ELSEVIER

Journal of Chromatography A, 880 (2000) 281–294

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Review

Herbicide and plant growth regulator analysis by capillary electrophoresis

Donna T. Eash, Rodney J. Bushway*

Department of Food Science and Human Nutrition, University of Maine, 5736 Holmes Hall, Orono, ME 04469-5736, USA

Abstract

Capillary electrophoresis (CE) is a relatively new analytical technique that is just beginning to be employed in the area of pesticide residue analysis. With the development of more sensitive detectors and in conjunction with CE separation powers, it should be a well accepted technique for pesticide residue analysis in the future. This review describes CE methods that have been developed to analyze herbicides and grow regulators in water, soil and food.

Keywords: Reviews; Pesticides; Organophosphorus compounds; Carboxylic acids; Triazines; Sulfonyl ureas; Plant hormones

Contents

1. Introduction

Pesticides are used in most areas of the world to some degree in order to control insects, weeds, fungi, rodents or other organisms. Approximately 4.5×10^9 pounds of chemicals are used in the USA in a typical year [1]. A weed is defined as a unwanted plant, and control of weeds is crucial for optimum crop growth. Weeds compete with the crop for light, moisture, and nutrients. Ever since agriculture existed man has in some way attempted to control the growth of weeds. At first, it was mainly by mechanical means such as plowing and hand picking weeds, but as agricultural fields expanded and the growth of industrialization began, other ways to control weeds were needed.

Controlling weeds with chemicals is not a new practice. At first chemicals such as rock salt, oil wastes, and copper salts were used. These chemicals

*Corresponding author. Fax: +1-207-5811-636.

0021-9673/00/$ – see front matter
PII: S0021-9673(00)00433-7

killed beneficial plants, and were mainly used to keep areas, such as railroad tracks, clear. What really was needed were chemicals that exhibited selective toxicity, wherein weeds were destroyed without damaging crops.

By the early 1900s there was some selective control of broad leaf weeds. A mixture of soluble copper salts and sulphuric acid was sprayed onto cereal crops. The selectivity was based on a physical factor, where the leaves of weeds were more effectively wetted due to their size and texture [2].

Herbicides are commonly used for controlling weeds in many of the agricultural and non-agricultural areas in the USA. Some herbicides exhibit intrinsic selectivity, whereby the weed species would succumb, but the crop would not. Not all herbicides possess this selectivity and are rather non-selective. The active ingredients that have herbicidal properties belong to a variety of chemical classes.

With the development of herbicides, careful monitoring of residue levels needs to be performed on crops, soil and water. Herbicide residues are commonly found in surface water, ground water, foods, as well as in soil, due to their persistence and water solubility. This creates the need for rapid, simple, and reliable methods for measuring residues. A variety of analytical methods, such as high-performance liquid chromatography (HPLC), gas chromatography (GC), thin-layer chromatography (TLC) and immunoassay, have been used for the analysis of herbicides. These analytical techniques have proven to be very reliable for the analysis of herbicide mixtures in samples, but these methods are often time-consuming and expensive due to sample preparation and instrumentation.

A relatively new analytical technique that is complementary to GC and HPLC is capillary electrophoresis (CE). CE is only beginning to find its niche in the area of pesticide analysis, and published methods to date cover a wide area of herbicides.

In CE, a fused-silica capillary is filled with some type of electrolytic solution known as the running buffer or background electrolyte. An electric field is applied to the capillary and cations migrate to the cathode and anions migrate to the anode. This is known as free zone capillary electrophoresis and is the most basic. The unique feature of CE is the development of an electroosmotic flow within the capillary. This is the ‘driving force’ of CE and causes all ions to migrate to the cathode, even negatively charged species.

The most common mode of CE is known as micellar electrokinetic chromatography (MEKC). In MEKC surfactants are added to the background electrolyte. Usually, the concentration of surfactant added exceeds the critical micellar concentration (CMC) so that micelles are formed. This will allow compounds to interact with the micelles to enhance the separation of neutral and similarly structured compounds. Surfactants can be classified as anionic (such as sodium dodecyl sulfate (SDS), the most common surfactant used), cationic and zwitterionic. A variety of other compounds, such as bile acids and vancomycin, can also be used as surfactants.

In MEKC the retention window extends from the migration of an unretained compound (t_0) to the migration of a compound that is completely solubilized by the micelle (t_{mc}). Compounds that interact with the micelle will migrate within this window. It is crucial to be able to control this window since it can affect peak capacity, resolution and analysis time. Surfactants that are charged in their natural environment have a predetermined retention window that cannot be altered. When using SDS, for example, the retention window is not affected by pH to a great extent. Cationic surfactants also have a retention window that stays relatively stable over a wide pH range.

Smith and co-workers [3–5] have introduced in situ charged micelles for some of their analyses. In situ charged micelles are based on the complexation of borate or borate ions with neutral surfactants that have polyolic polar head groups. Using these types of micelles the surface charge density of the micellar phases can be varied by either altering the borate or boronate concentration and/or pH of the running buffer. This will allow the retention window to vary for optimization of resolution and peak capacity.

CE offers many advantages over conventional chromatographic techniques. One of the greatest advantages is that no organic solvents are used in preparation of the running buffer. Organic solvents can be used as modifiers, but when this is done the levels only reach 5–30% of the total solvent. This is extremely cost effective since waste disposal is expensive as well as environmentally unsound. Some

other advantages of CE include small sample volume, automation, as well as decreased cost of capillaries when compared to HPLC columns or GC capillary columns. CE also can operate in numerous modes, such as MECK and isotachophoresis, as well as free zone CE. This allows for numerous possibilities when trying to separate a variety of compounds.

The largest drawback to CE is decreased sensitivity due to the on-line detection system. This problem is slowly being resolved with the introduction of high flow cell capillaries as well as new detectors. Sample stacking as well as pre-concentration techniques also aids to enhance sensitivity.

This review article will focus on the analysis of herbicides and plant growth regulators by capillary electrophoresis (see Tables 1 and 2).

2. Bipyridinium herbicides

Since paraquat and diquat are ionic species it would seem ideal to use CE for their analysis. In fact, numerous CE papers have been published to identify paraquat, diquat and difenzoquat. Stransky [6] quantified paraquat and diquat in water and soil samples using two different buffers by isotachophoresis. Most papers use capillary zone electrophoresis (CZE) for the identification of these herbicides. Galceran et al. [7] examined the effects of pH, temperature, applied voltage, buffer cation and injection mode on the separation of paraquat, diquat, and difenzoquat. Galceran et al. [8] in another paper separated paraquat, diquat, difenzoquat, chloremquat, and mepiquat in water samples by CZE with indirect UV detection. Methods have also been developed for matrices that include water [9,10], potatoes [11,12], soil, serum and urine [12].

3. Organophosphorus herbicides

Glyphosate is an organophosphorus herbicide. Tomita et al. [13] used CE to quantify glyphosate and its major metabolite (aminomethyl)phosphonic acid (AMPA) in serum. Prior to injection the samples were derivatized with *p*-toluenesulfonyl chloride and detected by UV at 240 nm. It was found with this method that both compounds resolved completely with no interferences. Recoveries were also found to be higher than those obtained by HPLC.

Cikalo et al. [14] analyzed glyphosate and AMPA in water. Phthalate was used as the background electrolyte with tetradecyltrimethylammonium bromide (TTAB) as a modifier. The polarity was reversed and the separation was completed in less than 4 min with indirect UV detection.

4. Carboxylic acid herbicides

Numerous CE methods have been developed for phenoxy acid herbicides. Jung and Brumley [15] were the first to derivatize the phenoxy acid herbicides. In their method the acids are activated with hydroxybenzotriazol (HBOT) and diidopropylcarbodiimide (DIC), then reacted with 5-(aminoacetamido)fluorescein in dimethylformamide. The phenoxy acid herbicides were separated in a single run by MEKC with laser-induced fluorescence (LIF) detection.

Mechref and El Rassi [16] fluorescently labeled phenoxy acid herbicides with 7-aminonaphthalene-1,3-disulfonic acid (ANDSA). The ANDSA-*o*-phenoxy acid derivatives were then detected by CE–LIF. It was also found that the ANDSA-phenoxy acid enantiomers exhibited higher chiral resolution than underivatized compounds in the presence of cyclodextrins in the running buffer. Several cyclodextrins were investigated in this study with 2,3,6-tri-*o*-methyl-β-cyclodextrin (TM-β-CD) producing the best enantioselectivity.

Mechref and El Rassi [17] evaluated two chiral alkylglucoside surfactants, *n*-octyl-(OG) and *n*-nonyl-β-D-glucopyranoside (NG) for the enantiomeric separation of phenoxy acid herbicides. They found that resolution could also be changed by manipulating surfactant concentration, ionic strength, pH and temperature of the system.

Wu et al. [18] developed a method for the separation of chlorophenoxy acids by MEKC. They investigated the effects of various surfactants including SDS, Brij 35, and cetyltrimethylammonium bromide (CTAB) as well as methanol. SDS combined with Brij 35 was found to produce the best separation for these compounds.

Table 1
Capillary electrophoresis methods for the analysis of herbicides and growth regulators[a]

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Crop water	CZE	Acetic acid, sodium acetate, pH 4.0	Fused silica, 50 μm I.D., L_{tot} 72 cm, L_{eff} 50 cm	15 kV	Water 2.9 μl Crop water 21 μl	UV 205 nm	Paraquat, diquat, difenzoquat	[9]
Potatoes	CZE	0.1 *M* phosphate, pH 2.5	Coated, 50 μm .D., L_{tot} 50 cm, L_{eff} 45.4 cm	45 μA	Paraquat 0.01 ppm Diquat 0.01 ppm	UV	Paraquat, diquat	[11]
Water	CZE	0.10 *M* sodium phosphate, pH 3.5 and 7.0	Fused silica, 50 μm I.D., L_{tot} 80 cm, L_{eff} 50 cm	15 kV	Paraquat 0.4 μg/ml Diquat 0.5 μg/ml	UV 258 and 308 nm	Paraquat, diquat	[10]
Soil potatoes, urine, serum	CZE	100 m*M* phosphate, 10% acetonitrile, pH 4.0	Fused silica, 75 μm I.D., L_{tot} 57 cm, L_{eff} 50 cm	12 kV	Varies with injection mode	DAD 258 and 310 nm	Paraquat, diquat	[12]
Not stated	CZE	Acetic acid, sodium acetate buffer, 100 m*M* NaCl, pH 4.0	Fused silica, 50 μm I.D., L_{tot} 72 cm L_{eff} 50 cm	15 kV	Not stated	UV 205 nm	Paraquat, diquat, difenzoquat	[7]
Water	MEKC	60 m*M* borate, 50 m*M* SDS, pH 9.2	Fused silica, L_{tot} 57 cm, L_{eff} 50 cm	22 kV	0.05 μm/ml	UV 214 nm	Simazine, cyanazine, atrazine, ametryne, propazine, prometryne, terbutryne	[31]
River water	MEKC	**A**: 10 m*M* sodium dihydrogenortho-phosphate, 25 m*M* SDS, pH 7 and 8 **B**: 10 m*M* sodium tetraborate, 25 m*M* SDS, pH 9.0 and 10.0	Fused silica, 75 μm I.D. L_{tot} 50 cm, L_{eff} 36 cm	10 kV	$3.5 \cdot 10^{-7}$ M	UV 225 nm	Atrazine, simazine	[32]
Water	CZE	0.02 *M* Tris adjusted to pH 3.0 with trichloroacetic acid, 30% ethanol	Fused silica, L_{tot} 40 cm	15 kV	$2 \cdot 10^{-6}$ M	UV 254 nm	Prometryne, terbutryne, desmetryne, simazine, atrazine	[30]
Not stated	CZE	**A**: 50 m*M* acetate, pH 3.8–5.6 **B**: Citrate–phosphate, pH 2.2–7.8 **C**: Citrate–HCl, pH 1.2–5.0	Fused silica, 75 μ I.D., L_{tot} 57 cm, L_{eff} 50 cm	20 kV	0.05 μg/ml	UV 230 nm	s-Triazines	[55]

Table 1. Continued

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Water	CZE	50 m*M* acetate, pH 4.65	Fused silica, 75 μm I.D., L_{tot} 57 cm, L_{eff} 50 cm	20 kV	Not stated	UV 230 and 214 nm	Atrazine	[29]
Wheat, barley, corn	MEKC	50 m*M* SDS, 25 m*M* sodium phosphate (monobasic), pH 6.15, adjusted with sodium phosphate dibasic	Fused silica, 75 μm I.D., L_{tot} 90 cm, L_{eff} 68 cm	25 kV	0.02 ppm, 0.035 ppm for rimsulfuron and Tribenuron methyl	UV 234 nm	Metsulfuron-methyl, Thifensulfuron-methyl, clorsulfuron, rimsulfuron, tribenuron-methyl	[38]
Soil	CZE	50 m*M* acetate, 25 m*M* TMBCD, pH 4.5	Fused silica, 75 μm I.D., L_{eff} 50 cm	20 kV	0.05 μg/ml	UV 230 nm	2,4-Dichloro-phenoxyacetic acid, dichloprop, mecoprop, fenoprop	[19]
Pond water	CZE	**A**: 10 m*M* Na_2HPO_4, 30 m*M* SDS, 8% methanol, pH 9.0 **B**: 10 m*M* $Na_2B_4O_7$, 30 m*M* SDS, 5 m*M* Brij 35, pH 9.2 **C**: 10 m*M* Na_2HPO_4, 30 m*M* SDS, pH 9.0 **D**: 10 m*M* $Na_2B_4O_7$, 100 m*M* NaCh, pH 9.3 **E**: 10 m*M* $Na_2B_4O_7$, 30 m*M* SDS, pH 9.2	Fused silica, 75 μ I.D., L_{eff} 50 cm	20–25 kV	UV 0.1 μg/ml, LIF 10 ng/ml	UV LIF Excitation 325 nm	**A**: Atrazine, simazine, alachlor, metolachlor **B**: Dicamba, 2,4-D **C**: Chlorimuron ethyl **D**: Dicamba, 2,4-D **E**: Chlorimuron ethyl	[25]
Milk	Isotachophoresis	40% methanol, 10 m*M* sodium acetate, pH 4.8, 0.2% (w/v) hydroxy-cellulose (leading electrolyte) 40% methanol, 20 m*M* acetic acid (terminating electrolyte)	**Preparation** PTFE, 8 mm I.D., L_{tot} 170 mm **Analytical** 0.2 mm I.D., L_{tot} 170 mm	10 μA	2 ng	Conductivity	Prometryne, desmetryne, terbutryne, atrazine (OH derivative), simatzine (OH derivative)	[34]
Not stated	MEKC	25 m*M* phosphate–borate, 100 m*M* SDS, 10 m*M* TBA, pH 8.7	Fused silica, 50 μm I.D., L_{eff} 40 cm	15 kV	30 pg	UV 214 nm	Imidazole, 1-methylimidazole, 2-methylimidazole, 4(5)-methylimidazole	[53]
Lake water	MEKC	Phosphate, 2 m*M* α-cyclodextrin, pH 5.6	Fused silica, 50 μm I.D., L_{tot} 47 cm, L_{eff} 40 cm	25 kV	1 ppb	UV 200 nm	Phenoxy acids: 2,4-DB, MCPB, 2,4-DP, 2,4-D, MCPA, 2,4,5-TP, 2,4,5-T	[20]

Table 1. Continued

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Tap water	CZE	20 *M* boric acid, 20 m*M* sodium borate, pH 9.0	Fused silica, 75 μm I.D., L_{eff} 40 cm	25 kV	10 pg	UV 214 nm	Metsulfuron, chlorsulfuron	[47]
Water	MEKC	10 m*M* pyrophosphate (PP), 10% methanol pH 2.5	Fused silica, 50 μm I.D., L_{tot} 72 cm, L_{eff} 50 cm	20 kV	0.8 μg/ml	UV 257 and 205 nm	Paraquat, diquat, difenzoquat, chlormequat, mepiquat	[8]
Water	MEKC	50 m*M* sodium borate, 22 m*M* SDS, 10% methanol	Fused silica, 75 μm I.D., L_{eff} 40 cm	25 kV	Not stated	UV	Chlorsulfuron, metsulfuron, triasulfuron, ethametsulfuron, tribenuron, bensulfuron, chlorimuron, rimsulfuron	[36]
Not stated	MEKC	0.02 *M* phosphate, 0.1 *M* SDS, Brij 35	Fused silica, L_{tot} 44 cm, L_{eff} 37 cm	15 kV	Not stated	UV	2,4-DP, 2,4-DB, MCPA, MCPP, MCPB, 2,4,5-TPA, 2,4,5-TPP, dicamba, 2,3,6-TB, bentazon	[18]
Not stated	MEKC	200 n*M* borate, 5 m*M* α-CD, pH 10.0	Fused silica, 50 μm I.D., L_{tot} 80 cm, L_{eff} 50 cm	20 kV	0.2 ppb	LIF	2,4-D, 2,4,5-T, 2-PPA, mecoprop, α,2,-CPPA, 2,3-CPPA, 2,4-CPPA, dichloprop, silvex	[16]
Production samples	CZE	**A**: 50 m*M* lithium acetate, pH 4.80 **B**: 30 m*M* lithium acetate, 20 g/l heptakis(2,6-di-*o*-methyl)-β-CB	Fused silica, 50 μm I.D., L_{tot} 79.5 cm, L_{eff} 63.1 cm	30 kV	$1 \cdot 10^{-5}$ M	UV 200 nm	MCCP, MD, i-MCCP, M, DP, D, MCPA	[21]
Soil	MEKC	30 m*M* borate, 80 m*M* SDS 14% methanol, 20% isopropanol, pH 7.0	Fused silica, 75 μm I.D., L_{eff} 63.1 cm	25 kV	10 ppb	UV 214 nm	Metsulfuron, chlorimuron, chlorsulfuron	[37]

Table 1. Continued

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Not stated	MEKC	200 m*M* sodium phosphate, 10–150 m*M* *n*-octyl-β-D-glucopyranoside, pH 6.5	Fused silica, 50 μm I.D., L_{tot} 57 cm, L_{eff} 50 cm	20 kV	Not stated	UV 230 nm	Dichlorprop, mecoprop, 2,4-CPPA 2,3-CPPA, 2,2-CPPA, 2-PPA, silvex	[17]
Water	MEKC	39 m*M* phosphate, 46 m*M* SDS, 1670 m*M* urea, 22.2% methanol	Fused silica, 50 μm I.D., L_{tot} 47 cm, L_{eff} 40 cm	30 kV	2 fg	LIF	2,4-D 2,4-DB, 2,4-DP, 2,4,5-T, MCBA MCPB, 2,4,5-T	[15]
Serum	CZE	0.1 *M* boric acid, 10% methanol, pH 9.6	Fused silica, 50 μm I.D., L_{tot} 72 cm	30 kV	0.1 μ/ml	UV 240 nm	Glyphosate, AMPA	[13]
Not stated	CZE	5 m*M* ammonium acetate (75:25), pH 5.0 (acetic acid)	Fused silica, 75 μm I.D., L_{tot} 1 m–35 cm	30–38 kV	30 pmol	Ion-spray mass spectrometry	Bensulfuron-methyl, sulfonmeturon-methyl, tribenuron-methyl, nicosulfuron, chlorimuron-ethyl, thifensulfuron-methyl, metsulfuron-methyl, chlorsulfuron	[39]
Not stated	CZE	Phosphate, pH 8.0	Fused silica, 50 μm I.D., L_{tot}	23 kV	<0.6 pg	UV 200 nm	2,4-D, 2,4,5-TP, 2,4-dichlorophenol, 2,4,5-trichlorophenol	[44]
Not stated	CZE	0.05 *M* phosphate, 0.01 *M* borate, 7.5 m*M* α-CD, 1.5 m*M* β-CB, 1.0 m*M* γ-CD, pH 7.54	Fused silica, 50 μm I.D., L_{eff} 50 cm	15 kV	Not stated	UV	IAA, IPA, IBA, GA, ANAA, BNAA, DCPAA, PCPAA, TCPAA	[40]
Water	MEKC	**Residue**: 50 m*M* sodium borate, 35 m*M* SDS, 10% methanol, pH 8.0 **Metabolites**: 50 m*M* sodium borate, 22 m*M* SDS, 10% methanol, pH 8.0	Fused silica, 75 μm I.D., L_{eff} 50 cm	25 kV	0.5 mg/l	UV 214 nm	Linuron, metolachlor, atrazine, metsulfuron	[26]
Not stated	MEKC	50 m*M* octylglucoside, 400 m*M* borate	Fused silica, 50 μm I.D., L_{tot} 80 cm, L_{eff} 50 cm	15 kV	Prometon 4.4 μ*M*, prometryne 8.3 μ*M*, propazine 3.0 μ*M*, butachlor 52.3 μ*M*	UV 210 nm	Prometon, prometryne, propazine, butachlor	[45]

Table 1. Continued

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Not stated	MEKC	30 m*M* phosphate, 80 m*M* DoTAC or 170 m*M* DTAC, pH 7.0	Fused silica, 50 μm I.D., L_{tot} 55/80 cm, L_{eff} 32.5/50 cm	10 or 20 kV	Not stated	UV	Monuron, fluometuron, metobromuron, disuron, diuron, linuron, chloroxuron	[27]
Soil	CZE	75 m*M* Britton Robinson, 6 m*M* vancomycin, pH 5.0	Polyacrylamide, 0.05 mm I.D., L_{tot} 37.5 cm, L_{eff} 33 cm	20 kV	$5 \cdot 10^{-7}$ M	UV	Mecoprop, fenoprop, dichlorprop, flamprop, haloxyfop, fluazifop, diclofop, fenoxaprop	[22]
Formulations	CZE	10 m*M* Dibasic sodium phosphate, pH 9.0	Fused silica, 75 μm I.D., L_{tot} 48.5 cm, L_{eff} 40 cm	75 μA	0.25 ppm	UV 220 nm	Maleic hydrazide	[41]
Potatoes, onions	MEKC	10 m*M* sodium phosphate, 40 m*M* cholic acid, pH 7.0	Fused silica, 75 μm I.D., L_{tot} 48.5 cm, L_{eff} 40 cm	30 μA	2.0 ppm	UV 220 nm	Maleic hydrazide	[42]
Not stated	CZE	100 m*M* β-alanine acetate, 50% methanol, 25 m*M* allyl-TER, pH 5.3	Fused silica, 50 μm I.D., L_{tot} 37 cm, L_{eff} 30 cm	20 or 30 kV	Not stated	UV 230 nm	Fluazifop, halossifop, fenoxaprop, flamprop	[24]
Not stated	MEKC	175 m*M* sodium phosphate, various OM levels	Fused silica, 50 μm I.D., L_{tot} 57 cm, L_{eff} 50 cm	25 kV	Not stated	UV 230 nm	Silvex, dichlorprop, mecoprop, 2,4-CPPA, 2,3-CPPA, 2,2-CPPA, 2-PPA	[50]
Not stated	CZE	Various amounts of cyclodextrins and sodium acetate in water	Fused silica, 50 μm I.D., L_{tot} 57 cm, L_{eff} 50 cm	25 kV	Not stated	UV	Imazaquin, diclofop, imazamethabenz	[54]
Not stated	CZE	50 m*M* phosphate, pH 6.5 Debinding electrolyte: 50 m*M* phosphate, 50% acetonitrile	**Pre**: Surface bound octadecyl, 50 μm I.D., L_{tot} 20 cm **Separation**: Fused silica, L_{tot} 60 cm, L_{eff} 30 cm	15 kV	0.1 μg/ml	UV 220 nm	Prometon, prometryne	[28]

Table 1. Continued

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Not stated	MEKC	Boric acid, MEGA	Fused silica, 50 μm I.D., L_{tot} 80 cm, L_{eff} 50 cm	15 kV	Not stated	UV 240 nm	Aldicarb, prometon, silvex, 2,4,5-T, propazine, prometryne, diazinon, butachlor	[3]
Water	MEKC	0.05 *M* SDS, 0.02 *M* borate–phosphate, pH 9.0	Fused silica, 50 μm I.D., L_{tot} 720 mm, L_{eff} 500 mm	Not stated	2–5 ppm	UV 210 nm	Asulam, thiuram, oxinecopper, iprodione, bensulfide	[57]
Not stated	CZE	3 parts ammonium acetate (50 m*M* pH 5.0) and 1 part acetonitrile	Fused silica, 50 μm I.D., L_{tot} 57 cm, L_{eff} 50 cm	30 kV	Not stated	UV 214 nm	Bensulfuron methyl, sulfonmeturon methyl, nicosulfuron, chlorimuron ethyl, thifensulfuron methyl, metsulfuron methyl, chlorsulfuron	[49]
River and drinking water	CZE	50 m*M* lithium acetate, pH 4.8	Fused silica, 50 μm I.D., L_{tot} 76 cm	30 kV	0.2–200 ppb depending on injection mode	UV 200 nm	MCPP, 2,4-DP, MCPA 2,4-D	[52]
Ground water	MEKC	50 m*M* SDS, 12 m*M* sodium phosphate, 10 m*M* borate, 15% methanol	Fused silica, 75 μm I.D., L_{tot} 48.5 cm, L_{eff} 40 cm	55 μA	0.38 ppm	UV 220, 225, 230, 247 nm	Hexazinone, metabolite B, metabolite D, metabolite A1, metabolite C, metabolite E	[33]
Drainage water	MEKC	12.5 m*M* Sodium borate 50 m*M* SDS, pH 9.0 with 0.5 *M* phosphoric acid	Fused silica, 50 μm I.D., L_{tot} 60 cm, L_{eff} 47 cm	23 kV	0.8 ppb	UV 210 nm	Metribuzin, bromacil, terbacil, hexazinone, triadimefon, DEET	[48]
Not stated	MEKC	**A**: 100 m*M* OM, 200 m*M* borate, pH 10.0	Fused silica, 50 μm I.D., L_{tot} 64 cm, L_{eff} 56 cm	187.5 V/cm	Fluometuron 4.2 pg, diruon 3.3 pg, chloroxuron 2.9 pg	UV 240 nm	**A**: Monuron, fluometuron, metobromuron, siduron, diruon, linuron, neburon, chloroxuron	[5]
		B: 200 m*M* borate, 100 m*M* OS or OM, pH 10.0					**B**: Aldicarb, prometon, propazine, prometryne, parathion, silvex, 2,4,5-T, 2,4-D	

Table 1. Continued

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Not stated	MEKC	60 m*M* γ-CD, 20 m*M* borate, 100 m*M* SDS, 15% methanol, pH 9.0	Fused silica, 75 μm I.D., L_{tot} 58 cm, L_{eff} 50 cm	15–30 kV	Not stated	UV 200 nm	Fenoprop methyl ester, mecoprop methyl ester, dichlorprop methyl ester	[23]
Water	MEKC	30 m*M* sodium borate, 30 m*M* SDS	Fused silica, 75 μm I.D., L_{tot} 500 mm	25 kV	Not stated	UV 214 nm	Tribenuron, chlorsulfuron, metsulfuron, paraquat, simazine, atrazine, linuron, terbuthylazine, alachlor, metolachlor, trifluralin	[35]
Water, wheat	MEKC	10 m*M* phthalate, 0.5 m*M* TTAB, pH 7.5 (with NaOH)	Fused silica, 50 μm I.D., L_{tot} 64 cm, L_{eff} 56 cm	Reverse 27.6 kV	0.6–0.8 μg/ml	Indirect UV 240 nm	Glyphosate, AMPA	[14]
Not stated	MEKC	100 m*M* surfactant, 200 m*M* borate, pH 10.0	Fused silica, 50 μm I.D., L_{tot} 64 cm, L_{eff} 56 cm	187.5 V/cm	Not stated	UV 240 nm	Monuron, fluometuron, metobromuron, siduron diuron, linuron, neburon, chloroxuron, aldicarb, prometon, propazine, prometryne, parathion	[4]
Not stated	MEKC	25 m*M* borate, sulfobutyl ether-β-CD organic modifiers at various concentrations	Fused silica, 50 μm I.D., L_{tot} 60 cm, L_{eff} 47 cm	20 kV	Not stated	UV 205 nm	Bromacil, chlorbufam, imazapyr, flamprop-isoproyl, flamprop free acid, fluazifop free acid, haloxyfor free acid	[46]
Not stated	MEKC	**A**: 5 m*M* phosphate 50 m*M* MEGA 9, 400 m*M* borate, pH 7.0 **B**: 5 m*M* phosphate, 50 m*M* MEGA 10, 400 m*M* borate, pH 5.0	Fused silica, 50 μm I.D., L_{tot} 80 cm, L_{eff} 50 cm	15 kV	Not stated	UV 240 nm	**A**: Silvex, 2,4,5-T, 2,4-D butyl ester, 2,4-D isopropyl ester, 2,4,5-T isopropyl ester **B**: Terbacil, monuron, fluometuron, metobromuron, siduron, diruon, linuron, neburon, chloroxuron	[51]

Table 1. Continued

Analyte matrix	Mode	Buffer	Capillary	Potential	LOD	Detection	Pesticides identified	Refs.
Water	CZE	**A**: 20 m*M* phosphate, pH 2.9 and 6.4 **B**: 5 m*M* ammonium acetate, 40% isopropanol	Fused silica, 50 μm I.D., L_{tot} 60 cm	18 kV or ~18 kV	Not stated	**A**: UV 230 **B**: Mass spectrometry	Dicamba, picloram, chloramben, acifluorfen, bentazon, 2,4-D, 2,4,5-TP, dichlorprop	[56]

[a] L_{tot}, Total length; L_{eff}, effective length; 2,4-DB, 4-(2,4-dichlorophenoxy)butyric acid; MCPB, 4-(4-chloro-methylphenoxy)butyric acid; 2,4-DP, 2-(2,4-dichlorophenoxy)propanoic acid; 2,4-D, (2,4-dichlorophenoxy)acetic acid; MCPA, (2-methyl-4-chlorophenoxy)acetic acid; 2,4,5-TP, (2,4,5-trichlorophenoxy)propionic acid; MCPP, 2-(4-chloro-2-methylphenoxy)propanoic acid; 2,4,5-TPA, (2,4,5-trichlorophenoxy)propionic acid so 2,4,5-TP and 2,4,5-TPA stand for the same compound along with 2,4,5-TPP; (2,3,6-trichlorophenoxy)butyric acid; PPa, phenoxypropionic acid; CPPA, chlorophenoxypropionic acid; MD, 2-(2-methyl-4,6-dichlorphenoxy)propionic acid; M, 2-(2-methylphenoxy)propionic acid; IAA, indole acetic acidl DP, 2-(2,4-dichlorophenoxy)propionic acid; D, 2,4-dichlorophenoxy acetic acid.

Garrison et al. [19] employed CZE for the separation and detection of 2,4-dichlorphenoxyacetic acid and three optically active phenoxy acid herbicides (dichlorprop, mecoprop, and fenoprop). A 50 m*M* acetate buffer at pH 4.5 gave the best separation at a wavelength of 230 nm.

Chiral analysis is important due to the various toxicity levels of enantiomers. HPLC can be used but a chiral stationary phase is needed for separation. The disadvantage to this approach is the cost of the columns. Also, a variety of columns may be needed to analyze similar racemic compounds [20,21]. However, in CE, cyclodextrins can be added to the aqueous running buffer to achieve chiral separations.

Disiderio et al. [22] achieved separation of mecoprop, fenoprop, dichlorprop, flamprop, haloxyfop, fluazifop, diclofor and fenozaprop in soil samples with the addition of vancomycin to the running buffer. Other methods have used γ-cyclodextrins [23] or ergot alkaloids such as 1-allylterguride as a chiral selector [24].

There also are some herbicides in this grouping derived from benzoic acid. The most important ones are dicamba and 2,3,6-TBA. CF–UV detection was employed for the detection of dicamba along with various other herbicides (atrazine, simazine, alachlor, metolachlor, 2,4-D, and chlorimuron ethyl) in pond water. CE–LIF was also used for the analysis of dicamba, 2,4-D and chlorimuron ethyl following derivatization with fluorescent reagents. The dicamba was derivatized with 4-bromomethyl-7-methoxycoumarin to give a limit of detection (LOD) of 10 ng/l [25].

5. Urea herbicides

The urea herbicides include diuron, fluometuron,

Table 2
Capillary electrophoresis methods for the analysis of herbicides

Analyte matrix	Mode	Leading ion	Counter ion	pH	Additive	Terminating electrolyte	pH	LOD	Pesticides identified	Ref.
Water, soil	Isotachophoresis	**A**: K^+ 10^{-2} mol/l	Acetate	4.7	0.05% PVA	Tris–acetate $5\cdot10^{-3}$	5	10 μg/kg	**A**: CCC	[6]
		B: K^+ 10^{-2} mol/l	Citrate	6.0	0.05% PVA	Tris–acetate $5\cdot10^{-3}$	5.8		**B**: Diquat	
		C: K^+ 10^{-2} mol/l	Diidotryosimate	7.4	0.05% PVA	Tris–acetate $5\cdot10^{-3}$	7.0		**C**: Paraquat	
		D: K^+ 10^{-2} mol/l	Acetate	5.0	0.05% PVA	Glycine $2\cdot10^{-2}$	5.0		**D**: s-Triazines	

linuron, chlorbromuron, chlortoluron, fenuron, metobromuron, metoxuron, monolinuron, chloroxuron and isoproturon. Dinelli et al. [26] analyzed linuron in water by using SDS as a micellar agent along with some other herbicides (metolachlor, atrazine, and metsulfuron). Smith et al. [5] separated eight urea herbicides in a standard mix by MEKC also.

Crosby and El Rassi [27] used cationic surfactants for the analysis of a mixture of urea herbicides. They found that the retention window could be increased when the size of the alkyl tail of the surfactant decreased. Separation was best achieved by MEKC with dodecyl- or decyltrimethylammonium chloride (DoTAC or DTAC) as the micellar phase.

6. Triazines

Cai and El Rassi [28] developed an on-line preconcentration method for the detection of prometon and prometryne using tandem octadecyl capillaries by CZE. Fused-silica capillaries were bound with octadecyl functions on their surface for on-line preconcentration of dilute samples. Two capillaries were needed for the analysis. First, a pre-concentration capillary and a second separation capillary composed of untreated fused silica. It was found that the coupled configuration increased the detectability in terms of solute concentration by a factor of 10–35 in comparison to CZE alone. Another advantage was that large volumes of sample could be injected without affecting the separation efficiency.

Depending on their application, triazine herbicides are subjected to various degradation processes that include photolysis, oxidation, hydrolysis, and biodegradation. These processes lead primarily to dealkylation of the amine groups in positions 4 and 6 and/or hydrolysis of the substituent in position 2. This latter process yields the hydroxy triazines that are found as contaminants in streams, lakes and well water. CE has been found to be a useful technique to study the degradation of atrazine in various conditions. Schmitt et al. [29] studied the effects of dissolved humic substances in the photodegradation pathway of atrazine.

It has also been observed that when sample extracts are stored in alcohol–water mixtures simazine and atrazine undergo solvolytic substitution reactions. Foret et al. [30] developed a CZE method to separate these triazine herbicides along with their solvolytic products.

Numerous methods have also been published that examine a large variety of the triazines in many different matrices. Martinez et al. [31] used SDS in a MEKC method to analyze simazine, cyanazine, atrazine, ametryne, propazine, prometryne, and terbutryne in water samples. They also investigated the effects of several electrophoretic parameters including injection conditions, pH, buffer concentration, surfactant concentration and applied voltage. River water was also analyzed by a micellar system employing SDS for atrazine and simazine [32]. Kubilius and Bushway [33] examined hexazinone and various metabolites in ground water by MEKC. Other matrices tested for triazines have included milk [34] by isotachophoresis, and soil [6].

7. Sulfonylurea herbicides

Numerous CE papers have been published regarding sulfonylurea detection. Dinelli et al. [35] analyzed chlorsulfuron and metsulfuron in tap water by CZE. Dinelli et al. [36] also examined the potential of CE for the separation and detection of nine metabolites of sulfonylurea herbicides in water. Dinelli et al. [37] also used solid-phase as a preconcentration technique along with MEKC to quantitate three sulfonylurea herbicides (chlorsulfuron, chlorimuron, and metsulfuron) from soil samples. The limit of detection were 10 ppb.

Krytinsky and Swineford [38] developed a method to separate and quantify metsulfuron methyl, thifensulfuron methyl, chlorsulfuron, rimsulfuron, and tribenuron methyl in various grains.

Most CE methods use UV detection. Garcia and Henion [39] were able to couple capillaries to a pneumatically assisted electrospray (ion spray) interface for separations with on line mass spectrometric (MS) detection. It was possible to separate an eight-component mixture within 5 min.

8. Plant growth regulators

Plant growth regulators have been analyzed primarily by HPLC or GC. Very few papers have

examined CE as an analytical technique. Yeo et al. [40] examined CE for the separation of nine plant growth regulators. Cyclodextrins and cholic acid were used as modifiers in the buffer to enhance selectivity.

Kubilius and Bushway [41] determined maleic hydrazide in potatoes and onions. A buffer of 10 m*M* sodium phosphate, 40 m*M* cholic acid (pH 7.0) gave optimum separation after a C_{18} clean up by solid-phase. Kubilius and Bushway also examined maleic hydrazide in formulations with a phosphate buffer [42].

Capillary electrophoresis offers one more analytical technique in method development for pesticide residues. An excellent review by El Rassi [43] focuses on three aspects of pesticide analysis by CE. El Rassi describes the various separation and detection systems for both chiral and achiral pesticides, pre-column derivatization of pesticides as well as sample concentration techniques. When examining the literature there are numerous papers detailing the analysis of herbicides by CE. The majority of articles use a form of water (i.e., lake, ground, drainage, river) or do not state the matrix used for analysis. Few articles focus on other types of 'real-world' samples such as fruits, vegetables, grains and soil. These types of matrices are more difficult to analyze due to sample concentration techniques and interfering compounds. This literature review is geared to be an aid for method development of herbicides, especially when using real world samples.

Acknowledgements

This study is Maine Agricultural Experiment Station paper No. 2387.

References

[1] A.L. Aspelin, Document 733-R-002, United States Environmental Protection Agency, 1997.
[2] R.J. Cremlyn, in: Agrochemicals Preparation and Mode of Action, Wiley, New York, 1991.
[3] J.T. Smith, Z. El Rassi, J. Microcol. Sep. 6 (1994) 127.
[4] J.T. Smith, Z. El Rassi, J. Chromatogr. A 685 (1994) 131.
[5] J.T. Smith, W. Nashabeh, Z. El Rassi, Anal. Chem. 66 (1994) 1119.
[6] Z. Stransyky, J. Chromatogr. A 32 (1985) 219.
[7] M.T. Galceran, M.C. Carneiro, L. Puignou, J. Chromatographia 39 (1994) 581.
[8] M.T. Galceran, M.C. Carneiro, M. Diez, L. Puignou, Chromatogr. A 782 (1997) 289.
[9] M.C. Cameiro, L. Puignou, M.T. Galceran, J. Chromatogr. A 669 (1994) 217.
[10] J. Cai, Z. El Rassi, J. Liq. Chromatogr. 15 (1992) 1193.
[11] Y. Wigfield, K.A. McCormack, R. Grant, J. Agric. Food Chem. 41 (1993) 2315.
[12] T. Perez-Ruiz, C. Martinez-Lozano, A. Sanz, V. Thomas, Chromatographia 43 (1996) 468.
[13] M. Tomita, T. Okuyama, Y. Nigo, B. Uno, S. Kawai, J. Chromatogr. 571 (1991) 324.
[14] M.G. Cikalo, D.M. Goodall, W. Matthews, J. Chromatogr. A 745 (1996) 189.
[15] M. Jung, W.C. Brumley, J. Chromatogr. A 717 (1995) 299.
[16] Y. Mechref, Z. El Rassi, Anal. Chem. 68 (1996) 1771.
[17] Y. Mechref, Z. El Rassi, J. Chromatogr. A 757 (1997) 263.
[18] Q. Wu, H.A. Claesssens, C.A. Cramers, Chromatographia 34 (1992) 25.
[19] A.W. Garrison, P. Schmitt, A. Kettrup, J. Chromatogr. A 688 (1994) 317.
[20] Y.Z. Hsieh, H.Y. Huang, J. Chromatogr. A 745 (1996) 217.
[21] M.W.F. Nielen, J. Chromatogr. 637 (1993) 81.
[22] C. Desiderio, C.M. Polcaro, P. Padglioni, S. Fanali, J. Chromatogr. 781 (1997) 503.
[23] Ph. Schmitt, A.W. Garrison, D. Freitag, A. Kettrup, Chromatogr. A 792 (1997) 419.
[24] B.A. Ingelse, J.C. Reijenga, M. Flieger, F.M. Everaerts, J. Chromatogr. A 791 (1997) 339.
[25] K.V. Penmetsa, R.B. Leidy, D. Shea, J. Chromatogr. A 745 (1996) 201.
[26] G. Dinelli, A. Bonetti, P. Catizone, G.C. Galletti, J. Chromatogr. A 656 (1994) 275.
[27] D. Crosby, Z. El Rassi, J. Liq. Chromatogr. 16 (1993) 2161.
[28] J. Cai, Z. El Rassi, J. Liq. Chromatogr. 15 (1992) 1179.
[29] Ph. Schmitt, D. Freitag, Y. Sanlaville, J. Lintelmann, A. Kettrup, J. Chromatogr. A 709 (1996) 215.
[30] F. Foret, V. Sustacek, P. Bocek, Electrophoresis 11 (1990) 95.
[31] R.C. Martinez, E.R. Gonzalo, A.I. Munoz Dominguez, J. Dominguez Alvarez, H. Mendez, J. Chromatogr. A 733 (1996) 349.
[32] C. Desiderio, S. Fanali, Electrophoresis 13 (1992) 698.
[33] D.T. Kubilius, R.J. Bushway, J. Chromatogr. A 793 (1998) 349.
[34] L. Krivankova, P. Bocek, J. Tekel, J. Kovacicova, Electrophoresis 10 (1989) 731.
[35] G. Dinelli, A. Vicari, P. Catizone, J. Agric. Food Chem. 41 (1993) 742.
[36] G. Dinelli, A. Vicari, A. Bonetti, J. Chromatogr. A 700 (1995) 195.
[37] G. Dinelli, A. Vicari, V. Brandolini, J. Chromatogr. A 700 (1995) 201.
[38] A.J. Krytinsky, D.M. Swineford, J. AOAC Int. 78 (1995) 1091.
[39] F. Garcia, J. Henion, J. Chromatogr. 606 (1992) 237.
[40] S.K. Yeo, H.K. Lee, S.F.Y. Li, J. Chromatogr. 594 (1992) 335.

[41] D.T. Kubililius, R.J. Bushway, J. Agric. Food Chem. 46 (1998) 4224.
[42] D.T. Kubilius, R.J. Bushway, J. AOAC Int. 81 (1998) 1109.
[43] Z. El Rassi, Electrophoresis 18 (1997) 2465.
[44] M. Aguilar, A. Farran, V. Marti, Sci. Total Environ. 132 (1993) 133.
[45] J. Cai, Z. El Rassi, J. Chromatogr. A 608 (1992) 31.
[46] C. Desiderio, C.M. Polcaro, S. Fanali, Electrophoresis 18 (1997) 227.
[47] G. Dinelli, A. Vicari, P. Catizone, J. Chromatogr. A 733 (1996) 337.
[48] Y. He, H.K. Lee, Electrophoresis 18 (1997) 2036.
[49] W.H. Matchett, W.C. Brumley, J. Cap. Electrophoresis 4 (1996) 199.
[50] Y. Mechref, Z. El Rassi, Chirality 8 (1996) 518.
[51] Y. Mechref, J.T. Smith, Z. El Rassi, J. Liq. Chromatogr. 18 (1995) 3769.
[52] M.W.F. Nielen, Trends Anal. Chem. 12 (1993) 345.
[53] C.P. Ong, C.L. Ng, H.K. Lee, S.F.Y. Li, J. Chromatogr. A 686 (1994) 319.
[54] K.V. Penmetsa, R.B. Leidy, D. Shea, J. Chromartogr. A 790 (1997) 225.
[55] Ph. Schmitt, A.W. Garrison, D. Freitag, A. Kettrup, J. Chromatogr. A 723 (1996) 169.
[56] X. Song, W.L. Budde, J. Chromatogr. A 829 (1998) 327.
[57] S. Wakida, S. Takeda, M. Yamine, A. Kawahara, K. Higashi, Anal. Sci. 7 (1991) 1109.