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Review

Solid-phase extraction coupling to capillary electrophoresis with emphasis on environmental analysis

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Abstract

This article reviews the status of solid-phase extraction (SPE) coupled with capillary electrophoresis (CE). It focuses on some of the organic pollutants which have captured the interest of analytical chemists — phenols, surfactants, dyes, polynuclear aromatic hydrocarbons (PAHs), aromatic and aliphatic amines, aromatic acids and aromatic sulfonic acids — and, in particular, on monitoring pesticides from different sources. It shows that the coupling of SPE to CE has considerable potential in the analysis of environmental pollutants.

Keywords: Reviews; Solid-phase extraction; Environmental analysis; Preconcentration; Surfactants; Polynuclear aromatic hydrocarbons; Dyes; Amines; Sulfonic acids; Pesticides; Phenols; Aromatic acids

Contents

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1. Introduction

In recent decades, pollutant compounds in the environment have been increasingly studied because of their toxicity, persistence and bioaccumulation. Hundreds of compounds have been identified, many of which have been qualified as priority by the US Environmental Protection Agency (EPA) and the European Union (EU). Most of these compounds are released into the environment as a consequence of human activity. The environment is subject to such excessive strains as farming, industry and densely populated areas which inflict serious damage on the ecological balance.

The main steps in environmental analysis have been described in the literature [1,2]. They are (i) sampling and sample preparation, (ii) clean-up and/or extraction, and (iii) final separation and qualitative and quantitative determination. Since analytes can be contained in a wide variety of matrices (i.e., aqueous samples can include rain and tap waters, river, marine and ground waters, and industrial waters; solid samples can include soils and sediments and other types of solid waste; and air samples) a considerable amount of effort has been made to deal with the handling of environmental samples before CE [2].

When applied in the environment, some of these pollutant compounds undergo degradation and dilution. Thus, they — and their metabolites — can only be determined at trace levels in environmental matrices with highly efficient separation methods which have good sensitivity and selectivity.

Chromatographic techniques — particularly gas chromatography (GC) and high-performance liquid chromatography (HPLC) — have certain characteristics which have given them a privileged position among the analytical techniques used in environmental analysis. GC is a very efficient technique with a high resolution power for volatile but non-thermally labile compounds, which can be coupled to very sensitive and specific detectors [3–5]. HPLC is suitable for determining soluble analytes and solves the problem of thermally labile and polar compounds which require a previous derivatization step if they are to be determined by GC [6,7].

In the environmental field, capillary electrophoresis (CE) is becoming increasingly popular as an important analytical technique which can complement the chromatographic techniques. The rapid expansion of research into both the instrumentation and applications of CE has demonstrated that it is an interesting tool for many analytical separations and that it is highly efficient at separating all sort of polar and non-polar compounds, including a wide variety of pollutants [8–18]. So, interesting reports in this field are being published continuously [19–21]. Moreover, the different modes of CE such as capillary zone electrophoresis (CZE), micellar electrokinetic capillary chromatography (MEKC) and capillary electrochromatography (CEC) have considerably increased the applicability of this technique. Many publications [8,17,20,21] have demonstrated that CE can be a good alternative for some environmental pollutants that are usually monitored by HPLC or GC.

Typically, CE separations are performed in fused-silica capillaries with internal diameters of 25–100 μm and they provide high theoretical plate numbers. These diameters, however, and the fact that only a small sample volume can be injected are responsible for the major limitation of the technique: its sensitivity, particularly with UV absorbance detection. The sensitivity of CE can be improved either by using a more sensitive detection method or by performing a preconcentration step before separation. This preconcentration step consist of either an extraction process like solid-phase extraction (SPE) [4,5,22–24] or the injection of larger sample volumes into the capillary by means of the different systems described in the literature [25–28].

The purpose of this review is to outline the status of SPE coupling with CE in the environmental field. The groups of compounds which have received most attention are phenols, surfactants, dyes, polynuclear aromatic hydrocarbons (PAHs), aromatic and aliphatic amines, and aromatic acids and aromatic sulfonic acids and pesticides. The review also shows that the different CE modes provide different separation efficiencies for many pollutants. Whenever possible, applications of the described procedures to real samples have been reported. The SPE-CE applications are summarised in Table 1.

2. Significant modes in capillary electrophoresis

Capillary electrophoresis has been increasingly

Table 1
Some environmental applications of SPE-CE

Compounds	SPE sorbent	CE mode	Electrophoretic buffer	Detection limits	Sample matrix	Ref.
Surfactants						
LAS	RP-C_{18} and SAX	CD-MEKC	250 m*M* borate, pH 8, 30% acetonitrile	1 mg l^{-1}	River and waste water samples	[92]
Sulfophenylcarboxylates	Carbopack B	CE	20 m*M* citrate buffer, pH 4 and 60 m*M* α-CD	μg l^{-1} range	Sewage water	[94]
PAHs						
16 US EPA priority PAHs	PDMS fiber (SPME)	CD-CZE	50 m*M* borate buffer, pH 9.2, 35 m*M* SB–β-CD, 10 m*M* M–β-CD and 4 m*M* α-CD	8–75 μg l^{-1}	Water samples	[53]
Dyes						
Sulfonated azo dyes	SDB disks and SCX cartridges	MEKC	50 m*M* boric/borate and 100 m*M* sodium cholate	μg g^{-1} (spiked levels)	Water and soil samples	[30]
8 Mono- and disulfonated commercial dyes	Isolute ENV+ and LiChrolut EN	MEKC	Ammonium acetate 9.2 m*M* and Brij 35 0.05%	10–150 μgl^{-1}	Groundwater samples	[107] [108]
4 Industrial dyes	SAX Bond Elut		20 m*M* Borate or 50 m*M* citric acid/10% acetonitrile	5×10^{-8}–1×10^{-7} M	Aqueous solutions	[109]
7 Synthetic dyes	SCX, C_{18} cartridges	MEKC	50 m*M* boric/borate, 100 m*M* sodium cholate and 10% acetone	μg g^{-1} (spiked levels)	Water and soil samples	[110]
Fluorescent dyes	SDVB		40 m*M* borate	10^{-4} M	Groundwater samples	[111]
Photoactive dyes	Amino and SAX columns	CZE	50 m*M* boric acid/10 m*M* sodium borate, pH 8.5	0.08–0.19 μg l^{-1}	Coffee cherries, green roasted beans	[112]
Aliphatic and aromatic amines						
Aliphatic amines	SCX cartridge-disks, C_{18}		5 m*M* Imidazole or 5.5 m*M* *N*-ethylbenzylamine	0.02 m*M*	Aqueous solutions	[113]
21 Aromatic amines	SDVB	CZE	50 m*M* phosphate, pH 2.35 and 7 m*M* 1,3-diaminopropane	0.06–1.8 mgl^{-1}	Real samples	[114]
Heterocyclic aromatic amines	Extrelut, Bond-elut, PRS, C_{18} cartridges	CZE	10 m*M* KCl–HCl (pH 2.2)	25–45 μg l^{-1}	Beef extract	[23]
4 Heterocyclic aromatic amines	Extrelut-20, C_{18} cartridges	CZE	30 m*M* Na_2PO_4, 30% methanol, and 20 m*M* NaCl at pH 2.0	0.08–0.16 mgl^{-1}	Cooked foods	[115]
Biogenic amines	C_{18}	MEKC	100 m*M* borate, pH 9.4 and 30 m*M* SDS	0.1 mg ml^{-1}	Soy samples	[116]
Aromatic acids and aromatic sulfonic acids						
Aromatic acids	Sep-Pak C_{18}	CZE	13 m*M* sodium borate pH 9.68	Low mg l^{-1}	Natural waters	[117]
21 Naphthalene sulfonates	C_{18}, SCX cartridge	CZE, MEKC	50 m*M* boric with 100 m*M* SDS or 15% acetonitrile	sub-μg l^{-1}	River water	[118] [119]
14 Aromatic sulfonates	SDVB (Lichrolut EN)	CZE	25 m*M* sodium borate, pH 9.3	μg/l range	Tap, river and seepage water samples	[120]
Pesticides						
Hydroxymetabolites of atrazine	Amberchrom resin	CZE	80 m*M* acetate, 62 m*M* phosphate buffer, pH 4.70	Sub-μg l^{-1}	Potable water	[121]
Triazines herbicides	C_{18}, Oasis HLB cartridges	CZE	acetonitrile–methanol (50:50, v/v), 7.5 m*M* perchloric acid and 17 m*M* SDS	0.01–0.05 μg l^{-1}	Natural waters	[122]
Chlorophenoxy acid herbicides	C_{18} disks	CD-CZE	0.1 *M* Na_2HPO_4, NaH_2PO_4, pH 5.6	Sub-μg l^{-1}	Lake water	[123]
Sulfonylurea herbicides	C_{18}, silica cartridges	CZE	50 m*M* acetate buffer, pH 4.76	Sub-μg kg^{-1}	Soil samples	[124]
Sulfonylurea herbicides	RP-102, SAX, alumina cartridges	CZE	50 m*M* ammonium acetate, 50 m*M* acetic acid, 12% acetonitrile	0.1 μg l^{-1}	Different water matrices	[31] [32]
Linuron, metalachlor, atrazine, and metsulfuron	C_{18} cartridges	MEKC	50 m*M* sodium borate, pH 8.0, 35 m*M* SDS, 10% methanol	μg l^{-1}	Tap water	[125]
Chlorsulfuron, chlorimuron and metsulfuron	C_{18} cartridges	MEKC	30 m*M* sodium borate, pH 7, 80 m*M* SDS, 14% MeOH, 20% isopropanol	10 μg l^{-1}	Soil samples	[126]

Table 1. Continued

Compounds	SPE sorbent	CE mode	Electrophoretic buffer	Detection limits	Sample matrix	Ref.
Monuron, linuron, diuron, isoproturon and monolinuron	C_{18} cartridges	MEKC	4 m*M* sodium tetraborate, 12 m*M* NaH_2PO_4, pH 7.0, 30 m*M* SDS	0.04 μg l^{-1}	Rain and surface water samples	[127]
Simazine, cyanazine, atrazine, ametryne, propazine, prometryne and terbutryne	C_{18} cartridges	MEKC	60 m*M* borate buffer, pH 9.2, and 50 m*M* SDS	Sub-μg l^{-1}	Natural waters	[128]
Pesticide mixture	Carbopack, C_{18} cartridges	MEKC	20 m*M* phosphate, pH 7, with 50 m*M* SDS and butanol	Sub-μg l^{-1}	Water samples	[41]
Triazine dione herbicide	ENVI-Carb cartridges	MEKC	12 m*M* Na_2HPO_4, 10 m*M* sodium borate, 50 m*M* SDS and 15% methanol	Sub-μg l^{-1}	Groundwater	[42]
Atrazine and terbutylazine metabolites	SDVB (LiChrolut EN)	MEKC	30 m*M* sodium borate, pH 9.3, 30 m*M* SDS	Sub-μg l^{-1}	Tap and river water	[129]
11 Carbamates	SDVB	MEKC	Sodium borate, 50 m*M* SDS and methanol	μg l^{-1}	Tap water	[130]
Carbamates and their hydrolytic metabolites	Activated carbon, RP-C_{18}, XAD-2, Florisil, Serdolit PAD I and LiChrolut-EN	MEKC	25 m*M* phosphate and 20 m*M* borate, pH 8, with 40 m*M* SDS	μg l^{-1}	River and pond water	[131]
2 Organotin compounds	C_{18}, C_8, phenyl functionalized sorbent, Amberlite XAD-2 and Amberlite XAD-4	CZE	20 m*M* tartaric acid, 20% methanol, 4 m*M* BTMA	μg l^{-1}	Natural waters	[132]
7 Enantiomeric pesticides	Oasis HLB cartridges	CD-MEKC	50 m*M* NaH_2PO_4, pH 7, 50 m*M* sodium cholate, 15 m*M* DM–β-CD	μg l^{-1}	Lake water	[133]
Carbamates and triazines	C_{18} cartridges	MEKC	50 m*M* borate, pH 8, 30 m*M* SDS	0.1 μg l^{-1}	Drinking water	[72]
6 Organonitrogen pesticides	C_{18} cartridges	MEKC	12.5 m*M* sodium borate, pH 9, 50 m*M* SDS	0.8 μg l^{-1}	Drainage water	[73]
9 Urea herbicides	C_{18} cartridge	CEC	NaH_2PO_4, pH 6/ACN 40:60 (v/v)	0.1 μg l^{-1}	Water samples	[134]
Triazines	On-line C_{18}	CZE	50 m*M* phosphate	μg l^{-1}	Water samples	[135]
Triazines	At line C_{18} SPE mini-column	MEKC	10 m*M* NaH_2PO_4, 60 m*M* SDS, 8% ACN, pH 9.5	μg l^{-1}	River water samples	[67]
Phenols						
11 EPA priority phenols	SDVB	CZE	20 m*M* borate, pH 9.9	μg l^{-1}	River and industrial waste water	[136]
Pentachlorophenol	Graphitized carbon black cartridges	CZE	40 m*M* sodium borate, pH 10	ng l^{-1}	Drinking water	[40]
Chloro- and nitrophenols	Cross-linked polystyrene cartridges	CZE	40 m*M* sodium borate, pH 9.8	μg l^{-1}	Tap waters	[138]
Pentachorophenol	On-column SPME (PA fiber)	CZE	20 m*M* sodium borate, pH 9.9	μg l^{-1}	Water samples	[52]
Chlorophenols	Cross-linked polystyrene–divinylbenzene copolymer cartridges	MEKC	50 m*M* *N*-(2-acetoamido)-2-aminoethanesulfonic acid (ACES) at pH 6.1 with 22 m*M* SDS	0.1 μg l^{-1}	River water	[140]
Miscellaneous						
Haloacetic acids	SAX, SDVB, graphitized carbon black, OASIS HLB	CZE	4 m*M* 2,6-naphthalene dicarboxylic acid, 0.5 m*M* CTAB (pH 7.5)	μg l^{-1}	Chlorinated waters	[38]
Metallo–cyanide complexes	Sep-Pak C_{18} cartridges	CZE	5 m*M* trimellitic acid, pH 9.5	mg l^{-1}	Leaching solutions from a gold mine	[143]
EDTA	SAX disks	CZE	30 m*M* ammonium formiate pH 3 with formic acid	0.15 μg l^{-1}	Water samples	[145]
Alkylphosphonic acids	Barium, silver and cartridges H^+	CZE	200 m*M* boric acid, 16 m*M* phenyl-phosphonic acid, 0.03% Triton X-100, 0.35 m*M* DDAOH, pH 4	1–50 μg l^{-1}	Water and soil samples	[147]

used in the last few years to separate and determine a wide range of analytes. CE have been extensively used in biomedical fields for such important analyses as DNA sequencing, protein identification, drug analysis, etc. More recently, CE is also being used in the field of environmental analysis. Environmental pollutants comprise a wide variety of compounds, and different strategies are required to separate them.

Capillary zone electrophoresis (CZE) separation is based on differences in the electrophoretic mobilities (determined by size and charge) of charged analytes in an electric field. However, since many environmental pollutants are uncharged or have very similar chemical structures, they often cannot be separated by CZE and micellar electrokinetic capillary chromatography (MEKC) has to be used. MEKC separations are based on the differential solubilization of the analytes in the micellar phase. So, they are partitioned between the micelle (the so-called pseudostationary phase) and the aqueous phase which means that they can be retained differently and then resolved, even when they have no charge or when the charged compounds are badly resolved by CZE.

Capillary electrochromatography (CEC) uses an electric field and an electroosmotic flow to drive solutes through a capillary column packed with a chromatographic type stationary phase. Separation is based on partitioning the analytes between the running buffer and the stationary phase, and, in the case of charged analytes, on their electrophoretic mobility.

3. Solid-phase extraction and solid-phase microextraction procedures

Preconcentration and clean-up systems such as liquid–liquid extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME) are needed to determine concentrations of pollutants in environmental samples. Nowadays, LLE is being replaced by SPE and SPME because they do not require large amounts of generally toxic and inflammable solvents, and the concentration step is cheaper and shorter.

Sometimes, before the analytes are separated, the sample must be cleaned up to avoid interferences. In some studies [23,29–32] SPE has been used as a clean-up and preconcentration technique so that the selectivity and limits of detection of the analytes are better. Krynitsky [31] presents an extraction/clean-up system for analysing sulfonylurea and sulfonamide herbicides by CE in marsh water. First of all, the samples were extracted with a reversed-phase RP-102 SPE cartridge and then the extract was cleaned up with a tandem system consisting of a strong-anion-exchange (SAX) SPE cartridge stacked on top of an alumina SPE cartridge. The extracts were clean enough to confirm $\mu g\ l^{-1}$ levels of the herbicides. Apart from the main goal of extracting traces of the compounds of interest and removing the interfering components from the matrix, SPE is also used to change the solvent (e.g., aqueous to organic) and store and transport the analytes [33].

Nowadays, new sorbents have been commercialised, mainly for the extraction of polar analytes: C_{18} specially designed for polar compounds [34,35], several styrene–divinylbenzene copolymers [22,36–38], graphitized carbon blacks [39–42], and poly-(divinylbenzene-Co-*N*-vinylpyrrolidone) copolymers [38,43,44].

Recently, a new extraction technique, solid-phase microextraction (SPME) has been introduced as an alternative to conventional techniques [45]. SPME is a rapid solvent-free technique for extracting organic compounds from environmental samples and it is easily automated with certain modifications [46]. SPME is based on the partition equilibrium of target analytes between a polymeric stationary phase, which is coated on a fused-silica fiber, and the sample matrix. SPME can easily be coupled to GC and, with some modifications, to LC and CE [47–53].

Very few applications of SPME in conjunction with CE have been reported. The SPME-CE coupling is more difficult than SPME-LC because the interface must allow for the introduction of the very small injection volumes used in CE. However, the miniature nature of the extraction fiber suggests that in the immediate future many SPME-CE separations will be developed. In environmental analysis, SPME with CE has been applied to determine 16 EPA priority PAHs using CD-modified CE [53]. A polydimethylsiloxane (PDMS) fiber was used to absorb the compounds from diluted samples and the analytes were directly released into the CE electrolyte stream,

using an adapter. Whang and Pawliszyn [52] designed an interface that enables the SPME fiber to be inserted directly into the injection end of a CE capillary. They prepared a 'custom-made' polyacrylate fiber to reach the SPME-CE interface (Fig. 1). This interface was tested for determining phenols in water samples.

The advantages of on-line over off-line SPE or SPME are that it is more sensitive and manipulates the samples less. This makes it more precise and easier to automate. Some studies have shown the potential of on-line SPE in CE [54–64]. A small amount of sorbent, either a bed of solid-phase packing material [57–62] or an adsorbing polymeric membrane [63,64] is placed on-line as a microcartridge at the inlet end of the capillary in the CE instrument. Recently Petersson et al. [62] presented the construction of an enrichment capillary to be used in on-line SPE-CE. The enrichment capillary was made small enough to be used in a commercial instrument and once installed in the CE instrument no manual handling was required. To prepare the enrichment capillary, three capillaries of two different inner diameters (I.D.s) were used. The smaller I.D. capillary was inserted between other capillaries with higher I.D.s and fixed with epoxy glue. Concentration factors of three to four orders of magnitude were reached.

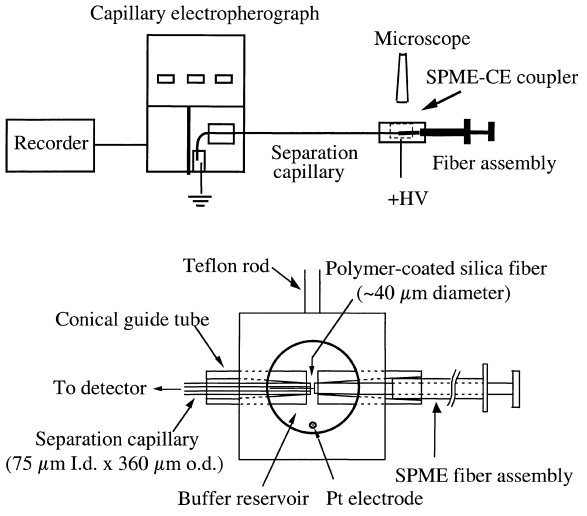

Fig. 1. Schematic of the SPME-CE system. Reproduced from Ref. [52], with permission of The Royal Society of Chemistry.

Veraart at al. [65] presented an at-line SPE device for CE. An automated SPE unit is connected to the CE instrument by means of a laboratory-made interface (Fig. 2). The polyetherether ketone (PEEK) tubing interface allows a continuous flow of the CE buffer through the interface and at the end of the SPE step the analytes are desorbed using a solvent that is flushed through the interface via a loop. The system was used to analyse about 900 complex biological samples for a year and the loop, interface and capillary did not block up during this period.

Valcárcel and co-workers [24,66,67] coupled an automated continuous flow system (CFS) for sample preconcentration to a commercial CE instrument using a mechanical and electronic interface. A SPE process was incorporated in the CFS for automatic preconcentration. The mechanical interface was a laboratory-made programmable arm which directly injected the sample into the sample vial in the autosampler of the CE instrument. The system enabled pesticides present in real samples at trace levels to be preconcentrated and determined completely automatically [67].

4. Other methods for manipulating sensitivity in CE

The sample size in CE is determined by the length of the sample introduction procedure. When the injection time increases, the length of the sample plug injected into the capillary also increases, and detection limits can be lower. However, the increase in the sample injection is limited by the impact of peak broadening, and can negatively influence the separation efficiency. To increase the amount of sample injected beyond the optimal conditions, but to still maintain high resolution, the sample matrix must be removed after the stacking process is completed [68–70]. One way of doing this is to pump the matrix out of the column using the electroosmotic flow. However, this pumping technique works only on ions that have negative mobility with respect to the electroosmotic flow. The main advantage of this system is that, without modifying the instrument, large volume injections give enrichment factors of more than 500, which make it possible to make analyses at low $\mu g\ l^{-1}$ levels.

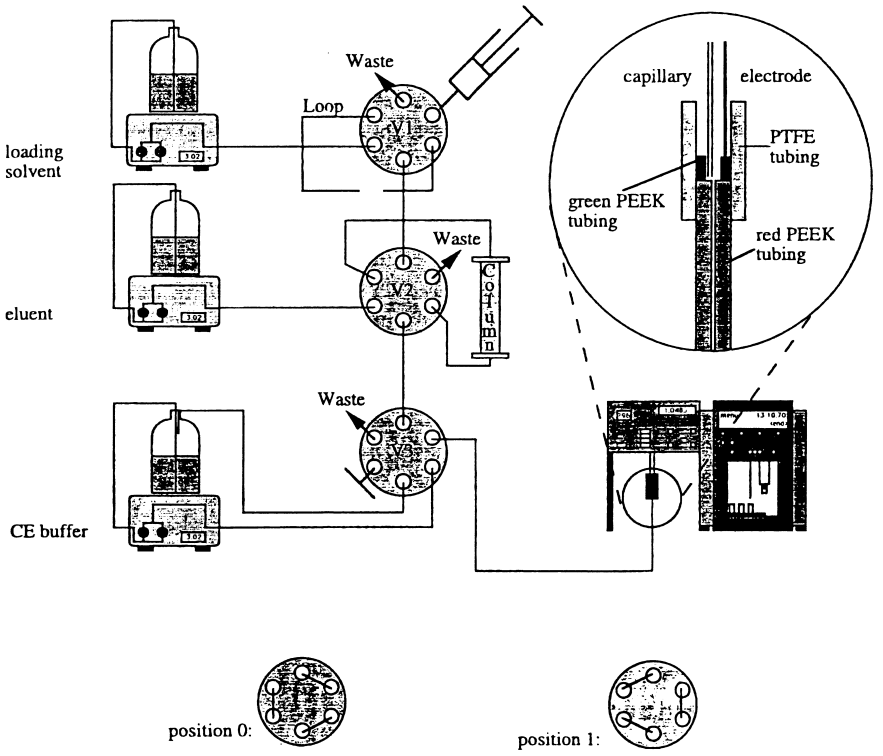

Fig. 2. Schematical representation of the LC–CE configuration. Reprinted with permission from Ref. [65].

The maximum filled length of sample which is possible without loss of any analytes using this technique has been studied theoretically [68]. Nevertheless, some authors [69,70] have concluded that results are good when the whole capillary is filled with the sample solution. Recently, this technique has been used in such environmental applications as the determination of phenols [69,71] and pesticides [72–75]. In all these examples, the limits of detection were reduced, and it can be seen that the technique can be used to separate and detect low amounts of analytes in relatively clean samples. However, it can be problematic in real samples in which the matrix components can interfere and mask the analytes of interest.

Isotachophoresis (ITP) is an electrophoretic technique which is carried out in a discontinuous buffer system. ITP can be used to preconcentrate samples in CE [76,77]. The on line ITP-CE combination can be used in several different arrangements [78–80]. With on line ITP-CE, two capillaries are connected. The ITP capillary enables the analytes to be concentrated and the matrix components to be removed, and the narrow-diameter CE capillary ensures the sensitivity of the analysis. The potential of the on-line ITP-CE technique has been shown by the environmental trace analysis of herbicides, such as diquat and paraquat, and other polar pollutants [78]. With ITP-CE, the minimum detectable concentration of these compounds can be reduced by a factor of 10^3–10^4 compared to single CE. The on-line coupling of ITP and CE has also been used to determine traces of iron in water at the $\mu g\ l^{-1}$ level [81]. Water samples from different sources showed that no peaks interfered in the iron determination.

Several research groups have carried out interesting studies with LC components coupled on-line to CE. Like on-line ITP-CE, two capillaries are coupled

together. The LC capillary is used for preconcentration and clean up, and traps the analytes when large sample volumes are loaded. The CE capillary separates the analytes retained in the LC capillary. The on-line LC–CE system has been used in samples which have higher salt concentrations than the CE electrolyte for which the electric field over the sample plug is too low and the peak sharpening effect is less effective [82]. When LC is coupled to CE, however, the peak shape of the analyte is the same for different salt concentrations.

5. SPE-CE applications

The review mainly focuses on organic pollutants of environmental interest, but the miscellaneous section discusses other applications, which are not the main focus of environmental analysis but they show that SPE-CE is increasingly applied to a broader range of compounds.

5.1. Surfactants

Surfactants are applied as complex homologous and isomeric mixtures in such household and industrial products as laundry detergents, cosmetics and pharmaceuticals. Surfactants have a toxic impact on aquatic organisms and long-term effects on soils and sediments after they have been deposited.

Surfactants present a variety of analytical problems: they are made up of many different components, they are not volatile and they occur as interferences in environmental analyses. CE, however, can provide high resolution separation of a wide variety of ionic and nonionic surfactants, and can analyse standard mixtures and industrial products, as well as complex formulations such as detergents, cosmetics, pharmaceuticals and environmental samples [83–86]. Likewise, homologous oligomers and isomers can be resolved in a short analysis time. Despite these advantages it has one main drawback: its detection limit is higher than the limit of chromatographic separations.

Linear alkylbenzenesulfonates (LAS) are the most widely used anionic surfactants in detergent formulations and they are the surfactants which have most been studied. They are present in commercial formulations as complex mixtures of C_{10}–C_{14} homologues and of the positional isomers which results from the attachment of the phenyl ring to the carbon atoms (from the second to the central one) of the linear alkyl chain. Due to their detergent properties, they have a toxic influence on aquatic organisms. Therefore, the selective and sensitive determination of LAS in environmental samples is of great importance [87,88].

CE is very suitable for determining LAS because they have both charge and UV absorbance. LAS have been determined as total LAS and separated into homologues and isomers in industrial and household formulations. Total LAS content, which is sufficient for general assessment of the pollution of waste water and surface water, can be determined by CZE using phosphate or borate buffers without adding organic solvents [89]. Homologous and isomeric separations are important in industrial and environmental samples, because detergent properties, biological degradation and aquatic toxicity depend on the alkyl chain length and the position of the phenyl.

Using organic solvents like acetonitrile as buffer modifiers, alkyl homologues of LAS can be separated [89–91]. The isomeric separation of LAS has been extensively studied by Vogt and co-workers [89,92]. They separated the LAS isomers using host–guest interactions with cyclodextrins in technical products [85,89] and they also described a method for almost complete resolution of LAS isomers based on the formation of association complexes with SDS in phosphate–acetonitrile buffers [92,93]. They applied both methods to determine total LAS and homologous distribution in various real samples after enrichment by SPE. They used a combination of RP-C_{18} columns and SAX cartridges to preconcentrate and clean up LAS. The SAX cartridge was used for the clean-up step to remove disturbing non-ionic compounds, to prevent an irreversible contamination of the inner capillary surface and to stop matrix components overlapping LAS peaks. In waste water samples, recoveries were high, but enrichments were low for the longer chain homologues. The limit of detection was found to be 1 mg l^{-1}. In sewage sludge samples (Fig. 3) LAS homologues were quantified at low mg g^{-1} levels and after SAX

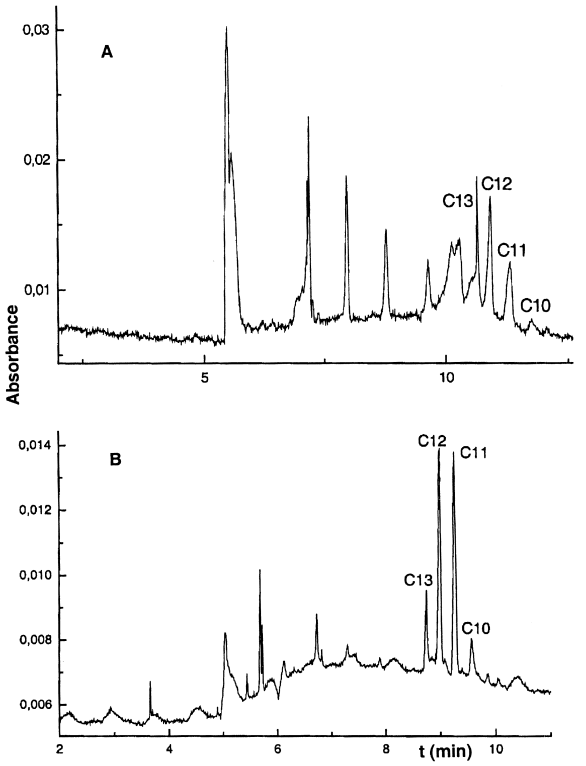

Fig. 3. Analysis of sewage sludge for LAS (a) after methanolic and SAX extraction. Capillary, 50/57 cm×75 μm I.D.; voltage, 25 kV; detection, UV at 200 nm; buffer, 250 m*M* borate (pH 8)–30% acetonitrile. Reproduced from Ref. [92], with permission of The Royal Society of Chemistry.

extraction recoveries were between 33.1 and 70.5%. The authors conclude that CE was efficient and sensitive enough to analyse LAS in samples such as household detergents, river waters, waste waters and sewage sludges. They recommend that the preconcentration process be carefully optimised according to sample composition.

Biodegradation of LAS leads to a series of mostly chiral isomeric sulfophenylcarboxylates (SPC) which can be detected in treated sewage effluents. CE was applied with α-cyclodextrin as the chiral selector to separate the enantiomers of *p*-sulfophenyl-2-butyrate (SP2B) and *p*-sulfophenyl-3-butyrate (SP3B) [94]. Using SPE on the graphitized carbon black Carbopack B sorbent, and applying a stacking technique in CE, chiral biodegradation intermediates were determined at the μg l^{-1} level in mechanically treated sewage effluent. Samples of filtered sewage water were passed through the Carbopack B cartridge, and the analytes were eluted with ammonium acetate in dichloromethane/methanol. The eluate was evaporated and the residues were redissolved in water and analysed by CE using citrate buffer containing α-CD, with a detection limit for SP3B of 0.1 μg l^{-1}.

Recently, considerable attention has been paid to the cleaning of processing equipment within the pharmaceutical industry to ensure that no cross-contamination of the manufactured product arises from material left over from a previously manufactured product. Although they did not use a preconditioning step, Altria et al. [95] reported that CE could be used with a simple, high-pH buffer to quantitatively monitor detergent residues at trace level after processing equipment had been cleaned. They improved the sensitivity of the CE analysis using indirect UV detection and low wavelengths (200 nm), where many solutes have enhanced UV activity. The limit of detection was found to be 0.6 mg l^{-1}, which meant that the method is well suited for routine purposes in the pharmaceutical industry.

5.2. Polycyclic aromatic hydrocarbons (PAHS)

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants of anthropogenic origin which are a potential health concern because of their toxicity, mutagenicity and carcinogenicity in animals. They can be detected in the atmosphere as well as in surface waters, sediments and soils. Several laws on water for public consumption include control over PAHs.

PAHs are difficult to separate using CZE because they are uncharged and highly hydrophobic. As reported in previous papers [16,96] a number of different approaches, such as MEKC [97,98], CD-modified CE [99–101] and CEC [102–104], have been used to separate these compounds. In order to improve the sensitivity detection compared to on-line absorbance detection, laser-induced fluorescence (LIF) detection has been used [105].

Luong and co-workers [53,99,106] developed several cyclodextrin-modified CE procedures to separate the 16 US EPA priority PAHs using LIF detection. A separation method using a mixture of a negatively charged β-CD and a neutral β-CD was able to separate the 16 US EPA priority PAHs as well

as other aromatic hydrocarbons with high efficiency in 20 min [106]. The method developed was used to analyse PAHs in contaminated soils. Soils were extracted using CO_2 supercritical fluid extraction (SFE), and the extract was provided in dichloromethane/methanol. The extracts were diluted 50-fold in methanol–water and analysed, providing sensitive detection of 11 of the 16 compounds at low $\mu g\ l^{-1}$ levels.

Nguyen and Luong [53] developed the first application of SPME with CD-modified CE using a UV detector to separate and analyse PAHs (Fig. 4). A hand-made PDMS fiber was used to absorb the 16 US EPA priority PAHs from the diluted sample until equilibrium was reached. Then, the SPME fiber was connected to a separation capillary via an adapter and the absorbed analytes were directly released into the CE buffer stream. The electrophoretic separation was performed using a mixture of α- and β-CDs in borate buffer. The highest limit of detection was 75 $\mu g\ l^{-1}$ for acenaphthene and the lowest was 8 $\mu g\ l^{-1}$ for pyrene. The reproducibility was very satisfactory with respect to migration time and peak area for repetitions in which the same capillary and adapter were used and the extraction fiber was discarded after each analysis. The sensitivity is only slightly lower than for CE equipped with LIF. Nguyen and Luong announced that work is currently in progress to couple SPME-CE for the detection and quantification of PAHs in contaminated soils and water.

The considerable number of PAH capillary electrophoretic separation procedures described in the bibliography show that it is a useful technique for separating PAHs. However, only a few environmental applications have been reported in the period covered by this review.

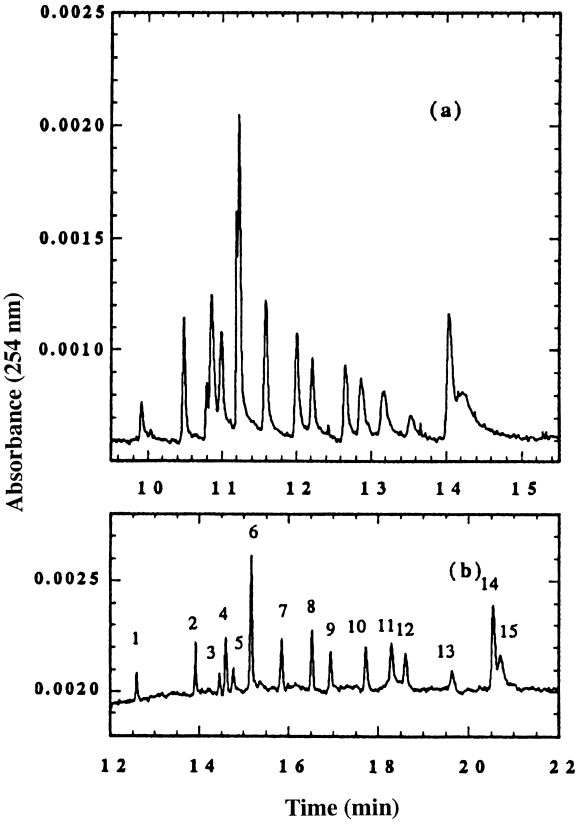

Fig. 4. Electropherograms obtained with 35 m*M* SB–β-CD, 10 m*M* M–β-CD, 4 m*M* α-CD in 50 m*M* borate buffer, pH 9.2. (a) Without microextraction, sample 40×, 57-cm capillary. (b) With microextraction, sample 4000×, 67-cm capillary. Peaks: (1) dibenz[*a,h*]anthracene, (2) acenaphthylene, (3) acenaphthene, (4) naphthalene, (5) fluorene, (6) anthracene, (7) phenanthrene, (8) chrysene, (9) benz[*a*]anthracene, (10) benzo(*k*)fluoranthene, (11) fluoranthene, (12) benzo[*a*]pyrene, (13) pyrene, (14) benzo[*b*]-fluoranthene, (15) indeno[1,2,3-*cd*]pyrene. Reprinted with permission from Ref. [53]. © 1998 American Chemical Society.

5.3. Dyes

Large quantities of dyes are produced and used in the manufacturing of various products such as textiles, paint pigments, printing inks and food colouring. Dyes are difficult to determine because they encompass many chemical functionalities with considerable differences in solubility, volatility, etc.

Sulfonated azo dyes are widely used in the textile industry to colour natural fibres. Their degradation products include amines which are known to be carcinogenic. Sulfonated azo dyes are incompatible with GC because they are nonvolatile and thermally unstable compounds, and some problems have been found in the determination of these compounds by LC. Although most of these compounds are charged, the MEKC mode is usually preferred to separate them.

Brumley and Brownrigg [30] used MEKC with borate at pH 8.3 and cholic acid as running buffer to determine 56 aromatic-containing organic acids

(AOCAs) including several azo and other dyes. They extracted two sulfonated azo dyes (Tryptan Blue and Orange II) and five aromatic organic acids by means of Empore polystyrene–divinylbenzene extraction disks and strong cation-exchange (SCX) cartridges. Spiked water samples were extracted by Empore disks and eluted in two ways: with an organic aqueous solvent and with an ion-pairing agent. Fractions were passed through the SCX cartridge. Solid samples were extracted by either sonication or Soxhlet methods, and the extracts were subsequently treated like the water samples. Recoveries for the polysulfonated dye Tryptan Blue in soil were only about 28% and this was attributed to the complex structure of the dye. In water, the recoveries were higher. The monosulfonated dye Orange II was extracted with good recoveries for both water and soil samples.

Schönsee et al. [107] reported a MEKC method for determining eight mono- and disulfonated commercial dyes. An automated off-line SPE (ASPEC XL) followed by a MEKC analysis was optimised. Separation by MEKC with a buffer of ammonium acetate and Brij 35 provided good efficiency, resolution and reproducibilities. Two highly crosslinked polystyrene–divinylbenzene sorbents, Isolute ENV+ and LiChrolut EN, were compared as solid phases for the extraction of spiked groundwater samples, obtaining best recoveries (up to 71%) when Isolute ENV+ was used. So, it was selected for further investigations. The UV detection limits of the dyes for the preconcentrated spiked water samples ranged between 10 and 150 $\mu g\ l^{-1}$. As is shown in Fig. 5 satisfactory results were obtained for spiked ground water samples.

Recently, the same authors [108] determined one monosulfonated (Mordant Yellow 8) and seven disulfonated azo dyes (Acid Red 1, Mordant Red 9, Acid Red 13, Acid Red 14, Acid Red 73, Acid Yellow 23 and Acid Blue 113) in spiked groundwater samples and industrial effluents by automated SPE coupled to CE with UV and MS detection. CE-MS was used to confirm that the dyes were present in the extracted water samples. For the CE-UV analysis, the MEKC separation was carried out using ammonium acetate and Brij 35 in water as electrophoretic buffer, but for the CE-MS analysis, no Brij 35 was added to the buffer solution because it was found to suppress the ionization. In both Refs. [107] and [108], Isolute ENV+ and LiChrolut EN were compared, but in Ref. [108] an amine base (TEA) was added to the solvent mixture to enhance the effectiveness of the elution step. Using Isolute ENV+ as sorbent and 100% MeOH (0.01% TEA) as eluent, recoveries varied from 64 to 83% for most dyes. With LiChrolut EN, and even when the eluent was optimised, recoveries were poorer (up to 49%). Sulfonated azo dyes were determined in real samples from industrial effluents, with detection limits between 10 and 150 $\mu g\ l^{-1}$ for CE/UV detection and from 100 to 800 $\mu g\ l^{-1}$ for CE-MS under time-scheduled selected-ion monitoring conditions. The selectivity of the technique was good, particularly in the analysis of industrial effluents, where the number of interferences is high.

Farry et al. [109] investigated the limits of detection of four structural types of industrial dyes given by CE. The dyes used were Malachite green (MG), Indigo Carmine (IC), Cibacron Blue 3GA (CB) and Remazol Black B (RB). Off-line concentration using SAX Bond Elut cartridges was found to be an effective method for concentrating the hydrolysed Remazol dyes from 1 l sample volumes. The SAX Bond Elut cartridge is a strong anion-exchanger which binds negatively charged species like the hydrolysed Remazol dyes. Such species were only eluted with a counter ion such as Cl^-. When 30% conc. HCl in MeOH was used, recoveries for hydrolysed Remazol dyes were about 90% and detection limits were in the range 5×10^{-8}–1×10^{-7} *M*, which are 20–50 times better than the limits obtained using on-capillary stacking with reverse polarity CE.

Brumley et al. [110] compared capillary liquid chromatography (cLC) with MEKC using LIF detection to separate synthetic dyes (Nuclear Fast Red, Cresol Red, Acid Red 151, Acid orange 8, Orange II, Acid Blue 40, Tropaeolin O). Both techniques were capable of resolving the compounds studied at high efficiency. The MEKC buffer consisted of boric acid/sodium borate, sodium cholate and acetone. Four dyes (Cresol Red, Acid Orange 8, Acid Blue 40, Tropaeolin O) were selected for detailed studies of the extraction/clean-up of the dyes from water and soil matrices. Water samples were extracted using the polystyrene–divinylbenzene Empore

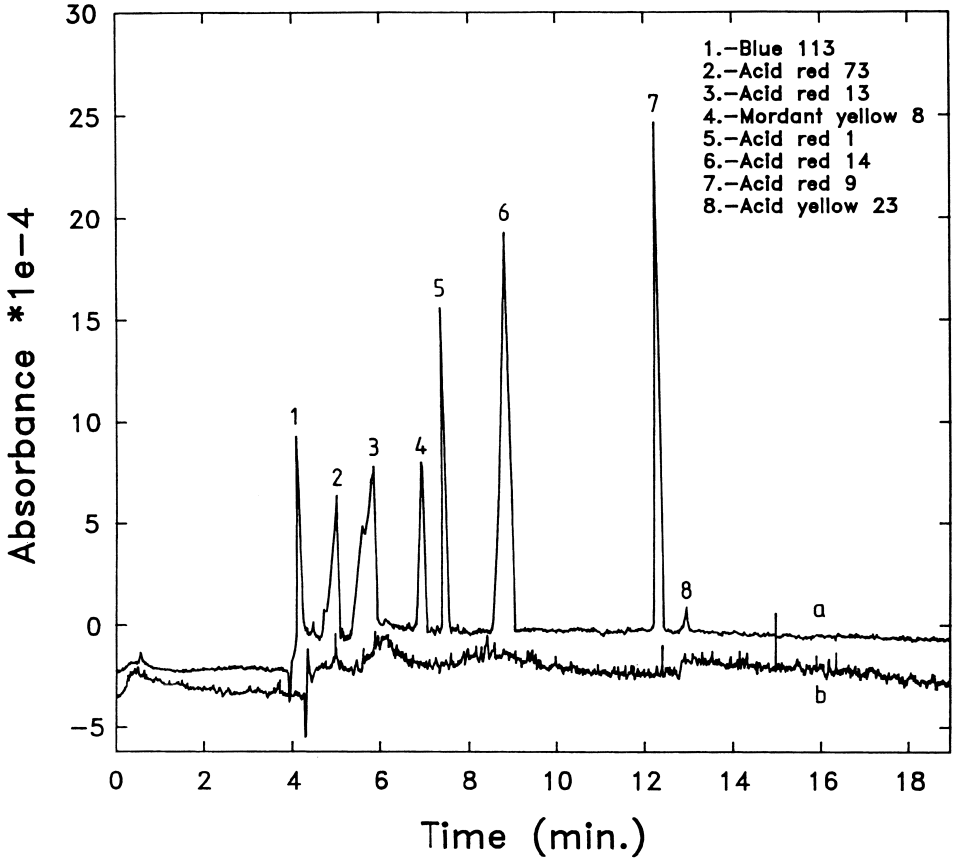

Fig. 5. (a) CE-UV (214 nm) electropherogram of the separation of eight sulfonated azo dyes spiked in groundwater (3 mg l^{-1}) after off-line SPE with Isolute ENV+ cartridges. Separation was carried out with a buffer solution of ammonium acetate 9.2 m*M* and Brij 35 0.05%. Peaks: (1) Acid Blue 113, (2) Acid Red 73, (3) Acid Red 13, (4) Mordant Yellow 8, (5) Acid Red 1, (6) Acid Red 14, (7) Acid Red 9, (8) Acid Yellow 23; concentration, 50 μg l^{-1}. (b) CE-UV (214 nm) electropherogram of an unspiked groundwater after SPE with Isolute cartridges. The injected blank was 20-fold higher concentrated than sample (a). Reprinted with permission from Ref. [107].

extraction disks. Water to be extracted was adjusted to pH 1 or solid cetyldiethylmethylammonium bromide (CEMA) was added to the spiked water for ion–pairing extraction. CEMA was removed from the extractant via an SCX cartridge. Both pH adjustment via acid and ion-pairing via cationic surfactant were investigated for isolating dyes. Recoveries of dyes from water at 1 mg l^{-1} were relatively good with both methods. Soils were extracted by sonication, and the diluted extract (pH 1) was passed through the Empore extraction disk. The compounds were isolated as for spiked water. An additional C_{18} SPE cartridge was used to clean up the samples isolated from the extraction disk. Recoveries were good (between 80 and 100%) for most compounds, except for Tropaeolin O, from 3 mg l^{-1} spiked soil samples. It was clear that MEKC and reverse phase cLC complemented each other because of their ability to quantitate and identify analytes, respectively.

Groundwater migration is an important factor which determines the distribution and fate of environmental pollutants originating from various waste sites. Fluorescent dyes can be used as groundwater migration tracers; they are a suitable choice because they are easily detected at low concentrations. Logically, CZE/LIF applications should be ideal for determining anionic or cationic dyes. In

CZE, the dyes are separated simply on the basis of their mobilities in aqueous buffers. Ferguson et al. [111] used CE/LIF detection to determine fluorescein dye as a tracer compound for groundwater migration and compared the results to those obtained with traditional spectrofluorimetry. Fluorescein was isolated from spiked deionized water samples or groundwater samples using SPE with styrene–divinylbenzene extraction disks. The SPE allowed the detection limit to be extended to 10^{-4} *M* in spiked water samples. The detection limits achieved by CE/LIF were as good as or better than those of traditional spectrofluorimetry, but specificity was increased because of the separation based on ion mobilities.

Alcantar-Licudine et al. [112] developed a method for analysing phloxine B and uranine. These photoactive dyes, were evaluated as fruit fly toxicants in coffee cherries and green roasted beans. The analytes were determined by HPLC and CZE using UV and fluorescence detection after clean-up with disposable amino cartridges. Several types of SPE columns (amino, SAX, cyano, diol, octadecyl, and phenyl) were first tested to cleanup the extracts. Amino and SAX were further investigated. The efficiency of the clean-up and elution was evaluated as recoveries of the dyes from the columns. The amino column was preferred because a higher concentration of base was required to elute the dyes from the SAX column. A mixture of MEOH–ACN–*n*-butylamine effectively extracted phloxine B and uranine, with good recoveries of each compound from both tested samples. The major advantages of CZE are the short analysis time and the inexpensive columns and aqueous buffer.

5.4. Aliphatic and aromatic amines

Aliphatic amines are commonly used chemicals: they are used as starting materials in the manufacturing of pharmaceuticals, insecticides, herbicides, fungicides, polymers, surfactants and rubber accelerators. The many commercial uses of aliphatic amines suggest that they will appear in the environment as pollutants. Thus, they are target analytes of several US EPA procedures.

Matchett and Brumley [113] used CE with indirect UV detection to determine several aliphatic amines (C_1–C_4 alkyl-substituted primary, secondary and tertiary amines) and some alkanolamines in water. Amines with similar mobilities were resolved by adding nonionic surfactants or selecting the pH and optimising the match between the mobility of amines and the running buffer. Various SPE adsorbents and systems for the preconcentration of such compounds were evaluated. Three adsorbent systems were examined: cation-exchange (SCX) cartridges, ion-pairing with C_{18} extraction disks and cation ion-exchange extraction disks. The average recoveries, from diluted aqueous solutions, for propyl-, dipropyl- and tripropylamine, using C_{18} extraction disks and sodiumdodecylbenzenesulfonate as ion pairing agent, were nearly 100%. Using cation-exchange disks, the recoveries for the same compounds compared well with the best ion-pairing results. Recoveries for some analytes, however, were disappointing. In particular, methyl- and ethylamine were not quantitatively recovered from the disks. Butyl-, dibutyl- and tributylamine approached quantitative recovery levels. The detection was in the range of 0.02 m*M* with preconcentration. These results demonstrated that CE with indirect UV detection is useful for determining organic amines in aqueous solutions and also that SPE can routinely achieve concentration factors in the order of 100-fold or more for selected analytes.

Substituted anilines and benzidines are widely used in the chemical industry as intermediates in the production of dyes, pesticides, pharmaceuticals, etc. These compounds are very well known because of their toxicity and suspected carcinogenicity. Owing to their high solubility in water, aromatic amines can easily permeate soil and contaminate groundwater. Cavallaro et al. [114] used a mixture of keto-derivatized and underivatized poly(styrene–divinylbenzene) copolymer for the selective SPE of 21 aromatic amines in environmental samples (Fig. 6). Before extraction, water samples were adjusted to pH 6.5–8, and the retained compounds were eluted with phosphoric acid in water–acetone. The extract was then analysed by CZE, using phosphate (pH 2.35) and 1,3-diaminopropane buffer, with UV detection. Linearity was good for all amines over more than 2 orders of magnitude of concentration. The limits of detection ranged from 0.06 to 1.8 mg l^{-1}. The recoveries for the amines were better than 82% except for the most hydrophilic ones, for which they

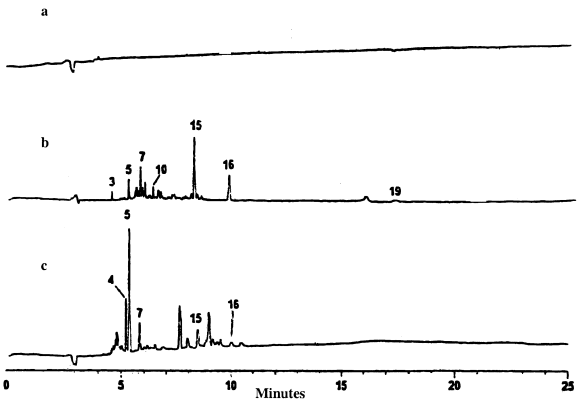

Fig. 6. Electropherograms of real samples after 1000-fold SPE preconcentration. (a) Tap water; (b) first layer groundwater. Peaks: (3) benzidine (2.7 μg/l), (5) aniline (1.8 μg/l), (7) *p*-anisidine (1.5 μg/l), (10) ethylaniline (0.5 μg/l), (15) *o*-chloroaniline (9.9 μg/l), (16) 3,4-dichloroaniline (2.9 μg/l), (19) 2,4-dichloroaniline (1.1 μg/l). (c) Soil sample from industrial plant. Peaks: (4) *o*-toluidine (600 μg/kg), (5) aniline (801 μg/kg), (7) *p*-anisidine (11.2 μg/kg), (15) *o*-chloroaniline (15.2 μg/kg), (16) 3,4-dichloroaniline (1.8 μg/kg). Buffer, 50 m*M* NaH_2PO_4–7 m*M* 1,3-diaminopropane (pH 2.35, adjusted with H_3PO_4); capillary, underivatized silica, 65 cm×50 μm I.D.; applied potential, 30 kV; detection, UV at 280 nm. Reprinted with permission from Ref. [114].

were about 60%. The proposed method is simple and fast, and complex matrices do not need to be prepared.

Heterocyclic aromatic amines (HAAs) are carcinogenic in rodents and may cause common human cancers as well. As reported in the literature, some beef flavours also contain potent mutagenic HAAs. Puignou et al. [23] developed a method to determine five HAAs by CE in a commercial meat extract. Sample preparation and clean up were carried out according to the method proposed by Gross using: EXtrelut extraction cartridges (a specially processed wide-pore kieselguhr with a high pore volume from Merck), the functionalized polystyrene–divinylbenzene Bond-elut polypropylsulfonyl silica gel sorbent and C_{18} cartridge. The absorbed HAAs were eluted from the C_{18} SPE column and analysed by CZE using KCl–HCl at pH 2.20 as running electrolyte. Detection limits ranged from 35 to 50 μg l^{-1} for hydrodynamic injection and from 25 to 45 μg l^{-1} for electrokinetic injection. CE separation proved to be an efficient technique for analysing complex matrices such as beef extracts; more than 25 peaks were resolved in a very short time, but only two HAAs, 2-amino-3,8-dimethylimidazo[4,5-*f*]quinoxaline (MeIQx) and 2-amino-3,4-dimethylimidazo[4,5-*f*]quinoline (MeIQ), were identified and quantified in the beef extract. They were quantified at 9.3 and 10.4 ng g^{-1} levels with recoveries of 77.7 and 66.6%, respectively. Selective and sensitive detectors were required to confirm the identities of the peaks resolved.

Mardones et al. [115] also developed a method for the simultaneous determination of four heterocyclic aromatic amines, 2-amino-3,8-dimethylimidazo[4,5-*f*]quinoline (IQ), 2-amino-3,8-dimethylimidazo[4,5-*f*]quinoxaline (MeIQx), 2-amino-3,4,8-trimethylimidazo[4,5-*f*]quinoxaline (4,8-DiMeIQx) and 2-amino - 1 - methyl - 6 - phenylimidazo[4,5 - *b*]pyridine (PHIP), in fried beefsteak, meat extract, and baked salmon. The Gross extraction procedure was also used for isolating the amines. Using Na_2PO_4, methanol, and NaCl at pH 2.0, the HAAs were separated within 20 min. The detection limits of this method were between 0.05 and 0.22 mg l^{-1} with hydrodynamic injection and, from 0.08 to 0.16 mg l^{-1} with electrokinetic injection. The method was applied to the analysis of real samples; recoveries ranged from 6% for PHIP to 91% for 4,8-DiMeIQx from various cooked foods. The recoveries of IQ, MeIQx and 4,8-DiMeIQx at concentrations within the range of interest provided a reliable quantification.

Biogenic amines can occur in a wide variety of foods such as soy sauce, fishery products, wine, or other fermented food. Biogenic amines may also have some potential carcinogenic effects. Arce et al. [24] reported the first method for the separating biogenic amines in wines using CE and indirect UV detection coupled with a minicolumn for SPE in a flow injection (FI) system [66]. Their objective was to determine the major biogenic amines which are normally found at levels above 1 mg l^{-1} in wine. Prior to separation by CE, the samples were cleaned-up to prevent interferences and concentrate the amines. A new interface for coupling FI with CE was developed to automate the treatment of samples and their transfer to the CE equipment. Weak cation-exchange adsorbents formed of carboxylic groups (CBA), and strong cation-exchangers (SCX) made

up of sulfonic groups and octadecylsilane (C_{18}) were tested and compared. The C_{18} minicolumn was chosen to concentrate the amines, which were separated within 15 min using copper(II) sulphate, formic acid and 18-crown-6 as running buffer and detected with limits of detection in the range 0.05–0.1 mg l^{-1}. The overall process was successfully used to identify biogenic amines in various types of wines. Rodriguez et al. [116] used ion-pair SPE to extract biogenic amines from soy sauce samples. Several variables were studied to establish conditions which led to the highest recoveries: type of ion-pairing agent, mode of extraction, and pH. With a C_{18} packing and dodecylbenzenesulfonic acid as ion-pair reagent, recoveries were high. The extracted amines were derivatized with fluorescein isothiocyanate, separated by MEKC and detected by LIF detection. Biogenic amines in soy samples were separated and quantified with detection limits in the order of 0.1 μg l^{-1}, depending on the sample source.

5.5. Aromatic acids and aromatic sulfonic acids

Aromatic acids such as vanillic, *p*-coumaric, ferulic and salicylic acid are important compounds in the aquatic environment. Distribution of these degradation products in the aquatic environment can provide basic information on the different sources of the overall dissolved organic matter. Deng et al. [117] developed a method for determining aromatic acids by CZE in combination with UV detection. The method was applied to analyse these compounds in natural waters. The aromatic acids were preconcentrated by means of SPE using Sep-Pak C_{18} PLUS cartridges at pH 2. Recoveries were quite successful for all compounds, except for the more polar ones, in 50 μ*M* spiked samples. The low recovery of the salicylic acid may be attributed to the high polarity and the low affinity for the non-polar packing material in the C_{18} PLUS column.

Aromatic sulfonates like benzene-, naphthalene-, anthraquinone- and stilbenesulfonates are widely used in industrial and domestic processes. Because of their low *n*-octanol–water partition coefficients (K_{ow}) they are highly mobile within the aquatic system. Therefore, they can easily pollute surface waters and pass through water treatment plants. The trace analysis of highly soluble aromatic sulfonates is still being developed and is not yet routine practice. Although they can be determined by CE, there are few reports about the analysis of such compounds and even fewer about real samples at trace levels [118,119].

Kok et al. [118] separated a mixture containing 21 naphthalene sulfonates in two runs, using a CZE and a MEKC. They analysed spiked river water samples using a three-step sample clean-up and enrichment procedure. Firstly, apolar interferences were removed using a C_{18} SPE column, and then the naphthalene sulfonates were trapped on a C_{18} column which was loaded with an ion-pair reagent (cetyltrimethylammonium bromide, CTMABr). Subsequently, the analytes were eluted with MeOH, which was then evaporated to dryness. Ion-pair reagents, like CTMABr, are non-volatile and cannot be removed during the final evaporation step and consequently they are still present in the final extract. Bearing in mind that ion-pair reagents will deteriorate the CE separation efficiency by influencing the EOF, a final clean-up step was added which used a SCX column to remove the ion-pair reagent was added. For most analytes, recoveries were between 78 and 108%.

Kok et al. [119] also combined the method described above with LIF detection so that the sensitivity could be improved and many real-life samples with lower concentrations could be analysed. The use of LIF detection is highly appropriate because these compounds show native fluorescence. However, rather expensive LIF detection systems have to be used because the absorption wavelengths of naphthalene sulfonates are relatively short. SPE increased the concentration by approximately 30-fold before the CE separation and the recoveries were between 50 and 100%, except for two amino-hydroxy substituted isomers which had a much lower value (<5%). The low to sub-μg l^{-1} detection limits enabled two naphthalenetrisulfonates and an aminonaphthalenedisulfonates to be identified and quantified in river water samples. The data obtained satisfactorily agree with those obtained by ion-pair HPLC.

Recently Loos and Niessner [120], proposed a new SPE enrichment procedure using the styrene–divinylbenzene adsorbent LiChrolut EN. They combined SPE and CE allowed 14 different aromatic sulfonates to be determined in water samples in the

low μg l^{-1} range (Fig. 7). After the LiChrolut EN cartridge had been conditioned, the spiked water samples adjusted to acidic pH were passed through the cartridge. The aromatic sulfonates were eluted with a MeOH:acetone solvent mixture. Separations were performed with a simple sodium borate buffer at pH 9.3. The recoveries for most of the sulfonates were >70% for the extraction from the spiked tap and river water. Very hydrophilic sulfonates cannot be extracted by this method. The detection limit of the combined method of SPE enrichment and CE analysis was approximately 0.1 μg l^{-1} for 200-ml water samples. The performance of the method was checked with the analysis of river and contaminated seepage water. No special sample pretreatment was applied with the tap and river waters. However, prior to enriching the seepage water with LiChrolut EN, a clean-up step with RP-C_{18} material was performed to remove interfering unpolar compounds.

5.6. Pesticides

Several hundred pesticides of a diverse chemical nature are currently used throughout world for agricultural purposes. Many of these organic compounds are positional, geometrical and optical isomers, which have been successfully analysed by CE.

Stutz et al. [121] used CZE-UV to determine the hydroxymetabolites of atrazine, one of the most extensively used herbicide in the world. They studied hydroxy-atrazine, desisopropylhydroxy-atrazine, desethylhydroxy-atrazine and ammeline and used an acetate–phosphate buffer for the separations. The method was applied to determine the herbicides in potable water using SPE with styrene–divinilbenzene and a methacrylate macroporous (Amberchrom resin) cartridge. The recoveries from fortified tap water at concentrations of 0.2 μg l^{-1} were: 95% for hydroxyatrazine, 70% for desethylhydroxyatrazine and 20%

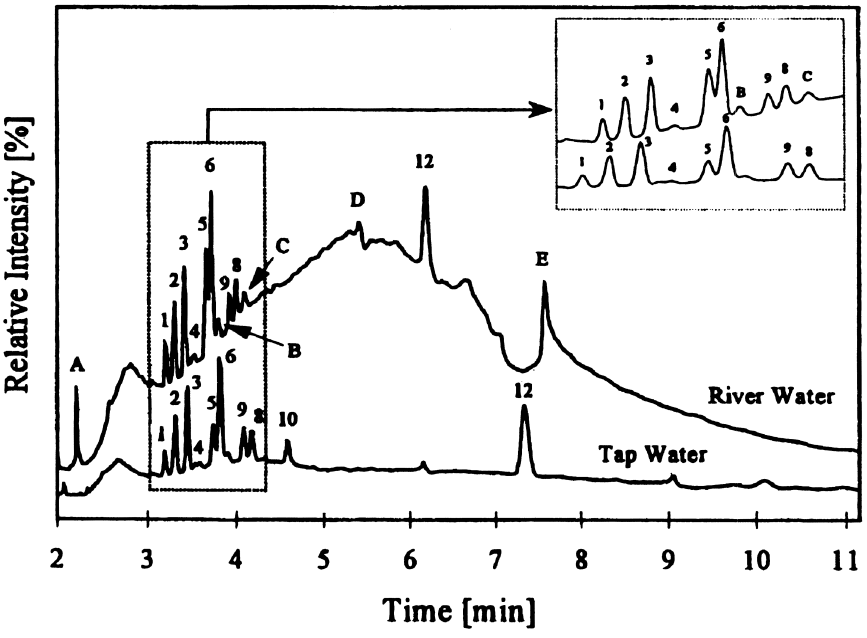

Fig. 7. Electropherogram of a river Isar extract after SPE with LiChrolut EN (enrichment factor 2000). Lower plot: 14-compound sulfonate standard at 5 mg/l. Conditions: running electrolyte, 25 m*M* sodium borate, pH 9.3; capillary 55 cm (45 cm to detection window)×75 μm I.D.; voltage, 25 kV; temperature, 30°C; pressure injection, 50 mbar for 12 s; UV detection at 230 nm. Peaks: (1) diphenylamine-4-sulfonate, (2) anthraquinone-2-sulfonate, (3) diphenyl-4-sulfonate, (4) 1-amino-5-naphthalenesulfonate, (5) 2-amino-1-naphthalenesulfonate, (6) naphthalene-1-sulfonate, (8) 4-chlorobenzenesulfonate, (9) toluene-4-sulfonate, (10) benzenesulfonate, (12) 1-naphthol-4-sulfonate. Reprinted with permission from Ref. [120].

for desisopropylhydroxyatrazine. However, because of its high polarity, ammeline was only slightly retained on Amberchrom resins and could not therefore be preconcentrated with this material.

Carabias-Martínez et al. [122] studied the determination of triazines herbicides at trace concentration levels (sub-μg l^{-1}) in natural waters after a preconcentration step using C_{18} and the poly(divinylbenzene-Co-*N*-vinylpyrrolidone) Oasis HLB cartridges in combination with non-aqueous CZE (Fig. 8). They observed that in deionized water both sorbents were satisfactory for analysing triazine herbicides. However, Oasis HLB was the most suitable for separation by non-aqueous CZE of natural waters. The separation medium was acetonitrile–methanol, perchloric acid and SDS. Finally, when this preconcentration step was combined with electrokinetic injection detection limits were low (between 0.01 and 0.05 μg l^{-1}, depending on the type of matrix analysed).

Most of the compounds used in the agrochemical industry contain chiral centres, with biological activity generally being limited to only one of the enantiomers. In order to increase the selectivity separation in CE, cyclodextrins (CD) are added to the buffer. Hsieh and Huang [123] developed a CZE method with CDs (α-CD and β-CD) to separate seven chlorophenoxy acid herbicides and their enantiomers at pH 5.6. This separation was used to determine these compounds in lake water. The herbicides were first extracted by a C_{18} disk and recoveries in the lake water ranged between 73 and 90%. The herbicide concentration increased 150 times when this preconcentration step was used and the detection limits in this sample were below 1 μg l^{-1}.

Menne et al. [124] studied the determination of sulfonylureas in soils by CZE at pH 4.76. The compounds were extracted with phosphate buffer from soil samples and then they were cleaned-up and preconcentrated by SPE. The phosphate extract was first passed through a C_{18} cartridge and the extract was passed through a second cartridge made of silica. Ethyl acetate containing 0.1% glacial acetic acid was used in both cases to elute the retained compounds with recoveries higher than 70% and standard deviations lower than 30% for most compounds. The authors observed that the method is not suitable for bensulfuron-methyl, probably because it is considerably adsorbed on the silica-phase SPE cartridge.

Hickes and Watrous [32] presented a method to determine 12 sulfonylurea herbicides in agricultural water. As in Krynitsky's study [31], the water was acidified with acetic acid and passed first through a RP-102 SPE cartridge and then through an alumina SPE cartridge to clean up the extract. In order to enhance the sensitivity of the method, an extended light path CE capillary and a high sensitivity optical Z-cell were used for residue analysis. The method was applied to three different water matrixes: reagent water, non-chlorinated water and surface water. Analyte recoveries for all matrices varied from 55 to 121%. The detection limit of the method was 0.1 μg l^{-1} and the matrix contribution was minimal.

Dinelli et al. [125] analysed the herbicides linuron, metalachlor, atrazine and metsulfuron using MEKC after a 1000-fold preconcentration step with a C_{18} SPE cartridge with recoveries about 87%. They determined these herbicides in tap water at the μg l^{-1} level. Dinelli et al. [126] have also used SPE

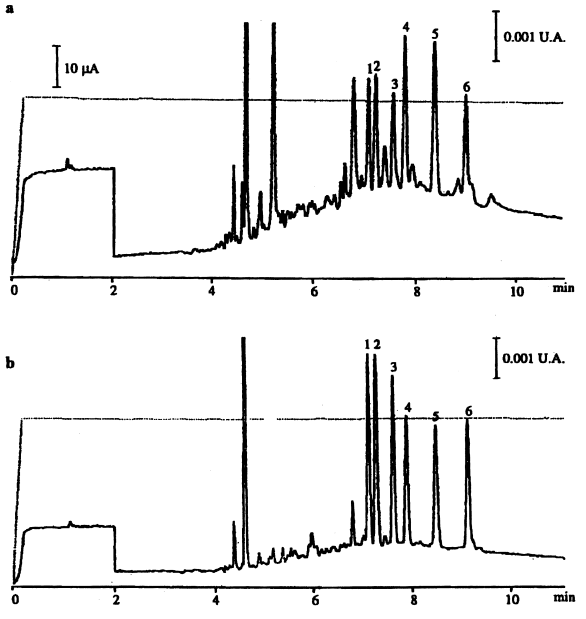

Fig. 8. Electropherograms of a 0.1 μg l^{-1} triazine-spiked neutral water samples of (a) river water and (b) drinking water, after SPE with an Oasis HLB cartridge. Peaks: (1) ametryne, (2) terbutryne, (3) prometryne, (4) simazine, (5) atrazine, (6) propazine. Buffer: MeOH–MeCN (50:50, v/v), 7.5 m*M* $HClO_4$, 17 m*M* SDS. Reprinted with permission from Ref. [122].

enrichment combined with MEKC to determine three sulfonylurea herbicides — chlorsulfuron, chlorimuron and metsulfuron — in soil samples. They used a sodium hydrogencarbonate solution to extract the herbicides from the soil sample and a C_{18} SPE cartridge to obtain an enrichment factor of 150 for the level of 10 μg l^{-1}, with recoveries of about 95%. More recently, Konda et al. [127] presented a MEKC application to determine five phenylurea herbicides (monuron, linuron, diuron, isoproturon and monolinuron) in rain- and surface-water samples at pH 7.0. The preconcentration step was carried out using a C_{18} cartridge. The samples were preconcentrated 2000 times (Fig. 9) and the detection limit for all compounds was 0.04 μg l^{-1}, except for diuron (0.02 μg l^{-1}).

Carabias-Martínez et al. [128] used MEKC with a C_{18} SPE preconcentration step to analyse triazine herbicides of environmental interest (simazine, cyanazine, atrazine, ametryne, propazine, prometryne and terbutryne) in water samples. The recoveries were studied using samples of bottled and tap waters and the results ranged between 79 and 130% at concentration of 0.3 and 0.5 μg l^{-1}.

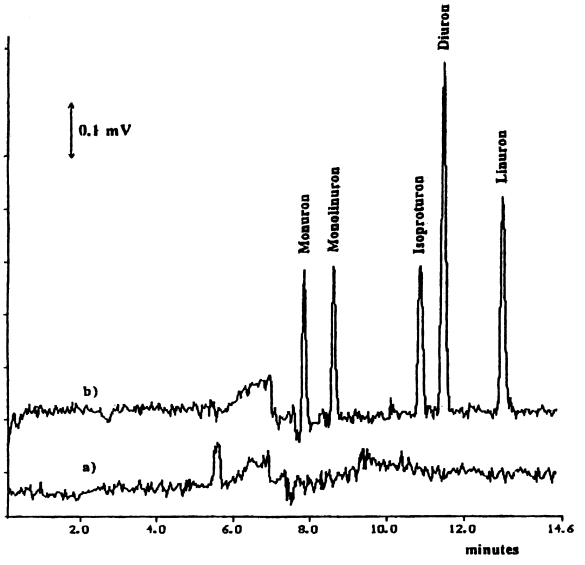

Fig. 9. Comparison between the electropherograms of (a) tap water concentrated 2000-fold and (b) tap water spiked at 0.1 μg l^{-1} and concentrated 2000-fold. Experimental conditions: buffer, 4 m*M* sodium tetraborate, 12 m*M* kH_2PO_4 (pH 7), 30 m*M* SDS; voltage, 30 kV; UV wavelength, 244 nm. Reprinted with permission from Ref. [127].

Farran et al. [41] used MEKC to analyse different mixtures of pesticides (triazine, phenylurea, phenoxyalkyl acid, carbamate and organophosphorous pesticide). The results were best when *n*-alcohols were used as mobile phase modifiers in phosphate with an SDS buffer. The authors evaluated off-line SPE process using the graphitized carbon black Carbopack, and C_{18} cartridges. When C_{18} cartridges were used the pH of the water sample was adjusted to 2. Nevertheless, the Carbopack B cartridges simultaneously extracted acidic and neutral pesticides with good recoveries (90–95% for phenylurea and phenoxyacid herbicides, at concentration of 0.4 μg l^{-1}) for spiked real water samples.

Hexazinone (a triazine dione herbicide) and its metabolites were separated and quantified in groundwater by MEKC [42]. These compounds were extracted from water using the graphitized non-porous carbon material Superclean ENVI-Carb. UV detection and extended light path capillaries were used and the buffer was composed of phosphate, borate, SDS and methanol. In this paper, the authors studied the recoveries for the compounds of interest at different concentration levels (between 0.5 and 5 μg l^{-1}). The recoveries for hexazinone ranged from 79 to 100%. The method was applied to several groundwater samples and the results were compared with those obtained by HPLC. The authors concluded that, in the samples studied, there was good agreement between both techniques.

Loos and Niessner [129] investigated the determination of the *N*-dealkylated chloro and hydroxy metabolites of atrazine, terbutylazine herbicides by SPE and CE-UV. They studied the styrene–divinylbenzene sorbent LiChrolut EN for the extraction of the herbicides. They also evaluated the separation of these compounds using CZE and MEKC. Hydroxy metabolites with pK_a values of 4.5–5.2 are quite well suited for CZE separation. However, with an acetate buffer, the addition of methanol as organic modifier and the best pH conditions, separation was not complete. For this reason, they suggested that MEKC with a sodium borate–SDS buffer should be used to separate these compounds. The limit of detection of SPE enrichment combined with MEKC analysis for hydroxy metabolites was between 0.1 and 0.25 μg l^{-1} and, with LiChrolut EN, the recoveries were better than when other conventional

sorbent materials were used. The only exception was ameline which was not detected in the samples after SPE because it was not extracted with this sorbent material.

Carbamates are a type of pesticide that have become increasingly important in recent years because they are used as insecticides, fungicides, nematocides, miticides and molluscicides. Some of these compounds have been separated using MEKC [41,130,131]. Rotilio and Rossi [130] analysed eleven compounds of the carbamate, thiocarbamate and dithiocarbamate classes of pesticides. They used MEKC with borate, SDS and a methanol buffer and an SPE step with a styrene–divinylbenzene cartridge to determine these compounds in tap water. The recovery values were between 50 and 92%, except for three compounds (thiophanate-methyl, thiram and cycloate) for which they were lower than 45%. Using this method the authors achieved detection limits at the $\mu g\ l^{-1}$ level.

Another example of carbamate pesticide determination using MEKC in environmental samples was presented by Molina et al. [131], who developed a method for determining *N*-methylcarbamate pesticides and their hydrolytic metabolites. The buffer used was composed of phosphate and borate with SDS. The samples were first preconcentrated by an SPE step and, for this reason, the authors studied different sorbent materials to find which was most suitable. Six sorbents — activated carbon, RP-C_{18}, the polystyrene–divinylbenzene copolymer XAD-2, the magnesium silicate Florisil, the unpolar polystyrene–divinylbenzene resine Serdolit PAD I and the highly crosslinked polystyrene–divinylbenzene sorbent LiChrolut EN) — were tested. LiChrolut EN showed the best sorption efficiency (close to 100%) using standard solutions at a concentration of 10 mg l^{-1}. The method was applied to determine the compounds in river water and pond water. Fig. 10 shows the electropherograms obtained for unspiked river water (A) and water spiked (B) with 0.5 $\mu g\ l^{-1}$ of each compound. Recoveries ranged from 82 to 108% at this level of concentration.

Organotin compounds are widely used in agriculture as insecticides, fungicides and biocides. Trojanowicz et al. [132] studied the separation of some of these compounds by CE. They used various sorbents such as C_{18}, C_8, phenyl functionalized

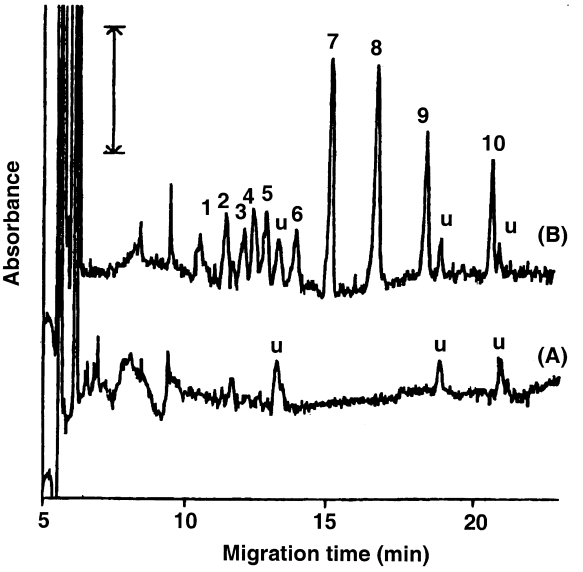

Fig. 10. Electropherogram of a trace-enriched 250-ml water sample with a LiChrolut EN cartridge. (A) Guadalquivir river water and (B) sample spiked with 0.5 $\mu g\ l^{-1}$. Peaks: (1) 4-dimethylamino-3-methyl phenol, (2) 2-isoproxyphenol, (3) propoxur, (4) 2,3-dihydro-2,2-dimethyl-7-benzofuranol, (5) carbofuran, (6) aminocarb, (7) 1-naphthol, (8) carbaryl, (9) 4-methylthio-3,5-xylenol, (10) methiocarb; 'u', unknown peaks. Experimental conditions: buffer, 20 m*M* borate, 25 m*M* phosphate and 40 m*M* SDS (pH 8); hydrodynamic injection, 0.5 p.s.i. for 10 s; detection wavelength, 202 nm for all compounds except 1-naphthol and carbaryl (214 nm). Reprinted with permission from Ref. [131].

sorbent, and the polystyrene–divinylbenzene copolymers: Amberlite XAD-2 and Amberlite XAD-4 to preconcentrate two organotin compounds, tributyltin chloride and triphenyltin chloride. They concluded that Amberlite XAD-2 was the most appropriate sorbent for the compounds studied. The method was applied to determine these compounds in various natural waters, and several inorganic salts were added to see how they affected the preconcentration step. The recovery values for these two organotin compounds were over 70% at $\mu g\ l^{-1}$ concentration levels.

Cyclodextrins have also been used in combination with MEKC to separate enantiomeric pesticides. Shea et al. [133] presented the separation of seven enantiomeric and isomeric pesticides using cyclodextrins with MEKC. The authors studied parameters

such as the type of surfactant and cyclodextrin. They used SDS and sodium cholate and six different cyclodextrins to separate the pesticides. Finally, the method was applied to separate the compounds in lake water at low μg l^{-1} levels using an SPE step. The samples were extracted using the poly(divinylbenzene-Co-*N*-vinylpyrrolidone) Oasis HLB cartridge and all the recoveries ranged between 45 and 89%.

To decrease the detection limits of pesticide analysis, some authors [72,73,134] have suggested using an enrichment process in two steps, such as SPE and sample stacking, in MEKC or CEC techniques. Süsse and Müller [72] proposed such a combination for analysing pesticides in drinking water by MEKC. The SPE preconcentration step used a C_{18} cartridge and the samples were stacked by first injecting a large volume of sample, then applying a high voltage with reverse polarity to remove the sample matrix and finally switching back the polarity to perform the separation. Under these enrichment conditions, the detection limits were lower than 0.1 μg l^{-1}. The same combination was used by He and Lee [73] to determine six organonitrogen pesticides (metribuzin, bromacil, terbacil, hexazinone, triadimefon and DEET) in drainage water by MEKC. The samples were stacked by injecting a large volume of sample dissolved in a buffer matrix that was less conductive than the one used in the MEKC separation. The recovery of the pesticides was over 80% at concentration of 5 μg l^{-1} except for DEET, that which it was 41 and the limit of detection was 0.8 μg l^{-1}.

El Rassi and Yang [134] investigated how to improve the sensitivity of detection by combining an SPE step and an on-line enrichment process to determine pesticides prior to CEC separation. They used CEC and octadecyl-silica (ODS) capillary columns to separate nine important urea herbicides. Due to the relatively strong affinity of the compounds to the ODS stationary phase, they were determined at low concentrations by on-line prolonged injections. They also showed that if the prolonged injection is preceded by the injection of a plug of water, the detection limits decrease. This plug led to a greater accumulation of dilute samples in a narrow band at the inlet of the CEC column. The authors combined this on-column sample enrichment with an off-line SPE C_{18} cartridge and observed that this procedure detected pesticide concentrations of 0.1 μg l^{-1}.

Several attempts have been made to automate on-line preconcentrations of pesticides with CE [67,135]. El Rassi and Cai [135] studied fused capillaries with surface-bound octadecyl functions for on-line preconcentration of dilute triazine samples before CZE. They showed that this coupled configuration could detect concentrations 10 and 35 times lower than CZE alone. More recently, Hinsmann et al. [67] used an automatic SPE system coupled to CE. They used a C_{18} SPE mini-column to separate seven pesticides by MEKC in spiked river water samples. Pesticides mixtures at concentrations of 50 μg l^{-1} were detected. Under optimal extraction conditions, recoveries were between 90 and 114% for most of the pesticides studied.

5.7. Phenols

Even small amounts of phenolic compounds can have a significant detrimental effect on water quality. At concentrations of less than 1 μg l^{-1}, the taste and odour of water are affected. The disinfection process with chloride aggravates odour and taste problems because of the formation of chlorinated phenolic compounds.

Phenols have been analysed by CZE or by MEKC [9,22,136–138]. Martínez et al. [136] analysed the eleven priority EPA phenols using a borate solution. An SPE step enabled these compounds to be detected at low μg l^{-1} levels. The off-line enrichment process was performed with a styrene–divinylbenzene EN-VI-Chrom P copolymer. They applied the method to determine phenolic compounds in river water and industrial waste water and in the latter case, little matrix effect was observed (Fig. 11).

Other authors have combined on-column sample stacking techniques with SPE preconcentration to reduce the limits of detection of phenolic compounds. For example, Tunes et al. [40] combined sample stacking techniques (with and without sample matrix removal) with the use of extended light path capillaries and off-line SPE preconcentration and they used CZE to monitor pentachlorophenol in drinking water at the level of international regulations (0.5 μg l^{-1}). SPE was carried out with

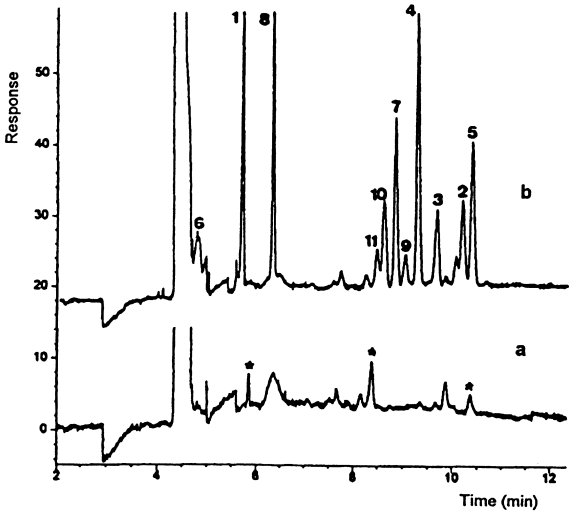

Fig. 11. Electropherogram obtained after ion-pair SPE extraction with an ENVI-Chrom P cartridge of 500 ml (a) Ebro river water and (b) Ebro river water spiked with phenolic compounds (50 μg l^{-1}). Peaks: (1) phenol, (2) 4-nitrophenol, (3) 2,4-dimethylphenol, (4) 2-chlorophenol, (5) 2-nitrophenol, (6) 2,4-dimethylphenol, (7) 2-methyl-4,6-dinitrophenol, (8) 4-chloro-3-methylphenol, (9) 2,4-dinitrophenol, (10) 2,4,6-trichlorophenol, (11) pentachlorophenol. Experimental conditions: buffer, 20 m*M* sodium tetraborate (pH 9.9); hydrodynamic injection, 50 mbar for 10 s; detection wavelength, 195 nm. Reprinted with permission from Ref. [22].

graphitized carbon black cartridges and the quantification limit was of 60 ng l^{-1}, which is suitable for monitoring drinking water. The recovery of pentachlorophenol from tap water was 95.8% at concentrations of 0.5 μg l^{-1}. The authors also made similar studies of chloro and nitrophenols [138] and the SPE process used cross-linked polystyrene cartridges with recovery values between 75.8 and 104.7%. Using this method, concentrations levels of 0.5 μg l^{-1} were determined in spiked tap water samples.

Whang and Pawliszyn [52] analysed the priority EPA phenols using an on-column SPME sampling technique with CE using a polyacrylate (PA) fiber as the extraction coating. The water samples were acidified to pH 2 and saturated with NaCl before extraction because in these conditions the extraction efficiency for phenols was significantly improved. Extraction was performed for 20 min in a stirred water sample which contained the spiked analytes. After extraction, the fiber was transferred to the interface and potential was then applied to perform the CE analysis. Using SPME-CE with UV detection, the concentration limit for pentachlorophenol — that is the phenolic compound that has the highest affinity for the PA coating — was determined to be 2 μg l^{-1}. However, the increase in sensitivity for other phenols was not as significant.

MEKC was also investigated for the separation of phenolic compounds [139–142]. Van Bruijnsvoort et al. [140] showed that MEKC could be used to separate and detect chlorophenols. They investigated MEKC coupled with electrochemical detection and combined with an SPE step, using of a highly cross-linked polystyrene–divinylbenzene copolymer. Of the 20 compounds studied, 17 were baseline separated and the detection limits were lower than 0.1 μg l^{-1} in river water samples.

5.8. Miscellaneous

SPE in combination with CE has been used to separate other types of environmental pollutants, such as haloacetic acids, metallo–cyanide complexes, ethylenediaminetetraacetic acid (EDTA), and chemical warfare agents (alkylphosphonic acids and their monoesters).

Haloacetic acids are disinfection water by-products and they can be found in high concentrations in water disinfected with chlorine. In order to determine these compounds at low concentration in tap water, Martínez et al. [38] studied four different commercial sorbents — quaternary ammonium anion exchanger, highly cross-linked styrene–divinylbenzene, graphitized carbon black and macroporous poly(divinylbenzene-co-*N*-vinylpyrrolidone) copolymer — for SPE extraction before being determined by CZE using indirect UV detection. The electrolyte used was 2,6-naphthalene dicarboxylic acid with hexadecyltrimethylammonium bromide as electroosmotic flow modifier. Using the highly cross-linked styrene–divinylbenzene sorbent, the recoveries in tap water were high (above 80% for dichloroacetic acid and trichloroacetic acid which are two of the most habitual haloacetic acids in chlorinated waters) and the detection limits were at the μg l^{-1} concentration level. However, a peak of the tap water matrix interfered with one of the compounds studied (monochloroacetic acid) which mean that it was determined less precisely (Fig. 12).

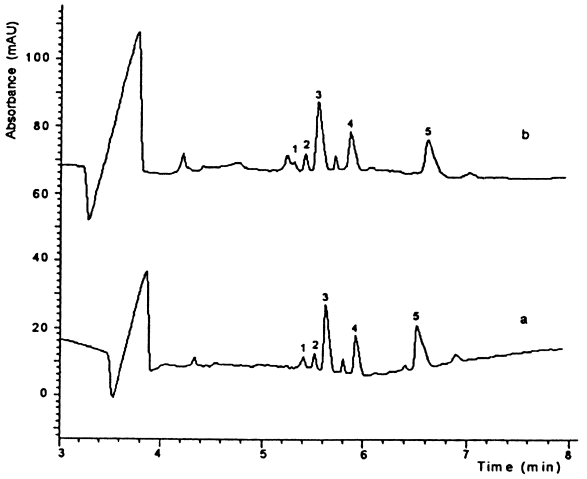

Fig. 12. Electropherogram obtained by passing (a) 500 ml of a standard solution of 25 μg l^{-1} of haloacetic acids and (b) 500 ml of tap water spiked at 25 μg l^{-1} level, through LiChrolut EN cartridge. Peaks: (1) monochloroacetic acid, (2) monobromoacetic acid, (3) dichloroacetic acid, (4) dibromoacetic acid, (5) trichloroacetic acid. Experimental conditions: 4 m*M* 2,6-naphthalenedicarboxylic acid and 0.5 m*M* hexadecyltrimethylammonium bromide, pH 7; hydrodynamic injection, 40 mbar for 20 s; indirect UV detection, 235 nm. Reprinted with permission from Ref. [38].

Cyanide is used in the metal processing industry for electroplating and it is likely to be present in the form of metallo–cyanide complexes in environmental samples at varying persistence and toxicology. Haddad et al. [143] studied the separation of these complexes by CZE. The electrolyte selected was phosphate–ethanolamine at pH 8.5. For sensitivity to be sufficient to determine these compounds in environmental applications, some metallo–cyanides can be preconcentrated using a Sep-Pak C_{18} SPE cartridge. In this study, experiments were carried out to determine the Au–cyano complex in leaching solutions from a gold mine. This procedure yielded a recovery of 103.6% for an aqueous standard containing 4 mg l^{-1} Au and a recovery of 83% for a real mine sample containing 1.3 mg l^{-1} Au. The authors explained the decrease in recovery by the fact that the real mine sample contained a relatively high concentration of anions, such as chloride and sulphate, which compete for the preconcentration sites on the Sep-Pak cartridge.

Ethylenediaminetetraacetic acid (EDTA) has been widely used to clean up radioactive and heavy metal wastes, and therefore it can be present at high levels at such waste sites. Several studies have shown that waste water treatment does not effectively remove EDTA from water and it is likely to be detectable in most water sources [144]. Henion and Sheppard [145] studied the determination of EDTA as the nickel chelate in environmental water by SPE and CE tandem mass spectrometry (MS). They developed an automated extraction procedure using an SPE disk. The procedure converts all free and chelate EDTA into the nickel chelate an then extracts it on strong anion-exchange extraction disks. The extracted was analysed by CZE using an amine-coated capillary column to separate anions and the electrolyte was formiate buffer, pH 3. To enhance the concentration detection limits of the method, a sample stacking technique was used. A small plug of water was injected into the CE capillary and then there was a large electrokinetic injection of the sample dissolved in water. The detection limits were 0.15 μg l^{-1} and the method was tested in a number of water samples from local sources. Finally, the authors concluded that the limits of detection of the method are at least five times lower than the best ones reported in the literature.

Chemical warfare agents are highly toxic and considerable effort has been made to identity, quantify, and neutralise them and their degradation products in a wide variety of matrixes [146,147]. Nassar et al. [147] studied alkylphosphonic acids and their monoesters, which are nerve agents, in environmental samples using CZE with electrokinetic injection to improve the sensitivity. The electrolyte used to reverse the electroosmotic flow was borate (pH 4), phenylphosphonic acid, Triton X-100 and didodecyldimethylammonium hydroxide (DDAOH). However, for electrokinetic injection enhancement for environmental samples to have greatest effect, the samples have to be cleaned up previously with ion-exchange cartridges. This clean-up step used sequential cartridges to remove sulphate (barium cartridge), chloride (silver cartridge), and cations (H^+ cartridge). When samples were passed through this stacked cartridge clean-up the detectability dramatically improved and the detection limits for the compounds studied were 1–2 μg l^{-1} for water samples and 25–50 μg l^{-1} for aqueous leachates of soil samples.

6. Nomenclature

ASPEC XL	Automated off-line SPE device
CD	Cyclodextrin
CE	Capillary electrophoresis
CEC	Capillary electrochromatography
cLC	Capillary liquid chromatography
CZE	Capillary zone electrophoresis
GC	Gas chromatography
HAAs	Heterocyclic aromatic amines
HPLC	High-performance liquid chromatography
I.D.	Inner diameter
ITP	Isotachophoresis
LAS	Linear alkylbenzenesulfonates
LIF detector	Laser-induced fluorescence detector
LLE	Liquid–liquid extraction
MEKC	Micellar electrokinetic capillary chromatography
MS	Mass spectrometry
ODS	Octadecyl-silica
PA	Polyacrylate
PAHs	Polycyclic aromatic hydrocarbons
PDMS	Polydimethylsiloxane
SAX	Strong anion-exchange cartridge
SCX	Strong cation-exchange cartridge
SDS	Sodium dodecyl sulphate
SFE	Supercritical fluid extraction
SPE	Solid-phase extraction
SPME	Solid-phase microextraction

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References

[1] G. Dinelli, A. Vicari, P. Catizone, J. Chromatogr. A 733 (1996) 337.
[2] W.C. Brumley, J. Chromatogr. Sci. 33 (1995) 670.
[3] J. Sherma, Anal. Chem. 67 (1995) 1R.
[4] C. Aguilar, F. Borrull, R.M. Marcé, LC–GC 14 (1996) 1048.
[5] M. Psathaki, E. Manoussaridou, E.G. Stephanou, J. Chromatogr. A 667 (1994) 241.
[6] I. Liska, E.K. Brouwer, A.G.L. Ostheimer, H. Lingeman, U.A.Th. Brinkman, R.B. Geerdink, W.H. Mulder, Int. J. Environ. Anal. Chem. 47 (1992) 267.
[7] H. Bagheri, J. Slobodnik, R.M. Marcé, R.T. Ghijsen, U.A.Th. Brinkman, Chromatographia 37 (1993) 159.
[8] M.W.F. Nielen, Trends Anal. Chem. 12 (1993) 345.
[9] I.C. Chen, C.W. Whang, J. Chin. Chem. Soc. 41 (1994) 419.
[10] Y.C. Chao, C.W. Whang, J. Chromatogr. A 663 (1994) 229.
[11] D. Kaniansky, F. Ivanyi, F.I. Onuska, Anal. Chem. 66 (1994) 1817.
[12] M. Berg, S.R. Mhler, R.P. Schwarzenbach, Anal. Chem. 67 (1995) 1860.
[13] R.S. Brown, J.H.T. Luang, O.H.J. Szolar, A. Halasz, J. Hawari, Anal. Chem. 68 (1996) 287.
[14] Ph. Schimtt, A.W. Garrison, D. Freitag, A. Kettrup, J. Chromatogr. A 723 (1996) 169.
[15] L. Song, Z. Xu, J. Kang, J. Cheng, J. Chromatogr. A 780 (1997) 297.
[16] G.W. Sovocool, W.C. Brumley, J.R. Donnelly, Electrophoresis 20 (1999) 3297.
[17] K. Heinig, C. Vogt, Electrophoresis 20 (1999) 3311.
[18] A. Karcher, Z. El Rassi, Electrophoresis 20 (1999) 3280.
[19] E. Dabek-Zlotorzynska, in: H. Shintany, J. Polonski (Eds.), Handbook of Capillary Electrophoresis Applications, Blackie Academic & Professional, London, 1997, p. 639.
[20] W.C. Brumley, LC–GC 13 (7) (1995) 556.
[21] E. Dabek-Zlotorzynska, Electrophoresis 18 (1997) 2453.
[22] D. Martínez, E. Pocurull, R.M. Marcé, F. Borrull, M. Calull, Chromatographia 43 (1996) 619.
[23] L. Puignou, J. Casal, F.J. Santos, M.T. Galceran, J. Chromatogr. A 769 (1997) 293.
[24] L. Arce, A. Ríos, M. Valcárcel, J. Chromatogr. A 803 (1998) 249.
[25] K. Grob, J. Chromatogr. A 703 (1995) 265.
[26] L. Mondello, G. Dugo, K.D. Bartle, J. Microcol. Sep. 8 (1996) 275.
[27] R.L. Chien, D.S. Burgi, Anal. Chem. 64 (1992) 489.
[28] A.K. Li, S.F.Y. Li, Analyst 120 (1995) 361.
[29] R. Saari-Nordhaus, J.M. Anderson, J. Chromatogr. A 706 (1995) 563.
[30] W.C. Brumley, C.M. Brownrigg, J. Chromatogr. 646 (1993) 377.
[31] A.J. Krynitsky, J. AOAC Int. 80 (1997) 392.
[32] H. Hickes, M. Watrous, J. AOAC Int. 82 (1999) 1523.
[33] I. Ferrer, D. Barceló, J. Chromatogr. A 778 (1997) 161.
[34] V. Pichon, M. Charpak, M.-C. Hennion, J. Chromatogr. A 795 (1998) 83.
[35] D. Puig, D. Barceló, Chromatographia 40 (1995) 435.
[36] N. Masqué, M. Galia, R.M. Marcé, F. Borrull, J. Chromatogr. A 771 (1997) 55.
[37] N. Masqué, M. Galia, R.M. Marcé, F. Borrull, Analyst 122 (1997) 425.
[38] D. Martínez, F. Borrull, M. Calull, J. Chromatogr. A 827 (1998) 105.
[39] J. Schulein, D. Martens, P. Spitzauer, A. Kettrup, Fresenius J. Anal. Chem. 352 (1995) 565.
[40] M.I. Tunes, M.C. Mejuto, R. Cela, J. Chromatogr. A 733 (1996) 395.

[41] A. Farran, S. Ruiz, C. Serra, M. Aguilar, J. Chromatogr. A 737 (1996) 109.
[42] D.T. Kubilius, R.J. Bushway, J. Chromatogr. A 793 (1998) 349.
[43] M. Peruzzi, G. Bartolucci, F. Cioni, J. Chromatogr. A 867 (2000) 169.
[44] R. Carabias-Martínez, E. Rodriguez-Gonzalo, J. Dominguez-Álvarez, J. Hernández-Mendez, J. Chromatogr. A 869 (2000) 451.
[45] J. Pawlinszyn, in: Solid Phase Microextraction: Theory and Practice, Wiley-VCH, New York, 1997.
[46] C.L. Arthur, L. Killam, K. Buchholz, J. Pawliszyn, Anal. Chem. 64 (1992) 1960.
[47] K. Jinno, T. Muramatsu, Y. Saito, Y. Kiso, S. Magdic, J. Pawliszyn, J. Chromatogr. A 754 (1996) 137.
[48] H. Daimon, J. Pawliszyn, Anal. Chem. 34 (1997) 365.
[49] R. Eisert, J. Pawliszyn, Anal. Chem. 69 (1996) 3140.
[50] A.A. Boyd-Boland, J. Pawliszyn, Anal. Chem. 68 (1996) 1521.
[51] S. Li, S.G. Weber, Anal. Chem. 69 (1997) 1217.
[52] C. Whang, J. Pawliszyn, Anal. Commun. 35 (1998) 353.
[53] A.L. Nguyen, J.H.T. Luong, Anal. Chem. 69 (1997) 1726.
[54] A.J. Tomlinson, L.M. Benson, N.A. Guzman, S. Naylor, J. Chromatogr. A 744 (1996) 3.
[55] A.J. Tomlinson, S. Naylor, J. Liq. Chromatogr. 18 (1995) 3591.
[56] S. Naylor, A.J. Tomlinson, Biomed. Chromatogr. 10 (1996) 325.
[57] M.E. Swartz, M. Merion, J. Chromatogr. 632 (1993) 209.
[58] I. Morita, J.-I. Sawada, J. Chromatogr. 641 (1993) 375.
[59] J.H. Beattie, R. Self, M.P. Richards, Electrophoresis 16 (1995) 322.
[60] M.A. Strausbauch, B.J. Madden, P.J. Wettstein, J.P. Landers, Electrophoresis 16 (1995) 541.
[61] D. Figeys, A. Ducret, R. Aebersold, J. Chromatogr. A 793 (1997) 295.
[62] M. Petersson, K.-G. Wahlund, S. Nilsson, J. Chromatogr. A 841 (1999) 249.
[63] A.J. Tomlinson, L.M. Benson, W.D. Braddock, R.P. Oda, S. Naylor, J. High Resolut. Chromatogr. 18 (1995) 381.
[64] Q. Yang, A.J. Tomlinson, S. Naylor, Anal. Chem. 71 (1999) 183A.
[65] J.R. Veraart, C. Gooijer, H. Lingeman, N.H. Velthorst, U.A.Th. Brinkman, J. Chromatogr. B 719 (1998) 199.
[66] L. Arce, A. Ríos, M. Valcárcel, J. Chromatogr. A 791 (1997) 279.
[67] P. Hinsmann, L. Arce, A. Ríos, M. Valcárcel, J. Chromatogr. A 866 (2000) 137.
[68] R.L. Chien, D.S. Burgi, Anal. Chem. 64 (1992) 489A.
[69] D. Martínez, F. Borrull, M. Calull, J. Chromatogr. A 788 (1997) 185.
[70] K. Li, S.F.Y. Li, Analyst 120 (1995) 361.
[71] J. Quirino, S. Terabe, Anal. Chem. 70 (1998) 149H.
[72] H. Süsse, H. Müller, J. Chromatogr. A 730 (1996) 337.
[73] Y. He, H.K. Lee, Electrophoresis 18 (1997) 2036.
[74] X. Song, W.L. Budde, J. Chromatogr. A 829 (1998) 327.
[75] T. Tegeler, Z. El Rassi, J. AOAC int. 82 (1999) 1542.
[76] S.A. Oehrle, J. Chromatogr. A 671 (1994) 383.
[77] J. Farré, F. Borrull, M. Calull, Chromatographia 47 (1998) 630.
[78] D. Kaniansky, F. Iványl, F.I. Onuska, Anal. Chem. 66 (1994) 1817.
[79] D. Kaniansky, I. Zelensky, A. Hybenova, F.I. Onuska, Anal. Chem. 66 (1994) 4258.
[80] L. Krivánková, P. Bocek, J. Chromatogr. B 689 (1997) 13.
[81] P. Blantný, F. Kvasnicka, E. Kenndler, J. Chromatogr. A 757 (1997) 297.
[82] J.R. Veraart, C. Gooijer, H. Lingeman, N.H. Velthorst, U.A.Th. Brinkman, Chromatographia 44 (1997) 581.
[83] K. Heinig, C. Vogt, Electrophoresis 20 (1999) 3311.
[84] C. Vogt, K. Heinig, Tenside Surf. Det. 35 (1998) 470.
[85] K. Heinig, C. Vogt, G. Werner, J. Chromatogr. A 745 (1996) 281.
[86] C. Vogt, K. Heinig, Fresenius J. Anal. Chem. 363 (1999) 612.
[87] J. de Ferrer, A. Moreno, M[a].T. Vaquero, L. Comellas, Tenside Surf. Det. 34 (1997) 278.
[88] H. Klotz, F. am Main, Tenside Surf. Det. 35 (1998) 459.
[89] C. Vogt, K. Heinig, B. Langer, J. Mattusch, G. Werner, Fresenius J. Anal. Chem. 352 (1995) 508.
[90] S. Chen, D.J. Pietrzyk, Anal. Chem 56 (1993) 2770.
[91] P.L. Desbene, C. Rony, B. Desmazieres, J.C. Jacquier, J. Chromatogr. 608 (1992) 375.
[92] K. Heinig, C. Vogt, G. Werner, Analyst 123 (1998) 349.
[93] K. Heinig, C. Vogt, G. Werner, J. Chromatogr. A 745 (1996) 281.
[94] C. Kanz, M. Nölke, T. Fleischmann, H.-P.E. Kohler, W. Giger, Anal. Chem. 70 (1998) 913.
[95] K.D. Altria, I. Gill, J.S. Howells, C.N. Luscombe, R.Z. Williams, Chromatographia 40 (1995) 527.
[96] E. Dabek-Zlotorzynska, Electrophoresis 18 (1997) 2453.
[97] C. Akbay, S.A. Shamsi, I.M. Warner, Electrophoresis 18 (1997) 253.
[98] T.W. Moy, P.L. Ferguson, A.H. Grange, W.H. Matchett, V.A. Kelliher, W.C. Brumley, J. Glassman, J.W. Farley, Electrophoresis 19 (1998) 2090.
[99] O.H.J. Szolar, R.S. Brown, J.H.T. Luong, Anal. Chem. 67 (1995) 3004.
[100] U. Krismann, W. Kleiböhmer, J. Chromatogr A 774 (1997) 193.
[101] B. Jimenez, D.G. Patterson, J. Grainger, Z. Liu, M.J. Gonzalez, M.L. Marina, J. Chromatogr. A 792 (1997) 411.
[102] A.L. Crego, J. Martinez, M.L. Marina, J. Chromatogr. A 869 (2000) 329.
[103] R. Stol, W.T. Kok, H. Poppe, J. Chromatogr. A 853 (1999) 45.
[104] R. Dadoo, R.N. Zare, C. Yan, D.S. Anex, Anal. Chem. 70 (1998) 4787.
[105] S. Nie, R. Dadoo, R.N. Zare, Anal. Chem. 65 (1993) 3571.
[106] R.S. Brown, J.T.H. Luong, O.H.J. Szolar, A. Halasz, J. Hawari, Anal. Chem. 68 (1996) 287.
[107] I. Schönsee, J. Riu, D. Barceló, Quím. Anal. 16 (1997) S243.
[108] J. Riu, I. Schönsee, D. Barceló, J. Mass Spectrom. 33 (1998) 653.

[109] L. Farry, D.A. Oxspring, W. Franking Smyth, R. Marchant, Anal. Chim. Acta 349 (1997) 221.
[110] W.C. Brumley, C.M. Brownrigg, A.H. Grange, J. Chromatogr. A 680 (1994) 635.
[111] P.L. Ferguson, A.H. Grange, W.C. Brumley, J.R. Donnely, J.W. Farley, Electrophoresis 19 (1998) 2252.
[112] J.P. Alcantar-Licudine, N.L. Bui, M.K. Kawate, Q.X. Li, J. Agric. Food Chem. 46 (1998) 1015.
[113] W.C. Matchett, W.C. Brumley, J. Liquid Chrom. Rel. Technol. 20 (1997) 79.
[114] A. Cavallaro, V. Piangerelli, F. Nerini, S. Cavalli, C. Reschiotto, J. Chromatogr. A 709 (1995) 361.
[115] C. Mardones, L. Arce, A. Rios, M. Valcarcel, Chromatographia 48 (1998) 700.
[116] I. Rodriguez, H.K. Lee, S.F.Y. Li, Electrophoresis 20 (1999) 1862.
[117] Y. Deng, X. Fan, A. Delgado, C. Nolan, K. Furton, Y. Zuo, R.D. Jones, J. Chromatogr. A 817 (1998) 145.
[118] S.J. Kok, E.H.M. Koster, C. Gooijer, N.H. Velthorst, U.A.Th. Brinkman, J. High Resolut. Chromatogr. 19 (1996) 99.
[119] S.J. Kok, E.M. Kristenson, C. Gooijer, N.H. Velthorst, U.A.Th. Brinkman, J. Chromatogr. A 771 (1997) 331.
[120] R. Loos, R. Niessner, J. Chromatogr. 822 (1998) 291.
[121] H. Stutz, K. Pitterstschatscher, H. Malissa, Mikrochim. Acta 128 (1998) 107.
[122] R. Carabias-Martínez, E. Rodríguez-Gonzalo, J. Domínguez-Álvarez, J. Hernández-Méndez, J. Chromatogr. A 869 (2000) 451.
[123] Y.-z. Hsieh, H.-Y. Huang, J. Chromatogr. A 745 (1996) 217.
[124] H.J. Menne, K. Janowitz, B.M. Berger, J. AOAC Int. 82 (1999) 1534.
[125] G. Dinelli, A. Bonetti, P. Catizone, G.C. Galletti, J. Chromatogr. B 656 (1994) 275.
[126] G. Dinelli, A. Vicari, V. Brandolini, J. Chromatogr. A 700 (1995) 201.
[127] L.N. Konda, M.B. Barroso, G. Morovjan, J. High Resolut. Chromatogr. 22 (1999) 171.
[128] R. Carabias Martínez, E. Rodríguez Gonzalo, A.I. Muñoz Domínguez Alvarez, J. Hernández Méndez, J. Chromatogr. A 733 (1996) 349.
[129] R. Loos, R. Niessner, J. Chromatogr. A 835 (1999) 217.
[130] M. Rossi, D. Rotilio, J. High Resolut. Chromatogr. 20 (1997) 265.
[131] M. Molina, D. Pérez-Bendito, M. Silva, Electrophoresis 20 (1999) 3439.
[132] M. Trojanowicz, E. Pobozy, B. Glöd, J. Kaniewska, J. Chromatogr. A 718 (1995) 329.
[133] D. Shea, K.V. Pentmetsa, R.B. Leidy, J. AOAC Int. 82 (1999) 1550.
[134] Z. El Rassi, C. Yang, Electrophoresis 20 (1999) 2337.
[135] Z. El Rassi, J. Cai, J. Liquid Chromatogr. 15 (1992) 1179.
[136] D. Martínez, E. Pocurull, R.M. Marcé, M. Calull, F. Borrull, J. Chromatogr. A 734 (1996) 367.
[137] D. Martínez, F. Borrull, M. Calull, J. Chromatogr. A 788 (1997) 185.
[138] I. Rodriguez, M.I. Turnes, M. Losada, M.H. Bollaín, M.C. Mejuto, R. Cela, J. Chromatogr. A 778 (1997) 279.
[139] W.C. Brumley, W.J. Jones, J. Chromatogr. A 680 (1994) 163.
[140] M. Van Bruijnsvoort, S.K. Sanghi, H. Poppe, W.T. Kok, J. Chromatogr. A 757 (1997) 203.
[141] G.-E. Lin, W.-C. Lin, W.-C. Ciou, J. Chromatogr. A 722 (1996) 333.
[142] G. Li, D.C. Locke, J. Chromatogr. A 734 (1996) 357.
[143] P.R. Haddad, W. Buchberger, J. Chromatogr. A 687 (1994) 343.
[144] F.G. Kari, W. Giger, Water Res. 30 (1996) 122.
[145] J. Henion, R.L. Sheppard, Electrophoresis 18 (1997) 287.
[146] A.-E.F. Nassar, S.V. Lucas, W.R. Jones, L.D. Hoffland, Anal. Chem. 70 (1998) 1085.
[147] A.-E.F. Nassar, S.V. Lucas, L.D. Hoffland, Anal. Chem. 71 (1999) 1285.