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Review

Monitoring of herbicide pollution in water by capillary electrophoresis

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Abstract

In recent years, capillary electrophoresis (CE) has demonstrated itself to be an extremely powerful analytical technique. However, CE has not yet been fully evaluated for the environmental analysis of herbicides. In this paper, the potential and drawbacks of CE for the separation and detection of herbicides in water sources are outlined. Details are given both on the applicability of CE to trace level monitoring of herbicides in water sources and on its usefulness in studies regarding the environmental behaviour of herbicides in water systems.

Keywords: Reviews; Water analysis; Capillary electrophoresis; Environmental analysis; Pesticides

Contents

1. Introduction

In the past, the techniques used to limit weed infestations and minimize competition were so-called "agronomic" methods, including crop rotation, tillage, and mowing. The introduction in the 1950s of chemical control reduced yield losses due to weeds to current values of 7–10% [1]. The primary function of herbicides is to protect agricultural crops from weeds and to prevent arable land from being overgrown by unwanted plants [2]. A variety of different organic chemicals with a broad range of molecular structure are employed as herbicides. The introduction of herbicides created a major change in agricultural practice, substituting chemical energy for mechanical and animal energy, reducing costs and increasing productivity [3]. In spite of the unquestionable advantages of herbicide use, the problem of the fate and behaviour of the herbicides released into the environment and the

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role of monitoring of the environment and of water sources have become extremely important. According to European Economic Community Directives [4], residues of single pesticides in drinking water must not be present at concentrations higher than 0.1 μg/l, and the concentration of total pesticides must not exceed 0.5 μg/l. In the USA, the EPA has established health advisory levels which are different for each pesticide and each water source examined. The situation in Europe and the USA is also completely different as concerns the choice of the analytical method for detecting each pesticide. In the USA, the EPA approves standard methods, including sampling and storage procedures, sample preparation, extraction, clean-up, determination and confirmation of identity for each water pollutant [5]. In Europe, in contrast, legislation does not prescribe the analytical scheme for the detection and determination of pollutants in water sources.

Most analytical schemes are currently based on gas and high-performance liquid chromatography (GC and HPLC), but various new technologies have entered the arena for serious consideration as routine methods [6]. The analytical goal of maximum detector response and improved sensitivity and selectivity are achieved by GC–atomic emission detection (GC–AED) and nuclear magnetic resonance (NMR) spectroscopy or, confirming the presence of residues with more confidence, using diode-array detection (HPLC–DAD), mass spectrometry (HPLC–MS and GC–MS) and Fourier transform infrared spectrometry (GC–FTIR). In recent years, capillary electrophoresis (CE) has developed into an exciting and extremely powerful technique [7]. CE has grown rapidly, as evidenced by the exponential trend in publications and citations on CE in the period 1980–93, and many new applications have been introduced into the field of analytical separations. The aim of this paper is to discuss the potential and drawbacks of CE both in the monitoring of herbicide water pollution and in laboratory studies concerning the environmental fate of herbicides. It is beyond the present scope to give a comprehensive bibliographic survey of these topics. This review will concentrate on some examples of the use of CE rather an attempt to enumerate the limited reports in the area of herbicide detection in water sources.

2. Water contamination by herbicides

Herbicides reach the water system through three main routes: transport by air flow, leaching and runoff. As concerns transport by air flow, the volatilization of herbicides during herbicide treatments and eolic erosion are involved. Vapour losses of most soil-applied herbicides are relatively small. However, compounds such as EPTC, triallate and trifluralin are particularly volatile, which can limit their weed control [8]. Generally, the herbicide formulation or incorporation in the soil limits the vapour losses after application. Recently, atrazine, amongst the most widely employed herbicides in the USA, was detected in rainfall during 1992–94 in central USA, in rainfall in the Great Lakes along the Canadian border and in rainfall and snow in southern Germany and the Bavarian Alps [9]. The concentrations of atrazine varied from 0.05 to 2 μg/l. Atrazine and deethylatrazine, as metabolites, were detected from 100 to 300 km from the nearest treated field. These data suggest that air flow in the atmosphere can cause long-range transport of herbicides and consequently contamination of water sources by rainfall.

In the USA and in most European countries, ground water is a major source of drinking water [10]. By means of leaching, herbicides can reach ground water, so causing contamination of the sources of drinking water. The fraction of a herbicide dose applied to the soil surface that leaches to ground water depends on several processes: transformation in the soil due to photochemical degradation, chemical and biological degradation, plant uptake, distribution over the three phases (solid–gas–liquid) in soil and transport in soil. In most cases, the contamination potential due to leaching seems to be limited [11]. Some workers [12,13] have reported for atrazine and its main metabolites a fraction of the dose applied ranging from 0.07% to 1%,

leached below sample depth (>60 cm). Similar results have also been obtained for other herbicides, such as dicamba, dinoseb, picloram and 2,4-5T [14,15].

Runoff is an important component of herbicide mobility. Herbicides are transported both dissolved in water and also associated with soil particles. In many cases, runoff is considered to be the main route of herbicide transport outside agricultural fields and of surface water pollution [16]. Therefore, herbicide losses from agriculture fields due to runoff represent a threat for water quality. The runoff losses depend on environmental factors, physico-chemical properties of herbicides and agronomic factors. Rainfall is an important environmental factor because the runoff itself and soil erosion are due to precipitation. In many cases, most herbicide losses are due to only one or two rainfall events [16]. The frequency of rainfall is also relevant, because frequent precipitation with low intensity leads to a decrease in the herbicide losses, increasing the leaching [17]. Finally, the time between the first rainfall event causing runoff and the herbicide application can influence dramatically the total losses of herbicides [18]. Runoff phenomena are very complex and parameters such as field slope, drain density and distance of the watershed can modify the runoff intensity [19,20]. The herbicides most often evaluated in runoff studies are triazines, owing to the large-scale use of these herbicides and in particular atrazine used for weed control in corn. In long-term studies under field-scale conditions, the mean losses of herbicides, as a percentage of the dose applied, ranged between 0.01 and 1% for bromoxynil, trifluralin, 2,4D, glyphosate, cyanazine, picloram, simazine and metribuzin [21–24], between 0.1 and 2% for alachlor and atrazine [25,26] and between 1% and 6% for paraquat [27]. Many review papers on this topic have shown that the environmental monitoring of different water sources permits an estimate only of existing pollution. On the other hand, in order to predict the potential for contamination by the herbicides, many different studies are necessary. For example, the physico-chemical parameters of herbicides play a basic role in all the main routes of water contamination. From this point of view, the use of analytical methods does not have to be limited to environmental monitoring, but may also be extended to laboratory and field environmental studies. In the next section, the potential of CE for the monitoring of herbicide pollution of water sources and its application to studies on the environmental fate of herbicides is discussed.

3. Separation of herbicides by capillary electrophoresis

CE is rapidly becoming an important tool for the separation of a wide variety of compounds, ranging in size from small ions to large biomolecules, such as proteins and nucleic acids. The main separation modes of CE are capillary zone electrophoresis (CZE), capillary gel electrophoresis (CGE), micellar electrokinetic capillary chromatography (MECC), capillary electrochromatography (CEC), capillary isoelectric focusing (CIEF) and capillary isotachophoresis (CITP). These techniques offer fast and highly efficient analyses for inorganic ions, metal chelates, pharmaceuticals and drugs, vitamins, amino acids, carbohydrates, proteins, nucleic acids, body fluids, polymers, coal and fuels, explosives, organic compounds, cells, viruses and bacteria [7]. The recent advances in instrumentation and the versatility of CE, i.e., various modes of separation, high resolving power and small sample requirement, have made possible a wide range of applications. However, the potential of CE has not been fully exploited in many fields of research, including environmental analyses for herbicides.

CE is known as a "nanoscale" separation technique. The power of CE in micro-separation is linked to the very small injection volume. Usually the capillary dimensions are between 2 and 200 μm I.D. and 10 and 100 cm length, resulting in a total column volume of only a few microlitres. Consequently, the loadability of the system ranges from 1 to 60 nl [28]. Despite its low loadability, CE performs very reproducible and efficient separations. This minute amount of

sample is a useful feature, especially for certain environmental studies. In fact, in analyses of environmental samples, such as ground and surface waters for the detection of herbicides at μg/l levels, the resulting sample volume available for detection and quantitation of the herbicides, after concentration and clean-up procedures, could be reduced. This small injection volume results in savings of sample for other subsequent analyses.

CE has attracted attention because of its very high chromatographic efficiency, with over 600 000 theoretical plates for species with molecular masses of several millions and greater than 10^6 theoretical plates for compounds with low molecular masses have been reported [29,30]. The reasons for this are due to the flat flow profile in CE and the inherently large internal surface area to volume ratio that exists within a separation channel of capillary dimensions [31]. The small capillary dimensions and on-column detection in CE permit a high detection sensitivity, in the range of femtomoles, without zone dispersion. Moreover, zone broadening problems, due to joints, fittings and connectors, that decrease the instrumental efficiency, are eliminated by the on-column detection [7]. The column efficiency in CE is about 10–20 times higher than that in HPLC and, when the selectivity is also optimized, CE resolves closely eluting peaks and separates a large number of compounds in a short retention time. The short CE separation time, due to its column efficiency, is a positive feature in the detection of herbicides in monitoring and environmental studies, especially when a large number of samples must be analysed. The reduced time of a single run makes the cost–benefit profile of CE favourable.

CE is a "hybrid" analytical tool, presenting some typical features of chromatographic techniques and some traits of traditional slab gel electrophoresis. As an example, MECC couples both the electrophoretic and chromatographic partitioning elements for the simultaneous separation of charged and neutral compounds, thereby providing some of the versatility of reversed-phase ion-pair chromatography along with the efficiency of CZE [32]. In Fig. 1 the versatility

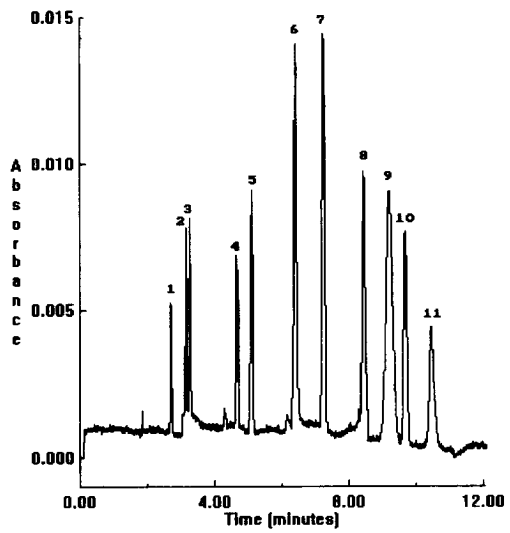

Fig. 1. MECC separations of eleven herbicides in distilled water at the mg/l level. Herbicides: 1 = tribenuron; 2 = chlorsulfuron; 3 = metsulfuron; 4 = paraquat; 5 = simazine; 6 = atrazine; 7 = linuron; 8 = terbuthylazine; 9 = alachlor; 10 = metolachlor; 11 = trifluralin. Conditions: herbicide concentration range, 1–2 mg/l; CE apparatus, P/ACE System 2000 (Beckman); capillary, 500 mm × 75 μm I.D.; operating voltage, 25 kV at 30°C; UV detection at 214 nm; separation buffer, 30 m*M* sodium borate–30 m*M* sodium dodecyl sulfate (pH 8.0). Unpublished data from the Department of Agronomy, University of Bologna, Italy.

and the efficiency of CE in the separation of herbicides are shown. It is possible in a short separation time to separate herbicides belonging to different chemical classes. In the same electropherogram, ionic herbicides (chlorsulfuron, metsulfuron and rimsulfuron), and various non-ionized herbicides (linuron, atrazine, terbuthylazine, simazine, cyanazine, metolachlor, alachlor and trifluralin) are separated. Simultaneous separations of up to 20 different pollutants by liquid and gel chromatographic techniques have been reported [33–35], but generally the physico-chemical properties of the analysed pollutants were closely related.

Another interesting characteristic of CE is its orthogonality compared with that of liquid chromatographic techniques. Techniques can be considered complementary to each other if the acquired data are orthogonal, so that more information can be obtained from the analysis.

Steuer et al. [36] defined the retention parameter χ_i as

$$\chi_i = (t_i - t_0)/\Delta t$$

where t_i is the retention time of analyte i, t_0 the retention time of the first-eluted analyte and Δt the total range of analysis time. The retention parameters were calculated for several herbicides and their degradation products with widely different chemical properties. The demonstration of the orthogonality between CE and HPLC in the separation of herbicides and their metabolites is shown in Fig. 2, where the retention parameters of CE are plotted against those of HPLC. No correlation is evidenced between the CE and HPLC retention parameters. Therefore, the coupling of these two analytical techniques provides a considerable benefit. The benefit of orthogonality was demonstrated also in a previous paper concerning the detection of terbuthylazine in ground water samples spiked at 0.2 μg/l by HPLC and CE [37]. The different positions of the matrix interferences in the HPLC and CE traces, next to the active ingredient (a.i.) peak, confirmed the non-redundant information from these independent analytical systems. Other useful traits of CE for monitoring routine analyses are the simplicity of the instrumentation, the low solvent consumption and the easy equipment maintenance with respect to chromatographic techniques.

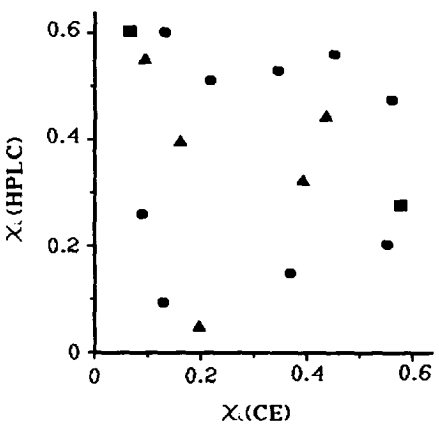

Fig. 2. Demonstration of the orthogonality between HPLC and CE. The HPLC gradient separations were carried out under reversed-phase conditions. HPLC conditions: HPLC Beckman System Gold 126 with two pumps and a Rheodyne Model 7725-i valve (20-μl loop); detector, Beckman diode-array Module 168; column, Beckman C_{18} Ultrasphere, 250 mm × 4.6 mm I.D., 5 μm particle size; mobile phase: eluent A, water (adjusted at pH 2.5 with phosphoric acid) 40%; eluent B, methanol 60% for 5 min; gradient from 40 to 30% A and from 60 to 70% B in 10 min; 5 min at 70% B before resetting; flow-rate, 1 ml/min; detection wavelength, 224 nm; injection volume, 20 μL. CE conditions as reported in Refs. [52], [53] and [60]. χ_i = Retention parameter. Compounds: ● = sulfonylurea herbicides and their metabolites; ▲ = triazine and urea herbicides; ■ = chloroacetanilide herbicides. Herbicide concentration range, 1–4 mg/l. Unpublished data from the Department of Agronomy, University of Bologna, Italy, and data from Refs. [52], [53] and [60].

At the same time, despite the many advantages of CE, there are some major limitations. Although the low loadability of the system allows the achievement of impressive detection limits, the corresponding measurable sample concentrations are still too high (of the order of mg/l) to permit trace level determinations of herbicide residues in water without 1000–5000-fold sample preconcentration by solid-phase extraction. In recent years, a wide range of detectors, such as laser-induced fluorescence, electrochemical, conductivity, Raman spectroscopic and radioisotopic, have been developed in order to enhance the CE concentration sensitivity with respect to the more widely employed UV and UV–Vis detectors.

Despite the simple basic set-up of CE instrumentation, the tuning of a CE separation is a complex and critical step. In order to optimize CE separations, several parameters must be taken into account, such as electrolyte buffer composition, capillary dimensions, capillary temperature, applied voltage and mode and time of injection. Usually, optimization procedures are easier in gas and liquid chromatography than in CE, because the only fundamental parameter set to achieve the desired selectivity and resolution is the mobile phase composition. To apply CE for monitoring analyses and environmental studies of herbicides, particular attention has to be devoted to the optimization of the separation in order to obtain the best selectivity in a complex matrix where many potential compounds may interfere. Different approaches have been proposed for the tuning of CE separations,

e.g., Plackett–Burman statistical design, theoretical approaches, computer simulation and the overlapping resolution mapping (ORM) procedure [7]. In a previous paper [38], a three-dimensional ORM scheme for the tuning of three interactive components of the electrolyte buffer was employed for the simultaneous detection at the μg/l level by MECC of three sulfonylurea herbicides in a complex matrix.

Although it might seem that each technique has its own points of strength and weakness, CE is not intended to compete with or simply be used as an alternative to GC and HPLC, but rather as a complementary method to chromatographic techniques to achieve more analytical information.

4. CE in water quality monitoring and environmental studies of herbicides

The main steps in the residue determination process are evidenced in the following sequence: sampling, sample preparation, extraction–concentration, clean-up, qualitative and quantitative determination and confirmation of identity. The improvement in each of these steps is evidenced by the extensive literature that appears each year [6]. As an example, new analytical tools permit the identification and quantitation of herbicide residues with higher accuracy and reproducibility than in the past. In the last 30 years, the concentration detection limit of herbicides has increased about 1000-fold, from 0.1 mg/l in the 1960s to less than 0.1 μg/l in the 1990s. However, the above-mentioned classical scheme is rapidly being modified and new trends in analytical protocols are appearing. Many analytical procedures for the determination of herbicides and their metabolites from an aqueous matrix are often tedious and expensive. The new analytical goals are to maximize the detector response for the components of interest while minimizing the response for interferences, controlling the analysis time and labour costs [39]. The application of multi-extraction and multi-determination methods for herbicides without clean-up procedures is common. Finally, despite the sensitivity potential of the analytical tools employed, the efficiency of water source monitoring depends on the quality of analysis. It is important not only that the measurement of the concentration value is made with high precision, but also that the level of the results obtained is compared. Comparability is increasing as a basic requirement, especially for long-term and wide-range monitoring programs. In order to provide comparable data, new approaches based on progress in instrumental equipment must be used directly for improving and therefore changing the available methods. At the same time, the traditional analytical tools must be employed in order to check and estimate the real share of a new analytical method.

The role of CE in water quality monitoring and environmental studies of herbicides must be considered taking into account the above-mentioned considerations. The application of CE, usually CZE, ITP and MECC, to the separation and determination of organic molecules in a wide range of matrices is rapidly expanding, although there are as yet only limited reports in the area of pesticide detection [40]. The herbicide derivatives of 1,3,5-triazines, namely prometryne, terbutryne, desmetryne, simazine and atrazine, have been separated by ITP and CZE and detected by UV spectrophotometry [41,42]. The long-term reproducibility of migration times was ca. 1% and the reproducibility of peak areas was 5%. In spite of the efficiency and separation speed of CZE for mixtures of triazine herbicides, Foret et al. [42] reported that the main limiting factor in CZE analysis for triazines was the sensitivity. In fact, the minimum detectable concentration in the injected sample was ca. $2 \cdot 10^{-6}$ mol/l of each triazine, corresponding to about 0.5–1 mg/l. However, it is important to note that the available extraction procedures allow the concentration of crude water samples by a factor of 1000 or more. Thus, the proposed CZE method for triazine analysis has a theoretical detection limit ranging between 0.5 and 1 μg/l.

Six urea herbicides, namely monuron, fluometuron, metobromuron, siduron, linuron and chloroxuron, were analysed by MECC using alkyltrimethylammonium chloride and bromide

surfactants [43]. The separation of a mixture of the six urea herbicides was best achieved when a MECC system of low hydrophobic phase and wide retention window, such as dodecyl- or decyltrimethylammonium chloride, was used as the micellar phase. The resolution of the six herbicides was obtained within 15 min and with an efficiency of ca. 150 000 theoretical plates per metre of capillary. The separation of nine plant growth regulators, including the herbicides 2,4D and 2,4,5-T, by CE has been described by Yeo et al. [44]. Cyclodextrins and cholic acid were used as modifiers in the electrolyte buffer to enhance selectivity. Satisfactory separation was obtained as concerns efficiency and reproducibility, but no mention of the applicability of the method for water monitoring purposes was reported. Other researchers [45] have also used CZE for the separation of 2,4D and 2,4,5-T and their corresponding phenols without mentioning its applicability to the analysis of water samples.

CZE methods have also been developed for the enantioseparation and detection of phenoxy acid herbicides (MCPB, MCPA and MCPP) and related impurities (including positional isomers) originating from production processes [46]. The selectivity of the separation was controlled and tuned by adding suitable cyclodextrin-type chiral selectors to the electrophoresis buffer. The CZE method showed good precision, linearity and long-term stability. The developed method was successfully applied to the analysis of real water samples and to the determination of their enantiopurity at concentrations ranging between 1 and 4 mg/l.

CZE with untreated fused-silica capillaries was evaluated in the separation and determination of paraquat and diquat [47]. As high as 200 000–300 000 theoretical plates per metre of capillary were obtained. The detection limits for paraquat and diquat with a UV detector were 15.4 and 16.8 fmol, respectively. Other herbicides, such as prometon, prometryne, propazine and butachlor, have been determined by MECC with low detection limits, ranging between 18 and 52 fmol [48]. Despite the impressive detection limits in terms of absolute amount, the concentration of components in a hypothetical water sample requires too high a concentration, of the order of 0.1–1 mg/l, for the direct determination of herbicides in water samples.

To avoid tedious sample preconcentration steps, an on-line preconcentration of triazines with tandem octadecyl capillaries–CZE was set up [49]. Fused-silica capillaries having surface-bond octadecyl functions were developed for the on-line preconcentration of dilute samples prior to CZE analysis. The performance of this system was evaluated with dilute solutions of prometon and prometryne. The on-line preconcentration was best achieved when oligomeric octadecyl capillaries with roughened inner walls were employed. The coupled configuration enhanced the detectability in terms of solute concentration by a factor of 10–35 compared with that obtained by CZE alone. In addition, the tandem system permits the introduction of a large volume without affecting the separation efficiency and reproducibility.

CE coupled to a pneumatically assisted electrospray (ionspray) interface with an on-line mass spectrometric detector has been employed for the detection and separation of eight sulfonylurea herbicides [50]. By using 35-cm fused-silica capillaries, the CE–MS determination of the eight sulfonylureas was accomplished within 5 min. Despite the encouraging applicability of CE–MS to sulfonylurea separation, the detection limit of about 400 mg/l is much higher than the μg/l level found in water samples. For this reason, a significant improvement in the MS detection limit will be required in order to use CE–MS for the direct determination of herbicides in water samples. The previous reports of the potential of CE for the monitoring of herbicide pollution in water have not yet provided realistic methods for the qualitative and quantitative determination of herbicides in real water samples at the μg/l level. A rapid and sensitive MECC method was developed for the determination of atrazine and simazine in river water samples fortified at 2–10 μg/l [51]. Samples were concentrated 200–500-fold by liquid–liquid extraction prior to MECC analysis and UV detection. Quantitative determination in water samples was achieved using an internal standard,

measuring the peak-area ratio. The two triazines were separated in less than 10 min with recoveries ranging between 80 and 117%. The estimated detection limit of the method was 0.4 μg/l in water for both herbicides.

The use of CZE with UV detection in our laboratory for the determination of two sulfonylurea herbicides, metsulfuron and chlorsulfuron, in tap water samples at the μg/l level has also been described [52]. Eleven water samples were fortified at 0.1–5 μg/l with metsulfuron and chlorsulfuron. Prior to the CZE analysis, the samples were concentrated 1000–10 000-fold by solid-phase extraction. The two herbicides were detected in 4 min with high accuracy and reproducibility. The average overall recovery, in the 0.1–5 μg/l range, was 96% for metsulfuron and 92% for chlorsulfuron. The detection limit was 0.1 μg/l for both herbicides, although it was possible to detect qualitatively the two herbicides at 0.01 μg/l. At concentrations lower than 0.1 μg/l, the presence of interfering compounds that arose from the SPE procedure did not permit the reliable quantitation of metsulfuron and chlorsulfuron.

Preliminary results from our laboratory on the detection of herbicides using MECC with UV detection have also been reported for the quantitation of five herbicides, namely rimsulfuron, linuron, atrazine, terbuthylazine and metolachlor, in drinking and surface waters [53,54]. The fortified water samples were concentrated by SPE. The limit of detection was 0.1 μg/l for the herbicides tested, except for metolachlor (1 μg/l). The overall average recovery was 95%. The application of this procedure to the analysis of a surface water sample containing metolachlor and terbuthylazine at μg/l levels gave results in good agreement with those obtained by HPLC.

Tap water and groundwater samples spiked with terbuthylazine were analysed by MECC, HPLC and a commercial enzyme immunoassay kit [37]. Over the range of concentrations tested (0.2–2.4 μg/l), the results obtained by the different methods were highly correlated. MECC proved to be viable for the detection in water of terbuthylazine with good resolution and reproducibility. The mean overall recovery of terbuthylazine was 99% and 94% in tap and groundwater, respectively. The concentration detection limit of MECC was higher than that of HPLC to detect the lowest concentration of the herbicide (0.2 μg/l), but the retention times were shorter. Moreover, MECC showed an on-column purification effect, as demonstrated by the fact that the area of the terbuthylazine peak in the electropherograms was 20% of the total area of the compounds detected, whereas in the HPLC traces the area of terbuthylazine peak was only 5% of the total area of compounds detected.

As an example of the use of CZE in the monitoring of water sources, the electropherograms of runoff water samples collected from sloping fields treated with an experimental sulfonylurea are shown in Fig. 3. The water samples were concentrated 1000-fold by solid-phase extraction before CZE analysis. It should be noted that the separation time was less than 5 min. The concentration detected in the runoff water sam-

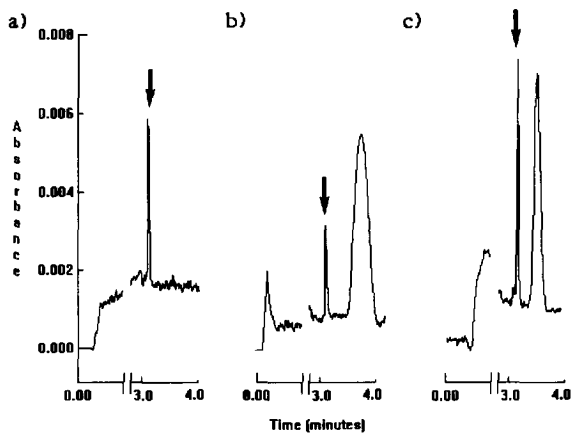

Fig. 3. Detection of an experimental sulfonylurea in a runoff water sample by CZE. (a) Sulfonylurea standard solution at 8 mg/l; (b) runoff water sample concentrated 1000-fold by SPE, according to Dinelli et al. [52]; (c) runoff water sample concentrated 1000-fold by SPE and fortified with 8 mg/l of the experimental sulfonylurea. The arrows indicate the sulfonylurea peak. Separation conditions: CE apparatus, P/ACE System 2000 (Beckman); capillary, 500 mm × 75 μm I.D.; operating voltage, 25 kV at 35°C; UV detection at 214 nm; separation buffer, 20 m*M* sodium borate–20 m*M* tetraborate (pH 8.5). Unpublished data from the Department of Agronomy, University of Bologna, Italy.

ple (Fig. 3b) was 4 μg/l. The confirmation of the peak identity was effected by fortification of the runoff water sample, on the basis of the retention time and peak-area increase (Fig. 3c).

However, apart from its potential in the trace level monitoring of herbicides in water sources, we would like to present evidence for the usefulness of CE in laboratory studies regarding the behaviour of herbicides in water. CE has already been employed in degradation studies of some sulfonylurea herbicides (e.g., triasulfuron, chlorsulfuron and metsulfuron) in aqueous solution [55]. Hydrolytic and microbial degradation are the major mechanisms of sulfonylurea dissipation [56]. Degradation rates of triasulfuron, metsulfuron and chlorsulfuron in water were determined by CE in the pH range 2–7.5 and over the temperature range 20–50°C. The data obtained were in agreement with those obtained under the same experimental conditions by other workers, using HPLC instead of CE for herbicide detection [57,58]. The degradation of the sulfonylurea herbicide rimsulfuron as a function of the temperature in aqueous solutions at pH 4 is reported in Fig. 4. The same samples were analysed by RP-HPLC and by CE. It is important to note that the half-lives measured by HPLC were well correlated with those registered by CE. These results suggest that the use of CE in water degradation studies of herbicides is highly reliable.

Another interesting application of CE is the detection in water of herbicide metabolites. In recent years, considerable interest has arisen in the detection and separation of herbicide metabolites, which are potential toxic compounds and interfering molecules in the water residue analysis for the active ingredient. The metabolites formed during hydrolysis of metsulfuron were analysed by CZE [53]. The degradation products were extracted from the aqueous solution by liquid–liquid partitioning and the extracts were analysed by CZE in order to verify their concentrations. The structures of the breakdown compounds were identified by GC–MS on the basis of their mass spectra and chromatographic retention times. The CZE and GC–MS data of metsulfuron metabolites permitted a degradation scheme for the parent herbicide in water to be formulated. Such a degradation pathway is in agreement with the literature [57–59].

The potential of MECC for the separation and detection of the metabolites of nine sulfonylurea herbicides in water has also been evaluated [60]. The formation patterns of hydrolytic metabolites of the nine sulfonylureas were obtained. A relationship between the structure of the sulfonylureas tested and the metabolites formed

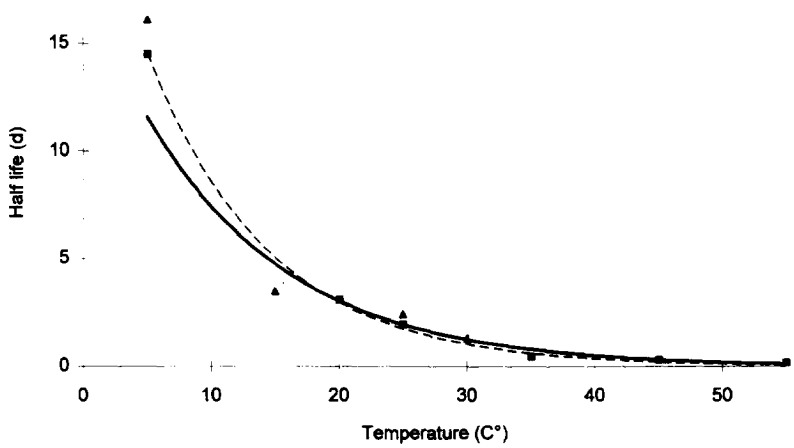

Fig. 4. Half-lives of rimsulfuron in pH 4 water as a function of temperature. ■---■ = samples analysed by CZE; ▲——▲ = samples analysed by HPLC. HPLC conditions as in Fig. 2; CE conditions as in Fig. 3. Unpublished data from the Department of Agronomy, University of Bologna, Italy.

was found: the non-*o*-benzene-substituted sulfonylureas gave only one metabolite, whereas the *o*-benzene-substituted sulfonylureas gave 4–6 metabolites.

5. Conclusion

The literature shows that CE is a suitable analytical technique for both mono- and multi-residue detection at the μg/l level of herbicides in water sources and for other studies related to the environmental behaviour of herbicides, such as chemical degradation and metabolite identification. The most important question to be considered is what the future potential of CE in environmental studies is. Although it is not easy to predict the future development of CE, we believe that the role of CE will depend on whether it will become as widely accepted as HPLC. Thus CE must not be considered as a rival but as a complementary tool to traditional chromatographic techniques. Moreover, in order to overcome the major drawback of CE, namely the limited loadability of the system, the development of highly sensitive and precise detection techniques will become a fundamental step to extend the use of CE in environmental studies. Despite the significant progress that has been already made in this direction, many capillary electromigration methods are mainly intended to achieve efficient and rapid separations. For this reason, further investigations are needed to evaluate effectively the role of CE in environmental studies.

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