



Capillary electromigration techniques applied to pollutant analysis—A review

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ABSTRACT

The analysis of pollutants such as pesticides, herbicides, insecticides, heavy metal ions, etc. is an important topic in the field of research, health, and the environment as these compounds, even if in traces, can create serious problems for the health of humans and animals. Therefore, reliable analytical methods, for the determination of these compounds, are requested. Among them, capillary electrophoretic techniques have been successfully applied for their separation and analysis. In this review paper, the main features of electromigration techniques (capillary zone electrophoresis, capillary isotachopheresis, capillary electrokinetic chromatography, and capillary electrochromatography) have been briefly reported. Selected applications reported in the period 2018–2023-March of the electromigration techniques applied to the analysis of pollutants are presented and discussed.

1. Introduction

The term pollutant includes any material or chemical compound that is not or cannot be used because it is worthless or unwanted. The use of these chemicals can cause several problems mainly related to contamination of water, soil, foods, air, ecosystem changes, and health.

Some examples of great social and scientific interest can be reported, e.g., plastic or microplastic material, heavy metal ions, pesticides, herbicides, insecticides, drugs, etc. [1–5].

Pesticides such as herbicides and insecticides are a class of pollutants, routinely used in agriculture to protect different crops from unwanted pests. Due to their intensive use, these compounds and/or their metabolites can be present in soil, water, vegetables, fruits, etc. The presence of pesticide residues is a risk to public health. Therefore, European Union, with Regulation (EC) No 396/2005, reported the definition of maximum residue levels (MRLs) of pesticides permitted in food or animal feed. MRL is the maximum value carefully assessed for a certain pesticide before its approval considering chemical properties, intended use, and careful analysis of residue behavior, and health risks (<https://www.efsa.europa.eu/en/topics/topic/pesticides>).

Considering the problems related to health, analytical methods are required to determine pesticide residues or other pollutants present in several matrices. These methods should offer appropriate performance, e.g., high sensitivity, analytes separation and resolution, good

repeatability and reproducibility, etc. Several analytical techniques have been applied to the analysis of pollutants including high-performance liquid chromatography (HPLC) [6], gas chromatography (GC) [7,8], supercritical fluid chromatography (SFC) [9–11]. In addition to the mentioned analytical techniques, miniaturized methods such as nano-liquid chromatography (nano-LC) [12,13] and capillary electromigration techniques (CE) [14,15] have also been used.

CE is an analytical technique offering some advantages such as high separation efficiency, high mass sensitivity, very good analytes resolution, use of minute volumes of both solvents and samples, etc. The analysis is carried out into capillaries of thin diameter (<100 μm I.D.) containing a background electrolyte (BGE) and applying a relatively high electric field strength (*E*). Compounds are detected, usually online, by UV or fluorescence systems, and in addition, mass spectrometry (MS) is also coupled with CE.

This review paper is presenting a short introduction about the features of electromigration techniques, and the application of these techniques to the analysis of pollutants reported in the literature in the period 2018–2023-March is also discussed.

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2. Capillary electrophoresis: general principles and instrumentation

2.1. General principles

CE is an analytical technique where the compounds' separation is achieved into a capillary (containing electrolytes) with small I.D. (<100 μm) under the influence of a relatively high electric field strength (500–1000 V/cm). The work done by Hjerten [16], where analytes were separated in free zone electrophoresis, was a fundamental step for the development of the modern CE. For the first time, compounds were separated in absence of supporting stabilizing material using complex instrumentation where quartz tubes of 1–3 mm were used. Zone broadening was minimized with the tube rotation. The usefulness of CE was shown by Jorgenson and Lukacs in 1981 [17,18] performing experiments into capillaries of 75 μm I.D. and applying a high electric field strength (30 kV/m). A very high separation efficiency and analytes resolution was demonstrated due to the high voltage applied and to the efficient dispersion of the Joule heat generated through the capillary wall.

In addition to capillary zone electrophoresis (CZE), other CE techniques, namely capillary isotachopheresis (CITP), capillary electrokinetic chromatography (CEKC), capillary isoelectric focusing (CIF) have been used for the separation and analysis of a large number of compounds.

In CZE analytes are separated in the capillary containing a selected background electrolyte (BGE). Charged compounds migrate to the cathode or the anode (cations and anions, respectively), and their migration is influenced by various parameters such as BGE composition, ionic strength, pH, organic solvent, etc. In addition, the separation voltage, the length, and the I.D. of the capillary have to be considered. An important parameter is the electrophoretic velocity v that can be calculated by the following equation:

$$v = \mu_e E \quad (1)$$

v and E are the ion velocity and the applied electric field strength, respectively, while μ_e

$$\mu_e = \frac{q}{6\pi\eta r} \quad (2)$$

Where q , η , and r are the ion's charge, medium viscosity, and ion radius, respectively.

From the two equations, it can be concluded that the higher the ion charge and the lower the radius, the higher the mobility can be observed; an increase in ion mobility and E will increase the velocity with an obvious reduction of analysis time. In addition, when q is zero (this is the case of uncharged compounds), the electrophoretic mobility is zero. Therefore these compounds cannot be analyzed by CZE. Terabe's group introduced CEKC showing the separation of some uncharged phenol compounds adding to the BGE sodium dodecyl sulfate (SDS). The analytes were moving to the cathode transported by a strong electroosmotic flow (EOF) and separated by the interaction with SDS [19]. CEKC has been successfully used for the separation of uncharged and charged compounds using other additives to the BGE such as charged cyclodextrins and in addition to SDS, other surfactants [15,20–22].

EOF is the movement of a bulk solution in the capillary due to the presence of a double layer on the wall and to the applied E . In the case of fused silica capillaries, the wall is negatively charged bonding positively charged ions coming from the BGE [18]. The velocity of the EOF can be calculated with the following equation:

$$v_{EOF} = \frac{\epsilon}{4\pi\eta} \zeta E \quad (3)$$

where, ϵ and ζ are the permittivity, and the zeta potential of the liquid-solid interface, respectively.

The EOF velocity can be modified by changing various parameters, e.

g., ionic strength of the BGE, organic solvent and type, pH, and temperature. An increase in the ionic strength causes a decrease in the EOF. An organic solvent modifies the zeta potential and buffer viscosity, the use of methanol or ethanol decreases the EOF, while acetonitrile has the opposite effect. Finally, the increase in temperature produces a decrease in viscosity (higher EOF). However, it is worth mentioning that these parameters are also influencing the ions' electrophoretic mobility [23].

Another interesting approach to changing the EOF considers the possibility to modify the capillary surface, e.g., changing the pH or adsorbing or bonding compounds. When using fused silica capillaries, the charge of the silanol groups on the wall can be low (pH < 2) or higher at higher pHs with consequent low and highest EOF (pH 2 and 7, respectively). The modification of the wall with a surfactant such as cetyltrimethylammonium bromide causes the change of the wall charge to positive reversing the EOF. Instead, the use of hydroxypropylcellulose [16] or poly(vinylalcohols) suppresses the EOF [23].

The EOF is an important driving force utilized with other electromigration techniques such as capillary electrochromatography (CEC). This technique combines the best features of both CE (high separation efficiency) and HPLC (high selectivity). The EOF is not depending on the particles' diameter and therefore experiments can be carried out with small particles with no problems with backpressure contrary to HPLC.

The separation of the analytes is performed into capillaries containing a stationary phase (SP) applying a high voltage. CEC was widely studied for the analysis of pharmaceutical [24,25], agrochemical [13], chiral [26–28] compounds, etc. The SPs used in CEC are usually the ones studied and applied in HPLC but contain charged/chargeable groups. They are included in the capillary as packed particles (p-CEC) or bonded/adsorbed on the wall (OT-CEC) or monolithic material (M-CEC). The features of p-CEC have been first reported by Pretorius et al. [29] focusing attention on the advantages of using an EOF (plug-like flow profile and no influence of the particle size and geometry) but in tubes of 1 mm I.D. Later on, p-CEC was performed on a capillary format [18,24,30–32]. Although good results have been obtained with p-CEC, problems are related to i) the preparation of packed capillaries that requires experience and skill (only a limited type of packed capillaries are commercially available), ii) bubble formation during the run due to the frits retaining the SP. Alternatively to the packed columns, monolithic material can be used, e.g., organic or inorganic polymers or mixed. In this case, there is no necessity to prepare frits and therefore minimize bubble formation. In addition, the SP can be bonded or adsorbed on the capillary wall working in an open capillary (OT-CEC). Although this last technique allows for overcoming some problems, its use is questionable, especially considering the low sample load and concentration sensitivity.

Another CE mode includes CITP which is a relatively old technique used for the analysis of only cations or anions, separately. The system considers a leading and a terminating electrolyte (LE and TE, respectively). The electrophoretic mobility of the analytes must be lower and higher than the one of LE and TE, respectively. The compounds reach a steady state, concentrating in the proper zones, and achieving high concentration sensitivity [33,34]. Often CITP is associated with CZE just exploiting this feature.

2.2. Instrumentation

Commercial instrumentation, introduced in 1990, can be used for all electromigration methods, however, to carry out CEC (p-CEC and M-CEC) experiments, it is necessary an external pressure, usually, 12 bar, to avoid bubble formation during the run. This drawback is usually caused by the frits retaining the stationary phase and/or by a not homogenous packing

The instrument contains two electrode compartments connected to a high voltage power supply, a capillary, a detector, a sampling system, and a control system; in addition, temperature control is also present. Conventional detectors such as UV and fluorescence are included and,

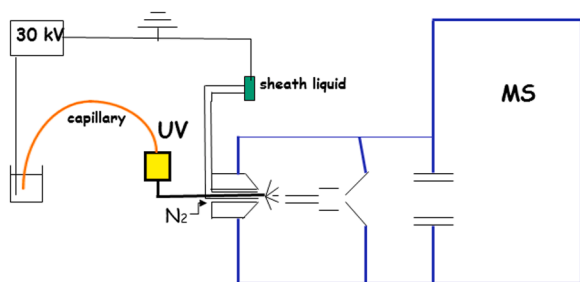


Fig. 1. Shows a scheme of CE-MS instrument where a SL interface is used. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

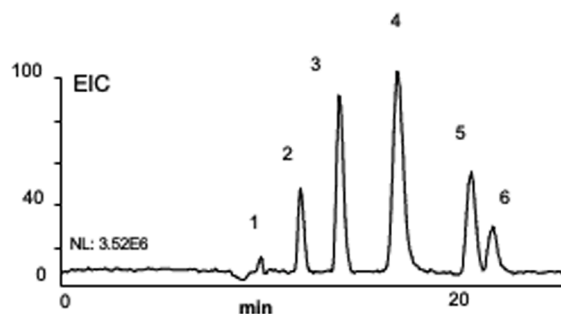
usually, the path length is the capillary diameter. However, recently the capacitively coupled contactless conductivity detector (C^4D) [35] or mass spectrometry (MS) [36,37] have been used. MS is not a simple detector offering higher concentration sensitivity but also allows analyte mass determination and compound characterization. However, the

coupling of electromigration techniques with MS is an issue due to the application of the high voltage for the CE analysis. For this purpose, there is a need for dedicated interfaces taking into account the high voltage. Recently, some review papers reported on this issue, e.g., [37–39].

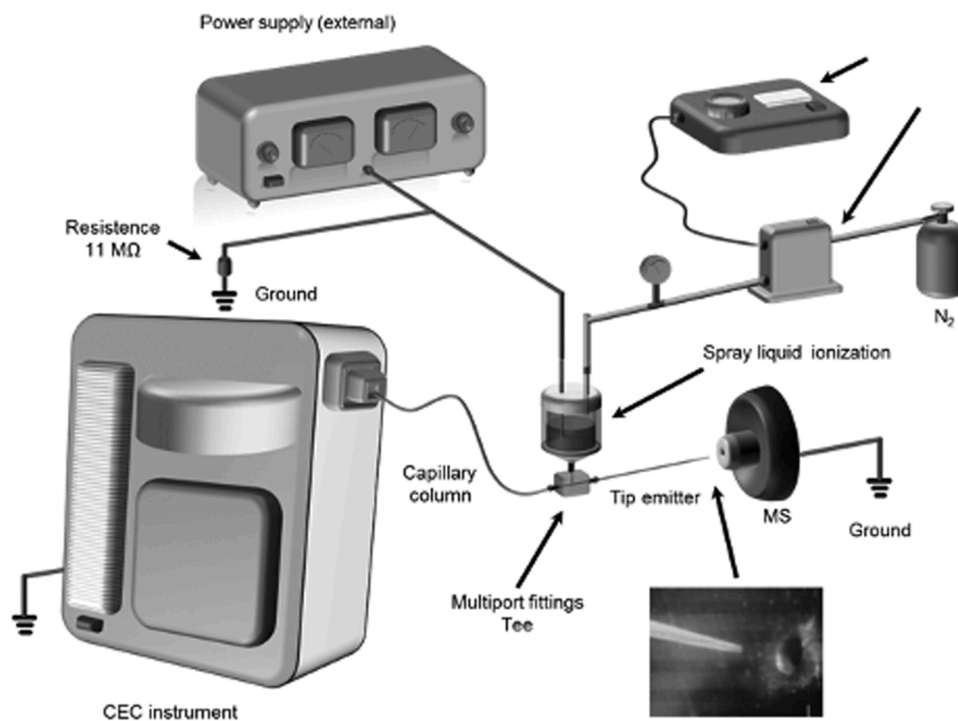
The electrospray interfaces (ESI) currently used for coupling CE and CEC with MS include sheathless (S_{less}), sheath liquid (SL), liquid junction (LJ), and pressurized LJ (p-LJ).

The usefulness of a S_{less} interface for CE experiments was first reported by Smith's group. In this setup, the capillary column was inserted into an electrospray needle, and the BGE allowed the separation and ionization of the compounds. Although good results were obtained, some drawbacks could be observed, e.g., long capillary (100 cm) and limited selection of the BGE [40]. Moini [41] proposed a modified S_{less} where the capillary had a porous end inserted into the electrospray needle containing a conductive solution (formic acid) for ionization. This type of interface was recently commercialized and has to be used with dedicated capillary columns.

SL interface is the most popular one and can be used with all CE instrumentation. SL was first proposed by Smith's group [42], here the



(a)



(b)

Fig. 2. (a and b. a) show the CEC-MS separation of standard compounds ((1) methamidophos, (2) fensulfothion, (3) fenamiphos, (4) isophenphos, (5) profenofos, (6) sulprofos) using a nano-LJ interface and b) reports the scheme of CEC-MS where a liquid junction interface is used. Modified from [44].

Table 1
Selected applications of electromigration techniques for pollutant analysis.

Compounds	Application/ Sample	Capillary	Experimental conditions	Detector	Remarks	References
Glyphosate and its metabolite (aminomethylphosphonic acid, AMPA)	Lyophilized tissue of marine mussels	Capillary 50 μ m I.D. x 48.5 cm	BGE, 30 mM borate buffer pH 9.2 and 10 mM dimethylated- β -CD 20 kV	Light-emitting diode-induced fluorescence (LEDIF)	CZE Derivatized with 4-fluoro-7-nitro-2,1,3-benzoxadiazole (NBD-F)	[65]
Triazine herbicides (atrazine, prometon, and prometryn)		50 μ m I.D. x 40.5 cm vinyl-functionalized covalent-organic framework	BGE, 20 mM ammonium acetate buffer (pH 4) with 40% (v/v) acetonitrile; -20 kV	UV/MS	OT-CEC	[78]
Fenuron and fluometuron	Lake water	50 μ m I.D. x 35 cm	BGE, 50 mM perfluorooctanoic acid and 100 mM ammonium hydroxide and 10% (v/v) isopropanol; 15 kV	MS	CEKC	[36]
Glyphosate and its metabolite (AMPA)	wheat flour	50 μ m I.D. x 80 cm	BGE, 50 mM sodium phosphate, pH 2.2 and 100 mM SDS; -25 kV	UV, 210 nm	CEKC	[69]
Herbicides (aldicarb, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), silvex, and prometon)	-	50 μ m I.D. x 57 cm	BGE, 10 mM disodium hydrogen phosphate, pH 7.6, containing 3.2 mg/L of MWCNTs 60 mM SDS and 10% (v/v) ACN	UV, 214	CEKC	[79]
Triazine herbicides (Terbutryn, prometryn, ametryn, prometon, propazine, atrazine, and simazine)	Honey, tomato and environmental water	50 μ m I.D. x 48.5 cm	BGE, 92 mM phosphate, 40 mM SDS and 15% (v/v) 1-propanol (pH = 2.6); -20 kV	UV, 220 nm	CEKC	[80]
Fluoroquinolones (ciprofloxacin, enrofloxacin, norfloxacin and ofloxacin)	Surface water	50 μ m I.D. x 64.5 cm	BGE, 15 mM sodium dihydrogen phosphate (pH 6.0) and 3 mM CTAB; -20 kV	UV, 275	CEKC	[22]
Glyphosate and its metabolites and its acetylated derivatives (aminomethyl phosphonic acid, glyoxylic acid, sarcosine, glycine, N-acetyl glyphosate, N-acetyl aminomethyl phosphonic acid, hydroxymethyl phosphonic acid)	Beer	50 μ m I.D. x 50.0 cm	BGE, 8.3 mM acetic acid + 21.8 mM ammonia pH 9.5 or 9.28 or 5.0 15 kV + assisted pressure 70 mbar	Conductivity detection, C ⁴ D	CZE Thermodynamic acidity constants and limiting ionic mobilities	[81]
2-hydroxy-s-triazines (2-Hydroxyatrazine, 2-hydroxydesethylatrazine, 2-hydroxyterbutylazine, and hydroxydesisopropylatrazine)	water	100 μ m I.D. x 100 cm	LE, 19 mM 1-ethylpiperazine and 20 mM pivalic acid at pH 6.60; TE, 8 mM 1-ethylpiperazine and 35 mM pivalic -20 kV SL, 5 mM acetic acid and 3 mM ammonium in 50% methanol	ESI-MS	ITP (computer simulation was used)	[82]
Agrochemicals	-	100 μ m I.D. x 25 cm packed with silica modified with immobilized amylose tris (3-chloro-5- methyl phenylcarbamate	Mobile phase: 1-H ₂ O (90:10, v/v) with 5 mM ammonium acetate 25 kV	UV 205 nm	CEC or nano-LC	[13]
Chlorophenols (2,4,6-trichlorophenol (TCP), 2,3,6-TCP, and 2,6-dichlorophenol)	Tap water	50 μ m I.D. x 60 cm	BGE, 240 mM sodium borate buffer of pH 9.2 20 kV	UV 214 nm	CZE Single bubble in-tube microextraction	[58]
Phosphorus-containing amino-acid-like herbicides (PAAHs) Glyphosate (GLYP) and glufosinate (GLUF) AMPA and 3- methylphosphinicpropionic acid (MPPA)	Baby foods	30 μ m I.D. x 50 cm	10% acetic acid in 10% methanol; -25 kV S _{less}	MS	CZE	[66]
Pesticides (pyrifenoxy, pirimicarb, cyprodinil, pyrimethanil)	-	15 μ m I.D. x 80 cm	BGE: 0.2 M acetic acid, pH 4 with ammonia. 20 kV S _{less}	MS	CZE	[14]
Fungicide and its metabolite (prothioconazole and prothioconazole-desthio)	Agrochemical ormulation; soil and sand samples	50 μ m I.D. x 58.5 cm	BGE, 100 mM borate buffer (pH 9.0) and 5 mM heptakis(2,3,6-tri-O-methyl)- β -CD	UV 205 nm	CZE	[77]

(continued on next page)

Table 1 (continued)

Compounds	Application/ Sample	Capillary	Experimental conditions	Detector	Remarks	References
Androstene-dione, testosterone, Progesterone, testosteroneglucuronide, hydrocortisone, androstene-dione, 17- α -hydroxyprogesterone, testosterone, 17- α -methyltestosterone, and Progesterone	Lake water	50 μ m I.D. x 80 or 60 cm	(TM- β -CD); 30 kV; or 10 mM sulfate- γ -CD in 75 mM borate buffer (pH 9.0) BGE: 20 mM ammonium acetate pH 9.68 Micelle plug BGE and 29.50 mM sodium dodecyl sulfate and 3.356 mM sodium taurocholate; 25 kV	UV 206 or 247 nm	CEKC	[15]
Steroids (androsterone, testosterone, progesterone, testosterone-glucuronide, hydrocortisone, 17- α -hydroxyprogesterone, and 17- α -methyltestosterone)	Raw water	50 μ m I.D. x 80 or 60 cm	BGE, 20 mM ammonium acetate pH 9.68-the PF contained SDS and sodium taurocholate 25 kV	UV 214, 220, 240, 247, and 260 nm	CEKC Partial filling. Results compared with UHPLC-MS	[83]
Herbicide (glyphosate)	Formulation	50 μ m I.D. x 65 cm	BGE, 20 mM MES/His-buffer (pH 6.1); 20 or -20 (+inlet 50 mbar) kV	Capacitively coupled contactless conductivity detector (C ⁴ D)	CZE	[35]
Trifluoroacetic acid (TFA) and difluoroacetic acid (DFA)	Fruit, grain, and vegetables	30 μ m I.D. x 91 cm	BGE, 5% acetic acid in 90:10 (v/v) water: methanol; -20 kV	MS	CZE In capillary ITP focusing	[70]
N-methylcarbamate pesticides (carbaryl, carbofuran, promecarb, 4-bromo-3,5-dimethylphenyl N-methylcarbamate, and methomyl)	Water	75 μ m I.D. x 80 cm	BGE, 15 mM borate buffer pH 11.5; 20 kV	UV	CZE	[59]
Pesticides (metolcarb, carbaryl, methomyl, aldicarb, carbofuran, isoprocarb, and pirimicarb)	Vegetables (cucumber, tomato, and cabbage)	25 μ m I.D. x 40 cm	BGE, phosphate buffer (pH 6.5) containing 45 mM NaCl and 25 mM β -cyclodextrin; 17 kV	ECL electrochemiluminescence	CZE	[71]
Aldehydes (formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde)	Water	50 μ m I.D. x 65 cm;	BGE, 120 mM sodium dodecyl sulfate and 40 mM borax in formamide/methanol (7:3, v/v); -26 kV	UV 360 nm	CZE Derivatization with 2, 4-dinitrophenylhydrazine (DNPH)	[60]
Glyphosate (N-(phosphonomethyl)glycine) and its major degradation product AMPA	Beer	50 μ m I.D. x 65 cm	BGE, 175 mM formic acid pH 2.8 with ammonia; 30 kV SL, 50:50 (v/v) isopropanol:water containing 0.01% formic acid	TOF-MS	CZE	[76]
Organic mercury compounds (methyl HG ⁺ , ethyl HG ⁺ , and phenylHg ⁺)	Fish	75 μ m I.D. x 60 cm	BGE, 25 mM borax buffer, pH = 9.3; 20 kV	UV 200 nm	CZE	[67]
Cyromazine and its metabolite (melamine)	Water, soil, and cucumber	23.5 μ m I.D. x 80 cm	BGE, 400 mM acetic acid; 18 kV	C ⁴ D	CZE	[61]
Herbicides (fenoprop, mecoprop, dichlorprop, 2-(4-chlorophenoxy)propionic acid, 2-(3-chlorophenoxy)propionic acid, and 2-phenoxypropionic acid)	-	50 μ m I.D. x 58.5 cm	BGE, 50 mM phosphate buffer (pH 7.0) and 4 mM hydroxypropyl- β -CD + 16 mM trimethylated- β -CD; 30 kV	UV 194 or 200 or 210 nm	CEKC	[84]
Organophosphorus pesticide (paraoxon)	Vegetable juice	50 μ m I.D. x 50 cm	BGE, 10 mM phosphate buffer at pH 8.0; 20 kV	UV 230 nm	OT-CEC Capillary containing at the inlet 1 cm enzymatic reactor	[72]
Metal ions pyriithione complexes	Water	coated 50 or 75 μ m I.D. x 55 or 59 cm	BGE, 20 mM borate buffer pH 9.7 + or - 30 kV SL, 5 mM ammonium acetate and 0.01% formic acid	ESI-MS or ICP-MS	CZE	[62]
Sulfonamides (sulfamethoxypyridazine, sulfamethoxydiazine, sulfamerazine, sulfamethazine and sulfamethoxazole)	Aquaculture waters	50 μ m I.D. x 51 cm	BGE, 30 mM borate buffer pH 7.60; 20 kV	UV 254 nm	CZE Samples extracted with ionic liquid-based hollow fiber	[63]

(continued on next page)

Table 1 (continued)

Compounds	Application/ Sample	Capillary	Experimental conditions	Detector	Remarks	References
Pesticides (chlorantraniliprole, kresoxim-methyl, and pyraclostrobin)	Apple	50 μ m I.D. x 30 cm	BGE, 90 mM borate buffer, 60 mM sodium dodecyl sulfate and 10 vol% ACN (pH 8.8); 25 kV	UV 200 nm	CEKC	[21]
Sulfonamides (sulfamethoxazole, sulfadimethoxine, sulfamethizole, and sulfaquinoxaline)		50 μ m I.D. x 60 cm	BGE, 0.2 mM CTAB and 2% methanol in 400 mM ammonium bicarbonate pH 8.5	UV	OT-CEC and OT-liquid chromatography	[86]
Thiabendazole, aminocarb, imazalil, atrazine, metazachlor, metoxuron, carbofuran, metosulam, and imazapyr	Corn	50 μ m I.D. x 58 cm poly(vinyl alcohol)-coated	BGE, 0.1 M formic acid (pH 2.4); 28 kV	MS/MS	CZE	[68]
Chlorophenols (4-chlorophenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 2,6-dichlorophenol)	Water	75 μ m I.D. x 50.2 cm	BGE, 20 mM Na ₂ B ₄ O ₇ ·10H ₂ O, pH 8.90 with 1 M NaOH; 20 kV	UV 214 nm	CZE	[87]
Phenols (phenol, 4-chlorophenol, pentachlorophenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2-chlorophenol, and 2,6-dichlorophenol)	Tap water	75 μ m I.D. x 50.2 cm	BGE, 20 mM Na ₂ B ₄ O ₇ ·10H ₂ O containing 10% v/v MeOH, pH 9.80; 20 kV	UV 195 nm	CZE	[88]
Hydrolyzed phenol carbamates (propoxur, carbofuran, 3-OH-carbofuran, carbaryl and bendiocarb)	Vegetable	25 μ m I.D. x 60 cm;	BGE, 50 mM buffer pH 9.8; 24 kV	Amperometric	CZE	[73]
Pesticides (methyl paraoxon, ethyl paraoxon, methyl parathion, fenitrothion, and ethyl parathion)	Artificial saliva or water	50 μ m I.D. x 31 cm	BGE, 20 mM 2-(N-morpholino)ethanesulfonic acid/histidine buffer (pH 5.0), 10 mM SDS; -20 kV	UV 273	CEKC	[89]
Chlorophenols (2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol)	Water	75 μ m I.D. x 50.2 cm	BGE, 20 mM Na ₂ B ₄ O ₇ ·10H ₂ O and 10% v/v acetonitrile pH 9.8; 20 kV	UV 214 nm	CZE	[52]
Phenoxy acid (fenoprop, mecoprop, dichlorprop, 2-(4-chlorophenoxy)propionic acid, 2-(3-chlorophenoxy)propionic acid, 2-phenoxypropionic acid) (chiral separation)	Water (river and waste)	50 μ m I.D. x 58.5 cm or 63.5 cm	BGE, 50 mM formate buffer (pH 5.0), 50 mM phosphate buffer (pH 7.0) and 7 mM hydroxypropyl-and 20 mM trimethylated- β -cyclodextrin; 25 kV	UV 210 nm	CZE	[53]
Antibiotics (Oxytetracycline, Chlortetracycline, Enrofloxacin, and Ciprofloxacin)	Wastewater	75 μ m I.D. x 60 cm	BGE, 100 mM phosphate-200 borate pH 3.0; 25 kV	UV 200 and 280 nm	CZE	[54]
Biogenic amines (putrescine, cadaverine, spermidine, spermine, histamine, phenylethylamine, tyramine, and tryptamine)	Seawater	50 μ m I.D. x 95 cm	BGE, 400 mM malic acid; 25 kV	C ⁴ D conductivity	CZE	[55]
Carbonyl pollutants (Formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, methylethyl ketone, crotonaldehyde, butyraldehyde, isovaleraldehyde, valeraldehyde, benzaldehyde, hexaldehyde, o-tolualdehyde, p-Tolualdehyde, and 2,5-dimethylbenzaldehyde)	Ambient particulate	50 μ m I.D. x 80 cm	BGE, 50 mM SDS, 20 mM sodium tetraborate and 20% (v/v) methanol, pH = 8; -24 kV	UV 360 nm	CEKC Analytes derivatized with 2,4-dinitrophenylhydrazine	[75]
Naproxen and diclofenac	Wastewater	100 μ m I.D. x 100	LE, 10 mM formic acid and TE, 10 mM propionic acid; -20 kV	MS	ITP HF-LPME on-line pre-concentration	[56]

Cetyltrimethylammonium bromide, CTAB; hollow fiber-based liquid phase microextraction, HF-LPME; leading electrolyte, LE; multiwall carbon nanotube, MWCNTs 2-(N-morpholino)ethanesulfonic acid, MES; sodium dodecyl sulfate, SDS; terminating electrolyte, TE.

capillary column was inserted into a coaxial tube connected with a sheath liquid, delivered at flow rates of 1–3 $\mu\text{L}/\text{min}$ and nitrogen. The sheath liquid reservoir was connected to the power supply for the CE analysis. Although good results have been obtained with this interface, there were some problems with concentration sensitivity and zone broadening. Considering that the flow on the column is usually 400–800 nL/min , the sheath liquid can cause turbulence mixing the separated zones and thus reducing resolution and concentration sensitivity.

Fig. 1 shows a scheme of CE-MS instrument where a SL interface is used.

This interface was difficult to use with CEC experiments especially when packed capillaries were employed. Alternatively, a LJ interface can be used for both CE and CEC. In LJ the separation capillary joins a tip into an electric compartment and the separated zones are transferred into the MS by an ionization solvent at a low flow rate. Good spray and CE stability, reduced turbulence, and high concentration sensitivity were shown by Karger's group [43] analyzing proteins or peptides by CZE-MS. The LJ interface was successfully applied in CEC for the separation of pollutants, e.g., methamidophos, fensulfothion, fenamiphos, isophenphos, profenofos, and sulprophos (see Fig. 2a). This separation was achieved with a laboratory made CEC instrumentation (see Fig. 2b). The interface (p-LJ) was miniaturized, in plastic material, with the possibility to join the column to the tip at zero volume [44] avoiding the use of a microscope to verify the distance capillary-tip for optimal results and saving time on the contrary of the one previously studied by our group [31]. In the p-LJ, the ionization liquid was delivered at a very low flow to produce a very good ionization.

3. Selected applications of electromigration techniques to the analysis of pollutants

In this section, some selected applications dealing with the pollutants analysis by using CE or CEC are reported. The period considered covers the years 2018–2023-March. During this time some review papers, dealing with this topic, have been reported, e.g., [3–5,45–51].

However, some of these reviews considered also other analytical techniques and/or compounds different from pollutants. In addition, in most of them, sample pre-concentration methods have also been reported (see Table 1).

The selected applications reported in this review include only works about the use of CE applied to the analysis of pollutants in water [15,36,52–64], food [65–69], vegetables [61,70–74], soil [61], fruit [21,70], ambient particulate [73,75], beer [76], agrochemical formulations [35,77].

3.1. Analysis of herbicides by capillary electrophoresis

Glyphosate (Glyp) is an herbicide widely used to kill weeds. It is included in Group 2nd of pollutants (probably carcinogenic to humans). This compound together with aminomethylphosphonic acid (AMPA), its microbial metabolite was analyzed by CZE after derivatization with 4-fluoro-7-nitro-2,1,3-benzoxadiazole for the detection with light-emitting diode-induced fluorescence detection. Samples, of marine mussels (*Mytilus galloprovincialis*) were hydrolyzed and analyzed. To avoid interferences during the CZE analysis, the BGE (borate buffer) was supplemented with 10 mM heptakis(2,6-di-O-methyl)- β -cyclodextrin. The analytical method was optimized, validated, and applied to mussel samples. Good sensitivity was obtained (LOQ of 0.2 and 1.0 $\mu\text{g}/\text{g}$). The authors analyzed six real samples finding AMPA in all of them (15.5–77.0 $\mu\text{g}/\text{g}$) and only in one they detected Glyp (11.3 $\mu\text{g}/\text{g}$) [65]. The same group also analyzed Glyp and AMPA in wheat using a CEKC method. Analytes were concentrated during injection (Field-amplified sample injection and sweeping CEKC) [69]. In this study, SDS was added to the BGE.

Glyp, glufosinate (Gluf), and their metabolites (3-methylphosphinopropionic acid-MPPA and AMPA) were analyzed by CZE

coupled with MS in some baby foods. Analyzed compounds were moving as anions. To increase the sensitivity, a pre-concentration method was developed by applying titanium dioxide-coated core-shell silica microspheres for the solid phase extraction (SPE). Low limits of quantitation (LOQs) between 0.3–1.6 ng/mL were obtained. The analysis of real commercial samples revealed the presence of only MPPA in two samples (6.2 ng/g and 7.4 ng/g) which were lower than the MRLs for any herbicides in baby foods (10 ng/g) [66].

Different types of herbicides, namely 2-hydroxy-s-triazines (2-hydroxyatrazine, 2-hydroxydesethylatrazine, 2-hydroxyterbutylazine, and hydroxydesisopropylatrazine) have been analyzed by Gebauer's group [82] utilizing an electrophoretic focusing employing a volatile electrolyte system 1-ethylpiperazine (LE) and pivalic acid (TE). The application of the inlet pressure allowed the use of MS detection. The use of ITP (concentrating effect) and MS offered excellent sensitivity (LODs in the range 0.5–1 nM, 100 ng/L). The optimized method was applied to the analysis of herbicides in tap and river waters.

Other herbicides (phenoxy acid family, namely fenoprop, mecoprop, dichlorprop, 2-(4-chlorophenoxy)propionic acid, 2-(3-chlorophenoxy)propionic acid, and 2-phenoxypropionic acid) have been analyzed by Marina's group [53] by using CZE but with UV detector. Since the goal of the authors was the analysis of chiral herbicides, the analytical method was optimized including in the BGE cyclodextrins (7 mM hydroxypropyl- and 20 mM trimethylated- β -cyclodextrin). The analysis of enantiomers is an important issue because the two stereoisomers could behave differently in the environment or humans, e.g., in the case of phenoxy acid herbicides, the *R*-enantiomer is biologically active. The method sensitivity was improved by applying a pre-concentration step based on an offline solid-phase extraction. The authors synthesized a material (mesoporous organosilica) where herbicides were retained with a reversed-phase/strong anionic exchange mixed mode. Limit of quantification (LOQ) were in the range 0.4 and 14.3 $\mu\text{g}/\text{L}$. The optimized method was validated and applied to the analysis of the studied compounds in the river and wastewater. In the analyzed samples, herbicides were not detected, and therefore, spiked samples were considered.

Chen et al. [36] carried out an interesting study using CEKC coupled with mass spectrometry (MS). It is known that the presence of additives in the BGE, when an MS detector is used, can cause problems for the detector and the sensitivity (ion suppression). In this study, a volatile additive (ammonium perfluorooctanoate) was used for the separation and analysis in lake water samples of two herbicides, namely fluometuron and fenuron. The same group investigated some triazine herbicides separation (prometon, prometryn, and atrazine) utilizing OT-CEC with the aim to develop new stationary phases. They developed new covalent organic frameworks (COFs) bonded to the capillary work as an SP. The material exhibits high porosity, strong hydrophobicity, and uniform mesoporous structure, with a narrow pore size distribution, and stability. The COF-V modified capillary was coupled to the MS detector and used for the herbicides analysis under a negative EOF due to the presence of amino groups on the wall [78].

In a recent study herbicides such as Glyp and its metabolites were studied to calculate the thermodynamic acidity constants and limiting electrophoretic mobilities utilizing a conductivity detector. Among the analyzed analytes, 2-methyl-4-chlorophenoxyacetic acid (MCPA), oxamic acid, and Glyp in spiked beer samples were determined by CE-MS [81]. The same group, in a previous study [35], although the aim was to study parameters affecting sensitivity with a new contactless conductivity detector, analyzed Glyp in its herbicide formulation with good results. The herbicide Glyp and its major degradation product AMPA were analyzed by CE-TOF-MS in beer samples. LOD for Glyp was < 5 $\mu\text{g}/\text{L}$, while for AMPA was 30.6 $\mu\text{g}/\text{L}$ with recoveries in the range 80–100%. To increase the sensitivity, a transient isotachopheresis method was also applied [76]. Herbicides with a different chemical structures including aldicarb, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), silvex, and prometon were studied as test compounds by using

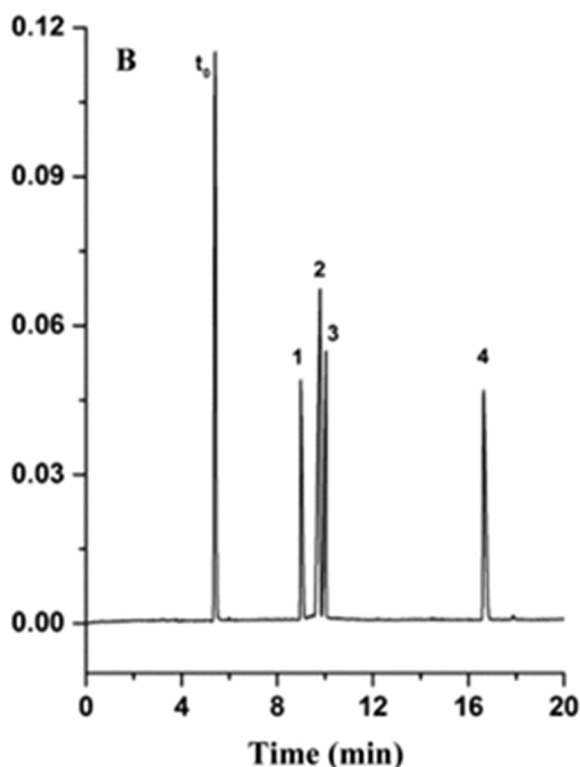


Fig. 3. Separation of four herbicides (1, aldicarb; 2, 2,4,5-T; 3, silvex; 4, prometon) by using CEKC. The BGE contained SDS-MWCNT-COOH. Modified from [79].

CEKC. The BGE was supplemented with multi-walled carbon nanotubes (MWCNTs) carboxylated (MWCNT-COOH) and sulfonated (MWCNT-SO₃H) all coated with SDS. Very good separation of the analytes was achieved by observing very high separation efficiency. The separation was due to differences in the partitioning of the analytes between the SDS nanoparticles and the hydro-organic phase and to other secondary interactions such as dipole-dipole, hydrogen bond, and π - π stacking [79].

Fig. 3 reports the separation of four herbicides by using CEKC

In a recent work, Casado et al. [84] reported an interesting separation of enantiomers of six herbicides by CE. The work is quite interesting considering that two enantiomers could have different effects and some formulations are produced with only one enantiomer. Compounds were resolved utilizing a mixture of cyclodextrins added to the BGE. The optimized method was not applied to real sample because the aim of the work was devoted to achieve a modeling-based optimization of a multicomponent mixture system (cyclodextrins) by CEKC.

3.2. Capillary electrophoresis, capillary electrokinetic chromatography, and capillary electrochromatography applied to the analysis of fungicides and insecticides

Insecticides and fungicides are compounds belonging to the class of pesticides widely used in agriculture to kill insects or parasitic fungus, respectively. Their residues can be dangerous for human and animal health causing also problems in the environment. In this section the analysis of insecticides and fungicides by electromigration techniques is reported.

In recent work, Furter and Hauser [14] separated by CZE-MS four fungicides (pyrifenoxy, cyprodinil, and pyrimethanil) and one insecticide (pirimicarb). Unfortunately, the optimized method was not applied to the analysis of real samples. In fact, this study was mainly devoted to the development of new instrumentation where the coupling of MS was

done with a sheathless electrospray ionization interface. The authors proposed firstly the analytes' separation and then the detection (ESI) pumping out separated compounds and BGE present in the capillary. The proposed method exhibited quite good sensitivity LOD in the range 0.36 and 0.76 μ M. Some triazoles fungicides (TAFs) were separated by CEKC. Penconazole, tebuconazole and cyproconazole in tomato fruit peel. The BGE contained a phosphate buffer in water/methanol mixture (80:20, v/v) modified with 15 mM of sodium dodecyl sulfate and sulphated γ -cyclodextrin. LOD and LOQ were in the range of 71–92 and 214–278 μ g/kg [85].

Agrochemical formulations have been analyzed for the determination of prothioconazole enantiomers (a fungicide). In the same work, Marina's group [77] analyzed this fungicide and its metabolite (prothioconazole-desthio) enantiomers to study the degradation of both compounds in soil and sand samples. For the CZE analysis authors used a BGE containing cyclodextrins, namely heptakis(2,3,6-tri-O-methyl)- β -cyclodextrin and a sulfated- γ -cyclodextrin, respectively. Reasonable LODs values were obtained (lower than 0.9 and 1.3 mg/L for prothioconazole and prothioconazole-desthio enantiomers, respectively) with good recovery (94–100%).

The residues of thiabendazole, aminocarb, imazalil, atrazine, metazachlor, metoxuron, carbofuran, metosulam, and imazapyr (fungicides or herbicides) were extracted from corn samples and their determination carried out by CZE-MS in less than 6 min. A very popular solid phase microextraction method ('Quick, Easy, Cheap, Effective, Rugged and Safe' - QuEChERS) was applied before the analysis. Very good LODs and LOQs (0.03 to 0.28 μ g/kg and 0.10 to 0.93 μ g/kg, respectively) were obtained. Although good quantitative results have been obtained, the CZE separation was not satisfactory because almost all analytes were not separated, the selectivity was due to the use of MS. Authors concluded that the obtained results achieved with CZE are comparable with those obtained with other methods but due to the use of the limited amount of solvents, CZE can be considered environmental friendly [68].

Three insecticides, namely chlorantraniliprole, kresoxim-methyl, and pyraclostrobin (neutral compounds) were analyzed by CEKC in ten min achieving good repeatability (RSD retention time and peak area 0.8–2.1 and 1.2–3.0%, respectively) with LODs in the range 1.8–6.4 ppb. To obtain a good sensitivity, the authors applied an interesting sample preparation method based on liquid extraction surface analysis (LESA) [21]. Recently Attig et al. [59] analyzed fungicides in spiked water samples. Although CE was used for the analysis, the study aimed to the optimization of a sample preparation method where ionic liquid (IL) in combination with magnetic multiwalled carbon nanotubes (MMWCNTs) were employed. LOQ in the range 5.6–9.3 ng/mL and recovery between 85.0% and 102.4% were obtained.

Seven carbamate pesticide residues (metolcarb, carbaryl, methomyl, aldicarb, carbofuran, isoprocarb, and pirimicarb) were analyzed in vegetables by using CE. Analytes were extracted by using a solid phase extraction (hollow fiber) procedure and detection was done with an electrochemiluminescence detector. Due to the extraction method and the detector used, good sensitivity was obtained (LOD, 0.1–0.5 μ g/L) [71].

The fungicide cyromazine and its main degradation compound (melamine) were analyzed in samples such as water, soil, and cucumber after a double surfactant-assisted electro-membrane extraction. The sensitivity obtained was not high probably due to the detector used (conductivity) [61].

Chlorophenols such as 2,4,6-trichlorophenol (TCP), 2,3,6-TCP, and 2,6-dichlorophenol are used as fungicides or herbicides in agriculture and they can be found in water. Jeong et al. [58] analyzed these compounds in tap water by CE. However, the main aim of the work was to propose a new enrichment method based on single bubble in-tube microextraction (ITME) coupled with CE. The enrichment factors of 2, 4,6-trichlorophenol (TCP), 2,3,6-TCP, and 2,6-dichlorophenol were 53, 41, and 60, respectively. LOQs were in the range of 5.6–8.3 ppb lower than 200 ppb reported by World Health Organization guidelines

for the analytes in water. Chlorophenols were also analyzed by Gao et al. [87] and by Ma et al. [88] in water samples using sample pre-concentration (field amplified sample injection and offline dispersive liquid-liquid microextraction combined with online pressure assisted electrokinetic injection, respectively). Enrichment factors were 61–1807 and 9–43, respectively. Gao et al. [52] also reported the analysis of some chlorophenols after a dispersive liquid-liquid microextraction (DLME) procedure. Acetonitrile (disperser solvent) and C_6H_5Cl (extraction solvent) were used for analyte extraction. Enrichment factors in the range 15–107 were obtained. Spiked samples of tap, lake, and river water were analyzed with recovery in the range 60.85–112.36% with acceptable RSD (1.31–11.38%).

Phenol carbamates (propraxur, carbofuran, 3-OH-carbofuran, carbaryl, and bendiocarb) were hydrolyzed and the products were analyzed by CE and detected with an amperometric detector in about 17 min. The proposed method was applied to the analysis of vegetables (cabbage, carrot, and pepper) [73].

Paraoxon, an insecticide, was quantified in a vegetable juice sample in an open-tubular immobilized enzyme microreactor (OT-IMER). The reactor was 1 cm at the inlet of the capillary and the online analysis of the activity and inhibition of acetylcholinesterase was achieved in 3 min. RSD was lower than 4%. LOD for paraoxon was 61 ng/mL. Recovery was in the range 89.6–105.9% [72]. Some organophosphorous insecticides, e.g., methyl paraoxon, ethyl paraoxon, methyl parathion, fenitrothion, and ethyl parathion were studied with CEKC and determined in artificial saliva and drinking water. SPE extraction was applied, however, the recovery was not satisfactory, while LODs were in the range 20–60 μm [89].

3.3. Miscellaneous

The applications of using CE for the analysis of pollutants include also other compounds such as steroids [15,83], trifluoroacetic acid (TFA) [70], aldehydes [60], carbonyl pollutants [75], organic mercury compounds [67], metal ions pyrithione complexes [62], sulfonamides [63,86], other antibiotics [22,54], biogenic amines [55] and nonsteroidal anti-inflammatory drugs (NSAIDs) [56].

Environmental water may contain residues of pharmaceutical and hormonal compounds. Among them, steroids need to be carefully analyzed because they can cause damage to humans. Siren and El Fellah [83] reported a very interesting study about the analysis of human-based steroids present in the intake wastewater of the water purification plant. Considering the presence of other interfering compounds, the low concentration of the analytes, and the low sensitivity of CE, the authors optimized an extraction method utilizing an SPE procedure. Analytes were quantified employing the partial filling micellar electrokinetic chromatography (PF-CEKC) and CZE based on the compounds' properties. The total steroid found in the influent water was 526 ng/L (calculated from quantified testosterone-glucoside, androstenedione, progesterone, and estradiol-glucoside). The authors concluded that, although a high volume of water (1 L) had to be used, considering the results, the proposed CE method could be an alternative to HPLC and GC. In a recent study, Siren et al. [15] applied CE to the analysis of steroids present in lake water. Excellent results (LOD) were obtained with the PF-CEKC (0.50, 0.48, 0.33, and 0.50 mg/L for androsterone, testosterone, progesterone, and testosterone-glucuronide, respectively).

In a recent work, some NSAIDs were studied by ITP coupled with MS. Very low LODs were obtained (100 ng/L), appropriate for the analysis of real samples (wastewater). The high sensitivity was obtained due to the use of MS, the concentrating effect of ITP, and an on-line sample preparation. The analysis of real samples revealed the presence of naproxen and diclofenac [56].

Due to the industrial production and use of TFA, this compound can be found in some environmental areas, e.g., water or residues of herbicides in several plants. Just for this, some agriculture products (cereals,

potatoes, grapes) were analyzed for the determination of TFA and DFA by using CE-MS. A sample pre-concentration and sample stacking method were also applied to increase the sensitivity. Very good LOD were obtained (9.3–44 $\mu\text{g}/\text{kg}$ and 7.8–26 $\mu\text{g}/\text{kg}$ for TFA and DFA, respectively) confirming the usefulness of the CE method [70].

Aldehydes are another type of pollutant compounds that can be found in particulate air, indoors, in water, etc. Due to the lack of chromophore groups, their determination is performed after derivatization with 2, 4-dinitrophenylhydrazine (2,4-DNPH). The excess of these derivatizing compounds can cause interferences in their extraction and analysis. A magnetic imprinted polymer was used to pre-concentrate aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde, and their analysis was performed with non-aqueous capillary electrophoresis (NACE) method. The obtained LOD was quite good, in the range 3.2–4.9 $\mu\text{g}/\text{L}$, and recovery was 87.3–99.8% and the method was applied to the analysis of the studied compounds in water samples [60]. The same aldehydes and other carbonyl pollutants have been investigated in ambient particulate (diameter < 2.5 μm ; PM_{2.5}). Magnetic molecularly imprinted microspheres were used to pre-concentrate the analytes before the CEKC analysis. LODs in the range 0.005–0.068 $\mu\text{g}\cdot\text{m}^{-3}$ were reported [75].

Organic mercury compounds are quite toxic pollutants that can be found in natural waters and marine products, e.g., fishes. Therefore they could be very dangerous for humans. In a recent study, Yang et al. [67] analyzed organic mercury in fish by CE after extraction with a zirconium-based metal-organic framework (MOF). With the proposed methods, LODs in the range 0.022–0.067 ng/mL, RSD- 3.2%, and recovery in the range 81.4–98.5% were obtained. The optimized methods were applied to the analysis of MeHg^+ , EtHg^+ , and PhHg^+ in fish samples. The analysis revealed the presence of MeHg^+ and EtHg^+ at a concentration of 0.15 and 1.53 $\mu\text{g}/\text{kg}$, respectively. Compared to other published methods, the proposed one resulted to offer a lower detection limit, reduced sample volume, and lower use of solvents.

Pyrithione is a biocide compound used as an active agent in some shampoos and other household products and commercialized as a complex with Zn or other metal ions. Therefore the complexes can be found in waters with consequent ecological risks. Authors performed leaching experiments of some antifouling paints containing Zn-pyrithione reporting the presence of only pyrithione (HPT) and dipyrithione (PT)₂ in the range 0.086–2.4 μm and 0.062–0.59 μm , respectively [62].

Sulfonamides are compounds belonging to a class of antibiotics widely used to treat both humans and animals. Since they are used in aquaculture, They have been found as residues in waters, soil, and tissues. Six of them were determined in aquaculture water by CE after applying an Ionic Liquid-based Hollow Fiber Liquid-Liquid-Liquid Microextraction method. LOD and enrichment factors were in the range 0.25 to 0.48 $\mu\text{g}/\text{L}$ and 122 to 230, respectively. The analysis of real samples revealed also the presence of sulfamerazine and sulfamethoxazole (0.52–1.60 $\mu\text{g}/\text{L}$ [63]. Other sulfonamides such as sulfamethoxazole, sulfadimethoxine, sulfamethizole were studied by Tarongoy et al. [86] by open-tubular electrochromatography (OT-CEC) and open-tubular liquid chromatography (OT-LC). In this work, cetyltrimethylammonium bromide (CTAB) was adsorbed on the capillary wall. Although analytes were resolved, a low separation efficiency was observed and the authors concluded that the use of capillaries of lower I. D. (10 μm) could resolve the problem. CE was also applied to the analysis of other antibiotics such as oxytetracycline, chlortetracycline, enrofloxacin, and ciprofloxacin in wastewater from pig farms. Oxytetracycline was detected and quantified in a real water sample at the concentration of 0.140 $\mu\text{g}/\text{mL}$ [54]. In another study, four fluoroquinolone antibiotics (ofloxacin, ciprofloxacin, norfloxacin, and enrofloxacin) were separated and quantified by CEKC employing a BGE (15 mM sodium dihydrogenphosphate at pH 6) supplemented with 3 mM CTAB applying a negative voltage. The antibiotics were found in river water samples at LOD level 1–2 $\mu\text{g}/\text{mL}$ [22].

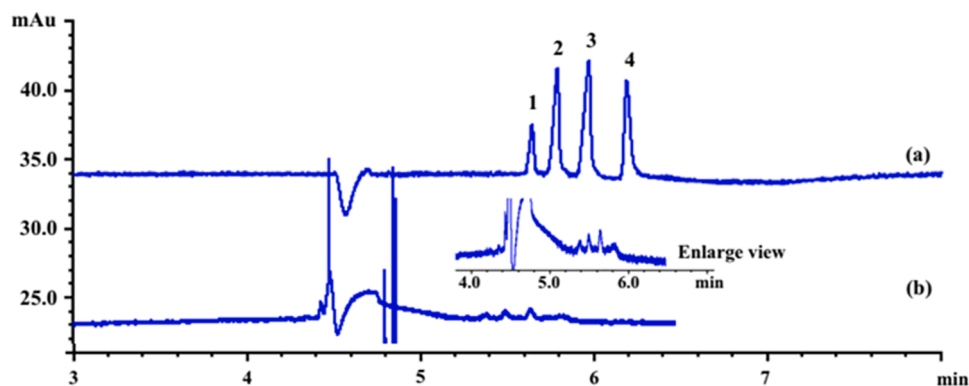


Fig. 4. Separation of 1 = ofloxacin, 2 = ciprofloxacin, 3 = norfloxacin and 4 = enrofloxacin a) standard compounds and b) Bang Pagong water sample by CEKC. Modified from [22]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Fig. 4 shows the separation of fluoroquinolone antibiotics in water samples.

Biogenic amines (BAs) are compounds that could be present in foods such as fruits, meats, fishes, etc. and their presence could be toxic. In water, these basic compounds could produce nitrosamines causing a carcinogenic effect. Therefore their determination is necessary for safety. Considering their chemical structure, and the presence of one or more amino groups, these compounds are easily analyzed by CZE. However, some of them do not contain UV-absorbing properties. Therefore in this work [55], a capacitively coupled contactless conductivity detections (C^4D) detector was used for their analysis by CE. Sea water samples were analyzed and none of the polyamines studied were found, therefore authors spiked analytes reporting quite interesting LODs (16–29 $\mu\text{g/L}$) and recoveries (77–93%). The proposed method could be an advantageous alternative to others where a derivatization procedure was necessary.

4. Conclusions

The analysis of pollutants such as pesticides, herbicides, insecticides, heavy metal ions, drug residues, aldehydes, etc. by using electromigration techniques has been reported in this review paper considering the results available in the literature published in the period 2018–2023-March. CE techniques offer high separation efficiency due to the use of capillaries of thin I.D., mainly due to the application of high voltages, and low generated current. Although these techniques exhibit high mass sensitivity, due to the low injected sample volumes, when applied to complex matrices, the sensitivity is questionable and therefore the use of sample pre-concentration and more sensitive detectors (e.g., MS) are necessary. This is shown in the reported selected applications in this review. Most of the applications reported the use of CZE, and a few considered CEKC and CEC. In some studies, chiral pollutants were also considered.

CRedit authorship contribution statement

Chiara Fanali: Writing – original draft, Conceptualization. **Susanna Della Posta:** Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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