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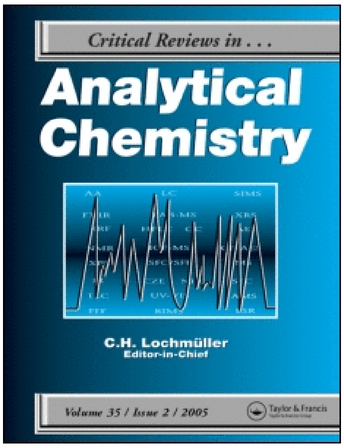

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A Review of Analysis of Pesticides Using Capillary Electrophoresis

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ABSTRACT: Capillary electrophoresis is a microvolume separation technique increasingly achieving recognition for use in the separation and determination of pesticides due to its relatively short analysis time, and nanoliter to picoliter sample volumes. Capillary electrophoresis is attracting considerable attention from many laboratories due to its simplicity. This overview discusses the applications of capillary electrophoresis for trace detection and determination of pesticides in pesticide formulations, environmental samples, and for chiral separations. The basic principles and improvements and their application in terms of increasing detection limits are discussed in this overview.

KEY WORDS: analysis, capillary electrophoresis, pesticides, environmental samples, reviews.

I. INTRODUCTION

In recent years, there has been a rapid development in capillary electrophoresis (CE) as an analytical technique. The popularity of the use of capillary electrophoresis in various analytical fields has been accelerated by its simplicity, high efficiency, selectivity, large separation capacity, and its relatively low cost. The basic theory is that on application of an electric field to a solution of charged molecules the movement starts. The mobility of the ion is governed by its charge-to-size ratio, and the size is dependent on the molecular weight, the three-dimensional structure, and the degree of solvation. The electrophoretic mobility is a balance between the electromotive and frictional forces and can be expressed as:

$$(\mu_{ep} = q/6\pi\eta r) \qquad (1)$$

where q = net charge, η = viscoscity, and r = ionic radius.

On the basis of their electric charge and the differences in the electrophoretic mobilities oppositely charged ions move in opposite directions, and smaller ions move faster than the large ions. The separation efficiency can be expressed as the number of the theoretical plates (N), and it is related to the applied voltage (V) and the mobility (μ) and the diffusion coeffficient (D) by the equation:

$$N = \mu V/2D \qquad (2)$$

It can be predicted from Eq. 2 that by applying high voltages efficient separation can be achieved. It is now adapted for the separation of large as well as small molecules. The advantages of the capillary electrophoresis are well known; heat dissipation in capillary tubes is good and temperature gradients can be kept to a minimum. This makes it possible to increase the voltage applied and thus to considerably decrease the analysis time, allowing a greater resolution. The analysis time can be shortened by using on-column detection and by processing data using a computer. The separation efficiency is mostly influenced by the inner diameter of the capillary, which is normally between 10 and 200 μm. Although excellent separation efficiencies are easily obtained in order to achieve quantitative and qualitative results, the shortage of sensitive detection systems may make obtaining these results difficult. The primary reason is the extreme degree of miniaturization involved. The growing interest in analyzing minute complex samples in which more

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than one species must be determined is one of the driving forces for the rapid development of capillary electrophoresis. Miniaturization (in situations with limited sample volumes and/or concentration) has been proven to be a great advantage, because in the miniaturized systems smaller injection volumes are required and inappropriate dilution of the analyte may be avoided.

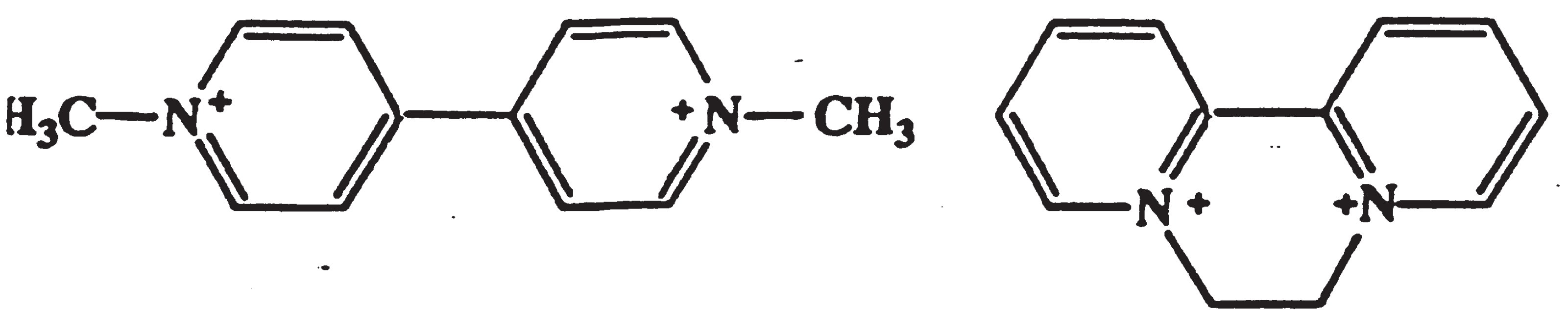
Capillary electrophoresis is superior to other separation techniques in many respects, for example, (1) CE is more efficient when compared with common liquid and gas separation techniques due to maximum theoretical plate number, (2) in CE nearly one-thousandth of the solvent is used when compared with HPLC, (3) the detection limit of CE is one-thousandth that for GC or HPLC, (4) detection limit as low as 10 yoctomolar (10×10^{-24} *M*) level (six molecules) may be attained using laser-induced fluorescence detection devices, (5) capillaries can be easily conditioned with buffer before the start of the analysis, (6) a wide range of analytes can be easily analyzed using CE. The main drawback of capillary electrophoresis is that it suffers from the mode of its detection system. The CE laser-induced fluorescence and photothermal systems offer sensitive detection devices at trace levels, but with other detection systems sufficient detection limits are not attainable.

Pesticides are the important and diverse environmental and agricultural species. Their determination in pesticide formulations, in feed and food, and in complex environmental matrices (e.g., water, soil, sludge, sediments, etc.) often requires separation methods capable of high efficiency, unique selectivity, and high sensitivity. Capillary electrophoretic methods for the analysis of pesticides were reviewed by Rassi[1] and summarized the various advantages and disadvantages of the use of different modes of capillary electrophoresis. In this review applications of capillary electrophoresis for the analysis of pesticides in environmental samples and enantiomer separation are demonstrated. The combinination of selective precolumn derivatization schemes, preconcentration techniques, and sensitive detection methods allows the determination of pesticides at the trace levels usually present in environmental samples. This review presents an up to date report on the applications of capillary electrophoresis for the analysis of pesticides.

II. APPLICATIONS OF CAPILLARY ELECTROPHORESIS

A. Isotachophoresis

Isotachophoresis involves the creation of sharp zone boundaries of analytes sandwiched between the zones (based on intrinsic mobilities) of leading and trailing electrolytes. The concentration of the analyte zone is electrically forced to become that of the leading electrolyte (called concentration effect.) This results in a varying electric field potential throughout the capillary (at constant current) such that all zones move at the same velocity. Isotachophoretic separations of the herbicides diquat (1,1´-ethylene-2,2´-bipyridylium ion) and paraquat (1,1´-dimethyl-2,2´-bipyridylium ion) (Figure 1) were performed by Walker et al.[2] in a glass microchip-etched channel and monitored on-chip by normal Raman spectroscopy. Microchips have large surface areas when compared with capillaries with similar internal cross sections. The chips efficiently dissipate heat generated by current flow. Even without active cooling, the operation of electrically driven separations at high fields proceeds with minimal sample heating. Heat dissipation is particularly useful for isotachophoresis (ITP) because high-concentration leading and trailing electrolytes are used. High voltage reduces the running time and therefore decreases interdiffusion of analyte zones that limit resolution. The 40-μm-wide and 75-μm-deep separation channels were chemically etched in a serpentine design to 21 cm total length. A 120-μm-thick glass cover slip was used to seal the channels. Separation held strengths up to 380 V/cm were used. The microchip was directly coupled to a Raman microprobe and no interfacing was required. Raman spectra were generated with a 2-W, 532-mn Nd:YAG laser and collected at 8 cm^{-1} resolution with a holographic transmissive spectrograph and a cryogenically cooled charged coupled device. Data acquisition was at 2 to 5 spectra/s. The experimental apparatus is shown in Figure 2. Raman isotachopherograms



Paraquat **Diquat**

FIGURE 1. Structure of paraquat and diquat. (Reproduced with permission from Reference 2.)

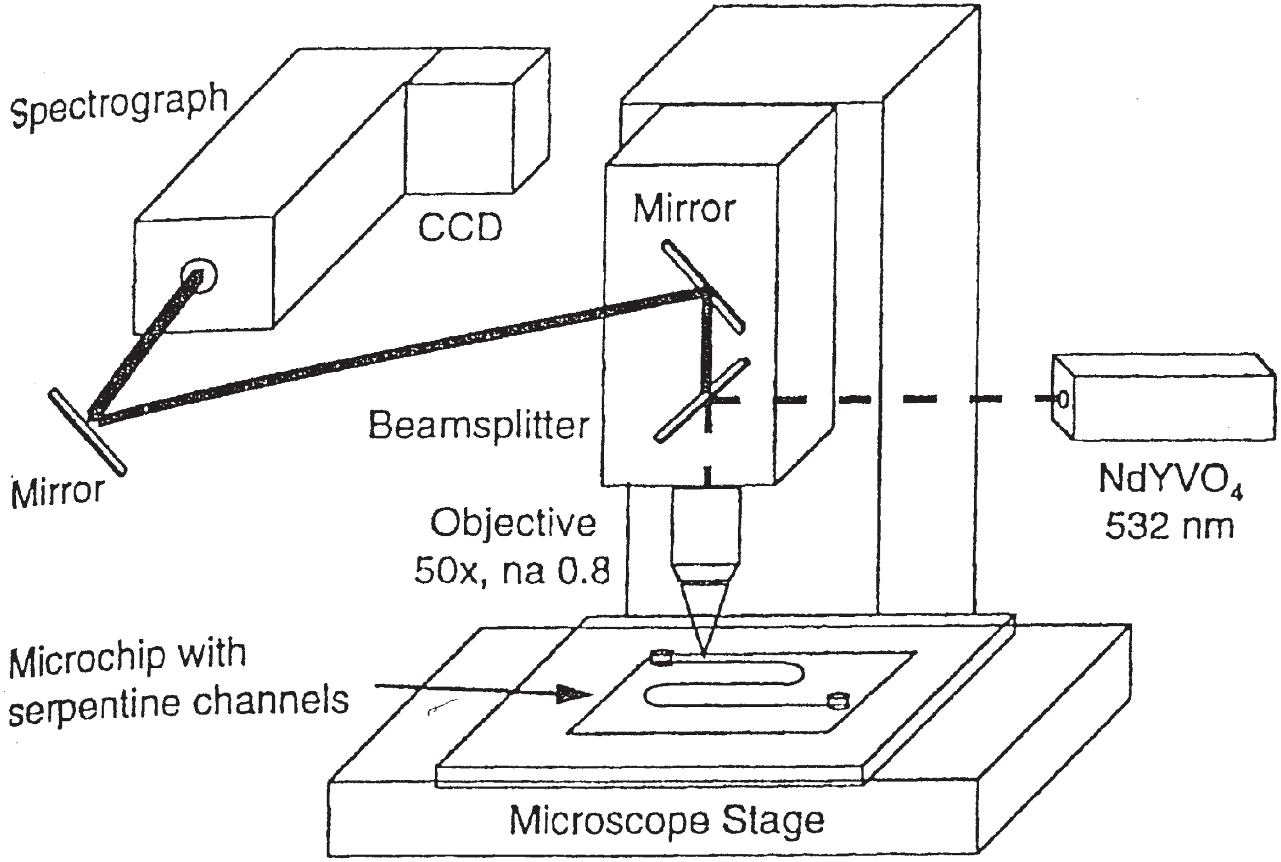


FIGURE 2. Diagram of the Raman spectroscopy/microchip isotachophoresis system. (Reproduced with permission from Reference 2.)

of the pesticides at starting concentrations (Figures 3 and 4) as low as 2.3×10^{-7} *M* (60 ppb paraquat/80 ppb diquat) were presented.

B. Micellar Electrokinetic Capillary Chromatography

Micellar electrokinetic capillary chromatography allow the separation of relatively unpolar pesticides, and its sensitivity is much increased when it is combined with preconcentration techniques. Penalver et al.[3] described the solid-phase microextraction (SPME) as a recent technique for sample preparation. The key feature of the review is the coupling of SPME with CE and its application for the analysis of environmental samples.

Faubel et al.[4] have separated nitrophenol pesticides (Figure 5) using micellar electrokinetic chromatography with thermal lens detection and compared their results with the normal UV detection. Micellar electrokinetic capillary chromatography (MECC) allows unpolar samples to be separated by a distribution of the substances between the aqueous electrophoretic buffer phase as carrier electrolyte and the micelles (pseudostationary phase) that arise when the concentration of the surfactant was higher than the critical micellar concentration. The schematic set up of the CE-TL detector is shown in Figure 6. The pesticides were separated by MECC and detected with a UV-VIS detector (linear UVIS 200, Thermo Separation Products) and the TL detector system. In Figure 7, the separation by the UV detector is shown; in Figure 8, the TL detector was used. The signal-to-noise ratio was significantly improved by the TL detector, thus allowing detection in the ppb range. The UV detector was fixed at a wavelength of 364 nm +/- 3 nm; the pump beam of the Tl detector delivered a power of 150 mW. Figures 9 and 10 shows the calibration curves of both detectors. The linearity of both methods was for a 75 μm capillary more than three orders of magnitude. The limit of detection with a signal-to-noise ratio of three was 1.1 ppm for DNOC for the UV-VIS detector and 23 ppb for the TL detector, which was a factor of 48 less than in usual absorbance spectroscopy. Table 1 shows the limit of detection of the pesticide 2-methyl-4,6-dinitrophenol (DNOC) with different detector system and different diameters of the capillary.

A micellar electrokinetic chromatographic method was developed by Kubilius and Bushway[5] to separate and quantify hexazinone and metabolites (Figure 11) in groundwater samples collected from U.S. Geological Survey monitoring wells after extraction using Supelclean ENVI-Carb solid-phase extraction tubes. Quantitation was performed using UV photodiode detection at 220, 225, 230, and 247 nm. Electropherogram of the separation of hexazinone and metabolites is shown in Figure 12. The linear regression for hexazinone was $y = 1.0073x + 0.219$ with a correlation coefficient of 0.96.

Capillary electrophoresis (CE) was used by Rossi and Rotilio[6] for the qualitative and quantitative analysis of the structurally different 11 compounds of the carbamate, thiocarbamate, and dithiocarbamate classes of pesticides with a large spectrum of chemical properties shown in Figure 13. Micellar electrokinetic chromatography (MEKC) was employed for the separation of these substances (Figure 14). Indicates good separation and sufficient sensitivity. Due to the nonpolar nature of some pesticides the addition of methanol to buffer improved the seaparation of these pesticides. The method was applied for the determination of carbamates in tapwater after preconcentration using a styrene-divinylbenzene polymer column with the solid phase extraction (SPE) technique.

Penmetsa, Leidy, and Shea[7] developed a capillary electrophoresetic (CE) method separately and determined residues of two sulfonylurea herbicides (primisulfuron and triasulfuron; in Figure15) in water and soil samples. Fortified water samples were extracted by solvent partitioning with methylene chloride and analyzed by CE (Figures 16 and 17). Fortified soil samples were extracted by shaking in methanol-phosphate buffer (1 + 1) followed by partitioning of the residues into methylene chloride and analysis by CE (Figure 18). The method was simple, rapid, and yielded recoveries greater than 90% for both herbicides fortified at 10 μg/l in lakewater samples and at 50 μg/kg in soil samples.

Lancas et al.[8] determined 2,4-D (2,4-dichlorophenoxyacetic acid) and dicamba (2-methoxy-3,6-

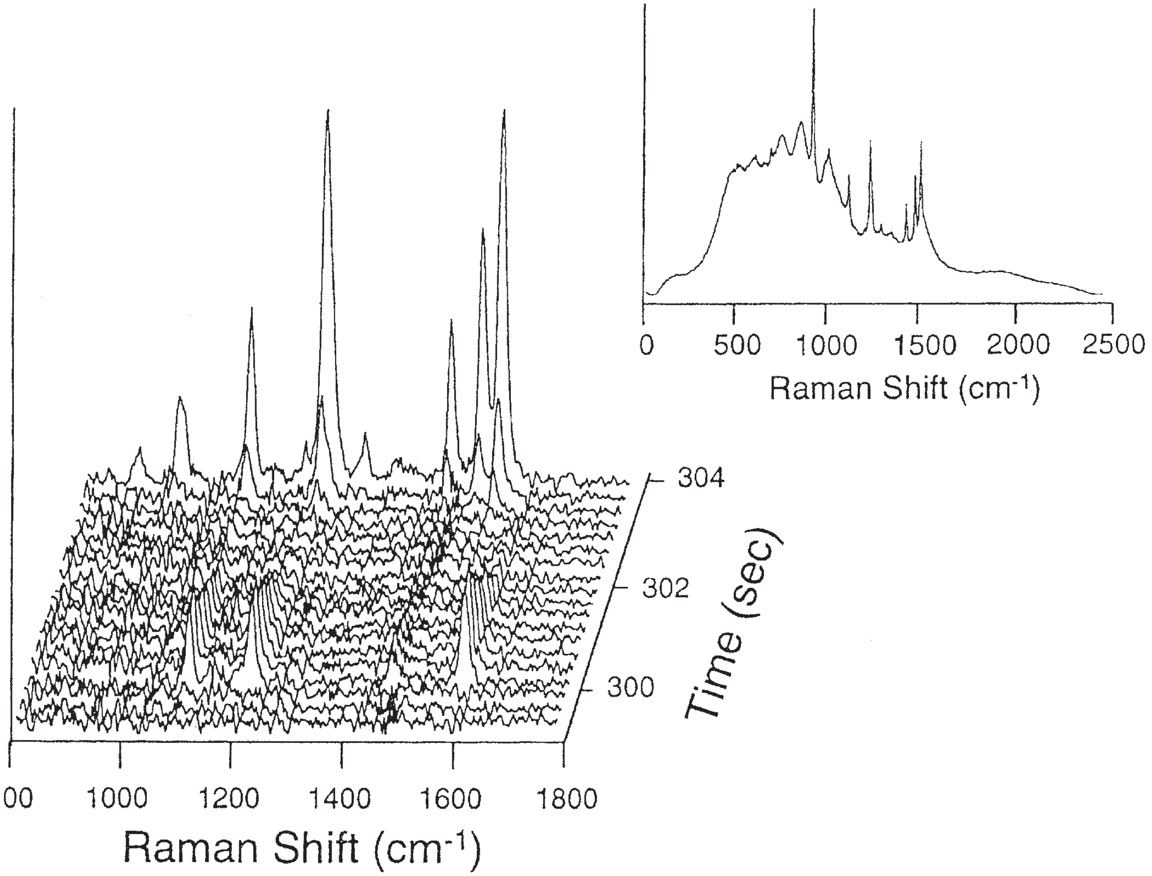


FIGURE 3. Raman isotachopherogram of herbicides at 2.3 × 10^{-6} *M* (600 ppb of paraquat/ 800 ppb diquat) in deionized water. Leading electrolyte 0.1 M H_2SO_4; trailing electrolyte 0.1 *M* Tris; sampled at 5 Hz; running voltage 8 kV; 60-s injection time at 4 kV. (Reproduced with permission from Reference 2.)

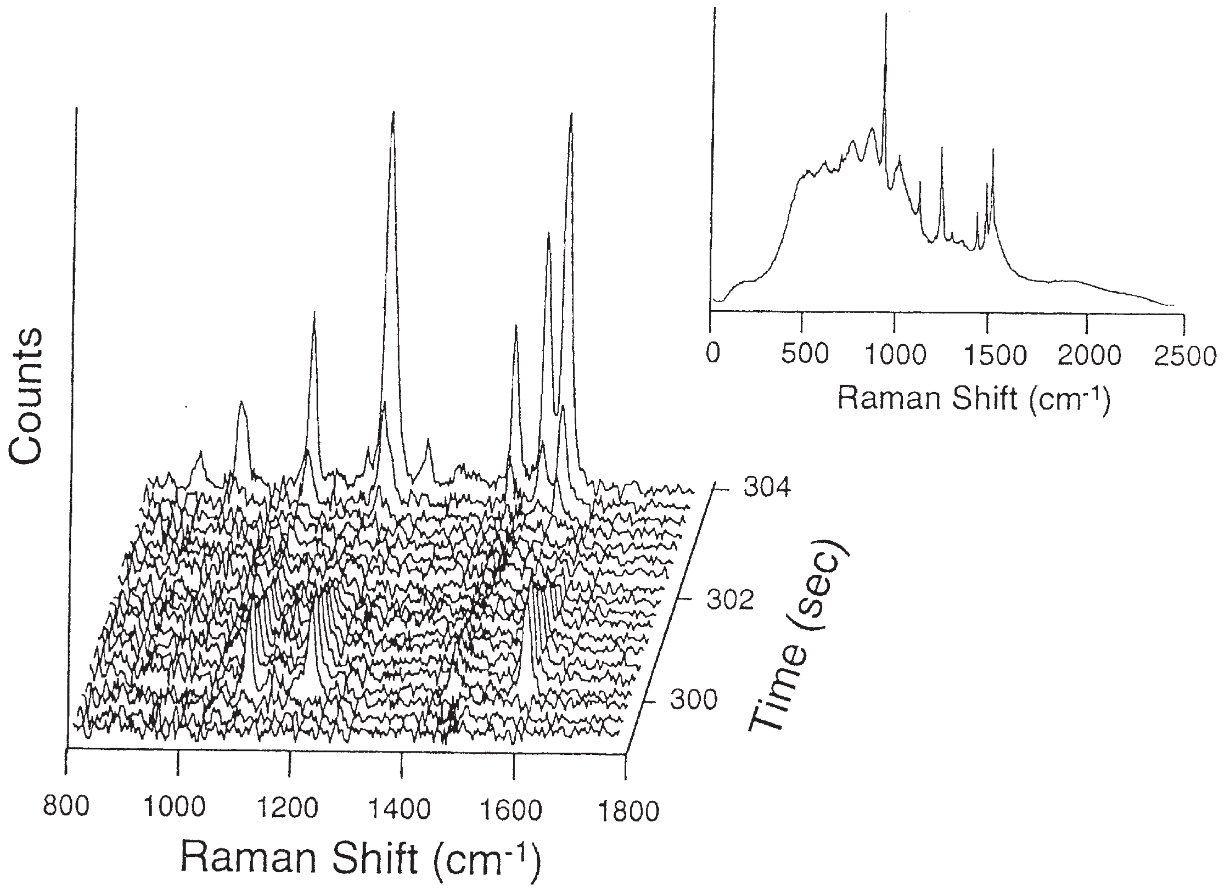


FIGURE 4. Raman isotachopherogram of herbicides at 2.3 × 10^{-7} *M* (60 ppb of paraquat/ 80 ppb diquat) in deionized water. Sampled at 2 Hz; 120-s injection time at 4 kV other conditions same as in Figure 5. (Reproduced with permission from Reference 2.)

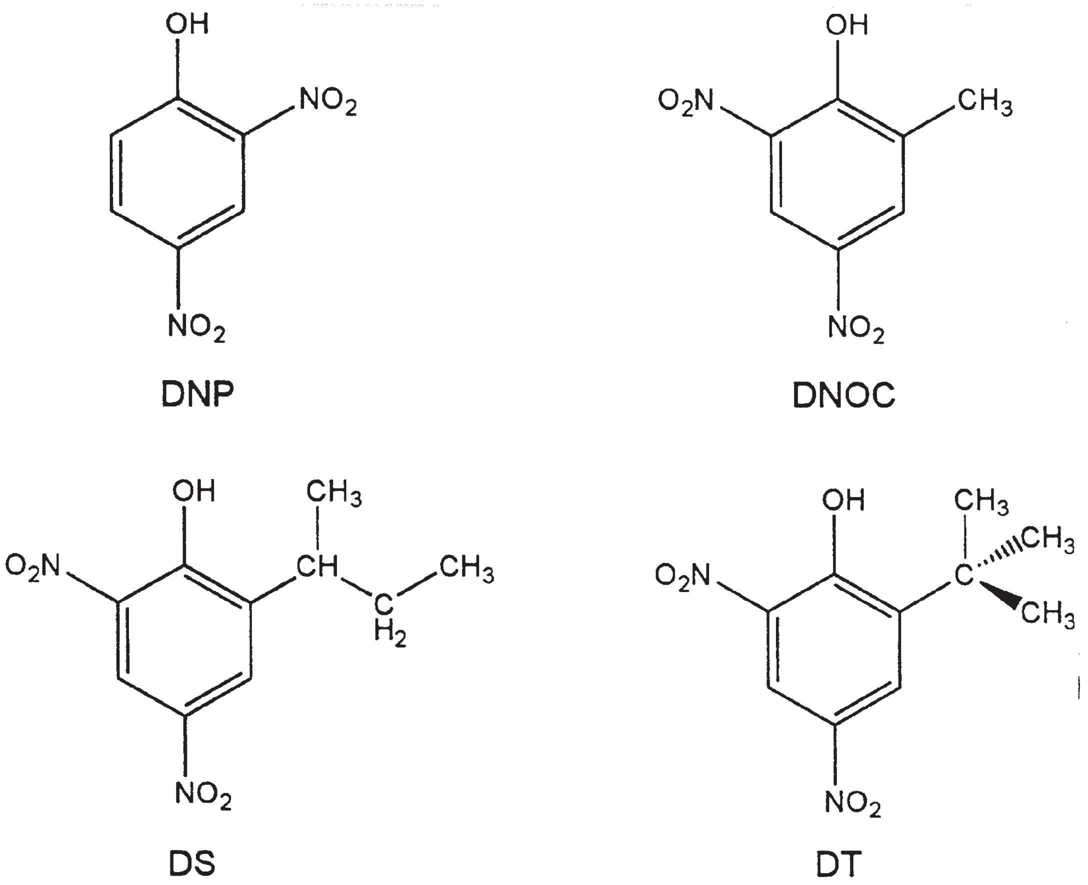


FIGURE 5. Strtucture of the nitro-phenol pesticides; DNP = 4,6-dinitrophenol, DNOC = 2-methyl-4,6-dinitrophenol, Dk,= 2-sek-butyl-4,6-dinitrophenol (dinoseb), DT = 2-tert-butyl-4,6-dinitrophenol (dinoterb). (Reproduced with permission from Reference 4.)

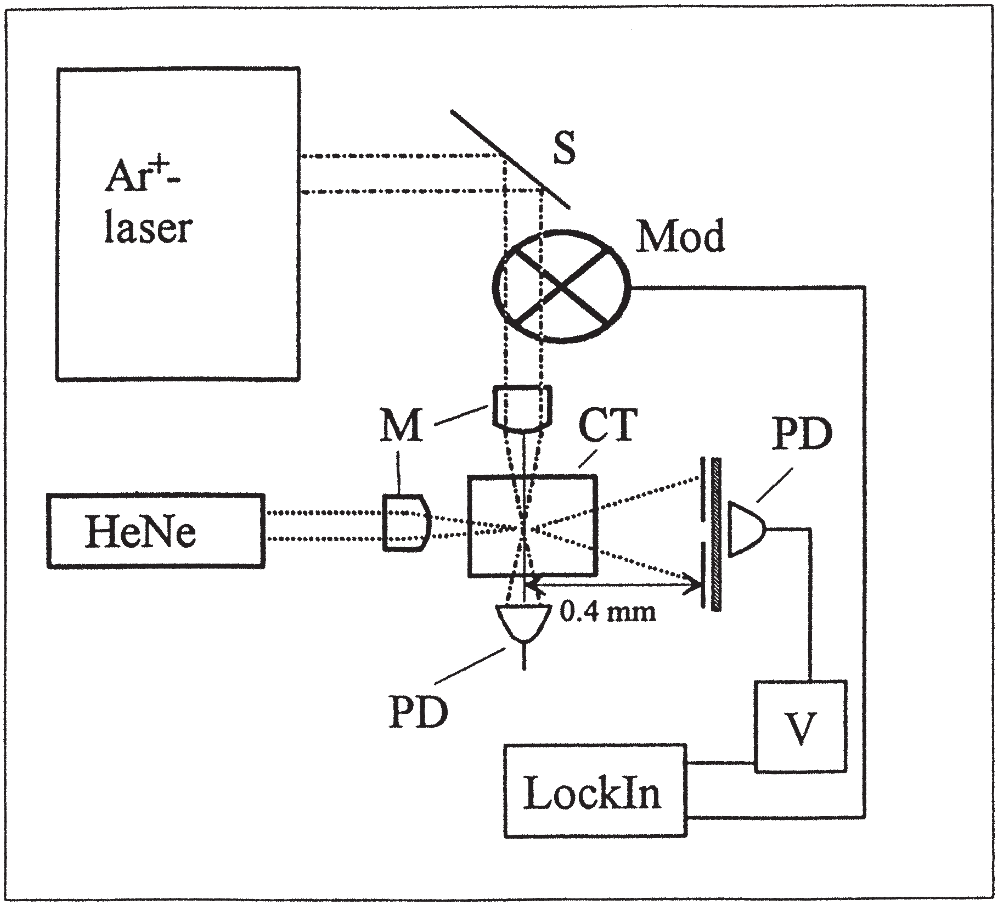


FIGURE 6. Schematic setup of the CE-TL detector. S = mirror, Mod=Chopper or acoustooptic modulator, M = microscope objective, CT = capillary tube, PD = photodiode, HeNe = helium neon laser, V = preamplifier, LockIn = LockIn-amplifier. (Reproduced with permission from Reference 4.)

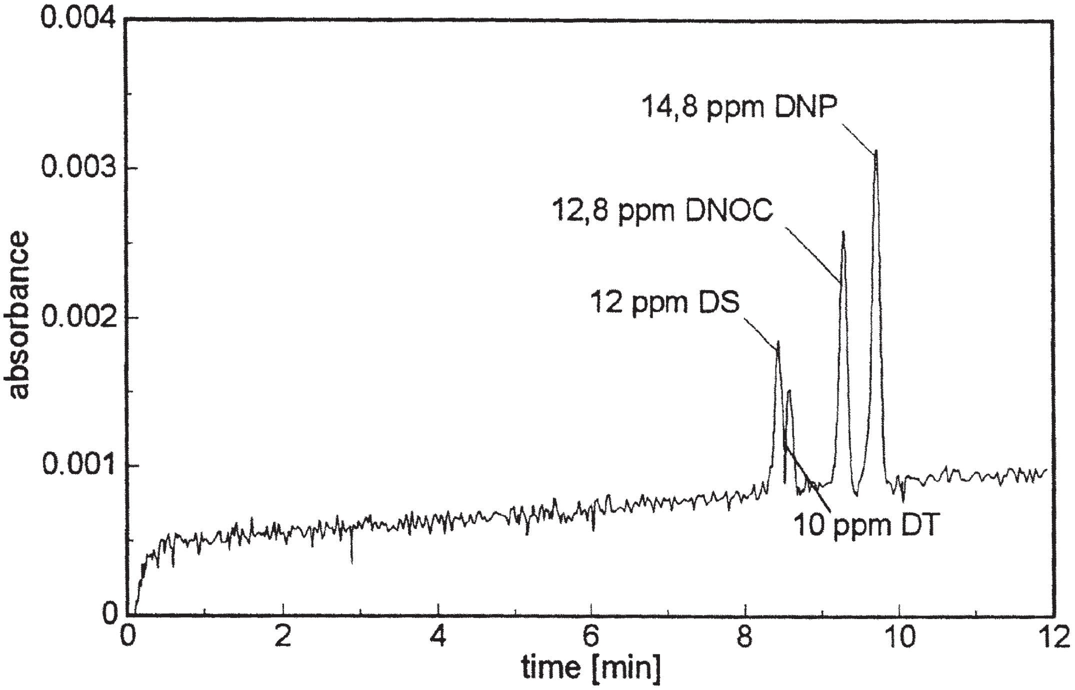


FIGURE 7. Capillary electropherogram of a mixture of pesticides with UV-detection with a 75-µm capillary. (Reproduced with permission from Reference 4.)

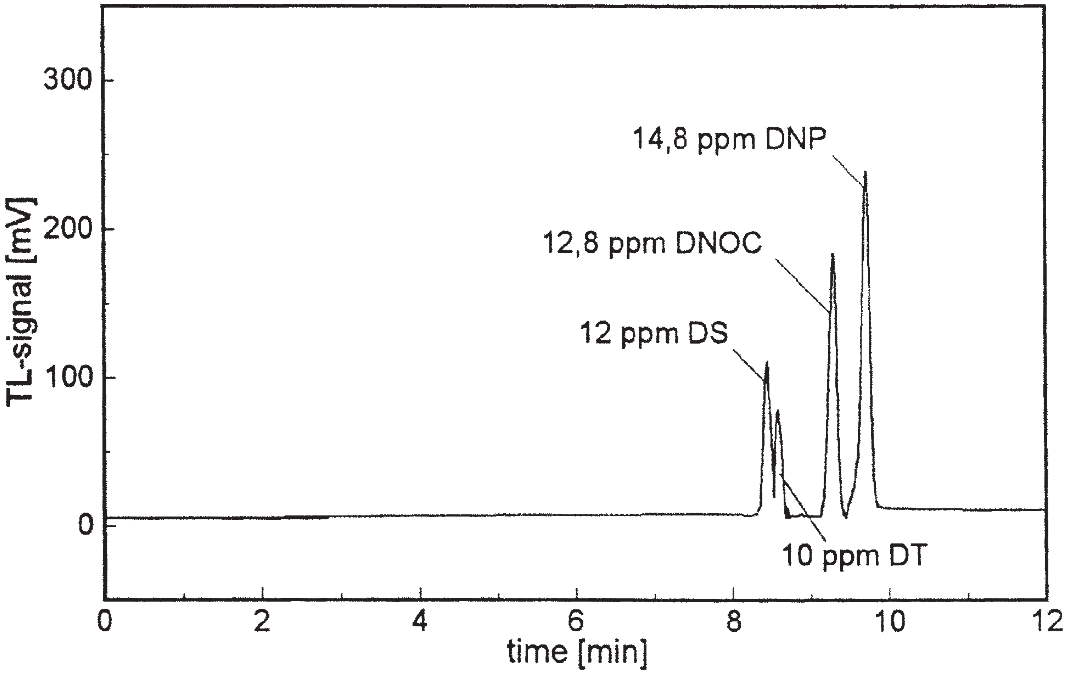


FIGURE 8. Capillary electropherogram of a mixture of pesticides with TL detection with a 75-µm capillary. (Reproduced with permission from Reference 4.)

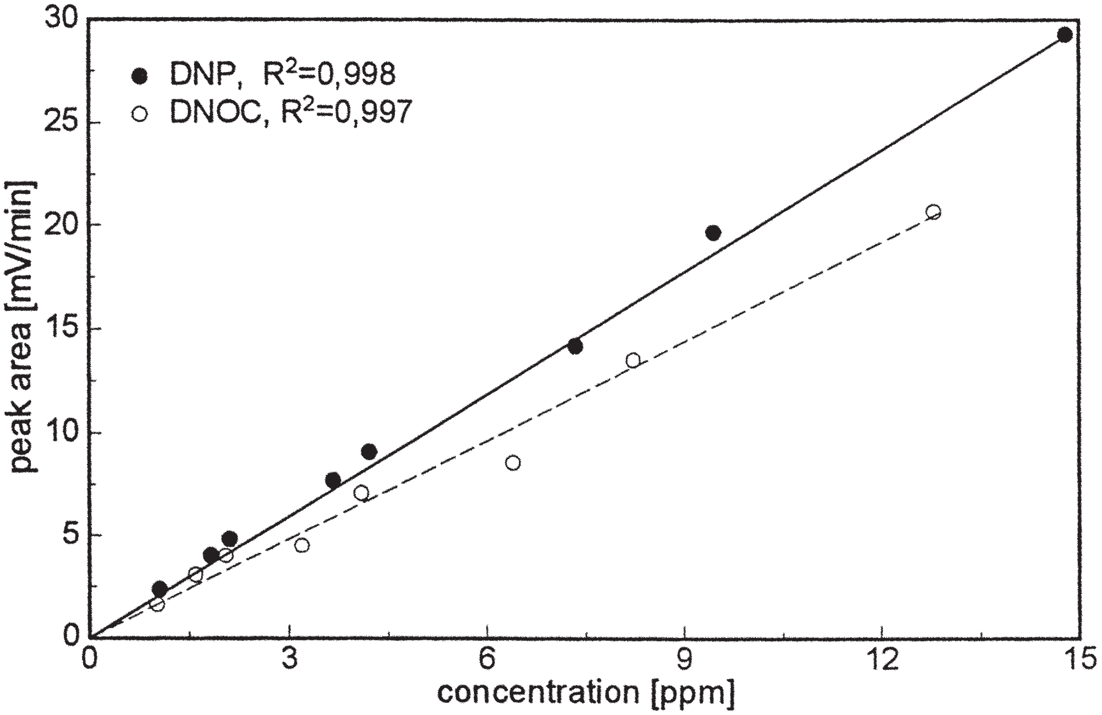


FIGURE 9. Calibration curve of the pesticides DNOC, DNP, with the UV detector. (Reproduced with permission from Reference 4.)

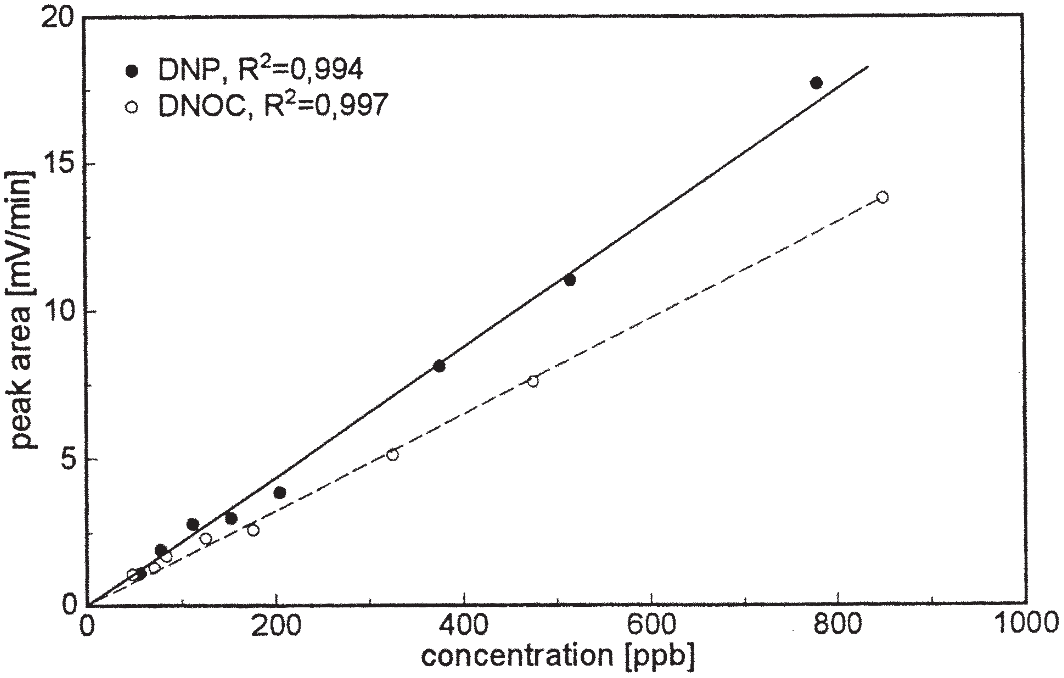


FIGURE 10. Calibration curve of the pesticides DNOC, DNP, with the TL detector. (Reproduced with permission from Reference 4.)

TABLE 1
Comparison of the Detection Limits for the Different Diameters of Capillary Using Thermal Lensing and UV/VIS Spectrometry

Capillary Internal diameter µm	CE-Capillary in UV/VIS in ppb	TL in ppb
50	2550	45
75	1100	23
100	815	23
200	405	23

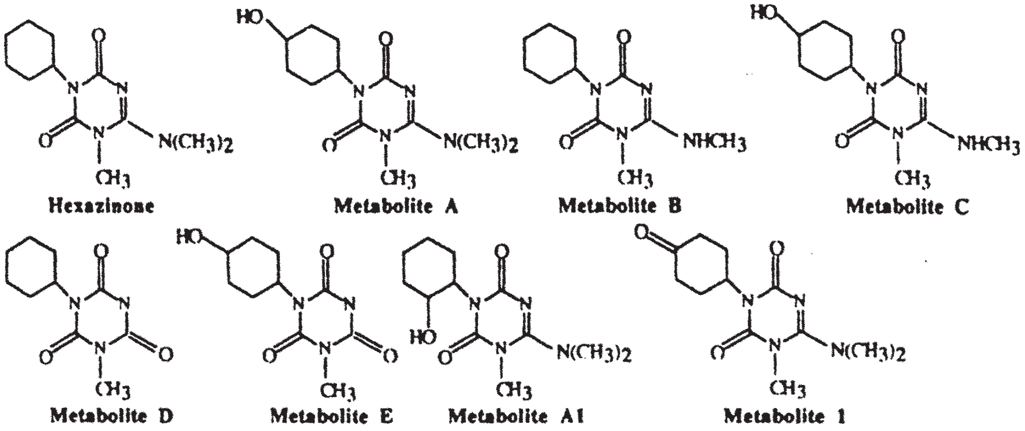


FIGURE 11. Chemical structure of hexazinone and its metabolites. (Reproduced with permission from Reference 5.)

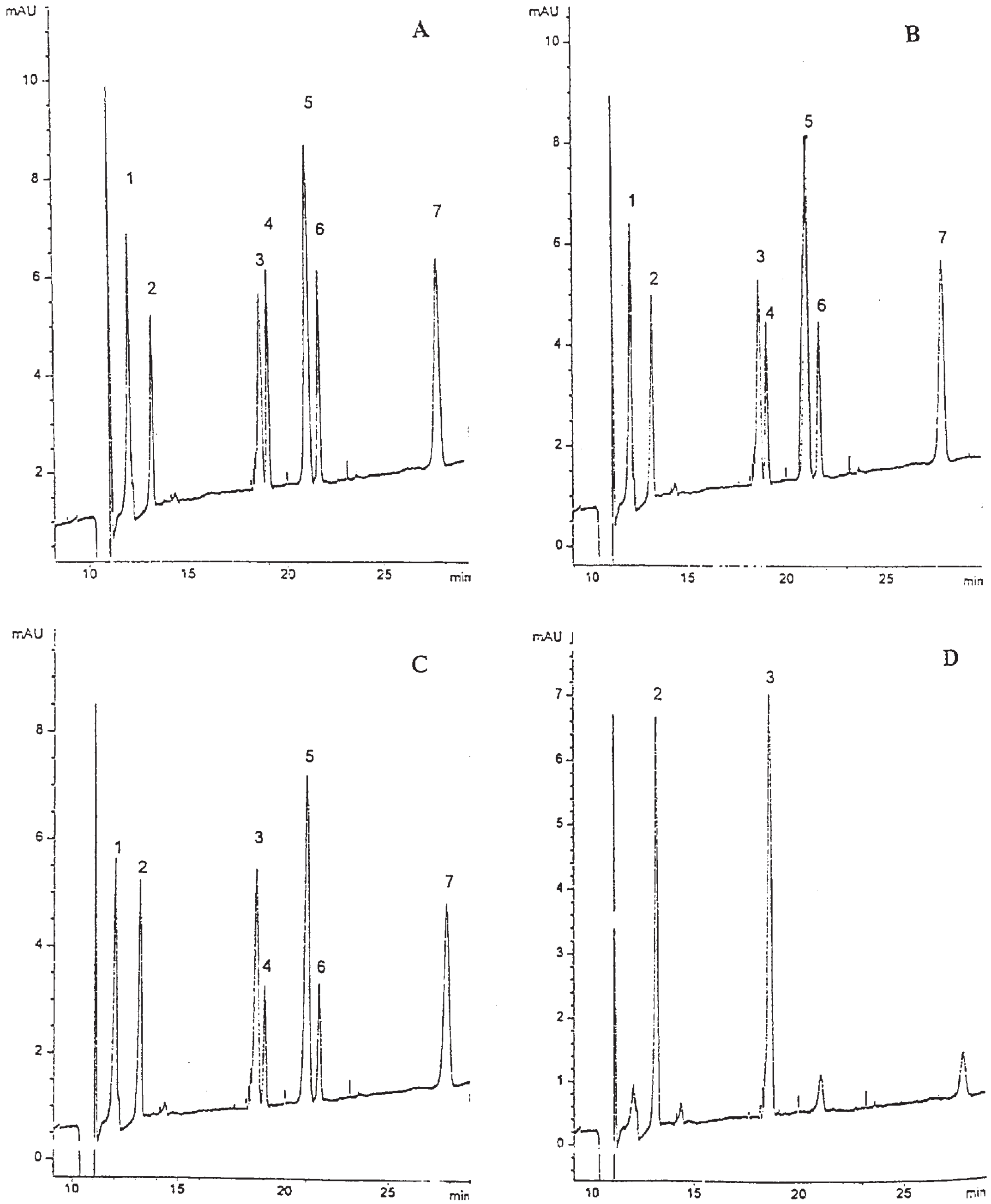


FIGURE 12. Electropherogram of the separation of hexazinone and metabolitesA = 220 nm; B = 225 nm; C = 230 nm; and D = 247 nm. Peaks 1 = metabolite C; 2 = metabolite A1; 3 = hexazinone; 4 = metabolite E; 5 = metabolite B; 6 = metabolite D; 7 = atrazine. Analysis conditions 48.5 cm × 75 μm I.D. capillary column; injection hydrodynamic (12 s at 60 mbar); 50 m*M* SDS, 12 m*M* sodium phosphate, 10 m*M* sodium borate and 15% methanol (pH 9.0) time 0 at 25 μA to 55 μA for first minute and then constant at 55 μA. (Reproduced with permission from Reference 5.)

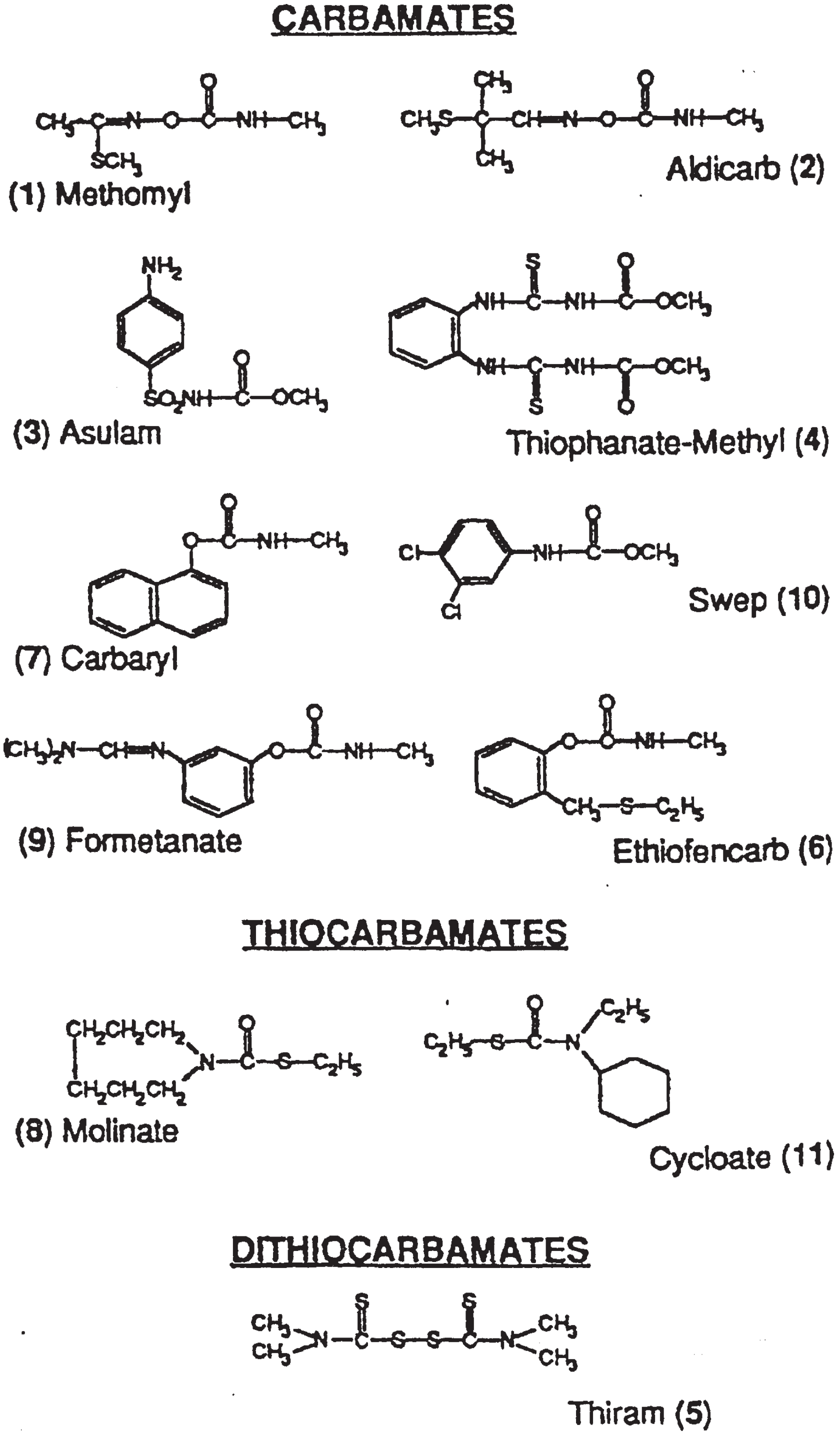


FIGURE 13. Chemical structure and name of the carbamate pesticides. (Reproduced with permission from Reference 6.)

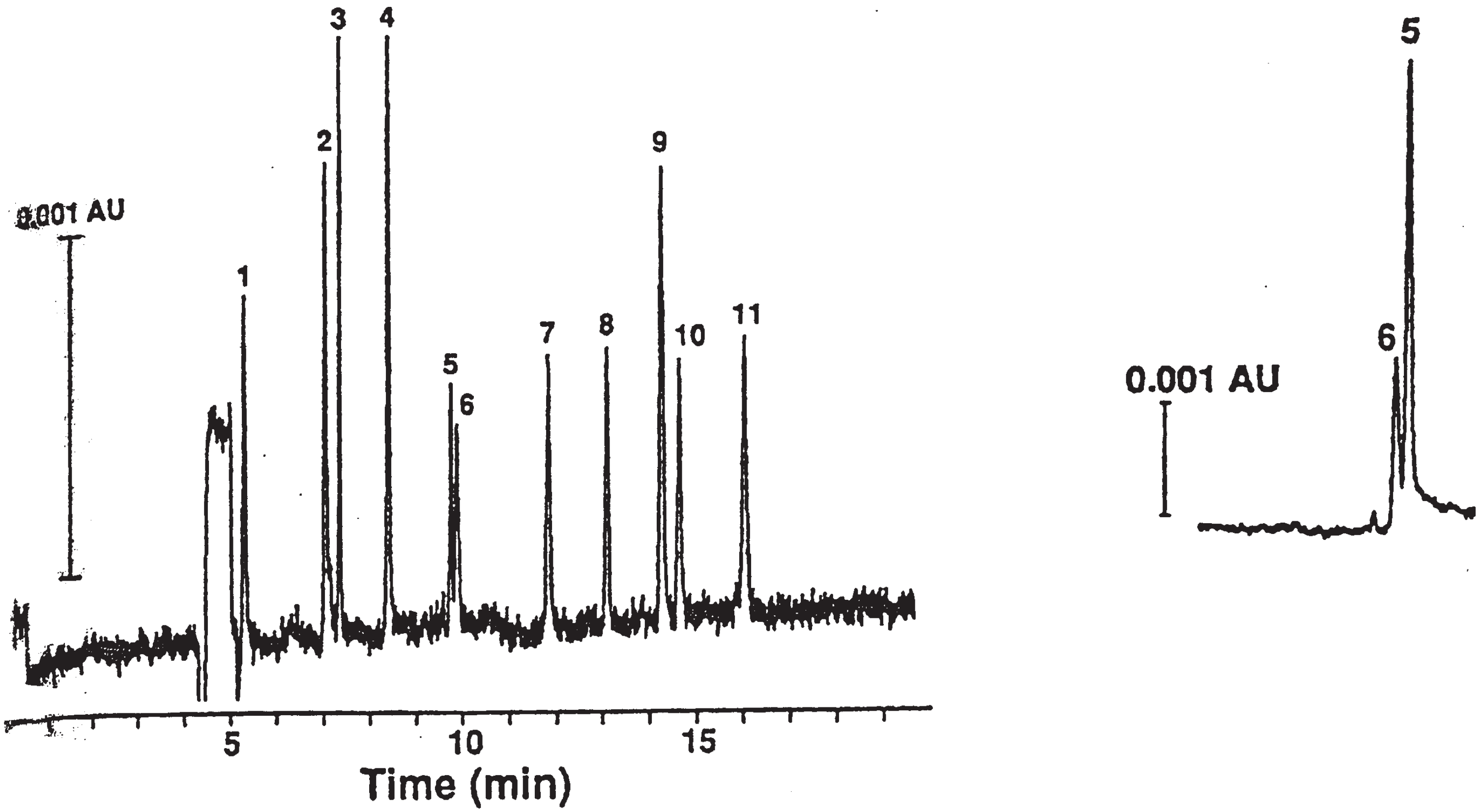
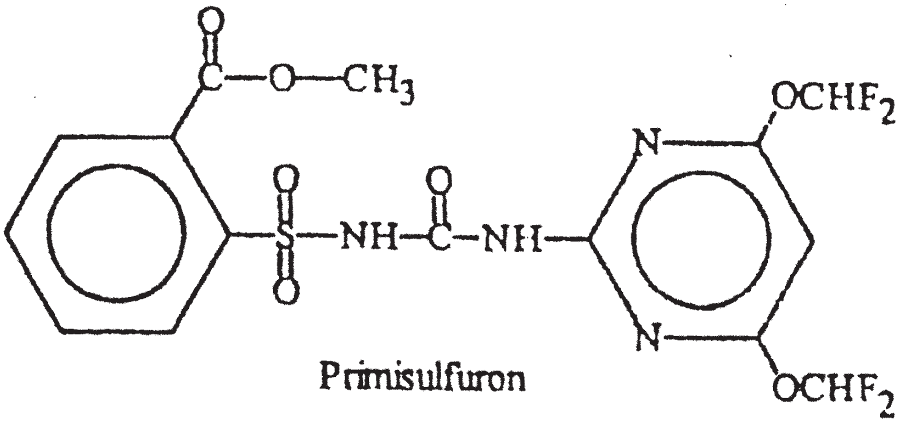
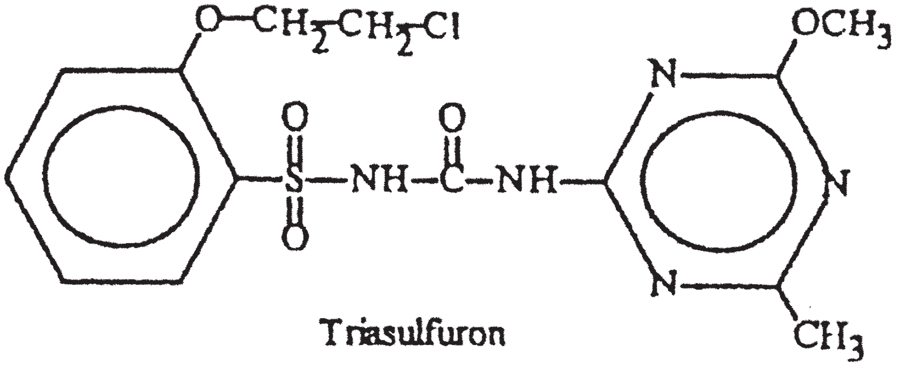


FIGURE 14. Micellar electrokinetic chromatography of mixtures of the eleven carbamate pesticides shown in Figure 1 (borate buffer 100 m*M*, SDS 50 m*M*, methyl alcohol 10% w/v, pH 8.2, 15 kV, 25°C). (Reproduced with permission from Reference 6.)



Primisulfuron



Triasulfuron

FIGURE 15. Structure of primisulfuron (Beacon) and trisulfuron (Amber). (Reproduced with permission from Reference 7.)

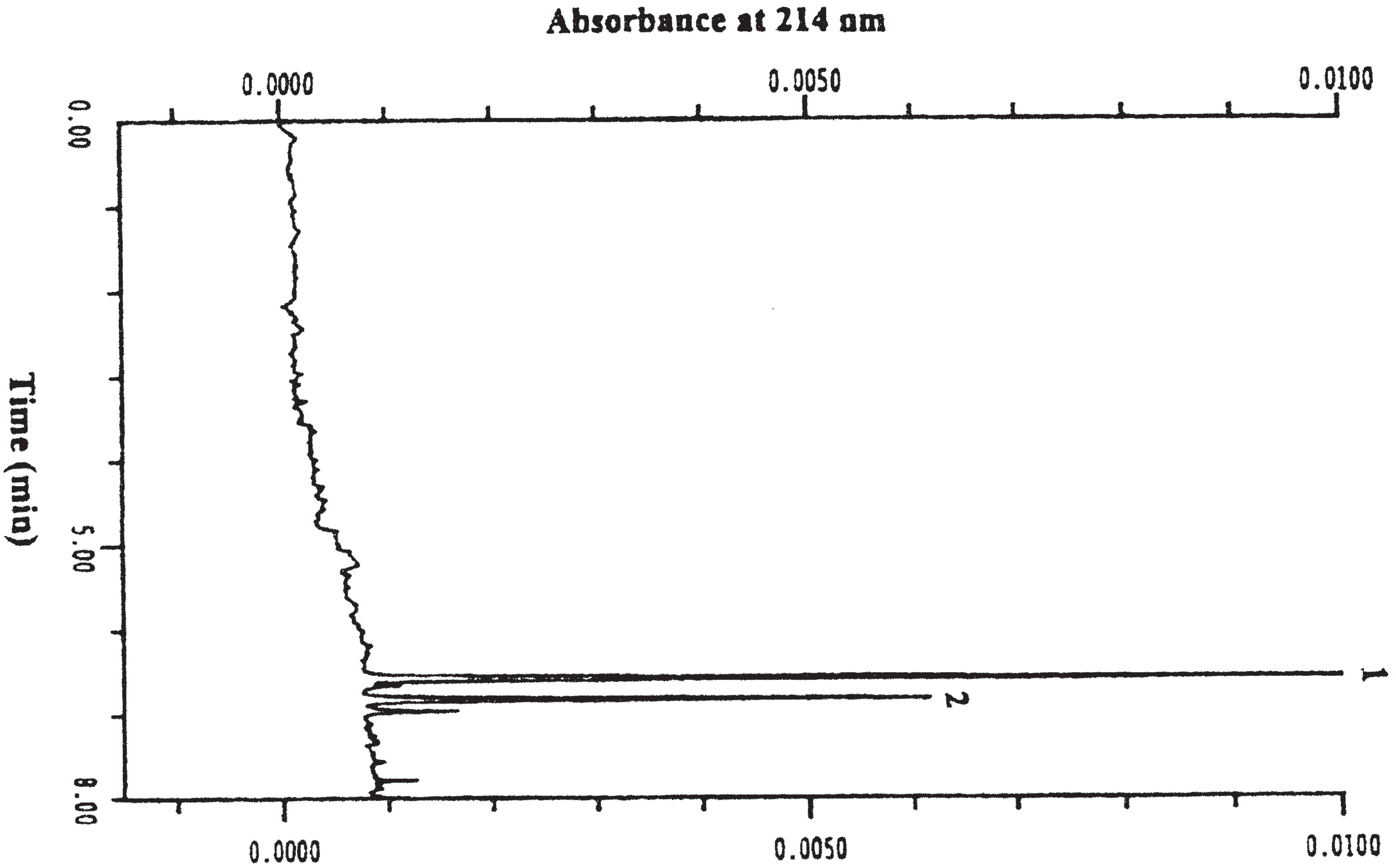


FIGURE 16. Electropherogram of a 10 μg/ml standard mixture in LC-grade water: (1) triasulfiron. Analysis conditions: 50 cm × 75 μm I.D. capillary column; pressure injection (10 s = 60 nl); 25 m*M* NaH_2PO_4 + 50 m*M* LiDS buffer, pH 6.5; 18 kV (63 μA); 214 nm UV absorbance. (Reproduced with permission from Reference 7.)

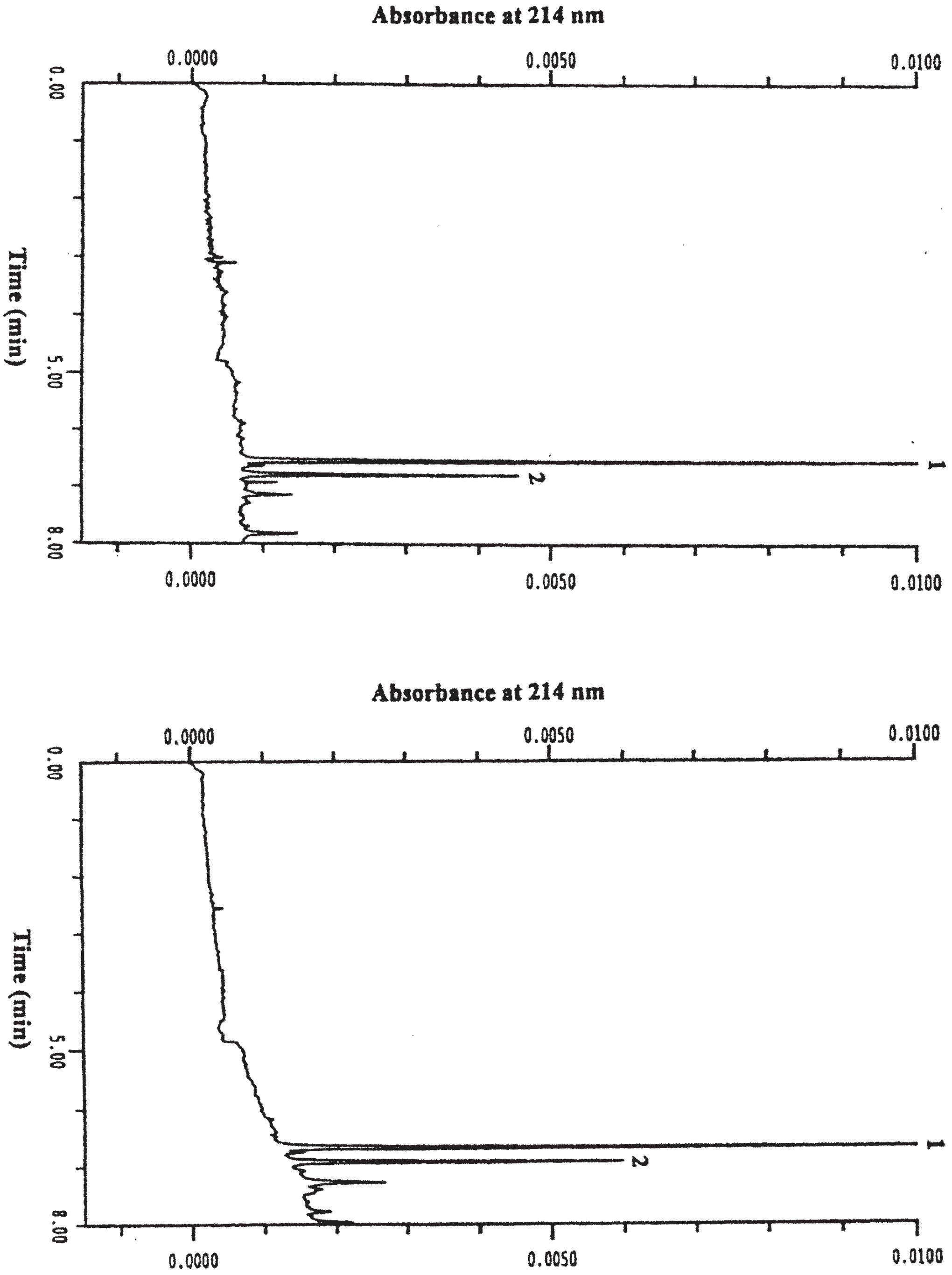


FIGURE 17. Electropherogram of (left) deionized water sample and (right) lake water sample fortified with 10 µg primisulfuron and triasulfuron followed by liquid-liquid extraction: (1) triasulfuron (2) primisulfuron. Analysis conditions are the same as in Figure 18. (Reproduced with permission from Reference 7.)

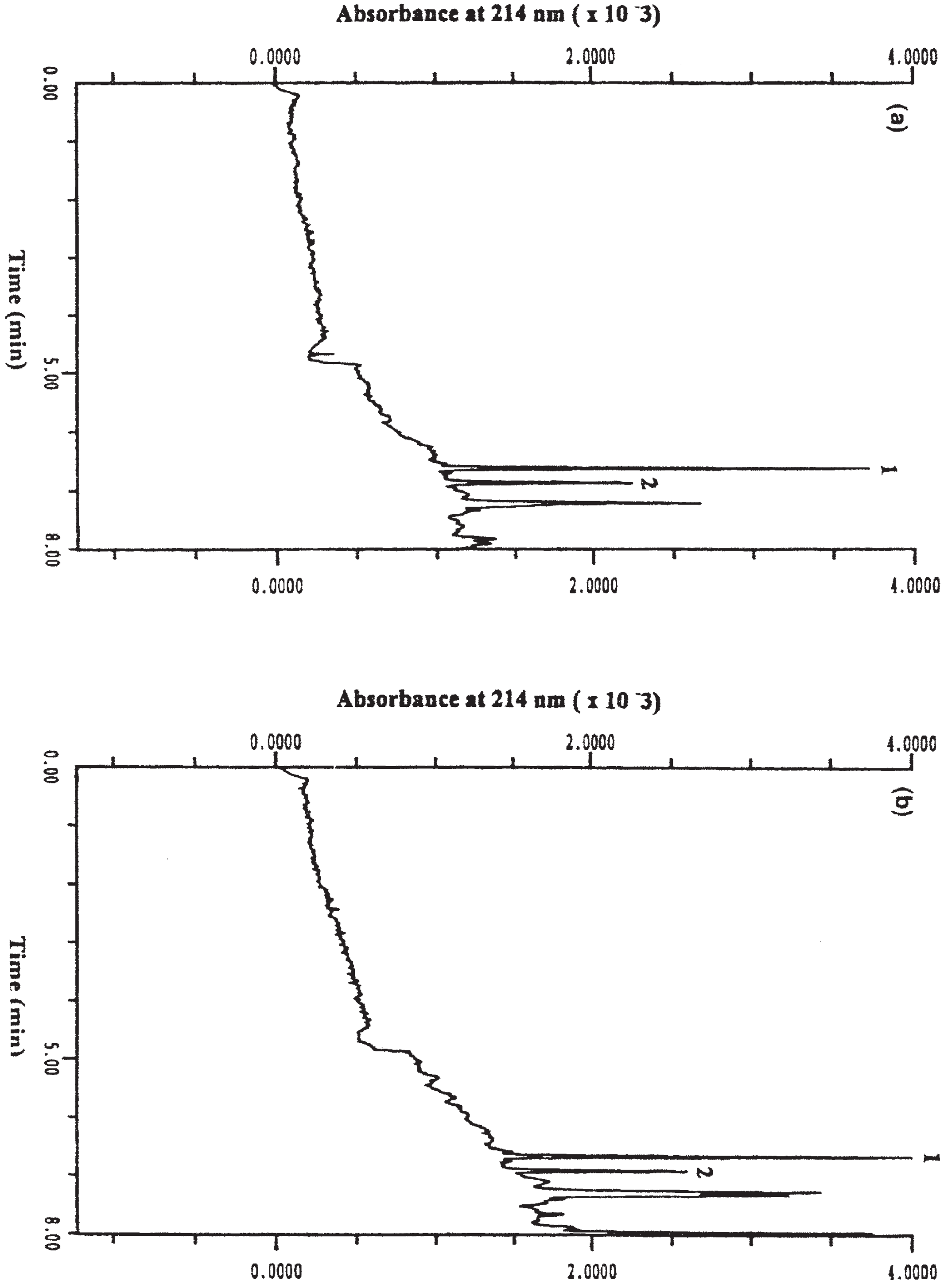


FIGURE 18. Electropherogram of (a) sandy loam soil and (b) clay loam soil fortified with 50 μg/kg primusulfuron and triasulfuron followed by extraction (1) triasulfuron (2) primisulfuron. Analysis conditions are the same as in Figure 18. (Reproduced with permission from Reference 7.)

dichlorobenzoic acid) residues in sugar cane, rice, and corn by a supercritical fluid extraction (SFE) method using a self-developed appartus and mixture of CO_2/acetone as extraction. The extracts were cleaned up after extraction by both liquid-liquid partition and a Florisil column. Micellar electrokinetic capillary chromatography (MEKC) coupled with ultraviolet on-column detection was used for the analysis of these pesticides. They attained the detection limits of ca. 0.6 pg for 2,4-D and Dicamba.

Wu, Lee, and Li[9] described a new method for the determination of ultra-trace levels of 12 *N*-methylcarbamates in drinking water via micellar electrokinetic chromatography (MEKC). The detection sensitivity was increased by first preconcentrating the sample using a C-18 bonded SPE cartridge and then further enriched through on-column stacking. This method permited separation and the UV detection of *N*-methylcarbamates at the 0.1-ppb level. The developed method for the determination of carbamates in drinking water was convenient and rapid and consumes practically no organic solvent.

In another approach, Loos and Niessner[10] investigated solid-phase extraction (SPE) with the styrene-divinylbenzene adsorbent LiChrolut EN for the extraction of the *s*-triazine herbicides atrazine and terbutylatrzine, their polar N-dealkylated degradation products deethylatrazine (DEA), disopropylatrazine (DUI) and ethylterbutylatrazine (DET), and for the hydrophilic hydroxytriazine degradation products (HTDPs) hydroxyatrazine (HA), hydroxyterbutylazine (HT), deethylhydroxyatrazine (DEHA), disopropylhydroxyatrazine (DMA), and diethyldisopropylhydroxyatrazine (ameline). Atrazine, terbutylazine, DEA, DIA, and DET were quantitatively extracted by LiChrolut EN. The chlorotriazines were analyzed by GC-MS and the HTDPs by capillary zone electrophoresis (CZE) and micellar electrokinetic capillary chromatography (MECC) (Figures 19, 20, 21). The combined method of SPE enrichment and CE analysis allows the determination of HTDPs in the low μg/l range.

C. Chiral Separations

About 25% of the compounds used in the agrochemical industry contain chiral centers and are produced and used as racemic mixtures. These compounds usually show enentiomeric selectivity, with biological activity generally residing in only one of the enantiomers. In addition, when racemic mixtures are applied, they often are degraded in the environment at different rates. The enantioselective phenomenon has important implications in the manufacture and the use of chiral agrochemicals. Thus, the separation and identification of the desired isomer is essential during the discovery of such compounds and also to support a product through development, registration, and production (quality assurance).

Capillary electrophoretic techniques for the separation of enantiomers were reviewed by Gubitz and Schmid.[11] In this review the separation principles and the chiral recognition mechanism were discussed, and a comprehensive collection of applications to drugs, pesticides, and other compounds of interest is reported in the form of tables.

Penmetsa, Leidy, and Shea[12] applied cyclodextrin-modified capillary zone electrophoresis (CD-CZE) to the enantiomeric and isomeric separation of three herbicides (imazaquin, diclofop, and imazamethabenz) shown in Figure 22. The enantiomers of imazaquin and diclofop, and the isomers of imazamethabenz could be resolved with a resolution of greater than or equal to 1.5 under the optimum conditions (Figure 23). When mixed cyclodextrins were used in the running buffer, the three herbicides were simultaneously separated in a single run (Figure 24). In addition, rapid (less than 3 min) enantiomeric separation was demonstrated using imazaquin as a model herbicide (Figure 25).

Desiderio et al.[13] used vancomycin as a chiral selector for the enantiomeric separation of several free acid herbicides, namely, aryloxypropionic (mecoprop, fenoprop, and dichlorprop), *N*-benzoyl-*N*-(3-chloro-4-fluorophenyl)-2-aminopropionic acid (flamprop) and aryloxyphenoxypropionic (haloxyfop, fluazifop, diclofop, and fenoxaprop) (Figure 26). The partial filling method was used in order to increase the sensitivity of the electrophoretic method; vancomycin was not present in the detector path during the detection due to its positive charge and to the absence/reduction of the electroosmotic flow at the operating pH. The pH, the

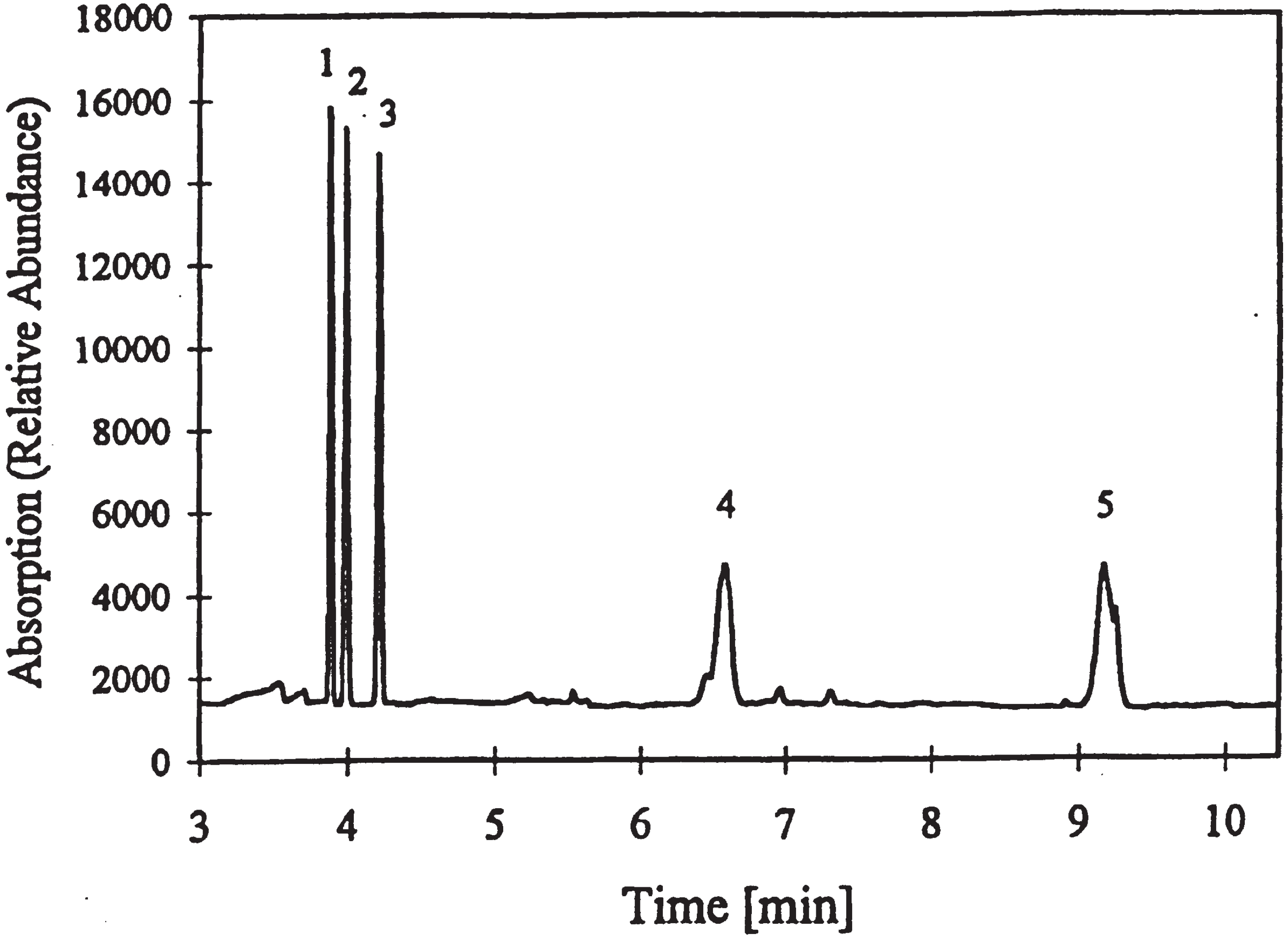


FIGURE 19. Electropherogram of compounds OH-triazines mixture containing 5 mg/l of each compound. Conditions running electrolyte 30 m*M* sodium borate- 30 m*M* SDS, pH 9.3, capillary 60 cm (50 cm to detection window) × 75 μm I.D., voltage 20 kV, temperature 30°C pressure injection 50 mbar for 12 s. UV detection at 210 nm. Peaks: 1= DIHA, 2= DEHA, 3 = ameline, 4 = HA, 5 = HT. (Reproduced with permission from Reference 10.)

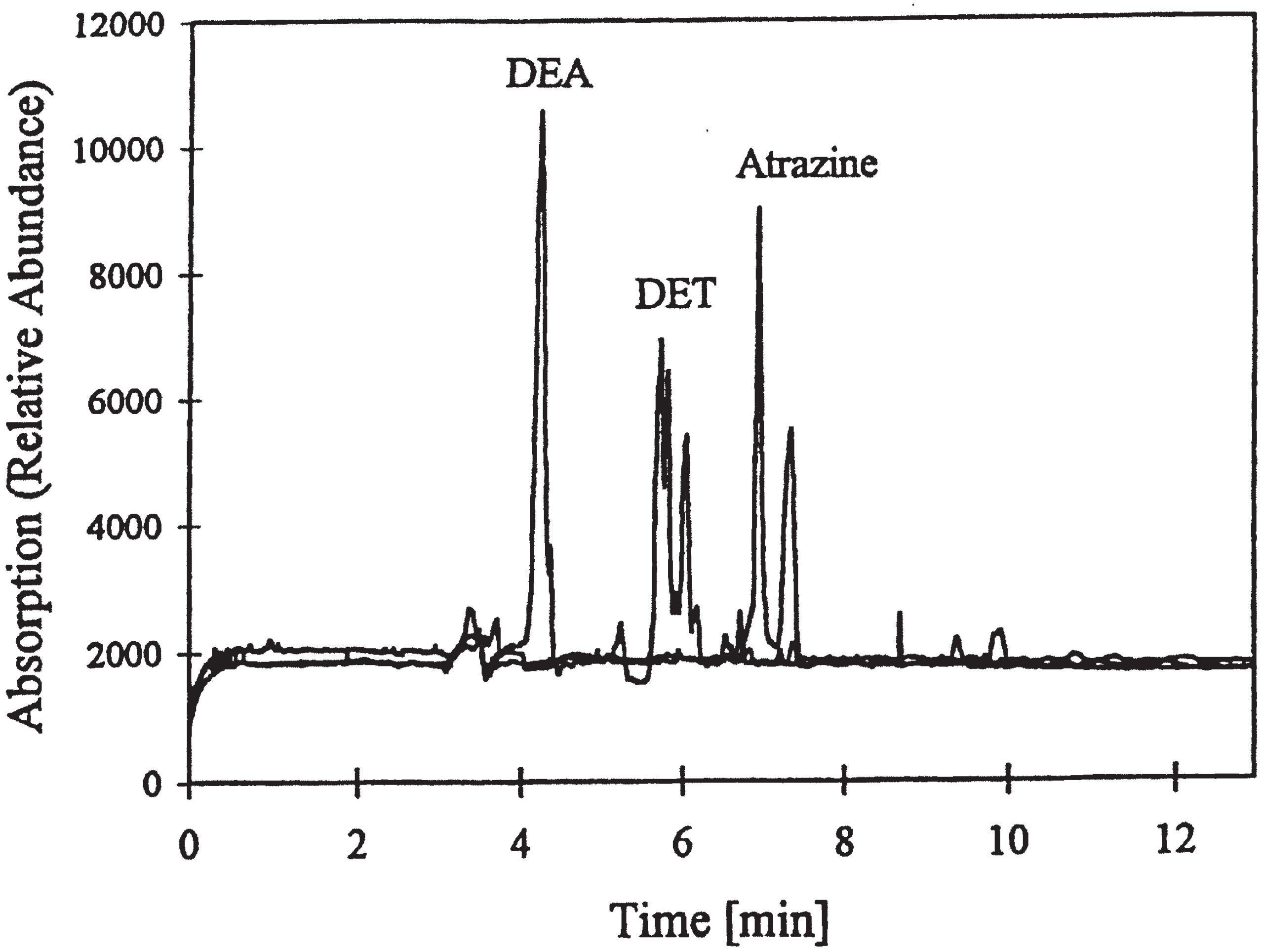


FIGURE 20. Electropherogram of chlorotriazines. Conditions same as in Figure 19. (Reproduced with permission from Reference 10.)

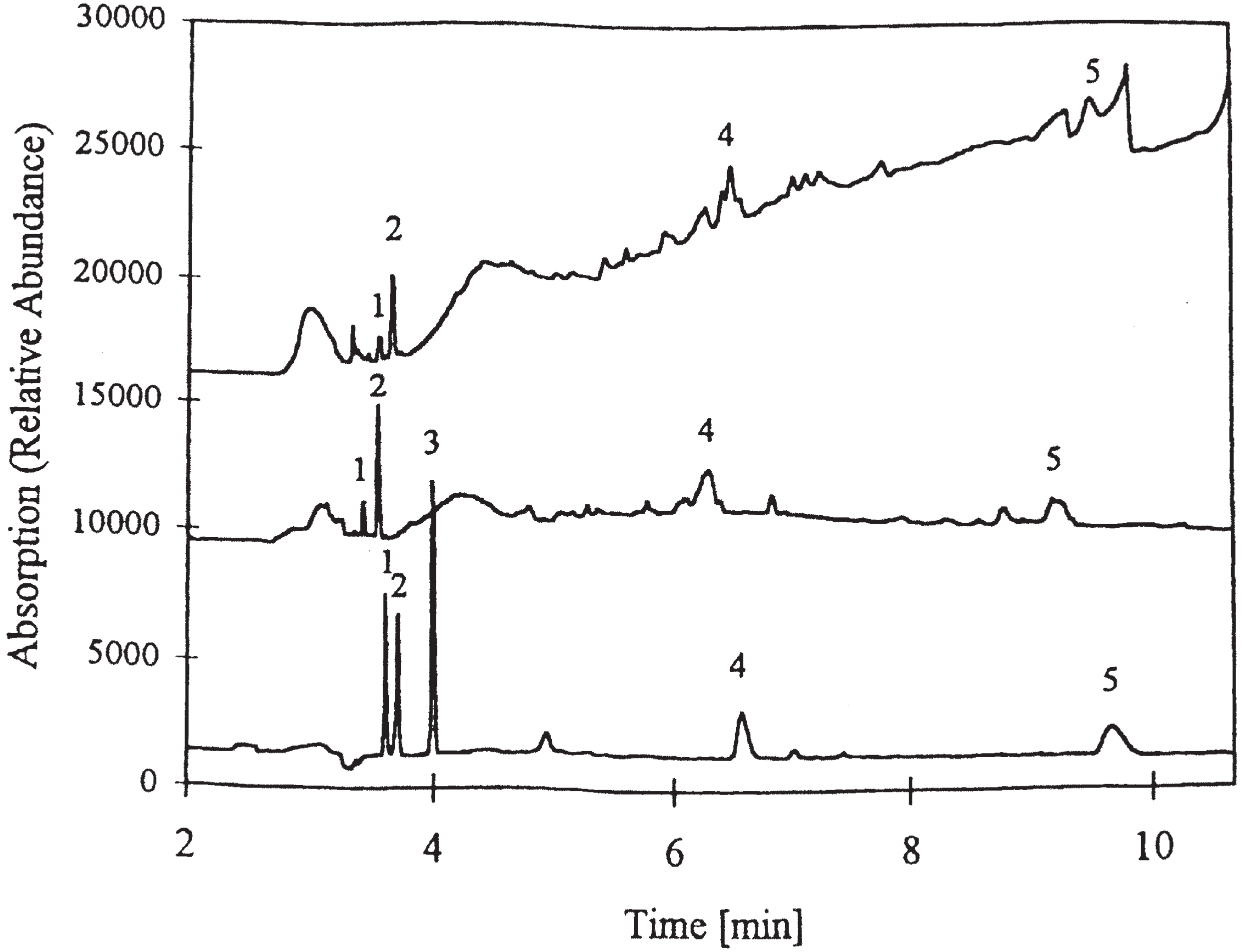
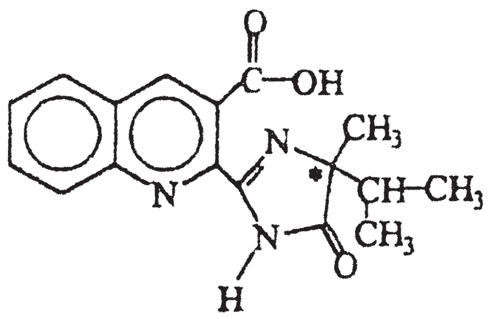
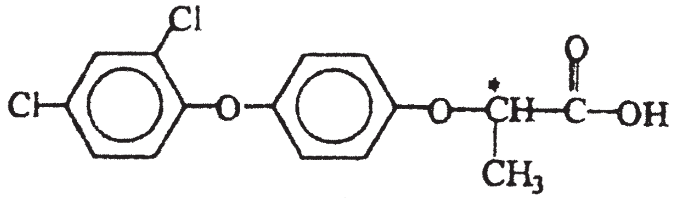


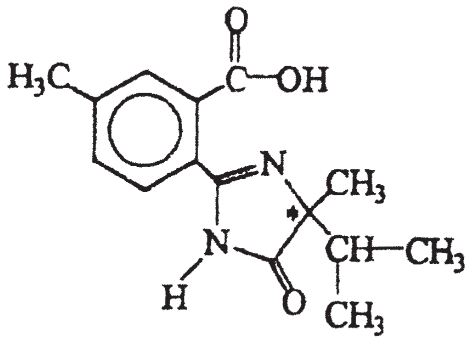
FIGURE 21. Electropherogram of OH-triazines spiked (2 µg/l) tap and river Isar water samples after SPE with LiChrolut EN (Enrichment factor 2000.) Conditions same as in Figure 19. Peaks: 1 = DIHA, 2 = DEHA, 3 = ameline, 4 = HA, 5 = HT. (Reproduced with permission from Reference 10.)



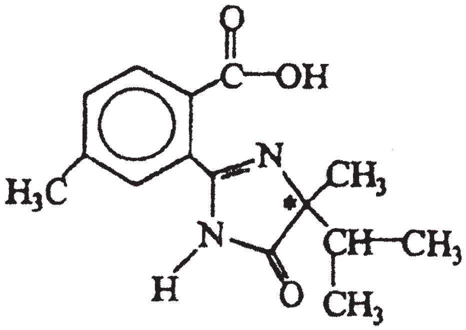
Imazaquin



Diclofop



Imazamethabenz (*m* - isomer)



Imazamethabenz (*p* - isomer)

FIGURE 22. Structure of herbicides; chiral center is indicated with an asterisk (*). (Reproduced with permission from Reference 12.)

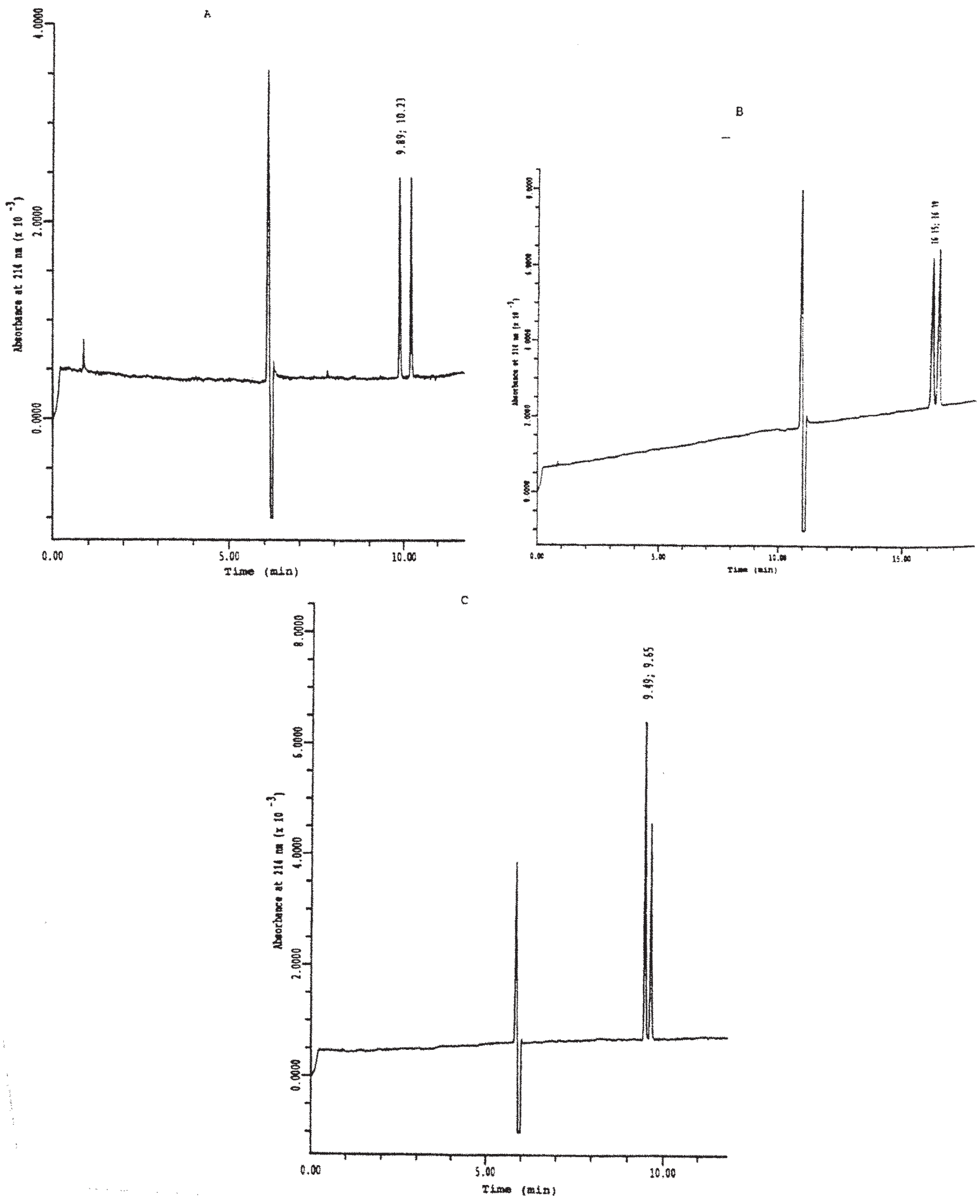


FIGURE 23. Separation of (A) imazaquin enantiomers, (B) diclofop enantiomers, and (C) Imazamethabenz isomers (9.49 min, para and 9.65 min, meta isomers). Analysis conditions: 57 cm (50 cm to detector) × 50 μm I.D. capillary column; pressure injection (2 s = 2.4 nl); 25 kV (35 μA); 214 nm UV absorbance. Buffer: (A) 50 m*M* sodium acetate + 10 m*M* DM-β-CD buffer, pH 4.6; (B) 50 m*M* sodium acetate + 10 m*M* TM-ß-CD buffer, pH 3.6; (C) 50 m*M* sodium acetate + 10 m*M* TM-ß -CD buffer, pH 4.6. (Reproduced with permission from Reference 12.)

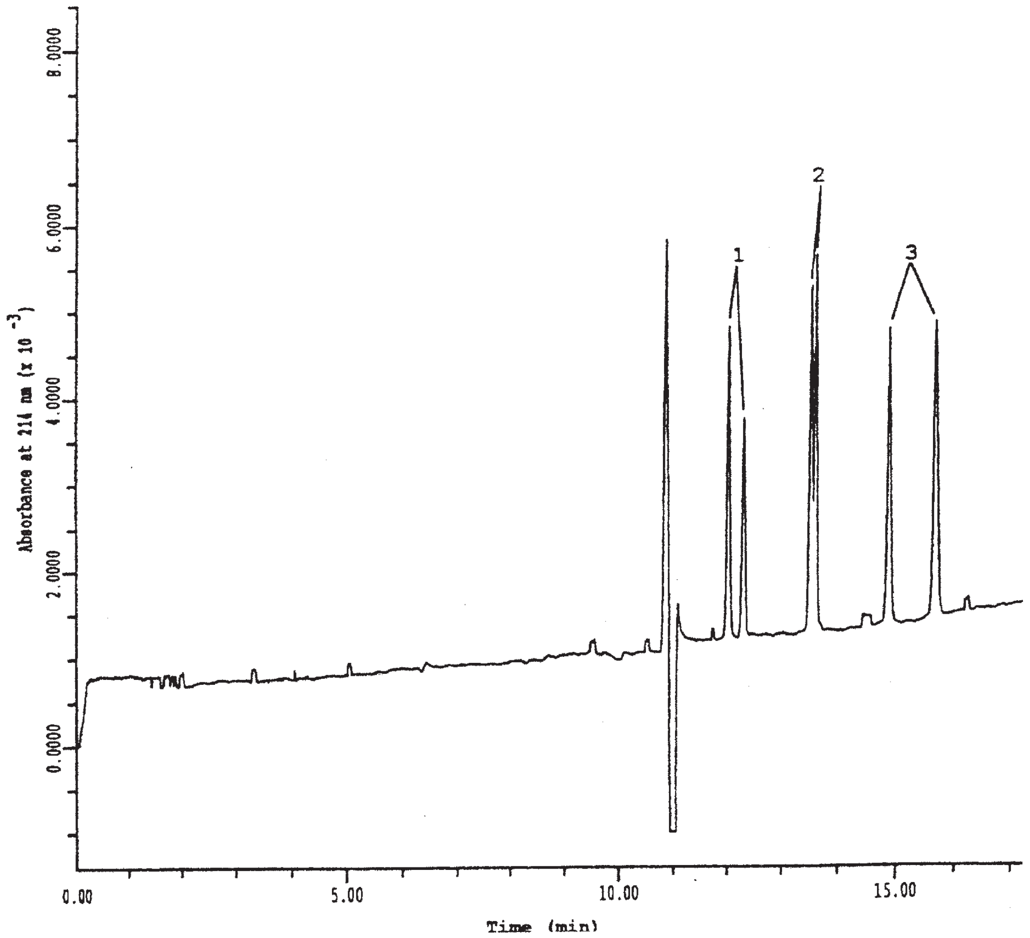


FIGURE 24. Simultaneous separation of herbicides using mixed cyclodextrins. (1) Imazamethabenz isomers (2) diclofop enantiomers and (3) imazaquin enentiomers. Analysis conditions: 57 cm (50 cm to the detector) x 50 µm I.D. capillary column; pressure injection (2 s = 2.4 nl); 50 m*M* sodium acetate + 10 m*M* DM- -CD + 10 m*M* TM-ß-CD buffer, pH 3.6; 25 kV (35 µA); 214 nm UV absorbance. (Reproduced with permission from Reference 12.)

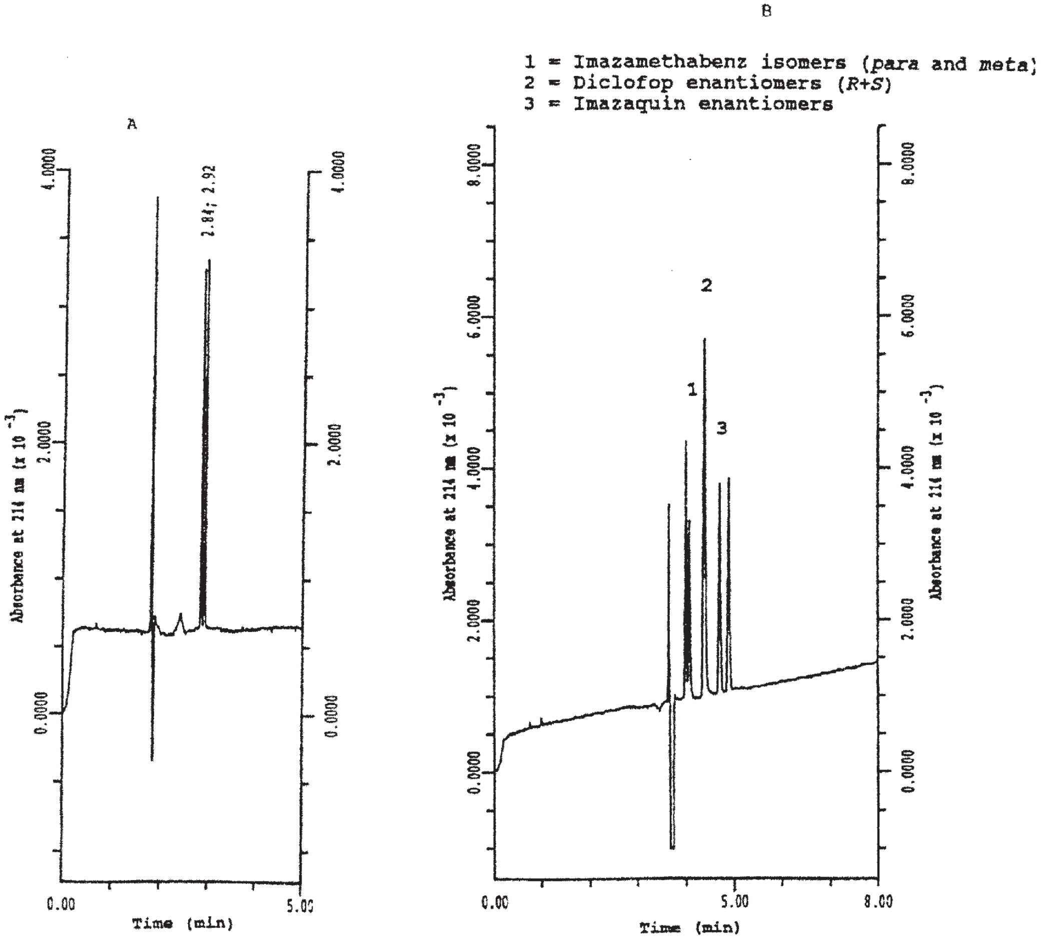
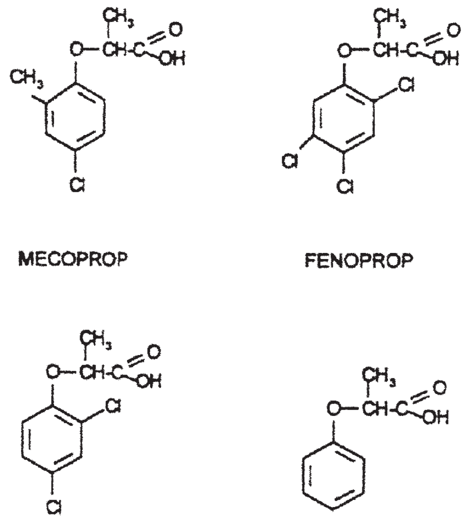


FIGURE 25. Rapid separation of imazaquin and (B) rapid simultaneous separation of the three herbicides. Analysis conditions: 27 cm (20 cm to detector) × 50 µm I.D. capillary column pressure injection (1 s = 2.4 nl); 12 kV; 214 nm UV absorbance. Buffer (A) 50 m*M* sodium acetate + 10 mM DM- ß -CD, pH 4.6 and (B) 50 m*M* sodium acetate + 10 m*M* DM-ß-CD+ 10 m*M* TM-ß-CD, pH 3.6. (Reproduced with permission from Reference 12.)

Aryloxy propionic acid herbicides



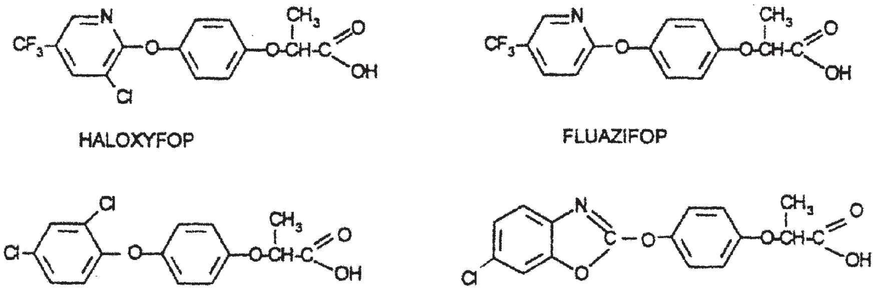
MECOPROP

FENOPROP

DICHLORPROP

2-PHENOXY PROPIONIC ACID

Aryloxyphenoxypropionic acid herbicides



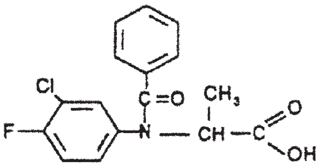
HALOXYFOP

FLUAZIFOP

DICLOFOP

FENOXAPROP

Amino propionic acid derivative



FLAMPROP

FIGURE 26. Chemical structre of acid herbicides. (Reproduced with permission from Reference 13.)

capillary temperature, and the vancomycin concentration influenced both effective mobility and resolution of the studied compounds (Figures 27 and 28). The optimized CE method was tested for the analysis of haloxyfop free acid metabolite in a soil sample spiked with racemic haloxyfop ethoxyethyl ester solution. The metabolite was a mixture of R and S enantiomers where the R form was about 72% (peak areas ratio). The method showed good precision for both migration time and corrected peak areas with a detection limit of 5×10^{-7} *M*.

Otsuka et al.[14] developed an on-line coupling of capillary electrophoresis and mass spectrometry (CE-MS) to the chiral separation of phenoxy acid herbicide enantiomers (Figure 26). The direct coupling of CD-CZE with EST-MS was examined as a complementary technique to UV detection. Heptakis (2,3,6-tri-*O*-methyl)- β -cyclodextrin (TM- β-CD) was used as a chiral selector. By using the negative-ionization mode along with a methanol-water-formic acid solution as a sheath liquid and nitrogen as a sheath gas, stereoselective separation separation shown in Figure 29 and the detection of three phenoxy acid herbicide enantiomers were successfully achieved.

Mechref and Elrassi[15] evaluated two chiral alkylglucoside surfactants, namely, *n*-octyl-(OG) and *n*-nonyl- β-D-glucopyranoside (NG) (Figure 30), in the enantiomeric separation dichloroprop, fenoprop, and mecocrop phenoxy acid herbicides (Figure 31). The enantiomeric resolution can be achieved by adjusting the surfactant concentration, ionic strength, pH, and separation temperature. The optimum surfactant concentration needed for maximum enantiomeric resolution varied among the different analytes and was an inverse function of the hydrophobicity of the phenoxy acid herbicides, with the most hydrophobic solute requiring less surfactant concentration for attaining a baseline enantiomeric resolution (Figures 32 and 33). It was observed that higher pH and an increase in micellar concentration at subambient temperature gives better enantiomeric resolution.

D. Analysis of Pesticides in Environemntal Samples

The literature shows that CE has not been fully exploited for the analysis of the environmental pollutants. Most of the publications giving rapid separation of substances were not used to analyze them in real environmental samples. However, both separation and analysis clearly demonstrated the high potential of CE in this field.

Chlorinated carboxylic acid herbicides are the important environmental pollutants nowadays. Song and Budde[16] applied capillary electrophoresis electrospray negative ion mass spectrometry (CE-ENI-MS) for the determination of chlorinated acid herbicides and several phenols in water. Sixteen acid herbicides were separated (Figure 34) as their anions in less than 40 min with a buffer consisting of 5 m*M* ammonium acetate in isopropanol + water (2 + 3, by volume) at pH 10. A sample stacking technique was used to provide lower detection limits, and a fortified drinking water sample was made pH 10 and analyzed without further processing (Figure 35). Quantitative analyses using selected ion monitoring and internal standardization provided good recoveries and precision.

Chlorpyrifos (Figure 36), an organophosphorous insecticide, was determined by Guardino et al.[17] in air, leaves, and soil in a greenhouse in order to establish performance differences between gas-chromatography with nitrogen-phosphorus detection (GC-NPD) and high-performance liquid chromatographic and capillary electrophoretic methods and to assess the farm workers risk of overexposure due to air exposure and/or skin contact with this compound. Results obtained indicated that the three analytical techniques, with the specific procedures described, can be used, although only GC-NPD provides an operative limit of detection in air. Chlorpyrifos levels in air are dependent on time and greenhouse ventilation, and workers should not go into the greenhouse before complete green house ventilation and aeration whereas it remains for a long time on leaf surfaces and soil (Figures 37, 38, and 39). Air samples could be analyzed by the three instrumental techniques, but the differences in the limits of detection (LOD) (0.01, 0.2, and 1 mg m^{-3} for GC, HPLC, and CE, respectively) were observed. As a consequence, specific instructions can be established for farm workers in order to avoid skin and respiratory exposure to chlorpyrifos.

Analytical techniques were developed by Schmitt-Kopplin[18] in capillary zone electrophoresis (CZE) and capillary electrokinetic chromatog-

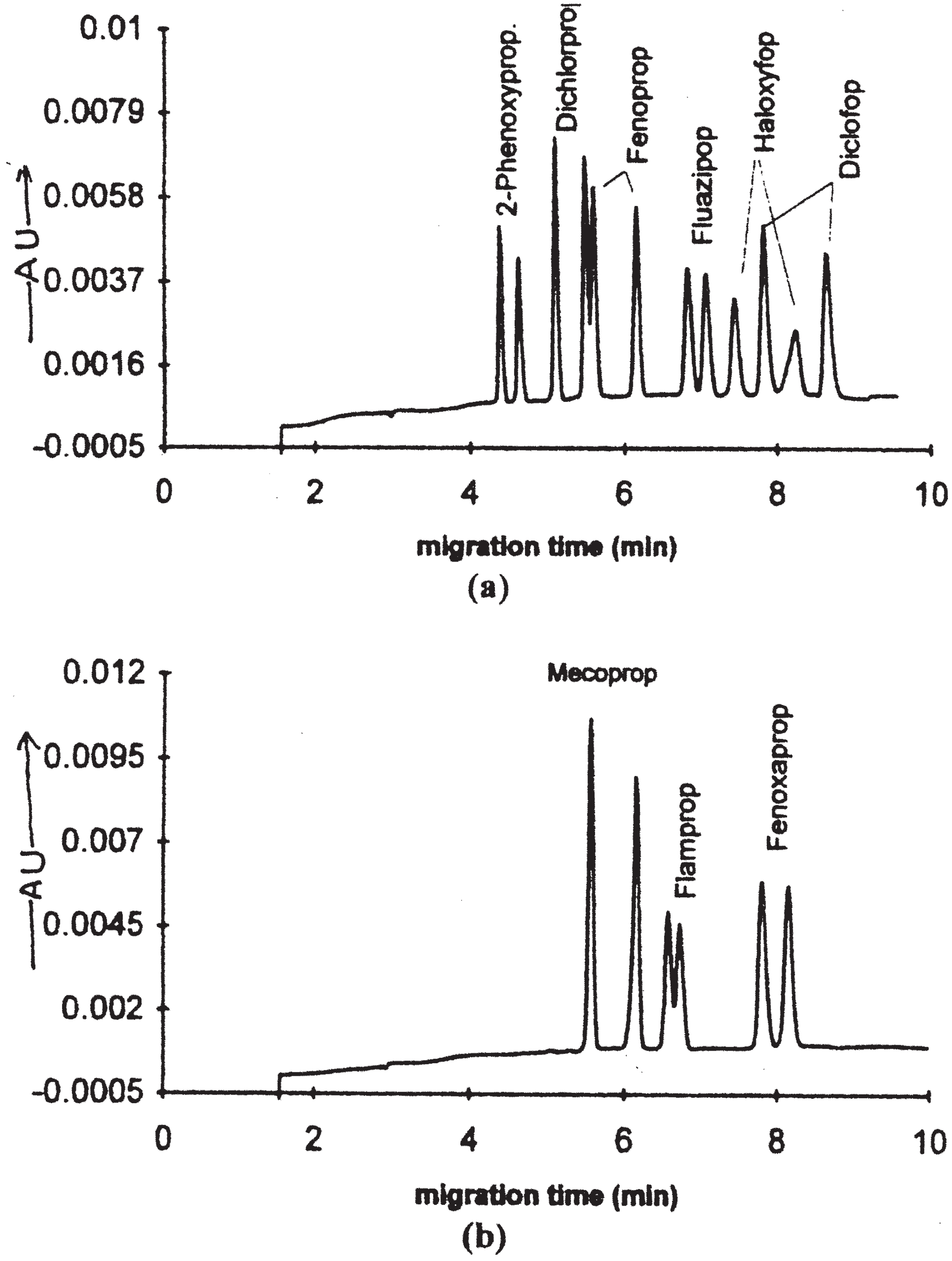


FIGURE 27. Electropherogram of the enenatiomeric separation of herbicides (a) 2 phenoxypropionic acid, dichloroprop, fenoprop, fluaziprop, haloxyfop and diclofop; (b) mecoprop, flamprop and fenoxaprop. Six mM of vancomycinn partial filling at 34.475 Pax30 s; applied voltage; 20 kV, 47 µA; analyte concentration was 10^{-4} *M* with exception of fenoprop and diclofop (5×10^{-5} *M*) and 2-phenoxypropionic acid (2×10^{-4} *M*). (Reproduced with permission from Reference 13.)

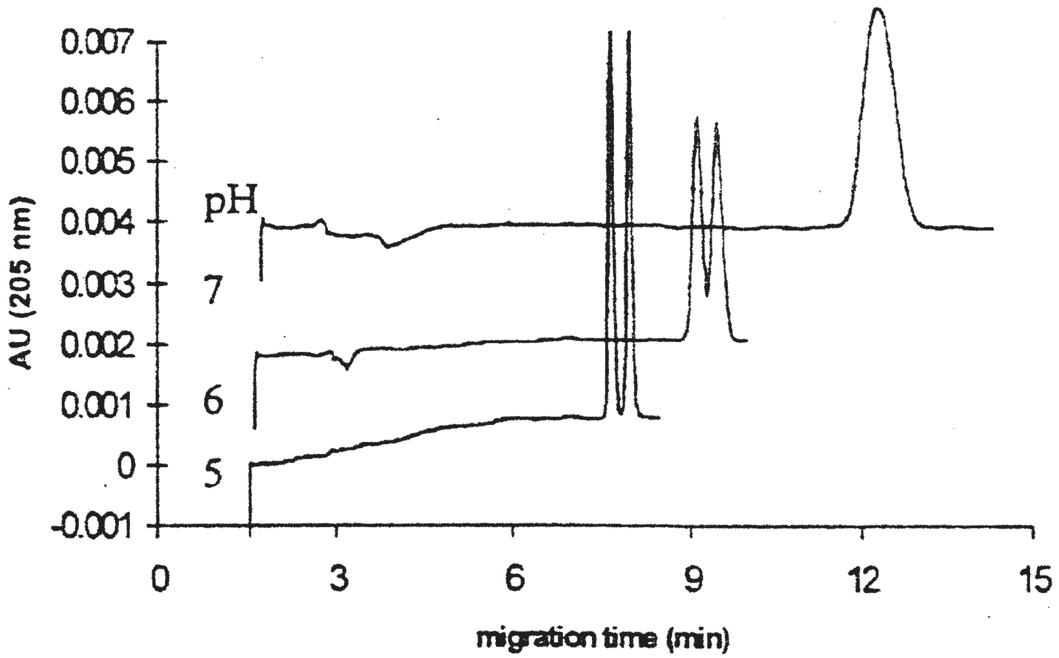


FIGURE 28. Electropherogram of fenoxaprop enenatiomeric separation at pH 5, 6, and 7. Background electrolyte, 75 mM Britton-Robinson buffer containing 6 m*M* of vancomycin; analyte concentration 10^{-4} *M*, applied voltage 20 kV, 47–72 μA and 25°C. (Reproduced with permission from Reference 13.)

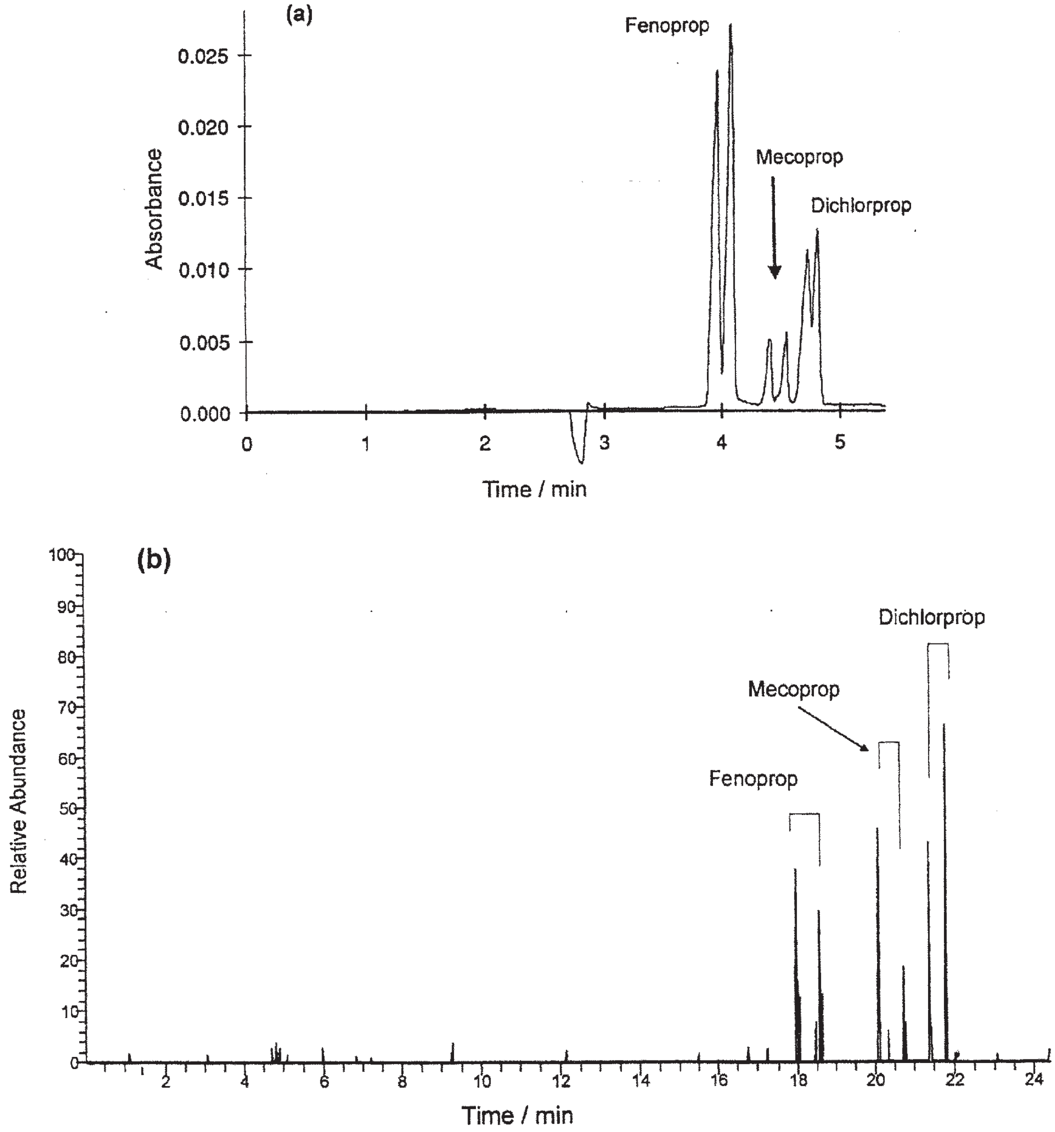


FIGURE 29. Enantioseparation of fenoprop, mecoprop, and dichlorprop by CD-CZE-ESI-MS with TM-β-CD. (a) UV electropherogramb (b) reconstructed masspherogram. CE conditions: separation solution, 20 m*M* TM-ß-CD in 50 m*M* ammonium acetate (pH 4.6); capillary 50 μm I.D. × 375 μm O.D., 980 mm in total length, 200, mm in UV effective; total applied voltage, 27.5 kV (net voltage applied across the capillary 30.5 kV); current, 16 μA; sample concentration, ca. 10^{-4} *M* each in acetonitrile. MS conditions: masspherogram reconstructed at m/z = 213 ± 0.5, 233 ± 0.5, and 267 ± 0.5. ESI capillary temperature, 250°C, sheath gas, nitrogen at 20 in an arbitrary value given by LCQ software. (Reproduced with permission from Reference 14.)

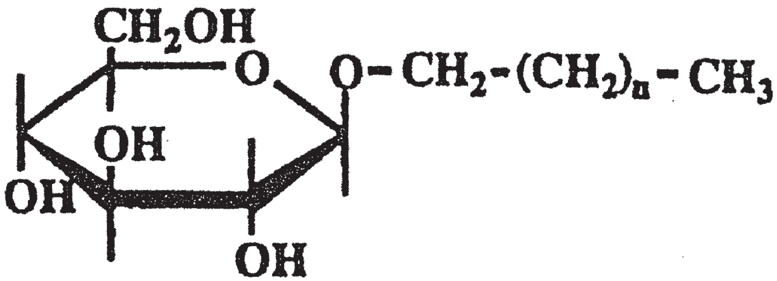
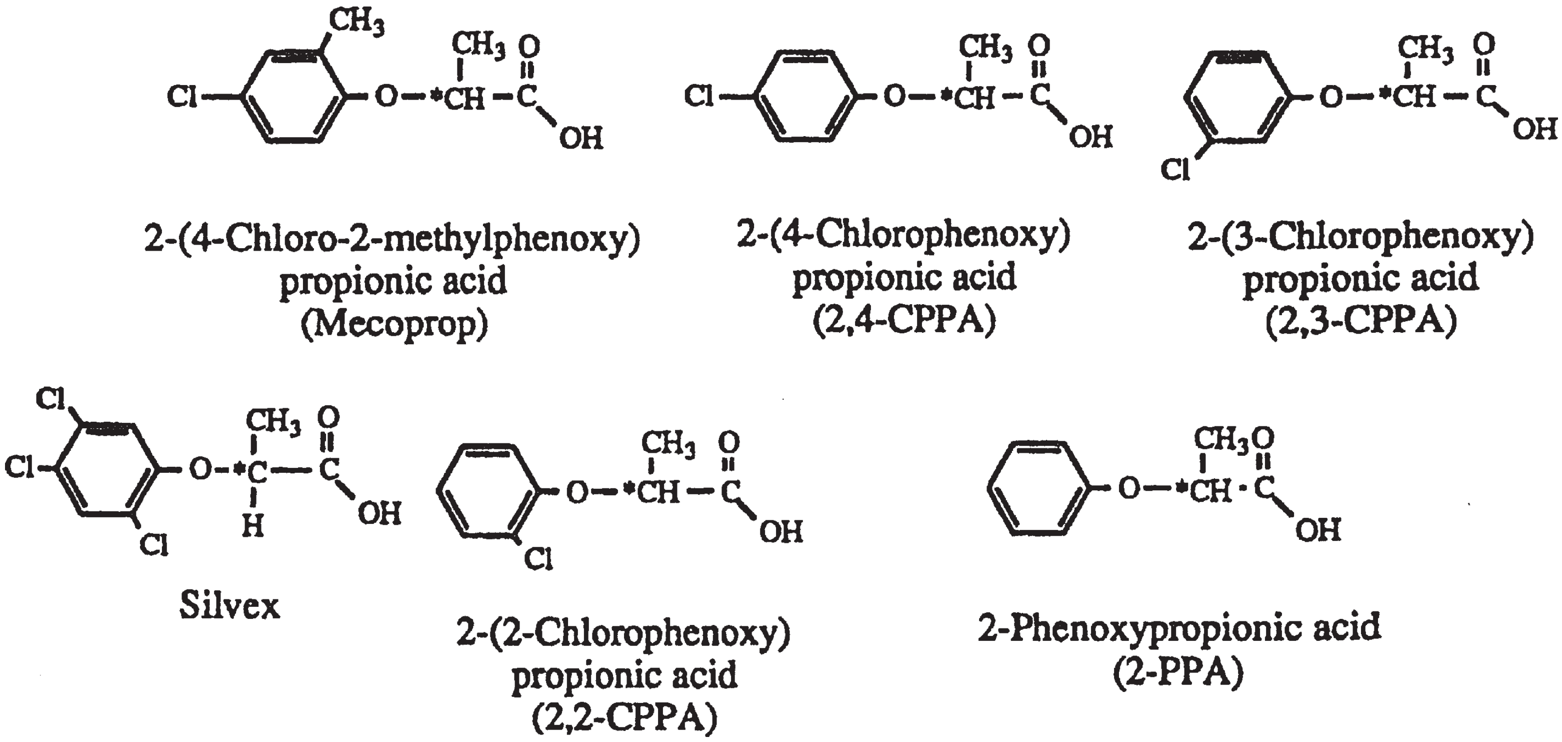
Structure and name of surfactant	Abbreviation
	
$n=6$: Octyl-β-D-glucopyranoside	OG
$n=7$: Nonyl-β-D-glucopyranoside	NG

FIGURE 30. Structure of the alkylglucopyranosides. (Reproduced with permission from Reference 15.)



2-(4-Chloro-2-methylphenoxy)
propionic acid
(Mecoprop)

2-(4-Chlorophenoxy)
propionic acid
(2,4-CPPA)

2-(3-Chlorophenoxy)
propionic acid
(2,3-CPPA)

Silvex

2-(2-Chlorophenoxy)
propionic acid
(2,2-CPPA)

2-Phenoxypropionic acid
(2-PPA)

FIGURE 31. Structure of the phenoxy acid herbicides. (Reproduced with permission from Reference 15.)

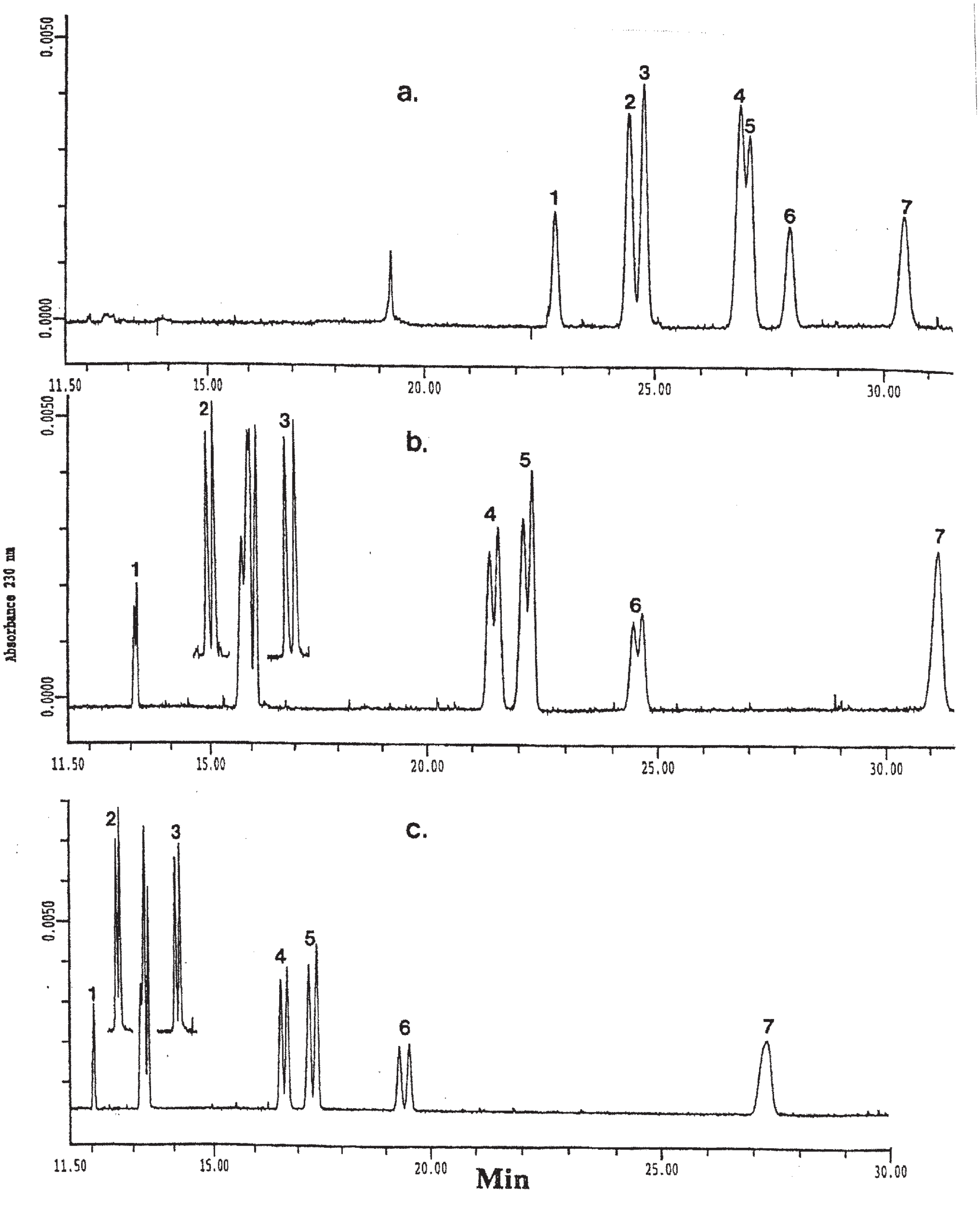


FIGURE 32. Electropherogram of phenoxy acid herbicides depicting the effect of OG concentration on enantiomeric resolution. Conditions running electrolyte, 200 mM sodium phosphate, pH 6.5, containing: (a) 10 m*M* OG, (b) 60 m*M* OG and (c) 150 m*M* OG; capillary, 57 cm (50 cm to to detection window) × 50 µm I.D.; voltage, 20 kV; temperature 15°C. Peaks: 1 = silvex, 2= dichlorprop, 3 = mecoprop, 4 = 2, 4-CPPA, 5 = 2,3-CPPA, 6 = 2,2-CPPA, 7 = 2-PPA. (Reproduced with permission from Reference 15.)

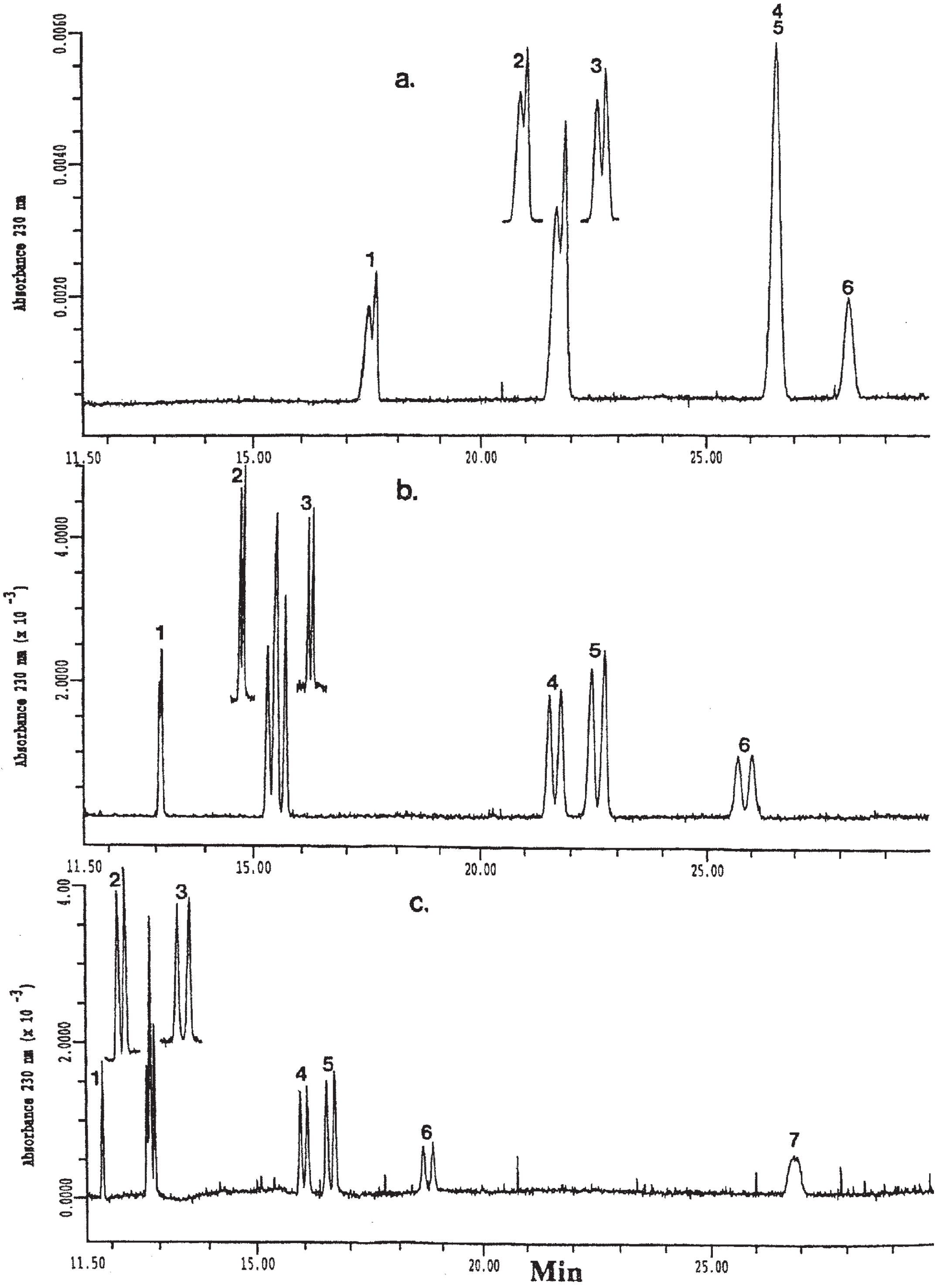


FIGURE 33. Electropherogram of phenoxy acid herbicides depicting the effect of NG concentration on enantiomeric resolution. Conditions running electrolyte, 200 m*M* sodium phosphate, pH 6.5, containing: (a) 10 m*M* NG, (b) 60 m*M* NG, and (c) 150 m*M* OG; capillary, 57 cm (50 cm to to detection window) × 50 μm I.D.; voltage, 20 kV; temperature 15°C. Peaks: 1 = silvex, 2 = dichlorprop, 3 = mecoprop, 4 = 2, 4-CPPA, 5 = 2,3-CPPA, 6 = 2,2-CPPA, 7 =2-PPA. (Reproduced with permission from Reference 15.)

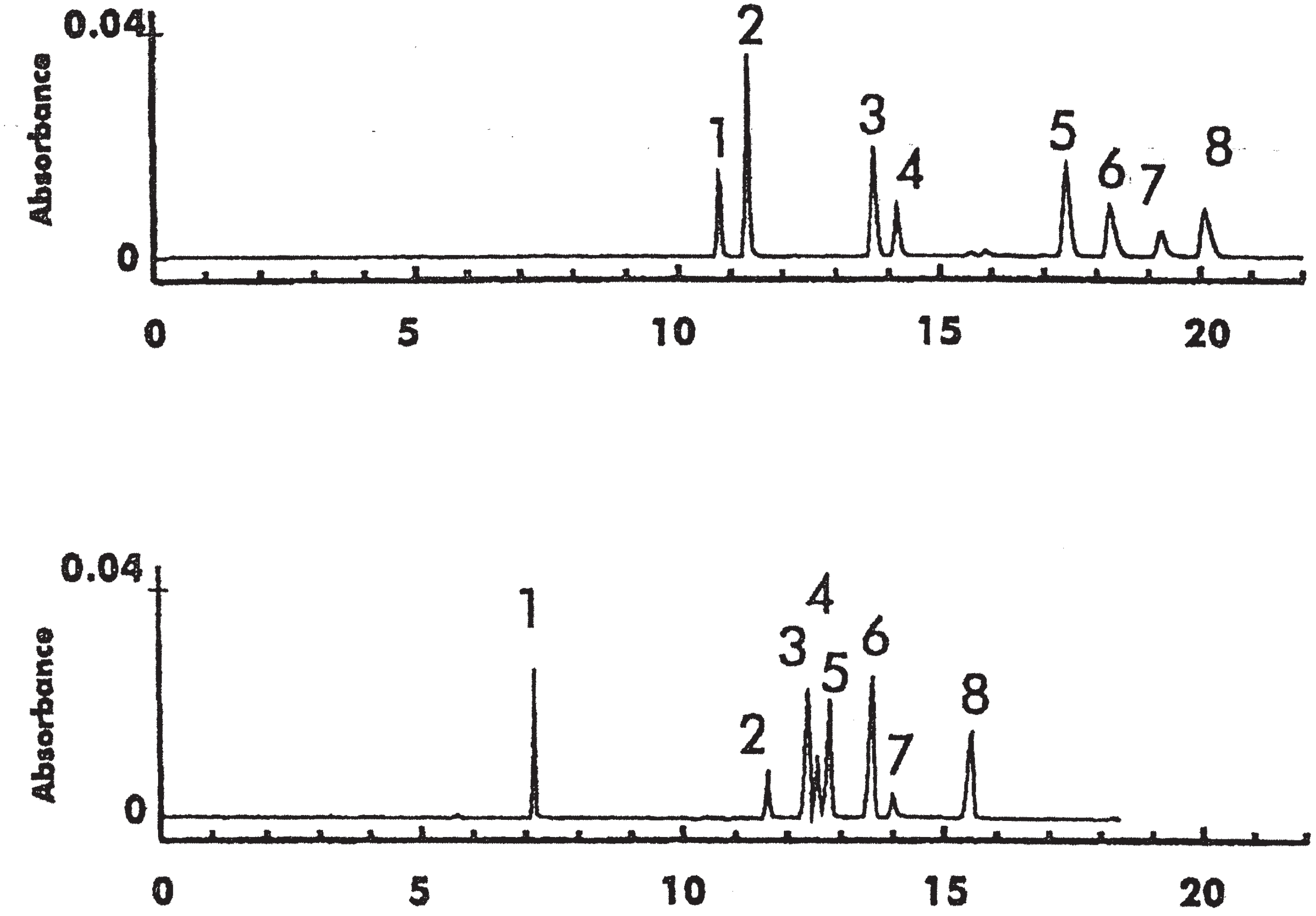


FIGURE 34. The upper electropherogram shows the separation of the eight group A compounds with UV detection: 1 = dicamba; 2 = picloram; 3 = chloramben; 4 = acifluorfen; 5 = bentazon; 6 = 2,4-D; 7 = 2,4,5-TP; 8 = dichlorprop. The lower electropherogram shows the separation the group B compounds: 1 = 4 —nitrophenol; 2 = 2,4-DB; 3 = MCPP; 4 = dinoseb; 5 = 2,4,5-T; 6 = MCPA; 7 = pentachlorophenol; 8 = 3,5 dichlorobenzoic acid. Time scale in min. (Reproduced with permission from Reference 16.)

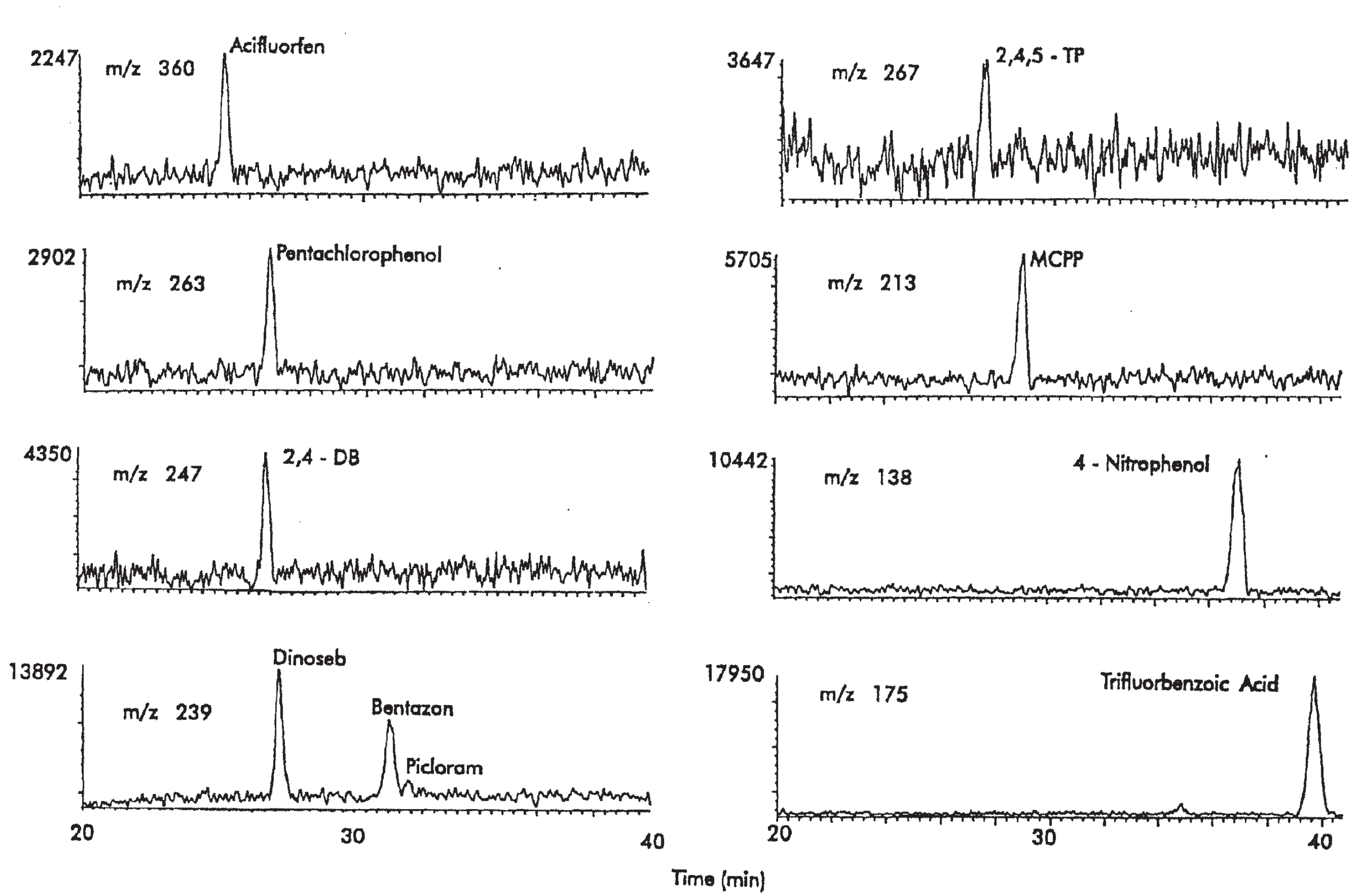


FIGURE 35. Selected ion electropherogram from the CE separation of nine of the analytes at the concentration of 50 µg/l and the internal standard at 250 µg/l with sample stacking on the CE column. (Reproduced with permission from Reference 16.)

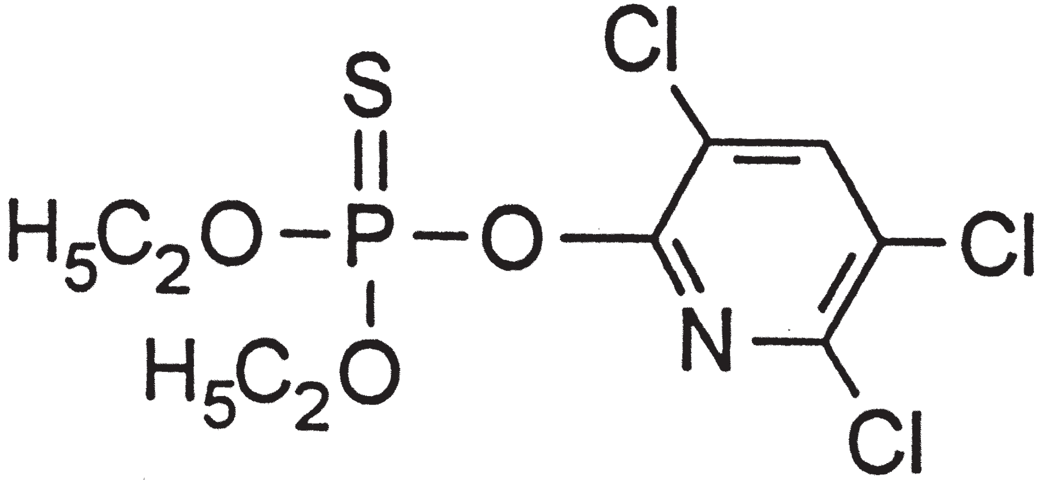


FIGURE 36. Structure of the chlorpyriphos. (Reproduced with permission from Reference 17.)

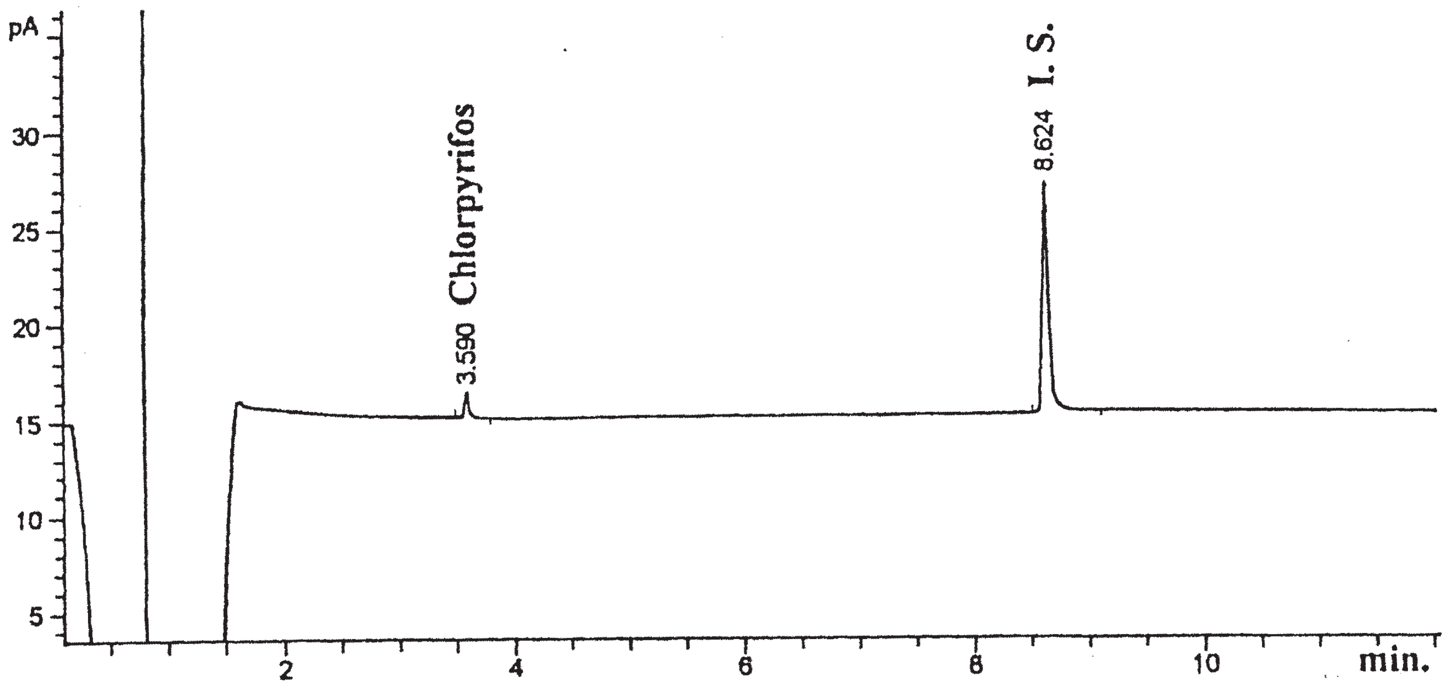


FIGURE 37. GC chromatogram of an air sample. (Reproduced with permission from Reference 17.)

raphy (CEKC) for the analysis of fluoroquinolone carboxylic acids (norfloxacin, ciprofloxacin, ofloxacin, enrofloxacin, danofloxacin) and their major degradation products. The charge densities were determined theoretically, and this formed the basis for the rapid development of the separation of the buffer system Enrofloxacin was determined by two CE methods with and without humic substances under natural sunlight conditions. The presence of humic substances in irradiated solution caused changes in the measured photodegradation product profile. Studies in affinity capillary electrophoresis (ACE) of enrofloxacin and its degradation products with the dissolved humic acids showed a lower adsorption potential of enrofloxacin to the humic phase than the degradation products. The adsorption of some photodegradation products to the dissolved humic matrix may explain the differences in the measured photodegradation products concentration in irradiated solutions. ACE turned out to be a rapid screening tool for the comparison of the adsorption potential of active ingredients and their degradation products to dissolved organic phases using very small amounts of sample.

Farran et al.[19] analyzed 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) herbicides by capillary electrophoresis (CE) by means of capillary zone electrophoresis (CZE) and micellar electrokinetic capillary chromatography (MECC). The CE separation of 2,4-D and MCPA in the presence of an organic modifier (acetonitrile), the use of a micellar system (sodium cholate), and the addition of different cyclodextrins. The use of acetonitrile resulted in the total separation of both herbicides in 15 min but with low efficiency and reproducibility values. On the other hand, the use of a micellar system solved the reproducibility problem but resulted in poor efficiency. Finally, when using α, β, or γ-cyclodextrins selectivity differences were observed, and the best results were obtained with the use of α-cyclodextrin. In this case, 2,4-D and MCPA were completely resolved with a high efficiency in less than 5 min.

E. Capillary Electrophoretic Separations

Tsai, Chen, and Her[20] used normal and reversed electroosmotic flow (EOF) capillary electrophoresis (CE) for the analysis of eight triazine herbicides (Figure 40). Reversed electro-osmotic flow capillary electrophoresis (EOF-CE), dynamically modified with cetyltrimethylammonium bromide (CTAB), provided better separation than normal CE. All eight triazines were baseline resolved under the optimum conditions (Figure 41). A sheath liquid was used in the on-line coupling of CE with electrospray mass spectrometry. The composition of the sheath liquid was found to be critical in the coupling of reversed EOF CE with MS. The resolution obtained in CE-UV can be preserved in CE-MS if the composition of the sheath liquid was similar to the running buffer (Figure 42). Although baseline resolution was not obtained with normal CE, the use of ESI-MS as the on-line detection method improved the quality of the compound identification. Reversed EOF CE-MS provided a better result than normal EOF CE-MS. Under these conditions triazines were identified both in retention time and in molecular mass. The composition of sheath liquid was more critical in reverse EOF CE-MS than in normal EOF CE-MS.

Fukumoto and Watarai[21] separated (structure of the pesticides shown in Figure 43) four kinds of pesticides 2-methyl-4-chlorophenoxyacetic acid, *o*,*o*-dimethyl-*o*-(3-methyl-4-nitrophenyl)-thiophosphate, *S*-benzyl di-iso-propylphosphorothiolate, and pentachloronitroben-zene (MCP, MEP, IBP, and PCNB) using capillary electrophoresis with some oil in water (o/w) microemulsions (μE-CE). In order to obtain information concerning the separation and/or migration mechanism μE-CE was carried out (Figures 44 and 45). The longest migration time for MCP was found in the case of surfactants with a sulfonate group, while the use of ones with a sulfate group led to the shortest migration time for MCP. The characteristic effect of the surfactants on the migration of MCP suggested a specific interaction with the interface of the microemulsion droplets. ^{31}P NMR (phosphorus nuclear magnetic resonance) measurement was carried out to get more detailed information about the microenvironment of the organophosphorus pesticides incorporated into the microemulsion. It was found that adsorption on the interface of the droplet contributed to a predominant interaction between the microemulsion and MEP, while in IBP the distribution into the droplet played an important role (Figures 46 and 47).

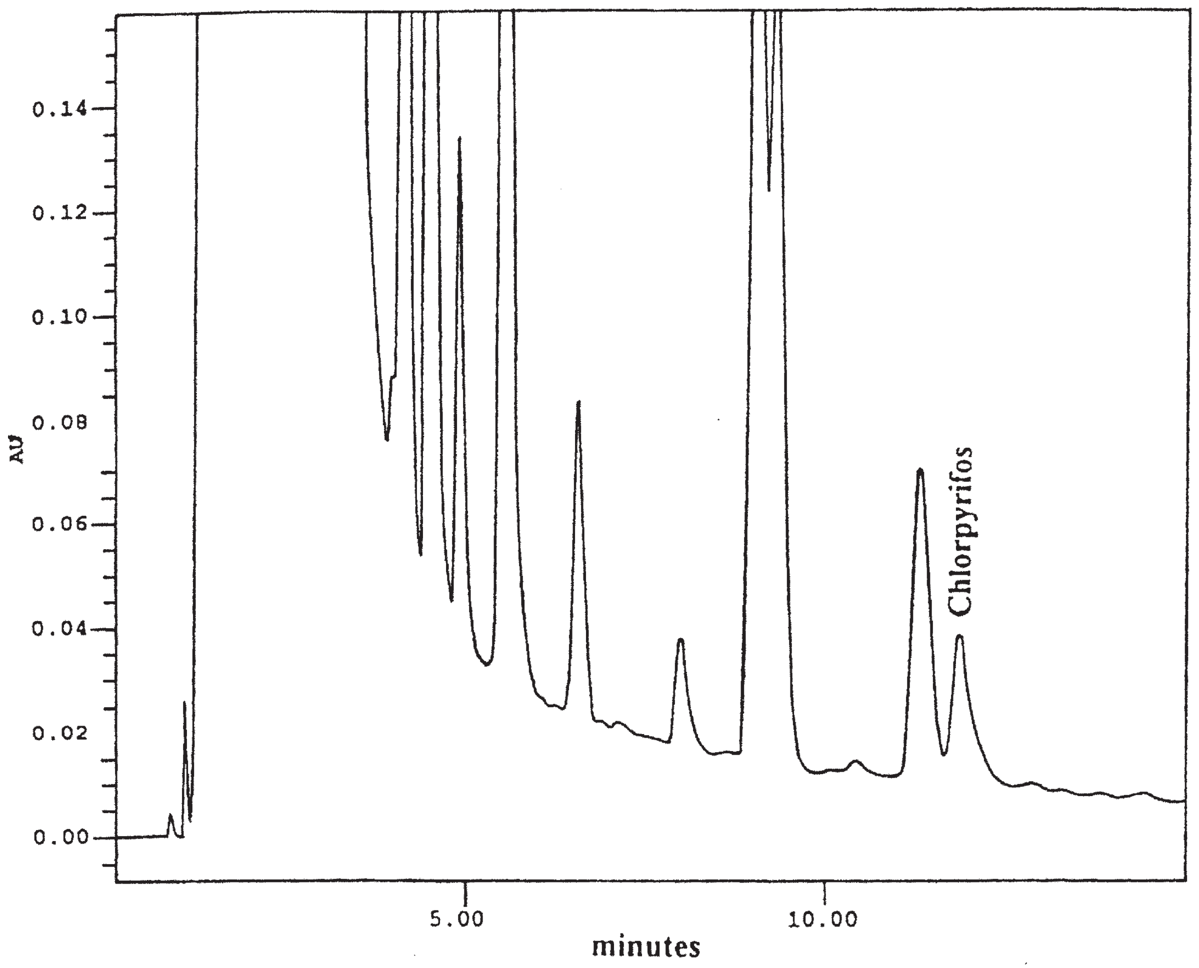


FIGURE 38. HPLC chromatogram of a leaf sample. (Reproduced with permission from Reference 17.)

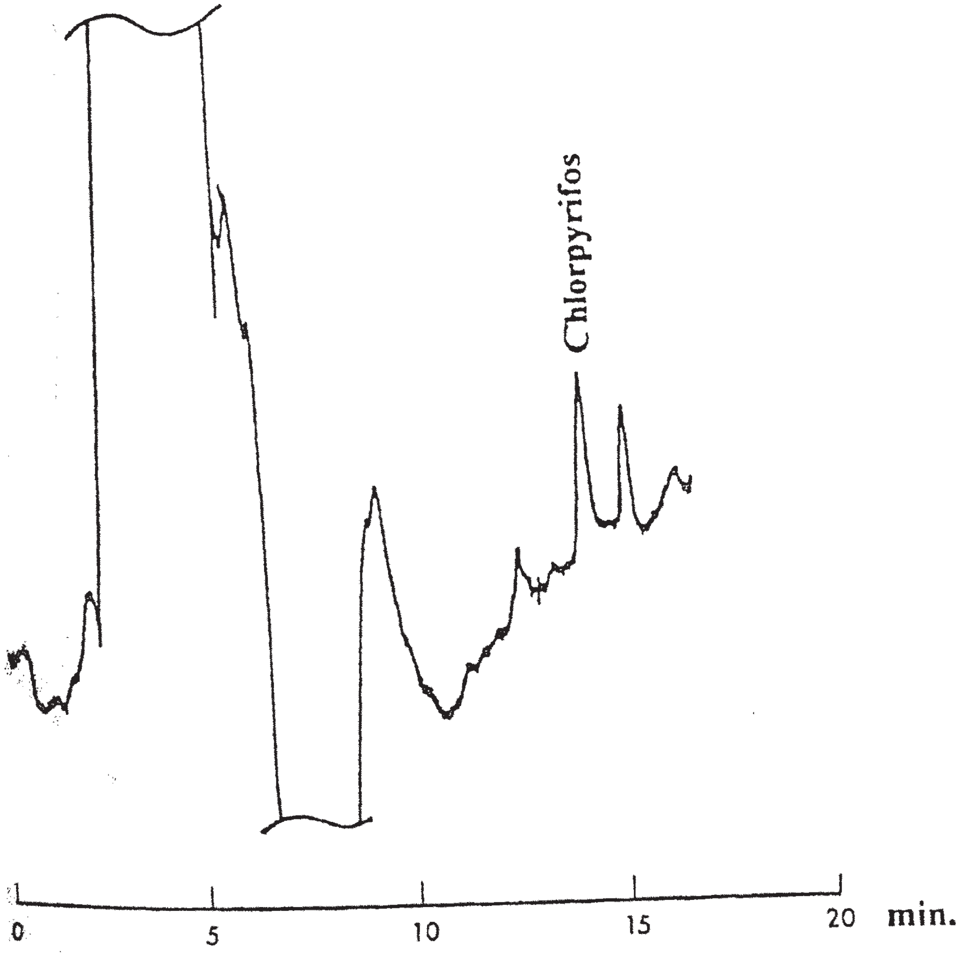
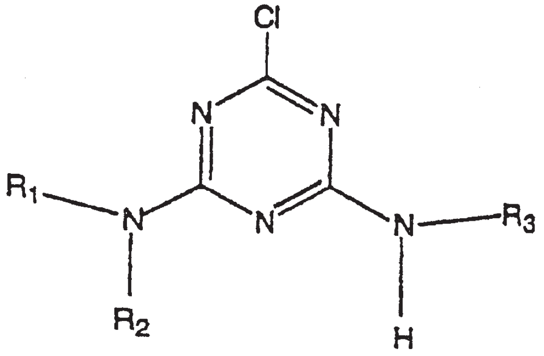
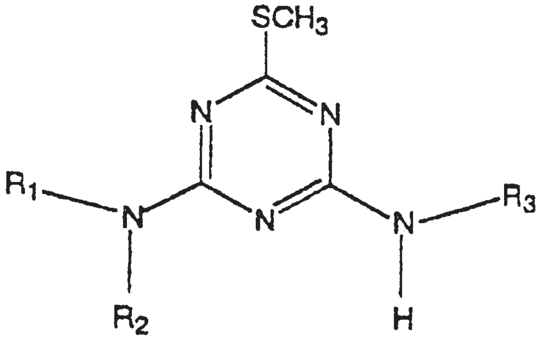


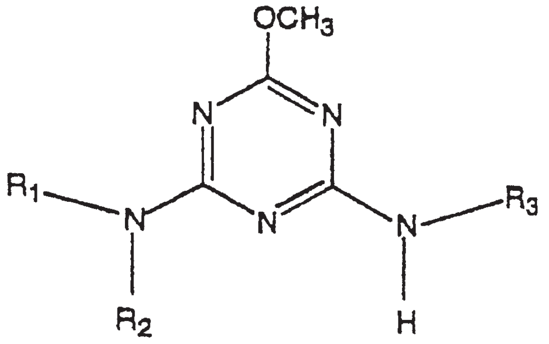
FIGURE 39. CE electropherogram of a soil sample. (Reproduced with permission from Reference 17.)



	R_1	R_2	R_3
Simazine	H	Et	Et
Atrazine	H	Et	*i*-Pr
Propazine	H	*i*-Pr	*i*-Pr



	R_1	R_2	R_3
Ametryn	H	Et	*i*-Pr
Prometryn	H	*i*-Pr	*i*-Pr
Terbutryne	H	Et	*t*-Bu
Simetryn	H	Et	Et



	R_1	R_2	R_3
Prometon	H	*i*-Pr	*i*-Pr

FIGURE 40. Structures of triazines. Et = Ethyl; i-Pr = isopropyl; t-But = tert-butyl. (Reproduced with permission from Reference 20.)

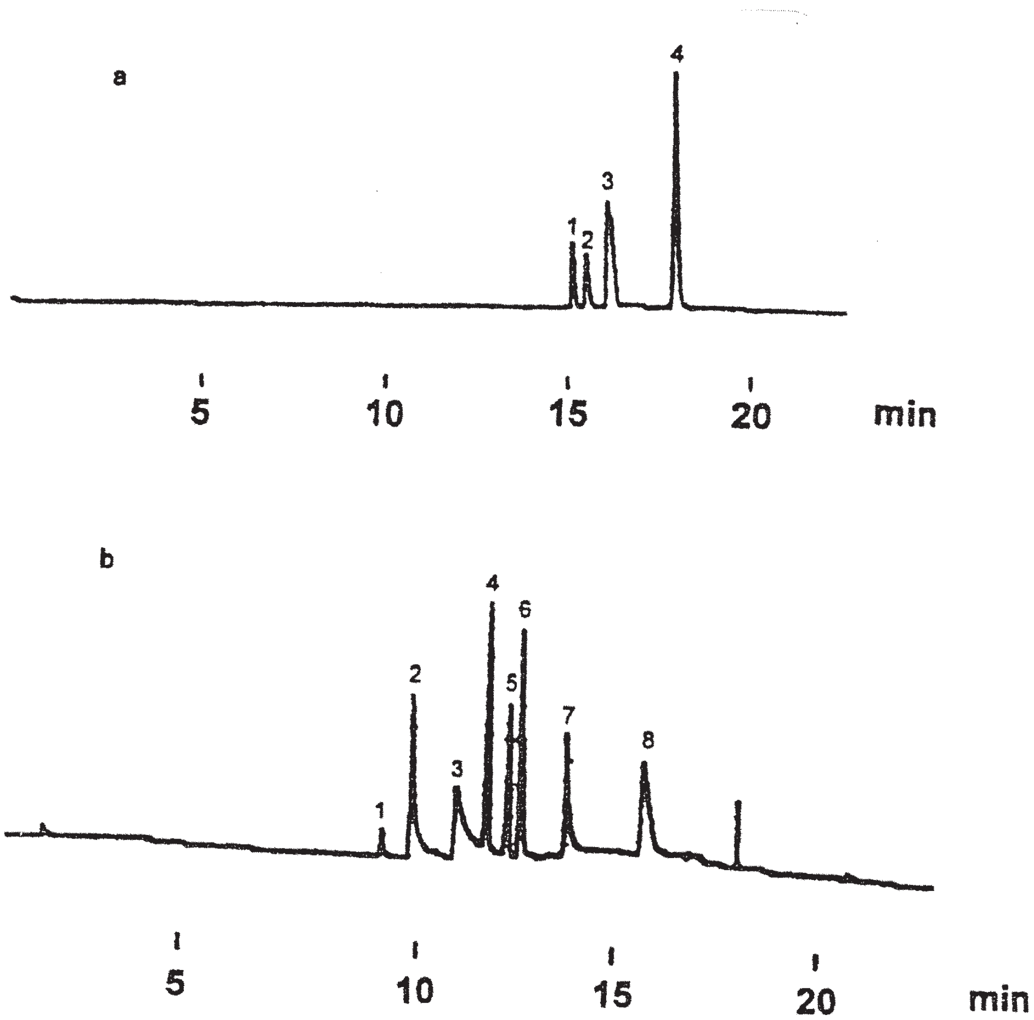


FIGURE 41. Electropherogram of triazines by normal -CE. An 80 cm × 50 μm I.D. fused-silica capillary was used with 50 m*M* ammonium acetate at pH 4.5 as the running buffer. The potential was +20 kV and the detection wavelength was 230 nm. Sample (50 μg/ml) was injected electrokinetically at 10 kV for 10 s. Peaks were assigned as (1) prometon, (2) terbutyrene, (3) prometryn, ametryn, simetryn, (4) propazine, atrazine, simazine. (b) Electropherogram of eight triazines by reversed EOF CE. An 80 cm × 50 mm I.D. fused-silica capillary tubing was used with 50 m*M* ammonium acetate containing 0.7 m*M* CTAB at pH 3.85 as the running buffer. The potential was —20 kV for 10 s. Peaks were assigned as (1) simazine, (2) atrazine, (3) propazine, (4) simetryn, (5) ametryn, (6) prometon, (7) prometryn, (8) terbutryne. (Reproduced with permission from Reference 20.)

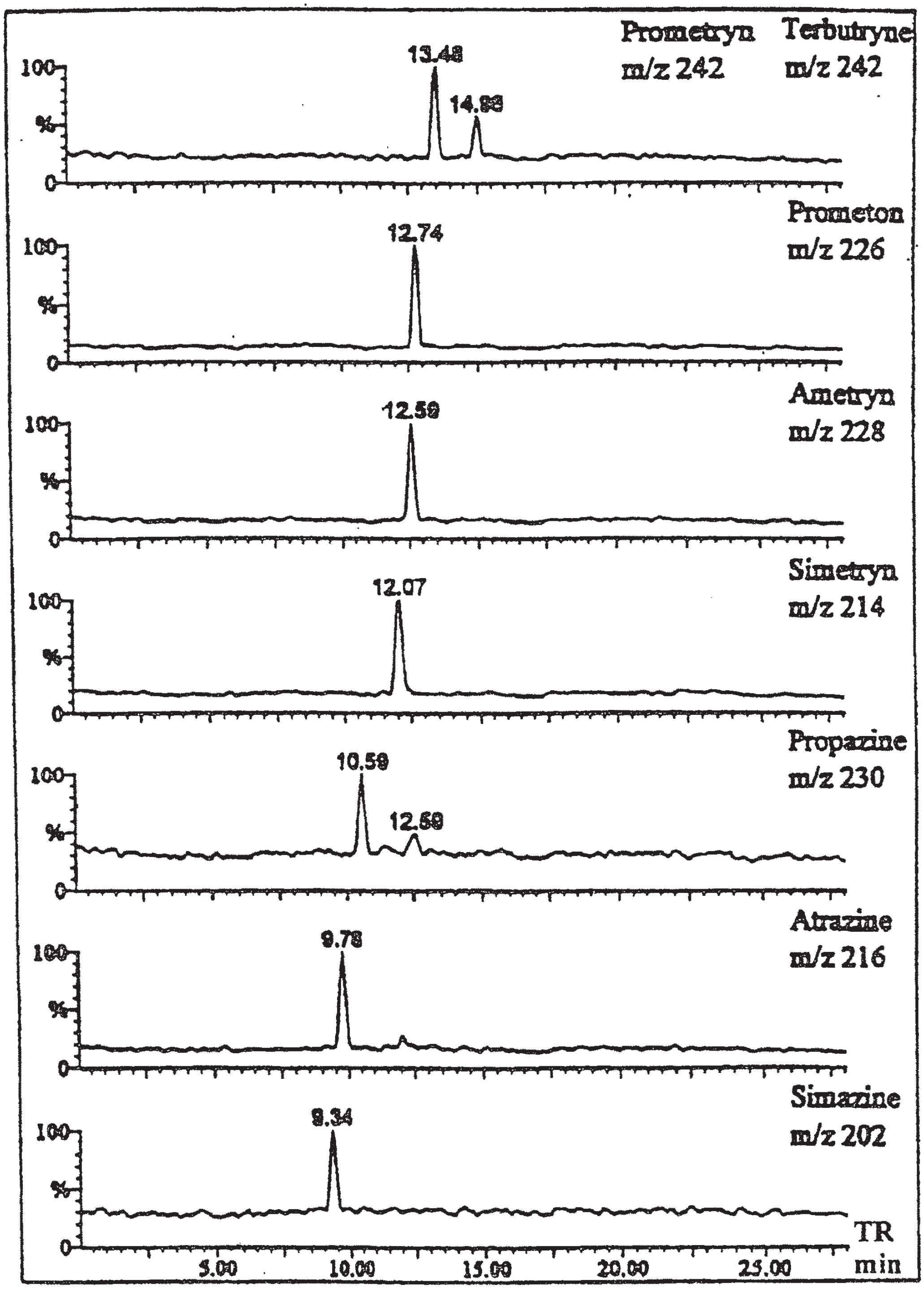
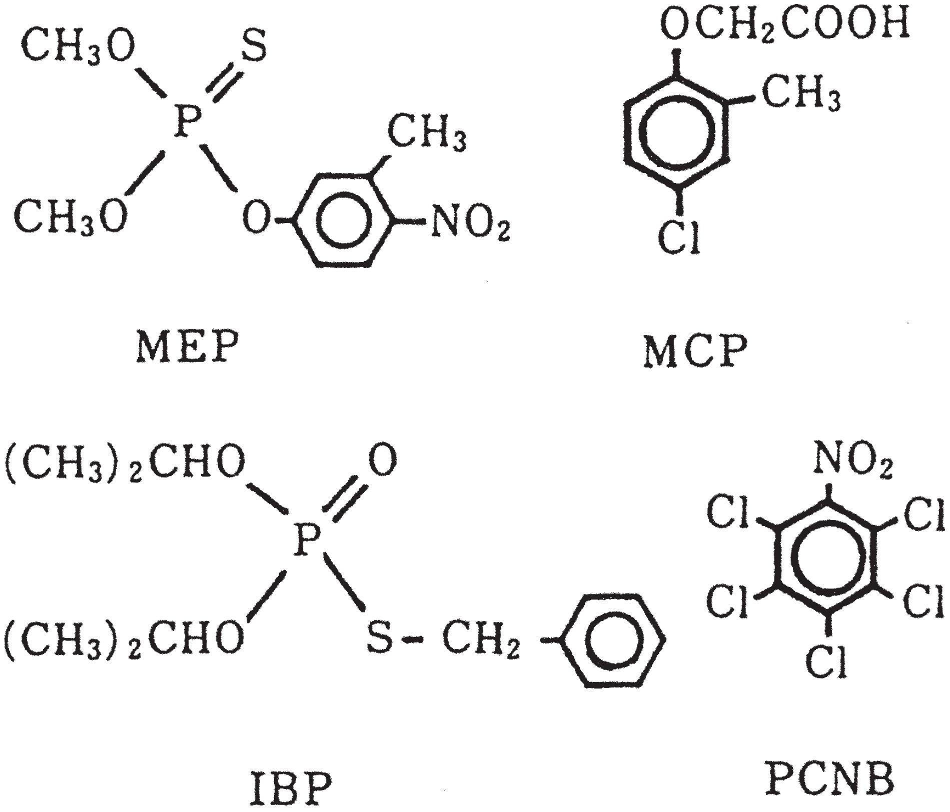


FIGURE 42. Selected—ion electropherograms of eight triazines by reversed EOF CE-MS. Sheath liquid composition was 90% methanol-water (80:20) + 10% 50 m*M* ammonium acetate at pH 3.85. Other conditions same as in b. The additional peak at 12.59 min with m/z 230 was the M+2 isotope peak (S atom) of ametryn. (Reproduced with permission from Reference 20.)



MEP MCP

IBP PCNB

FIGURE 43. Chemical formulae for MEP, MCP, IBP, and PCNB. (Reproduced with permission from Reference 21.)

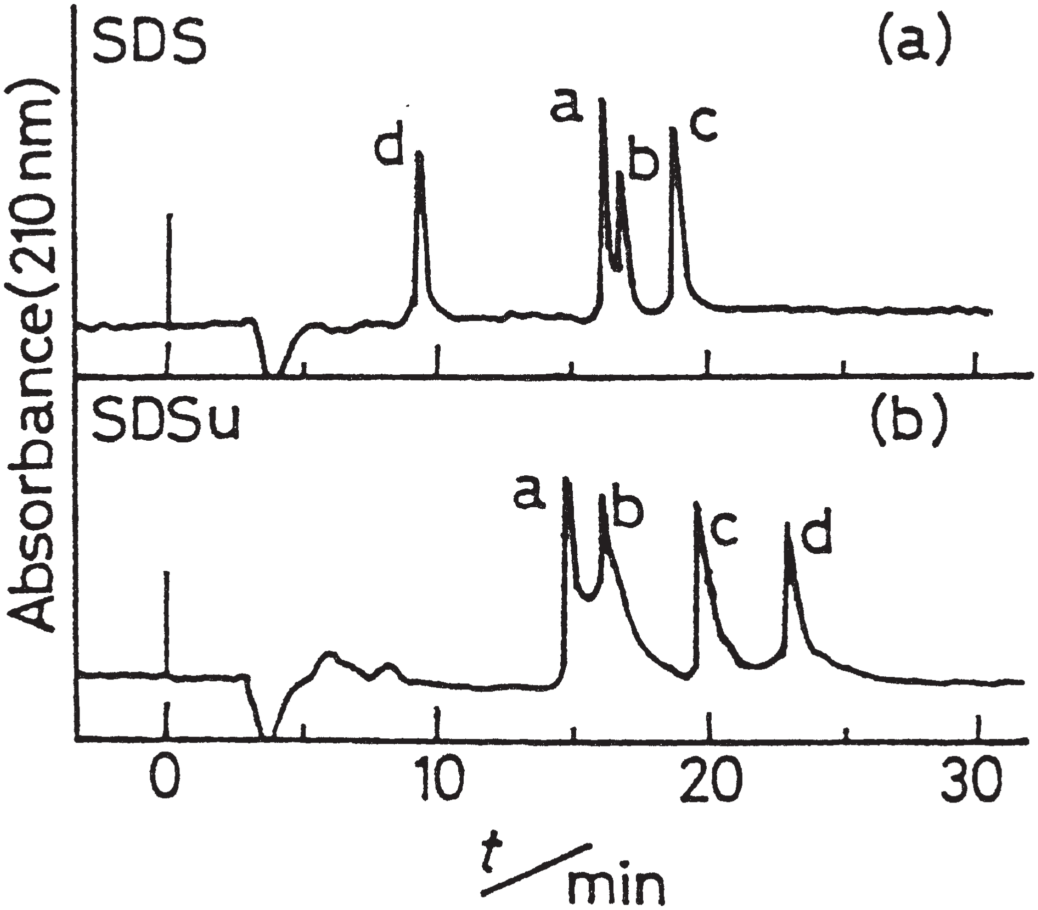


FIGURE 44. Electropherogram of four kinds of pesticides in SDS and SDSu microemulsions. a: MEP; b: IBP; c: PCNB; d: MCP. Migrating solution (wt%): SDS (or SDSu) 3.3/ butanol 6.6/ heptane0.8/5 m*M* Na_2CO_3 buffer 89.3; Applied voltage: 15 kV, T: 25°C. (Reproduced with permission from Reference 21.)

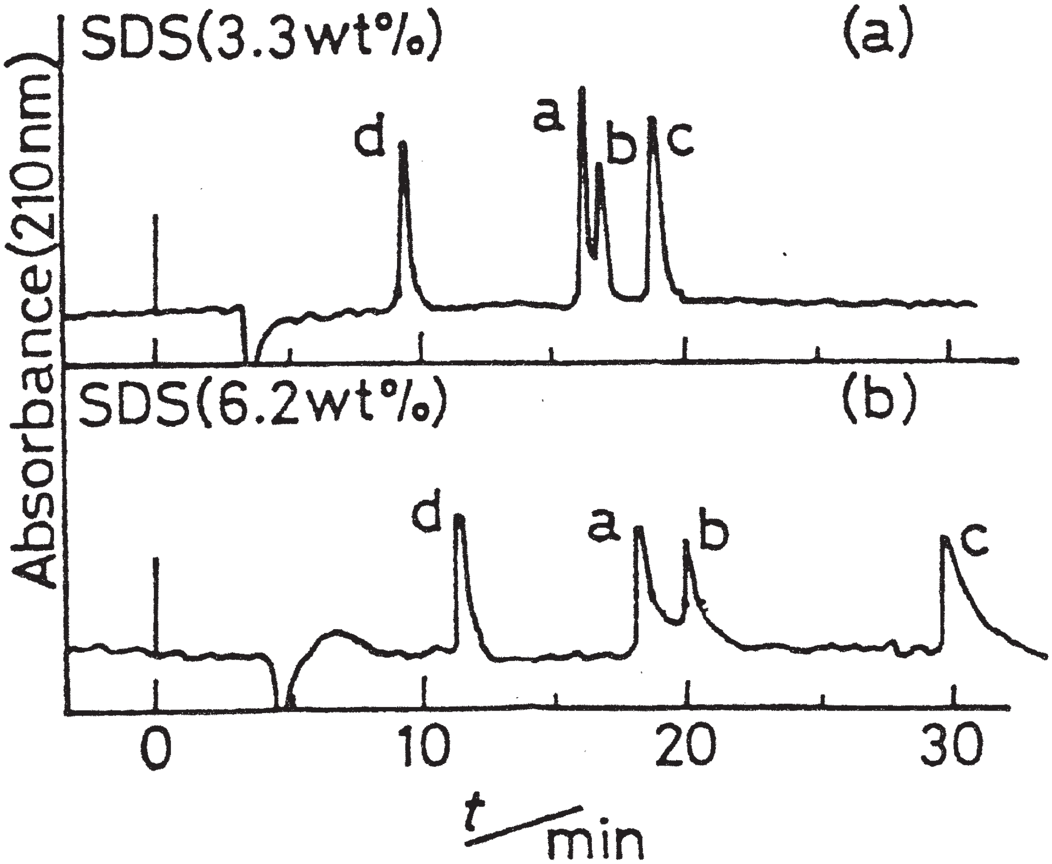


FIGURE 45. Electropherogram of four kinds of pesticides in two SDS microemulsions. a: MEP; b: IBP; c: PCNB; d: MCP. Experimental conditions same as in Figure 44. Migrating solution (wt%): SDS (6.2/butanol 12.4 /heptane 4.9/5 m*M* Na_2CO_3 buffer 76.5; Applied voltage: 15 kV, T: 25°C. (Reproduced with permission from Reference 21.)

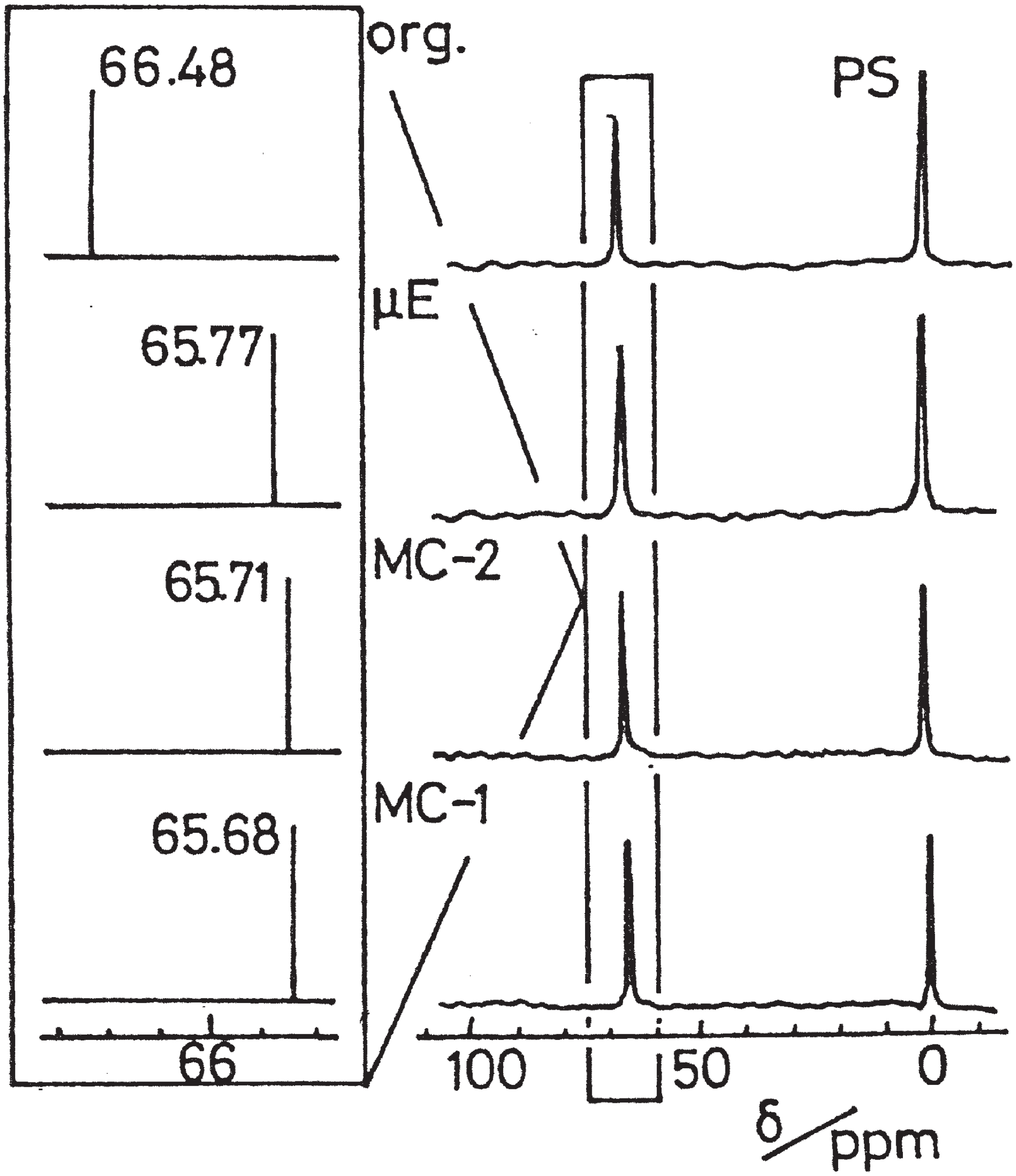


FIGURE 46. ^{31}P-NMR spectra of MEP in MC-1. MC-2, μE, and org. solutions PS: H_3PO_4 (in D_2O); MC-1: SDS+5 m*M* Na_2CO_3 buffer; μE: migrating solution is the same as in Figure 44a; org: butanol+ heptane. (Reproduced with permission from Reference 21.)

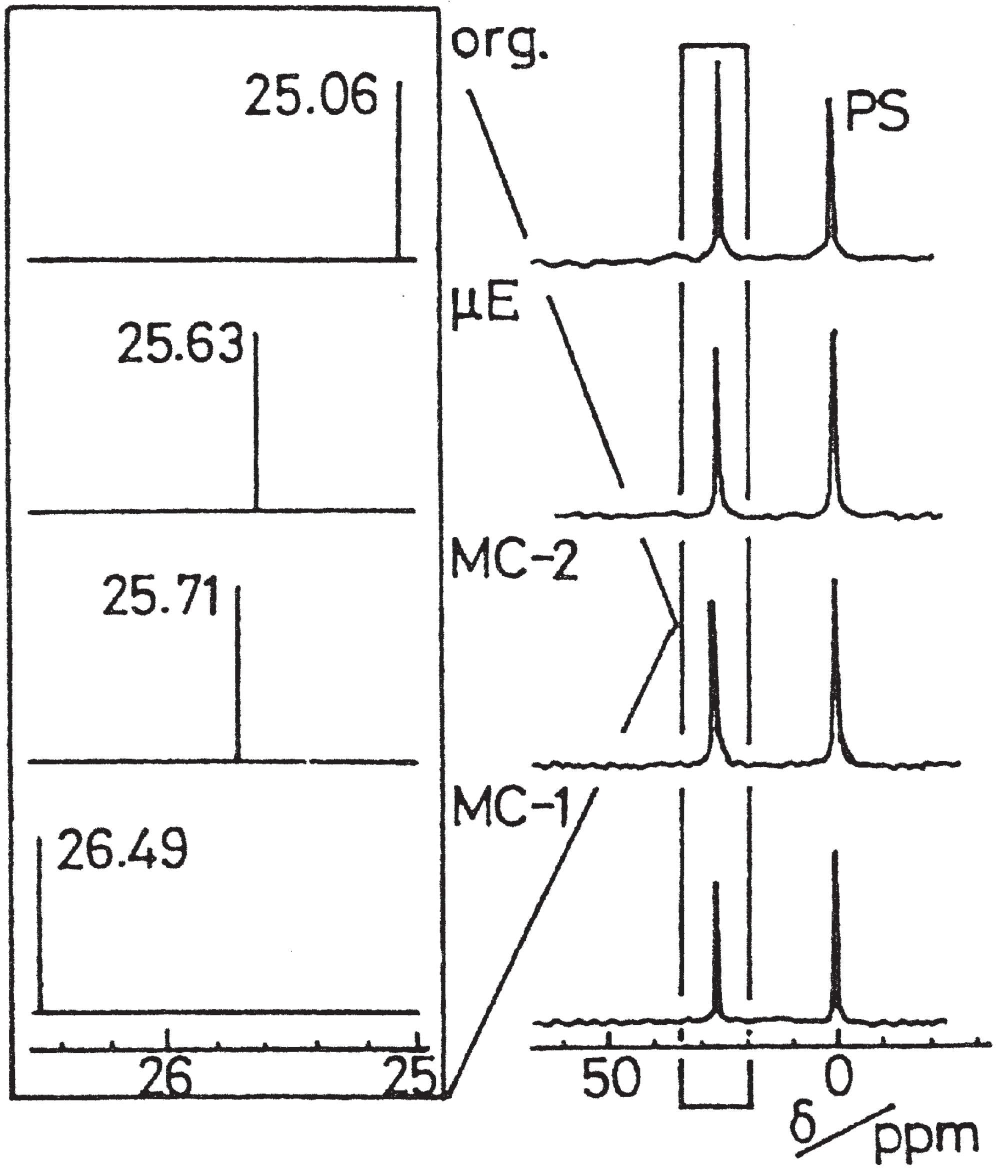


FIGURE 47. ^{31}P-NMR spectra of IBP in MC-1. MC-2, µE, and org. solutions. PS: H_3PO_4 (in D_2O); experimental conditions are the same as in Figure 44. (Reproduced with permission from Reference 47.)

A method was developed by Nitowski et al.[22] for the determination of sodium dimethyldithiocarbamate using capillary electrophoresis with a UV detector. The capillary electropherogram is shown in Figure 48. The relative standard deviations for the analysis of the compound were 2.7 and 12.8% for 528 and 37 μg ml^{-1} concentrations, respectively. The detection limit for sodium dimethydithiocarbamate in waste water was established at 1 μg ml^{-1} using 2-ml samples without preconcentration of the sample with stringent analysis controls and routinely to 10 μg ml^{-1}.

A simple and sensitive capillary elecrophoretic method was developed by Malik, Seidel, and Faubel[23] for the separation and determination of disodium ethylenebis (dithiocarbamate) (nabam) and sodium diethyldithiocarbamate (NaDDC) in boric acid buffer (pH 9.2) using UV detector. The separation (Figure 49) is dependent on pH, and the nature of the buffer and the detection limits (S/N = 3) were 1.56×10^{-6} mol dm^{-3} and 2.48×10^{-6} mol dm^{-3}, and the linear calibration range was three orders of magnitude for nabam and NaDDC, respectively. The method was applied successfully to the direct analysis of water and wheat samples spiked with nabam.

A new sequential uniform design procedure was developed by Chan et al.[24] The uniform design-based number-theoretic method, developed statistically, was used for the optimization of electrophoretic separation. The procedure was illustrated by the complete separation of standard dithiocarbamate (DTC) compounds, that is, sodium diethyldithiocarbamate, sodium dimethyldithiocarbamate, ammonium pyrrolidinethiocarbamate, sodium butylyldithiocarbamate, and sodium octylyldithiocarbamate by capillary electrophoresis, and the separation is shown in Figure 50. In order to optimize the conditions, three different experimental parameters that are pH of carrier buffer, running voltage, and temperature of the capillary were investigated. Using this procedure, these five DTC compounds, by changing one variable at a time, were completely separated by this procedure whereas by normal CE techniques these were not separated.

A simple and sensitive capillary elecrophoretic method with UV detection was developed by Malik, Seidel, and Faubel[25] for the determination of Ferbam (ferric dimethyldithiocarbamate) in boric acid buffer after its acidic decomposition and complexation with EDTA as Fe-EDTA$^-$ complex. The determination is dependent on the pH and the nature of the buffer solutions. In this method the detection limits (S/N = 3) is 1.8×10^{-6} mol/L (0.7 mg/kg). The relative standard deviation for the analysis of 50 μg/ml was reported to be 2.9%. The method was applied successfully for the analysis of wheat samples spiked with Ferbam. The applicability of capillary electrophoresis as a useful tool for the rapid analysis of Ferbam is demonstrated.

Baroso et al.[26] described the application of capillary electrophoresis in the micellar mode to the separation and quantitative determination of five phenylurea herbicides, viz, monuron, linuron, diuron, isoproturon, and monolinuron, in water samples. Using uncoated fused silica capillary and phosphate-borate buffer (pH 7.0) containing SDS, the five pesticides are resolved in less than 15 min and quantitatively determined by an ultraviolet detector at 244 nm. The method was applied for the determination of these herbicides in environmental and drinking water samples at the minimum residue levels (MRLs) (0.1 μg/L) after solid-phase extraction (SPE) preconcentration procedure.

III. CONCLUSIONS

Capillary electrophoresis has been applied successfully for the analysis of pesticides and their enantiomer separations. Capillary electrophoresis suffers from drawbacks in its detection system and so has become a less selective technique. During the last few years many improvements and modifications in the detector systems have been reported in the literature in order to increase the limit of detection. The combination of the capillary electrophoresis with laser-induced fluorescence detection is highly promising for the analysis of pesticides, but it is not applicable to all systems and therefore photothermal methods are more useful. Present literature lacks the applications of these photothermal methods to capillary electrophoresis, and only a few applications are reported in present literature. Despite the significant progress that has been made in this direction,

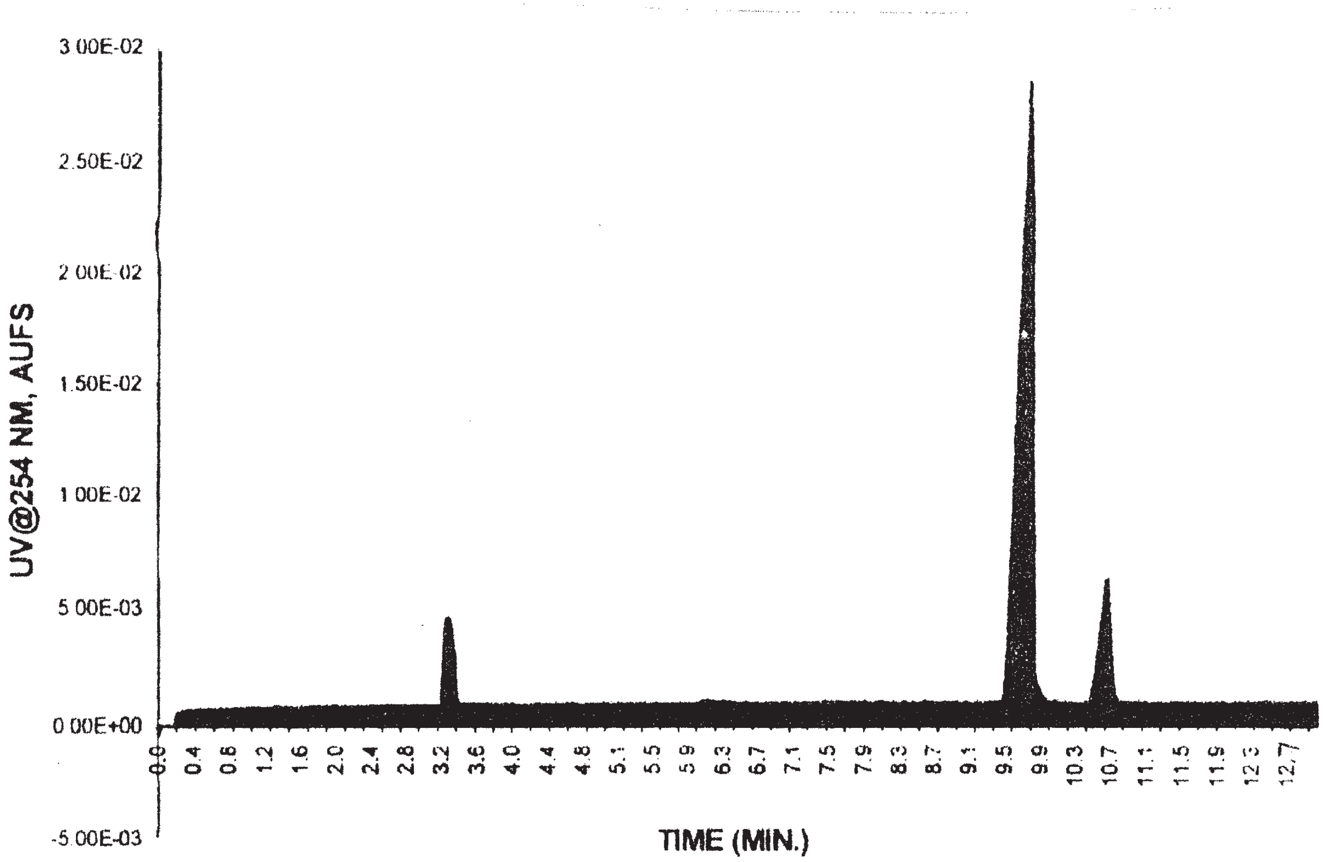


FIGURE 48. Analysis of sodium dimethyldithiocarbamate standard (10.7 min) separated from the *p*-hydroxybenzoic acid internal standard (9.6 min). Analytical conditions: capillary sulfonic acid (high-EOF)-coated fused silica (37 cm × 50 µm I.D.); electrolyte 25 m*M* sodium phosphate buffer (pH 6.5); constant current mode; 50 µA (Approximately 26 kV applied); detection UV absorbance at 254 nm. (Reproduced with permission from Reference 22.)

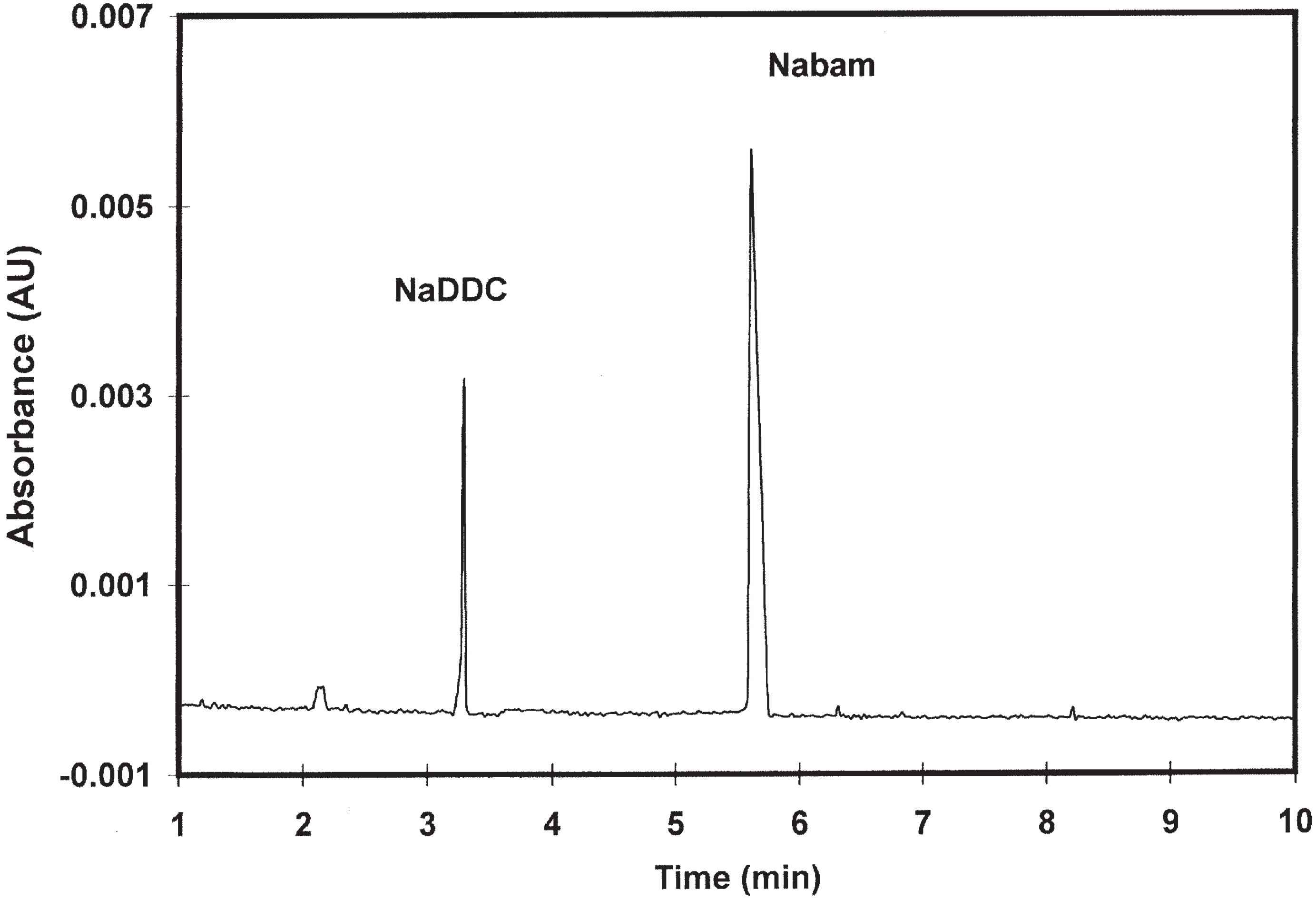


FIGURE 49. Capillary electropherogram of Nabam (0.08 m*M*) and NaDDC (0.03 m*M*) using 1.25 mM boric acid buffer (pH 9.0) as the carrieer electrolyte, voltage applied 30 kV, detection by the UV absorbance at 254 nm. (Reproduced with permission from Reference 23.)

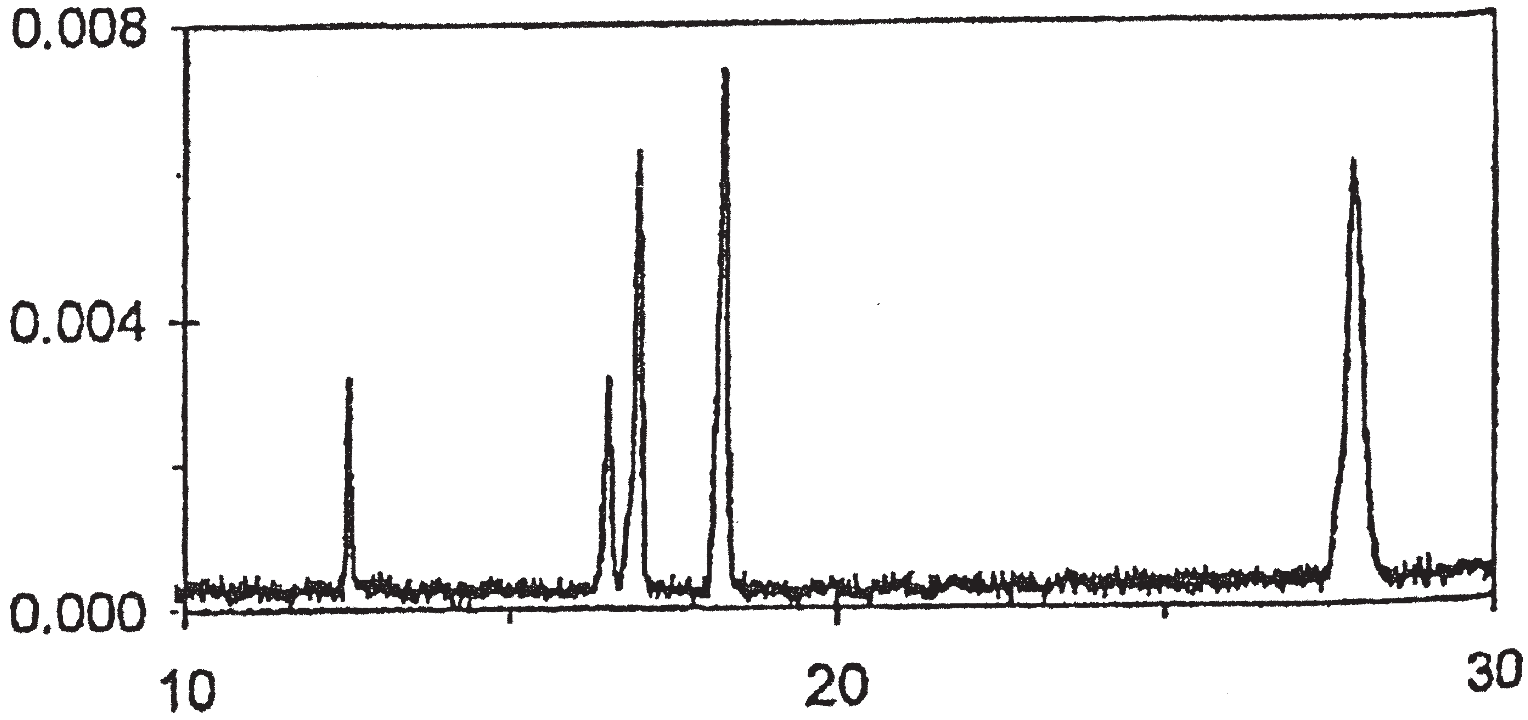


FIGURE 50. The electropherogram of the five dithiocarbamates. Conditions: Concentration of methanol: 6%; Buffer concentration; 15 m*M*; and running voltage 15 kV. The units or the x-axis is retention time in minutes and that for the y-axis is is absorbance. (Reproduced with permission from Reference 24.)

TABLE 2
Comparison of the Detection Limits for Different Detectors Used for the Capillary Electrophoresis

Detection mode	Approx. Linear range [M] (S/N=2 or 3)	Approx. Mass LOD (Mol)	Advantages	Disadvantages
UV/VIS Absorbance	$10^{-6} - 10^{-3}$	10^{-15}	Easy to use	Not so sensitive
Indirect UV/VIS Absorbance	$10^{-5} - 10^{-3}$	10^{-14}	selective and sensitive	Comparatively less sensitive and imposes limits on choices of buffer
Optical absorbance (LED)	$10^{-6} - 10^{-3}$	10^{-15}	selective and sensitive	Comparatively more sensitive and selective in detection
Laser induced Fluorescence	$10^{-18} - 10^{-12}$	10^{-21}	Highly sensitive	Selective and expensive
Mass Spectrometry	$10^{-12} - 10^{-9}$	10^{-15}	Highly sensitive	Selective and expensive
ICP-MS	$10^{-12} - 10^{-9}$	10^{-21}	Highly sensitive	Selective and expensive
Microchip based CE	$10^{-13} - 10^{-9}$	10^{-21}	Short analysis time, selective	Separation is difficult
Photothermal (Thermal Lensing)	$10^{-18} - 10^{-12}$	10^{-21}	Highly sensitive, short analysis time	Expensive and difficult to handle

many capillary electromigrations methods are mainly intended to achieve efficient and rapid separations. For this reason, further investigations are needed to evaluate the potential of capillary electrophoresis as a rapid separation technique for the estimation of pesticides.

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