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Review

# Strategies for chromatographic analysis of pesticide residues in water

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## Abstract

A review is presented of the modern techniques and approaches in methods for pesticide residue analysis in water matrices. The state of the art of the individual steps (extraction, clean-up, separation, identification, quantitation) of the chromatographic methods is reviewed with emphasis laid on emerging techniques which have gained popularity. The new approaches are discussed with respect to their relevancy to the requirements for increasing the sensitivity of detection and reliability of identification and quantitation at low levels of concentrations, arising from the European Community Drinking Water Directive.

*Keywords:* Reviews; Environmental analysis; Water analysis; Extraction methods; Pesticides

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## 1. Introduction

The Maximum Admissible Concentration of pesticides in drinking water, defined by European Community Drinking Water Directive as  $0.1 \mu\text{g l}^{-1}$  for individual pesticides and as  $0.5 \mu\text{g l}^{-1}$  for the

sum of pesticides [1] posed certain demands to the analytical methods for pesticide residue determination. It initiated intensive research activities to increase the sensitivity of the methods and their reliability at low levels of concentrations. The efforts to increase the validity of peak identification were

essential for avoiding false positive results. The necessity to extract large volumes of water samples gave rise to the development of new techniques for sample pretreatment. As matrix effects from the water can cause errors in determination and quantitation, reduction of the matrix interferences was also an important goal in the efforts to develop adequate methodology and techniques capable of determining the environmentally important pesticides in water samples.

The goal of the work was to review the emerging techniques and approaches in the basic steps of chromatographic methods for pesticide analyses in different types of water.

## 2. Sample pretreatment

### 2.1. Liquid–liquid extraction

Extraction methods are continually being revised and improved with new technologies. Liquid–liquid extraction (LLE) is the classical approach for pesticide extraction from water samples [2–11]. It is performed by repetitive extraction of 500–1000 ml samples in a separatory funnel and dichloromethane is the most popular solvent [3–9] because it is capable of extracting compounds with a wide range of polarities and is easy to evaporate. There are numerous examples on the application of this simple technique but only a few general works will be mentioned. Different experimental procedures based on dichloromethane LLE from aqueous media of semi-volatile analytes (including halogenated pesticides) listed in the EPA Target Compounds List have been evaluated [12]. EPA methods 8120 [13] and 8140 [14] use LLE procedure for analysis of 15 organochlorine (OC) and 21 organophosphorus (OP) pesticides respectively in water samples. For extraction of acidic herbicides from aqueous samples, adjustment to  $\text{pH} < 2$ , followed by LLE with diethyl ether or dichloromethane were used [15,16].

This classical approach shows many disadvantages. It is not applicable to automation of the analytical procedure, requires large volumes of toxic solvents and is time consuming. Formation of stable

emulsions often occurs especially with highly polluted surface waters. Single continuous LLE has been recommended for samples which form emulsions or are otherwise difficult to extract by the separatory funnel procedure [12,17]. It is performed in continuous extractors, designed to extract large volumes, for instance 1 l water with solvents heavier than water. The extractors, attached to boiling flasks containing 500 ml dichloromethane are refluxed for 18 h. The procedure allows for changing the pH of the aqueous matrix and collection of separate fractions of the extract. The continuous LLE is recommended as an effective and labor saving procedure but it is time and toxic solvent consuming and is used as an alternative when LLE is not applicable [18].

Although the traditional LLE is considered a disadvantageous procedure, some recent studies are reported on development of new modifications. Micro liquid–liquid extraction (MLLE) was developed as a simple alternative method for analysis of organic compounds in water [19]. This approach was applied for determination of the herbicide alachlor and two of its metabolites [20]. The principle of MLLE is the extraction of a large volume of water (400 ml) with a very small volume of solvent (500  $\mu\text{l}$  of toluene) that can be directly applied for GC analysis without an evaporation step. This is particularly useful for determination of volatile compounds. A vigorous shaking and salting out of the analytes and the organic solvent from water by saturation with sodium chloride was absolutely necessary to achieve sufficient recovery (80–100%). In comparison with solid-phase extraction (SPE) this technique was less expensive and time consuming. MLLE was reported to show less co-extractives than SPE but this statement is to some extent inexplicable taking into account that a properly designed SPE procedure allows for the possibility of separation of analytes from a certain part of impurities. Confirmation with analysis of various types of water will be necessary. The limit of determination of both techniques was similar. Still, SPE showed better results, 10  $\text{ng l}^{-1}$  was the minimum detectable concentration of alachlor by SPE, and 25  $\text{ng l}^{-1}$  by MLLE. Applicability of this approach to extraction of different classes of pesticides from water has not been studied in the literature known to us.

## 2.2. Solid-phase extraction

A substantially new approach to aqueous sample preparation techniques is SPE. It offers advantages such as time saving, solvent reduction, elimination of emulsions, trace enrichment, and a high potential for automation. The advantages of SPE have not yet been fully realized in the isolation of pesticide residues from all matrices, but SPE has been adapted to environmental water analysis with good results.

Currently SPE is predominant in analytical methods used for pesticide residues in water matrices. Conventional LLE has been largely replaced by procedures utilizing solid-phase partition. The basic steps associated with these procedures include column conditioning by rinsing with the solvent used to elute the analytes followed by methanol and water to improve reproducibility and reduce background contaminants. The sorbent is not allowed to dry before the water sample is added. The samples (1 l) are forced through the column usually at flow-rates between 5–10 ml min<sup>-1</sup> and the column is dried under vacuum. Weak solvents are used first for elution of impurities. Finally the analytes are eluted with stronger solvents designed to elute completely the pesticides while leaving as many impurities as possible on the column. Ethyl acetate and dichloromethane are the most popular elution solvents for SPE. Various types of sorbents and techniques have been developed and applied. Chemically bonded silica-based sorbents are generally used in SPE columns. The non-polar octadecyl (C<sub>18</sub>) is the most common sorbent used in pesticide analysis. It has been used to extract compounds belonging to different chemical classes and within a wide range of polarities—triazines [21,22] as well as some of their polar decomposition products—hydroxy-*s*-triazines [23], urea herbicides [20], *N*-methylcarbamate pesticides and their polar metabolites [24–26], OC [27,28] and OP insecticides [29,30], triazole and pyrimidine pesticides [31]. Multiresidue methods [32–34] including a large number of pesticides (up to 128) of different classes have been developed using C<sub>18</sub> bonded silica cartridges. Mixed sorbents of C<sub>18</sub> and phenyl (PH) bonded phases in single column have also been used in multiresidue procedures to increase the retention power and the range

of extracted compounds [35]. C<sub>18</sub> sorbents were not effective for extraction of very polar compounds: dimethoat, metomyl and aldicarb were poorly recovered [30,32] from spiked water samples. Application of more polar sorbents—PH, cyanopropyl (CN), did not give satisfactory results. Hydroxydealkyltriazines could not be enriched on C<sub>18</sub> [23].

In order to reduce the breakthrough of the early eluting polar compounds larger amounts of sorbents - up to 2 g have been applied, especially in multiresidue methods [22,34]. Still, recoveries of very polar compounds such as desisopropylatrazine could not be improved by the use of more column material [22].

Acidic compounds such as phenoxyalcanoic acids and other acidic herbicides have been successfully extracted on C<sub>18</sub> bonded silica cartridges under strong acidic (pH<2) conditions [36–38]. Adjusting the pH of the water sample below the pK<sub>a</sub> of the acidic herbicides was essential in order to increase the retention capacity of RP system to these compounds. Since the bonded silica sorbents are not stable at such conditions, an alternative approach using ion-pairing mechanism with triethylamine as counter ion was recently developed for SPE of acidic compounds under mild conditions, at nearly neutral pH [39].

The volumes of water samples extracted on cartridges with different sorbents have been usually in the range of 0.5–1 l, but large volumes, up to 8–10 l [35,40] have been preconcentrated in some cases. The sample volumes should be considered carefully with respect to increasing the determination limits from one side and from the other—with respect to the possibilities of decreasing the recoveries, especially of the early eluting compounds, due to their breakthrough during preconcentration [41]. Passing large volumes through the cartridge materials could result in plugging and channeling; as optimum flow-rates are about 10 ml min<sup>-1</sup> [42], the use of SPE cartridges for large sample volumes is a time consuming process [38].

These shortcomings of the extraction cartridges have been overcome with a new technique—SPE discs. The use of SPE discs has been described in more recent studies [43–46]. The membrane extraction discs have been used as an alternative to

cartridge SPE. Higher flow-rates can be applied with the SPE discs and the extraction time is much shorter [47–49]. They do not get plugged and channeling does not occur.  $C_{18}$  discs exhibited better blanks than  $C_{18}$  cartridges [50]. The comparison of both SPE techniques—cartridges and discs show also some disadvantages of the latter. They require 4–6 times higher consumption of eluents [47] and are about 4 times more expensive.

Extraction discs can be used in off-line mode [51,52] and in on-line mode using a membrane holder [45,53].

$C_{18}$  sorbents seem to be inappropriate for some pesticides, especially very polar and very non-polar compounds. Enrichment on synthetic polymer resins—styrene divinylbenzene copolymers (SDB) in cartridges or in SPE discs has been applied in recent studies as an alternative to  $C_{18}$  bonded silica SPE [38,40,41,48]. Improvement of the results for recoveries, relative standard deviations and determination limits with SDB Empore discs were reported in comparison with  $C_{18}$  Empore discs [38,54], especially with more polar compounds such as acidic herbicides. The observations on the recoveries obtained with SDB discs in comparison with  $C_{18}$  discs under acidic conditions were controversial. An improvement in the recoveries of acidic herbicides and phenols with SDB discs under  $\text{pH} < 2$  was reported in some articles [48,54,55] while in other studies [38] SDB discs showed worse recovery rates under acidic conditions in comparison with  $C_{18}$  discs.

An alternative sorbent, especially effective for SPE of acidic pesticides from water is Carbopack B, composed of non-porous spherical graphite particles. Studies on the application of Carbopack B in preconcentration of different classes of pesticides (OP, triazines, phenylureas, carbamates, phenoxyacids, acetanilides, phenols) are described by Di Corcia et al. [56–58]. Graphitized carbon black cartridges offer the advantage of being able to extract simultaneously basic/neutral and acidic compounds. They appeared to be superior to other sorbents for extraction of very polar compounds (phenols, polar metabolites of atrazine). Among the various extraction techniques compared, that employing 1 g graphitized carbon black cartridges and reextraction by back-flushing had the highest ability to retain

hydrophilic pesticides from large water volumes [58]. The sorption mechanism is almost unknown and some cases of obtaining very high standard deviations and determination limits cannot be explained [38].

A useful technique has been developed in recent years to increase the effectiveness of pesticide residues analysis in water. It is based on on-line enrichment of the analytes from aqueous samples on small cartridges filled with a suitable reversed-phase sorbent and subsequent direct determination utilizing switching to analytical HPLC columns [59]. The advantages of this approach are time saving and a high potential for automation.

On-line SPE, followed by HPLC coupled with diode array detector (DAD) or MS, represents a rapid, robust and very selective approach to identification and quantitation of pesticides in water matrix. This technique has been applied to various pesticide classes including chlorophenoxyacids [48,60,61], OP [62,63], OC [64], carbamates [65], chlorotriazines [66]. It has been successfully applied in multiresidue analysis of 51 compounds representing six groups of pesticides, differing strongly in polarities [41]. Relatively low recoveries were obtained only with very polar compounds due to their early elution and breakthrough during enrichment. This effect was similar with all sorbent materials studied— $C_{18}$  bonded silica and two styrenedivinylbenzene copolymers. Attempts to reduce the breakthrough by using larger amounts of adsorbents would lead to extreme peak broadening, particularly for early eluting compounds. When highly hydrophobic materials (SDB) were used for preconcentration, strong band broadening was observed, leading to overlapping peaks in the chromatogram [41,62]. This effect made the analysis of complex mixtures impossible. The combination of almost identical materials (i.e.,  $C_{18}/C_8$ ) in both precolumn and analytical column was considered more adequate as the band broadening of early eluting compounds was reduced [41].

A negative matrix effect due mainly to humic substances presented in real waters has often been reported [41,46,48,67,68]. Peak interferences and low recoveries were attributed to the formation of pesticide–humic complexes that could not be sufficiently extracted by the adsorbents used [67]. A

separation of humic acids on Florisil cartridges was applied in a method for HPLC with UV detection analysis of pesticides in water [22].

### 2.3. Coupled-column liquid chromatography

A possibility for increasing the selectivity between the interferences and analytes by utilizing coupled-column HPLC with column switching has been reported [69]. The basic procedure involves several steps: the crude sample extract is injected on the first chromatographic column where a pre-separation is performed with a certain volume of the first mobile phase. During this step the more polar interferences are removed. Just before the first analyte starts to elute, the first column is switched on-line with the second analytical column where the separation of the analytes is performed using a second mobile phase. The advantages of this approach are suitability for automation, increase of the sensitivity by introduction of larger sample volumes under controlled bandbroadening conditions, improvement of selectivity by transferring accurate volumes containing only the analytes of interest to the second analytical column. This technique has been applied to analysis of several pesticides in aqueous matrices: ETU [70], iprodione [71], bromacil, diuron and 3,4-dichloroaniline [72], bentazone [73]. Its successful performance depends on the optimization of two important parameters - the choice of the first separation column and the eluotropic strength of the clean-up solvent. In order to extend the applicability of this technique to simultaneous determination of pesticides with different polarities, a computer aided chromatogram simulation was developed for optimizing the conditions of coupled-column HPLC combined with step-gradient elution [74]. The coupled-column liquid chromatography is not generally applicable in laboratory practice because the optimization of the conditions for clean-up and separation of pesticides especially for multiresidue analysis requires special skills, and simultaneous determination of analytes with different polarities is difficult.

### 2.4. Solid-phase microextraction

Routine monitoring studies on pesticide pollution

of water require development of rapid methods of analysis. Recently a very simple and rapid technique has been developed based on solid-phase microextraction (SPME) [75,76]. The extraction and concentration steps are focused in one single step. It is accomplished on fused-silica fiber coated with an immobilized stationary phase (polyacrylate or polydimethylsiloxane) for the extraction without making use of any solvents. The fiber is exposed to the sample for an optimized adsorption time (25 min) until equilibrium is achieved. The transport of the analytes from the aqueous phase to the polymeric microphase is controlled by diffusion and can be enhanced by stirring the water sample. Small sample volumes (down to 3 ml) could be used without loss of sensitivity because the total amount of the extracted sample is used. The fibers are directly introduced into the heated split-splitless injector of GC. The same fiber can be used repeatedly. The extraction efficiency strongly depends on the polarity of individual compounds. The polyacrylate phase has higher affinity to less polar compounds. Addition of sodium chloride to the aqueous sample could be used to increase the extraction efficiency for the polar compounds. This approach has been applied to determination of various groups of pesticides—OP, triazines, dinitroanilines and good accuracy and precision were reported [76].

SPME procedure has been developed for analysis of organic pollutants in water using pencil lead as sorbent and subsequent thermal desorption [77].

### 2.5. Supercritical fluid extraction

Supercritical fluid extraction (SFE) is a principally new approach which is gaining popularity as a sample preparation technique. One of the biggest advantages of SFE over the standard LLE is that it can be done with nonpolluting fluids such as CO<sub>2</sub>. It is the most widely used supercritical solvent which is a natural component of the air and after decompression it can be allowed to escape without environmental concern. The remaining extracts are clean of organic solvents [78].

Fluids are defined as supercritical when they are maintained at temperatures and pressures above the

critical point. At these conditions the substance can not be liquified regardless the pressure exerted to it but possesses properties of both liquid and gas. Supercritical fluids exhibit several unique properties that make them desirable as extraction solvents. One of the most interesting properties is that the solvent strength of the supercritical fluid is directly related to its density. Since the density of the fluid is a function of its pressure and temperature, a solvent with specific solvating strength can be obtained by precise control of the pressure and temperature. It leads to the ability to perform a very selective extraction. Higher molecular weight compounds can be dissolved as the pressure of the fluid increases. If the pressure is reduced the fluid loses its solvating ability and the extracted compounds fall out of solution.

Another advantage of supercritical fluids is that their diffusivities are higher and the viscosities are lower in comparison with many organic solvents. These properties of supercritical fluids allow them to promote rapid mass transfer and faster solute extractions.

SFE has been used for analysis mainly in soils, animal and plant tissues of various classes of pesticides: OC [79–81], urea herbicides [82,83], sulfonyleureas [84], compounds with different polarities—pyrethroids, carbamates, ureas, OP, OC, triazines [85], *s*-triazines [86], OP and OC [87,88].

Addition of co-solvents (entrainers or modifiers) to the primary solvent proved to be useful for enhancing the extraction efficiency of the compounds of interest. Methanol is the most common co-solvent added to CO<sub>2</sub>. One of the reasons for addition of entrainers is to overcome matrix effects. Pesticides strongly bound to the matrix (for instance bound residues in soil and plant tissues) are not recovered by pure CO<sub>2</sub>. The use of methanol or acetone in addition to CO<sub>2</sub> is necessary to obtain quantitative recoveries [80,89]. A second reason is that CO<sub>2</sub> is an excellent solvent for non-polar compounds, but it is not good for polar ones. Addition of entrainers is necessary to increase the polarity of the primary solvent and its strength for extraction of polar compounds [82–84].

Direct SFE has been used only in a few cases to extract analytes from an aqueous matrix [90,91]. The moderate solubility of water in supercritical CO<sub>2</sub> can

lead to problems such as restrictor plugging due to ice formation and difficulties in removal of water from the extracts [92]. A successful approach to overcoming these problems has been developed by combining SPE with SFE [93–95]. C<sub>18</sub> Empore discs have been used to trap analytes prior to elution with supercritical fluid. The effectiveness of CO<sub>2</sub> selectivity to polar and non-polar pesticides has been demonstrated in separation of OP from OC pesticides under different extraction conditions [95].

An interesting application of SFE is reported [96] for the isolation and trace enrichment of pesticides in freeze-dried water samples used in interlaboratory studies. The SFE with CO<sub>2</sub> resulted in better recovery and selectivity than LLE. The extraction efficiency depended on solubility of the analytes in the supercritical fluid and in the water matrix.

A substantial reduction of analysis time is another advantage of SFE as no clean-up of the extracts is necessary.

The availability of SFE instrumentation is a limitation for application of this technique in laboratory practice.

### 3. Determination

Chromatographic methods are most widely used for analytical separation, identification and quantitation of pesticide residues in different matrices including water. Application of selective and highly sensitive detection systems is essential in water analysis because of the very low level of admissible concentrations of pesticide residues in water.

#### 3.1. Gas chromatography

GC is preferably used for analysis of volatile and thermostable pesticides. In combination with selective detectors such as NPD and ECD it became a routine technique in pesticide analysis in water [6,9,30,31,47,97,98]. Capillary and megabore capillary columns have replaced the traditional packed columns. Fused capillary columns with bonded phases of different polarities (non-polar HP-1, Ultra-1; low polar SE-54, HP-5, DB-5, Ultra-2, CP Sil 8;

medium polar DB-1701, CP Sil 19; or polar CP Wax); internal diameters (0.2–0.53 mm); film thickness (0.12–1  $\mu\text{m}$ ); lengths (15–30 m) or others were reported. Ionic compounds, such as phenoxyalcanoic acids also can be determined by GC with ECD after derivatization to their methyl-, 2-chloroethyl-, 2,2,2-trichloroethyl- and pentafluorobenzyl- (PFB) esters [99]. For water analysis PFB esters were preferable because of the higher sensitivity [36,99].

As chromatography is a poor identification technique, hyphenated techniques have been developed and have gained popularity for increasing the selectivity and certainty of identification. GC–MS has become the preferred analytical technique. In multiresidue pesticide determination in water it is used either for confirmation of the results obtained with GC–ECD, NPD [31,96] or as a primary method [100]. Three modes of GC–MS operation are generally available: electron impact (EI), positive chemical ionization (PCI) and negative chemical ionization (NCI) [101]. GC–MS in EI mode using selected ion monitoring (SIM) is commonly used in determination of different classes of pesticides in water [23,35,100,102]. NCI and PCI are good alternative ionization methods, which offer, depending on the compounds, better selectivity and/or sensitivity than EI. GC–MS with NCI is a selective approach particularly suitable for confirming the presence of OC and OP in environmental samples. GC–MS–PCI has been applied for confirming triazines [103] and OP with their sulphoxides and sulphones [104] in water samples. GC–MS with PCI or NCI and SIM of two or three characteristic fragment ions are strongly recommended for determination of triazines and OP respectively in dirty extracts since diagnostic ions are at higher  $m/z$  values and consequently less interference from the matrix will appear [105]. A drawback of this approach is that only a few libraries of standard mass spectra for PCI and NCI GC–MS are available and they must be built in each laboratory.

A sophisticated technique using GC–MS–MS has been reported to enable analysis of pesticides and their metabolites at trace level in the presence of many interfering compounds. A limited number of examples are present in the literature on application of this technique. In PCI mode it has been employed for the determination of triazine and acetanilide herbicides in water [103].

### 3.2. HPLC

HPLC is the method of choice for thermally unstable and ionic compounds which are not amenable to GC. Environmentally important pesticides such as carbamates, urea- and phenoxyacid herbicides, polar metabolites of triazines, benzimidazoles and others are among these compounds. RP-HPLC columns containing mainly  $C_{18}$  bonded silica sorbents [4,21,22,32,37,106] and in some cases  $C_8$  [24,41] and CN- [37] bonded silica are used for analytical separation. Narrow-bore, 3 mm I.D. columns [41] and 3  $\mu\text{m}$  particles [22,38] have been applied in recent studies. Gradient elution with a large change in mobile phases composition is used for multiresidue analysis. Buffer solutions with pH adjusted below the  $pK_a$  values of the acidic compounds ( $\text{pH} < 2$ ) are commonly used in order to increase the retention capacity of RP sorbents for HPLC separation of acidic herbicides [48,107]. A possibility to increase the separation efficiency and retention capacity for acidic herbicides in RP-HPLC under mild conditions, at nearly neutral pH utilizing an ion-pairing mechanism has been reported [39].

UV-detection with variable wavelength has been the routinely used technique, enabling sufficient sensitivity (0.1  $\text{ng ml}^{-1}$  or less) for most pesticides to be achieved [37,106,108]. The problem of identification, typical of chromatographic methods, can not be solved with the application of UV-detectors. An increase of confirmation ability has been achieved with DAD. This technique has been reported most often in multiresidue HPLC analysis of pesticides in aqueous samples [4,21,22,32,38,48]. In order to increase the validity of identification, the absorption spectra of the compounds have been compared to reference substances [21,22]. Substance detection at several different wavelengths has been performed for better identification. Low recoveries for some substances have been observed with DAD caused by the matrix interferences [46,48]. Application of DAD capable of automatically identifying compounds by utilizing a multiple spectral comparison technique enhances attainment of correct results in automatic systems for pesticide measurement in drinking water [109]. Multi-component analysis has been reported in the same article to provide quantitative accuracy for peaks that co-elute due to inadequate resolution.

Recently DAD has been applied in a fully automated HPLC system for trace-level determination of polar pollutants in water using an automated cartridge-exchange system for on-line trace enrichment, gradient elution and optimized HPLC parameters for 18 pollutants in various types of waters [110].

The combination of HPLC with MS provides possibilities for overcoming the problems arising out of the matrix interferences. Different types of interfaces for connection of MS to HPLC are possible (including transport systems, direct liquid introduction, atmospheric pressure ionization, particle beam, continuous flow-fast atom bombardment, thermospray, electrospray) [111]. Thermospray (TSP) is the most widely used interface in HPLC–MS reported in pesticide residue methodology because the TSP ionization in general leads to simple mass spectra, resulting in high sensitivity when time scheduled SIM is applied. This technique has been employed in methods for determination of a variety of individual classes of pesticides such as carbamates [112], OP [113,114], ureas [115], acidic herbicides [48], fungicides [46], triazines [116,117], sulfonyleureas [118] and others, but currently there are few multiresidue methods based on this technique [34,41,119]. Two MS modes are applied routinely—positive ion (PI) and negative ion (NI). The choice between them depends on the compounds determined, the latter appearing to be much more sensitive to electronegative compounds [48,105]. Determination of 128 pesticides under different HPLC conditions has been reported [34] when operating in PI and NI modes. For improvement of selectivity and sensitivity postcolumn techniques have been applied such as addition of aqueous buffer solution and external ionization media [120]. Identification and determination of co-eluting compounds has been possible by comparison of their different characteristic ions. In critical cases different confirmatory techniques have been shown to be adequate to distinguish between analytes: variation of interface temperatures, MS–MS techniques [34], use of external ionization media [121], repeller-induced spectral changes [122], additional cluster ions with solvent or additive molecules, complementary PI and NI spectra [34].

The other interface techniques have been scarcely used in pesticide analysis. Electrospray (ESP) ioniza-

tion has been applied recently in high-flow mode for determination of OP pesticides [123]. An advantage of this technique in comparison with TSP is that no degradation occurs under ESP conditions thus it is very useful for determination of compounds which are easily thermodegraded such as trichlorfon. An important feature of ESP is that it gives better structural information than TSP and can be used for identification of unknown compounds. Higher sensitivities (about 100 times) have been reported with LC–ESP–MS for several OP insecticides as compared to LC–TSP–MS.

Particle beam interface giving electron ionization spectra has been reported to have an advantage over the TSP technique for HPLC–MS determination of chlorinated phenoxy acid herbicides because it provided an excellent confirmation based on numerous and highly reproducible diagnostic fragmentation ions [124].

Limitations for general application of these advanced techniques are the high costs of the instrumentation and the complexity of its exploitation.

### 3.3. High-performance thin-layer chromatography

High-performance thin-layer chromatography (HPTLC) is not the method of choice for pesticide residue analysis in water. As compared to the advanced techniques described above it is not considered as prospective. In recent years there are a very limited number of articles on the application of this technique in pesticide residue analysis and particularly in water samples. An example will be given to show the possibilities of HPTLC utilizing modern techniques for increasing applicability for this purpose [125]. The migration distances of 275 active substances have been determined utilizing automated multiple development with a standardized elution gradient and a second gradient for verification. The UV-spectra in reflected light, measured on the HPTLC plate, have been stored in a library program. This technique has been reported to be suitable for routine identification and quantitative determination of pesticides in water samples and especially of thermally unstable compounds such as phenylureas, carbamates and others, not amenable to GC. As the compounds studied differ in their UV



absorbance, the range of sensitivities is wide. Some pesticides lack a strong chromophore in the UV region for sensitive detection. Hence UV detection is not well suited for universal application. The equipment used in the HPTLC method described is not much simpler or cheaper if compared to HPLC or GC but the possibilities for determination of multiresidues at low concentrations are more limited.

#### 4. Conclusions

The main contemporary goal in pesticide residue analysis of environmental waters is increasing the sensitivity of detection in compliance with the high demands for drinking water quality. Improvement of the selectivity and development of reliable confirmatory techniques are adequate approaches for eliminating false positive results. The necessity to enhance the control of water pollution gives rise to development of techniques and methods leading to minimization of the analysis time by simplification of sample preparation procedures and increasing the sample throughput by automation. Efforts have also been focused on reducing the consumption of hazardous solvents as this is essential for environmental safety.

The presented review clearly indicates that there is a rapidly developing response of analytical chemists to residue problems. The enormous growth in techniques and ideas is strong evidence that the difficult analytical problems related to determination of pesticide residues in water can be solved by experience and inventive imagination.

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