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Review

Comparison of gas and liquid chromatography for analysing polar pesticides in water samples

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Abstract

This review describes the applications of gas chromatography (GC) and liquid chromatography (LC) in the analysis of selected groups of pesticides in water. The attention is focussed on the most popular (in terms of amounts produced and applied) pesticide classes, i.e., carbamates, phenylureas, triazines, phenoxy acetic acid derivatives and chlorinated phenols. The use of GC and LC for the analysis of these compounds in water samples in the past and at present is reviewed separately for each group. Sample concentration and detection techniques are discussed in relation to their influence on the performance of the particular separation technique. Special attention is given to mass spectrometry (MS) because it is the most intensively developed detection technique in environmental analysis. The potential of another novel approach – large volume injections into the GC – is discussed separately.Methods using GC or LC coupled to an appropriate detector and using suitable sample handling procedures provide detection limits typically in the range of 0.001–1 ppb. At these levels, target or unknown compounds can be determined/identified by means of their retention and spectral characteristics. Principally, most of the analytes can be determined by both techniques, however, GC methods, when applicable, still have the advantages of great separation efficiency, high speed of analysis and the availability of a wide range of highly sensitive detectors; on the other hand, LC is often a method of choice when polar, non-volatile or thermolabile compounds are to be analyzed. Neither of the two separation techniques reviewed seems to have an overall priority in environmental analysis of pesticides. They can be considered as complementary.

Keywords: Reviews; Water analysis; Environmental analysis; Pesticides

Contents

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1. Introduction

The demand for efficient agricultural production evokes the increasing development and subsequent production of a large number of various substances and preparations used for destroying pests. The extent of the application of the most popular pesticides reaches thousands of tons per pesticide annually in many countries and the diversity of the insecticides, herbicides, growth regulators, fungicides and other applied substances is increasing rapidly. However, in addition to definite advantages for the food production efficiency, this phenomenon has also an increasing negative impact on the environment. The transport of pesticides out of their area of application results in the presence and subsequent accumulation of these compounds or their various degradation products in many parts of the global environmental system. As an example the impaired quality of the surface waters, ground waters and other parts of the hydrosphere can be mentioned [1]. To prevent water pollution by pesticides, precise information on their concentration levels in the aquifer is necessary. For this purpose various analytical techniques such as spectrometry, total halogen methods and biological methods were used in the past. The situation was remarkably improved by the introduction of chromatographic methods in the 1960s. The preference for these methods is a result of the fact, that in conjunction with various sample handling and detection techniques, they are able to provide a very extensive analytical information.

In the early period of environmental pollution control, the organochlorine pesticides were probably the most popular group of compounds and were the focus of research efforts of analytical chemists. Because of the highly hydrophobic character and relatively high thermal stability of organochlorine pesticides, GC soon became the method of choice for their determination. Compared to other separation techniques, GC had the best separation possibilities and, by that time, relatively most efficient equipment available (e.g., when compared to LC). Later, the introduction of capillary columns increased its separation ability. The use of the highly sensitive electron capture detector (ECD) and other selective GC detectors such as the nitrogen-phosphorus detector (NPD), flame photometric detector (FPD) and subsequent coupling of GC columns to a mass spectrometer further increased the prevalence of GC over the other analytical techniques used in pesticide as well as in the organic water pollution analysis. Nowadays, the gas chromatograph is still an important and widely used instrument for routine pesticide residue analysis [2] mainly due to its versatility and sensitivity. However, since the late seventies, another separation technique, the LC, started to acquire more and more attention from the analysts. Although this method had some drawbacks, the most serious being the lack of the sensitivity and the difficulties in the direct linking with MS, an obvious shift in pesticide development towards the more hydrophilic compounds forced chromatographers to pay more attention to the theoretically almost unlimited separation possibilities available when a liquid mobile phase was used. Progress in that area has been also supported by the development of more efficient packing materials and by the introduction of the reversed phases. LC was well suited to the demands for a non-destructive selective

analytical technique, especially required for new types and classes of thermally unstable and highly polar pesticides and conjugated metabolites, where the application of GC often failed.

The present situation in the field of pesticide analysis can be characterized as a coexistence between these two chromatographic techniques, which sometimes might look as a silent competition in providing the maximal information flow in analyses of particular groups of compounds. Nowadays, both techniques can offer several advantages. GC has an advantage in the existence of a large amount of retention time data, often based on standardized retention indexes, which can be helpful for identification or confirmation purposes. Other advantages are a high separation efficiency, an availability of a wide scale of extremely sensitive detectors and a high speed of analysis. The information obtained from a GC method can be enlarged by using a combination of different columns and detectors simultaneously [3–5]. The amount of retention data available can also save time during method development. The previously described ease of GC–MS and also availability of GC–FTIR/MS, GC–atomic emission detection (AED) and other hyphenated techniques make identification in GC very efficient and upgraded. Moreover, in GC many new developments in the sample introduction process were introduced within last decade. The most important are the introduction of retention gap and related on-column injection, loop-type and programmed temperature vaporizer (PTV) injector interfaces and their various modifications [6]. With these techniques, often reported as 'LC–GC' or 'solid-phase extraction (SPE)–GC' coupling, an actual sample volume analyzed by GC can be increased from the conventional 1 μl up to several tens of milliliters. This leads to a substantial improvement in sensitivity.

The advantages of LC for pesticide and environmental analysis have been already reviewed [1,7–9]. In addition to cases where LC can be used as a much better alternative because of obvious drawbacks of GC (e.g., in case of polar, non-volatile or thermolabile compounds and direct introduction of aqueous samples), this method becomes more attractive also because of large improvements in the detection techniques in the past decade. Next to the most common UV, the application of the reaction detection (mainly post-column derivatization) [10] and, especially, fluorescence and chemiluminiscence techniques [11] lowered the detection limits and remarkably improved the selectivity of the detection. The development of on-line precolumn trace enrichment procedures also helped to increase the sensitivity and, moreover, made the whole analysis easy to automate.

Progress in LC–MS coupling in recent years remarkably improved the possibility of identification and/or confirmation of unknown compounds at concentration levels comparable to those in GC–MS. After solving initial technical difficulties during the combination of high-pressure and high-mass flow LC to the vacuum of MS, numerous interfaces were being developed and successfully applied in environmental analysis. The review will deal mainly with, at present, the most popular LC–MS interfaces: thermospray (TSP), particle beam (PB) and atmospheric pressure ionization (API) [12,13]. API includes a group of interfaces, commonly addressed as electrospray (ESP), ionspray (ISP) and atmospheric pressure chemical ionization (APCI) [14,15]. The direct liquid introduction (DLI) [16,17] and moving-belt (MB) [18,19] interfaces have been rarely used within the last six years and therefore they will be discussed more briefly.

The aim of this review is to demonstrate the potential and the possibilities of GC and LC when used in aqueous samples for analysis of four groups of the most frequently applied pesticides with relatively increased polarity. Multiresidue methods are discussed separately. Because of the very dynamic development of MS-hyphenated techniques, their increased use in pesticide analysis, and the promising results obtained with large volume injections in GC, particular attention is given to these concepts. The advantages and drawbacks of LC and GC techniques are discussed and the trends for the future are outlined. Even though some of the particular topics discussed in this paper have already been reviewed, this review should provide a comprehensive view on the present and past possibilities of GC and LC in analysis of polar pesticides in water.

2. Carbamates

In the past decades carbamates have become very important in the field of the pest control. Because of

the persistence of the organochlorine pesticides and the toxicity of the organophosphorus pesticides and their metabolites, the carbamates offered a viable alternative. In the past it was felt, that since the carbamates were labile and would not persist in the environment, there was no need for analysis of these compounds. This lack of interest might also have resulted from the fact that, at that time, monitoring studies usually did not find carbamates in the water environment. The most probable reason was, that while the residue procedures for the organochlorine pesticides were usually reported in the ppt range, carbamate analyses had detection limits usually in the ppb range [20]. Nowadays the situation has changed, because there are more sensitive analytical procedures available and because, even though the half-lives of most of the carbamates in natural waters are not very long their residues are persistent enough to be found in the water environment after point source events such as land run-off or accidental spills.

The carbamates, or N-substituted carbamic acid esters (RO-C(O)-NR′R″), can be divided into three subclasses, i.e., N-methyl-aryl carbamates, N-methyl-oxime carbamates and N-substituted aryl ester carbamates. In this paper the main attention will be given to GC and LC analysis of the N-methylcarbamates because they are the most often used compounds from this group.

2.1. GC

The direct GC analysis of N-methylcarbamates often led to their breakdown in the injection port or in the column during the analysis. The reason was that the elevated temperature caused the decomposition of most of the N-methylcarbamates to their respective phenols. There were two solutions available for this problem : (a) preparation of more stable derivatives or (b) the use of lower temperatures and short analysis times.

The development of derivatization techniques for carbamates in gas chromatography had its origins in the 1960s and 1970s, then their applications slowly decreased [21]. Generally, these techniques can be divided into the analysis of the derivatives of the carbamates and the analysis of the derivatives of their hydrolysis products. A study on the use of various agents for direct carbamate derivatization was published [20,22]. Except for the fact that derivatized carbamates are more stable under heat stress, the addition of several electron-capturing components to the molecule remarkably increases the sensitivity when ECD is used [23,24].

In order to avoid the additional labor needed for derivatization techniques, another approach in GC carbamate analysis was to adjust the separation conditions to make them suitable for direct carbamate analysis. Lower temperatures, short columns and PTV injectors were usually used [25,26]. Zhong et al. [27] investigated the temperature of the injection port and found the peak areas to be sensitive to this factor. Levesque and Mallet [28] used a 1.2-m packed column containing OV-17 stationary phase for the GLC analysis of aminocarb and its derivatives and applied this method to water also [29]. Leppert et al. [30] used a 122-cm glass column packed with 2% OV 101 on Chromosorb W-HP for the determination of carbofuran and carbosulfan residues in water. Here, the critical temperature for carbosulfan was 210°C and for carbofuran 155°C and good recoveries were achieved for both compounds at the 10 ppb level. After their extraction from water, a 2.6-m fused silica DB 5 capillary column was used to separate aldicarb and its derivatives [31]. Instead of the usual use of short columns, Nash [32] used a long glass capillary column (60 m×0.75 mm I.D.) for analysis of carbofuran after its SPE from shallow well water and found the method to be accurate. Non-derivatization methods use often an NPD detector which, even though not as sensitive as the ECD for halogenated carbamate derivatives, enables the analytical method to reach detection limits below the ppb range. Moreover, the use of NPD improves the selectivity of the detection.

2.2. LC

The use of LC for carbamate analysis is another solution for problems encountered during their GC separation. The easiest way to analyze carbamates in water by LC is to extract them using liquid–liquid extraction (LLE) or SPE and then to separate them in the reversed-phase column with subsequent UV detection [33–35] but other LC detectors such as UV diode array detection (DAD) [36], electrochemical

[37] and fluorescence [38,39] have been also employed.

One of the advantages of LC methods is an easy application of the on-line trace enrichment. Procedures were published, for carbofuran [40] and carbaryl [41], where several milliliters of the water sample were flushed onto the analytical column so that the solutes were concentrated at the head of the column. A multiresidue method using this 'large-volume injection' into a short analytical column is discussed further in Section 7 [42]. An alternative approach is the use of a precolumn for concentration of the sample . Despite the somewhat longer analysis time, it prolongs the life-time of the analytical column and allows the introduction of a clean-up step. Marvin et al. [43] described an automated on-line SPE method for the determination of benomyl, carbendazim and other pesticides in drinking water in conjunction with LC and UV detection. The often insufficient sensitivity obtained with UV detection can be increased by the use of fluorescent detection of carbamates containing fluorophores [44]. Precolumn or postcolumn derivatization is needed for the other carbamates. In the precolumn mode, the phenols, which are the hydrolysis products of carbamates, can react with dansyl chloride to produce dansyl derivatives which are separated and detected [45]. The postcolumn mode, which is the most frequently applied derivatization technique for carbamates, is based on the reaction of the other degradation product, methylamine, with *o*-phthalaldehyde (OPA) or *o*-phthalaldehyde/2-mercaptoethanol (OPA/MERC), in order to produce highly fluorescent 1-hydroxyethylthio-2-methylisoindole. This method was introduced by Moye et al. [46] and has been widely recognized for its sensitivity and selectivity for carbamates. After the method was refined [47,48], it was found to be suitable for a multicarbamate insecticide residue determination reaching nanogram and/or subnanogram levels. To simplify the complex post-column derivatization system, Nondek et al. [49] introduced the use of the solid-phase reactor containing an anion exchanger for the hydrolysis of the N-methylcarbamates. This elegant method was later refined and was suitable for a larger amount of carbamates [50]. Generally, the postcolumn fluorogenic derivatization is a powerful technique for the N-methylcarbamate residue analysis in water and it is also included in standard U.S. EPA methods within the Method 531.1 [9]. With this method it is possible to reach low detection limits at the ppt level. Derivatization with OPA-2-mercaptoethanol after SPE and postcolumn solid-phase hydrolysis was used for the analysis of a large group of carbamates and their sulphone and sulphoxide degradation products [38,51]. The analytes contained in 50-ml samples were first trapped on a disposable SPE cartridge and next, eluted with 1 ml of acetonitrile and a 100-μl aliquot was injected into the analytical system. Detection of all carbamates at levels below 30 ng/l was possible with this method. The method was later automated by means of the OSP-2A (automated cartridge exchange and valve switching unit) [52] and, with the sample volume being reduced to 5 ml, up to 30 samples per hour could be analyzed. Another approach for the sensitive detection of the carbamates is their fluorescent detection after UV photolysis. The use of this technique for the detection of various carbamates in groundwater provided detection limits of 2–3 ppb [53]. Comprehensive information on derivatization techniques used in carbamate analysis can be found in [54].

Simultaneously, with the development of derivatization techniques, the efforts to enhance the sensitivity provided by conventional UV detectors for LC led to the testing of electrochemical detection for carbamate analysis. Mayer and Greenberg [55] reported the detection of eight carbamates using a flow cell with a wax-impregnated graphite electrode. They worked at the positive potential limit for this electrode and obtained limits of detection below 5 ng for some compounds. The use of UV and electrochemical detection in series also enabled them to monitor compounds with similar retention times. Anderson et al. [56,57] proposed the use of the Kel-F-graphite electrode for the direct detection of carbamate pesticides in water. They obtained detection limits in the program range and the sensitivity was 60-fold improved compared to other reports for glassy carbon electrodes under identical conditions, or for alternative LC detectors. Apart from their high sensitivity, the problem in the use of electrochemical detectors is the maintainance of their operation ability. One reason is the accumulation of the reaction products on the surface of the electrode

resulting in the blockage of the active surface. To avoid this drawback, in situ cleaning by pulsing the electrode periodically to extreme potentials can be used. Application of this technique with a platinum working electrode for the determination of carbamates provided detection limits in the nanogram to picogram range, depending on the compound, the potential applied and the retention time [58]. An effort has also been made to couple another spectral detection, FTIR spectrometer, to LC. The application of this hyphenated technique to carbamate mixture analysis provided valuable spectral information but the sensitivity was rather low [59].

2.3. MS

A mass spectrometer coupled to GC was used for the development of the rapid specific method, which allowed the detection of carbofuran in water at the 0.5–1 μg/l level after its extraction with dichloromethane [60]. GC–MS was also found to be effective for the parallel analysis of aldicarb and aldicarb nitrile with a greatly reduced possibility of misidentification [31]. These two compounds could not be analyzed together by LC using conventional detectors since aldicarb nitrile neither absorbed in the UV nor hydrolyzed to form methylamine which is used after reaction with OPA in fluorescence detection. However, because of problems with their GC analysis, LC–MS is usually preferred for most carbamates. Since coupling of LC and MS has been applied, carbamates, together with other pesticides, have been studied using all the major interfaces. Reports have appeared on the use of MB [61,62], DLI [63], PB [64], TSP [65,66] and API [67,68] interfaces coupled to a variety of MS detectors.

An application of the on-line column-switching technique prior to LC–TSP–MS allowed the detection of the total content of carbendazim, benomyl and thiophanate-methyl in water at levels below 0.02 μg/l [69]. Miles [64] studied the carbamate pesticide aldicarb and its degradation products, aldicarb sulphoxide and aldicarb sulphone, by a variety of methods, including GC–MS, LC–TSP-MS and LC–PB-MS. Even though the PB can be coupled to a conventional LC with flow-rates up to 1 ml/min, it suffers from several disadvantages, the main one being the low sensitivity due to inefficient sample transfer through the interface. This drawback can be compensated by on-line coupling to SPE. A 100-ml sample was preconcentrated on small cartridges (10 mm×3.0 mm I.D.) packed with the C_{18} or polymeric sorbent, connected to the LC–PB-MS [70]. With this approach, detection limits of 0.1–8 μg/l were obtained for a group of 17 carbamates in the full-scan EI mode. The CI experiments with a larger group of 48 carbamates and their degradation products had shown the best performance in positive ion mode (PCI) with ammonia as a reagent gas. Both GC–MS and LC–PB-MS spectra could be identified by the library search, however, only 28 from the 48 carbamates could be satisfactorily detected by GC–MS.

The LC–MS coupling is at present dominated by the developments of the new API interfaces. Their major advantages are an excellent sensitivity, already being compared to GC–MS, and the possibility of gaining additional structural information by means of collision-induced dissociation (CID) in the pre-analyzer region. The disadvantage of the first ESP interfaces was that the low flow-rates (typically less than 10 μl/min) were not compatible with the conventional LC. The situation improved with the recent high-flow ESP (ISP) and APCI which can be operated at flow-rates of up to 2 ml/min. The ISP- and APCI-MS were compared to the more established TSP and PB methods in a detailed study on N-methylcarbamates [67]. As expected, the TSP-MS spectra provided the least structural information of all techniques tested; the most sensitive appeared to be the APCI-MS with approximately ten-fold better detection limits than ISP and TSP. The PB-MS was in some instances almost four orders of magnitude less sensitive than APCI-MS. Detection limits of 40 ppt of carbofuran in surface water and 2.5 ppb in crude potato extract were obtained by the ISP-MS in on-line coupling with selective immunoaffinity trapping [71].

To summarize all different approaches for the carbamate analysis, more attention is given to LC techniques nowadays. At present, the main goals in this area are to further refine techniques using fluorescence and electrochemical detection and to implement LC–MS methods, especially those using API interfacing, on a routine basis. A lot of attention is paid to sample concentration and numerous SPE

methods in off-line or on-line configuration that are used prior to LC separation. LC separation is easy to automate and several fully-automated systems (e.g., with UV DAD) are already used in routine monitoring. Since these methods often incorporate also other groups of pesticides as well they are discussed in more detail in the section 'Multiresidue methods'.

With regard to GC, the development of new columns capable of separating carbamates at lower temperatures and wider use of the 'cold' on-column or PTV injectors could increase the frequency of the use of GC. This would certainly be interesting for highly specific determinations with an MS detector.

3. Substituted urea herbicides

Substituted phenylurea herbicides are widely used in agriculture for a selective control of weeds. They are persistent chemicals and soil-based residues can remain for several months following application. They are able to be transported from agricultural and other treated areas via air, surface run-off and by leaching and accidental spills near wells and water bodies. Both GC and LC techniques can be used for determination of these compounds.

3.1. GC

In the direct GC separation of substituted phenylureas, difficulties frequently arise because of the rapid thermal decomposition of some of these compounds into their isocyanates and aliphatic amines. The cause of this thermal breakdown was ascribed to the presence of the amide hydrogen atom, since substitution of this position with a methyl group provided thermostable compounds amenable to GC [72]. Several authors described the direct analysis of phenylureas [73,74], but later it was pointed out that they, most probably, determined the corresponding pyrolysis products, isocyanates [75,76]. Grob [76] made attempts to evaluate capillary GC for the analysis of thermolabile phenylurea herbicides. After the comparison of several columns and optimization of the GC procedure he divided urons into several groups according to the ease of their GC analysis. The compounds with a methoxy group on the nitrogen atom, e.g., monolinuron and linuron, were found to be relatively stable and most easily analyzable. On the other hand, diuron, metoxuron and neburon were classified as 'impossible' for a GC analysis due to reasonable difficulties in their analysis when the usual conditions and columns are used.

To overcome the difficulties with the GC analysis of substituted ureas, various derivatization procedures can be applied. Principally, it is possible to modify the phenylureas directly to make them stable for GC analysis or to analyze anilines, which are hydrolysis products of phenylureas. As an example, analysis of heptafluorobutyric acid (HFBA) derivatives of anilines [77] and phenylureas [78] can be given. The use of other types of derivatization of urea herbicides (e.g., alkylation) has been also reported [79]

3.2. LC

To overcome difficulties with the thermal stability of the phenylurea herbicides, the choice of LC is another alternative in the same way as it was for carbamates. To separate phenylureas, both normal [80] and reversed-phases [80,81] were used. For the detection the simplest choice is an UV spectrometer [82]. The spectral information can be increased when a UV diode-array detector is used [83]. The connection of an additional detector in series with the UV detector increases the selectivity of the detection procedure. Schussler [81] proposed simultaneous UV/electrochemical detection of isoproturon, chlorotoluron and linuron after their LLE from surface and tap waters. Photolabile analytes, after passing the UV detector cell, can be detected by a photoconductivity detector [80]. The proper operation of this detector requires a sufficiently polar mobile phase to facilitate free ion formation and efficient charge transfer in the photoconductivity process. In addition to the use of these common LC detectors, efforts were made in coupling typical GC detectors to LC columns. The electron capture detector was used in the analysis of phenylurea herbicides after their derivatization with HFBA [84]. To increase the response of the ECD, a derivatization procedure was used in this case. A packed-capillary reversed-phase liquid chromatography was coupled with ECD by Zegers et al. [85]. Among representatives of several groups of polar compounds linuron could be detected at minimum

amounts of 70 pg, corresponding to its sub-ppb levels in surface water. The use of the chemical modification of analytes for better sensitivity can be also applied when common LC detectors are used. After the introduction of a suitable fluorophor into the skeleton of the analyte, a fluorescence spectrophotometer can be used for detection. Lantos et al. [86] described the analysis of metoxuron and its breakdown products in water by LC with fluorescence detection after their pre-column dansyl derivatization. Using LLE for the isolation they obtained detection limits of 1 ppb. Another derivatization procedure was based on a reaction of the photolysis products with OPA to produce fluorescent molecules [87] (see also section on carbamates). An increased selectivity, required for the analysis of complex samples, was reached when electrochemical detectors were used for determination of phenylureas. Nielen et al. [88] applied this technique and found it to be a sensitive screening method for phenylurea herbicides in surface water without an extensive sample pretreatment. Almost all analytes that they tested could be determined at sub-ppb levels. They observed a certain sensitivity drop due to the contamination of the electrode, but this drawback might be suppressed by pulsing the electrode periodically to high potentials. The already mentioned drawback in the analysis of phenylureas is that they are often detected with their corresponding anilines. It usually leads to a high complexity in the analyzed mixture and, subsequently, to difficulties or errors in data interpretation. An attempt to develop a multiresidue method exploiting the combination of GC and LC techniques was done by De Kok et al. [89]. They made a primary fractionation using normal-phase LC and derivatized the fractions with HFBA to obtain a sensitive GC–ECD detection. They presented several schemes to be used in environmental analysis differing in their complexity and the final information provided [90]. Using these schemes, phenylurea herbicides and their corresponding anilines could be detected at the 0.01–0.1 ppb level in the surface water with a satisfactory repeatability. A simpler approach for the detection of phenylurea herbicides in the presence of their anilines was proposed by Goewie et al. [91]. They used a precolumn packed with a support containing 2-amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) loaded with platinum (IV) as an aniline filter. At least 0.1 ppm of anilines could be removed from aqueous solutions containing trace amounts of phenylurea herbicides. Consequently, they determined phenylureas by LC–UV detection after the on-line trace enrichment on an C_{18}-bonded silica precolumn. Filter precolumns containing platinum were able to be regenerated. The coupled column RPLC with UV detection using direct large-volume injections of up to 4 ml was used for the rapid and sensitive determination of isoproturon in water samples [92]. The adverse impact of the interfering humic substances, which is usually observed when on-line SPE–LC systems are applied, has been minimized when, in the analysis of six phenylureas in natural water, an on-line dialysis step was introduced [93]. For analysis of 250 ml tap water; detection limits were 0.1 ppb.

3.3. MS

Phenylureas were among the first compounds to be analyzed in environmental applications of LC–MS techniques. Using DLI-MS coupled to reversed-phase LC [94] 15 phenylureas could be detected at amounts as low as 100 pg. However, the method required micro-LC and detection limits were in the ppm range. Maris et al. [95] described LC separation of ureas followed by the DLI-MS. Using an on-line trace enrichment of a 10-ml sample and a mass spectrometer operating in the selected ion (SIM) monitoring mode, they obtained detection limits at the 10-ppb level. Despite the promising results, many technical problems of the DLI interfacing hampered further developments and the TSP interface because of its robustness and availability is preferred for the analysis of phenylureas [96,97]. The on-line SPE of 50-ml surface water samples coupled to LC–TSP-MS was used for the study of fifteen phenylureas by Bagheri et al. [97]. Time-scheduled SIM detection limits for all compounds except linuron (60 ppt) and chlorobromuron (120 ppt) were found to be 5–15 ppt and the presence of monuron and isoproturon at low ppt levels in river Rhine water was confirmed. Both LC–TSP-MS and SFC–TSP-MS were used for analysis of diuron [98]. It was shown that variation of the repeller voltage may sometimes be used to obtain structure-specific fragmentation. The use of

on-line SPE of 100–250-ml samples combined with LC–PB-MS allowed sensitive detection of four phenylureas at 30–50 ppt level under full-scan EI conditions [99]. In addition to several industrial pollutants, low-ppt levels of chlortoluron and diuron were found in surface water. The combined EI and methane-PCI data were used for the identification of 3,4-dichloroaniline, a breakdown product of diuron. A similar set of phenylureas was studied by Minnaard et al. [42]. In this work, a single (precolumn-size) column was used for both sample enrichment and separation. The four (from six) phenylureas could be detected and identified in surface water from their EI spectra at 1 ppb level; the SIM improved detection limits about ten-fold. Another method of improvement the sensitivity of the PB-MS for phenylureas was shown by Mattina [100] who added a structurally similar compound (phenylurea) to the LC eluent in order to improve the transfer efficiency through the interface. With this method, it was possible to detect 0.2 ppb of diuron and 0.5 ppb of linuron.

Generally, the present situation for the analysis of the phenylurea herbicides in water is similar to that for carbamates. Despite the possibilities of the GC and the detection schemes available for the analyses of complex mixtures [90], LC seems to be more popular in recent years when the number of methods published are considered. LC methods originally tried to overcome the lack of the sensitivity by the introduction of various derivatization steps. Naturally, this created larger demands on the skill of operators and the presence of many steps in an analytical method also increased the possibility of error. Therefore, efforts were focussed on the simplification and optimization of a LC method. To speed up the analyses and to increase the throughput of samples, on-line SPE–LC procedures were often introduced. The use of such systems for the analysis of the phenylurea herbicides can be found in earlier literature [82,88,95,101]; nowadays phenylureas are mostly analyzed within multiresidue methods [36,83,102,103]. Improved separation ability of LC columns, sensitive UV DAD or MS detectors and the use of solid phase for the trace enrichment enabled low-ppt detection limits to be reached in these methods.

Further developments in the analysis of phenylureas in water can be expected mostly in the LC techniques since in GC applications the problems are generally similar to those mentioned for carbamates. In LC the improvement and the simplification of the detection by introduction of powerful and easy-to-operate derivatization systems can be one alternative for future progress, however, the present state of LC–MS analysis predicts the preference of analysts for this technique as the method-of-choice.

4. Triazines

Triazines are among the most widely used herbicides in agriculture today and they are applied to growing crops as well as directly to the soil. These herbicides, especially atrazine and simazine, are among the most persistent herbicides in use. Their transport in the environment, e.g., by leaching, run-off or accidental spills can cause pollution of aquatic systems. The triazines are degraded by chemical and biological processes. Their major breakdown products in soils and waters are the respective hydroxy-triazines which are formed primarily by chemically induced hydrolytic reactions [104]. For triazine analysis both GC and LC can be used.

4.1. GC

Because of their relatively less polar nature but still sufficient volatility, the separation of the triazine herbicides on the GC column is not problematic and it does not suffer from the breakdown problems observed by carbamates and phenylurea herbicides. Triazines can be easily chromatographed without a derivatization procedure since they provide a strong response if suitable detectors are used. The preferred and the most commonly used detector is the nitrogen-phosphorus detector (NPD) sometimes referred to as alkali flame ionization detector, which provides high selectivity and sensitivity for triazines [105–107]. ECD can be also applied especially for multiresidue methods which include other organochlorinated pesticides [108]. The classical analytical procedure for triazines consisted of the liquid–liquid extraction of the water sample, concentration of the extract by evaporation followed by programmed temperature separation with NPD detection [109].

However, the higher efficiency of SPE in the recovery of triazines almost totally converted the sample enrichment procedure from LLE to SPE. The usual detection limits for the determination of triazines with NPD after an appropriate trace enrichment are 10–100 ppt. Certain problems during a GC analysis of triazines have to be faced when there is a need for the direct analysis of polar hydroxy derivatives and other degradation products. The hydroxy derivatives can be separated by GC after derivatization [110]

4.2. LC

Triazines are mostly separated on reversed-phase columns [105,111–114]. Since they have a strong absorption of the UV light between 210–240 nm, UV is the most common method of detection in LC [112–118]. The DAD detector was used to improve identification [83,102,105,119]. To increase the sensitivity of the detection, investigations on the use of the electrochemical detectors were performed [111,120,121], but only some of the authors claimed better sensitivity when compared to UV detection [120,121]. One advantage of electrochemical detection is the enhanced selectivity [111]. Triazines are usually also included in the multiresidue methods discussed further in Section 6 .

To obtain higher sensitivity in the LC method for environmental analysis, a trace enrichment is generally required. For triazines the classical LLE was applied [116,117,119], but, at present, it is more often replaced by SPE in the off-line mode [83,96,105,118] or in the on-line configuration [102,122,123] which is less labour-intensive, easy to automate and providing a large sample throughput [112]. On-line techniques using ion exchangers were applied to chlorotriazine and some pesticide degradation products, e.g. hydroxyatrazine and phenoxyacetic acids [124–126].

When GC and LC are used in one on-line system, they provide a highly efficient method. With a loop-type interface, Grob and Li [127] concentrated 10 ml of sample on an alkyl-bonded silica LC column and, after isocratic separation with methanol–water–*n*-propanol solvent, transferred 150 μl heart-cut fraction containing atrazine into the GC. The detection limit of the method with an NPD detector was in the range of 3–5 ng/l and the whole procedure was fully automated. A similar approach was also used by Pico et al. [128], referred to as SPE–GC. This hyphenated technique enabled utilization of various GC detectors (FID, NPD, FPD) and provided detection limits lower than 0.1 μg/l. LC–GC and/or SPE–GC applications will be discussed more thoroughly in the section on large volume injections into GC.

4.3. MS

The coupling of GC with a variety of MS detectors, including magnetic sector, quadrupole, ion trap or triple quadrupole, is well documented for triazines [129–133]. However, similar to previously discussed classes of pesticides, triazines are usually included in the multiresidue GC–MS methods. Rostad et al. [131] showed that GC with tandem MS operated in PCI mode (GC–PCI–MS–MS) provided speed and selectivity which can be extremely useful in the rapid analysis of trace concentrations of selected compounds in complex environmental matrices. The quantitative performance of the GC–MS analysis can be even increased if isotopically labeled analytes are used as internal standards. This technique, called isotope dilution (ID), uses the ratio of the naturally abundant and the stable labeled isotope for the determination of the naturally abundant compound. Due to the similarity between the compound and its isotope, method accuracy and precision are not affected by the sample matrix. However, a serious disadvantage of the ID technique is the need for a labeled internal standard for every analyte investigated. The use of ID GC–MS for the determination of triazines in water was published by several authors who found this technique to be very successful for the environmental organic pollution analysis [129,132–134]. Off-line SPE on polymeric sorbent followed by GC–MS was used for analysis of twelve triazines in surface and drinking water [135]. Authors examined PCI and NCI modes with methane and isobutane as reagent gases next in addition to classical EI. The EI MS was found to be more sensitive than CI and atrazine and simazine were detected and identified in real water samples at 10–80 ng/l levels. Absolute lowest detectable amounts of the triazines obtained by GC–EI-MS technique were between 2–12 pg in SIM mode. EI

and CI operation modes were compared also by Stan and Bockhorn [136] an Durand and Barceló [137], however, some differences in relative intensities of base peaks in spectra obtained under various experimental conditions and from different instruments can be seen.

Regarding the rapid development of the LC–MS technology, many of the statements which refer to GC–MS above are valid also for LC–MS. After the initial analyses of triazines by open-tubular LC–MS and LC–DLI-MS [138] the more robust TSP was preferred and several applications proved its capacities for sensitive detection of environmental samples with the selective removal of problematic matrix interferences [96,139–141]. LC–TSP-MS is often used as a complementary technique to GC–MS for the identification or characterization of degradation products of various pesticides. Barceló et al. [142] studied the photodegradation of fenitrothion and propazine in various water samples. Aliquots of the spiked samples were injected directly into the LC system and the combined data from LC–UV DAD and LC–TSP-MS led to the identification of four degradation products of propazine. An off-line trace enrichment on C_{18}-bonded silica or ion-exchange sorbents was used prior to LC–TSP-MS, for the analysis of atrazine and its metabolites in water [143]. Both chlorotriazine and hydroxytriazine metabolites could be detected at levels comparable to those from LC–UV DAD (ca. 1 ng). However, the conclusion drawn from all of the above studies was that the spectral information from the TSP-MS is in many instances not sufficient for the elucidation of the structure. This encouraged intensive research on the coupling of a TSP interface with tandem-MS, mainly with the goal of obtaining relevant structural information from the daughter ion spectra [144–146]. Abián et al. [144] investigated both qualitative and quantitative aspects of the PI- and NI-mode detection in LC–TSP-MS and LC–TSP-MS–MS for the identification of six triazines and their degradation products. Despite encouraging results, the technique still requires an experienced operator and several operational parameters have to be adjusted separately for each compound.

As it can be seen from publications, reports and standard methods available (see also Section 7: 'Large-volume injections into GC'), GC is still a more powerful technique than LC for many triazines due to its simplicity, lower detection limits and efficient coupling to the mass spectrometer. LC chromatography, however, has been developed to be a suitable alternative which has advantages over GC when an analysis of labile triazines or more polar derivatives and degradation products (hydroxytriazines) is required.

5. Chlorophenols and phenoxyalkanoic acids

Analyses of compounds belonging to these two groups of pesticides are usually based on similar principles owing to their acidic character. Chlorophenols and phenoxyalkanoic acids (sometimes also called phenoxyacetic acid herbicides) can be detected within the same method which is sometimes required since chlorophenoxyalkanoic acids can degrade into chlorophenols. Both groups of pesticides are often transported to aquatic systems via indirect contamination from droplet drift after spraying operations, via water run-off from treated agricultural areas, through leachate from landfill sites or after accidental spills. Chlorophenols, being also often used in manufacturing processes for resins, plastics, pulp and paper, dyes and pharmaceuticals can be introduced to water from waste water discharges. Because of their toxicity and the amounts applied, the monitoring of both groups of pesticides is highly important. GC and LC are the most used analytical techniques nowadays for these acidic pollutants.

5.1. GC

For the preconcentration of acidic pesticides prior to GC analysis the most usual techniques are SPE or LLE after acidification of the water sample. The direct analysis of phenoxyalkanoic acids by GC is obstructed due to their acidic character and low volatility. Chlorophenols can be directly separated by GC if a properly deactivated column is used. Peak tailing can be reduced when, for example, a methylvinyl silicone fused-silica capillary column is used [147]. The use of a polyester stationary phase deactivated by phosphoric acid has similar effects. The most used derivatization procedures in environmental applications are acetylation of chlorophenols,

methylation of phenoxyalkanoic acids and, for both groups, the preparation of pentafluorobenzyl derivatives. Methylation of phenoxyalkanoic acids is the traditional approach which is less laborious when compared to, for example, esterification methods. It was used for the analysis of several acid herbicides in water with a detection limit 0.1 to 1.0 ppb [148]. Diazomethane is also applied in U.S. EPA Method 515.1 for determination of chlorinated acids in water by GC–ECD [149]. The use of diazomethane has, however, several disadvantages. It is a rather toxic reagent and has explosive properties requiring very careful treatment. In addition to that, the response of ECD to methyl derivatives is sometimes weak and varies from one chemical to another. To improve the sensitivity of analytes, pentafluorobenzylation was suggested as a suitable derivatization technique for both chlorophenols [150] and phenoxyalkanoic acids [151]. PFB derivatives provide a sufficient ECD response and they are often the method of choice when phenols or acids with low or no amount of halogen atoms are to be analyzed. They have been applied for analyses of chlorophenols and phenoxyalkanoic acids in various types of waters [152–154]. Hillman and Bachmann [155] introduced an on-line system for supercritical fluid derivatization and extraction connected with capillary GC–ECD. The advantage of SFE is the higher rate of the reaction of analytes with pentafluorobenzylbromide (PFBB) in the supercritical phase. In addition to PFBB, several other halogen containing reagents as, for example, heptafluorobutylimidazol or boron trichloride-2-chloroethanol have been used to improve the sensitivity of ECD to phenols and acids. Lamparski and Nestrick [156] determined trace phenols in water as heptafluorobutyryl derivatives with the detection limits at a low-ppb level. Acetylation is a convenient approach for chlorophenols as it reduces the laborious derivatization procedure. Acetylation exploits the fact that the presence of halogen atoms in these compounds enables them to be detected sensitively by ECD. The advantage of this method is that in the analysis of the water samples the acetylation can be performed directly in water by addition of acetic anhydride and adjustment of the reaction conditions. Acetates can be then isolated by LLE [157,158] or SPE [159]. The modified procedure used SPE of phenols from acidified water samples, elution with an organic solvent and derivatization of phenols in the eluate [160]. NPD can be used for the detection of some derivatives as well. This provides more selective response and, thus, an extensive clean-up is not necessary. Preparation of 2-cyanoethyldimethyl(diethyl)aminosilane (CEDMSDEA) derivatives of acidic herbicides was proved to be a good alternative to ECD-sensitive derivatization for the determination of acids in water [161]. The reproducibility of the proposed method as well as detection limits obtained (0.01–0.1 ppb) were comparable to that of the ECD. CEDMSDEA derivatives have been prepared also for chlorophenols [162]. Another promising spectrometric detection technique for GC is FTIR. Malissa et al. [163] described the determination of chlorophenols in surface water by capillary GC–FTIR spectroscopy. The proposed method was able, similar to GC–MS, to identify water pollutants. But, despite progress in the instrumentation, the sensitivity of FTIR detection is still markedly lower than MS.

5.2. LC

As it could be seen, the usual way to obtain a good separation of acidic herbicides in GC is by chemical derivatization. To avoid this procedure HPLC can be applied for their direct analysis. LC determination of phenols and substituted derivatives has been reviewed recently [164]. For the LC separation of acidic herbicides reversed-phases are most frequently used [165,166]. The simplest detection technique is based on the UV absorption of acidic herbicides. Phenoxyalkanoic acids have two local UV absorption maxima. First is at 230–235 nm and the second at 280 nm. The use of detection at 230 nm is usually preferred because of its higher sensitivity [167,168]. When a water matrix contained a significant amount of interfering components or a high UV wavelength cut-off buffer was employed, the detection at 280 nm had to be chosen even though it was six times less sensitive [165,166]. In order to obtain an improved selectivity for phenoxyalkanoic acids, Fayyad et al. [169] used 1,10-phenanthroline as a mobile phase additive and indirect photometric detection at 510 nm.

Chlorophenols can be detected at 220 nm [170] or 280 nm in the same way as phenoxyalkanoic acids,

[171]. Since the use of UV detection for the analysis of water samples often suffers from an excessive number of interferences, some authors tried to utilize electrochemical detection. The sensitivity they obtained was usually at the same level as in UV detection, but a cleaner background enabled a more selective detection [172–174]. Another approach on how to improve the selectivity of the detection of chlorophenols in complex water matrices was suggested by Werkhoven-Goewie et al. [175]. For lower chlorophenols they used a post-column photoconversion to phenol by UV irradiation followed by fluorescence detection. The method was applied to river water and found to be very selective. The reversed-phase LC was coupled to a GC detector (ECD) for analysis of six chlorophenols [85]. Relatively large volume injections of 15 μl allowed detection limits of ca. 150 ppt in surface water.

For the preconcentration of acidic herbicides from water samples, both LLE [172,176] and off-line SPE [166–168] were employed. An elegant example of the use of a sorbent combination is trapping of phenoxyalkanoic acids and other matrix components from water on non-specific graphitized carbon black followed by elution and selective retrapping of phenoxyalkanoic acids on an anion exchanger. The acidic eluate from the anion exchanger was analyzed by LC [167]. The same group also reported a similar approach with a single graphitized carbon black cartridge for the analysis of eleven phenols. Using 0.5–2 l of water sample they obtained detection limits for most of the analytes in the sub-ppt range [177]. Membrane extraction disks impregnated with C_{18}, polystyrene-divinylbenzene (PS-DVB) or acetyl-PC-DVB resin beads were used for off-line SPE of 16 nitro-, chloro- and methyl-substituted phenols from 200–500 ml of aqueous samples. After elution with an organic solvent, GC or LC was used for quantitative determinations [178]. The best recoveries were obtained with acetyl PS-DVB. When thick (3-mm) membranes packed in the 7-mm I.D. precolumns were used, only 0.75 ml of methanol was needed for elution of analytes and the SPE method seems to be robust and quick. A popular preconcentration technique for acidic herbicides in recent years is the on-line SPE. So-called precolumn switching techniques are very efficient procedures because of their speed and large enrichment factors their use in analyses for chlorophenols and phenoxyalkanoic acids in water has been well documented [165,170,173,175]. An on-line SPE–LC with UV DAD detection was used for a systematic study of retention properties of a group of thirteen substituted phenols [179] on five different analytical columns. With 50 ml of surface water enriched on a non-selective PLRP-S and a selective ENVI-Chrom P precolumn in series, the limits of detection for phenol and its chlorinated substituents were between 0.05–0.6 ppb. The potential of on-line coupling of the porous graphitic carbon precolumn with a carbon-packed analytical column was demonstrated for several polar phenolic compounds in the study by Coquart and Henion [180]. Despite some peak broadening, analytes could be detected at the 0.2 ppb level in 50 ml of drinking water and the method appears to be suited also for analyses of other classes of polar compounds. To remove the macromolecules that interfere with analytes in on-line systems from aqueous samples, the electrodialysis sample treatment was tested in the analysis of phenoxy acids [181]. The authors reported partial improvement in the selectivity but this approach still requires further study. An interesting sample-handling alternative for acidic herbicides is the use of supported liquid membrane techniques [182].

Higher selectivity and/or sensitivity in LC analysis of acidic pesticides can be reached via various derivatization techniques. For the detection of chlorophenols in river water, De Ruiter et al. [183] used pre-column dansylation of analytes followed by separation and post-column photochemical UV irradiation of the dansyl derivatives. They obtained an improved selectivity in comparison with the usual detection techniques. Kwakman et al. [184] employed a different approach for LC analysis of chlorophenols in water. They used lissamine rhodamine B sulphonyl chloride as a pre-column labeling reagent for the peroxyoxalate chemiluminiscence detection and obtained a detection limit of 0.2 ppb using only 0.5 ml of water sample.

5.3. MS

Similarly, as for previous groups of pesticides, an efficient detector for the identification and determi-

nation of chlorophenols and phenoxyalkanoic acids by a GC method is a mass spectrometer. The direct analysis of chlorophenols is included in U.S. EPA priority pollutants GC–MS procedures which are used commonly nowadays. Generally, chlorophenols can be analyzed by MS directly [185,186] or after their derivatization [158]. A similar procedure is available for chlorinated acids. Infante and Perez [187] presented an analytical method utilizing SPE with C_{18}, elution with methylenechloride, derivatization with diazomethane and MS detection. They reported detection limits in the low ng/l range. It is also possible to use the isotope dilution GC–MS, already mentioned in the chapter on triazine analysis, which is an excellent technique for the removal of interferences and for the improvement of the reproducibility. Lopez Avila et al. [188] found that the sensitivity of ID GC–MS was comparable to that of GC–ECD for the determination of 2,4-D and dicamba in water. Tang and Ho [189] utilized ITD-MS for the testing of the membrane extraction disk enrichment followed by supercritical fluid elution and GC of phenols from water. All underivatized phenols, with the exception of free phenol, were quantitatively recovered from water. In-situ aqueous acetylation required longer sample preparation time, but the phenol derivatives formed were easier to recover from the water sample, easier to chromatograph and were detected more sensitively.

As regards the LC–MS, an on-line extraction system with a phase separator was used in a post-column mode in order to selectively remove non-volatile buffers or ion-pair reagents prior to DLI-MS [190] or TSP-MS [191]. The phenoxy acid herbicides 2,4-D, 2,4,5-T and silvex were used as model compounds; the electronegative chlorines caused a superior response in the negative ion (NI) mode compared to that in the positive ion (PI) mode. This effect was even enhanced with the addition of a halogenated modifier to the LC eluent for various chlorophenols, 2,4-D and 2,4,5-T [192]. Similar experiments, with chloroacetonitrile in the mobile phase, were performed in the TSP-NI-MS analysis of chlorophenols [193]. The selectivity of TSP-NI-MS for chlorophenols was demonstrated also by Barceló [140]; signal intensities in the PI mode were about three orders of magnitude higher than those in the NI mode and lowest detectable amounts ranged from 5 to 50 ng. A technique of segmented-flow extraction into a non-polar solvent was used for determination of organophosphorus insecticides, chlorophenols and phenoxyacetic acids by LC–TSP-MS [194].

Chlorinated phenoxyacetic acid derivatives could be detected by LC–PB-MS at low-ppb levels upon the addition of a structurally similar 'carrier compound' to the eluent. Methane-NCI, combined with SIM, led to limits of detection of ca. 1 ppb for 2,4-D, 2,4,5-T and silvex [195]. LC–PB-MS of chlorinated phenoxyacetic acid derivatives allowed their identification, but showed that quantification was not reliable, because instrument response factors varied widely over a limited period of time [196,197]. Successful identification could be carried out by comparison with common EI library spectra and only small differences in the relative ion intensities were observed [196]. Evidence for thermal decomposition of chlorinated phenoxyacetic acid herbicides in LC–PB-MS was obtained by Betowski et al. [198].

GC and LC are equally suitable for the analysis of acidic herbicides as for triazines. The use of relatively simple derivatization procedures, SPE and the efficiency of the GC–MS analysis often make GC the preferred technique for the environmental analysis of chlorophenols and phenoxyalkanoic acids. Moreover, the use of deactivated capillary columns allows direct GC separation of chlorophenols. In addition to FID and MS these compounds can also be directly and sensitively detected by ECD due to presence of chlorine atoms. Thus, very efficient, sensitive and fast GC methods are available.

LC is usually preferred for the analysis of phenoxyalkanoic acids and chlorophenols in multiresidue on-line or off-line methods where no derivatization is required. Moreover, the use of on-line SPE allows the development of a robust, sensitive and fast method. Present developments in LC–MS make this technique very promising for the future. The wider dissemination of the use of derivatization techniques in LC is hindered by their sophisticated nature, even though they enable a high selectivity.

6. Multiresidue methods

The obvious practicality of the determination of numerous pesticides within one analytical run has led

to a rapid development of multiresidue methods in both GC and LC. As it is apparent from the text below, most of the multiresidue methods employ MS for the detection (that is why a separate section on GC analysis is omitted from this chapter). This results from the fact that retention-time-based identifications and determinations of environmental pollutants are no longer sufficient and additional spectral information is usually required.

6.1. LC

A multiresidue method for a group of phenylureas and triazines was developed by Pichon et al. [199]. An on-line SPE of 150-ml sample on a PLRP-S precolumn followed by LC–UV was used; detection limits obtained for surface water samples were between 0.05–0.3 μg/l. Pesticides atrazine and diuron were found in the Seine River at 0.3 and 1.1 μg/l levels, respectively. A systematic study on the suitability of precolumn sorbents in on-line combination with a C_{18} analytical column was presented by Liška et al. [200]. Breakthrough volumes and peak broadening aspects of diuron, atrazine, 2-nitrophenol, aniline and 2-chloroaniline were shown for ten different sorbents, including C_{18}, polymeric, ion-exchange and carbon materials. In addition, an influence of humic substances on analyte trapping efficiency was discussed. It was concluded that the styrene-divinylbenzene copolymer is the best suited material for on-line combination with a C_{18} analytical column and that humic substances are only partially contributing to the matrix peak observed in surface water. A comparison of the different sorbents has shown that the retention on apolar copolymers was 25 to 40 times higher than the retention obtained with C_{18} silicas [201]. Chiron and Barceló [39] used on-line solid-phase disk extraction followed by UV–VIS and post-column fluorescence detection for the analysis of various pesticides in drinking water. The proposed method met the requirements established by the European Community Directive on the Quality of Water Intended for Human Consumption (DWD-CEC) and permitted determination of ten pesticides and their transformation products at levels below 0.1 μg/l. The potential of LC for multiresidue analysis was shown by Di Corcia et al. [202]. The separation of 71 base-neutral pesticides and, in a separate run, 18 additional acidic pesticides was carried out on C_{18} and Cyano columns after off-line sample enrichment on Carbopack cartridges. Detection limits obtained with the method were typically below 0.1 μg/l. Both, C_{18} and cation-exchange membrane extraction disks, packed in a small pre-column-type membrane holder, were used for simultaneous on-line trace enrichment of thirteen acidic, basic as well as polar neutral analytes from surface water [203]. Using LC–UV and 20-ml samples the detection limits of most analytes were between 0.5–2 μg/l and the disks could be reused up to ten times. Liška et al. [204] presented a rapid screening on-line SPE-LC method designed for an early-warning system of over 50 pesticides in surface water. It allowed the separation of most compounds with detection limits of about 1–5 μg/l after preconcentration of 30 ml of sample. A fully automated LC method using on-line trace enrichment and DAD detection was developed by Slobodnik et al. [36]. Validation results for 27 pesticides were presented and calibration graphs were linear in the range of 0.1–7 μg/l.

6.2. MS

The styrene-divinylbenzene (ST-DVB) and C_{18} Empore extraction discs were used for trace-enrichment of 1 liter of surface water samples spiked with numerous carbamates, chlorinated pesticides, organophosphorous herbicides, triazines, anilides and phenylureas and acidic herbicides [205]. From among 32 analytes, 14 could not be detected with the LLE method whereas all compounds were determined by the SPE procedure. The stability of individual pesticides enriched on disks was also discussed. A similar approach using bonded-silica cartridges was reported by Benfenati et al. [206]. An off-line SPE and GC–ITD has been used for multiresidue analysis of 245 pesticides in the work of Cairns et al. [207,208]. Pesticides were determined in fruit and vegetable matrices, however, the general conclusions relating to EI and CI spectra formation are of importance also for water analysis.

For the LC–MS analysis of water samples TSP is, at present, the most often used interface. The potential of TSP with non-polar, normal-phase LC solvents (*n*-hexane, cyclohexane and dichlorome-

thane) for the analysis of pesticides has been evaluated [191]. In the PI mode, detection limits were improved about ten-fold for all test compounds when using a normal-phase instead of a reversed-phase eluent. In the NI mode both types of eluent showed the same sensitivity for several chlorophenols. Using full-scan TSP-MS, detection limits for nine most commonly used groups of pesticides varied between 1 and 200 ng in both PI and NI. This is in agreement with the results of a study on the determination of phenoxyacetic acids and chlorotriazines using cyclohexane as an LC eluent [209]. In this case, good sensitivity was obtained in the PI mode. TSP-MS [210] detection was used for the on-line SPE-LC analysis of selected pesticides. The detection limits ranging from 0.01 to 0.09 μg/l were found acceptable for target compound analysis in environmental studies, e.g. for the determination of 'alarm level' (1–3 μg/l) quantities in surface water. Barceló and co-workers [140,211–214] reported studies on organophosphorus insecticides, chlorophenols, triazines, phenylureas, phenoxyacetic acids and carbamates. They found that TSP was a suitable tool for straightforward analysis of most of tested compounds. Carbamates, phenoxyacetic acids, chlorinated aliphatic acids, phenylurea herbicides and oxime fungicides were determined in environmental samples with TSP after off-line preconcentration [215]. Preconcentration was performed by means of LLE and SPE for soil and water samples, respectively. Analytes were then separated by gradient LC, with ammonium acetate in the mobile phase. Under full-scan conditions, various pesticides could be detected in liquid samples at the 0.1–1 μg/l level, with estimated detection limits at the 10 ng/l level. Chlorine-containing analytes (e.g., carbaryl, linuron) were determined in the NI mode. The addition of ammonium acetate led to improved sensitivity for triazines with detection limits of 20–60 ng. In addition, the adduct ions generated with ammonium formate, from triazines, phenylureas, chlorinated phenoxyacetic acids [216] and carbamates [217], provided complementary structural information which enabled unambiguous molecular-weight assignment for unknown pesticides. Detection limits (using SIM) for simazine, atrazine and propazine were 5 μg/l while carbamates could be detected at the 50 μg/l level, under full-scan conditions. The same authors [218] gave an overview of the use of ammonium formate or acetate, non-polar solvents, or chloroacetonitrile to obtain structural information from TSP mass spectra of a variety of carbamates, chlorinated phenoxyacetic acids, chlorotriazines, organophosphorus insecticides and phenylurea herbicides. Effects of various additives in the LC eluent on the sensitivity and selectivity in LC–TSP-MS of 55 pesticides were studied in detail by Vreeken et al. [219]. Full-scan detection limits for fifteen different groups of pesticides ranged usually from 20 to 200 ng. TSP–LC-MS was used in an interlaboratory study on the analysis of carbamate and phenylurea pesticides in the low mg/l range [220]. Results from nine laboratories showed an intra-laboratory precision of analyses expressed in terms of R.S.D. ranging from 6.5 to 33.1%, R.S.D. for inter-laboratory precision ranged from 29.8 to 98.2%. The authors reported the day-to-day variations of TSP spectra as the most important parameter in the production of the unsatisfactory results. A similar validation of TSP-MS and PB-MS methods, was given by Jones et al. [221].

Bellar and Budde explored the potential of off-line extraction and concentration techniques for the development of a broad-spectrum method for the determination of non-volatile target compounds in aqueous environmental samples [222]. They used liquid–liquid and liquid–solid extraction and subsequent gradient LC separation for samples spiked with carbamate, triazine, sulphonylurea, phenylurea and organophosphorus compounds. With the liquid–liquid preconcentration procedure applied to pesticide levels of 2–50 μg/l, detection limits for 34 analytes varied from 0.2 μg/l for cyanazine to 18 μg/l for linuron in the filament off, PI mode. Detection limits obtained via liquid–solid extraction, applied to pesticide levels of 20–500 μg/l, were approximately ten times higher. Volmer et al. [66] used off-line SPE and LC–TSP-MS, for the determination of pesticides in water samples. From a selection of 128 environmental pollutants, 95 compounds could be detected at the 0.1 μg/l level by using eleven samples, gradient elution, post-column addition of the TSP buffer and PI time-scheduled SIM detection. A similar method was used by Chiron et al. [223] for the determination of thirty pesticides and various degradation products. Nine carbamates,

triazines and anilides were found in surface and ground water samples at the 0.01–0.5 μg/l level. Both on-line and off-line SPE coupled with LC–TSP-MS were used for environmental monitoring of a series of nitrogen- and phosphorus-containing pesticides [224]. SIM detection limits for 51 selected compounds varied between 40–600 pg injected on-column which is equivalent to less than 100 ng/l in drinking water. In addition, structure–spectrum relations were investigated by means of APCI, ESP, fast atom bombardment (FAB), 252Cf plasma desorption and CID for several pesticides. LC–TSP-tandem-MS was used by Kienhuis for the screening of twenty pesticides [146]. Because of the difficulties encountered when using the MS–MS in the usual daughter, parent or neutral loss scan mode, a radio frequency-only daughter scan mode (RFD) was used in order to obtain more spectral information for the analytes studied. An off-line trace enrichment procedure with a carbon phase, followed by an LC separation, was used for the determination of ten pesticides. Using 500 ml of spiked river Rhine water samples, 1 μg/l of each analyte could be detected. The TSP interface was coupled to a double-focusing magnetic sector instrument for the analysis of phenylurea and triazine pesticides in the study of Hammond et al. [96]. Off-line concentration of eleven samples to 0.1 ml and injection of a 20-μl aliquot onto the analytical column was suggested to obtain detection limits of 10 ng/l in the SIM mode. Recent progress in the field of environmental LC–TSP-MS is summarized in reviews by Lamoree et al. [17], Barceló [225] and Arpino [226].

The first systematic study on pesticides using a particle beam interface was published in 1990 [227]. In this pioneering work, classical EI spectra were obtained for carbamates and phenylurea herbicides with instrument detection limits ranging from 10 to 440 ng in the full-scan mode. More than 100 compounds from the U.S. EPA National Pesticide Survey (NPS) were used in a study on the feasibility of LC–PB-MS for the identification and quantification of residues of non-volatile pesticides in ground water [228]. Detection limits were estimated to range from 5 ng, for carboxim sulphoxide, to 50 ng, for disulphoton sulphoxide. In a similar study on 40 NPS compounds [229], detection limits were found to be between 0.4 and 19.2 ng. The use of LC–PB-MS for the analysis of effluent from waste water treatment plants was shown to be complementary to GC–MS analysis [230]. Off-line sample preconcentration of 10 l waste water samples to 1 ml was followed by gradient LC, with the addition of 0.01% ammonium acetate as a carrier. The detection limit for triclocarban was found to be in the low-μg/l range. Obviously, identification of low concentrations of non-target compounds by LC–PB-MS is feasible, but large samples must be available and preconcentration should be carried out. In a study following the successful coupling of microflow LC and PB-MS [231], the performance of the set-up was tested with 45 selected pesticides (among others: carbamates, triazines, anilides, polychlorophenoxyacetic acids, organophosphorus and phenylurea compounds) [103]. Using off-line SPE with graphitized carbon black material, pesticides were transferred from 2-l water samples to 100-μl aliquots. Detection limits, in the SIM mode, ranged from 1 to 40 ng of analyte injected with an injection volume of 60 nl. The authors reported a better response for high water content LC eluents during gradient runs (as compared to conventional-size PB) and linear calibration curves. A significant reduction in solvent consumption resulted in less contamination of the ion source and the pumping system.

Atmospheric pressure ionization interface dominates present developments in the field of LC–MS. A mixture of selected carbamates and phenylureas was analyzed by means of simultaneous ISP-MS and APCI-MS (with heated pneumatic nebulisation), using gradient LC with ammonium formate as an additive [232]. The double detection was achieved by splitting the effluent of the analytical column (0.4 ml/min) to deliver approx. 20 μl/min to the APCI interface. A potential of 20–40 V over the ion sampling capillary and the first skimmer was used to effect solvent cluster breaking and pre-analyzer CID; this resulted in an improved signal-to-noise ratio. The observed difference in the TIC responses from ISP and APCI was attributed to thermolability of the analytes and to differences in the ionization mechanism. The CID-ISP and CID-APCI mass spectra displayed several characteristic fragment ions. Unfortunately, no detection limits or repeatability data were reported. Seventeen pesticides from the US EPA NPS of ground water contaminants, e.g. tri-

azines, carbamates, phenylureas and organophosphorus compounds, were analyzed by LC–APCI-MS [68,233]. Detection limits ranged from 0.8 to 10 ng under full-scan conditions, and from 0.01 to 1 ng under SIM conditions. It was shown that full-scan APCI-MS detection was less sensitive to differences in analyte structure (ranging 10-fold) than TSP-MS (range varied 50-fold) or PB-MS (range varied 150-fold), at least for the tested pesticides.

The introduction of a high-flow LC–ISP-MS system [234] looks very promising for the future utilization of LC–MS in environmental analysis. Conventional LC flow-rates of 1–2 ml/min were used in ISP with a heated ion sampling capillary and a liquid shield. This system was reported to provide mass spectra of low-ng quantities of compounds with on-column injections. Non-volatile phosphate buffers in LC eluent could be used without major problems. A 100-ng/l concentration of mexacarbate could be detected in spiked pond water, after SPE of a 150-ml sample over a C_{18} cartridge; the entire extract, which contained 3 ng of the analyte, was injected on-column. Mexacarbate, monuron, propoxur and siduron were determined in the SIM mode, using 10–25 ng on-column injections. Carbamates could be detected at low-ng levels, using gradient LC for separation. The high-flow ISP system parameters have been studied more recently by the same group, using alkyl benzoate esters, monuron and carbofuran as model compounds [235]. Recently, Voyksner summarized the potential of LC–API-MS for environmental analysis [236], using the determination of carbamates and aromatic amines by means of LC–APCI-MS and LC–ESP-MS as examples. The possibility of efficient ionization and the gain of structural information by pre-analyzer CID are mentioned as main advantages of the API-based techniques. The author concludes that acid and basic compounds are most effectively analyzed by LC–ESP-MS, while less polar compounds are more amenable to LC–APCI-MS.

7. Large-volume injections into GC

The weakest part of GC is undoubtedly a sample introduction. Nowadays, the injection volume in a common GC has to be close to 1 μl. This means that, if an aliquot from a usual volume of concentrated sample (50 μl–1 ml) is taken, only several percents of the extracted analyte are analyzed. A solution to this unfavorable situation is the use of a retention gap placed between injector and analytical column enabling the injection of a 10–100 μl volume. Then, the normal-phase LC can be used for a direct introduction of a heart-cut fraction into the GC using a loop-type interface. Similarly, SPE can be employed for sample concentration and, after selective removal of water and salts from the pre-column sorbent, it can be connected on-line with a GC using an on-line interface. The off-line SPE–GC configuration using large volume injection is also possible. The off-line approach, with an injection of 200-μl sample extract, was successfully applied for the multiresidue analysis of eighteen pesticides present in surface water at ng/l levels with recoveries between 90–100% and (R.S.D.) of 7–14% [237].

Direct injections of water-containing solvents into GC discriminate low-temperature boiling compounds and also, present retention gaps are not water resistant. Therefore, easy-to-automate on-line LLE–GC and SPE–GC with a water removal step are preferred nowadays. A continuous extraction system with and without two-phase derivatization was developed by Ballesteros et al. for a group of phenolic compounds [238] and carbamate pesticides [239], where the aqueous sample was extracted with ethyl acetate, the extract was stored in the loop and injected into GC via a heated transfer line by the carrier gas. The same set-up was used also for simultaneous on-line extraction and derivatization of the phenols with an *n*-hexane–acetic anhydride mixture. Aryl-N-methyl carbamates were converted to the corresponding phenols using a basic sodium hydroxide and detected as above. FID detection limits were at 100 μg/l level with R.S.D. of 1.9–3.9%. On-line SPE on small (10–20 mm×1–4 mm I.D.) precolumns is already a well-established technique in valve-switching LC. Aqueous samples of 10–200 ml can be enriched on the precolumn sorbent of choice, e.g. alkyl-bonded silica, polymeric material, specific ion-exchange sorbent or materials loaded with immobilized antibodies. Analytes of interest are concentrated in a small volume of the precolumn, typically 20–50 μl, and, after water removal, on-line eluted into the GC system. The detection limits obtained are at the low

ng/l level and the systems can be fully-automated [240,241]. The SPE–GC procedure can be coupled to most of existing GC detectors and it was already demonstrated for the FID [242], NPD [240] and MS [241]. The SPE–GC system with a 'drying cartridge' was applied for analysis of 10 ml water samples spiked with s-triazine herbicides at the 0.3–2 μg/l level [243]. The cartridge, containing sodium sulphate, was introduced before the GC injector to remove residual water from the precolumn to avoid peak-tailing of high-boiling analytes. As an alternative, a nitrogen purge drying was successfully applied with the membrane extraction disks or polymeric sorbent packed in a small precolumn [240,241]. An on-line SPE–GC was successfully coupled with FID, NPD and FPD detectors for determinations of numerous triazines, organophosphorus and sulphur containing pesticides in natural waters [128]. A drying cartridge introduced between the PLRP-S precolumn and GC retention gap efficiently removed traces of water from the desorption solvent ethyl acetate and ca. 100 analyses were performed without deterioration of the chromatographic performance. Using 10 ml tap water sample volumes the detection limits were lower than 0.1 μg/l with all detectors. Atrazine and diazinon were found at levels from 20–300 ng/l in river waters from four European countries. An on-line SPE–GC–MS was used for a low ng/l detection of five triazines in river water samples [244]. Sample volume of 1 ml was concentrated on a short polymer-packed precolumn, dried with nitrogen, desorbed with ethyl acetate and a fraction of 60 μl was introduced into the retention gap of GC. Each of the compounds could be identified from the full-scan MS spectra at the 200 ng/l level; when using the SIM mode, detection limits were between 10–20 ng/l. It should be noted that the precolumn is generally used for trace enrichment of 50–100 ml rather than 1 ml sample volumes which would allow, in this particular case, detection of pg/l levels. In the follow-up study of the same group [245] the system was used for full-scan and SIM detection of atrazine and simazine with detection limits of 30 pg and 5 pg, respectively. The capabilities of the system were demonstrated for multiresidue identifications of 168 pollutants spiked into surface water at the 1 μg/l level. An AED detector coupled to SPE–GC was utilized for analysis of drinking, surface and waste waters [246,247]. An on-line SPE on a Tenax sorbent held in the liner of a PTV injector was studied by Vreuls et al. [248]. After removal of water and drying of the sorbent with a flow of carrier gas the analytes were thermally desorbed and analyzed by GC. The method was applied for the analysis of ten chlorinated phenols and benzenes at the 10 μg/l level. A modified system was successfully used for analysis of pesticides and industrial pollutants in surface water [249] with recoveries of 70 to 110% (R.S.D. 2–10%). Unfortunately, deposited salts and suspended matter break down chemically labile compounds and a frequent change of insert was required for analyses of real samples.

8. Conclusions

The solving of the dilemma of technique selection for the analysis of polar pesticides is usually based on several factors. The most important factors are the behavior of the analyte in the chromatographic system; the need of analyte derivatization and the labour required for it; the personal preference of the analyst for a particular technique; the availability of the technique in the laboratory and the general purpose of the analysis.

The behavior of the analyte in the GC or LC column is the main criterion for selection of the separation method. Usually, most environmental analysts still prefer capillary GC because of its high separation efficiency, easier maintenance and operation and problem-free connection to the mass spectrometer. They start to consider an alternative approach only when an analyte is not directly amenable to GC separation. In the seventies and early eighties it was usually derivatization prior to GC, however, during the last decade the preference for LC has increased. In recent years only LC applications are of practical importance for carbamates and phenylureas. The situation is different for triazines and chlorophenols, where both separation techniques are applicable. In this case the decision is based on the criteria mentioned above, i.e., tradition, possession of know-how in the particular technique and the availability of the instrument. Another decision-supporting factor is the purpose of the analysis. This can be

illustrated by the example of the automated monitoring of triazines. The need of a simple on-line enrichment predetermines the use of on-line SPE–LC rather than on-line SPE–GC. The latter technique is available but its continuous unattended operation requires a skilled operator because of its relatively sophisticated character. Nowadays, derivatization techniques for GC and LC analysis of polar pesticides are being also reported and some of them (e.g., OPA derivatization in carbamate analysis, methylation or PFBB reaction of acidic herbicides) are also widely utilized in routine methods. Since MS became a favorite detector in pesticide analysis the need for its utilization often influenced the choice of the separation technique towards GC. On the other hand, a remarkable progress in LC–MS techniques during last decade decreases this preference for GC.

Thus, a general conclusion can be made that, when there is a need for the development of a multiresidue method for polar pesticides, LC is usually the technique of choice. On the other hand, when the target method for triazines or acidic herbicides is to be applied, both GC and LC are available. However, a GC method is usually preferred as a consequence of the historical development of environmental analysis. This choice is usually supported by the high separation efficiency and related peak capacity of modern GC. But whatever preferences for either of the two reviewed techniques could be considered it must be concluded that recent advances in environmental analysis and the need for the acquisition of complex and relevant data from water pollution monitoring systems stress the complementary roles of GC and LC.

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