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Review

Analysis of agrochemicals by capillary electrophoresis

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Abstract

An increasing amount of articles using capillary electrophoresis as an investigation tool for pesticides and environmental pollutants were found over the last few years in analytical chemistry oriented journals. This review covers a wide literature range of the 1990s and concentrates on the analysis of organic agrochemicals (herbicides, fungicides, insecticides, acaricides, etc.) with capillary electrophoresis (capillary zone electrophoresis, micellar electrokinetic chromatography with CE–UV–visible or laser-induced fluorescence detection) as well as with the on-coming hyphenated techniques like capillary electrophoresis–electrospray ionization mass spectrometry. The principal preconcentration methods that allowed real sample analysis with CE are also briefly discussed. The pesticides, the separation methods, the used electrolytes, the detection types, the detection limits and the preconcentration methods were classified and presented in tabulated form as a rapid information tool.

Keywords: Reviews; Environmental analysis; Water analysis; Soil; Food analysis; Pesticides

Contents

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1. Introduction

Capillary electrophoresis (CE) has been increasingly used in the last decade, in the medical [1,2] and the biochemical sectors [3,4]. Recent reviews show the increasing need of method development in CE and capillary electrochromatography (CEC) in the analysis of DNA, proteins and peptides, clinical and forensic samples [5]. Capillary gel electrophoresis (CGE), capillary isotachophoresis (cITP) and capillary isoelectric focusing (cIEF) are widely used for the separation of biomolecules such as proteins, DNA, polysaccharides [6] and found only very specific environmental applications [7–10].

Separations with capillary zone electrophoresis (CZE) [11,12] and micellar electrokinetic chromatography (MEKC) [13] cover a wide range of analytes of various polarity, from ionized (anionic or cationic) to neutral components. The selectivity and resolution of the separations are directly controlled by different buffer additives (solvents, complexing agents, polymers) [14,15]. More complex buffer compositions involving different chiral selectors like cyclodextrins, polysaccharides, proteins or macrocyclic antibiotics, allow additionally the separation of isomeric compounds [16,17]. From previous reviews, CZE and MEKC have up to now found the best response in the analysis of environmental samples in contents of pesticides, inorganic [9] and organic pollutants [18–23] in environmental matrices. CE complements and for some separations even replaces classical chromatographic techniques [gas chromatography (GC) or high-performance liquid chromatography (HPLC)] by combining automatization with high separation efficiency for low sample amounts (miniaturization). The running costs in CE (low amount of running buffer, aqueous electrolyte and fused-silica capillary) are very low as compared with chromatographic packing materials with which high amounts of organic solvents have to be used [18]. Furthermore, a rapid conditioning of the separation system allows a high flexibility of the analysis methods within the same day. All these together make CE a rather ''ecological'' separation technique worth being developed for many specific routine applications.

Within this manuscript our interest concentrated on the published articles on the analysis of organic agrochemicals by CE (CE–UV–visible, CE–laser-induced fluorescence and CE–mass spectrometry) from the mid-1990s to now; some reviews already focused on environmental applications of CE and CEC [18–23]. The collected information is presented in tabulated form. We particularly focused on the information concerning the nature of the probes (real samples from water, food, soils or stock solutions), the preconcentration techniques like solid-phase extraction (SPE), supercritical fluid extraction (SFE) or field-amplified injection (FAI) and the separation conditions (buffer systems, appropriate wavelengths, type of detection. Not only the ''traditional'' UV–visible and LIF devices, but also selective mass spectroscopic detection were shown to be promising in environmental application of CE.

2. Tabulated list of agrochemical and capillary electrophoresis separation methods

Agrochemicals cover different chemical classes of organic components from ionizable to neutral substances. The annual worldwide use of agrochemical

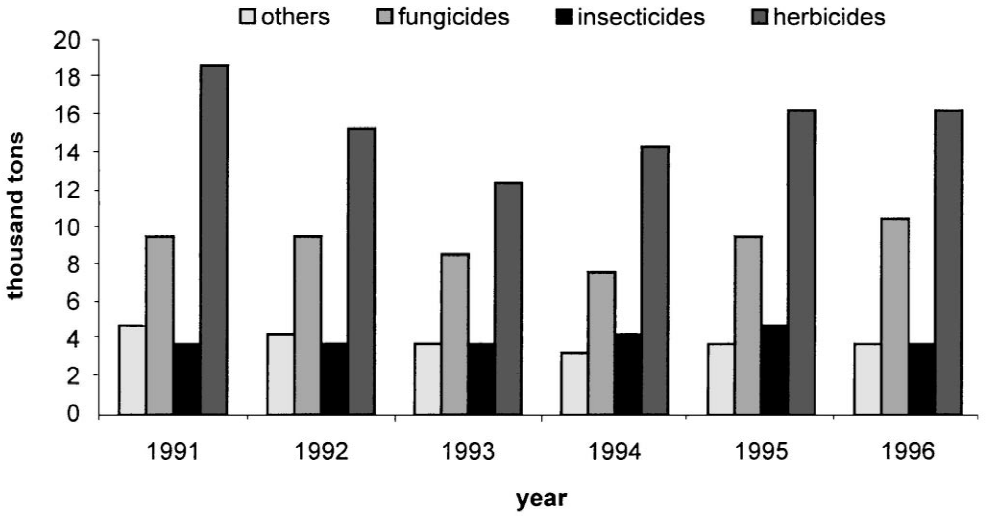


Fig. 1. Pesticides production in Germany from 1991 to 1996 [source: Ministerium für Ernährung, Landwirtschaft und Forsten, Germany, 1998].

is in the million tons per year and in Germany alone is higher than $3 \cdot 10^7$ kg; the herbicides class is the most important, followed by fungicides and insecticides (Fig. 1).

The structures of the analyzed agrochemicals with their typical representatives are shown in Fig. 2 for a rapid compound identification.

Tables 1 and 2 summarize the found references (over 60 records in the last few years) in terms of pesticide classes, separation methods, electrolytes, detection methods, matrices and extraction methods as well as the detection limits (as far as this information was available in the cited articles). We distinguished the articles where separation techniques were developed for the different agrochemical classes with standard solutions (Table 1) from the articles where real samples were analyzed (Table 2).

3. Type of analyzed samples

3.1. Commercial formulations

CE finds more and more applications in quality control in the analysis of pharmaceuticals, excipients, preservatives or products in biochemical synthesis [90–92]. In the agrochemical sector CE could be successfully used for the analysis of the active molecules (racemate contents) in commercial formulations prior to their field application:

(i) Gallant containing 125 g/l racemic haloxyfop ethoxyethyl ester [83], (ii) Effix [flamprop isopropyl pure *R*-(−)-isomer] [84], blasticidin-S [86], (iii) Foxtril (400 g/l racemic dichlorprop, 187.5 g/l bifenox, 75.5 g/l ioxynil) [68].

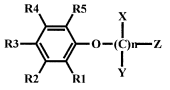
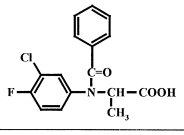
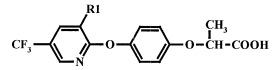
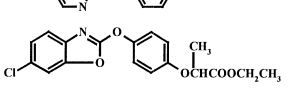
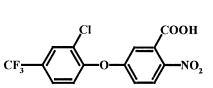
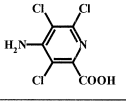
3.2. Environmental real samples

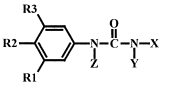
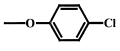
The identification and quantification of pesticides and their metabolites in real matrices was investigated in ground- and surface water, in soils as well as in various food samples.

It is especially important to analyze the effects of the matrices on the recoveries (during sample concentration) and responses (during quantification) of the pesticides by CE prior to the analysis of the real samples. For this reason, the different environmental samples were usually analyzed after spiking them with the pesticides of interest.

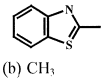
The different analyzed real matrices from Tables 1 and 2 are listed below:

(1) Water: deionized/distilled water [60,69,72, 76,81], pond water [57,67], tap water [58,62,70,88], ground water [81], river water [81], lake water [45,48], drinking water [89,92].

Pesticide classes	Structure Formula	Name	n	X	Y	Z	R_1	R_2	R_3	R_4	R_5
Chlorinated acid herbicides and related compounds		2,4 - D	1	H	H	COOH	Cl	H	Cl	H	H
		2,4 - DB	3	H	H	COOH	Cl	H	Cl	H	H
		MCPA	1	H	H	COOH	CH_3	H	Cl	H	H
		MCPB	3	H	H	COOH	CH_3	H	Cl	H	H
		2,4,5 -T	1	H	H	COOH	Cl	H	Cl	Cl	H
		2,4,5 - TP	1	CH_3	H	COOH	Cl	H	Cl	Cl	H
		2,4 - DP	1	CH_3	H	COOH	Cl	H	Cl	H	H
		MCPP	1	CH_3	H	COOH	CH_3	H	Cl	H	H
		2,4 – CPPA	1	CH_3	H	COOH	H	H	Cl	H	H
		2,3 – CPPA	1	CH_3	H	COOH	H	Cl	H	H	H
		2,2 - CPPA	1	CH_3	H	COOH	Cl	H	H	H	H
		2 - PPA	1	CH_3	H	COOH	H	H	H	H	H
		dicamba	1	H	H	H	Cl	H	Cl	H	COOH
		chloramben	0	no oxygen benzene	on ring	COOH	Cl	NH_2	H	Cl	H
		diclofop	1	H	CH_3	COOH	H	H	Cl	H	Cl
		flamprop									
		fluazifop					H				
		fenoxaprop-ethyl					Cl				
		acifluorfen									
		picloram									

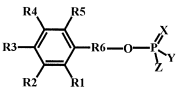
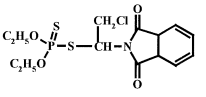
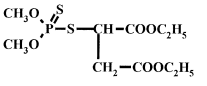
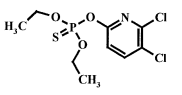
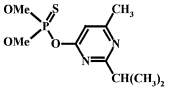
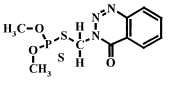
Pesticide classes	Structure Formula	Name	R_1	R_2	R_3	X	Y	Z
Phenlurea		monuron	H	Cl	H	CH_3	CH_3	H
		fluometuron	CF_3	H	H	CH_3	CH_3	H
		metobromuron	H	Br	H	OCH_3	CH_3	H
		diuron	H	Cl	Cl	CH_3	CH_3	H
		linuron	Cl	Cl	H	CH_3	OCH_3	H
		chlortoluron	Cl	CH_3	H	CH_3	CH_3	H
		fenuron	H	H	H	CH_3	CH_3	H
		isoproturon	H	$(CH_3)_2CH$	H	CH_3	CH_3	H
		metoxuron	Cl	OCH_3	H	CH_3	CH_3	H
		monolinuron	H	Cl	H	CH_3	OCH_3	H
		methabenz-thiazuron	(a)	(a)	(a)	CH_3	H	(b)
		neburon	H	Cl	Cl	C_4H_9	CH_3	H
		chloroxuron	H		H	CH_3	CH_3	H
		siduron	H	H	H		H	H

(a) instead of benzene-ring:

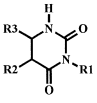


(b) CH_3

Fig. 2. Structures of the analyzed pesticides listed in Tables 1 and 2.

Pesticide classes	Structure Formula	Name	X	Y	Z	R_1	R_2	R_3	R_4	R 5	R 6
Organo-phosphorus		fenamifos	O	$NHCH(CH_3)_2$	OCH_2CH_3	H	CH_3	SCH_3	H	H	-
		isofenfos	S	$NHCH(CH_3)_2$	OCH_2CH_3	H	H	H	H	(a)	-
		ruelene	O	OCH_3	$NHCH_3$	Cl	H	(b)	H	H	-
		chlorfenviphos	O	OC_2H_5	OC_2H_5	Cl	H	Cl	H	H	(c)
		parathion	S	OC_2H_5	OC_2H_5	H	H	NO_2	H	H	H
dialifos		malathion									
chlorpyrifos		diazinon									
azinphos methyl											

(a) $COOCH(CH_3)_2$
(b) $C(CH_3)_2$
(c) $C{=}CCl$

Pesticide classes	Structure Formula	Name	R_1	R_2	X	Y	Z	N-Y-Z
Organonitrogen		metribuzin	NH_2	-	SCH_3	N	$C(CH_3)_3$	N-Y=Z
		hexazinone		-	=O	$N(CH_3)_2$	$N-CH_3$	N=Y-Z
		hexazinone derivatives	substituded cyclohexane -ring	-	=O	$N(CH_3)_2$	$N-CH_3$	$N-CH_3$
		DEET	$CHCH_3$		N	$CHCH_3$	-	-
		triadimefon		$C(CH_3)_3$	O		-	-
		bromacil			Br	CH_3		
		terbacil	$C(CH_3)_3$		Cl	CH_3		

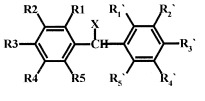
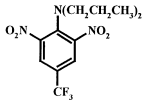
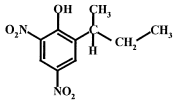
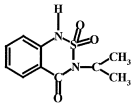
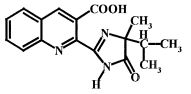
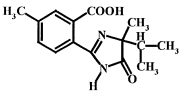
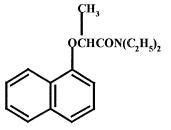
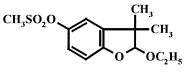
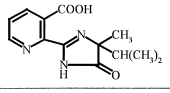
Pesticide classes	Structure Formula	Name	R_1	R_2	R_3	R4	R5	R1`	R2`	R3`	R4`	R5`	X
Organo-chlorine		p,p`-DDT	H	H	Cl	H	H	H	H	Cl	H	H	CCl_3
		o,p`-DDT	H	H	H	H	Cl	H	H	Cl	H	H	CCl_3
		p,p`-DDD	H	H	Cl	H	H	H	H	Cl	H	H	$CHCl_2$
		o,p`-DDD	H	H	H	H	Cl	H	H	Cl	H	H	$CHCl_2$
		p,p`-DDE	H	H	Cl	H	H	H	H	Cl	H	H	CCl_2
		o,p`-DDE	Cl	H	H	H	H	H	H	Cl	H	H	CCl_2

Fig. 2. (*continued*).

Pesticide classes	Structure Formula	Name
Nitrobenzene amine		trifluralin
Nitrophenol		dinoseb
Benzothiadiazin		bentazon
		imazaquin
		imazamethabenz (m-isomer)
		napropamide
		ethofumesate
		imazapyr

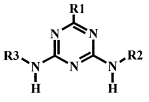
Pesticide classes	Structure Formula	Name	R_1	R_2	R_3
s-Triazines		atrazine	Cl	$CH(CH_3)_2$	CH_2CH_3
		simazine	Cl	CH_2CH_3	CH_2CH_3
		propazine	Cl	$CH(CH_3)_2$	$CH(CH_3)_2$
		terbutylazine	Cl	$C(CH_3)_3$	CH_2CH_3
		cyanazine	Cl	CH_2CH_3	$C(CH_3)_2CN$
		terbutryn	SCH_3	$CH(CH_3)_2$	CH_2CH_3
		desmetryn	SCH_3	$CH(CH_3)_2$	CH_3
		simetryn	SCH_3	CH_2CH_3	CH_2CH_3
		prometryn	SCH_3	$CH(CH_3)_2$	$CH(CH_3)_2$
		ametryn	SCH_3	$CH(CH_3)_2$	CH_2CH_3
		atraton	OCH_3	$CH(CH_3)_2$	CH_2CH_3
		prometon	OCH_3	$CH(CH_3)_2$	$CH(CH_3)_2$
		hydroxymetabolites of triazines above	OH	"	"
		dealkylated metabolites of triazines above	"	"	H

Fig. 2. (*continued*).

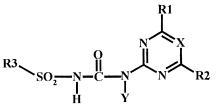
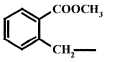
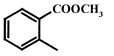
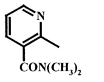
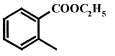
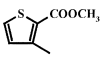
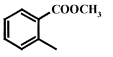
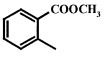
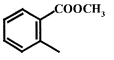
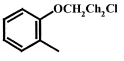
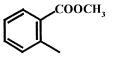
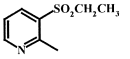
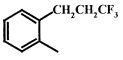
Pesticide classes	Structure Formula	Name	X	Y	R_1	R_2	R_3
Sulfonylurea		bensulfuron methyl	C	H	OCH_3	OCH_3	
		sulfometuron methyl	C	H	CH_3	CH_3	
		nicosulfuron	C	H	OCH_3	OCH_3	
		chlorimuron ethyl	C	H	OCH_3	Cl	
		thifensulfuron methyl	N	H	OCH_3	CH_3	
		metsulfuron methyl	N	H	CH_3	CH_3	
		tribenuron methyl	N	CH_3	CH_3	OCH_3	
		ethametsulfuron-methyl	N	H	OCH_2CH_3	$NHCH_3$	
		triasulfuron	N	H	OCH_3	CH_3	
		primisulfuron-methyl	C	H	OCF_2H	OCF_2H	
		chlorsulfuron	N	H	OCH_3	CH_3	
		amidosulfuron	C	H	OCH_3	OCH_3	$N(CH_3)SO_2CH_3$
		rimsulfuron	N	H	OCH_3	OCH_3	
		CGA 152`005	N	H	CH_3	OCH_3	

Fig. 2. (*continued*).

(2) Soils: agriculture soils [28,61,68,72,83,93], sea sand [75].

(3) Food: crops such as sugar cane, rice, corn [73], wheat, barley [64], vegetables such as potatoes [61], fruits such as soybeans [66].

CE is only part of a complete analysis setup in the separation of pesticides from real matrices which includes isolation, purification and preconcentration steps [94]. As with CE the injection volumes are in the nanoliter range the sample preparation (purification and concentration) is an essential step prior to analysis.

4. Extraction and concentration procedures

Mainly five preconcentration methods were found to be used for the components listed in Fig. 2: SPE; LLE (liquid–liquid extraction); sample stacking, FAI

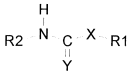
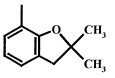
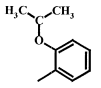
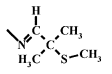
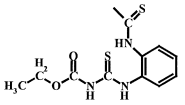
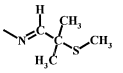
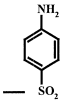
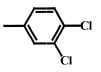
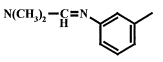
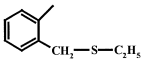
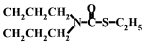
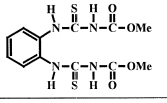
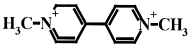
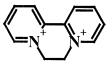
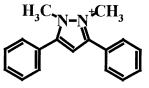
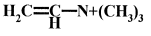
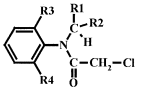
Pesticide classes	Structure Formula	Name	R_1	R_2	X	Y
Carbamates		prophame	$-CH(CH_3)_2$		O	O
		carbofuran		CH_3	O	O
		propoxur		CH_3	O	O
		methomyl		CH_3	O	O
		thiophanate methyl		CH_2CH_3	O	O
		dimethoate		CH_3	CH_2	O
		thiram		two CH_3 on nitrogen	S	S
		aldicarb		CH_3	O	O
		methomyl		CH_3	O	O
		asulam		CH_3	O	O
		carbaryl		CH_3	O	O
		swep		CH_3	O	O
		formetanate		CH_3	O	O
		ethiofencarb		CH_3	O	O
		cycloate	 (C_2H_5 instead H on nitrogen)	CH_2CH_3	S	O
		molinate				
		thiophanate-methyl				

Fig. 2. (*continued*).

Quaternary Ammonium "Quats"		paraquat
		diquat
		difenzoquat
	$ClCH_2CH_2N^+(CH_3)_3$	chlormequat
		mepiquat
	$HO(CH_2)_2N^+(CH_3)_3$	choline chloride
	$(CH_3)_3N^+H$	triethylamine-HCl
		trimethylvinylammonium hydroxide

Pesticide classes	Structure Formula	Name	R_1	R_2	R3	R4
Acetamid		metolachlor	CH_3	CH_2COCH_3	CH_3	CH_2CH_3
		alachlor	H	OCH_3	CH_2CH_3	CH_2CH_3
		butachlor	H	OC_4H_9	CH_2CH_3	CH_2CH_3

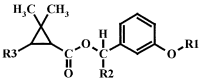
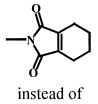
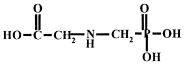
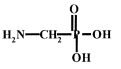
Pesticide classes	Structure Formula	Name	R_1	R_2	R3
Pyrethroid		permethrin		H	$C=C-Cl_2$
		cypermethrin		C≡N	$C=C-Cl_2$
		fenpropathrin		C≡N	$(H_3C)_2$
		phenothrin		H	$C=C-(CH_3)_2$
		sanmarton		C≡N	
		tetramethrin	 instead of 	H	$(H_3C)_2$-C=CH

Fig. 2. (*continued*).

Pesticide classes	Structure Formula	Name
Triorganotin	$(CH_3)_3SnCl$	trimethyltin-Cl
	$(C_2H_5)_3SnCl$	triethyltin-Cl
	$(C_3H_7)_3SnCl$	tripropyltin-Cl
	$[CH_3(CH_2)_3]_3SnCl$	tributyltin-Cl
	$(C_6H_5)_3SnCl$	triphenyltin-Cl

Pesticide classes	Structure Formula	Name
Phosphonic Acid		glyphosphate
		aminomethylphosphonic acid (AMPA)

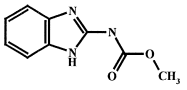
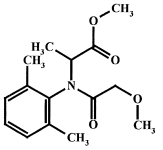
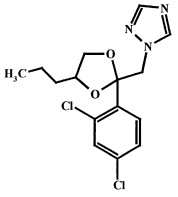
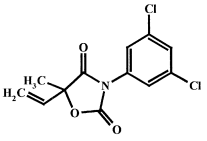
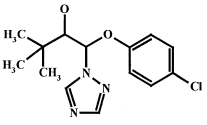
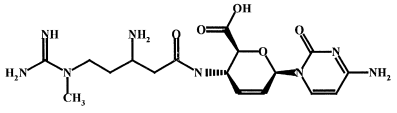
Pesticide classes	Structure Formula	Name
Benzimidazole		carbendazim
Methoxyacetyl-xylyl-alaninate		metalaxyl
Triazole		propicanazole
Oxaoldinedione		vinclozolin
Triazole		triadimenol
Enopyranuronic acid		blasticidin-S

Fig. 2. (*continued*).

Table 1
Pesticide classes analyzed with capillary electrophoresis from standard solutions[a]

Pesticide class	Pesticides	Method	Electrolytes	Detection methods, detection limit (DL)	Ref.
Phenoxy acid	Dichlorprop, mecoprop, 2,4-CPPA, 2,3-CPPA, 2,2-CPPA, 2-PPA, (silvex)	CZE	250 m*M* phosphate, pH 6.5 50 m*M* NG (nonyl-β-D-glucopyranoside or 70 m*M* OG (*n*-octyl-β-D-glucopyranoside)	UV, λ=230 nm	[24]
Pyrethroid	Chrysanthemic acid metabolites		Review on chiral glycosidic surfactants		[25]
s-Triazine	Chloro-, hydroxy-, methoxy-, thiomethyl *s*-triazine	CZE	50 m*M* citrate–hydrochloric acid, pH 2.2	UV, λ=230 nm DL: 0.05 mg/l	[26]
Phenoxy acid	2,4-D, MCPA	CZE	(a) 10 m*M* phosphate, 6 m*M* borate, pH 9.3, 50% acetonitrile	UV, λ=200 nm	[27]
		MEKC	(b) 10 m*M* phosphate, 6 m*M* borate, pH 9.3, 50 *M* sodium cholate, 35% acetonitrile	DL: 2,4-D: 0.15 mg/l MCPA: 0.15 mg/l	
		CZE	(c) 10 m*M* phosphate, 6 m*M* borate, pH 9.3, 5 m*M* α-CD		
Imidazolinone, phenoxy acid	Imazaquin, imazamethabenz, diclofop,	CZE	50 m*M* acetate, pH 3.6, 10 m*M* DM-β-CD, 10 m*M* TM-β-CD	UV, λ=214 nm DL: 10 mg/l	[28]
Phenoxy acid	2,4-D, dichlorprop, mecoprop, fenoprop	CZE	50 m*M* acetate, pH 4.5; for enantiomers: idem+25 m*M* TM-β-CD	UV, λ=230 nm DL: 0.05 mg/l	[29]
Organophosphorus Phenoxy acid methylester Organochlorine	Ruelene, isofenphos, dialifos, fenamifos, malathion Fenoprop, mecoprop, dichlorprop-methyl ester *p,p′*-DDT, *p,p′*-DDD, *o,p′*-DDT, *o,p′*-DDD, *p,p′*-DDE, *o,p′*-DDE	MEKC MEKC	(a) 20 m*M* borate, pH 9,100 m*M* SDS, 40 m*M* DM-β-CD (b) 20 m*M* borate, pH 9,100 m*M* SDS, 60 m*M* γ-CD, 15% methanol	UV, λ=200 nm	[30]
Acetamide	Metolachlor isomers: aS1′R, aS1′S, aR1R, aR1′S	MEKC MEKC MEKC	(c) 20 m*M* borate, pH 9, 50 m*M* SDS, 20 m*M* γ-CD, 20% acetonitrile (d) 20 m*M* borate, pH 9, 100 m*M* SDS (three of four isomers separated) 5 m*M* borate, pH 8, 30 m*M* SDS		
Carbamate organophosphorus, s-triazine	Prophame, propoxur carbofuran, methyl-, ethyl-parathion, chlorfenvinphos atrazine, simazine, desmetryn			UV-Scanner: λ=200–300 nm DL: 0.08–0.13 mg/l	[31]
Pyrethroid	Permethrin, phenotrin, sanmarton, cypermethrin, fenpropathrin (with and without derivatization with ANDSA)	CZE	50 m*M* phosphate, pH 7.0	UV (a) λ=200 nm, (b) λ=255 nm LIF λ_{ex}=325, 488 nm DL underivatized: UV $4.5\cdot10^{-5}$ *M* LIF $2.5\cdot10^{-5}$ *M* DL derivatized: UV $3.2\cdot10^{-5}$ *M* LIF $9.3\cdot10^{-5}$ *M*	[32]
s-Triazine	12 hydroxytriazines, ametryn, atraton	MEKC	10 m*M* phosphate, pH 7.0, 50 m*M* SDS, (25% isopropanol)	UV, λ=210, 230, 254 nm	[33]
s-Triazine	Ametryn, terbutryn, prometryn, simazine, atrazine, propazine	NACE	10 m*M* perchloric acid in 50% (v/v) acetonitrile in methanol, 20 m*M* SDS	UV, λ=214 nm	[34,35]
Sulfonylurea	Bensulfuron methyl, sulfometuron methyl, nicosulfuron, chlorsulfuron, chlorimuron ethyl, thifensulfuron methyl, metsulfuron methyl,	CZE	25 m*M* acetate, pH 5–acetontrile (3:1)	UV, λ=214 nm DL: $4\cdot10^{-4}$ *M*	[36]
Phenoxy acid, phenylurea	2,4-D, 2,4-DP, 2,4,5-T, 2,4-DB fenuron, monuron, diuron, monolinuron, linuron	MEKC	20 m*M* phosphate, borate pH 7, 0.07 *M* SDS	UV, λ=205 nm	[37]

Table 1. Continued

Pesticide class	Pesticides	Method	Electrolytes	Detection methods, detection limit (DL)	Ref.
Sulfonylurea	Bensulfuron methyl, sulfometuron methyl, ethametsulfuron-methyl, tribenuron methyl, triasulfuron, chlorimuron ethyl, nicosulfuron, thifensulfuron methyl primisulfuron methyl, metsulfuron methyl, chlorsulfuron, amidosulfuron	CZE	50 m*M* acetate, pH 4.76, 1.86 mol/l acetonitrile	UV, λ=239, 220 nm	[38]
s-Triazine, phenoxy acid, urea	Prometon propazine, prometryn silvex, 2,4,5-T, 2,4-D; monuron, diuron, chloroxoron, fluometuron, linuron, metobromuron, neburon,	MEKC MEKC	(a) 200 m*M* 1-butaneboronic acid, pH 10, 104 m*M* HG (heptyl-β-D-glucopyranoside) or 28 m*M* DG (decyl-β-D-glucopyranoside) (b) 200 m*M* 1-butaneboronic acid buffer, pH 11, 125 m*M* HG or 28 m*M* DG	UV, s-triazine, phenoxy acid: λ=231 nm (b) urea: λ=240 nm	[39]
s-Triazine	Hydroxytriazines	CZE	50 m*M* acetate, pH 4.65,	UV, λ=214, 230 nm	[7,40]
Phenoxy acid	Silvex-enantiomers; (Troger's base, dansyl amino acids)	MEKC	400 m*M* borate pH 10, 50 m*M* deoxy big CHAP[*N*,*N*-bis-(3-D-glucon-amidopropyl)-deoxycholamide]	UV, λ=240 nm	[41]
s-Triazine, acetamide, phenoxy acid, sulfurcarbamate, organophosphorus	Prometon, prometryn, propazine butachlor; silvex, 2,4,5-T; aldicarb; diazinon	MEKC MEKC	(a) 125 m*M* borate, pH 10, 100 m*M* MEGA 8 (octanyl-*N*-methylglucamide) (b) 125 m*M* borate, pH 10, 50 m*M* MEGA 10 (decanoyl-*N*-methylglucamide)	UV, λ=240 nm	[42]
Quaternary ammonium	Paraquat, diquat, difenzoquat	CZE	10 m*M* acetate, pH 4, 100 m*M* sodium chloride	UV, λ=205 nm	[43]
Phenylurea, phenoxy acid	Diuron, fenuron, linuron, mono- linuron, monuron; dichlorprop, 2,4-D, 2,4,5-T, 2,4-DB	MEKC	20 m*M* phosphate, pH 7, 50 m*M* SDS, 50 m*M* *n*-heptanol or 4.59 *M* methanol	UV, λ=205 nm	[44]
Phenylurea	Monuron, diuron, fluometuron, siduron, metobromuron, linuron, neburon, chloroxuron	MEKC	(a) 200 m*M* borate, pH 10, 100 m*M* OS (OM, OG, MEGA-9)	UV, λ=240 nm	[45]
s-Triazine, phenoxy acid, sulfurcarbamate, organophosphorus	Prometon, propazine, prometryn silvex, 2,4,5-T, 2,4-D; aldicarb; parathion	 MEKC	(OM: octyl-β-D-maltopyranoside OS: *n*-octanoylsucrose OG: octyl-β-D-glucopyranoside MEGA 9: nonanoyl-*N*-methylglucamide) (b) 200 m*M* borate, pH 10, 100 m*M* OG (OM, OS, MEGA-9)		
Triazole	Triadimenol	MEKC	(a) 200 m*M* borate/20 m*M* phosphate, pH 9.1, 0.05 m*M* SDS, (b) 20 m*M* hydroxypropyl-β-CD (enantiomers) 20% methanol	DAD, λ=220 nm	[46]
Phenoxy acid	Dicamba, 2,4,5-T, 2,4-D, silvex, dichlorprop, MCPP, MCPA, 2,4-DB	CZE	19 m*M* phosphate buffer, pH 2.9, 0.75 m*M* hexamethoniumhydroxide (reversed-EOF)	UV, λ=230 nm	[47]
Phenoxy acid	MCPA, 2,4-D, MCPB, dicamba, mecoprop, dichlorprop	CZE	75 m*M* acetate, pH 4	UV, λ=230 nm	[48]
Carbamate phenylurea,	Carbofuran, phenmedipham, diuron, chlortoluron, fenuron, isoproturon, linuron, monuron methabenzthiazuron, metoxuron metobromuron, monolinuron	MEKC	10 m*M* disodiumtetraborate, 10 m*M* boric acid (a) +80 m*M* SDS (b) +20 m*M* SDS with each 3 *M* urea (c) +20 m*M* SDS without urea	UV, λ=254 nm	[49]
s-Triazine	Simazine, atrazine, propazine, ametryn, prometryn, terbutryne, simetryn, prometon	CZE	50 m*M* acetate, pH 3.85, 0.7 m*M* cetyltrimethylammonium bromide (CTAB) for reversed-EOF	UV, λ=230 nm; ESI-MS	[50]
Phenoxy acid	Dichlorprop, fenoprop, mecoprop	CZE	50 m*M* acetate, pH 4.6, 20 m*M* TM-β-cyclodextrin	UV, λ=230 nm ESI-MS	[51]

Table 1. Continued

Pesticide class	Pesticides	Method	Electrolytes	Detection methods, detection limit (DL)	Ref.
s-Triazine	Atrazine, propazine, ametryn, prometryn	MEKC	20 m*M* acetate, pH 6.8, 25 m*M* SDS	UV, λ=226 nm; ESI-MS	[52]
Phenoxy acid	MCPP, 2,4-DP, 2,4-D, MCPA	CZE	10 m*M* acetate, pH 4.8	ESI-MS	[53]
Quaternary ammonium	Chlormequatchloride, choline chloride, trimethylamine-hydrochloride, trimethylvinyl-ammoniumchloride	CZE	10 m*M* creatinine, pH 3.6	Indirect UV, λ=200 nm ESI-MS DL: 5 mg/l	[54]
s-Triazine	Atrazine, desethylatrazine, desisopropylatrazine, simazine	MEKC MEKC	(a) 10 m*M* acetate, pH 7, 10 m*M* SDS (b) 10 m*M* acetate, pH 5.9, 10 m*M* SDS	(a) UV, λ=226 nm (b) ESI-MS	[55]
Quaternary ammonium	Paraquat, diquat	CZE	5 m*M* electrolyte (sodium acetate; ammonium hydrogencarbonate; ammonium acetate; ammonium formate, ammonium citrate), 0.5–1.5% acetic acid, pH 3.9, in methanol–water (50:50, v/v)	UV, λ=210 nm ESI-MS	[56]

[a] ANDSA=7-aminoaphthalene-1,3-disulfonic acid; CD=cyclodextrin; CPPA=Chlorphenoxypropionic acid; DB=(dichlorophenoxy)butryic acid; DP=(dichlorophenoxy)propanoic acid; MCPA=(2-methyl-4-chlorophenoxy)acetic acid; MCPP=2-(4-chloro-2-methylphenoxy)propanoic acid; PPA=Phenoxypropionic acid; SDS=sodium dodecyl sulfate; TM=trimethyl; other abbreviations defined in the table or in the text.

or FAC (field amplified concentration); PLE (pressurized liquid extraction); SFE.

4.1. Solid-phase extraction

SPE constitutes the most used preconcentration technique prior to CE analysis. The sorbents used for analysis are in the most presented cases non-polar C_{18} materials that retain the analytes by hydrophobic interactions [95]. Coextracted substances from the matrices may interfere in the separation/detection of the analytes [96]. These preconcentrations were usually performed off-line by using SPE microcolumns and only in a few attempts was the on-line-modus with CE tried for the analysis of pesticides [97]. For more detailed information on SPE please refer to Ref. [98], a review which places an emphasis on method development, sorbents and coupling with liquid chromatography in both biological and environmental areas.

4.2. Liquid–liquid extraction

LLE is a classical extraction method with a long history, but with several drawbacks: (i) many clean-up steps must be included (low selectivity); (ii) the recoveries are often insufficient, (iii) high consumption of solvents are needed (the usually used solvents were methylene chloride [28,50,53,73,83] and hexane [66]).

4.3. Supercritical fluid extraction

SFE uses the physico–chemical properties of supercritical fluids (mainly CO_2 and possible solvent additives) [100] for the extraction of the pesticides {acetone: CO_2 (10:90) (70°C, 100 atm=$10.1\cdot10^3$ kPa) was used in Ref. [73]}. It needed rather a long time in some examples, because intermediate washing and drying steps had to be involved [69].

4.4. Pressurized liquid extraction

PLE is a relative new technique similar to LLE and employs increased temperatures and pressure in order to speed up the extraction [in the found example the extraction solvent was acetonitrile–50 m*M* HCl (pH 2) (7:3), 50°C, 2000 p.s.i.=$13.8\cdot10^3$ kPa] [66]. PLE works according to the principle of static extraction with superheated liquids. Originally PLE was developed for the sample preparation in environmental analysis and found application in the extraction of medicinal plants [99].

Table 2
Pesticide classes analyzed with capillary electrophoresis from real environmental matrices[a]

Pesticide class	Pesticides	Method	Electrolytes	Detection method and limit (DL)	Matrix analyzed, extractions	Ref.
s-Triazine, acetamide, phenoxy acid	Atrazine, simazine, alachlor, metolachlor dicamba, 2,4-D	MEKC	(a) 10 m*M* phosphate, pH 9.0, 30 m*M* SDS, 8% methanol	UV: λ=214 nm DL UV: triazines: 0.1 μg/l	Pond-water: LLE with methylene chloride	[57]
		MEKC	(b) 10 m*M* borate, pH 9.2, 30 m*M* SDS, 5 m*M* Brij35			
Sulfonylurea	Chlorimuronethyl: *after derivatization with BMC (4-bromo-methyl-7-methoxy- coumarin) *after derivatization with dansylchloride	MEKC	(c) 10 m*M* phosphate, pH 9.0, 30 m*M* SDS	alachlor: 1.0 μg/l LIF: λ_{ex}=325 nm dicamba, 2,4-D, chlorimuronethyl DL LIF: 10 ng/l	Deionized water: SPE with ethyl acetate, ethyl acetate–methylene chloride (1:1, v/v), methylene chloride	
Quaternary ammonium	Paraquat, diquat, difenzoquat, chlormequat (cq), mepiquat (mq)	CZE	10 m*M* 1-(4-pyridyl)-pyridinium chloride–HCl (PP), pH 2.5, 10% methanol	Indirect UV, λ=205, 257 nm DL: 0.8 μg/l for mq, cq	Tap water	[58]
Organonitrogen	Hexazinone and metabolites C, A1, E, B, D; (atrazine as internal standard)	MEKC	12 m*M* sodium phosphate 10 m*M* sodium borate pH 9, 50 m*M* SDS, 15% methanol	DAD, hex., A1: (247 nm), C (230 nm), B, D (225 nm), atrazin E (220 nm)	Groundwater SPE with methylene chloride	[59]
Phenoxy acid	2,4-D, 2,4-DB, 2,4-DP, 2,4,5-TP, MCPA, MCPB, 2,4,5-T, MCPP, derivatized with 5-(aminoacetoamido)fluorescein	MEKC	39 m*M* phospate, pH 6.5, 1670 m*M* urea, 46 m*M* SDS, 22.2% methanol	LIF, λ_{ex}=488 nm DL 2 fg for 4-nl injection	Distilled water, SPE with methanol	[60]
Quaternary ammonium	Paraquat, diquat	CZE	100 m*M* phosphate, pH 4.0, 10% acetonitrile	DAD, λ=258, 310 nm, DL: 0.25–0.36 n*M*	Herbicides in water, soil, potatoes, urine serum	[61]
s-Triazine	Atrazine, terbutylazine, desethylatrazine, desisopropylatrazine, desethylterbutylatrazine, hydroxyatrazine (HA), ameline hydroxyterbuthylazine (HT), desethylhydroxyat. (DEHA), desisopropylhydroxyat. (DIHA)	CZE,	(a) 100 m*M* acetate, pH 4.6, 10% methanol for OH-triazines	UV, λ=210 nm DL CZE: DIHA, DEHA, ameline 0.2 mg/l HA, HT 0.5 mg/l	Tap water, river water, s-triazine-contaminated groundwater	[62]
		MEKC +GC–MS	(b) 30 m*M* borate, pH 9.3, 30 m*M* SDS	DL SPE-CZE: 0.5–1.25 μg/l for 200-ml sample	SPE (LiChrolut EN) with methanol–acetone (3:2, v/v)	
Phenoxy acid, phenylurea, s-triazine, carbamate, organophosphorus	2,4-D, 2,4,5-T, diuron, atrazine, simazine, terbutryn dimethoate, azinphos methyl, chlorpyriphos methyl chlorpyriphos ethyl, carbaryl	MEKC	(a) 20 m*M* phosphate, pH 7, 50 m*M* SDS, 20 m*M* borate 8.8% *n*-butanol	UV, λ=200, 225 nm	Off-line-SPE (Carbopack B with methylene chloride, methanol, 0.016 *M* KOH and C_{18} with methanol) field amplified injection	[63]
		MEKC	(b) pH 9, 50 m*M* SDS, 40% methanol			
Sulfonylurea	Metsulfuron methyl thiofensulfuron-methyl, rimsulfuron, chlorsulfuron, tribenuron methyl	MEKC	25 m*M* phosphate, pH 6.15, 50 m*M* SDS	UV, λ=234 nm DL: 0.02 mg/l, DL rim., triben.: 0.035 mg/l	Wheat, barley, corn (a) Homogenisation with acetonitrile, extraction with *n*-hexane (b) Clean-up with cation-exchange-SPE	[64]

Organophosphorus	Chlorpyrifos	CZE +GC +HPLC	10 m*M* phosphate, 6 m*M* borate, 25% acetonitrile, 50 m*M* SDS or NADCh (sodiumdeoxycholate)	UV, λ=? DL air sample: 1 mg/m^3	Air, leaves, soil	[65]
Nitrobencoic acid, Phenoxy acid, Benzothiadiazin, Sulfonylurea	Acifluorfen (A), 2,4-D, bentazon (B), thifensulforon-methyl (T), chlorimuron-ethyl (C) imazaquin (I),	CZE	50 m*M* acetate, pH 4.75	UV, λ=240 nm DL: (ng/g) A: 36, B: C: 11,T: 11 2,4-D: 85, I: 52	Soybeans PLE, clean-up with LLE with *n*-hexane/SPE with C_{18}	[66]
Phenoxy acid	2,4-DB, MCPB, 2,4-DP, 2,4-D, MCPA 2,4,5-TP, 2,4,5-T	CZE	(a) Phosphate, pH 5.6, 2 m*M* α-CD (b) Phosphate, pH 5.6, 4 m*M* α-CD/1 m*M* β-CD	UV, λ=200 nm DL: $<$1 μg/l	Lake water SPE with methanol	[67]
Phenoxy acid	Foxtril formulation: dichlorprop, ioxynil, bifenox	CZE CZE	(a) 50 m*M* acetate, pH 4.65 (b) 50 m*M* acetate, pH 4.65 +25 m*M* TM-β-CD	UV, λ=230 nm DL dichlorprop: 0.05 μg/g soil	Foxtril and soil after application of Foxtril extraction with acetonitrile–water–glacial acetic acid (80:20:2); methylene chloride–hydrochloric acid	[68]
Benzimidazole, Methoxyacetyl- xylylalaninate, Tiazole, Oxaoldinedione	Carbendazim (c), metalaxyl (m), propiconazole (p), vinclozolin (v)	MEKC	10 m*M* phosphate, pH 7, 100 m*M* cholate, 10% methanol	UV, λ=214 nm DL: (m): 10 μg/l, (c): 5 μg/l (p): 20 μg/l, (v): 5 μg/l	Deionized water lake water LLE (methylene chloride)	[69]
Sulfonylurea, acetamide, *s*-triazine	Linuron, metsulfuron, metolachlor, atrazine	MEKC MEKC	(a) 50 m*M* borate, pH 8, 35 m*M* SDS, 10% methanol (b) 50 m*M* borate, pH 8, 22 m*M* SDS, 10% methanol (metabolites)	UV, λ=214 nm	Tap water, drinking water SPE (methylene chloride)	[70]
Sulfonylurea Sulfonamide	Bensulfuron methyl, sulfmeturon methyl, triasulfuron, chlorsulfuron, flumetsulam, nicosulfuron, triflusulfuron methyl, chlorimuron ethyl, Prosuluron, thifensulfuron methyl, primisulfuron methyl, metsulfuron methyl, halosulfuron methyl	CZE +LC–MS	50 m*M* acetate, pH 4.75, 12% acetonitrile	UV, λ=240 nm	Marsh water SPE with methanol Clean-up with strong-ion-exchange SPE on alumina SPE with 0.5% acetic acid in methylene chloride	[71]
Sulfonylurea	Chlorsulfuron, tribenuron, metsulfuronmethyl, bensulfuron, triasulfuron, chlorimuron, rimsulfuron, ethametsulfuron, CGA 152'005	MEKC	50 m*M* borate, pH 8.0, 22 m*M* SDS, 10% methanol		Distilled water	[72]
Phenoxy acid, benzoic acid	2,4-D, dicamba	MEKC	50 m*M* borate, pH 8.3, 25 m*M* SDS	UV, λ=254 nm DL: ca. 0.6 pg	Crops (sugar cane, rice, corn) treated with 2,4-D and dicamba, SFE with CO_2–acetone, clean-up: LLE with diethylether	[73]

Table 2. Continued

Pesticide class	Pesticides	Method	Electrolytes	Detection method and limit (DL)	Matrix analyzed, extractions	Ref.
Phosphonic acid	Glyphosphate, aminomethylphosphonic acid (AMPA)	CZE	10 m*M* phthalate, pH 7.5, 0.5 m*M* TTAB	Indirect UV, λ=240, 350 nm DL: 0.01 μM (2 ng/nl)	Milled wheat, stacking from water, field amplified injection	[74]
Diorganotin (DT), triorganotin (TT)	Trimethyltin (TMT), triethyltin (TET), tripropyltin (TPT), tributyltin (TBT), triphenyltin (TPhT)	CZE CZE	(a) 5 m*M* acetate, pH 4.5, 4 m*M* 4-aminopyridine (4-AP) (b) 5 m*M* acetate, pH 4.5, 4 m*M* 4-aminopyridine (4-AP), 15 m*M* α-CD	Indirect UV, λ=261 nm DL (TT): 2 μM DL (DT): 10-20 μM	Sea-sand standard reference material (SRM) PACS-1 from National Research Council of Canada (NRCC, Ottawa, Canada)	[75]
Sulfonylurea	Chlorsulfuron, chlorimuron, metsulfuron	MEKC	30 m*M* borate, pH 7.0, 80 m*M* SDS, 14% methanol 20% isopropanol	UV, λ=214 nm DL: 10 ng/l	Soil SPE with methanol–water (1:1, v/v)	[76]
Sulfonylurea	Primisulfuron, triasulfuron	CZE	25 m*M* phosphate, pH 6.5, 50 m*M* lithium dodecyl sulfate	UV, λ=214 nm DL: 0.2 mg/l (primisulfuron) 0.1 mg/l (triasulfuron)	Deionized water, lake water, soil, (a) extraction with methylene chloride (b) extraction with methanol–phosphate (1:1) and methylene chloride	[77]
Carbamate organophosphorus, *s*-triazine phenoxy acid phenylurea	Prophame, carbofuran, parathionethyl, chlorfenviphos simazine, desmetryn 2,4-D diuron	MEKC	5 m*M* borate, pH 8.0, 30 m*M* SDS	UV, DAD λ=190–365 nm DL in ng/ml: 2,4-D 0.08 Diuron 0.08 Prophame 0.02 Atrazine 0.014 Parathionethyl 0.04	Drinking water SPE with methanol combined with sample stacking	[78]
s-Triazine	Atrazine, cyanazine, simazine, propazine, ametryn, prometryn, terbutryn	MEKC	60 m*M* borate, pH 9.2, 50 m*M* SDS	UV, λ=214 nm DL: 0.05 μg/ml DL (SPE) 0.2 ng/ml	Water, SPE with methanol	[79]
Triorganotin	Trimethyltin (TMT), triethyltin (TET), tributyltin (TBT), tripropyltin (TPT)	CZE +HPLC	20 m*M* tartraric acid, 20% methanol, 4 m*M* CTAB, pH 2.6	UV, λ=220 nm DL: TMT: 0.16 mg/l TET: 0.24 mg/l TBT: 0.29 mg/l TPT: 0.009 mg/l	SPE (XAD-2) with methanol	[80]

Sulfonylurea quaternary ammonium *s*-triazine Phenylurea acetamide	Tribenuron, chlorsulfuron, metsulfuron paraquat simazine, atrazine, terbuthylazine linuron metolachlor, alachlor, trifluralin	MEKC	30 m*M* borate, pH 8.0, 30 m*M* SDS	UV, λ=214 nm	Distilled water	[81]
Organonitrogen	Metribuzin, bromacil, terbacil, hexazinone, DEET, triadimefon	MEKC	12.5 m*M* borate, pH 9, 50 m*M* SDS	UV, λ=210 nm DL: 0.8 ng/l (without DEET)	Drainage ditch water near a highway after rainfall, (a) off-column-SPE: with acetonitrile (b) on-column-FAC: with 1.2 m*M* borate, 5 m*M* SDS (10-fold diluted buffer)	[82]
Phenoxy acid	Mecoprop, fenoprop, dichlorprop, flamprop, haloxyfop, fluazifop, diclofop, fenoxaprop	CZE	75 m*M* Britton–Robinson buffer (boric, acetic, phosphoric acid), pH 5, 6 m*M* vancomycin	UV, λ=190–210 nm DL per enantiomer: $5 \cdot 10^{-7}$ *M*	Soil and Gallant, 72 h incubation at room temperature, extraction with methylene chloride	[83]
Bonzothiadiazin, organonitrogen, Chlorinated acid herbicides	Naproamide, flampropisopropyl bromacil, chlorbufam, imazapyr, flamprop acid, fluazifop acid, haloxyfop acid, ethofumesate	CZE	25 m*M* borate, pH 9, 20–80 mg/ml SBE-β-CD	UV, λ=205 nm	Commercial formulation Effix	[84]
Rotenticide	Sodium monofluoracetate	CZE (reversed-EOF)	5 m*M* phthalate, pH 4.61, 0.3 m*M* CTAB 5 m*M* 4-hydroxybenzoate, pH 9.49, 0.3 m*M* CTAB	Indirect UV, (a) λ=230 nm (b) λ=249 nm DL: 0.4 μg/ml	Rotenticide bait	[85]
Enopyranuronic acid	Blasticidin-S	CZE	67 m*M* phosphate, pH 7	UV, λ=265 nm DL: 0.2 μg/ml	Commercial formulated blasticidin-S	[86]
Phenylurea	Monuron, linuron, diuron, isoproturon, monolinuron	MEKC	4 m*M* borate, 12 m*M* phosphate, pH 7, 30 m*M* SDS	UV, λ=244 nm DL: diuron 0.02 ng/ml others 0.04 ng/ml	Water, SPE with acetone	[87]
Carbamate, thicarbamate, dithiocarbamates	Methomyl, aldicarb, asulam, thiophanate-methyl, cabaryl, swep, formetanate, molinate, ethiofencarb, cycloate, thiram	MEKC	100 m*M* borate pH 8.2, 50 m*M* SDS, 10% methanol	UV, λ=230 nm DL: carbaryl and asulam: 1–38 ng/ml cycloate 158 ng/ml	Tap water, SPE with acetonitrile	[88]
Benzothiadiazin, chlorinated acid herbicides, nitrophenol	Bentazon, dinoseb, chloramben, 4-nitrophenol, acifluorfen, pentachlorphenol, dicamba, picloram, dichlorprop, 2,4-D, 3,5 dichlorbenzoic acid, 2,4,5-TP, 2,4-DB acid	CZE	20 m*M* posphate, pH 2.9 or 6.4, 5 m*M* acetate in isopropanol–water (40:60), pH 10	(a) UV, λ=230 nm; ESI-MS DL: 8–250 μg/l	Drinking-water, sample stacking	[89]

[a] DEET=N,N-Diethyl-3-methyl-benzamide; SBE=sulfobutyl ether; for other abbreviations see tables and text.

4.5. On-line sample stacking, field-amplified injection and concentration

FAI is done during electrokinetic injection, and FAC or sample stacking is possible after hydrodynamic injection [63]. In both cases a large volume of analyte is diluted in distilled water or in run buffer (about 1:10). FAI and sample stacking are based on the principle, that in diluted buffer or water the electric field is much stronger than in the buffer system. By applying high voltages (normal: anode⇒cathode; reversed: cathode⇒anode) the anionic analyte migrates up to the border between water (diluted buffer) and the separation buffer. When they reach this interface the ions slow down and concentrate in a sharp sample band. In reversed-polarity FAC the polarity is changed after concentration in the sample band [63]. In FAC the injection time can vary from 45 s [74] to 120 s [63] as a function of the column length.

5. Capillary electrophoresis separation methods used for the analysis of agrochemicals

From the various different CE techniques, CZE and MEKC were found in Tables 1 and 2 to have the most applications in environmental fields.

6. Detection modes

6.1. UV–visible and laser-induced fluorescence detection

Two ‘‘traditional’’ detection modes were used for analyzing pesticides by CE: UV–visible (direct and indirect modus) and LIF.

The use of LIF detection (after or without derivatization) could in some cases compensate for low sensitivity problems caused by the use of UV–visible detection [51].

Apart from the classical UV–visible detection, the following detection modes were used for the analysis of the agrochemicals presented in Tables 1 and 2:

(1) UV–visible: phenoxy acid [24,25,27–30,37,39, 41, 42, 44, 45, 47, 48, 51,57,63,66–68,73,78,83,84, 89], *s*-triazine [26,31,33–35,39,40,42,44,50,52, 55,62,63,70,78,79,81], carbamate [31,42,45,49, 63,78,88], organophosphorus [30,31,42,45,63, 65], organonitrogen [59,82,84], organochlorine [30], acetamide [30,42,70], pyrethroid [32], sulfonylurea [36,38,64,70–72,76–78,81], urea [37,39,44,45,49,63,87], quaternary ammonium [43,56], organotin [80], triorganotin [80], blasticidin-S [86].
(2) Diode array detection (DAD): diquat and paraquat [61], triadimenol [46].
(3) Indirect UV–visible: glyphosphate [50], quaternary ammonium salts [54], sodium monofluoracetate [60], quaternary ammonium salts [20], organotin compounds [59].
(4) LIF: fluorescein-derivatized phenoxy acids [37,97], pyrethroid insecticides [63], derivatized dicamba, 2,4-D, chlorimuronethyl [41].

6.2. Electrospray mass spectrometry detection

Although GC–MS and LC–MS are already well established and practiced analytical systems for the structure identification of pesticides [101–106], up to now only a few research groups developed methods to analyze pesticides with CE–MS [50–55,89]. The limitations of low sensitivity and the buffer systems needed to be adapted to the MS detection. A higher volatility is needed in order to avoid losses in electrospray efficiency and ion source contamination [55]. New technology now also offers the possibility to use more usual buffers (phosphate, borate) at low molar concentrations. Advances in ion source technology, the use of compatible buffers and the decreasing costs of benchtop MS instruments will surely increase the applicability of CE–MS in the future [107]. For more detailed information about CE–MS and some biological, pharmaceutical and environmental applications one can refer to the review in Ref. [108].

That only few examples are found in MEKC or chiral CE methods coupled with MS detection [51] shows the need for method development in this field [109].

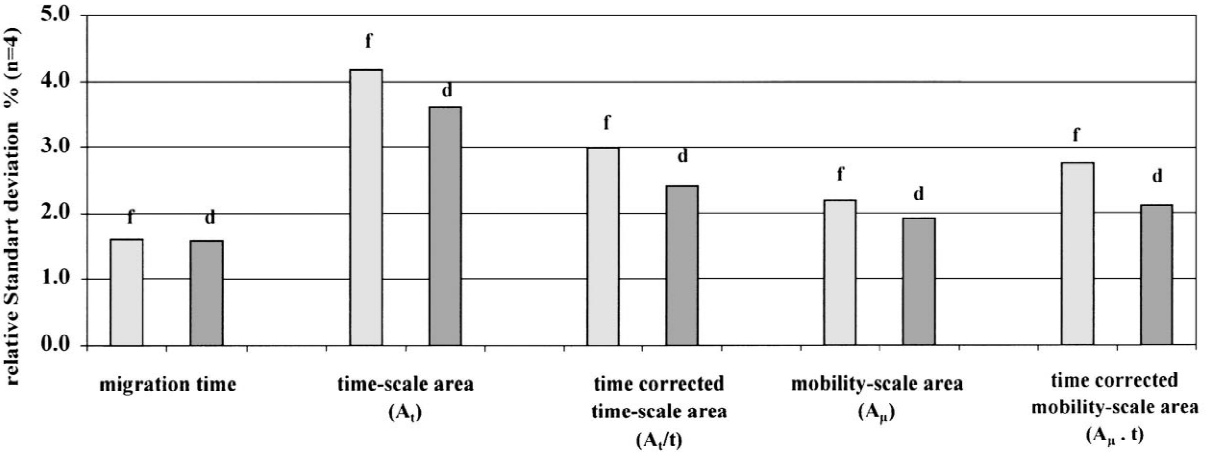


Fig. 3. Relative standard deviations (%) of a replicate ($n=4$) measurement of fenoprop (f) and mecoprop (m) in migration time (t), peak area from time scale electropherograms (A_t) with respective time corrected areas (A_t/t), and peak area from mobility scale converted electropherograms (A_μ) with respective time corrected areas ($A_\mu \cdot t$).

7. Quantitative analysis

Quantification is one of the key points when analyzing pesticides from real matrices. In most articles presented in Tables 1 and 2 the quantification was performed with the CE software tools derived from chromatographic techniques, by using external or internal standards (spiking), reproducibility assurance and standard curve calibrations on a time-scale basis.

CE has reached a point where the advances in instrumental technology allow a good reproducibility of migration times and peak signals from run-to-run and from day-to-day. In uncoated capillaries however, the electroosmotic flow (EOF) – hardly controllable and dependent on the capillary inner surface conditions – is the driving force and influences directly the migration times of the analytes (in both CZE and MEKC). Small changes in EOF can have big influences on the migration times of an analyte (as a function of column length and voltage). A direct implication is that the characterizing parameter for the identification of an analyte can thus not be the migration time but rather its effective mobility. For peak tracking (i.e., pesticides in real matrices) the comparison of the effective mobilities instead of migration times should be used systematically and for the qualitative comparison of complete electropherograms some strategies have been developed. These includes the definition of ''quantity of charge'' [110], the transformation of the electropherogram in the ''1/time domain'' [111] or in the ''effective mobility scale'' (μ_{eff} scale) [112–114]. Up to now these strategies are only applicable off-line and not with the chromatography-derived software currently on the market. The latter approach (μ_{eff} scaling) not only allows a good peak tracking but also quantitative implications as shown in Fig. 3; the reproducibility in the quantification parameters is increased with the time corrected areas (usual procedure) and even more when analyzing the peaks in the effective mobility scale. Modifications of the chromatographic derived CE software taking more account the electrophoretic processes prior to data analysis should be proposed in a near future [115].

8. Outlook – advanced techniques in the analysis of pesticides

CE is now generally accepted as an analytical tool in many research fields but still shows many limitations, especially because of its low sensitivity which may be contradictory at a first glance at the analysis of agrochemicals present in trace amounts from environmental matrices. CE only needs low amounts

of sample (nanoliter range) and an increase in the sensitivity by improving the hardware seems to be reaching its limits. This shows the necessity in developing strategies in sample preparation, cleaning and concentration prior to CE analysis. Some recent trends are on-line methods allowing sample concentration and CE analysis in one step as with the sweeping techniques, LC–CE coupling, on-line SPE–CE and solid-phase microextraction (SPME) [115].

Another on-coming field is the development of non-aqueous separation methods of neutral and charged agrochemicals with many advantages when coupling CE to MS.

8.1. On-line preconcentration methods

8.1.1. On-line solid-phase extraction

The on-line preconcentration of triazine herbicides with packed material C_{18} (''interactive capillaries'') was initially described by Cai and El Rassi in 1992 [97]. Commercially available ''concentration capillaries'' with packing material (C_8) at the injection end of the capillary were already proposed for the analysis of pharmaceuticals [116]. In Refs. [117,118], the ''extractor tube'' was proposed in polyethylene (in that example 5 mm×310 μm I.D. with C_{18} packing material).

In the environmental sector on-line SPE is promising as a rapid concentration/separation tool. The enhancement of the sensitivity by increasing the concentration by a factor of 7000 for the analysis of the cationic drug terbutaline with UV detection has been shown in Ref. [119]. Within this method, some matrix effects could be minimized (on-line clean-up) and the concentration limit of detection improved (on-line concentration). Even complex peptide mixtures derived by tryptic digestion of proteins (for example: bovine serum albumin, BSA) are analyzed successfully [120]. With an automatic on-line SPE–CE system *s*-triazines could be enriched 12-fold from fortified water samples, down to a concentration of 50 μg/l [121] showing thus good potentialities in this combined technique.

8.1.2. Sample sweeping in electrokinetic chromatography

Sample sweeping is the extension to neutral components of sample stacking techniques for charged analytes [122]. The detection sensitivity of both charged and neutral components can be significantly improved only by choosing adequate sweeping conditions [123]. The method allows a sample zone sharpening corresponding to up a 5000-fold concentration of dilute analyte in MEKC. With only this on-column concentration technique, lake water spiked with fenoprop could be analyzed to enantiomer concentrations lower than 10 ppb [124].

8.1.3. Membrane-based sample preparation

Prior to CE separation membrane extraction/concentration was proposed [125]. In the supported liquid membrane (SLM) technique either the porous membrane is impregnated with a water-immiscible organic solvent or the membrane consists of a non-porous silicon rubber. The pH is an essential parameter, so that at the ''donor-side'' the pH must be adjusted to the value, where the analyte is uncharged and can be easily extracted into the membrane (-liquid). At the ''acceptor-side'' a proper pH must be chosen for ionization of the analytes. They do not have to remigrate into the membrane. Separation is based on size-exclusion [125]. In the environmental sector preconcentration with SLMs has been applied for the analysis of phenoxy acids, sulfonylureas, triazines and other herbicides [125].

8.2. Non-aqueous capillary electrophoresis

MEKC was commonly used for the analyzing of pesticides (see Table 1). When coupling CE with electrospray MS the main disadvantage is the non-volatility of the surfactants. Thus the loss in electrospray efficiency and ion source contamination is the consequence [55].

In order to avoid these problems non-aqueous media can be used for the separation of less polar substances; for instance lipophilic peptides and therapeutic drugs were separated successfully with an acetate buffer used together with acetic acid in methanol [126] and sulfonylurea herbicides using acetate buffer and acetonitrile [36]. Combined off-line with conventional SPE technique, six *s*-triazines could be analyzed from natural waters down to sub-ppb levels with a good day-to-day precision [127]. The development of methods for the analyzing

of pesticides by non-aqueous CE (NACE)–electrospray ionization (ESI) MS should also be taken into consideration in environmental analysis.

9. Conclusions

This tabulated review article pointed out the high potential of CE in the analysis of pesticides and summarized the optimum conditions in buffer systems, pH, sample analyzed and preconcentration methods for various classes of pesticides. The sample preparation becomes a critical point when analyzing environmental samples (concentrations in trace amounts) with CE which is generally known not to be as sensitive as classical chromatographic methods. The actual developments go in the direction of on-line concentration/clean-up/separation including solid phase, sweeping techniques, membrane- and isotachophoresis-based extraction/concentration. For the separations a trend is given with non-aqueous buffer systems that are also applicable when using ESI-MS detection. After more than 10 years of development to routine analysis in many chemical and biochemical fields, CE still offers many possibility and challenges in the separation area of environmental chemistry.

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