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Review

Analysis of environmental pollutants by capillary electrophoresis with emphasis on micellar electrokinetic chromatography

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Abstract

This review surveys analysis of environmental pollutants by capillary electrophoresis with emphasis on the commonly used pseudo-stationary-phase micelles. Other pseudo-stationary phases are also included for a systematic description. Manipulating the sensitivity, which is important for trace analysis, is also reviewed for environmental samples. For some typical environmental pollutants, systematic description of their separation and analysis is based on different pseudo-stationary phases. The potential of capillary electrophoresis in analysis of environmental pollutants is clearly demonstrated with a bright future. © 1997 Elsevier Science B.V.

Contents

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1. Introduction

Applications of capillary electrophoresis (CE) are exploding. Revolutionized from traditional electrophoresis, CE has been extensively used in the separation of biological macromolecules. However, the separation of neutral compounds had been prohibited until Terabe et al. developed micellar electrokinetic chromatography (MEKC) in 1984 [1]. Now more and more micelles and other pseudo-stationary phases for CE have been developed, and this renders CE fairly versatile to separate different and almost all molecules. For the analysis of environmental pollutants, CE possesses many unique advantages such as small sample volumes, high mass sensitivity, high separation efficiency, low cost of columns, easy rinsing of the column, low consumption of reagents, simple methodology and short analysis time, etc. Based on different separation principle and instrumentation, CE can provide complementary separation for gas chromatography (GC) and high-performance liquid chromatography (HPLC).

Environmental pollutants comprise a variety of compounds from inorganic anions and cations, ionizable organic compounds, moderately hydrophobic organic compounds to highly hydrophobic organic compounds. Correspondingly, different separation strategies are needed for their separation. Although this review is primarily dedicated to the topical issue of micelles as separation media in chromatography and electrophoresis, it was finally decided to include other separation media with emphasis on micelles. Micelles have been really mainly employed as separation media in CE, but other separation media cannot be absolutely divided from micelles. For example, oligomerized surfactants and macromolecules can be categorized as monomolecular pseudo-stationary phases, but they mimic micelles and are also considered as micelles with critical micelle concentration (CMC) approaching zero. Although

cyclodextrins (CDs) have definite differences from micelles, they are also monomolecular pseudo-stationary phases. Another example is hydrophobic interaction EKC in which surfactants cannot form micelles because of high concentration of organic solvents, but its separation mechanism is similar to MEKC. Furthermore, solvophobic association CZE has a separation process similar to hydrophobic interaction EKC.

In this paper, separation and analysis of environmental pollutants by CE are described mainly on the basis of different CZE buffer modifiers or pseudo-stationary phases. Manipulating the sensitivity, which is important for trace analysis, is also introduced for environmental samples. The potential of CE in analysis of environmental pollutants is clearly demonstrated with a bright future.

2. Separation strategies for environmental pollutants

2.1. Capillary zone electrophoresis (CZE) and its variants with pseudo-stationary phases

2.1.1. CZE

CZE separation is based on different electrophoretic mobilities of the analytes. It is very suitable to separate inorganic anions, cations and other low mass molecules. This belongs to the category of capillary ion electrophoresis (CIE). As this review emphasizes the use of MEKC, we skip over CIE. Some reviews are recommended: [2–4]. CZE is also suitable to separate ionizable organic environmental pollutants, it will be included in Section 4 as well for systematic description of the CE separation of typical environmental pollutants. In CZE, the buffer pH is the most important factor for separation, except for the separation of completely ionized ions. The optimum pH for the separation of analytes having very similar pK_a values has been calculated to be close to the pK_a values [5]. However, many environmental pollutants are related isomers or have very close chemical structures, so CZE often cannot provide sufficient resolution. Then various EKC techniques have been developed. CZE has also been used in modified fashions with pseudo-stationary phases.

2.1.2. CD-modified CZE (CD-CZE)

CZE separation can be modified by using neutral CDs as additives. Host–guest interaction between CDs and analytes affords changes in electrophoretic mobilities of the analytes and a chance to improve separation. This strategy has been extensively adopted in chiral separation. Actually, it was firstly used by Terabe et al. [6] to separate nitrophenol isomers. The addition of α-CD caused reversed elution order of *o*- and *p*-isomers.

2.1.3. Organic solvent-modified CZE

Basically, addition of organic solvent to CZE buffer can decrease electroosmotic and electrophoretic mobility and then subsequently increase resolution. In 1987, Fujiwara and Honda [7] investigated the addition of methanol and acetonitrile in CZE buffer on the separation of positional isomers of amino-, hydroxyl-, and methyl-benzoic acids. As a result, the separation was much improved and complete separation was achieved.

2.1.4. Solvophobic association CZE

This technique was firstly reported by Walbroehl and Jorgenson [8]. In this report, tetrahexylammonium perchlorate (THxAP) was dissolved in acetonitrile modified with varying amounts of water. When polynuclear aromatic hydrocarbons (PAHs) dissolved in this medium, they underwent a solvophobic association with the THxA ion, forming a positively charged species which then enabled their separation. The resolution was increased by increasing water content from 0 to 50% or the concentration of THxAP from 0 to 50 m*M*. This was due to more favorable solvophobic association, which was proved by Shi and Friz in a systematic study [9]. It should be noted that the electroosmotic mobility and the electrophoretic mobility had the same direction. It was also observed that pH was also an important variable. The electroosmotic mobility increased with increasing pH, leveling off at pH 10.5, while the electrophoretic mobilities of analytes remained virtually constant. Then lower pH resulted in better resolution. The type of ammonium salt was also important. Tetraheptylammonium bromide (THpAB) gave higher resolution than THxAP. The use of

tetraoctylammonium was abandoned owing to low solubility.

Recently a new solvophobic association CZE system by addition of sodium dioctylsulfosuccinate (DOSS) to water-acetonitrile solvent was developed by Shi and Friz [10]. Now PAHs moved in the opposite direction of electroosmotic flow (EOF) because they possessed negative charge after solvophobic association. Higher water content was again observed resulting in higher resolution. However, the analysis time was not very long because of higher EOF at higher water content. Higher DOSS concentration also led to better resolution, but analysis time became longer due to lower EOF at higher DOSS concentration. It was shown that DOSS was more effective than quaternary ammonium ions for larger separation windows and less interaction with capillary wall. However, quaternary ammonium is advantageous because the largest most hydrophobic molecules appear first, in the presence of much larger amounts of more polar molecules.

2.1.5. Polymer-modified CZE

Recently, neutral polymers have been extensively used as additives in CZE for the separation of biochemicals as well as diasteromers. They have also been used to separate environmental compounds. Addition of polyethylene glycol (PEG) and/or polyvinylpyrrolidone (PVP) as pseudo-stationary phases was found to be a novel separation parameter in CZE. In the separation of substituted and unsubstituted benzoic acids used as model analytes, attractive interaction with PEG was observed for the analytes with hydroxyl, amide, or amine groups [11]. This interaction was attributed to hydrogen bond formation. The concentration and the polymer length of PEG can control the net strength of the interaction and then the observed separation. In the separation of nine synthetic organic dyes [12], the electrophoretic mobility of the analytes was adjusted by the addition of PEG and PVP. Significantly improved and baseline separation was then achieved. It was found that PEG has less influence than PVP on the selectivity. It was demonstrated by cluster analysis that the relative decrease in the electrophoretic mobility of the dyes correlated with the number of benzoaromatic rings in the analyte molecules.

2.2. Micellar electrokinetic chromatography (MEKC) with various micelles

While CZE separation is based on different electrophoretic mobilities of charged analytes, MEKC was developed in 1984 by Terabe et al. [1] for the separation of both neutral and ionizable analytes. In MEKC, ionic surfactants are added to the buffer to form micelles, then the MEKC system is composed of an aqueous phase and a micellar phase. Under applied voltage, the aqueous phase has an electroosmotic mobility u_{eo} and the micellar phase has an electrophoretic mobility u_{ep}. Because u_{ep} is less than u_{eo} with an opposite direction, they all move toward detector, resulting in a fast-moving aqueous phase at a velocity of v_{eo} and a slow-moving micellar phase at velocity of v_{mc}. Neutral compounds experience chromatographic partition between the two phases leading to different retention. Resolution equation was derived by Terabe et al. in 1985 [13].

$$R_s = \frac{\sqrt{N}}{4} \cdot \frac{\alpha - 1}{\alpha} \cdot \frac{k_2'}{k_2' - 1} \cdot \frac{1 - t_o/t_{mc}}{1 + (t_o/t_{mc})k_1'}$$

Where N is the number of theoretical plates, α is the selectivity factor equal to k_2'/k_1', k' is the capacity factor, t_o and t_{mc} are the migration time of water and micelle, respectively. The equation clearly shows that resolution in MEKC can be manipulated by three parameters: separation efficiency, N, capacity factor, k', and retention window, t_o/t_{mc}. It can be derived from the equation that, unlike chromatography, larger k' of adjacent peaks cannot lead to better resolution in MEKC. Nevertheless, for a given value of t_o/t_{mc}, there is an optimum value of k' that maximizes resolution which is equal to $(t_{mc}/t_o)^{1/2}$ [14,15]. On the other hand, for a given value of k', the wider the retention window is (i.e., the smaller the ratio t_o/t_{mc}), the larger the resolution is. A higher separation efficiency can always result in better resolution.

Sepaniak and Cole [16] had intensively investigated the parameters affecting efficiency in MEKC. While many parameters, such as longitudinal diffusion and thermal dispersion, affecting efficiency in MEKC perform alike in CZE, resistance to mass transfer has a significant effect. High surfactant concentration where the intermicelle distance is

decreased can result in higher efficiency. The micelle polydispersity also affects efficiency [17], which is significant only for analytes having large k'. The effect can be leveled out by the dynamic exchange of the micellar size.

2.2.1. Use of sodium dodecyl sulfate (SDS) micelles

Investigation by Terabe and co-workers [1,13,18,19] showed that, at constant voltage, t_o remained constant irrespective of SDS concentration, while t_{mc}, k' and current increased with an increase in SDS concentration [13]. The t_o/t_{mc} decreased from 0.28 for 30 m*M* SDS to 0.18 for 150 m*M* SDS. The ratio t_o/t_{mc} remained constant irrespective of applied voltage and current. When the pH of the buffer was varied from 5.5 to 9, no significant change in u_{eo} and u_{ep} was observed, leading to a constant t_o/t_{mc} [18]. However, when the pH was below 5.5, u_{eo} decreased with decreasing pH while u_{ep} was also constant [19]. Actually, t_o/t_{mc} was negative when the pH was below 5.5, which meant that not all analyte can be detected in the cathode end. These results clearly suggested that the SDS micellar system is more suitable for separating moderately water-soluble compounds that have k' values in the range of 1–5 and the resolution can only be less manipulated by changing the concentration of SDS. Hydrophobic compounds having a k' value larger than 5 are almost totally incorporated in micelles due to the pronounced unbalance in the hydrophile-lipophile character of SDS.

2.2.1.1. Use of coated column

Attempts to change the retention window of the SDS micellar system was first conducted by coating the fused-silica capillary inner wall [18,20]: with the non-polar polymethylsiloxane coating the EOF was increased giving shorter analysis time and poorer resolution, but EOF decreased with the polar PEG coating resulting in much longer analysis time and improved resolution.

2.2.1.2. Use of organic solvent modifier

Resolution as well as selectivity can be altered by the addition of organic solvents to buffer [21–23]. The organic solvents modify the retention mechanism by shifting the partition equilibrium of an analyte towards the bulk aqueous phase because it decreases the polarity of the buffer. Selectivity is enhanced by the addition of organic solvents because the shift in equilibrium is greater for hydrophobic analytes compared to hydrophilic ones. However, the addition of an organic solvent at high percentages above 15% drops column efficiency because of micelle polydispersity, and migration times become prohibitive. Some organic solvents, such as methanol and isopropanol, were found to extend the retention window because they can interact with the capillary inner wall and, as a result, slowed down EOF, while acetonitrile and dioxane did not appreciably affect EOF [21,24]. Sepaniak and co-workers [22,23] were the first to report the use of gradient elution in MEKC. It can shorten the analysis time while maintaining the resolution.

2.2.1.3. Use of urea as modifier

Terabe et al. [25] first reported the successful separation of hydrophobic compounds, such as PAHs, by using urea as modifier in the SDS micellar system. The log k' values decreased linearly with increasing concentration of urea. This effect was explained in terms of a diminished water structure (so-called 'iceberg') around a hydrophobic analyte by the addition of urea to the aqueous solution. The t_o/t_{mc} also decreased from 0.269 to 0.175 at 8.0 *M* urea because t_{mc} increased more than t_o.

2.2.1.4. Use of CD modifier (CD-MEKC)

Addition of a neutral CD in the SDS micellar system was first reported by Terabe et al. for the separation of highly hydrophobic compounds [26]. CD-MEKC has also been extensively used in chiral separation. A neutral CD has a hydrophilic outside surface, which means that they do not interact with the micelle and migrate with the bulk solution, behaving as another pseudo-stationary phase. A water-insoluble hydrophobic analyte is partitioned between the micelle and CD phases resulting in a decreased k'. It was observed that the use of γ-CD was more effective than β-CD, though β-CD has a cavity of diameter very suitable for the inclusion of the analytes. This was explained by taking into consideration the fact that an SDS molecule was probably co-included with a hydrophobic molecule. Further investigations by Terabe et al. and other

authors [27–30] supported this conclusion. The use of α-CD was less effective and resulted in higher k' values than β-CD [29]. Though the use of hydroxypropyl-γ-CD (HPγCD) resulted lower k' than γ-CD, the separation became worse because of the narrower range in k' [30]. Copper and Sepaniak [30] theoretically calculated the energies for various host–guest combinations, and then the corrected elution order was predicted. Jinno and Sawada concluded, by the relationship between log k' and the hydrophobicity log P of PAHs, that the hydrophobic interaction between CD and PAHs can mainly control the migration of PAHs when using a coated capillary [31], while it was not the case when using an uncoated capillary [32].

2.2.1.5. Use of mixed micelles

The addition of neutral surfactants such as Brij 35 [33] and PEG 400 monolaurate [34,35] to SDS micelles can change the selectivity, but shorten the retention window. Recently, Ahuja et al. [36] reported that equal but opposite u_{ep} and u_{eo} values were obtained at a specific Brij 35 concentration mixed with 20 m*M* SDS, thereby producing a 'stationary' micellar phase. Infinite elution ranges were obtained at pH 7.0 with 30 m*M* Brij 35 using a coated capillary, and at pH 6.2 with 12 m*M* Brij 35 using an uncoated capillary.

2.2.1.6. Use of SDS homologs

Using surfactants other than SDS was another way to alter resolution and selectivity. SDS homologs such as sodium tetradecyl sulfate (STS) [13] and sodium decyl sulfate [37] were evaluated. STS exhibited a narrower retention window than SDS, and sodium dodecyl sulfate enlarged the retention window but resulted in irreproducible times.

2.2.2. Use of alkyltrimethylammonium micelles

Crosby and El Rassi [38] intensively evaluated a series of alkyltrimethylammonium (C_{10}-, C_{12}-, C_{14}-, C_{16}-) chloride and bromide surfactants for MEKC. With these cationic micellar phases, t_o was largely unaffected by the length of the alkyl chain of the surfactant, while t_{mc} increased with decreasing the length of the alkyl tail. The net result was an increase in the retention window as the size of the alkyl tail of the surfactant decreased. The retention window stayed almost the same when the micelle counterions were changed from chloride to bromide, pH changed from 4.5 to 9.0 or the surfactant-ionized head changed from ammonium to sulfate (i.e., dodecyltrimethylammonium chloride (DoTAC) and SDS). At constant micellized surfactant concentration, the capacity factors of neutral analytes increased linearly with increasing alkyl chain length of the surfactant.

2.2.3. Use of bile salts micelles

Bile salts exhibit the useful chromatographic properties: to form chiral micelles. This makes them useful in recognizing specific enantiomeric conformations. Further, bile salt monomers are more polar than SDS, and lead to a general reduction of k' values of hydrophobic compounds. This is particularly advantageous for the separation of PAHs. Also, the bile salt micelle resembles a reversed or inverted micelle, so it can tolerate a high concentration of organic solvents. Sodium cholate with methanol were successfully used to separate PAHs [39].

2.2.4. Use of in situ charged micelles

El Rassi and co-workers [40–47] recently introduced several types of in situ charged micelles for MEKC. These new micellar phases are essential anionic complexes formed between alkyl– or steroidal–glycoside surfactants and borate anions. In situ charged micelles possess many unique and attractive features. (A) The surface charge density and then the retention window increase substantially with an increase in pH (pH>8.0) or borate concentration (25–400 m*M*), but the k' value of an analyte remained constant irrespective of pH and borate concentration. (B) Due to the more balanced hydrophile–lipophile character, the k' values obtained with them are lower than those obtained with alkyl ionic surfactants. This makes them useful for separating more hydrophobic compounds. (C) Some in situ charged micelles have chiral selectivity [46].

A study of homologous surfactants [45] revealed that, at constant micellized surfactant concentration, the retention window remained constant as the length of the surfactant alkyl tail increased when the molar ratio of surfactant:borate was maintained the same (1:1). In addition, the k' values of neutral analytes increased linearly with increasing alkyl chain length

of the surfactant. The nature of the sugar head groups of these surfactant, i.e., sucrose, β-D-glucopyranoside, β-D-maltopyranoside and glucamide were also evaluated for their influence on the retention window [42]. Nonanoyl-N-methylglucamide (MEGA 9) has 2- or 3-fold greater affinity for borate than *n*-octanoylsucrose (OS), octyl-β-D-glucopyranoside (OG) and octyl-β-D-maltopyranoside (OM) because it possesses an acyclic sugar residue which allows the hydroxyl groups to change their conformation. Under favorable conditions, the u_{ep} value of MEGA 9 can be increased very close to the u_{ep} of SDS. However, the u_{eo} value of these surfactant systems decreased with an increase in pH or borate concentration, due to higher ionic strength or viscosity, the peaks then tended to appear late in comparison with SDS. Butylboronate was also used instead of borate to form in situ branched and charged surfactants with alkylglucosides [43]. The butylboronate can also be incorporated into the micelle, decreasing CMC and increasing the hydrophobicity of the micelle. The net result is an in situ charged micellar entity whose hydrophobic character is dynamically altered.

Recently, it has even been reported that the MEGA surfactants can be used at neutral and acidic pH to 3.5 [47], which is not the case for SDS micelles, as indicated above. This is advantageous for the separation of acidic compounds, which can experience partial association in acidic pH. The studies which were performed at high borate concentration, up to 1000 m*M*, suggested the formation of polyborates, which increased the ionic strength and viscosity of the buffer without further increasing the surface charge density of the micelle. This led to decreased u_{eo} and u_{ep} values at increasing borate concentration, with a net increase in the retention window. The u_{eo} and u_{ep} values increased slightly from pH 3.5 to 6.5 by almost the same factor with an almost constant retention window.

2.2.5. Use of disodium 5,12-bis(dodecyloxymethyl)-4,7,10,13-(tetraoxa)-1,16-hexadecanedisulfonate (DBTD) micelles

Tanaka et al. [48] reported the use of DBTD (a surfactant with two ionic groups and two lipophilic chains) micelles as a pseudo-stationary phase for MEKC. Compared with the widely used SDS, this new surfactant exhibited different selectivity and gave lower k' values and a wider retention window. MEKC can be performed at surfactant concentrations almost one order of magnitude lower because of the low CMC.

2.2.6. Use of sodium 10-undecylenate (SUA) and sodium 10-undecylsulfate (SUS) oligomers

Palmer and co-workers [49,50] developed a monomolecular pseudo-stationary phase, SUA oligomer, for MEKC. The oligomer affords high stability in the presence of organic solvents, and this enables the retention to be adjusted by simple addition of organic solvents, such that hydrophobic compounds can be analyzed. Its high electrophoretic mobility when employed in mixed mobile phases also provides a wide retention window. The electrophoretic and chromatographic properties of the oligomeric phase indicate a change in the structure of the oligomer with changes in solvation. This results in a non-linear plot of log k' against the content of organic solvent, which is not the case with reversed-phase liquid chromatography (RPLC). This approach is limited by the solubility of the oligomer, which begins to precipitate at ca. 60% methanol or 55% acetonitrile. Other problems, such as increasing retention times and cloudiness in the anodic buffer after several runs, can be resolved by employing fresh buffer for each run. Recently, SUS oligomer was also synthesized and used as a pseudo-stationary phase for MEKC by Palmer and Terabe [51]. The CMC of this molecular surfactant was confirmed to be zero by a plot of k' versus the concentration of the surfactant with intercepts approaching zero. This oligomer is also more stable in mixed mobile phase than SDS micelles and has a higher electrophoretic mobility and thus a wider retention window. The SUS oligomer is superior to SUA oligomer because it can be used at pH values less than 8 and no cloudiness in the anodic vial was observed in any cases. This is benefited by the strong acidic character of the sulfate group.

2.2.7. Use of butyl acrylate–butyl methacrylate–methacrylic acid copolymers sodium salts (BBMA) micelles

BBMA is a group of high molecular surfactants. They were utilized as pseudo-stationary phase by

Ozaki et al. [52]. The separation selectivity was different, especially for naphthalene derivatives in comparison with SDS micelles. The retention window became wider with increasing pH from 4.8 to 6.8 and was almost constant between 7 and 9. The k' decreased with an increase in pH. The retention window and k' increased with an increase in the content of methacrylic acid in the polymer. The high efficiency suggested that the distribution of the molecular mass of BBMA did not cause a serious loss of efficiency.

2.2.8. Use of dendrimers

Starburst dendrimers (poly(amidoamines): SBDs) were successfully used as pseudo-stationary phases by Tanaka et al. [53,54]. The SBDs were prepared by the Michael addition of a N–H group of a core molecule (*p*-xylylenediamine = X or ammonia = A) to the double bond of methyl acrylate first (a SBD of half-generation), and then subsequent aminolysis with ethylenediamine (a SBD of full-generation). The synthesis procedure was then repeated several times. By hydrolyzing the ester group of half-generation SBDs, a carboxylate form of SBD functioning similar to anionic micelles was obtained, whereas full-generation SBDs functioned similarly to cationic micelles. The effects of pH on EOF were determined for both, with results indicating that EOF in the direction of the cathode was above pH 7 for half-generation SBDs, and that EOF in the direction of the anode was below pH 11 for full-generation SBDs.

It was observed that binding of analyte increased with the size of the SBDs, leading to an improved separation with SBDs of higher generation. Differences in selectivity between the full-generation and half-generation SBDs were also observed. The SBD system also showed different selectivity from MEKC with either SDS or cetyltrimethylammonium chloride (CTAC) micelles. Generally, the SBDs showed little selectivity for alkyl groups and clear preference for aromatic compounds, especially for rigid, planar PAHs. However, the k' values for aromatic compounds with the SBDs were much smaller than k' values with micelles of a similar size. The k' for naphthol was 0.61 for 5 m*M* SBD(X, G = 4.0) at pH 5.0, compared with 3.1 for 30 m*M* SDS at pH 7.0. The separation efficiency was slightly lower. Size monodispersity and slow equilibration associated with polymeric pseudo-stationary phases can work against each other affecting the efficiency.

Half-generation SBD(X, G = 3.5) was partial alkylated [55]. The resulted SBD(X)-C_8 and SBD(X)-C_{12} possessed six and 14 alkyl groups per molecule on average, respectively, out of 32 terminal groups on the SBD. SBD(X)-C_8 and SBD(X)-C_{12} showed a large increase in retention and separation compared with the parent SBD. However, SBD(X)-C_{12} was too hydrophobic and showed a similar retention to SDS micelles. SBD(X)-C_8 was less hydrophobic and contributed to smaller partition coefficients for hydrophobic compounds. In the presence of methanol, SBD(X)-C_8 and SBD(X)-C_{12} resulted in a wide retention window at high methanol content, even an infinite retention window at a content of above 60–80%. SBD(X)-C_{12} can even maintain its hydrophobicity at a content of 90% methanol, which is advantageous for separating PAHs. The results, showing a nearly linear relation between log k' and methanol content for SBD(X)-C_{12}, indicated the possibility for the optimization of separation by simply changing the methanol content to manipulate the analyte retentions as in RPLC.

Diaminobutane-based poly(propyleneimine) dendrimers were also successfully used as pseudo-stationary phases by Muijselaar et al. [56]. The dendrimers were prepared by the Michael addition of a primary amine to acrylonitrile followed by the heterogeneously catalyzed hydrogenation of the nitrile to primary amine. These nitrile-terminated dendrimers were subsequently transformed into carboxylic acid-terminated dendrimers by treatment with hydrochloric acid and then functioned similar to anionic surfactant micelles. These dendrimers were successfully used to separate some aromatic compounds and different selectivities from SDS micelles were observed.

2.2.9. Use of ionenes

Some preliminary experiments were conducted to use [3,22]-ionene as pseudo-stationary phases [57]. The [*x*,*y*]-ionenes are some cationic polyelectrolytes of molecules consisting of dimethylammonium chain centers interconnected by alternating alkyl chain segments containing *x* and *y* methylene groups. Such hydrophobic ionenes can form intramolecular aggre-

gates and function as micelle-mimetic agents. However, they are soluble and stable in solutions containing a very high percentage of organic solvents. Successful separation of naphthalene and fluorene was achieved with 2.4 ppm [3,22]-ionene in 20% (v/v) methanol.

2.3. Other kinds of electrokinetic chromatography (EKC)

2.3.1. Hydrophobic interaction EKC

In 50% acetonitrile, 50 m*M* SDS or 20 m*M* cetyltrimethylammonium bromide (CTAB) were successfully used as pseudo-stationary phases to separate alkyl (C_{18}, C_{20}, C_{22}, C_{24}) aryl ketone homologs [58]. Micelles were not believed to form because of the high concentration of organic solvent. The separation mechanism was attributed to hydrophobic interaction between surfactants and alkyl aryl ketones. With CTAB, EOF was suppressed and the free CTAB monomers migrated towards the detector which was different from MEKC using CTAB micelles.

2.3.2. CDEKC

Charged CD derivatives can be used instead of surfactants in MEKC as pseudo-stationary phases. In this case, only host–guest interaction between the CD derivative and the analyte operates as a distribution process. By using carboxymethyl-β-CD (CMβCD), Terabe et al. [6] successfully separated alkyl benzoates, isomers of cresol, nitroaniline, chloroaniline, dinitrobenzene, nitrophenol, xylidine and xylenol in 1985. The retention window t_o/t_{CD} was reported to be equal to 0.7, which is much higher than that in the SDS micellar system. In the last 2 or 3 years, CDEKC has been used increasingly for chiral separation.

2.3.3. CD-CDEKC

Using neutral and charged CD mixtures as pseudo-stationary phases was first reported for chiral separation. The separation was effected on the basis of differential partition of analytes between the two relatively moving CD pseudo-stationary phases. The system was soon evaluated for the separation of PAHs [59,60]. Two neutral CDs, HPβCD and methyl-β-CD (MβCD), and two negatively charged CDs, CMβCD and sulfobutyl ether-β-CD (SBβCD), in different combinations were evaluated by Szolar et al. [60]. The use of 30 m*M* HPβCD and 45 m*M* CMβCD was successful in quantitatively separating a mixture of PAHs. The order of migration for the PAHs was roughly largest-to-smallest molecule, indicating a general trend where large molecules partitioned more to HPβCD, whereas smaller molecules preferred CMβCD. The separation was somewhat serendipitous since the use of MβCD instead of HPβCD was unable to achieve the same degree of separation at any concentration ratio. The use of 20 m*M* MβCD and 15 m*M* SBβCD was also successful in quantitatively separating the above mixture of PAHs. The order of migration was different from the HPβCD–CMβCD system, with a trend where smaller molecules partitioned to the MβCD and larger molecules to the SBβCD, though the trend was not as rigidly followed as in the previous case. As before, the separation was somewhat serendipitous as replacing MβCD with HPβCD resulted in the inability to separate benzo[*a*]pyrene (BaP) and pyrene. In both systems, the separation efficiencies of the PAHs which emerged last were lower owing to the polydispersity of charged CDs. The SBβCD–MβCD system was superior to the HPβCD–CMβCD system because a lower SBβCD concentration was used. Then lower ionic strength and, consequently, shorter analysis time, lower current and excellent reproducibility resulted. A 35-m*M* SBβCD, 15-m*M* MβCD system was soon extended for analysis of the 16 PAHs listed by United States Environmental Protection Agency (US EPA) as priority pollutants, and satisfactory separation was achieved in under 20 min [61]. Sepaniak et al. [59] also developed a system containing 8 m*M* β-CD, 1 m*M* γ-CD and 10 m*M* CMβCD with 30% methanol for the separation of anthracene, pyrene, chrysene, and BaP.

The use of CDs exclusively, without micelles, resulted in dramatically reduced sensitivity, compared with MEKC, to parameters such as temperature and separation potential. The method of development for this system is quite straightforward. The only choices to be made are the CD derivatives and concentrations to be used. However, CD-derivative combinations must be tested empirically with each analyte mixture to determine the applicability for separation, although an initial choice may be

assisted by previous knowledge of inclusion complex properties.

2.3.4. Calixarene EKC

Shohat and Grushka [62] reported initial results that demonstrate the value of calixarenes as a pseudo-stationary phase. Calixarenes are macrocyclic oligomers having the shape of a conical case. Their inner cavity can accommodate various guest molecules, similar to other macrocyclic molecules, such as crown ethers and CDs. The separation of chlorinated phenols, benzenediols and toluidines was achieved by using *p*-sulfonate calix[6]rene when the analytes were uncharged and largely unresolved. Retention behaviors were also investigated.

2.3.5. Microemulsion EKC

Miroemulsions are prepared by mixing surfactant, oil (hydrocarbons), cosurfactant (always medium alkyl chain alcohol) and water. Similar to micelles, microemulsions are also thermodynamically stable aggregates. Oil-in-water microemulsions were first used as pseudo-stationary phases by Watarai [63]. Later the fundamental characteristics of microemulsion EKC were studied in comparison with MEKC for the separation of some model mixtures, including phenol derivatives and six phenylurea herbicides, by Terabe et al. [65] and Song et al. [34]. Microemulsion EKC is superior to MEKC from the viewpoint of an easily extended retention window through an increase in the surfactant concentration. The k' values in microemulsion EKC were observed to be lower for phenylureas than MEKC [34]. Microemulsion EKC can also provide some different selectivities from MEKC.

2.3.6. Suspension EKC

Bachmann et al. [66] reported the use of a suspension of reversed chromatographic particles with a diameter of 1.5 μm as a pseudo-stationary phase. A buffer containing SDS was used to coat the particles and form a stable suspension. The velocity of the particles (17.7 cm/min) was larger than EOF and in the opposite direction. To avoid problems arising with optical detection (light scattering of the particle), a discontinuous experiment set-up was used. The separation of nine phenol derivatives was presented. The capacity factor of the chromatographic separation was varied by changing the particle concentration, independent of other parameters.

2.3.7. Ion-exchange EKC

In CZE, the electrophoretic separation of a mixture having very similar electrophoretic mobilities over a wide pH range, such as isomers of strong acids and bases, is almost impossible. Terabe and Isemura [67] developed an ion-exchange EKC with polymer ions additives such as poly-(diallyldimethylammonium chloride) (PDDAC) and (diethylamino)ethyldextran (DEAE-dextran) to solve this problem. Isomers of naphthalenesulfonate and naphthalenedisulfonate dynamically interacted with the polymer cation differently, resulting in apparently different electrophoretic mobilities, and successful separation.

3. Manipulating sensitivity

Currently the most often used detection technique in CE is UV absorbance with limit of detection (LOD) below the order of 10^{-6} *M*. It is not sensitive enough for environmental trace analysis. Even so, CE still has impressive mass sensitivity which can compete with the best GC system because of very low injected sample volume. Now various approaches have been developed to enhance concentration sensitivity for CE. Albin et al. [68] presented a review in this field. So, in this section, we will only introduce some techniques which have been used in environmental analysis.

3.1. Use of detection cells with extended optical path length

In CE, the optical path length for detection is limited by the narrow diameter of the capillary column due to on-column detection. Many authors [68] have designed various special detection cells, such as Z-cells, rectangular cells, multireflection cells, along the column end cells, and bubble cells, etc., to extend the optical path length. Although these cells have enhanced sensitivity from several to several tens of folds, they have also posed difficulty in the manufacture and manipulation. They can even

decrease separation efficiency. The bubble cell is now commercially available and has been used in environmental analysis with an enhanced sensitivity of more than three-fold [61,69].

3.2. Use of alternative detection techniques

Laser-induced fluorescence (LIF) can provide LOD several orders lower than UV absorbance. PAHs are natively fluorescent and suitable for LIF detection. Imasaka et al. [70] first designed an LIF detector for PAHs with a blue semiconductor laser. The LOD for 1-aminoanthracene was 1×10^{-8} *M*. However, the emission wavelength of the laser is 415 nm, which is too long for excitation of many PAHs. Later, they [71] used a He–Cd laser for excitation and obtained a LOD of 7×10^{-9} *M* for 9,10-dimethylanthracene. The He–Cd laser has a strong emission line at 325 nm, which is better matched with the optical absorption of PAHs. Sepaniak and co-workers [72] also designed a LIF detector using a He–Cd laser for detection of PAHs. Moreover, a commercially available instrument for capillary electrophoresis, P/ACE 5000 (Beckman, Fullerton, CA), included a LIF detector with a HeCd laser. It was used to monitor PAHs with detection limit typically in the low ppb range [60,61]. Nie et al. [73] even reported a LOD as low as 6×10^{-11} *M* for 2-methyl- and 9-methylanthracene (with maximum optical absorption at 254 nm) by using deep-UV laser excitation at 257 nm. A close match of excitation wavelength and optical absorption led to significant improvement in the achieved detection limit. Moreover, careful adjustment of the optical devices to reject a high fluorescence background was also important, especially for deep-UV LIF detection where the fluorescence background is even higher. A high numerical aperture microscope objective (minimal autofluorescence and high-UV transmission) was coupled with an adjustable precision slit in a confocal configuration, i.e., positioning the sample and the slit exactly at the two focal points of the objective. By adjusting the slit to exactly match the image size, the intense capillary wall fluorescence was efficiently separated from the analyte signal. Brumley et al. [74] also demonstrated LIF detection of erythrosin B dye from spiked soil.

However, most environmental pollutants are not intrinsically fluorescent, in this case LIF cannot be used until a suitable fluorophore is introduced into their molecules. Fortunately, a large section of chemical literature covers fluorescent labeling techniques. In 1995, Jung and Brumley [75] developed a novel derivatization procedure for LIF detection of phenoxy acid herbicides. In this procedure, the acids were activated by hydroxybenzotroazol (HDBT) and diisopropylcarbodiimide (DIC) and reacted with 5-(aminoacetamido)fluorescein in N,N-dimethylformamide (DMF) at ambient temperature. The reaction was complete for most analytes after 3 h, whereas it took 18 h for MCPB and 2,4-DB. The many side products yielded as a result of the large excess of the derivative reagent did not interfere, because their peaks were fortunately concentrated in the first part of the electrophorogram. The LOD was 0.5 ppb. However, handling and derivatization for practical reasons required a minimum of ca. 1 ng herbicides. Mechref and El Rassi [76] also developed a derivatization procedure for LIF detection of phenoxy acid herbicides. In this procedure, the acids reacted with 7-aminonaphthalene-1,3-disulfonic acid (ANDSA) in 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) aqueous solution at ambient temperature. The reaction was complete after 2 h stirring. This derivatization was very quantitative (99.7% yield) and produced stable derivatives and no side products. The LOD was 0.2 ppb.

An alternative to derivatizing non-fluorescent analytes is the use of indirect LIF detection. Actually, indirect UV detection is widely used in CIE. Briefly, indirect detection is a result of decreased signal from the fluorescing/absorbing reagent in running buffer, which is caused by displacement of the reagent with non-fluorescing/absorbing analytes. Indirect LIF detection for capillary separation was reviewed by Yeung and Kuhr [77]. Recently, Chao and Whang [78] performed indirect LIF detection of 11 phenols listed by the US EPA as priority pollutants with 1 m*M* fluorescein in 15 m*M* sodium borate buffer at pH 9.9. The displacement was based on local charge neutrality. The LOD was in the 10^{-6} to 10^{-7} *M* range. Indirect LIF detection is also possible with MEKC. The sensitivity relies upon the different quantum efficiency of the fluorescent reagent in the

two phases. Generally, the quantum efficiency of the fluorescent reagents is significantly enhanced in the micellar phase, and the displacement of it from the micellar phase to aqueous phase by the analytes caused a concomitant reduction in the fluorescence signal. Quenching of the fluorescent reagent by some analytes can enhance the sensitivity. Amankwa and Kuhr [79] realized indirect LIF detection of phenols by MEKC with quinine sulfate as fluorescent reagent, while Swaile et al. [80] achieved this with 1-anilinonaphthalene-8-sulfonate. Indirect fluorescence detection of herbicides was reported by Smith and El Rassi [41] using N-phenyl-1-naphthylamine as fluorescent reagent. Recently, Kennedy et al. [81] performed indirect LIF of high explosives using MEKC with fluorescein and rhodamine B as fluorescent reagents. However, the achieved sensitivity was poor, lower than direct UV detection. This can be attributed to the less effective displacement mechanism.

Amperometric detection is advantageous because the LOD remains constant irrespective of the inner diameter of the capillary column. In amperometric detection, LOD can reach 10^{-8} M [64]. Unfortunately, this type of detection has not been fully exploited in the analysis of environmental pollutants. Gaitonde and Pathak [82] detected phenol and chlorophenols in wastewater by amperometric detection. Mass spectrometry (MS) is one of the most powerful detection methods for obtaining structural information on separated analytes. Determination of organophosphonic acids and sulfonylurea herbicides using ion spray MS was demonstrated by Kostiainen and Bruins [83], Carcia and Heion [84], respectively. However, CE–MS is still not generally considered for routine analysis. The major limitation is its relatively poor concentration sensitivity. The use of non-volatile buffer is generally avoided, and compromises are often made in choosing appropriate separation conditions. Moreover, the coupling of MEKC with MS is difficult due to the presence of high concentration SDS in the running buffer, which can cause low ionization efficiency. However, current research is rapidly changing this situation by developing new CE–MS interfaces, more sensitive MS instrumentation and novel pseudo-stationary phases.

3.3. On-column preconcentration by sample stacking

Sample stacking occurs when the injected sample has a lower ionic strength than the running buffer. Then the applied voltage is not distributed uniformly along the capillary in the two regions. The field strength is higher in the sample zone, which results in higher migration velocity of an analyte ion, whereas the field strength is lower in the buffer zone, which results in lower migration velocity of the analyte ion. The analyte ion will then stack up at the stationary boundary between the two zones, thereby increasing its concentration. Sample stacking in CZE was reviewed by Chien and Burgi [85] and Song et al. [86].

In the simplest form of sample stacking, a large plug of sample dissolved in water is introduced hydrodynamically into the capillary; the LOD can thus be improved by a factor of 10. However, if the sample zone is too long, laminar flow, which originates from the different local EOF caused by the non-uniform distribution of the applied voltage, will occur and de-stack the stacked analyte ion. Chien and co-workers provided an elegant and simple method for removing the relatively large sample matrix zone during or after the stacking stage by taking advantage of EOF [85,86]. For anionic analytes, this involves field polarity reversion after the capillary is filled with sample. Then the sample matrix is pushed out of the capillary from the injection end by EOF, while anionic analytes move with a very high velocity towards the boundary between the sample and the buffer. The field polarity is switched back when the boundary is approaching the injection end of the capillary, which is indicated by the current approaching 95% of its highest value, i.e., the current when the capillary is solely filled with buffer. The LOD can then be improved by a factor of 200. The preconcentration of cationic analytes is similar, but demands a reversed electroosmotic flow. Sample stacking can also be performed by electrokinetic injection with LOD improved by a factor of 1000, however the reproducibility is very poor.

Nielen [87] used large-volume sample stacking with matrix removal as an on-column preconcen-

tration technique in the analysis of phenoxy acid herbicides. The reproducibility in this procedure was compared to normal injection, giving a result of typically 4.0 vs. 1.2% for peak area and no differences for migration time. It was indicated that this preconcentration technique requires samples having a relatively low and reproducible conductivity. A sample pretreatment procedure involving C_{18} membrane disks for simultaneous filtration and solid-phase extraction (SPE) clean-up was then developed. The achieved LODs were 50 ppt for drinking water and 100 ppt for river water, where sample stacking contributed an enrichment factor of 200 and SPE only 20. Song et al. [88,89] systematically investigated normal sample stacking with hydrodynamic injection, and proved that the ionic strength of samples had significant effect on sensitivity. Higher ionic strength of a sample resulted in high LOD, and lower ionic strength of a sample led to lower LOD. Carneiro et al. [90] performed sample stacking by electrokinetic injection in the analysis of cationic herbicides. The achieved LOD was 31 ppb for crop water. It was indicated that sample matrix effected the accuracy and precision of the determination. Oxspring et al. [91] compared large-volume sample stacking after matrix removal with sample stacking by electrokinetic injection in the analysis of reactive dyes. Respective reproducibility of 3.3 and 60% was obtained. Recently, large-volume sample stacking with matrix removal was used by Carro-Diaz et al. [92] in the analysis of methylmercury with a LOD of 12 ppb. It was also used by Turnes et al. [69] in the determination of pentachlorophenol in tap water with a LOD of 60 ppt, where an enrichment factor of 33 was attributed to SPE and 3 to bubble cell.

Sample stacking can also be used in MEKC. For ionic analytes, the procedure is the same as in CZE. However, for neutral analytes the procedure has to be modified a little. Liu et al. [93] reported the accomplishment of sample stacking of neutral analytes by dissolving them in a micellar solution with a low concentration just above CMC. The micelles were stacked up under applied voltage, and caused stacking of neutral analytes. Normal and reversed-field polarity was used and produced 75–85-fold increase in sensitivity for 1,2,4,7- and 1,2,4,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Recently, Susse and Muller [94] used sample stacking with reversed-field polarity as an on-column preconcentration technique for the analysis of pesticides by MEKC. LODs between 0.01 and 0.1 ppb were achieved, where 30-fold preconcentration was attributed to sample stacking and 250-fold to SPE.

3.4. On-line preconcentration by isotachophoresis (ITP)

Unlike CZE, ITP is realized in a discontinuous buffer system rather than a continuous one. The analyte ions migrate between a leading ion having the highest mobility and a terminating ion having the lowest mobility in the buffer system. Under applied voltage, the analyte ions stack up and migrate as consecutive zones, according to their mobility, between the leading and terminating ions. From the point of view of trace analysis, ITP can be considered a good preconcentration technique for CZE. Kaniansky et al. [95] constructed a column-coupling configuration CE equipment for on-line ITP-CZE analysis of paraquat and diquat in tap and lake water. A careful selection of the leading, terminating ions and counterion (potassium, tris and citrate) gave a high sample load of 90 μl. The herbicides were then analyzed with a LOD of 1×10^{-9} *M*. Despite the impressive LOD, the on-line coupled ITP–CZE instrument is complicated and not commercially available. Recently, ITP–CZE has been shown to be capable of being performed in a single capillary by taking advantage of a counterflow. Moreover, ITP can also be performed before CZE separation as a transient preconcentration step in commercial CE instruments by carefully selecting the CZE electrolyte as a leading or terminating electrolyte to form an ITP buffer system with an additional electrolyte. These two techniques were recently reviewed by Mazereeuw et al. [96].

3.5. Preconcentration by solid-phase extraction (SPE)

SPE is a preconcentration technique capable of providing concentration factors of $10–10^6$, especially effective for aqueous samples. A large section of off-line preconcentration techniques now covers

SPE, which can be transferred to CE. Cai and El Rassi [97] even described the use of an on-line coupled C_{18}-coated column for performing SPE preconcentration of prometon and prometryne before CZE separation. However, because of the low amount of the wall-coated stationary phase, the enrichment factors were limited to 10–35-fold.

4. Separation and analysis of environmental pollutants

4.1. Polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorodibenzo-p-dioxins (PCDDs)

Primarily PAHs, PCBs and PCDDs appear to be singularly unsuited to CE analysis because of their similar and extreme hydrophobicity. However, this problem has been well solved with many recently developed separation strategies (see Section 2). These separation strategies have been mainly devoted to the separation of PAHs, and a comparison is demonstrated in Table 1. Some very good and excellent separations are illustrated in Fig. 1 Fig. 2 Fig. 3 Fig. 4.

The method developed by Bruggemann and Freitag [98], which is described as No. 4 in Table 1, has a LOD of 10 ppm. It was used to quantify the PAH content of soil samples (heath sand) deliberately contaminated with a mixture of standard PAHs. The soil was extracted with cyclohexane and acetonitrile for analysis. The quantification was unsatisfactory, as only 45–90% of original amount was recovered. Further efforts need to be directed towards the optimization of the extraction procedure. The method developed by Brown et al. [61], which is described as No. 18 in Table 1, has LODs typically in the low ppb level. Contaminated soil was extracted using CO_2 supercritical fluid extraction (SFE), and the extract was provided in dichloromethane, methanol, or a 50:50 mixture. The extracts were diluted 50-fold in 60:40 methanol–water and analyzed. HPLC was used to verify the concentration of six components in the sample, giving fairly good agreement, though with a possible systematic underestimation of the concentration by the CE method.

There are two available reports concerning the separation of PCBs. Terabe et al. [26] successfully separated 11 isomers of trichlorobiphenyls by CD-MEKC using 100 m*M* SDS, 60 m*M* γ-CD and 2 *M* urea at pH 8.0. In the other report, Marina et al. [103] successfully separated 12 of 14 commercially available chiral PCBs individually into their enantiomers also by CD-MEKC using SDS micelles. This was the first time that PCBs 88, 171 and 196 had been separated into their two enantiomers. Multicomponent separation of nine chiral PCBs (the other three can overlap with them) had also been performed (see Fig. 5).

Terabe et al. [26] also reported successful separations of three pairs of TCDD isomers by CD-MEKC using 100 m*M* SDS, 60 m*M* γ-CD and 2 *M* urea at pH 8.0. Recently Grainger et al. [104] used CD-MEKC to examine isomer differentiation of PCDD isomer pair components. The buffer consisted of 100 m*M* SDS, 40 m*M* γ-CD, 5 *M* urea and 100 m*M* borate at pH 9. All of the PCDD isomer pairs analyzed were baseline separated, with electrophorograms showing 11 peaks for the 12 mono- and dichlorinated isomers, 14 peaks for the trichlorinated isomers, 21 peaks for the 22 TCDD isomers, and 14 peaks for the pentachlorinated isomers. The determination results agreed well with the results determined by GC–MS, GC–FITR, HPLC/NPO, ^{13}C NMR[13] and ^{1}H NMR[12] methods.

4.2. Herbicides

CE has been used to separate herbicides, including triazines, paraquat and diquat, organophosphorous compounds, carbamates, sulfonylureas, phenoxy acids and phenylureas, etc. Recently, the potential and drawbacks of CE for the monitoring of herbicide water pollution were discussed by Dinelli et al. [105].

Triazine herbicides are basic species which can protonize in acidic buffer. Their separation can then be simply carried out by CZE. Foret et al. [106] reported the successful separation of hydroxy simazine, hydroxy atrazine, methoxy simazine, methoxy atrazine, desmetryne, terbutryne and prometryne at pH 3.0 in 30% ethanol.

Paraquat and diquat are ammonium salts, their separation by CZE is straightforward. However, their adsorption to the capillary inner wall can prevent

Table 1
Separation of PAHs by various separation media

No.	Separation mode	Compounds	Separation media	Field strength (V/cm)	Analysis time (min)	Performance[a]	Refs.
1	CZE	5 homologs	25 m*M* THxAP, 50% acetonitrile	200	28	Good	[8]
2	CZE	16 homologs	50 m*M* THpAB, 40% acetonitrile, 8 m*M* borate, pH 9.2	200	28	Very good	[9]
3	CZE	23 homologs	50 m*M* DOSS, 40% acetonitrile, 8 m*M* borate, pH 9.0	380	22	Very good	[10]
4	MEKC	7 homologs	85 m*M* SDS, 50% acetonitrile, 8.5 m*M* borate, pH 9.9	1070	9	Good	[98]
5	MEKC	10 homologs	50 m*M* SDS, 40% ethanol, 20 m*M* KH_2PO_4–5 m*M* $N_aB_4O_7$	400	36	Good	[99,100]
6	MEKC	9 homologs	50 m*M* SDS, 8 *M* urea, 20 m*M* borate–20 m*M* phosphate, pH 9.0	310	—	Good	[24]
7	CD-MEKC	16 homologs	100 m*M* SDS, 20 m*M* γ-CD, 5 *M* urea, 100 m*M* borate, pH 9.0	310	60	Very good	[27]([26,28,29])[b]
8	CD-MEKC	6 anthracene derivatives	100 m*M* SDS, 30 m*M* γ-CD, 5 *M* urea, 100 m*M* borate	330	38	Very good	[71]
9	CD-MEKC	7 BaP derivatives	20 m*M* SDS, 15 m*M* γ-CD, 5% 2-propanol, 10 m*M* NaH_2PO_4–6 m*M* $Na_2B_4O_7$	415	14	Very good	[30]
10	MEKC	7 homologs	100 m*M* CTAB, 25% acetonitrile, 50 m*M* borate, pH 9.5	345	20	Not good	[98]
11	MEKC	3 homologs	50 m*M* sodium cholate, 20% methanol, 10 m*M* Na_2HPO_4–6 m*M* $Na_2B_4O_7$	380	20	Good	[40]
12	MEKC	6 homologs	70 m*M* sodium deoxycholate, 20% DMF, 20 m*M* Tris–10 m*M* NaH_2PO_4	330	18	Good	[101]
13	CD-MEKC	16 homologs	100 m*M* sodium cholate, 30 m*M* γ-CD, 50 m*M* borate, pH 8.35	440	13	Not good	[42]
14	MEKC	5 homologs	50 m*M* MEGA 10, 50 m*M* borate, pH 10.0	190	15	Not good	[41]
15	MEKC	10 homologs	5 m*M* SUA oligomer, 35% acetonitrile, 20 m*M* borate, pH 8.2	200	33	Very good	[50]
16	MEKC	12 homologs	0.4% SUS oligomer, 60% methanol or 40% acetonitrile, 12.5 m*M* sodium tetraborate	390	30	Very good	[51]
17	MEKC	8 homologs	5 m*M* SBD(X)-C_{12}, 90% methanol, 20 m*M* borate, pH 10.1	500	15	Good	[55]
18	CD-CDEKC	16 homologs	35 m*M* SBβCD, 15 m*M* MβCD, 50 m*M* borate, pH 9.2	525	20	Excellent	[61]([60])[b]

[a] Refer to approximately estimated resolution of 16 priority PAHs listed by the US EPA.
[b] Relevant references.

their separation. This was solved by using high ionic strength buffer containing 20 m*M* NaCl [107] or a coated column together with low pH [108]. The later method proposed by Wigfield et al. [108] was then used to simultaneously determine the residues of paraquat and diquat in potatoes. The potato samples

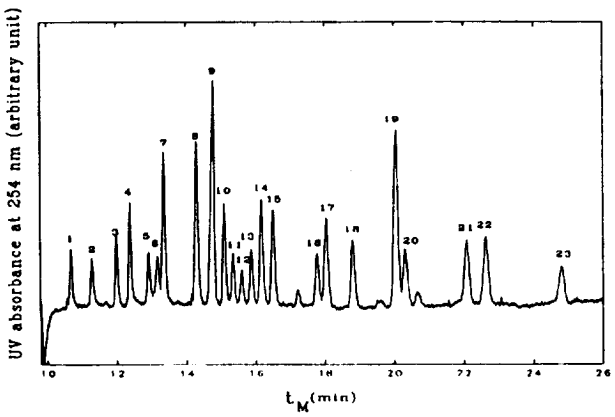

Fig. 1. Separation of polynuclear aromatic hydrocarbons (PAHs) by solvaphobic association capillary zone electrophoresis (solvaphobic association CZE). Buffer: 50 m*M* DOSS, 8 m*M* sodium borate, 36% (v/v) acetonitrile, pH 9.0. Capillary: 50 μm I.D., 52.5 cm effective length. Applied voltage: 20 kV. Injection: gravity, 10 cm for 30 s. Sample: in water–acetonitrile (~30%, v/v) containing about 30 m*M* DOSS. Detection: UV at 254 nm. Peaks: 1, acetophenone; 2, nitrobenzene; 3, unidentified; 4, 5,6-benzoquinoline; 5, benzophenone; 6, azulene; 7, naphthalene; 8, acenaphthylene; 9, acenaphthene; 10, fluorene; 11, 3-aminofluoranthene; 12, 9,10-dimethylbenz[*a*]anthracene; 13, benz[*a*]anthracene; 14, phenanthrene; 15, anthracene; 16, fluoranthene; 17, pyrene; 18, 2,3-benzofluorene; 19, chrysene; 20, 2,3-benzphenathrene; 21, perylene; 22, benzo[*a*]pyrene; 23, benzo[*g,h,i*]perylene. (Reprinted with permission from Ref. [10]. Copyright (1995) American Chemical Society.)

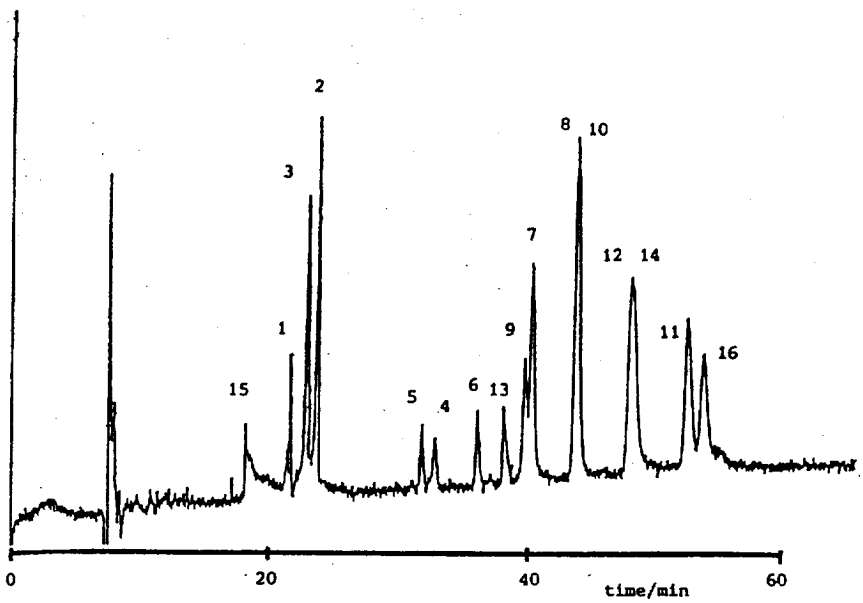

Fig. 2. Separation of polynuclear aromatic hydrocarbons (PAHs) by cyclodextrin modified micellar electrokinetic chromatography (CD-MEKC). Buffer: 20 m*M* γ-CD, 5 *M* urea, 100 m*M* SDS, 100 m*M* borate, pH 9.0. Capillary: 80 cm×50 μm I.D. (60 cm effective length). Applied voltage: 25 kV. Sample: 100–500 ppm in methanol. Detection: UV at 210 nm. Peaks: 1, naphthalene; 2, acenaphthene; 3, acenaphthylene; 4, fluorene; 5, anthracene; 6, phenanthrene; 7, pyrene; 8, fluoanthene; 9, chrysene; 10, benz[*a*]anthracene; 11, benzo[*b*]fluoranthene; 12, benzo[*k*]fluoranthene; 13, benzo[*a*]pyrene; 14, dibenz[*a,h*]anthracene; 15, benzo[*g,h,i*]perylene; 16, indeno[1,2,3-*cd*]pyrene. (Reprinted with permission from Ref. [27].)

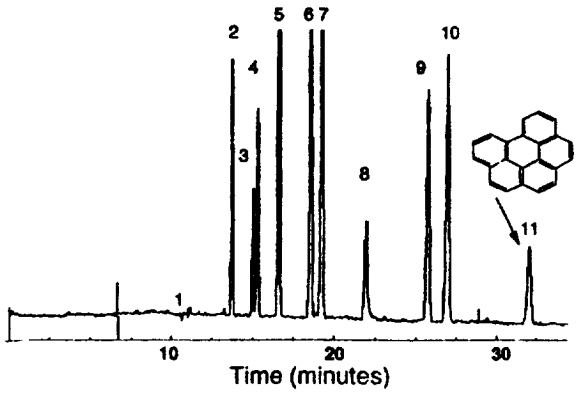

Fig. 3. Separation of polynuclear aromatic hydrocarbons (PAHs) by micellar electrokinetic chromatography (MEKC) using monomolecular pseudo-stationary phase. Buffer: 5 m*M* SUA oligomer, 20 m*M* sodium borate, 35% acetonitrile, pH 8.2. Capillary: 100 μm I.D., 50 cm effective length. Separation potential: 200 V/cm. Sample: 20 ppm in buffer, or at the limit of solubility, whichever was lower. Detection: UV at 275 nm. Peaks: 1, methanol; 2, naphthalene; 3, acenaphthene; 4, fluorene; 5, phenanthrene; 7, pyrene; 8, chrysene; 9, benzo[*b*]fluoranthene; 10, benzo[*a*]pyrene; 11, benzo[*g,h,i*]perylene. (Reprinted with permission from Ref. [49].)

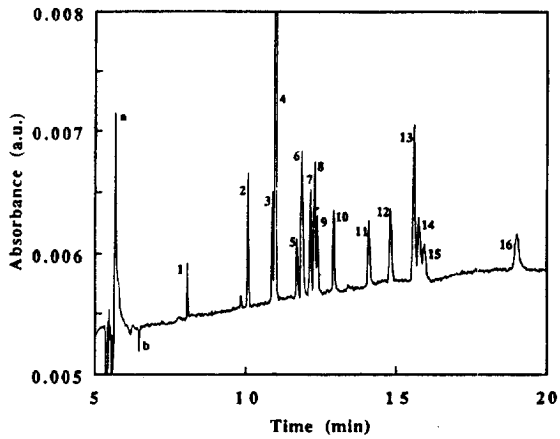

Fig. 4. Separation of polynuclear aromatic hydrocarbons (PAHs) by electrokinetic chromatography using neutral and charged cyclodextrin mixtrures as pseudo-stationary phases (CD-CDEKC). Buffer: 35 m*M* SBβCD, 15 m*M* MβCD, 50 m*M* borate, pH 9.2. Capillary: 57 cm×50 μm I.D. (50 cm effective length). Applied voltage: 30 kV. Injection: vacuum, 0.5 p.s.i. for 2.5–7 s (1 p.s.i.=6894.76 Pa). Sample: 5–100 ppb in methanol. Detection: UV at 254 nm. Peaks: 1, dibenz[*a,h*]anthracene; 2, naphthalene; 3, fluorene; 4, anthracene; 5, acenaphthylene; 6, acenaphthylene; 7, chrysene; 8, phenanthrene; 9, benz[*a*]anthracen; 10, benzo[*k*]-fluoranthene; 11, benzo[*a*]pyrene; 12, fluoranthene; 13, benzo[*b*]-fluoranthene; 14, indeno[1,2,3-*cd*]pyrene; 15, pyrene; 16, benzo-[*g,h,i*]perylene. (Reprinted with permission from Ref. [61]. Copyright (1996) American Chemical Society.)

were chopped into fine pieces and sonicated with 6 *M* HCl for 30 min. After the mixture settled, the herbicides were isolated by SPE with a silica gel Sep-Pak cartridge. Following the addition of an internal standard (N,N′-tetramethylene-2,2′-bipyridinium dibromide), the extract was analyzed with mean recoveries of over 70% and R.S.D. of 9.8 and 10.6% ($n=20$) for paraquat and diquat, respectively, at 0.05–1.0 ppm fortification level. The final LOD was 0.01 ppm. Recently Carneiro et al. [90] reported a successful separation of paraquat, diquat and difenzoquat with a buffer containing 100 m*M* NaCl at pH 4.0. This separation was used to determine the herbicides in crop water by direct electrokinetic injection. The achieved LODs were below 30 ppb. The R.S.D. values of the analysis were below 5%.

The separation of alkylphosphonic acids is also straightforward by CZE. However, the alkylphosphonic acids do not absorb or fluoresce in the UV or visible spectral. Pianetti et al. [109] monitored C_1- to C_4-alkylphosphonic acids by indirect UV detection with 10 m*M* phenylphosphonic acid at pH 6.0. Kostiainen and Bruins [83] detected four alkylphosphonic acids by using ion spray MS. Tomita et al. [110] separated and quantitated glyphosate and its major metabolite, aminomethylphosphonic acid (AMPA), in serum. The two compounds, after derivatization with *p*-toluenesulfonyl chloride, were clearly separated with a pH 9.6 buffer containing 10% methanol. The LOD for both derivatives was 0.1 ppm in spiked sera. The recoveries for glyphosate and AMPA were 87.9–88.8% and 78.4–86.9% with R.S.D. values of 3.5–6.2% and 1.5–5.3% ($n=5$), respectively, at 0.5–20 ppm spiked level.

Sulfonylureas also have acid–base equilibrium in aqueous solution, so their separation can be fulfilled by CZE at appropriate pH. Dinelli et al. [111] reported the successful separation of metsulfuron and chlorsulfuron at pH 9.0. This method was used to detect metsulfuron and chlorsulfuron in tap water with LODs of 0.16 ppm. The sample was preconcentrated by SPE with a C_{18} column. The enrichment factors were 50 000 and 20 000 times for 0.01 and 0.05 ppb samples, respectively. The average overall

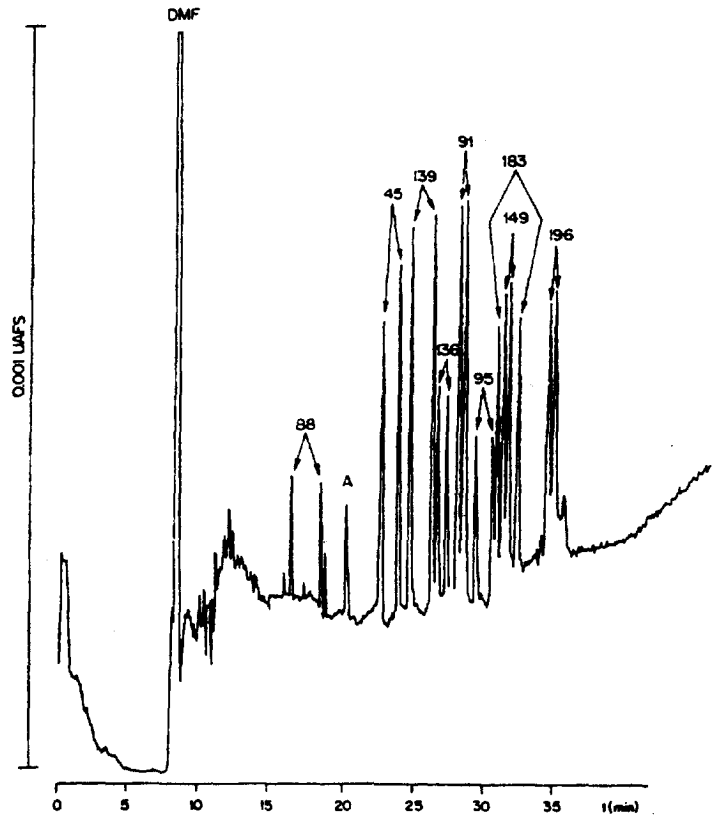

Fig. 5. Separation of chiral polychlorinated biphenyls (PCBs) by cyclodextrin-modified micellar electrokinetic chromatography (CD-MEKC). Buffer: 110 m*M* SDS, 2 m*M* urea, 50 m*M* γ-CD, 100 m*M* MES (2-(N-cyclohexylamino)ethanesulphonic acid), pH 10.0. Capillary: 65 cm×50 μm I.D. (50.5 cm effective length). Applied voltage: 15 kV. Injection: pressure, 20 mbar for 0.02 min. Sample: 100 ppm in DMF. Detection: UV at 235 nm. Each pair of enantiomers is identified by a number according to the Ballschmiter nomenclature. (Reprinted with permission from Ref. [103].)

recoveries, in the 0.1–5 ppb range, were 96.32±15.58% for metsulfuron and 92.25±9.52% for chlorsulfuron in 11 replicates. Carcia and Heion [84] separated bensulfuron methyl, sulfometuron methyl, tribenuron methyl, nicosulfuron, chlorimuron ethyl, thifensulfuron methyl, metsulfuron methyl and chlorsulfuron at pH 5.

The separation of phenoxy acids by CZE can also be successful. Nielen [112] reported a successful separation of 2,4-D, MCPA, M, MCPP, 2,4-DP and MD at pH 4.80. This separation was later used to determine herbicides in drinking and river water [87]. The samples were first cleaned-up by SPE with a C_{18} membrane disk and then preconcentrated by large-volume sample stacking with matrix removal. The achieved LODs were 50 and 100 ppt for drinking and river water, respectively. The recoveries of the herbicides were 98–103% for drinking water and 55–81% for river water at 0.5 ppb level. Garrisson et al. [113] separated 2,4-D, 2,4-DP, MCPP and 2,4,5-TP at pH 4.45.

CD-CZE was used to enhance the separation of phenoxy acid herbicides, even to separate them into their enantiomers [76,112,113]. Mechref and El Rassi [76] reported a separation of ANDSA-derivatized phenoxy acid herbicides, as many as nine isomers was separated in a single run with addition of α-CD at pH 10.0. The high pH was used to eliminate any enantiomeric separation. At acidic pH, 2-PPA and its seven isomers 2,2-CPPA, 2,3-CPPA, 2,4-CPPA, 2,4-DP, 2,4,5-TP, MCPP and MD or their ANDSA-derivatized products can be baseline re-

solved into their enantiomers provided a suitable CD is used [76,112,113]. CD derivatives such as α-CD, β-CD, γ-CD, HPγCD, 2,6-di-O-methyl-β-CD (DMβCD) and 2,3,6-tri-O-methyl-β-CD (TMβCD) were used for this purpose. They provided extremely different enantiomeric selectivity. The TMβCD afforded the best enantiomeric separation while γ-CD the worst. It is then obvious that a CZE buffer system composed of mixed CDs should yield unique chiral selectivity that cannot be achieved by either CD alone (see Fig. 6) [76]. 2,4,5-TP was also partially separated into its enantiomers by use of in situ charged Deoxy Big CHAP micelles at pH 10.0 [46].

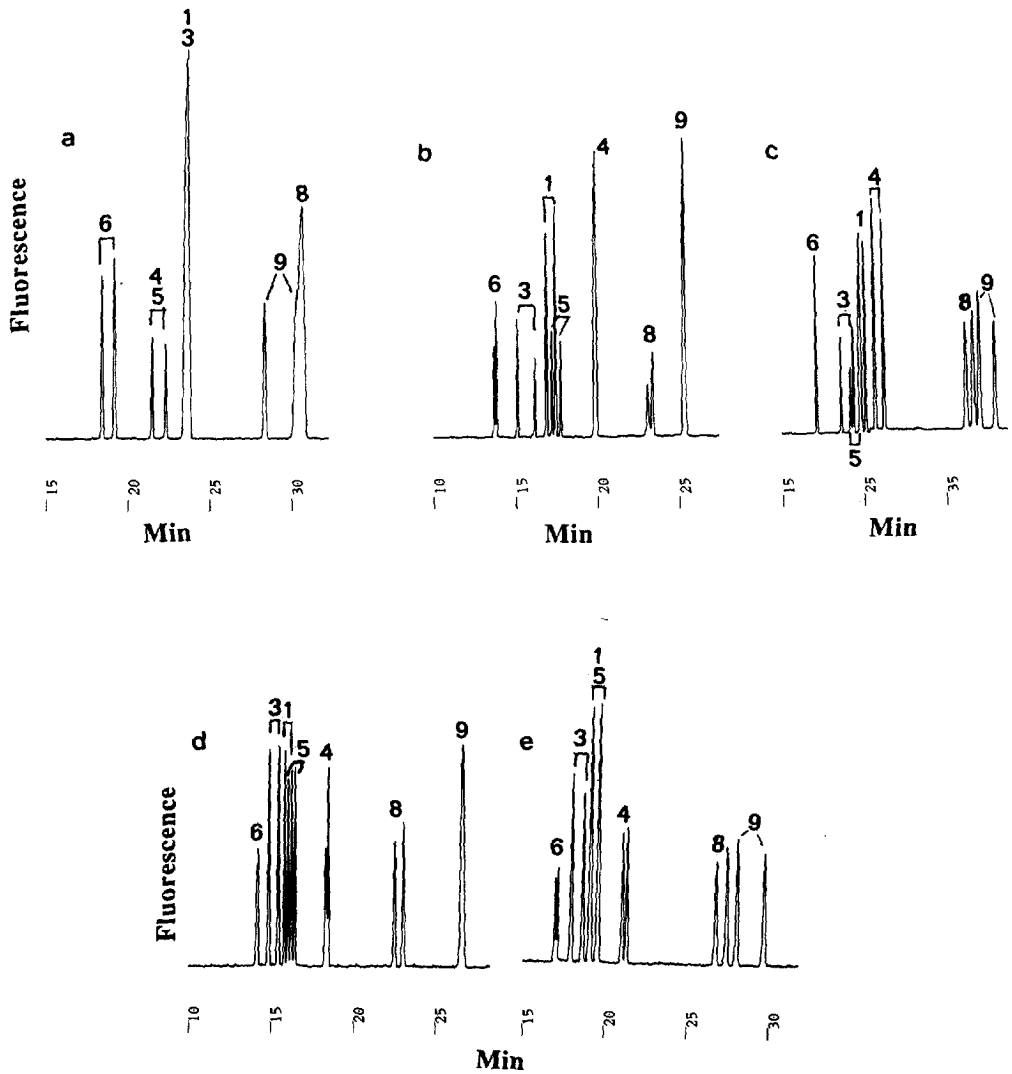

Fig. 6. Separation of chiral phenoxy acid herbicides derivatized with 7-aminonaphthalene-1,3-disulfonic acid (ANDSA) by cyclodextrin (CD) or mixed CDs modified capillary zone electrophoresis (CD-CZE). Buffer: 25 m*M* sodium phosphate, 600 m*M* borate, pH 5.0, containing (a) 5 m*M* β-CD, (b) 5 m*M* TMβCD, (c) 5 m*M* each of β-CD and TMβCD, (d) 5 m*M* β-CD and 30 m*M* TMβCD, (e) 30 m*M* TMβCD. Capillary: 80 cm×50 μm I.D. (50 cm effective length). Applied voltage: 20 kV. Injection: gravity, 15 cm for 5s. Sample: 5×10^{-5} *M*; see text for derivatization procedure. Detection: lamp-operated fluorescence. Peaks: 1, 2,4-DP; 3, MCPP; 4, 2,3-CPPA; 5, 2,4-CPPA; 6, 2,4,5-TP; 8, 2,2-CPPA; 9, 2-PPA. (Reprinted with permission from Ref. [76]. Copyright (1996) American Chemical Society.)

CZE separation of the above herbicides can be enhanced by MEKC. Cai and El Rassi [40] reported the separation of prometon, prometryne, prapazine and butachor by use of in situ charged OG micelles at neutral and basic pH. The separation of simazine and atrazine was accomplished, using 25 m*M* SDS at pH 8, by Desiderio and Fanali [114]. The method was used for the determination of herbicides in river water. The samples were preconcentrated 200-fold by chloroform extraction. Recoveries tested in triplicate at $1-5\times10^{-8}$ *M* were 80–117% with an R.S.D. of 2.6–17.3%. The LODs were 1.75×10^{-9} *M* or 0.38 and 0.35 ppb, respectively, for atrazine and simazine. The separation of seven triazine herbicides was accomplished by Martinez et al. [115] with 50 m*M* SDS at pH 9.2. The optimized MEKC method was applied to determine these herbicides in bottled and tap water. The 100-ml samples were preconcentrated by SPE with Sep-Pak C_{18} cartridges and dissolved in 200 μl of 10% (v/v) methanol–borate buffer. The LODs were 0.1 ppb for tertutryne and 0.2 ppb for all the other herbicides. The recoveries of the herbicides ranged from 79–130% with R.S.D. of 9–10% ($n=4$) at spiked concentration levels of 0.3 and 0.5 ppb. A representative electrophorogram of a bottled water sample at a spiked concentration level of 0.3 ppb is shown in Fig. 7.

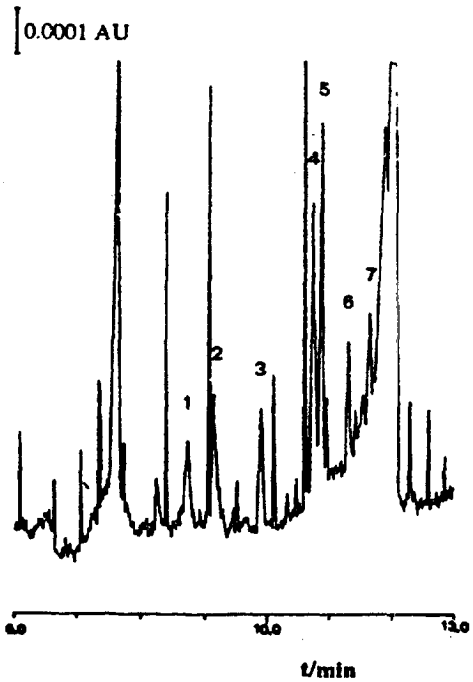

Fig. 7. Determination of seven triazine herbicides in a bottled water sample by micellar electrokinetic chromatography (MEKC). Buffer: 50 m*M* SDS, 60 m*M* borate, pH 9.2. Capillary: 57 cm×75 μm I.D. (50 cm effective length). Applied voltage: 22 kV. Injection: pressure, 85 p.s.i. for 10 s. Sample: after SPE preconcentration of 100 ml at spiked concentration level of 0.3 ppb to 200 μl. Detection: UV at 214 nm. Peaks: 1, simazine; 2, cyanazine; 3, atrazine; 4, ametryne; 5, propazine; 6, prometryne; 7, terbutryne. (Reprinted with permission from Ref. [115].)

Wu et al. [116] reported the separation of as many as 10 phenoxy acid herbicides by using 100 m*M* SDS with 3 m*M* Brij 35 to form mixed micelles. However, the separation of phenoxy acid ester was difficult because of the fact that esters hydrolyze readily in alkaline media. Meter et al. [47] solved this problem by using in situ charged MEGA 9 micelles at pH 7.0. Phenoxy acid herbicides 2,4-D, 2,4,5-T and 2,4,5-TP, together with 3-nitrobenzoic acid, 4-chlorobenzenesulfonic acid, orange II and trypan blue, were separated with 100 m*M* sodium cholate at pH 8.3 by Brumley and Brownrigg [117]. This method was used to determine the compounds in water and soil. The soil samples were extracted with a water–methanol (25:75, v/v) solvent by sonication. The extracts of the soil and water samples were then extracted at pH 2 on C_{18} SPE disks. The non-retained acids at pH 2 on C_{18} disks were retained on disks at pH 6 using an ion-pairing agent, cetyldiethylmethylammonium bromide (CEMA). The recoveries were 38.1 to 101% in water with R.S.D. of 6.7–46% ($n=3$), and 26.5–94.4% in soil with R.S.D. of 6.7–55% ($n=3$) at 0.1–1.0 ppm concentration level. The 5-(aminoacetamido) fluorescein-derivatized products of 10 phenoxy acid herbicides were separated, by Jung and Brumley [75], using a micellar system containing 46 m*M* SDS and 1670 m*M* urea in 22.2% methanol at pH 7.0. The LOD after LIF detection was 0.5 ppb. Water samples were purified by SPE with C_{18} membrane disks at pH 5.7 and then trapped at pH 1.5. Recoveries in the 60–80% range were obtained for most herbicides. Because of the insufficient derivatization time of 2 h, MCPB and 2,4-DB were barely visible. After long derivatization times, the background noise level resulting from side reactions was found to be higher. Extracts of real samples may contain compounds that

can enhance the decomposition of the derivatizing reagent.

Susse and Muller [118] separated a mixture of three triazine, three organophosphorous compounds and three carbamate herbicides by using 30 m*M* SDS at pH 8. Another mixture of nine herbicides containing triazines, phenoxy acids and organphosphorous compounds was separated by using various (OS, OG, OM and MEGA 9) in situ charged micelles [45].

Dinelli [119] optimized a buffer containing 80 m*M* SDS, 14% methanol and 20% isopropanol at pH 7, using an overlapping resolution mapping (ORM) scheme to separate metsulfuron, chlorimuron and chlorsulfuron. The LODs were 0.63 ppm for chlorimuron and 0.5 ppm for metsulfuron and chlorimuron. This method was used to determine herbicide residues in soil. The samples were treated firstly by extraction with 0.1 *M* sodium hydrogencarbonate at pH 7.8, then by SPE with a C_{18} column. This treatment gave a 100-fold enrichment of the herbicides. Subsequent determination gave the average overall recovery, in the 20–50 ppb range, of 95.4±16.1% ($n=18$). Krynitsky and Swineford [120] separated five sulfonylurea herbicides by use of 50 m*M* SDS at pH 6.15. This method was applied to analyze herbicide residues in wheat, barley and corn. The sample treatment involved acetonitrile extraction, hexane partitioning, SPE with an SCX (aromatic sulfonic acid) cation-exchange cartridge and acetonitrile–methylene chloride (5:95) extraction. The analysis gave typical recoveries of 73–118% with R.S.D. of 3–18% at the 0.05-ppm level, and 72–103% with R.S.D. of 2–8% at the 0.2-ppm level. The LODs were in the 0.02–0.035-ppm range. A representative electrophorogram of a wheat sample at a spiked concentration of 0.05 ppm is shown in Fig. 8.

The herbicides metsulfuron, atrazine, metolachlor and linuron spiked in drinking water were analyzed by MEKC with a buffer containing 30 m*M* SDS in 10% methanol at pH 8.0 by Dinelli et al. [121]. The LOD for the herbicides after a 1000-fold concentration step by SPE with C_{18} columns was 0.5 ppb. The average overall recovery for the four herbicides in the concentration rang of 1–50 ppb was 78.2±11.6%. Furthermore, the hydrolysis products of metsulfuron were analyzed by MEKC with a buffer containing 50 m*M* SDS in 10% methanol at pH 8.0. On the basis of the MEKC and GC–MS data on the metsulfuron breakdown products, a hypothetical degradation scheme for metsulfuron in water was formulated. Metabolites of sulfonylurea herbicides in aqueous solution have also been separated by MEKC using SDS micelle in 10% methanol at pH 8.0 [122].

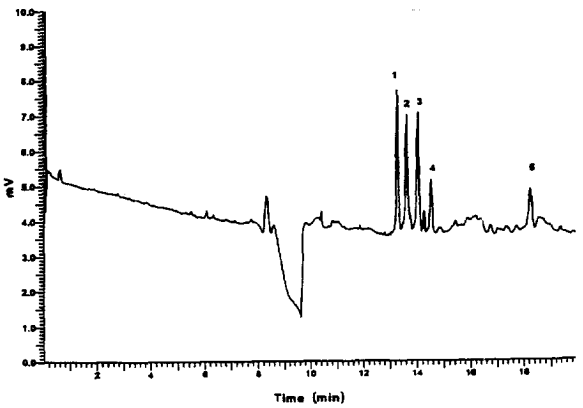

Fig. 8. Determination of five sulfonylurea herbicides in wheat by micellar electrokinetic chromatography (MEKC). Buffer: 50 m*M* SDS, 25 m*M* sodium phosphate, pH 6.15. Capillary: 90 cm×75 μm I.D. (68 cm effective length). Applied voltage: 25 kV. Injection: vacuum, 12.7 mmHg for 9 s. Sample: spiked concentration level of 0.05 ppm; see text for extraction and clean-up procedure. Detection: UV at 234 nm. Peaks: 1, metsulfuron methyl; 2, thifensulfuron methyl; 3, chlorsulfuron; 4, rimsulfuron; 5, tribenuron methyl. (Reprinted from The Journal of AOAC International, 1995, Volume 78, Number 4, pp. 1091–1096. Copyright, 1995, by AOAC International, Inc.)

Phenylurea herbicides are neutral in aqueous solution, they cannot be separated by CZE. Song et al. [34] successfully separated six phenylurea herbicides and chlorsulfuron by SDS micellar, SDS and PEG 400 monolaurate mixed micellar, and microemulsion (SDS, *n*-butanol and octane) EKC. Crosby and El Rassi [38] successfully separated six phenylurea herbicides by use of alkyltrimethylammonium micelles. The separation was best achieved when DoTAC or decyltrimethylammonium was used because they had low hydrophobic-phase ratio and wide retention window, resulting in medium capacity factors of the herbicides. When tetradecyltrimethylammonium (TTAC) was used, the separation was slightly less effective because of high capacity factors. However, the separation was enhanced by

the inclusion of small amounts of octyltrimethylammonium chloride into TTAC micellar phase. This was because the mixed micelle had a decreased hydrophobic phase ratio and increased retention window. The separation of phenylurea herbicides is more effective by using in situ charged micelles, because of their more balanced hydrophile–lipophile character compared to ionic surfactants. Nine phenylurea herbicides can be easily separated at neural, basic and even acidic buffer [42–47]. Modification of the SDS micellar system by urea [123] can also provide better resolution of phenylurea herbicides: an electrophorogram of 10 phenylurea and two carbamate herbicides is shown in Fig. 9. Farran and Ruiz [124] also reported the simultaneous separation of four phenoxy acid and five phenylurea herbicides by using 70 m*M* SDS at pH 7.0. Recently, they [125] further studied the effect of aliphatic alcohols (methanol, butanol, pentanol, hexanol and heptanol) on the separation. It was found that optimal alcohol concentration decreased as chain length increased.

4.3. Phenols

Phenols are weak acids which can dissociate in aqueous solution. So CZE can be used to separate phenols. Gaitonde and Pathak [82] separated 11 phenol derivatives including phenol and seven chlorophenols at pH 8.0. Amperometric detection was used with a LOD of 0.001 ppb after electrokinetic injection of standards dissolved in 1:1 water–methanol (sample stacking occurred). This method was used to monitor phenol and chlorophenols in waste water. The waste water was extracted by 1:1 chloroform–diethyl ether and then diluted with buffer solution at a ratio of 1:1. Electrokinetic injection of the sample resulted in a LOD of 0.05 ppb.

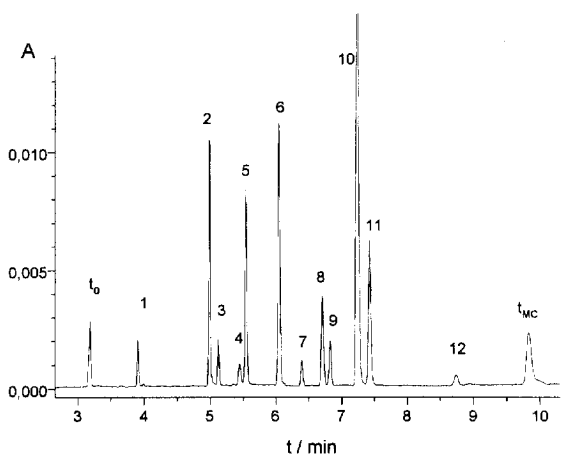

Fig. 9. Separation of 10 phenylurea and two carbamate herbicides by micellar electrokinetic chromatography (MEKC). Buffer: 35 m*M* SDS, 3.25 *M* urea, 10 m*M* $Na_2B_4O_7$, 10 m*M* H_3BO_3, pH 9.2. Capillary: 56.5 cm×75 μm I.D. (50 cm effective length). Applied voltage: 25 kV. Injection: pressure, 2.0 s. Detection: UV at 254 nm. Peaks: 1, fenuron; 2, monuron; 3, metoxuron; 4, monolinuron; 5, carbofuran; 6, metobromuron; 7, chlortoluron; 8, isoproturon; 9, diuron; 10, metabenzthiazuron; 11, linuron; 12, phenmedipham. (Reprinted with permission from Ref. [123].)

Specific physico-chemical models were developed to describe the migration behavior of phenols as a function of pH and pK_a for separation optimization [126–128]. Gonnord and Collet [129] optimized the CZE separation of 13 chlorophenols with a pK_a range from 4.74 to 8.52 and obtained an optimum pH of 6.9. Smith and Khaledi [128] optimized the CZE separation of eight substituted phenols with pK_a values in the range from 7.04 to 10.28 and obtained an optimum pH of 10.5. Lin et al. [130] optimized the separation of six isomeric dichlorophenols and got an optimum pH very close to the mean value of the analyte pK_a.

A very good separation of 11 phenols listed by the US EPA as priority pollutants was reported by Chao and Whang [78]. The electrophorogram is shown in Fig. 10. Indirect LIF detection was used with LOD in the ppb range, and the linear dynamic range was generally more than 2 orders of magnitude. This method was applied to the determination of phenols in two industrial wastewater samples taken from a coke plant. The sample preparation procedure was just filtration and dilution. The separation of pentachlorophenol from the other eight chlorophenols was accomplished at pH 10 by Turnes et al. [69]. The LOD was 60 ppt after a combined preconcentration procedure of SPE and large-volume sample stacking with matrix removal. The recovery of the pentachlorophenol from tap water was 95.8±2.7% ($n=5$) at 0.5 ppb.

Recently, Masselter and Zemann [131] reported a very fast separation of 12 phenol derivatives within 5 min. A high pH value of 11 was chosen. A reversal of EOF to reduce analysis time by migration of the phenols in the same direction of EOF was achieved by using 0.07 m*M* CTAB or 0.001% hexadimethrine bromide (HDB). The addition of organic solvents

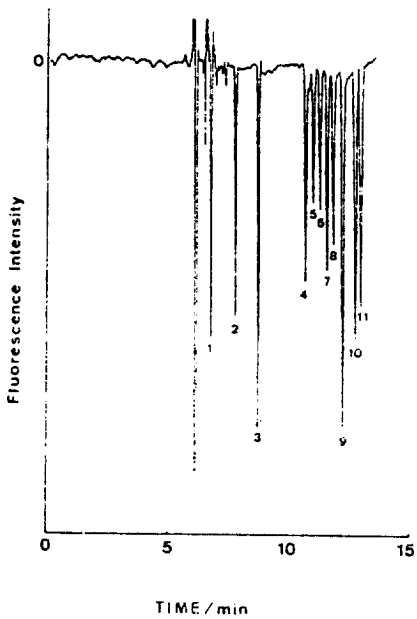

Fig. 10. Separation of the 11 phenols listed by the US EPA as priority pollutants by capillary zone electrophoresis (CZE). Buffer: 15 m*M* borate (pH 9.9) containing 1 m*M* fluorescein. Capillary: 50 cm×20 μm I.D. (45 cm effective length). Applied voltage: 9 kV. Injection: 9 kV for 2 s. Sample: 0.4–25.2 ppb in methanol. Detection: indirect LIF. Peaks: 1, 2,4-dimethylphenol; 2, phenol; 3, 4-chloro-3-methylphenol; 4, pentachlorophenol; 5, 2,4,6-trichlorophenol; 6, 2,4-dichlorophenol; 7, 2-methyl-4,6-dinitrophenol; 8, 2-chlorophenol; 9, 2,4-dinitrophenol; 10, 4-nitrophenol; 11, 2-nitrophenol. (Reprinted with permission from Ref. [78].)

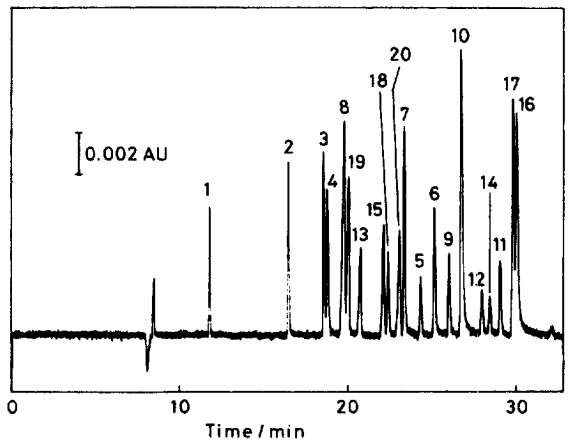

Fig. 11. Separation of all the isomeric chlorinated phenols including phenol by micellar electrokinetic chromatography (MEKC). Buffer: 70 m*M* SDS, 50 m*M* sodium dihydrogen phosphate, 25 m*M* sodium borate, pH 7.0. Capillary: 65 cm×50 μm I.D. (50 cm effective length). Applied voltage: 10 kV. Sample: dissolved in methanol or methanol–water (1:1). Detection: UV at 220 nm. Peaks: 1, phenol; 2, 2-chloro; 3, 3-chloro; 4, 4-chloro; 5, 2,3-dichloro; 6, 2,4-dichloro; 7, 2,5-dichloro; 8, 2,6-dichloro; 9, 3,4-dichloro; 10, 3,5-dichloro; 11, 2,3,4-trichloro; 12, 2,3,5-tetrachloro; 13, 2,3,6-trichloro; 14, 2,4,5-trichloro; 15, 2,4,6-trichloro; 16, 3,4,5-trichloro; 17, 2,3,4,5-tetrachloro; 18, 2,3,4,6-tetrachloro; 19, 2,3,5,6-tetrachloro; 20, pentachloro. (Reprinted with permission from Ref. [133].)

(methanol, ethanol, 1-propanol, 2-propanol and acetonitrile) significantly improved peak shapes and enabled the baseline separation, although a little longer separation time resulted. Previously, they [132] also separated the three isomers of cresol at pH 2.0, with 0.00022% HDB and 44% ethanol or isopropanol within 5 min.

MEKC can provide enhanced resolution of phenols in comparison with CZE. Terabe et al. [1] separated a mixture of 14 phenols, including three cresol isomers, three monochlorophenol isomers and six xylenol isomers with 50 m*M* SDS at pH 7.0. Otsuka et al. [133,134] reported a separation of all the 19 isomers of chlorophenols, including phenol, with 70 m*M* SDS at pH 7.0: the electrophorogram is shown in Fig. 11. CZE separation of all chlorophenol isomers has not been reported until now. Ong et al. [135] separated all 11 phenols as priority pollutants with 50 m*M* SDS at pH 6.6. However, the analysis time of 48 min is much longer than the CZE separation of 15 min reported by Chao and Whang [78]. Brumley and Jone [102] also reported a separation of phenols using 100 m*M* sodium cholate in 10% acetone at pH 8.35.

In MEKC of ionizable phenols, separation mechanisms are complicated by the effect of combined electrophoretic and chromatographic migration on separation. Chromatographic migration is also complicated by the ion-pair formation between the charged analytes and the opposite charged surfactants. However, there are still physico-chemical models developed by Khaledi and co-workers [136–138] to describe their migration behavior as a function of pH, pK_a, k' and the micellar concentration. Optimum separation conditions can then be determined. Recently Lin and co-workers [139,140] investigated the migration factor and electrophoretic mobility of each isomeric species of dichlorophenols as a function of micelle concentration and buffer pH. Comparison of separation in MEKC and CZE

showed completely different or reversed elution orders.

Phenols have also been used as standards to evaluate novel pseudo-stationary phases [6,62,65,66].

4.4. Nitroaromatic and other chemical warfare-related compounds

Nitroaromatic compounds are main the organic constituents of gunshot and explosives. In 1991, Northrop et al. [141] demonstrated a separation of 26 organic gunshot and high-explosive constituents standards by using 25 m*M* SDS at 2.5 m*M* borate buffer. All compounds were baseline resolved within 10 min, except that three pairs (3,4-dinitrotoluene–2-nitrotoluene, 2,3-dinitrotoluene–4-nitrotoluene and 1,5-dinitronaphthalene–1,8-dinitronaphthalene) co-eluted: the electrophorogram is shown in Fig. 12. The separation conditions were later adopted by

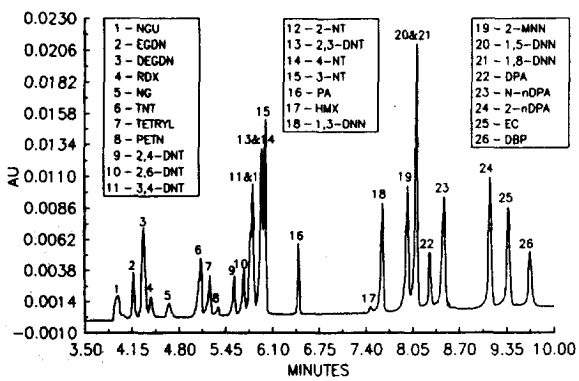

Fig. 12. Separation of 26 organic gunshot and high-explosive constituents by micellar electrokinetic chromatography (MEKC). Buffer: 25 m*M* SDS, 2.5 m*M* borate. Capillary: 67 cm×100 μm I.D. (62 cm effective length). Applied voltage: 20 kV. Injection: 5 kV for 2 s. Sample: 5×10^{-6} *M* in buffer. Detection: UV at 220 nm. Peaks: 1, nitroguanidine; 2, ethylene glycol dinitrate; 3, diethylene glycol dinitrate; 4, 1,3,5-trinitro-1,3,5-triazacyclohexane; 5, nitroglycerine; 6, 2,4,6-trinitrotoluene; 7, 2,4,6,N-tetranitro-N-methylaniline; 8, pentaerythritol tetranitrate; 9, 2,4-dinitrotoluene; 10, 2,6-dinitrotoluene; 11, 3,4-dinitrotoluene; 12, 2-nitrotoluene; 13, 2,3-dinitrotoluene; 14, 4-nitrotoluene; 15, 3-nitrotoluene; 16, picric acid; 17, 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane; 18, 1,3-dinitronaphthalene; 19, 2-nitronaphthalene; 20, 1,5-dinitronaphthalene; 21, 1,8-dinitronaphthalene; 22, diphenylamine; 23, N-nitrosodiphenylamine; 24, 2-nitrodiphenylamine; 25, ethylcentralite; 26, dibutyl phthalate. (Reprinted with permission from Ref. [141]. Copyright (1991) American Chemical Society.)

Northrop and McCrehan [142] in analysis of gunshot residues for forensic investigation, and by Kleiboehmer et al. [143] in analysis of explosive residues in heavily contaminated soils at military facilities associated with weapons production. Because the concentrations of these residues were relatively high, the analysis was accomplished by MEKC with UV detection without preconcentration. A comparative study between MEKC and HPLC by Kleiboehmer [143] showed that there was not much difference in the reproducibility of retention time and peak area for standards, whereas HPLC had better reproducibility for contaminated soil samples. Yik et al. [144] also reported a separation of nitroaromatic compounds by MEKC with SDS micelles. Gu et al. [145] separated six isomers of trinitrotoluene with mixed micelles of 40 m*M* SDS and 7 m*M* Brij 15 at pH 8–10. In 1995, Pyell and Butehorn [123] optimized a separation buffer containing 55 m*M* SDS and 1.8 m*M* urea at pH 9.3 for the separation of nine isomers of mono-, di- and tri-nitrotoluenes within 8 min. MEKC was also used to separate six sulfur-containing chemical warfare-related compounds by Cheicante et al. [146]. A buffer containing 100 m*M* SDS at pH 9.0 was used and successful separation was finished within 10 min. The LODs were well within the goal of 1–10 ppm.

4.5. Amines

Based on their positive charge in acidic solution, aniline can be easily separated by CZE. Nielen [147] separated phenyldiamine isomers at pH 4.8, while Jacquier et al. [126] separated chloroaniline isomers at pH 3.75. In 1995, Cavallaro et al. [148] separated 21 anilines at pH 2.35 with 7 m*M* 1,3-diaminopropane as buffer modifier to slow EOF and improve resolution: the electrophorogram is shown in Fig. 13. In this separation, all anilines had LODs of 0.06–1.8 ppm. Recoveries for surface water samples spiked with 20 ppm of anilines were better than 82%, except for the most hydrophilic ones: ca. 60%. The proposed method was used to analyze groundwater samples after SPE extraction with a 20:80 (w/w) mixture of keto-derivatized and underivatized poly-(styrene-divinylbenzene)copolymer, and soil samples after methylene chloride extraction. The samples had contemporaneous extraction of phenols and neutral

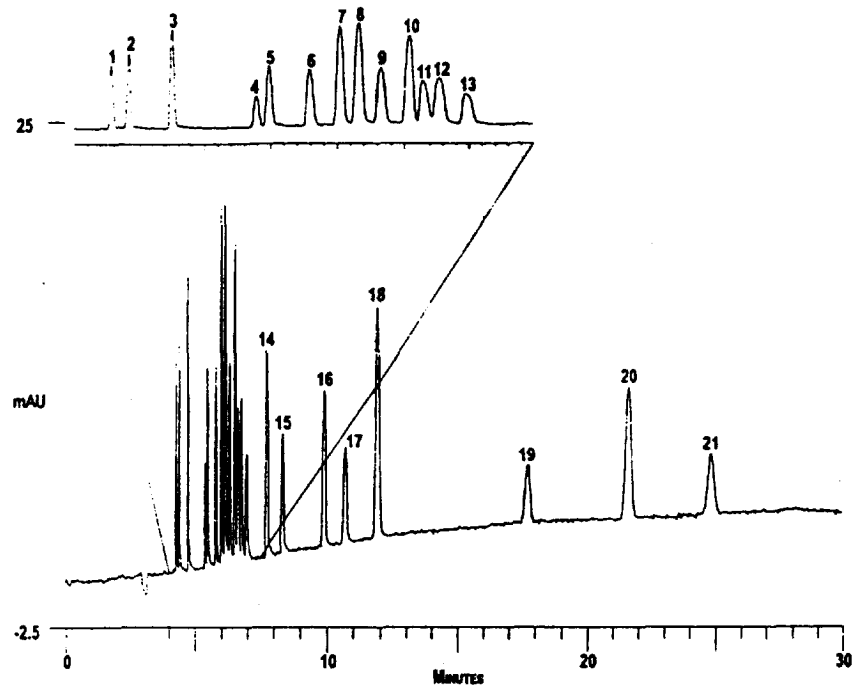

Fig. 13. Separation of 21 anilines by capillary zone electrophoresis (CZE). Buffer: 50 m*M* NaH_2PO_4, 7 m*M* 1,3-diaminopropane, pH 2.35 adjusted with H_3PO_4. Capillary: 65 cm×50 μm I.D. (60 cm effective length). Applied voltage: 30 kV. Injection: gravity, 10 cm for 30 s. Sample: 5–36 mg/ml in 150 m*M* H_3PO_4. Detection: UV at 280 nm. Peaks: 1, pyridine; 2, *p*-phenylenediamine; 3, benzidine; 4, *o*-toluidine; 5, aniline; 6, N,N-dimethylaniline; 7, *p*-anisidine; 8, *p*-chloroaniline; 9, *m*-chloroaniline; 10, ethylaniline; 11, α-naphthylamine; 12, diethylaniline; 13, N-(1-naphthyl)ethylenediamine; 14, 4-aminophenazone; 15, *o*-chloroaniline; 16, 3,4-dichloroaniline; 17, 3,3′-dichlorobenzidine; 18, 2-methyl-3-nitroaniline; 19, 2,4-dichloroaniline; 20, 2,3-dichloroaniline; 21, 2,5-dichloroaniline. (Reprinted with permission from Ref. [148].)

compounds, but did not interfere the CZE determination.

Anilines have also been separated by MEKC. Pyell and Butehorn [149] optimized a buffer containing 60 m*M* SDS at pH 9.3 for the separation of seven methylnitroanilines. Brumley and Jones [102] reported a separation of anilines by using 100 m*M* SDS in 10% acetone or 30 m*M* γ-CD at pH 8.35. Takeda et al. [150] separated 10 anilines, including eight which have been found in environmental water by GC–MS in Japan, by using a buffer containing 50 m*M* SDS and 8 m*M* γ-CD at pH 6.2. Diphenylamine and N-nitrosodiphenylamine cannot be directly distinguished by GC–MS because N-nitrosodiphenylamine decomposed at the temperature of GC injection ports or columns.

Other amines have also been separated by CE. Aliphatic amines derivatized by 7-chloro-4-nitrobenz-2-oxa-1,3-diazole (NBD-Cl) were separated using an SDS micellar system with isopropanol or acetonitrile gradient elution [22,23]. Three nitrosamines listed by the US EPA as priority pollutants were separated by Ng et al. [153]. Because of neutral, polar and low molecular weight, nitrosamines cannot be separated by MEKC with SDS micelles. Ng et al. [153] proposed a combined packed and open-tubular column for their separation. The injection end of an open-tubular column was jointed to a section of teflon tubing which was packed with HPLC stationary phase (0.13–0.5 mm in thickness) with both ends supported by teflon wool. The subsequent separation using a buffer containing 40 m*M* SDS at pH 6.6 was greatly improved. Wu et al. optimized a CZE separation of 12 heterocyclic amines by orthogonal array design (OAD) [151] and combined OAD and ORM schemes [152]. The optimum buffer should contain

15–30% methanol at pH 2.0. Pyell and Butehorn [123] optimized a MEKC separation of 16 *p*-nitrobenzoyl chloride-derivatized biogenic amines. The optimum buffer contained 55 m*M* SDS and 2.0 m*M* urea at pH 9.3.

4.6. Aromatic sulfonic acids and carboxylic acids

Brumley [154] first evaluated CE as a qualitative tool in the analysis of an environmental sample for eight aromatic sulfonic acids. The separation was successful at pH 8.3 by CZE. A leachate from a hazardous waste site was also separated. Later Brumley and Brownrigg [117] reported a separation of aromatic sulfonic acids by MEKC using a buffer containing 100 m*M* cholic acid at pH 8.3. Recently Kok et al. [155] tried to separate 21 amino- and hydroxy-substituted naphthalene sulfonic acids, which included multiple isomeric compounds. By using a buffer containing 50 m*M* boric acid–borate and 100 m*M* SDS at pH 8.7, all the analytes except three isomers of naphthalene trisulfonic acids were completely separated: the electrophorogram is shown in Fig. 14. By using a buffer containing 50 m*M* boric acid–borate and 15% acetonitrile at pH 8.7, the three isomers of naphthalene trisulfonic acids were almost completely separated, but some other isomers co-eluted. The LODs obtained for the individual compounds typically were 20 ppb. River water samples spiked at this concentration were cleaned using a simple three-step procedure (C_{18} SPE column clean-up, C_{18} SPE column with CTAB trap, SCX SPE column clean-up) and then analyzed, with overall recoveries in the 78–108% range at a spiking level of 1×10^{-6} *M*.

Aromatic carboxylic acids were often used as standards to study effect of various parameters on CZE separation [6,7,11,156] and evaluate proposed physical-chemical models for CZE optimization [127,157]. Friedl and Kenndler [157] even optimized

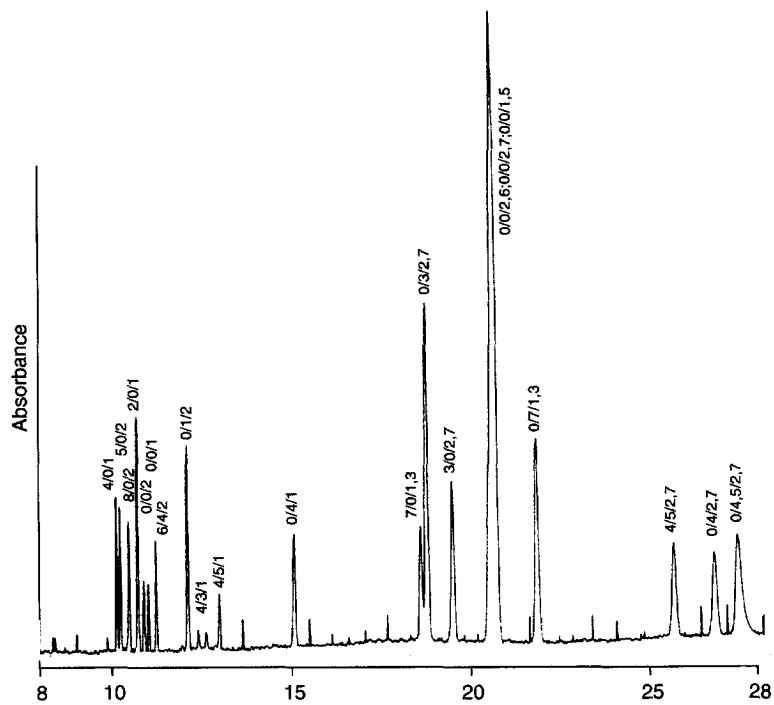

Fig. 14. Separation of 21 naphthalene sulfonic acids by micellar electrokinetic chromatography (MEKC). Buffer: 100 m*M* SDS, 50 m*M* boric acid/borate, pH 8.7. Capillary: 85 cm×75 μm I.D. (70 cm effective length). Applied voltage: 30 kV. Injection: pressure, 50 mbar for 0.1 min. Sample 5×10^{-6} *M* in water. Detection: UV at 230 nm. Peaks: the individual compounds are indicated by the substituent positions on the naphthalene skeleton as follows: positions of NH_2 groups/positions of OH groups/positions of SO_3^- groups. The label 'zero' indicates the absence of that particular group. (Reprinted with permission from Ref. [155].)

a CZE separation of all the six isomers of benzene di- and tri-carboxylic acid at pH 4.33. However, it was found that a change of the pH as small as 0.04 may have a dramatic influence on the resolution. Khaled and McNair [158] preferred to separate these isomers at pH 9–10.7, away from the pK_a of the acids. However, CZE separation was unsuccessful. The addition of α-, β- or γ-CD resulted in total separation of all the isomers.

4.7. Organometallic compounds

Medina et al. [159] analyzed organomercury compounds in biological samples of marine origin by CZE. Organomercurials were extracted from the samples by means of the classical Westoo procedure, thus giving organomercury–cysteine complexes. Methylmercury, ethylmercury, phenylmercury and inorganic mercury complexed with 0.1% cysteine were separated by CZE at pH 8.35 in 10% methanol. The LOD was 0.13 ppm. Studies showed that only 72% of methylmercury initially present was extracted, and the recovery was significantly affected by the matrix. However, the analyses of real samples were corrected for the extraction losses, and then data were obtained in good agreement with GC, as well as certified values for the reference material analyzed. Recently, Carro-Diaz et al. [92] determined methylmercury by CZE using sample stacking as preconcentration method. They separated methylmercury from the excess cysteine at pH 8.24. The LOD was 12 ppb. The method was tested, using different reference materials with certified methylmercury contents, with very good agreement.

Morin et al. [160] separated arsenite, arsenate, monomethylarsonic acid and dimethylarsonic acid by CZE at pH 4.5–6.5 with on-column UV detection at 190 nm.

Han et al. [161] separated dimethyltin, dibutyltin and tributyltin by CZE at pH 2.65. Pyridine with a concentration of 5 m*M* provided the indirect UV detection of the analytes at 254 nm. The LODs were about 1–10 ppm. When the pH was greater than 3.5, 0.8 m*M* CTAB was added to buffer to improve the peak shapes. The LODs were 10–30 ppm. In 1995, Pobozy et al. [162] compared the analysis of trimethyltin (TMT), triethyltin (TET), tributyltin (TBT) and triphenyltin (TPT) by HPLC and CZE. In both cases, indirect UV detection by using benzyltrimethylammonium (BTMA) for TMT, TET and TBT and direct UV detection for TPT were applied. A better separation of analytes and very low detection limits by CZE, ca. 0.3 ppm for indirect detection, 0.009 ppm for direct detection, were observed. The CZE buffer was composed of 20 m*M* tartaric acid, 20% methanol, 4 m*M* BTMA at pH 2.6. Tartaric acid was used as complexing agent to modify the apparent mobility of analytes and improve the separation of TBT and TPT. SPE was employed as preconcentration method for real environmental applications. Among the five different commercial non-polar sorbents examined for SPE of TBT and TPT, the best results were obtained with XAD-2 with mean recovery of 100% and R.S.D. of 3% ($n=3$). The use of SPE improved the detectability by about 3 orders of magnitude.

MEKC was also used to separate organometallic compounds. Ng et al. [163] separated trimethyllead, triethyllead, diphenylselenide and phenylselenyl by MEKC using a buffer containing 50 m*M* SDS and 5 m*M* β-CD at pH 6.0. The LODs at 210 nm UV were 26–67 ppm. Recoveries of distilled water extracted with chloroform were 80–104%. Li et al. [164] also separated trimethyllead, triethyllead, trimethyltin, dibutyltin and tributyltin by MEKC using a buffer containing 50 m*M* SDS at pH 7.65. Enrichment of the analytes in water samples was performed by liquid–liquid extraction and SPE using a C_{18} membrane disk. The membrane disk extraction proved to be a good technique for overcoming the problems encountered in solvent extraction, such as emulsification, larger labor requirement and time consumption. The recoveries were ca. 90% with R.S.D. of 5–8%, except for trimethyltin with a recovery of 49.7% and R.S.D. of 11.0%. The LODs after 1000-fold preconcentration were in the range of 1.1–5.2 ppb.

4.8. Phthalate esters

There are two available reports concerning the separation of phthalate esters by MEKC. Six phthalate esters were separated by Ong et al. [165] using a buffer containing 10 m*M* SDS at pH 6.0. Ten phthalate esters including all six phthalate esters listed by the US EPA as priority pollutants were separated by Takeda et al. [166] using a buffer

containing 50 m*M* SDS in 20% methanol at pH 9.0. Two phthalate esters, di-*n*-octyl- and bis(2-ethylhexyl) phthalate were so hydrophobic that they co-eluted with the micelle and could not be resolved. Separation time was also very long, about 60 min. They should be separated with less hydrophobic micellar systems.

4.9. Carbonyls

There are two available reports concerning the separation of carbonyls by CE in literature. In one report [167], 30 m*M* sodium bisulfite was added to CZE buffer. Benzaldehydes reacted with bisulfite and then were charged. A simultaneous CZE separation at pH 7.3 enabled 13 different hydroxy- and methoxy-substituted benzaldehydes to be separated within 8 min. In the other report [168], nine carbonyls were derivatized with 5-(dimethylamino)-naphthalene-1-sulfonehydrazide (DNSH) and then separated by CZE at pH 7.1 within 8 min.

4.10. Dyes

Siren and Sulkava [169] described a CZE separation at pH 10.8 for routine screening of black reactive dyes and black acid dyes, isolated from cotton and wool materials. Oxspring et al. [91] separated four of six reactive dyes (four remazol dyes and two cibacron dyes) and all their hydrolyzed dyes using a buffer containing 10% acetonitrile at pH 3.25. In 1995, Blatny et al. [12] reported a CZE buffer containing 0.5% PEG and 0.01% PVP at pH 6.5 for the separation of nine synthetic organic dyes, including seven azo compounds, used as coloring for textiles, in polyacrylamide-coated capillaries. Blatny et al. [170] also separated five synthetic triphenylmethane dyes used as colorants for textiles by CZE at pH 3 with 1% PVP. Separation conditions enabling the complete resolution of 11 permitted food colorants and some of their subspecies by CZE were determined by Masar et al. [171] as 5 m*M* β-CD, 0.2% PEG in 30 m*M* TES (N-tris(hydroxymethyl)methyl-2-aminoethane sulfonic acid)–8 m*M* imidazole buffer at pH 6.84. A 300-μm I.D. capillary tube made of fluorinated ethylene–propylene copolymer in a hydrodynamically closed separation compartment was used. The capillary could accommodate 90-nl sample injection volumes, thus providing a LOD of 11–30 ppb for standards prepared in 1 m*M* Na_2SO_4. In 1995, Razee et al. [172] reported improved reproducibility and peak shape in determination of seven food additive dyestuffs by CZE after addition of β-CD to running buffer. This is because interaction between the dyes and the capillary inner wall was alleviated.

Evans and Beaumonts [173] separated diverse range of dyes and dye intermediates with a MEKC buffer containing 20–50 m*M* SDS at pH 9–10. It was found that MEKC using SDS was more effective than using CTAB for the separation of dyes. Burkinshaw et al. [174] successfully used MEKC with 40 m*M* SDS at pH 9.3 to separate several sulfonated, cationic, pyridine-based or water-insoluble dye intermediates and two azo-sulfonated dyes. The separation of aqueous insoluble, electrically neutral dye intermediates was completed by using 20 m*M* SDS in 50% acetonitrile at pH 10. Suzuki et al. [175] reported that four xanthene dyes and three azo dyes which are members of the 12 synthetic tar dyes permitted for use as food additives in Japan were separated by MEKC with a buffer containing 10 m*M* SDS at pH 8.0. Brumley et al. [74] reported that seven monosulfonated dyes, which encompass structures including azo, diazo, triarylmethane and anthraquinone moieties, were separated using a buffer containing 100 m*M* sodium cholate in 10% acetone at pH 8.35. Recovery data for spiked water and soil samples were relatively good. Both pH adjustment via acid and ion-pairing via a cationic surfactant were investigated for isolating the dyes. In 1995, Sainthorant et al. [176] reported a separation of 14 phenylenediamine, aminophenol and phenol derivatives for quality control of oxidative dye production by using 150 m*M* SDS at pH 7 or 60 m*M* CTAC at pH 9.5.

5. Conclusion

The literature shows that CE has not been fully exploited for the analysis of environmental pollutants. A large section of the relevant publications dealt with efficient and rapid separation of standards and were not to be used to analyze them in real environmental samples. However, both separation

and analysis clearly demonstrated the high potential of CE in this field. Currently GC and HPLC are the main analytical techniques in the analysis of environmental pollutants. GC is advantageous for two reasons. Firstly, it provides fast and efficient separation with high capacity. Secondly, the gas mobile-phase permits many reliable, selective and sensitive detectors for trace analysis. Especially, GC is relatively simple to couple with MS, which is now the best analytical technique for identifying and quantifying trace components in the complex matrix of environmental samples. However, for the separation of polar, acidic or basic, and thermally labile compounds, GC is always not amenable without derivatization procedures. So, their analysis is more often carried out by HPLC. However, HPLC may suffer from long analysis time, and low efficiency, resolution and sensitivity. CE possesses the first advantages of GC. Unfortunately, the detection methods in CE are not different from those used in HPLC, and even more problems have been encountered in the most often used optical detection methods, simply because of the limited optical path length. If the concentration of pollutants in environmental samples is high, CE may compete with HPLC to complement GC. However, this situation is hardly encountered. The simple on-column preconcentration technique in CE, large-volume sample stacking with matrix removal, can compensate fpr this shortcoming and afford CE with sensitivity comparable to HPLC. Before the on-column preconcentration procedure, an off-line preconcentration procedure (often SPE) is needed not only to further enhance sensitivity but also to provide a relative low and reproducible conductivity for the sample. Although SPE can provide sufficient enrichment of samples for CE, the use of on-column preconcentration can decrease the sample volume processed by SPE, and shorten the time for pouring the sample through the cartridge. Then, CE can be considered at least as good as HPLC in the analysis of environmental pollutants. Based on different separation principles, CE can provide complementary analysis both for GC and HPLC. Moreover, many sensitive detection methods for CE such as thermo-optical absorbance [177], chemiluminescence [178] and inductively coupled plasma mass spectrometry (ICPMS) [179–181], etc., are developing, they can certainly render CE more versatile in detecting trace level environmental pollutants.

6. Abbreviations

ANDSA	7-aminonaphthalene-1,3-disulfonic acid
BaP	benzo[*a*]pyrene
CD	cyclodextrin
CE	capillary electrophoresis
CIE	capillary ion electrophoresis
CMC	critical micelle concentration
CMβCD	carboxymethyl-β-CD
2,2-CPPA	2-(2-chlorophenoxy)-propionic acid
2,3-CPPA	2-(3-chlorophenoxy)-propionic acid
2,4-CPPA	2-(4-chlorophenoxy)-propionic acid
CTAB (C)	cetyltrimethylammonium bromide (chloride)
CZE	capillary zone electrophoresis
2,4-D	2,4-dichlorophenoxy-acetic acid
2,4-DB	4-(2,4-dichlorophenoxy)-butyric acid
DMβCD	2,6-di-O-methyl-β-CD
DMF	N,N-dimethylformamide
DOSS	dioctylsulfosuccinate
DoTAC	dodecyltrimethylammonium chloride
2,4-DP	2-(2,4-dichlorophenoxy)-propionic acid
EKC	electrokinetic chromatography
EOF	electroosmotic flow
GC	gas chromatography
HPγCD	hydroxypropyl-γ-CD
HPLC	high-performance liquid chromatography
ITP	isotachophoresis
LIF	laser-induced fluorescence
LOD	limit of detection
M	2-(2-methyl)-propionic acid
MβCD	methyl-β-CD
MCPA	2-methyl-4-chlorophenoxy-acetic acid
MCPB	4-(2-methyl-4-chloro-phenoxy)-butyric acid
MCPP	2-(2-methyl-4-chloro-phenoxy)-propionic acid
MD	2-(4,6-dichlorophenoxy)-propionic acid
MEGA 9	nonanoyl-N-methylglucamide
MEKC	micellar electrokinetic chromatography
MS	mass spectrometry
OG	octyl-β-D-glucopyranoside
OM	octyl-β-D-maltopyranoside

OS	*n*-octanoylsucrose
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorodibenzo-*p*-dioxin
PEG	polyethylene glycol
pK_a	negative logarithm of acid association constant
2-PPA	2-phenoxy-propionic acid
PVP	polyvinylpyrrolidone
RPLC	reversed-phase liquid chromatography
SBβCD	sulfobutyl ether-β-CD
SDS	sodium dodecyl sulfate
SPE	solid-phase extraction
SUA	sodium 10-undecylenate
SUS	sodium 10-undecylsulfate
2,4,5-T	2,4,5-trichlorophenoxy-acetic acid
TCDD	tetrachlorodibenzo-*p*-dioxin
THpAB	tetraheptylammonium bromide
THxAP	tetrahexylammonium perchlorate
TMβCD	2,3,6-tri-O-methyl-β-CD
2,4,5-TP	2-(2,4,5-trichlorophenoxy)-propionic acid
US EPA	United States Environmental Protection Agency

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