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Review

Chemical modification of analytes in speciation analysis by capillary electrophoresis, liquid chromatography and gas chromatography

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Abstract

Chemical modification of target analytes is widely used in modern analytical methods. This review focuses on the application of chemical modification techniques in the simultaneous analysis of metallic species by capillary electrophoresis, liquid chromatography and gas chromatography. Emphasis is placed on the procedures relating to analyses carried out by capillary electrophoresis. The development of this topic in the past five years is evaluated for liquid chromatography and gas chromatography. The advantages, performance and application in real samples are compared for the three techniques.

Keywords: Reviews; Speciation; Metal cations; Organotin compounds; Organometallic compounds; Organolead compounds

Contents

1. Introduction

According to Florence's description [1], the speciation of an element is the determination of the individual physico–chemical forms of that element which together make up its total concentration in a sample. The importance of speciation analysis has been intensively emphasized [1,2]. Speciation analysis of metal elements attracts particular attention

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because of the characteristics, industrial consumption, and toxic influence of different metal species after being released into the environment [2]. Generally, the physico–chemical forms of the metallic species under study usually encompass different oxidation states, e.g., Cr(III) and Cr(VI), Fe(II) and Fe(III), V(IV) and V(V) [3–6], different complexation states, e.g., Pt(II) and Pt(IV) chloro-complexes [7], different association states, e.g., organometallic compounds and oxoanions [8,9], and different metal-binding states, e.g., some metal-containing proteins [10,11].

In numerous methodologies developed to date for speciation analysis, a few analytical techniques are applicable for simultaneous separation and detection of multiple species of an element, or of multi-elements. Of these techniques, gas chromatography (GC) and liquid chromatography (LC) are most commonly used, as indicated by the numerous reviews and procedures published [12–14]. Capillary electrophoresis (CE) is a comparatively new separation technique. Applicability of using CE as an alternative way for speciation analysis has been explored during the past five years [3,15–17].

As is known, volatile organometallic compounds can be directly detected by GC, provided they are thermally stable. It is also possible to use LC and CE for direct analysis of some metallic species with UV detection [18,19]. However, most metallic compounds have low volatility [2], and hence are not suitable for direct GC analysis. Additionally, the physico–chemical properties of many metallic species make direct detection impossible. For example, some organoselenium and organomercurials are thermally sensitive [20], and most metallic species are UV transparent. Sometimes, the sensitivity achieved by direct detection does not meet the requirement in real sample analysis [21]. Therefore, chemical modification of the target analytes, which transforms the existing states of the analyte to another, are applied to facilitate their analysis [22,23].

In most cases, analytical schemes for speciation analysis by CE, LC and GC rely on the combination of three basic stages and their interfacing design at the instrumental level: analyte pre-concentration, separation and selective detection (single or multi-element).

Depending on the nature of analytes, sample matrix, and the analytical approach, chemical modification has found wide applications. For example, chemical modification techniques have been used independently [24], or in combination with liquid–liquid extraction (LLE) [25], solid-phase extraction (SPE) [26], solid-phase microextraction (SPME) [27], microwave-assisted extraction [28], and field-amplified sample injection (FASI) [15,29], etc., for sample treatment and analyte pre-concentration.

Efforts have also been made to use chemical modification techniques to improve separation and enhance detection signals in speciation analysis by GC and LC [21,27]. Combined with common detection approaches [i.e., flame photometric detection (FPD) [30], electron-capture detection (ECD) [12], ultraviolet spectroscopy (UV) [15], fluorescence detection (FD) [31]], and the element-specific detection techniques, such as atomic absorption spectrometry (AAS) [13], atomic emission spectrometry (AES) [32], mass spectrometry (MS) [33], and inductively coupled plasma mass spectrometry (ICP-MS) [34]), both GC and LC have been applied to speciation analysis of many elements, including tin, lead, mercury, selenium, chromium, arsenic, vanadium, iron, platinum [12,30,35–37] etc. These documents considered most aspects of speciation analysis, including sample storage and preparation, analyte enrichment, separation optimization, detection improvement, interference and real sample analyses [1,12–14,38,39].

Since the early 1990s, interest in using CE for speciation analysis has increased [8–10]. More recently, reviews on selectivity control [40], and the state-of-the-art advancement [41] in metal speciation by CE have become available.

This work focuses on chemical modification techniques in speciation analysis by CE, LC and GC. Considerable attention is paid to complexation or derivatization in speciation analysis by CE. Because numerous works and comprehensive reviews on the use of complexation or derivatization in speciation analysis are well documented for LC and GC, emphasis was placed on the currently developed procedures. Comparison among three techniques with use of complexation or derivatization for speciation analysis is made, and the current strengths and limitations of CE methods are discussed. The

performance of CE is also critically evaluated in relationship to LC and GC in separation, detection and application. While the work cited in the CE section was performed in the past decade, because of the relative newness of CE, most of that in the LC and GC sections are more recent (since 1992).

2. Chemical modification of analytes

According to Nondek's description two independent interaction mechanisms operate at the molecular level in liquids: nonspecific van der Waals forces and specific interactions involving the transfer of electrons (charge) between interacting molecules [22]. The chemical modification of analytes conducted in solutions follows the same principles.

Based on the nature of analytes and the products formed, different modifications can be performed. The two most commonly used approaches relevant to specific interactions are ''derivatization'' and ''complexation''. The energetics of specific interactions involved in derivatization are usually much higher than those in complexation, and reactions taking place in derivatization are irreversible [42]. Besides, new covalent bonds will form in derivatization [22]. Therefore, derivatization is a more permanent modification than complexation. While the terms ''complexation'' and ''derivatization'' are frequently encountered when modification is used in CE [43], or in GC [44], respectively, both are used synonymously in LC [22,45]. Depending on the stability of the products formed, complexation can be further divided into complete complexation, partially complexation, association and ion-pairing [40].

In CE, besides the above two approaches, micelle–analyte interaction [43] provides a unique means of chemical modification. Taking advantages of such interaction, Terabe et al. [46] introduced the separation mode of micelle electrokinetic chromatography (MEKC), and extended the application of CE to weak and neutral compounds. Because no transfer of electron is involved between the interaction molecules, this type of chemical modification can thus be treated as a nonspecific van der Waals force modification process.

In relation to the separation process, chemical modification can be performed in three ways, namely, pre-column, on-column or post-column [21]. Pre-column and on-column modifications are simple and commonly used procedures. Post-column modification as a viable means has been mostly used to facilitate detection, such as fluorescence detection or chemoluminescence detection [47,48]. ''On-line'' or ''off-line'' are also used to describe the respective modification modes [45,49]. In GC, the initial sample volume is different, for on-line and off-line methods. In the former, as much as several hundred milliliters of sample may be used. With off-line hyphenated systems, the sample injected is limited to microliter volumes.

A problem encountered sometimes by using chemical modification for speciation analysis is the possible loss of speciation information in the original sample. For example, when the fraction of free versus bound ions is of interest, or when species and its complexes originally existing in the sample under study are less stable than the complexes formed as a result of the added complexing agent [50], the use of that complexing agent will cause problems in identifying the original species. Therefore, attention must be given to choosing modification methods and appropriate reagents, and in controlling operational conditions governing the modification process.

3. Chemical modification for speciation analysis by CE

In CE, there is much that can be done to improve separation or enhance detection. For speciation analysis, two approaches are usually adopted. Most employ chemical modification, such as derivatization, complexation, ion dissociation and ion pairing. Regulation of the rate of electroosmotic flow (EOF) is the other. For the analysis of inorganic metal species and organometallic compounds, complexation presents the most valuable chemical modification approach [18,40]. Studies which have been done include both theoretical and application aspects.

3.1. Theoretical model and description of migration behavior

In CE, some theoretical models have been pro-

posed to describe the migration behavior of analytes such as inorganic metal ions, enantiomers and other organic compounds [51–53]. Based on a 1:1 dynamic complexation between organic analytes, which were used as model compounds, and additives in an aqueous system, Chen et al. [53] proposed a comprehensive theory in CE to describe the migration behavior of analytes involving dynamic equilibria. In the cases when a complexing agent, a surfactant and a buffer solution co-exist in the separation electrolyte, multiple secondary equilibria must be considered simultaneously. Liu and Lee [54] proposed a multiple complexation model to describe the migration behavior of different species–complexing reagent complexes of lead, mercury and selenium. In a separation electrolyte which contains the analytes, triethylenetetraminehexaacetic acid (TTHA), sodium dodecyl sulphate (SDS), and a phosphorate-borax buffer (at a certain pH value), multiple complexing equilibria, i.e., the analytes–complexing reagent equilibrium, analytes–hydroxo equilibrium, and analytes–SDS equilibrium, are taken into consideration [54]. The migration behavior of the species can be expressed using the following equation:

$$\mu_{\text{eff}} = \mu_0\delta_A + \sum\mu^n_{AY}\sum\delta^n_{AY} + \mu_{AS}\delta_{AS} + \sum\mu^m_{AOH}\sum\delta^m_{AOH}$$
$$= \frac{\mu_0 + C_y\sum\mu_{AY}\sum(\beta^n_{AY}\delta^n_y) + \mu_{AS}\beta_{AS}[SDS^-] + \sum\mu^m_{AOH}\sum(\beta^m_{AOH}[OH^-]^m)}{1 + C_y\sum(\beta^n_{AY}\delta^n_y) + \beta_{AS}[SDS^-] + \sum(\beta^m_{AOH}[OH^-]^m)} \quad (1)$$

where μ_{eff} is the effective electrophoretic mobility of the analyte; μ_0 represents the electrophoretic mobility of the free analyte, and μ_{AY}, μ_{AS} and μ_{AOH} are the electrophoretic mobilities of the various complexed species. β values are stability constants. δ values are the molar fractions of polyaminocarboxylic acid at different anionic forms which are capable of reacting with the analytes with considering its protonation in aqueous solutions. This equation is similar to that in Chen's general expression for mobility derived from the dynamic complexation model [53], and presents a typical example of multiple equilibria in CE. Additionally, this equation gives a general expression of the analyte migration behavior for speciation analysis by CE. It establishes a link between the mobility of the analytes and the different β values, and the condition-dependent parameters, i.e., pH of the buffer, and concentrations of the complexing agent and SDS. Therefore, variation in migration can be predicted and explained by changes in these factors.

When analytes are modified under MEKC conditions, the theory developed by Terabe et al. and other workers is applicable [46,55,56].

3.2. Application of chemical modification for speciation analysis by CE

This section gives an overview of the applications of complexation in speciation analysis by CE developed to date. Several reagents are applicable for this purpose. These include sulphur-containing derivatizing agents, e.g., diethyldithiocarbamate (DDTC), polyaminocarboxylic acids, e.g., nitriloacetic acid (NTA) [15], ethylenediaminetetraacetic acid (EDTA) [16], 1,2-cyclohexanediaminetetraacetic acid (CDTA) [3], diethylenetetraminepentaacetic acid (DTPA) [57], and TTHA [54], hydroxocarboxylates, e.g., tartrate, oxalate and citrate [58], α-amino acids, e.g., cysteine [59,60], cyclodextrins (CDs), e.g., α-CD [61] and β-CD [62], and anionic surfactants, e.g., SDS. Amongst them, complexing agents of the aminocarboxylic acid family (mono-α-amino acid and polyaminocarboxylic acids) receive much attention. Particular emphasis is given to the speciation analysis of different oxidation states and organometallic compounds. For a quick review, Table 1 provides the reader with a comprehensive listing of references to specific speciation methodologies involving analyte modification.

To the best of our knowledge, only two procedures developed to date made use of derivatizing reagents for speciation analysis by CE. Li et al. [25] used sodium diethyldithiocarbamate (NaDDTC) to extract organolead and organotin compounds from water samples into hexane. In combination with SPE, >1000-fold enrichment of the species was achieved, allowing the detection of the species at the low part-per-billion levels. In another study [66], metallic species of mercury [methylmercury (MeHg), ethylmercury (EtHg), phenylmercury (PhHg) and Hg(II)] were analyzed after derivatization by dithizone sulphonate.

Although many of the sulphur-containing derivatizing reagents have very good photometric

Table 1
Derivatization and complexation for speciation analysis by capillary electrophoresis

Species	Detection method	Reagent and technical details	LOD	Sample	Ref.
Cr (III), Cr (VI)	UV	CDTA		Rinse water	[3]
Fe(II), Fe(III)	UV	EDTA			[16]
Cr (III), Cr (VI)	UV	EDTA + CTAB	1.5, 5 mg/l		[63]
Fe(II), Fe(III)	UV	EDTA + *o*-phen	10 pg		[64]
V(IV), V(V)	UV	EDTA	0.1, 0.4 mg/l	Catalyst–leachate	[65]
TML, TEL, DPhSe, PhSeC,	UV	MEKC + β-cyclodextrin	20, 8, 9, 18 pg	Water	[62]
TMT, TBT, TML, TEL	UV	DDTC + SPE + MEKC	5.2, 1.1, 1.9, 1.5 ppb	Rain water and drainage water	[25]
MeHg	UV	Cysteine			[59]
MeHg, EtHg, PhHg, Hg(II)	UV	Dithizone sulphonate (DzS)	Low μg/l		[66]
TMT, TET, TBT, TPhT		Tartaric acid, β-CD, or camphorsulphonic acid + SPE	0.16, 0.24, 0.29, 0.009 mg/l		[17]
TML, TEL, DPhL, PhHg, PSC, DPS, Pb(II), Hg(II), Hg(I), Se(IV)	UV	NTA + FASI	80, 40, 2.48, 0.41, 5.31, 10, 110, 130, 0.54, 0.2 μg/l	Tap water	[15]
TML, TEL, DPhL, PhHg, MeHg, EtHg, PSC, DPS, Pb(II), Hg(II), Se(IV)	UV	DTPA	Sub-mg/l	Water	[57]
TML, TEL, DPhL, PhHg, PSC, DPS, Pb(II), Hg(II), Se(IV)	UV	TTHA + FASI	369, 2.42, 0.3, 0.25, 2.0, 390, 0.11, 0.14, 0.34 μg/l	Sea water	[54]
TMT, TET, TPT, TBT, TPhT	Indirect UV	α-CD	2–20 μM	Marine sediment	[61]
MeHg	UV	Cysteine + FASI	12 ng/g	CRMs	[29]
DMT, DBT, TBT	UV	Oxalate or citrate	1.3, 11.2, 9,9 ppm		[58]
As(III), As(V), MMA, DMA	UV	Dodecyltrimethyl-ammonium phosphate	15 (As^{III}), 19 (As^{V}) ppb		[60]
As(III), As(V), DMA, AsF_6(V), Se(IV), Se(VI)	conductivity	CTAB	0.045, 0.076, 0.04 0.085, 0.065, 0.07 μg/ml	Water	[67]
Se(IV), Se(VI), selenocysteine, selenomethione	UV	Tetramethylammonium bromide	Several ppm		[68]
Humic substances (free ionic form and the complexed forms	Indirect UV	Fe(II) or Hg(II)			[69]
Cereal proteins	UV	Cu(II)		Flour	[10]
Hg(II)–FA and Fe(III)–FA	UV	CDTA			[70]
Zn(HP) and Zn(PP), Cu(HP) and Cu(PP)	UV	MEKC			[71]
Mg(chlorophyll C_1), Mg(chlorophyll C_2)	UV	MEKC			[72]
Ca-binding and Zn-binding proteins	UV	EDTA + MEKC			[73]
TML, TEL, DPhL, PhHg, PSC, DPS, Pb(II), Hg(II), Hg(I), Se(IV)	UV	EDTA + FASI	1.4, 5.6, 0.65, 0.41, 4.6, 110, 0.15, 0.48, 1.1, 0.35 μg/l	Tap water	[84]

properties [74], their application in CE is limited. This is mainly attributed to the low solubility in aqueous media of most of the derivatization products formed or the reagents themselves [45,74].

In speciation analysis by CE, complexation using aminocarboxylic acids or polyhydroxocarboxylates has attracted much attention. Compared to the sulphur-containing reagents, an advantage of amino-

carboxylic acids or polyhydroxocarboxylates lies in their or their salts' good solubility in water [74], and this makes them more suitable for CE analysis. Moreover, in aqueous media, the dissociation and presence of aminocarboxylic acids or polyhydroxycarboxylates are acid-dependence [75]. Therefore, the formation of complexes as well as the charge of complexes formed can be controlled by the variation in pH.

To date, speciation analysis using complexing agent has been most extensively studied. Speciation analysis using EDTA as complexing agent has been performed for inorganic metal ions at different oxidation states, including Fe(II) and Fe(III) [16,64,76], V(IV) and V(V) [6,65], and Cr(III) and Cr(VI) [16,63]. Analysis was also carried out with CDTA as chelating agent for Fe(II) and Fe(III) [6], and Cr(III) and Cr(VI) [3,4].

Polyaminocarboxylic acids have been used for the simultaneous speciation analysis of inorganic and organometallic species [15,54,57]. A method was developed to use NTA as both pre-separation and on-column complexing reagent in the analysis of lead, mercury and selenium species [15]. Nine species were eluted within 25 min under hydrodynamic injection mode (Fig. 1).

Cysteine is an α-amino acid. It can form stable complexes with mercury. An interesting application was carried out to use cysteine as complexing agent in the speciation analysis of organomercurials [59]. In a weakly basic buffer, 1:2 organomercurial–cysteine complexes were formed, and the separation was accomplished. However, baseline separation of methylmercury and ethylmercury could not be achieved.

Polyhydroxocarboxylates are another important type of complexing agents with weak complexing ability than aminocarboxylic acids. Compared to aminocarboxylic acids, they are weak complexing agents. In CE, the most successful application of polyhydroxocarboxylates is when they are used as complexing agents in the analysis of metal ions [77]. In cases where weaker complexation is adopted for speciation analysis by CE, polyhydroxocarboxylates are also the preferred choice. Oxalate and citrate were found to be critical in the separation of organotin compounds [58]. Under weakly acidic conditions, oxalate and citrate complexed with di-

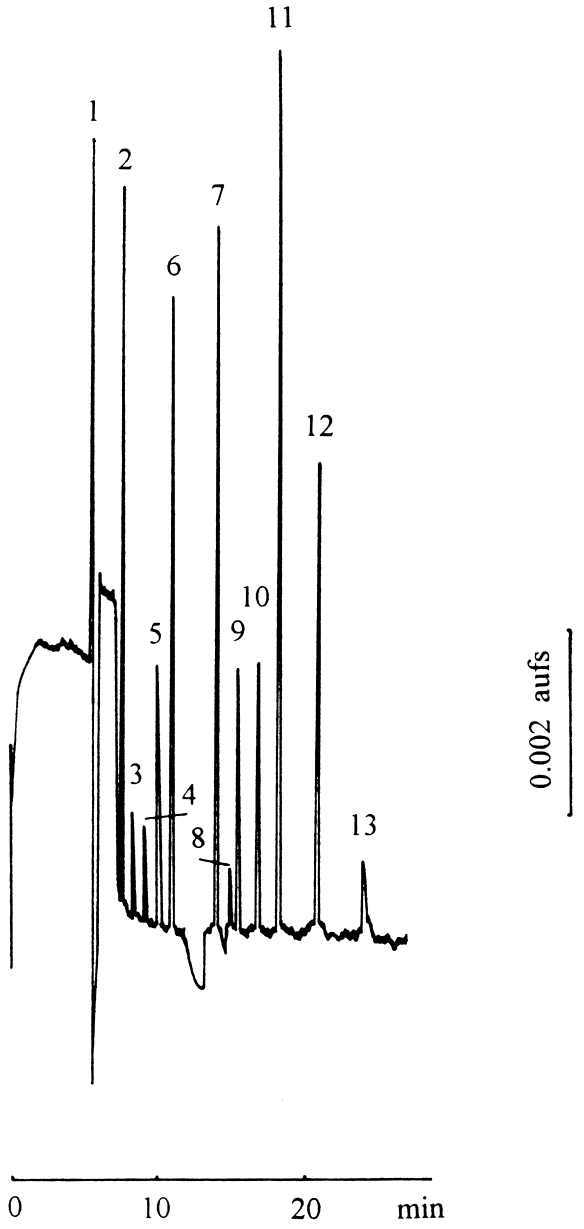

Fig. 1. Electropherogram of 10 species using nitrilotriacetic acid as complexing agent. Column: fused-silica capillary (63 cm×50 μm I.D.) with 50 cm length for separation; injection: 50 mbar× 0.1 min; voltage: 20 kV; detection: 200 nm. Separation electrolyte: pH 7.0, 40 m*M* NaH_2PO_4–$Na_2B_4O_7$ buffer, 40 m*M* SDS, and 5.0 m*M* NTA; sample mixture: pH 6.0, 40 m*M* NaH_2PO_4–$Na_2B_4O_7$ buffer and 5.0 m*M* NTA. Peaks: 1=MeOH; 2=DPLC; 3=Hg(II); 4=Pb(II); 5=PSC; 6=TMLC; 7=PMA; 8 and 9=Hg(I); 10=Se(IV); 11=TELC; 12=DPS; 13=NTA (reproduced with permission from Ref. [15]).

methyltin and dibutyltin, and thus exerted influence on their electrophoretic mobilities and resolution. In addition, the complexing agents were also useful in preventing the organotins from hydrolysis under the working conditions. In another procedure [17], four organotins were separated by using an electrolyte that contained tartaric acid as complexing agent. Besides its influence on the apparent mobility of complexed analytes, an increase in tartaric acid concentration also improved the detection of the trialkytins under indirect UV detection mode.

Using cyclodextrins is popular in CE to enhance selectivity, especially for chiral separation [43]. In speciation analysis by CE, various cyclodextrins are also applicable for this purpose. In a procedure of the analysis of organotin cations, separation of di- and triorganotins was achieved with the addition of α-CD to the electrophoretic buffer [61]. In another study, the formation of inclusion complexes between β-CD and organotins allowed the resolution of tributyl- and triphenyltins [17].

While capillary zone electrophoresis (CZE) is suitable for the speciation of charged species, MEKC extends the range of CE applications to neutral compounds. An application of using MEKC was carried out by Ng et al. in the simultaneous detection of organolead and organoselenium compounds by CE [62]. A clear variation in electrophoretic mobility was obtained for TML, TEL, PhSe and DPSe by changing the SDS concentration in the electrophoretic buffer. For speciation analysis by CE, SDS also plays a role in detection. Under direct UV detection mode at 200 nm [15], enhancement in detection signals was obtained for lead, mercury and selenium species with an increase in SDS concentration across a certain range. SDS used above its critical micellar concentration was also found necessary for detection of organotin and lead compounds in another study [25].

Besides anionic surfactants, cationic surfactants like alkylammonium compounds, e.g., cetyltrimethylammonium bromide (CTAB) and tetradecyltrimethylammonium bromide (TDTAB), have also found their applications in speciation analysis by CE [67,68]. Nevertheless, they are mostly used as an EOF regulator rather than for analytes modification.

In some cases, different methods can be used simultaneously for analyte modification to achieve better separation [15,57,62]. Analysis of multi-lead, mercury and selenium species was carried out when complexation and MEKC were used in combination [57]. In this work (Fig. 2), DTPA was the complexing agent for both off-line and on-line modification of the species, and SDS effectively modified the electrophoretic mobilities of TML, TEL and DPSe. Ng et al. [62] employed β-CD and MEKC to study four organometallic compounds by CE. While the increase in SDS concentration prolonged the migration time of analytes due to the micelle–analyte interaction, β-CD acted as a competitor against SDS on analytes through host–guest complexation, and exerted influence on resolution and total migration time.

Besides the above applications, another interesting consideration of analyte modification techniques is to study the structure, activity and characteristics of metal-binding organic molecules. Characterization of metal–fulvic acid (FA) interaction was carried out by Norten and Zlotorzynska [70]. CDTA was added to the CE separation buffer; it displaced Hg(II) and Fe(III) from their corresponding fulvic acid complexes, and formed UV-absorbing complexes. Through this way, the existence of a particular metal–fulvic acid complex could be identified. In another study, a MEKC method was developed for speciation analysis of copper-binding and zinc-binding haematoporphyrin and protoporphyrin substances [71]. The binding shift of calcium-binding and zinc-binding proteins was studied by Kajiwara [73] with the use of a separation buffer of EDTA plus micellar SDS. In a study by O'Keeffe et al. [10], metal–polyaminocarboxylate complexation was chosen as a model interaction to investigate the effect of metals on proteins. These studies provide essential examples of using CE as an approach to investigate the role that trace elements play in the structures and functions of biological macromolecules.

To date, most of the speciation analyses carried out by CE are still being performed using conventional UV detectors whose detection sensitivity is lower than those of the element-specific detectors. Recently, the applicability of coupling CE to MS or ICP-MS for speciation analysis has been explored [50]. Much attention has been paid to CE–ICP-MS [50,78,79] because the high selectivity of ICP spectrometry allows resolution of the chemical separation

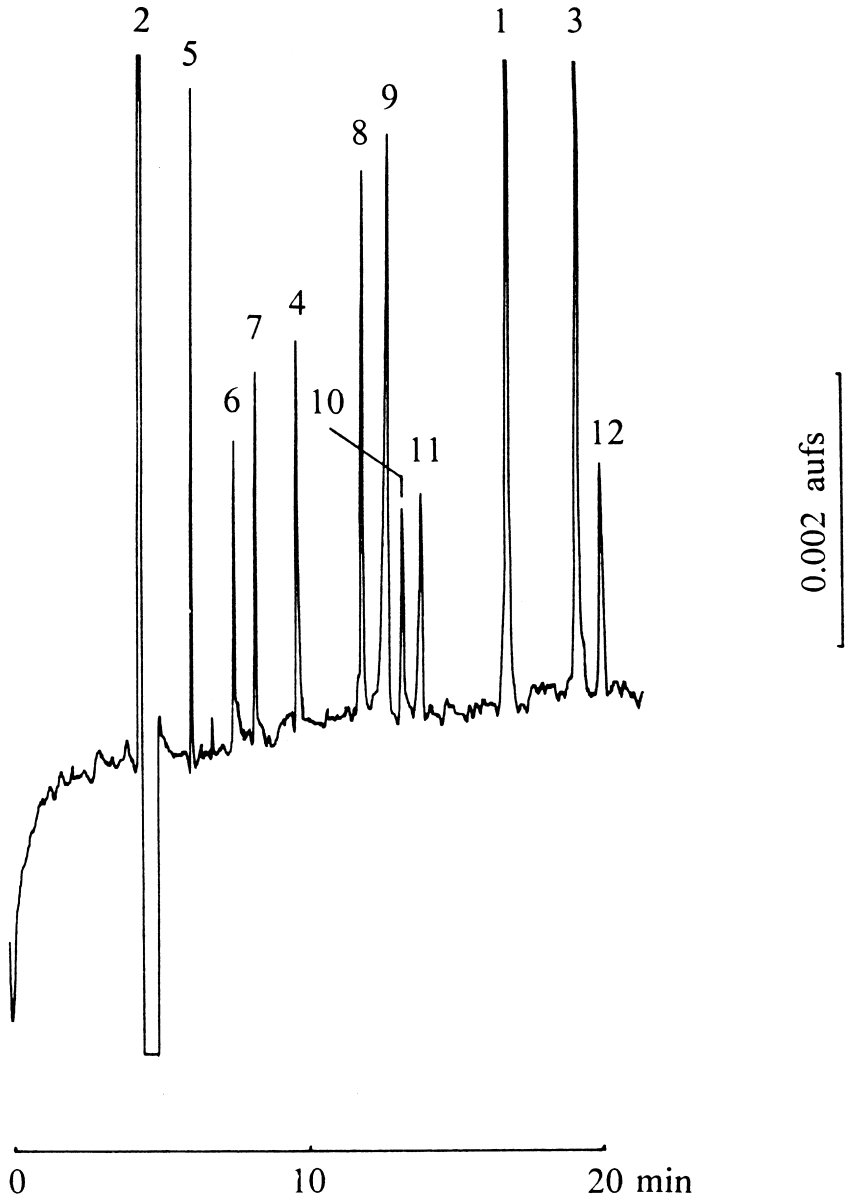

Fig. 2. Electropherogram of 11 species generated with complexation and MEKC. Column: fused-silica capillary (65 cm×50 μm I.D.) with 51.5 cm length for separation; injection: 50 mbar×0.1 min; voltage: 20 kV; detection: 200 nm. Separation electrolyte: pH 7.25, 40 m*M* NaH_2PO_4–$Na_2B_4O_7$ buffer, 5 m*M* DTPA, and 2.5 m*M* SDS; sample mixture: running electrolyte and analytes. Peaks: 1=TELC; 2=MeOH; 3=DPS; 4=TMLC; 5=DPLC; 6=Pb(II); 7=PSC; 8=PMA; 9=EtHg; 10=Hg(II); 11=MeHg; 12=Se(IV).

to be traded off for rapid analysis times, and there is thus no need to resolve completely species containing different elements, from one another. Recognizing the incompatibility in sample flow-rates between CE (a few nl/min) and ICP-MS (in the order of ml/min), efforts have been made to overcome this limitation by using uniquely designed interfaces, such as concentric, pneumatic nebulizer [50], direct injection nebulizer [78], concentric tube nebulizer and cross-flow nebulizer [79]. With its successful

application in speciation analysis [50,79], CE–ICP-MS has heralded a novel approach in this realm of analytical chemistry.

3.3. Combination of complexation and FASI in speciation analysis by CE

Several techniques have been reported to be capable of improving sensitivity in CE analysis [80]. Among the developed approaches, field-amplified stacking injection (FASI) is the most promising [81,82]. It takes advantage of electrophoretic migration and electroosmosis, and has been demonstrated to achieve over 100-fold enhancement in detection for charged analytes [83]. To perform FASI, samples are usually prepared in water, or in a diluted buffer solution which is of the same composition as the separation electrolyte. When a high voltage is applied across the buffer-filled capillary column, an amplified field is generated at the injection point, thus ensuring on-line stacking. Through polarity-switching of the electrodes during the stacking process [83], both positive and negative analytes can be enriched within a single analysis. In CE, an advantage of introducing complexation for speciation analysis is to facilitate FASI. Therefore, if the complexes formed are also electrically charged and stable, FASI is applicable.

FASI has been used to analyze methylmercury after its complexation with cysteine under a weakly basic condition where a 1:2 analyte–cysteine complex was formed, and FASI was carried out for the negatively charged complex at the anodic end of the capillary [29]. A 10-fold detection enhancement which enabled a detection limit ($S/N=3$) of 12 ng/g was obtained. FASI was performed in speciation analysis of lead, mercury and selenium using polyaminocarboxylic acids as complexing agents [15,54,84]. Very high enhancement in detection was achieved by TTHA as complexing agent and FASI for the speciation analysis of different lead, mercury and selenium species [54]. Because TTHA is a strong complexing agent, stable complexes can be formed. Moreover, under the weakly basic conditions, TTHA is mainly present in -4 anionic form; this may result in the formation of highly negatively charged complexes (-1 to -3), permitting effective stacking. Under the optimum conditions, as high as 1500-fold detection enhancement was achievable (Fig. 3a and b). Moreover, this procedure also provided resolution of Ca(II), Mg(II) and Na(I), which are the three common interfering ions in many aqueous samples.

Although FASI technique has many intrinsic advantages, its application in real-world samples has not yet been well exploited. As has been demonstrated [82], FASI is based on the electrical charge of the analytes. When sample ions are stacked under the amplified field, impurity ions will also be simultaneously concentrated. For real sample analysis, it is important that the differences in stability constants of the formed complexes are great enough for CE resolution. In addition, real-world samples are usually complicated in matrix and ion composition. During the stacking process, the variation in electrical current, which is caused by the change in ionic strength, is different from each other depending on the sample matrices. Because the stacking time is usually shorter than 1 min, it is difficult to monitor precisely the electrical current or stop the stacking potential at the right time. In order to resolve the impurities from the analytes in real sample analysis, the choice of a suitable complexing agent that can provide sufficient differentiation in stability constants of the analytes is thus critical.

4. Complexation and derivatization in speciation analysis by LC

LC is an ideal approach to speciation analysis. Before the introduction of CE procedures, LC was the primary technique used for the simultaneous speciation of inorganic metallic species. Reversed-phase LC (RPLC), ion-pair chromatography (IPC) and ion-exchange chromatography (IEC) are the three commonly adopted separation modes [45]. A number of monographs and reviews are available which describe these techniques [19,22,42]. The methodologies developed in the past few years relating to analytes modification for speciation analysis by LC are summarized in Table 2.

Much emphasis has been placed on the analysis of mercuric compounds, and lead and tin species. Simultaneous speciation of multi-elements has also

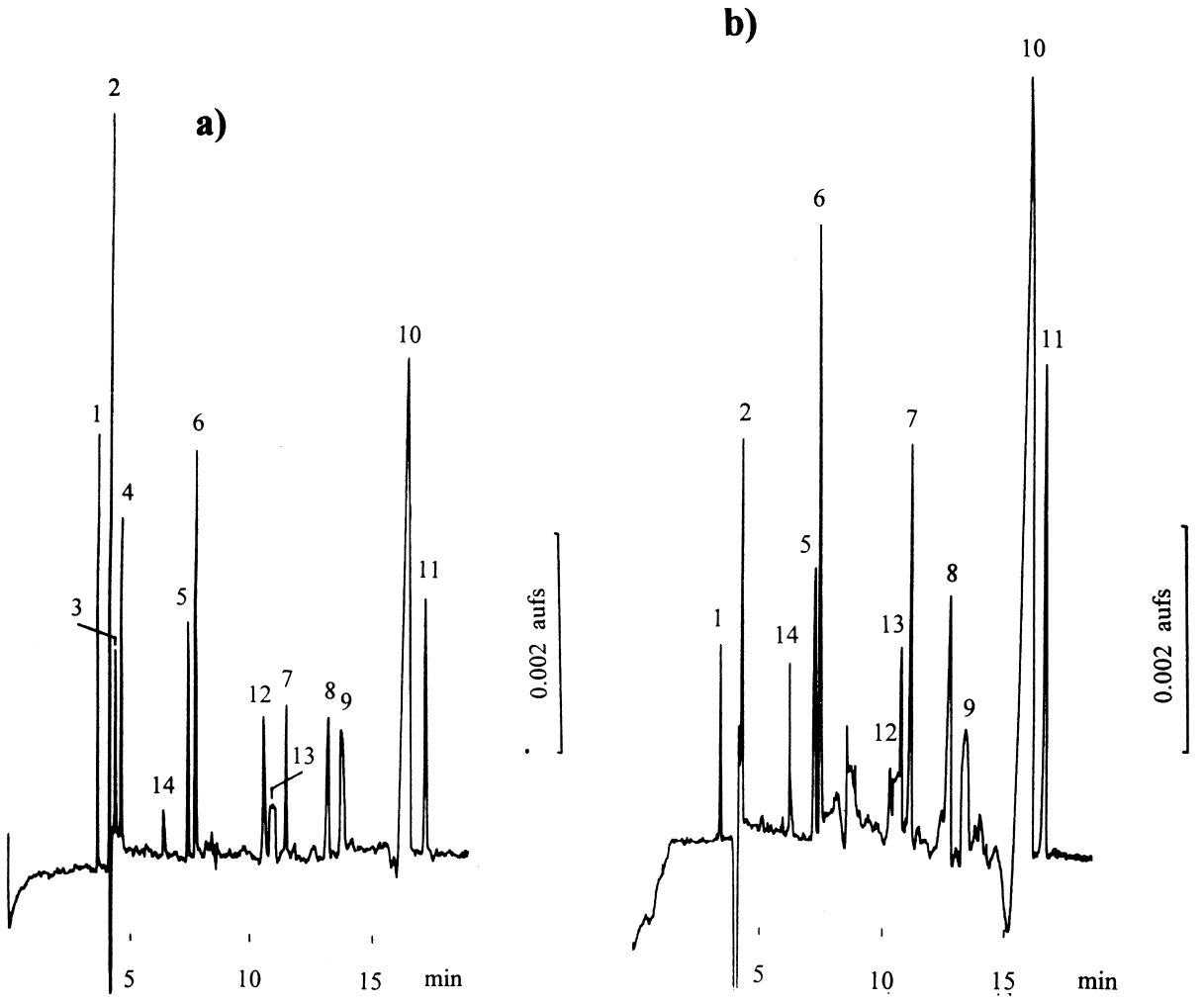

Fig. 3. Electropherograms of lead, mercury and selenium compounds generated under hydrodynamic injection and FASI. Column: fused-silica capillary (64.5 cm×50 μm I.D.) with 52 cm length for separation; voltage for separation: 20 kV; detection: 200 nm. (a) Hydrodynamic injection: 50 mbar×0.1 min; separation electrolyte: pH 7.5, 40 m*M* NaH_2PO_4–$Na_2B_4O_7$ buffer, 2.5 m*M* TTHA, and 2.0 m*M* SDS; sample mixture: pH 7.5, 40 m*M* NaH_2PO_4–$Na_2B_4O_7$ buffer, 5.0 m*M* TTHA, and analytes. (b) FASI: +10 kV 2.0 min, and −10 kV until electric current reached 95% of that of the beginning of sample stacking; separation electrolyte: pH 7.5, 40 m*M* NaH_2PO_4–$Na_2B_4O_7$ buffer, 2.5 m*M* TTHA, and 2.0 m*M* SDS; sample mixture: pH 7.5, 0.2 m*M* NaH_2PO_4–$Na_2B_4O_7$ buffer, 0.025 m*M* TTHA, and analytes. Peaks: 1=TELC [(a) 73.7 μg/ml; (b) 0.37 μg/ml] (enhancement factor (EF): 279-fold); 2=MeOH; 3=DPS* [(a)12.5; (b) –]; 4=TMLC** [(a) 63.5; (b) –]; 5=PSC [(a) 70.0; (b) 0.35] (EF: 461); 6=DPLC [(a) 31.8; (b) 0.16] (EF: 340); 7=Pb(II) [(a) 8.95; (b) 0.045] (EF: 1490); 8=Se(IV) [(a) 19.5; (b) 0.32] (EF: 870); 9=PMA [(a) 25.0; (b) 0.12] (EF: 607); 10=TTHA; 11=Hg(II) [(a) 16.5; (b) 0.082] (EF: 813); 12=Mg(II)*** [(a) 1.9; (b) 0.01]; 13=Ca(II)*** [(a) 6.1; (b) 0.03]; and 14=Na(I)*** [(a) 7.1; (b) 0.035]. * Neutral compound – no enhancement factor under FASI. ** Compound co-migrates with EOF marker – enhancement factor not calculated. *** Interfering ions under consideration in sample matrix. (Reproduced with permission from Anal. Chem., July 1998, 70, pp. 2666–2675. Copyright 1998 American Chemical Society [54]).

been carried out. The modification reagents used included derivatizing agents, polyaminocarboxylic acids and surfactants.

For the analysis of organometallic compounds, derivatizing agents containing sulphur, including substituted dithiocarbamates [89], thioglicolate

Table 2
Derivatization and complexation for speciation analysis by high-performance liquid chromatography

Species	Method	Reagent and technical details	LOD	Sample analysis	Ref.
TTML, TTEL, MeHg, EtHg, PhHg	IPC–ICP-MS	Ammonium pentanesulphate	0.2 pg	Urine reference material	[85]
TTML, TTEL, TPhL, Pb(II)	IPC–ICP-MS	Sodium pentanesulphate			[86]
TML, TEL, DML, DEL, MeHg, EtHg	Reversed-phase high-performance LC (RPLC)–UV	Methyl thioglicolate	270–800 ng/l		[87]
MeHg, EtHg, PhHg, Hg(II)	RPLC–AAS	Ammonium tetramethylene-dithiocarbamate	0.015–0.5 μg/l		[88]
MeHg, EtHg, MeOEHg, EtOEHg, PhHg, Hg(II)	RPLC–spectrophotometry	*N*,*N*-disubstituted dithiocarbamate			[89]
MeHg, EtOEHg	LC–UV–post-column oxidation–cold vapor-AAS	Chelate of Hg+ preconcentration	0.5 ng/l		[90]
MeHg, EtHg, Hg(II)	RPLC–ICP-MS	2-mercaptoethanol	0.4–0.8 ppb	CRM dogfish muscle	[91]
MeHg, EtHg, Hg(II)	RPLC–cold vapor-AAS	Cysteine	0.1 ng in Hg	Waste water	[92]
MeHg, EtHg, Hg(II)	RPLC–cold vapor-AAS	Cysteine + $NaBH_4$	0.1, 0.04, 0.02 μg/l	Tap water	[93]
MeHg, EtHg, PhMeHg, PhHg, Hg(II)	IPC–UV	tetraalkylammonium bromide	0.2–8.0 (175–255) ng	River water	[94]
TPhT, TMT, TBT, TML, TEL	IEC–FD	3-Hydroxyflavone (Triton X-100 medium) + solid-phase extraction	0.02 ng	Seawater	[31]
TMT, TET, TBT, TPhT,	IPC–indirect UV	Benzyltrimethyl-ammonium chloride	0.15–2.5 mg/l	Natural water	[17]
TMT, TET, TPT, TBT, TPhT	IPC–ICP-MS	Pentanesulphonate	2.8–16 pg Sn	Harbour sediment and water	[95]
Cr(III), Cr(VI)	RP-IPC–UV	EDTA			[96]
Cr(III), Cr(VI)	RP-IPC–UV	EDTA + tetrabutyl ammonium bromide	0.02, 0.8 mg/l	Waste water	[97]
Cr(III), Cr(VI)	IEC–UV	EDTA + tetrabutyl ammonium bromide			[98]
Cr(III), Cr(VI)	IEC–ICP-MS	EDTA	80–88 ng/l	Water	[99]
Cr(III), Cr(VI)	IEC–spectrophotometry	DPC; DCTA	2.5, 1.8 ng/l; 4.5, 1.5 ng/l	River water	[100]
Cr(III), Cr(VI)	IEC–ICP-AES	EDTA	0.4, 1.0 ppb	CRM water	[101]
DML, TML, DEL, TEL, MeHg, EtHg	RPLC–UV	Mercaptoethanol + methyl thioglycolate	12, 17, 31, 32, 25, 19 ng		[102]
Fe(II), Fe(III)	IEC–spectrophotometry	PDCA + PAR		Rock	[48]
Hg(II), MeHg, EtHg	RPLC–UV	Mercaptoethanol			[103]
MeHg, EtHg, PhHg, Hg(II)	RPLC–spectrophotometry	dithizone	0.1, 0.3, 0.1, 0.1 ng	Natural water	[104]

[87,102], mercaptoethanol [101] and dithizone [104], attracted the most attention. An example was presented by Falter et al. [89], in the speciation analysis of mercuric species, i.e., inorganic, methyl-, ethyl-, methoxyethyl-, ethoxyethyl- and phenylmercury. Three *N*,*N*-disubstituted dithiocarbamates, hexamethyleneammonium (HMA)-hexamethylene-dithiocarbamate (HMDC) and DDTC, were used for pre-separation enrichment, and as an eluent additive. The best results were obtained with pyrrolidinedithiocarbamate (PDDC). In another application of determining ionic organolead and organomercury species, Bettmer et al. [102] used mercaptoethanol and thioglycolate for pre-separation enrichment and on-column derivatization, respectively. A typical liquid chromatogram is shown in Fig. 4. Six compounds of organo-mercurials and lead were separated in 35 min, with detection limits at μg/ml levels.

Procedures relevant to speciation analysis using other derivatizing reagents are also available in the literature such as 3-hydroxyflavone for fluorescent

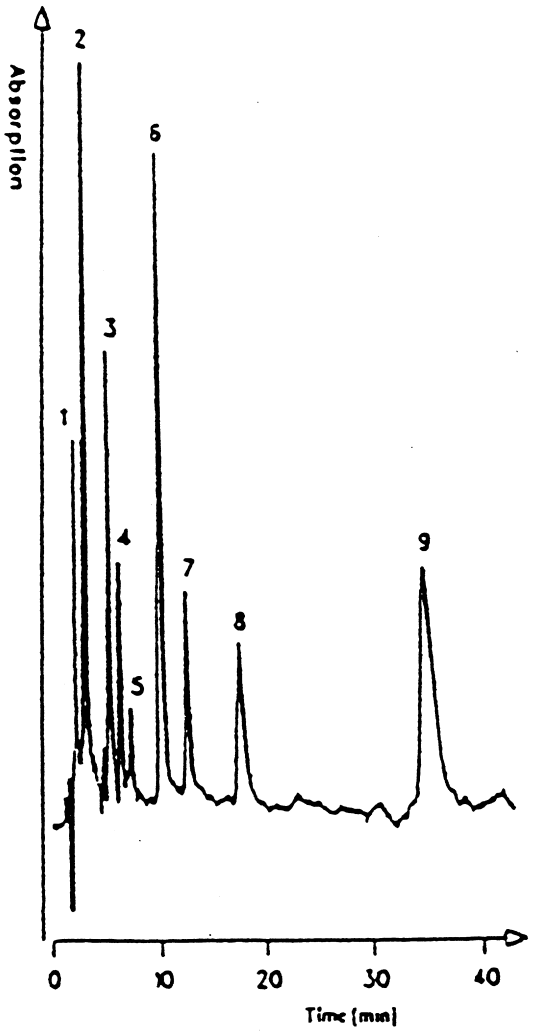

Fig. 4. LC chromatogram of lead and mercury compounds. Stationary phase: Hypersil ODS 100-5, 250 mm×4 mm; mobile phase: methanol–0.1 mol/l citric acid (40:60, v/v), adjusted to pH 5.8, 0.02% (v/v) methylthioglycolate; detection, 235 nm at 0.04 a.u.f.s. Peaks: 1=Methanol; 2=methyl thioglycolate; 3=81 ng of TML; 4=226 ng of MeHg; 5=impurity from methyl thioglycolate; 6=129 ng of DML; 7=208 ng of EtHg; 8=238 ng of DEL; 9=246 ng of TriEL. (Reproduced with permission from Ref. [102]).

detection [31], and pyridylazoresorcinol (PAR) for photometric detection [48].

Polyaminocarboxylic acids have been mainly used as complexing agents for the determination of different oxidation states of inorganic species. An ion chromatographic separation of chromium (Cr) species of its EDTA complexes has been reported [99]. In another application, Cr(III) was separated from Cr(VI) on an anion-exchange column based on its CDTA complex [100]. In this procedures, a complexing agent and an ion-pairing agent were applied to ensure off-line complexation of Cr(III) and on-column modification of Cr(VI).

Surfactants, in either cationic- or anionic- forms, are the third type of modification reagents used in speciation analysis by LC. Through ion-exchange or ion-pairing techniques, speciation analysis has been carried out for organotin, lead and mercuric compounds [17,85,86,94].

5. Derivatization in speciation analysis by GC

Derivatization techniques employed for speciation analysis by GC have usually consisted of: (a) hydride generation, (b) extraction into an organic solvent and derivatization with an alkylating agent, and (c) in situ ethylation in the aqueous sample with sodium tetraethylborate ($NaBEt_4$), followed by head-space analysis (Table 3). Due to the concerted efforts placed in this area since the 1970s, derivatization methods of hydride generation and alkylation with Grignard reagents have been well established for elements such as Sn, Se, As, Bi, Te, Sb, and most of the light alkylated Pb and Hg species. In the 1990s, the use of aqueous ethylation with $NaBEt_4$ has attracted intensive attention due to its unique merits [30]. Besides attention paid to the analytes pre-concentration, separation and detection strategies in speciation, several articles described the comparison of the derivatization approaches used in speciation analysis by GC have been recently published [32,120].

Alkylation of organometallic compounds using Grignard reagents can provide quick derivatization for organotin, mercury, lead and other elements [121]. An important application of using a Grignard reagent for speciation analysis of organotins was demonstrated by Liu et al. [118] in the simultaneous separation and detection by GC–atomic emission detection (AED) (Fig. 5). Depending on the characteristics of the target, alkylating reagents with different alkyl-groups, including methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl- and phenyl-, are available [32]. Alkylation by Grignard reagent with longer

Table 3
Derivatization for speciation analysis by gas chromatography

Species	Detection method	Derivatization and technical details	LOD	Sample analysis	Ref.
Butyltin	MS	Grignard reagent	0.15 pg (Bu_3SnMe)	Sediments, CRMs	[105]
TBT, DBT, MBT, TphT, DphT, MphT	AED	Grignard reagent, $NaBEt_4$		Mussels	[32]
MBT, DBT, TBT, MphT, DphT, TphT,	FPD	$NaBEt_4$	0.4–0.8 ng/l, 0.7–2.1 ng/l	CRM, aqueous samples	[30]
MBT, DBT, TBT, TphT	FPD, AED	$NaBEt_4$ + MAE		CRM (fish tissue)	[106]
MBT, DBT, TBT	AAS	$NaBEt_4$	5 ng/l	CRMs	[107]
MBT, DBT, TBT	AES, AAS	Tropolone + $NaBEt_4$, DDTC + Grignard reagent		Sediments, harbors and dry-docks	[13]
MBT, DBT, TBT, TBT	FPD	$NaBH_4$ + quartz surface-induced emission	5, 18, 2, 0.3 (pg)	Water	[108]
MBT, DBT, TBT	FPD	Tropolone + SPE	6, 4, 3 ng/l	Seawater	[26]
MMT, MeBT, TeET, MBT, TPT, DBT, MPhT, TBT, MocT, TeBT, MdoT, TPhT, DDoT	FPD	$NaBEt_4$ + quantitative MAE	4–73 pg	CRM sediments	[28]
MMT, DET, DBT	Cryogenic trapping–AAS	$NaBH_4$, $NaBEt_4$			[109]
MMT, MBT, DBT, TBT	AAS	$NaBH_4$			[110]
MBT, DBT, TBT	AAS	$NaBH_4$, $NaBEt_4$	0.2, 0.1, 0.44 ng Sn/g	Sediment	[111]
Ionic MBT and alkyllead	Plasma AED	Grignard reagent	0.5, 0.2 (pg)	CRMs	[41]
Organotin, lead and mercury	ICP-MS	$NaBEt_4$	0.34–2.1 ng/l Sn	CRMs	[39]
TML, TEL	Microwave induced plasma–AED	Grignard reagent	0.5, 0.85 ng/l	River water	[112]
Selenomethionine	Microwave induced plasma–AES, FPD, MS, AAS	Esterification + acrylation		Wheat	[113]
Hg^{2+}, MeHg	Cryogenic trapping–AAS	$NaBH_4$ + MAE	3 ng/g	CRMs	[114]
Organotin and lead	AED	$NaBEt_4$ + SPME	0.09 Sn, 0.08 Pb (pg)	Slurry samples	[27]
Methylated mercury, tin and lead, and Hg(II)	Cryogenic trapping–AED	$NaBEt_4$	0.6, 0.15, 0.2, 2 ng/l	River, soil and run-off water	[115]
BT and PT, pentylated DMGe, TMGe and TeBGe	FPD	Grignard reagent, $NaBEt_4$	0.7–2.3, 50–100 pg	Water, sediments	[116]
Organic tin, lead, mercury	ICP-MS	$NaBEt_4$		Sediments	[33]
Selenium(IV)	Microwave induced plasma–AES	$NaBEt_4$	8 ng/l	Water	[117]
Organotin, lead and mercury	AED	Grignard reagent	1.0–2.5 μg/l		[118]
Organolead and tin	AAS	$NaBEt_4$			[119]

alkyl-groups, i.e., pentyl- and hexyl-, have the advantage of providing derivatization compounds with relatively low volatility which allows easy pre-concentration steps in the sample pretreatment without any special precautious, and are most commonly used. In contrast, propylation, ethylation and methylation produce highly volatile compounds, and partial losses during the pre-concentration steps may occur. This can lead to lower accuracy and recovery.

Compared to hydride generation, ethylation by $NaBEt_4$ provides more reproducible results and is not affected by inorganic interferents [111]. In addition, the detection limits of some organometallic compounds can be significantly improved by ethylation because it is a foam-free derivatization [111].

In comparison to Grignard reagents, $NaBEt_4$ is stable in water and so the derivatization can take place in aqueous media [113]. This provides aqueous

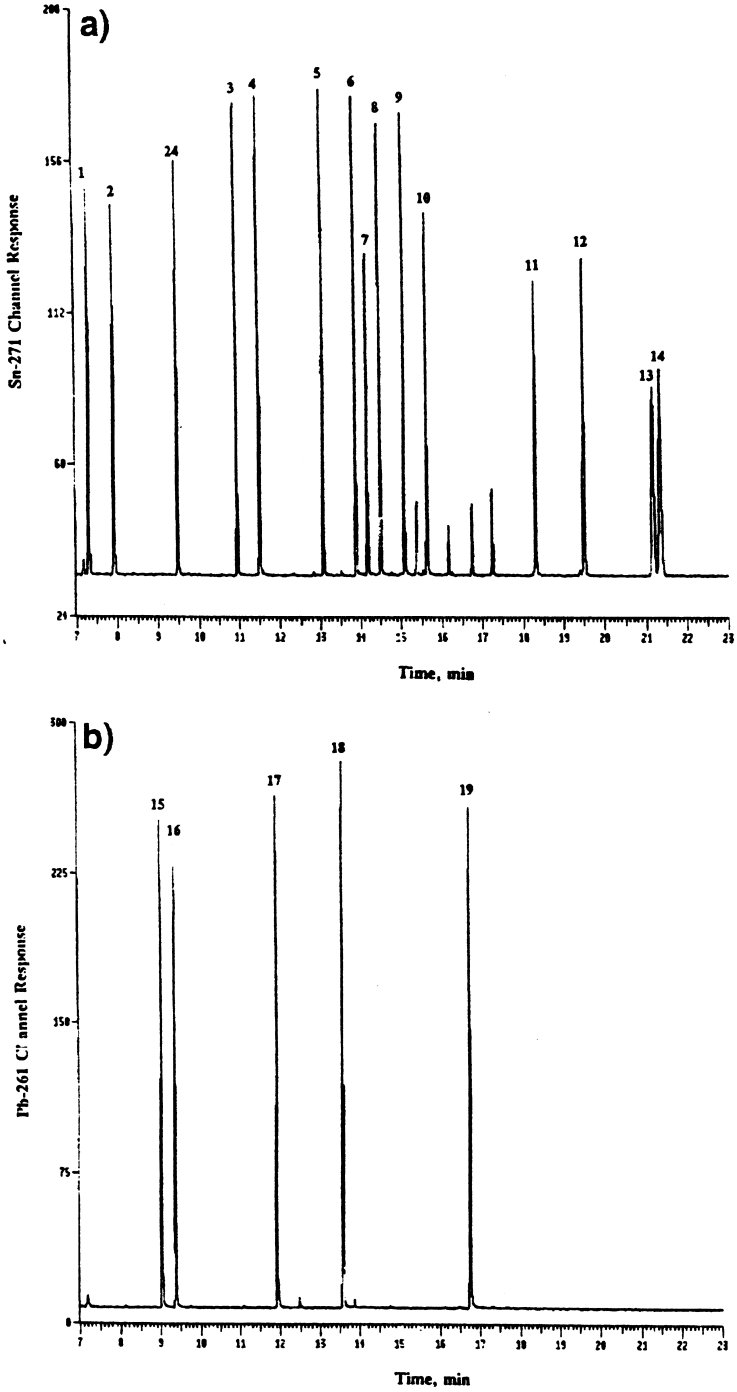

Fig. 5. GC–AED chromatograms of a multi-component organotin, organolead and organomercury standard. (a) Sn-271 channel, (b) Pb-261 channel and (c) Hg-254 channel; the concentration of each compound was 250 ng/ml as metal (Sn, Pb, or Hg). Peaks: 1=TML; 2=TTET; 3=TET; 4=DMT; 5=DET; 6=TTBT; 7=MMT; 8=TBT; 9=DBT; 10=MBT; 11=DPhT; 12=TPhT; 13=TTCHT; 14=TTPhT; 15=TML; 16=TTEL; 17=TEL; 18=TPL; 19=TPhL; 20=MeHg; 21=EtHg; 22=PhHg; 23=HeHg; 24=trimethylphenyltin (internal standard 1); 25=bis(trimethylsilymethyl)-mercury (internal standard 2). (Reproduced with permission from Ref. [118]).

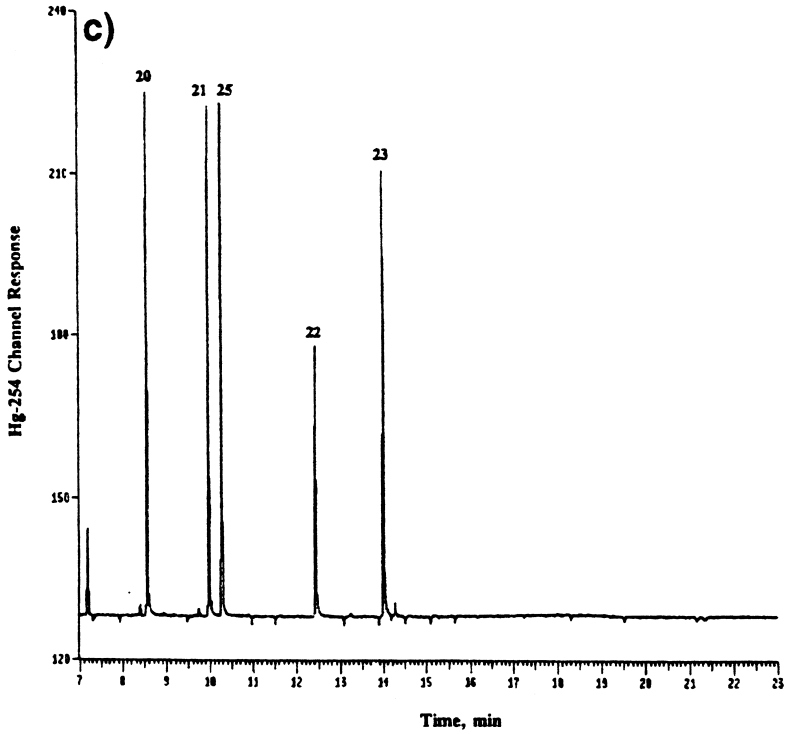

Fig. 5. (*continued*)

ethylation an advantage over alkylation in speciation analysis of water samples.

Hydride generation is in turn easier to handle than aqueous ethylation or alkylation [111]. It is shown to be slightly more sensitive than ethylation for some species, and requires shorter reaction and purge times in the reactor than the aqueous ethylation method does. However, hydride generation is not suitable for the accurate analysis of lead and mercury species of environmental samples because the hydrides of both organometallic compounds are not very stable, or are prone to dismutation reaction [21]. This has lead to the decline of hydride generation by $NaBH_4$ in speciation analysis.

In addition to the three common approaches described previously, other derivatization methods have also been used. A method was carried out for the determination of selenomethionine in wheat samples [113]. Both esterification and acrylation was used to transform the carboxylic and the amino groups separately to facilitate GC analysis. Tropolone was employed as a derivatizing reagent in another application for the determination of organotin compounds [26].

6. Comparison of analyte modification techniques in speciation analysis by CE, LC and GC

Chemical modification presents a valuable means for speciation analysis in CE, LC or GC, and bridges the three analytical techniques. Knowledge about advantages and drawbacks of the three analytical techniques can provide helpful information in the development of new speciation procedures.

By converting the analytes from their existing forms, chemical modification renders them suitable for separation and detection. Many of the procedures developed to date are capable of enabling simultaneous modification for multi-species or multi-elements [53,104,118]. Another common feature of conducting modification for metal speciation by the three techniques is that this approach is commonly

effective for ionic species [21]. Moreover, most of the modification methods can be used in combination with other sample treatment strategies such as extraction and enrichment procedures.

Table 4 gives a brief comparison of speciation analysis using analytes modification by CE, LC and GC. Reagents for modification are similar in CE and LC. Separation in both can be performed under aqueous conditions. In principle, detection methods used in LC are also applicable to CE.

However, chemical modification in speciation analysis by CE, LC or GC is distinguished, in purpose, reagent used, operation conditions, performance and application from one another, caused by their inherent features. In CE, separation is based on the difference in electrophoretic mobility under high voltage [43], and is due to the electrophoretic mobility of an analyte being proportional to its charge-to-size ratio [43]. An important aim of analyte modification in CE is to increase or fine-tune the charge-to-size ratio among different analytes, and hence to improve separation. In LC, the role of modification is to affect partition coefficients of analytes between the mobile phase and stationary phase, and thus control retention times and resolution [45]. For GC, chemical modification is usually performed to adjust the volatility of analytes to facilitate their analysis [113].

Numerous reagents have been used for chemical modification of metallic species in GC, LC and CE. In GC, in accordance with hydride generation, ethylation, or alkylation, $NaBH_4$, $NaBEt_4$, and various Grignard reagents are utilized, respectively. In LC and CE, a great variety of reagents have been used, and provide advantage procedures over GC. Further, compared to CE which aqueous medium is preferred for speciation analyses, those by LC can be performed in aqueous or non-aqueous conditions. This allows the use of most of sulphur-containing reagents for speciation analysis by LC. In general, complexation and derivatization procedures for speciation analysis by CE or LC are usually simple and easy-to-use. In GC, they are composed of many steps, and thus more complicated. When Grignard reagents are used for example, precautions need be taken because they are sensitive to moisture, and sulphuric acid which is used to decompose the excess reagent after derivatization procedure is agitate and strongly corrosive. To overcome this problem in speciation by GC, one- or two-step protocols have been developed for sample preparation and analytes pre-concentration [12,122]. A typical procedure is to perform simultaneously in aqueous solution the microwave-assisted dissolution of sample, ethylation of analytes with $NaBEt_4$, and extraction of modified analytes with organic solvent [122].

In speciation analysis using chemical modification, an important aspect that differentiates CE from LC or GC is detection. The mass detection limit reported by CE is in a similar range to GC. When using UV for detection, the best results obtained by CE exhibit better limits of detection (LODs) than those of LC in the analysis of organometallic compounds [123].

Table 4
Comparison of the speciation analysis using analyte modification by CE, LC and GC

Method	Preferred operation media	Detection technique	Reagent for modification	Compatability with other sample treatment procedures	LOD	Application	Ref.
CE	Aqueous	UV, FD	Derivatizing agents, complexing agents, surfactants	LLE, SPE, FASI	Sub-μg/l–mg/l	Water	[15,54] [63,65]
LC	Aqueous, non-aqueous	AAS, AED, FD, ICP-MS, UV	Derivatizing agents, complexing agents, surfactants	LLE, SPE	ng/l–sub-mg/l	Water, rock	[87,88,90] [93,97] [99,100]
GC	Non-aqueous	AAS, AED, ECD, FPD, ICP-MS, MS	Grignard reagents, $NaBEt_4$, $NaBH_4$	LLE, SPE, SPME, MAE, cryogenic trapping	sub-ng/l–low-μg/l	Air, soil, rock, water, tissues	[26,30,34] [106,112,115] [117,118]

However, GC is usually superior to CE by providing much better detection sensitivity in terms of concentration. In many cases, LC is also more sensitive than CE in determining inorganic species. These are mainly attributed to both GC and LC being more compatible to numerous element-specific detection techniques, e.g., AAS, AES, MS and ICP-MS.

For real sample analysis, modification methods have been used in GC for the analysis of different organometallic compounds in soils, sediments, waters and marine organisms [13,26,32,115]. The methods developed for LC are mainly focused on water samples. In CE, although major efforts are still being concentrated on the development of separation and detection strategies, applications involving analytes modification have been sporadically reported in speciation analysis of water samples and reference materials.

Although CE, LC and GC have been used in the speciation analysis of inorganic and organic metal species, it is noted that most studies have been performed using GC as far as speciation of organometallic compounds is concerned. While LC is very suitable for the analysis of inorganic species, CE has found its potential for the determination of both inorganic and organic metals.

7. Conclusions

Of the three techniques that employ analyte modification for speciation analysis, GC has been arguably the most successful and most frequently used approach. This is because of the technique's high separation efficiency, versatile detection methods, well-developed analyte-modification strategies, and a wide range of sample pretreatment procedures. Analyte modification has also been well demonstrated for LC analysis. However, based on reports in the past few years there has been a slight declining interest in using LC for metal speciation, possibly due to the increasing popularity of CE in this area. CE has proved to be an alternative technique of great potential because of its better compatibility to aqueous media than GC, and higher separation efficiencies for charged analytes and rapid sample throughput than LC.

8. Abbreviations

DBT	Dibutyltin
DDoT	Didodecyltin
DEL	Diethyllead
DET	Diethyltin
DMA	Dimethylarsenite
DMGe	Dimethylgermanium
DML	Dimethyllead
DMT	Dimethyltin
DPhC	Diphenylcarbazide
DPhL	Diphenyllead
DphT	Diphenyltin
DPLC	Diphenyllead chloride
DPS, DPhSe	Diphenyl selenide
EtHg	Ethylmercury
EtOEHg	Ethoxyethylmercury
HeHg	Heptylmercury
MBT	Monobutyltin
MDoT	Monododecyltin
MeBT	Methylbutyltin
MeHg	Methylmercury
MeOEHg	Methoxyethylmercury
MMA	Monomethylarsenite
MMT	Monomethyltin
MOcT	Monooctyltin
MphT	Monophenyltin
PhHg	Phenylmercury
PhMgBr	Phenylmagnesium bromide
PSC, PhSeC	Phenylselenyl chloride
TBT	Tributyltin
TeBT	Tetrabutyltin
TeET	Tetraethyltin
TEL, TELC	Triethyllead
TET	Triethyltin
TML, TMLC	Trimethyllead
TMPhT	Trimethylphenyltin
TMT	Trimethyltin
TPhL	Triphenyllead
TPL	Tripropyllead
TPhT	Triphenyltin
TPT	Tripropyltin
TTBGe	Tetrabutyldermanium
TTBT	Tetrabutyltin
TTCHT	Tetracyclohexytin
TTEL	Tetraethyllead
TTET	Tetraphenyltin
TTMGe	Tetramethylgermanium

TTML	Tetramethyllead
TTPhT	Tetraphenyltin

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