

GC-MS and LC-MS evaluation of pesticide degradation products generated through advanced oxidation processes: An overview

A. Agüera and A.R. Fernández-Alba*

Pesticide Residue Research Group, University of Almeria, 04071 Almeria, Spain

This article provides an overview of the application of GC-MS and LC-MS techniques for carrying out pesticide degradation studies by means of advanced oxidation processes (AOPs). The attention is focused on the crucial role of these techniques in the evaluation of degradation products (DPs) produced through the application of these oxidative treatments. Advantages and limitations of the application of different GC-MS and LC-MS approaches are outlined. Further, the DPs produced under different AOPs treatments of a large number of compounds belonging to the major pesticide families: triazines, organophosphorous and halogen containing compounds are presented.

Introduction

The presence of pesticides in waters constitutes a pervasive problem and there is a growing concern about reducing the pesticide contamination. A major point source of pesticide pollution is the water generated by agricultural processes and pesticide manufacturing plants. The waste water from those may have pesticide concentrations of up to 500 mg/L. Developments in the field of water management have made several chemical oxidative degradation processes known as Advanced Oxidation Processes (AOPs) available. These processes are quite efficient for pesticide degradation [1,2]. The various AOPs such as heterogeneous photocatalysis and ozonation are clean, fast and effective degradation treatments for the detoxification of polluted water that contains pesticides and other organic compounds [1-6].

All AOPs are mainly based on the direct attack of oxidative molecules such as ozone or the reaction of free radicals with the organic compounds [7]. The hydroxyl radical (HO^\cdot) is usually the major reactive intermediate responsible for organic substrate oxidation. Free radicals, HO_2^\cdot and O_2^\cdot , are also involved in the degradation processes, but these radicals are less reactive than the free hydroxyl radical [8]. The hydroxyl radical reacts strongly with most of the organic species by hydrogen abstraction or electrophilic addition to double bonds. Free radicals further react with molecular oxygen, resulting in a peroxy radical, that initiates a sequence of oxidative degradation reactions [9]. Complete

compound mineralization of parent compounds is usually not feasible and the presence of intermediates or degradation products (DPs) appears to be unavoidable with all AOPs [1].

Because hydroxyl radicals react non-selectively, numerous DPs will be formed en-route to complete mineralization. Chemical analysis of such complex mixture is difficult. In most cases where AOPs are applied, no attention is paid to the formation of DPs; hence, process evaluation and comparison with alternative degradation methods is difficult. A more complex understanding of the DPs is necessary, because some of them may be more toxic and environmentally persistent than the parent compound.

Several significant problems are faced during any adequate analytical evaluation of the pesticide DPs in water: (i) the number of DPs generated is usually high (>15) and the concentration range is broad; (ii) the range of polarity of the DPs obtained is very large; and (iii) a lack of prior knowledge and the complexity of the chemical structures produced can lead to a situation whereby the needed analytical standards are not available. Figure 1 (from Ref. [10]) shows the proposed degradation products of atrazine treated with ozone indicating 21 DPs.

Therefore, to analyze a water reaction mixture containing one or several pesticides and their DPs generated through AOP treatments, it is necessary to have analytical screening methods available that permit separation and identification of compounds with very different hydrophilic-hydrophobic characteristics. The methods should be suited also to a broad range of concentration.

In practice, the evaluation of DPs in water is possible only through application of sophisticated analytical tools. Unequivocal identification of DPs can be carried out by means of complex techniques such as GC-HRMS [11], NMR [12], FT-IR [13], LC-MS/MS [14], etc., but these methods are usually difficult or time-consuming. GC-MS and LC-MS based techniques are generally a good choice for rapid analytical work even when a definite assignment of definitive chemical structures is not possible and, therefore, only tentative degradation pathways can be proposed.

The aim of this work is to present an overview of the current GC-MS and LC-MS analytical methods as applied to pesticide chemical oxidation studies in water. Various aspects of sample handling, evaluation and identification of pesticide DPs are discussed. The degradation products of

* To whom correspondence should be addressed.

Chlorinated

Hydroxylated
(observed after methylation)

Dehalogenated

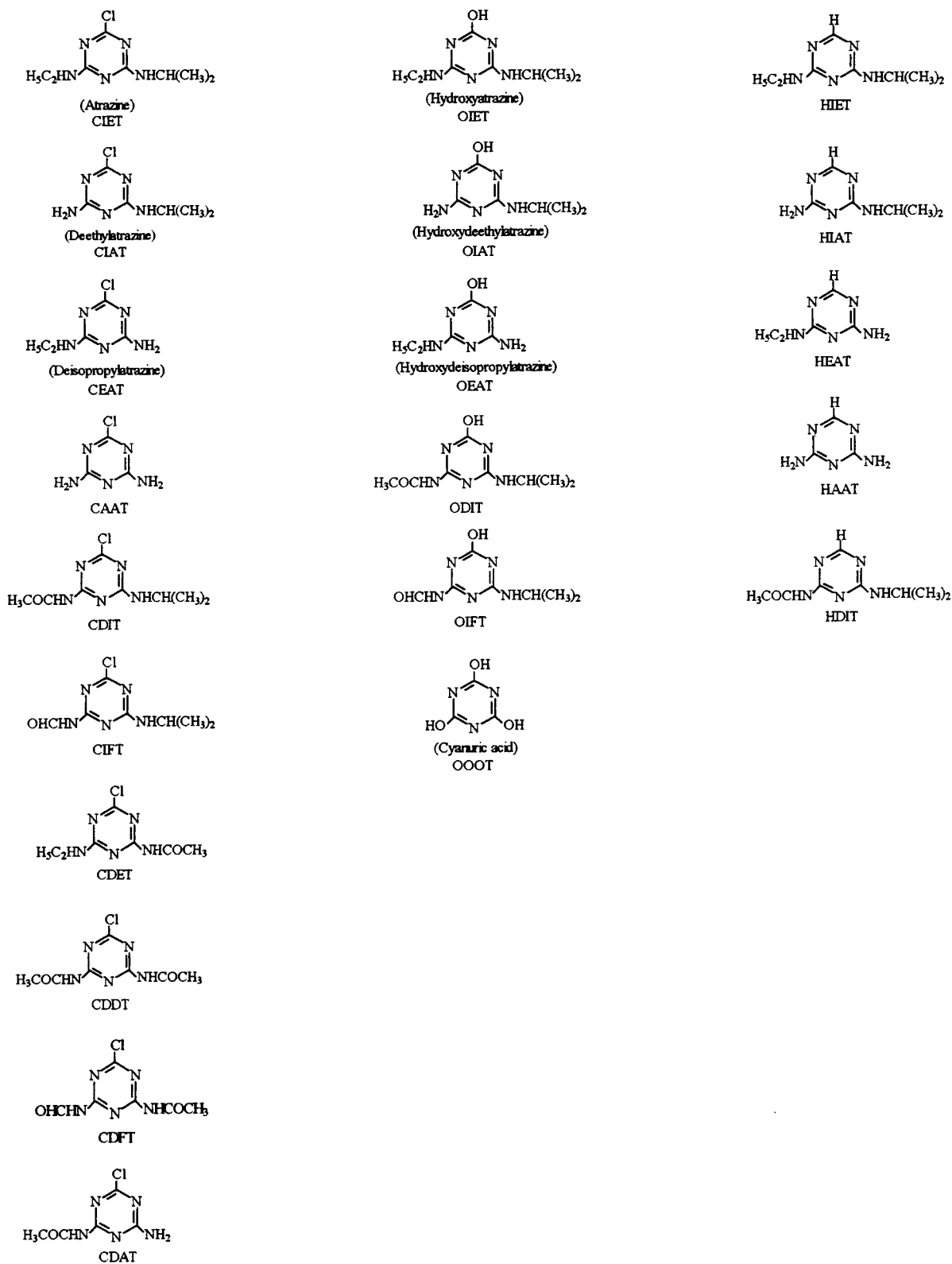


Figure 1. Atrazine ozonation products (from Ref. [10]).

some relevant pesticide families undergoing AOPs are also reviewed.

Sample handling procedures

Common sample handling procedures in chemically treated water analysis involve the use of either a liquid-liquid extraction (LLE) or a liquid-solid extraction (LSE). Because identification of degradation products in water has to be carried out at sub ppm levels (at least above 10 µg/L) for possible toxicity reasons, a 10 – 50 times preconcentration step is usually necessary. Extraction volumes should not normally exceed 50 mL in order to discard systematic additional sample clean-up before analysis, when dealing with waste waters, and to limit analyte breakthroughs in LSE procedures.

LLE by using an appropriate solvent such as ethyl acetate, dichloromethane, diethylether etc. [13,15,16] is usually the method of choice, but losses of the more polar compounds and important matrix interferences can occur [11,17]. From a practical point of view, LLE has an important disadvantage: difficult-to-break emulsions are sometimes found when treated waste water is extracted as well as the need of several sample handling steps.

Lately, LSE is gaining acceptance mainly because: (i) as far as GC-MS analyses are concerned, the LSE method generates less matrix interferences than when LLE is used [18]; (ii) new LSE sorbents are able to trap DPs of a large range of polarities and selectivity may be introduced in the preconcentration step by using different sorbents (e.g. C₁₈ and end-capped C₁₈; porous polymers, PRP-1 or PLRP-S; carbon modified materials, etc.) and different water pH values [19]. Ion exchange properties are generally not relevant, because inorganic salt contents in waste waters are normally high (> 20 g/L). A sequential extraction scheme using different LSE sorbents can be contemplated to identify as many DPs as possible. Firstly, a C₁₈ phase can select all neutral hydrophobic compounds at pH 7 and the major part of the pesticide formulating agents. Secondly, at pH 7 the C₁₈ filtrates can be passed through a polymeric sorbent, where compounds of medium polarity are retained. During a third and fourth step, samples can be acidified to pH 4.5 and pH 2.5, respectively, for extraction of the majority of acidic compounds with a polymeric or carbon type sorbent [20]. The advantages of Lichrolut EN and Isolute ENV+ polymeric sorbent materials over C₁₈ materials are that polymeric sorbents can be used at pH 2 – 13 without decomposition and can therefore extract a large array of DPs with different polarities. Such materials have been successfully used for the characterization of organic pollutants in industrial effluents [21] and for the extraction of polar DPs of pyrimethanil from industrial waters after a treatment by heterogeneous photocatalysis [22]. When dealing with polymeric sorbents, problems may arise with multifunctional compounds such as aminophenols or cyanuric acid, the ultimate degradation product of atrazine. Such hydrophilic compounds (Log *P*_{oct} < 0) can be recovered by means of carbon materials, porous graphitic carbon or non-porous graphitized black carbon. For instance, polar oxime derivatives of pyrimiphos methyl after ozonation could be analysed by using an Envicarb material [17]. However, chemical breakthrough volumes are strongly

influenced by the amount and the nature of matrix interferences. The influence of other organic compounds present, which often account for more than 50% of the total organic carbon present in the water, has rarely been studied systematically. In such conditions, before routine use of the LSE procedure in pesticide degradation studies, comparison with LLE results are still highly recommended. Finally, the ultimate degradation products tend to be aliphatic acids of 2-4 carbon chain length (e.g. oxalic or formic acids) which are not recovered with LSE extraction methods. Samples can either be freeze or vacuum dried [10,23] or can be extracted with diethyl ether [13] prior to esterification and analysis of these organic acid products. To our knowledge, solid phase microextraction (SPME) has not been reported, but its use will probably become significant in the near future because this methodology would allow a rapid assessment of the performance of the AOP reactors.

Identification of degradation products

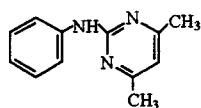
GC-MS based methods

Gas chromatography-mass spectrometry (GC-MS) is by far the most frequent analysis tool for identifying DPs. Important advantages of the GC-MS based methods are: (i) the high amount of structural information yielded and the possibility of using commercial libraries which make the identification of unknown DPs feasible; (ii) the ruggedness and reliability of the GC-MS interface; and (iii) the high sensitivity and separation efficiency which avoid the overlapping of compounds with similar structures. Figure 2 (from Ref. [22]) shows the proposed degradation products of pyrimethanil under TiO₂ photocatalytic treatment where 16 DPs were identified by GC-MS analysis in the 0.03 – 4 ppm concentration range.

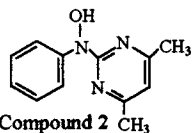
However, the GC-MS methods have important drawbacks as a consequence of their low capacity for analyzing very polar, less volatile and thermally unstable compounds. In order to increase the range of DPs covered by the GC-MS methods, the dried extracts may be derivatized with diazomethane [10], BF₃/MeOH [17], BSTFA [2], etc., prior to chromatography. These methods represent an interesting alternative, but their use can cause degradation of the DPs, due to severe derivatizing conditions (heating, acidic pH). Apart from introducing additional stages into the analysis, derivatization can result in a large variability in the apparent recovery, making the quantitative evaluation of the DPs unfeasible [10]. In addition, unwanted compounds may be formed during derivatization because of the presence of other extraneous compounds (e.g., formulating agents, fulvic acids, etc.) and their degradation products (Fig. 3). Consequently, the derivatization approach has limited usefulness [1,9,11]. Another approach in GC-MS analysis of DPs is the use of high polarity columns such as the polyethylene glycol type (Fig. 4). This approach is limited by the column's stability and bleeding at high temperatures. Very few studies have reported using this strategy [22].

Identification of DPs is usually carried out on the basis of their EI mass spectra, mainly because structural elucidation can easily be achieved by comparing the spectrum of the unknown compound with published spectra either from

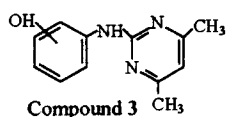
PYRIMETHANIL
AND
HYDROXY DERIVATIVES



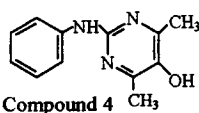
PYRIMETHANIL



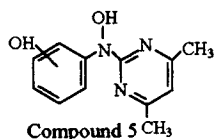
Compound 2



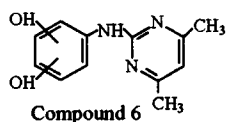
Compound 3



Compound 4

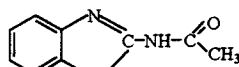


Compound 5

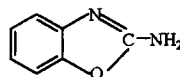


Compound 6

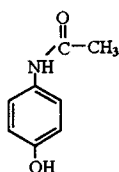
PHENYL DERIVATIVES



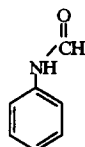
Compound 13



Compound 11



Compound 12



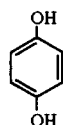
Compound 10



Compound 14

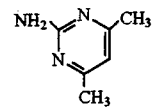


Compound 7



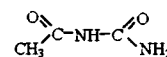
Compound 9

PYRIMIDIL DERIVATIVES

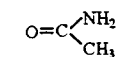


Compound 1

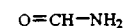
OPEN CHAIN DERIVATIVES



Compound 8



Compound 15



Compound 16

Figure 2. Degradation products for Pyrimethanil during TiO₂ photocatalytic treatment in waste water. All products were identified by GC-MS (from Ref. [22])

data bases or from research papers. A disadvantage of the EI mode is that it does not usually provide molecular weight information [24]. Additional and very useful structural information on DPs can be obtained using the chemical ionization mode (CI), especially for determining the DPs' molecular weights (Mw). Few studies rely on GC-MS with chemical ionization (CI) mode for DP identification, mainly because in quadrupole technology additional instrumentation is required for positive and negative CI analysis [10,20]. In ion trap (IT) technology, switching from EI to CI can be

achieved very easily providing rapid information on the molecular weight of the DPs. However, this technique can produce for some compounds spectra with a high percentage of EI spectrum fragments overlapping the CI spectrum and protonated molecular ions with low relative abundances (< 50%) [18]. Figure 5 (from Ref. [25]) illustrates to what extent GC-ITMS can be used as a powerful analytical tool for DP identification. Figure 5A depicts the full scan GC-IT mass spectrum of chloronicotinic acid ($M_w=157$) one of the major DPs of Imidacloprid under TiO₂ photocatalysis.

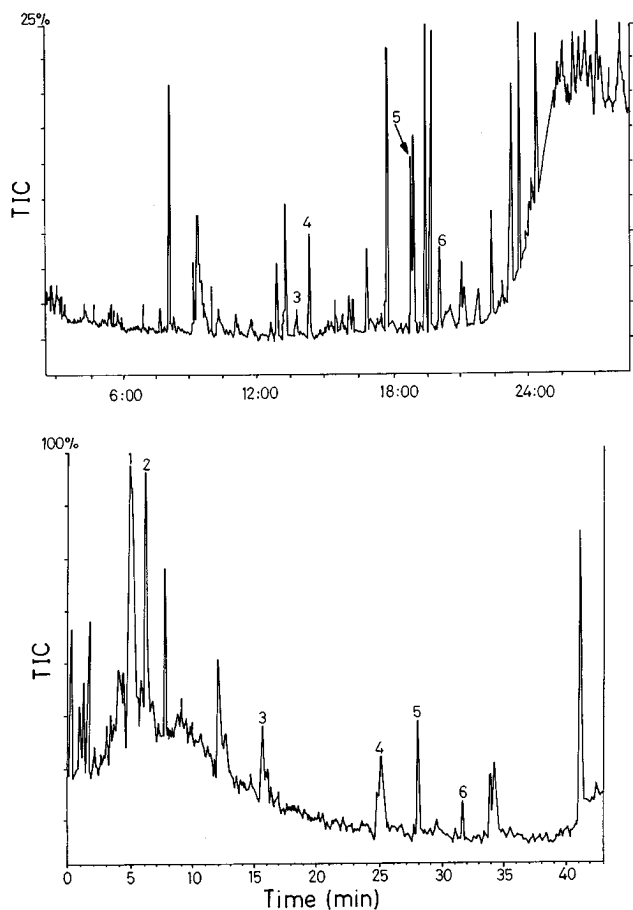


Figure 3. Methyl Pyrimiphos ozonation products in waste water solution. A) GC-MS chromatogram in EI mode after 80 min of ozone treatment and BF_3/MeOH derivatization procedure. B) LC-APCI-MS (positive mode) chromatogram obtained from the same sample. Peaks 1 and 2 correspond to hydroxy derivatives. Unnumbered peaks correspond to matrix compounds (from Ref. [17]).

The figure shows four fragment patterns with high relative abundances ($> 30\%$) at $m/z = 157$, 139, 112 and 76, respectively, allowing the elucidation of its structure by comparison of its spectrum with those available in a data base. Confirmation of the molecular weight was obtained by the CI mass spectrum using acetonitrile as reagent gas which exhibited the $[\text{M}+\text{H}]^+$ ion ($m/z = 158$) as the base peak. Figure 5B shows similar results with another chloronicotinic aldehyde, another important DP of Imidacloprid. From a knowledge of the M_w and an interpretation of the fragmentation pattern, it is possible to hypothesize a molecular structure. However, even the EI mass spectrum does not provide enough information on the position of the functional groups (e.g., the position of a hydroxyl group in a benzyl ring). A comparison with a commercially available standard is required for unequivocal confirmation. When DPs are not commercially available, they may have to be synthesized [12]. Another possibility is to use a high resolution EI GC-MS technique after fraction collection from LC-UV analysis [14]. NMR is not adequate for identification purposes in view of the very low concentration of DPs formed in many cases.

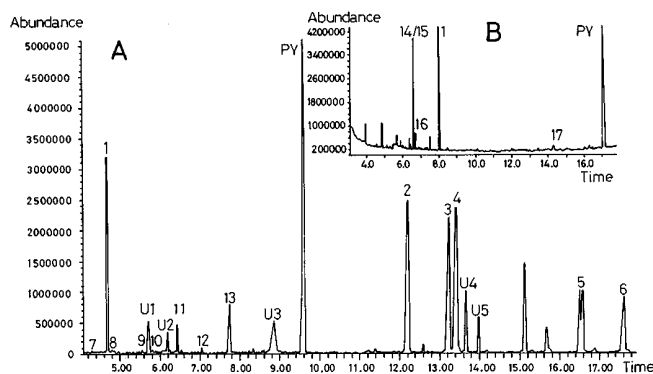


Figure 4. Pyrimethanil photocatalytic products. A) GC-MS chromatogram in EI mode by using a capillary column phenylmethylsilicone type. B) By using a capillary column polyethylene glycol type. Numbered peaks corresponding to figure 2 (from Ref. [22]).

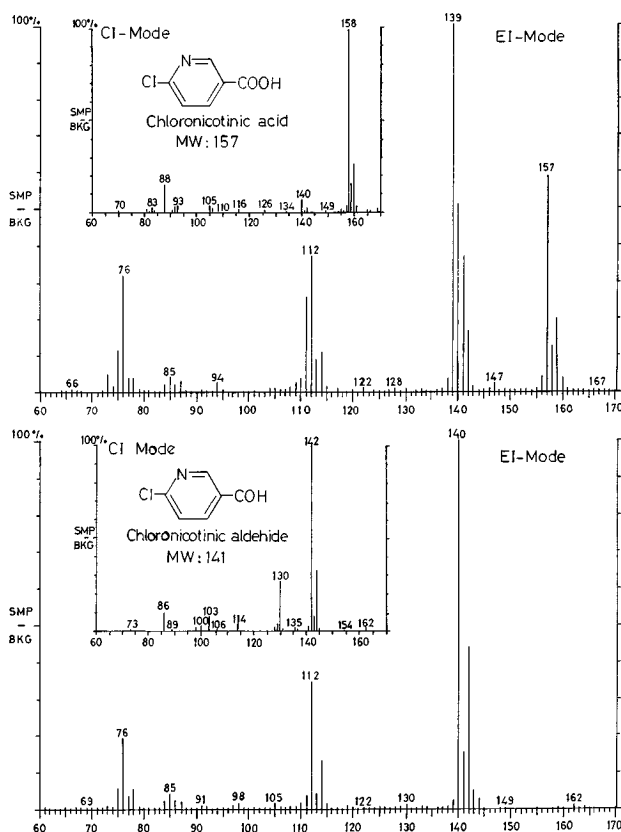


Figure 5. GC-MS spectra in EI and CI modes corresponding to two degradation products of Imidacloprid under TiO_2 photocatalytic treatment (from Ref. [25]).

LC-MS based methods

Liquid chromatography-mass spectrometry (LC-MS) techniques are gaining acceptance in order to determine both parent compounds and their DPs. LC techniques present several advantages over GC: (i) little or no sample clean-up is required; (ii) highly polar, less volatile and thermally

labile compounds are more easily analyzed; and (iii) direct analysis of the samples avoids the possibility of polar DPs escaping during extraction procedures. However the use of LC-MS has been mainly hindered by a lack of a robust universal LC-MS interface [24].

Thermospray and particle beam LC-MS interfaces have been used for the analysis of different classes of pesticides and their DPs [24,26] in photolysis experiments. However, confirmation of compounds can be difficult in thermospray, because of the insufficient fragmentation as well as difficulties with thermally labile compounds. The particle beam technique has the advantage that mass spectra resembling reference EI spectra are produced, but sensitivity for polar analytes is generally low and often the technique cannot ionize non-volatile compounds.

Developments in atmospheric pressure ionization (API) interfaces allow obtaining similar structural information as chemical ionization techniques, hence overcoming the limitations of other LC-MS interfacing devices [24]. Either electrospray (ESP)/ionspray (ISP) and atmospheric-pressure chemical ionization (APCI) interfacing systems have expanded the applicability of LC-MS in these studies, mainly because of the high sensitivity and structural information that can be obtained [1,24]. The major role of LC-

MS in pesticide degradation studies are: (i) to check the DPs molecular weight, and (ii) to detect DPs which are not directly amenable to GC-MS techniques. High flow positive electrospray (ISP) appears to be the most suitable ionization mode for identification of the DPs, since formation of Na⁺ and K⁺ adduct ions allows the confirmation of the DPs' molecular weights in many cases and protonated molecular ions are usually the base peak of the spectrum.

Table I (from Ref. [17]) illustrates to what extent LC-API-MS can be used as a powerful analytical tool for DPs identification. As shown, compounds 1 and 2 are detected by ISP and APCI; however, they are not detected when GC-MS is applied. ISP allows a better confirmation of the DPs molecular weights with the [M+H]⁺ ion as the base peak as well as the formation of Na⁺ or K⁺ adduct ions. In addition, the negative mode is a good tool for the confirmation of the *M_w* of the DPs detected in the positive mode. In some cases the negative mode allows the detection of ionic compounds such as phenols or acidic compounds that do not show a response in the positive mode. Conversely, APCI gives more fragmentation patterns, but molecular weight is not easily discerned, because vaporization of the mobile phase is required at temperatures of 300 – 400 °C and degradation of thermolabile DPs can take place. An increase of extraction potential values provides additional structural information.

Table I. Main ions and their relative abundances (RA) of each degradation product detected after a 80 min ozone treatment of formulated pyrimiphos methyl using either GC/Ion Trap-MS (positive CI or EI) after sample derivatization with BF₃/MeOH or LC-API-MS (positive APCI or ISP interfaces).

COMPOUND	Positive ISP Ions	Positive APCI Ions	EI Ions (RA %)	Positive CI Ions
1 <i>M_w</i> 157	[M+H] ⁺ (100) [M+Na] ⁺ (6) [M+K] ⁺ (5)	[M+H] ⁺ (100) [M-41] ⁺ (41) [M-16] ⁺ (11)	n.d.	n.d.
2 <i>M_w</i> 169	[M+H] ⁺ (100) [M+Na] ⁺ (5)	[M+H] ⁺ (100) [M-41] ⁺ (12) [M-16] ⁺ (15)	n.d.	n.d.
3 <i>M_w</i> 195	[M+H] ⁺ (92) [M+Na] ⁺ (6) [M+K] ⁺ (5)	[M+H] ⁺ (100) [M-41] ⁺ (51) [M-69] ⁺ (12)	178 (12); 149 (32) 135 (41); 121 (22) 77 (15)	[M+H] ⁺ (31) [M-31] ⁺ (100)
4 <i>M_w</i> 277	[M+H] ⁺ (100)	[M+H] ⁺ (18) [M-27] ⁺ (100) [M-91] ⁺ (21)	177 (100); 262 (61) 233 (31); 152 (43) 135 (49); 125 (15) 109 (13)	[M+H] ⁺ (100)
5 <i>M_w</i> 319	[M+H] ⁺ (100) [M+Na] ⁺ (7) [M-41] ⁺ (42)	[M+H] ⁺ (5) [M-41] ⁺ (100) [M-73] ⁺ (26)	319 (100); 305 (8) 290 (30); 276 (45) 151 (25); 125 (22) 109 (12)	[M+H] ⁺ (100)
6 Pirimiphos methyl <i>M_w</i> 305	[M+H] ⁺ (100) [M-141] ⁺ (11)	[M+H] ⁺ (100) [M-27] ⁺ (15) [M-141] ⁺ (92) [M-169] ⁺ (23)	305 (31); 290 (100) 276 (72); 233 (51) 180 (42); 151 (25) 125 (22); 109 (11)	[M+H] ⁺ (100)

No more than three clear fragment ions are generally obtained making the DPs structure elucidation difficult (Tab. I). However, the main structural characteristics such as the preservation of the aromatic ring and the nature of the functional groups can be obtained. Further structural information requires an adequate analysis of these DPs by using the GC-MS systems, making both techniques GC-MS and LC-MS complementary.

In this respect, figure 3 (from Ref. [17]) depicts two chromatograms obtained after 1h treatment by ozone of methyl pyrimiphos in an industrial waste water sample. In the upper chromatogram, GC-EI-MS allowed the detection of three major DPs (compounds 3,4,5) while LC-APCI-MS allowed, in the lower chromatogram, the detection of two additional compounds (1 and 2). From the structural information obtained by both techniques (Tab. I) a tentative elucidation of the five DPs is feasible. Although generally capable, LC-MS presents important weaknesses as a consequence of the lack of structural information that is usually achieved and the lower sensitivity and discriminating power with respect to GC-MS. These facts can frequently prevent DPs identification as a consequence of low detection threshold or overlapping peaks [27] from compounds with similar chemical structures, a common occurrence in AOPs degradation processes. A comparison of figures 2, 4 and 6 (from Ref. [22]) illustrates to what extent a low discrimination capacity and lower sensitivity limits LC-MS identification compared to GC-MS. Figure 6 shows the chromatograms obtained after 300 min of TiO₂ photocatalytic treatment of Pyrimethanil. Both APCI and ES yielded information about six chromatographic peaks (peak numbers correspond to DPs shown in Fig. 2). However, peak 1 in figure 6 is the result of the overlapping of compound 1 with compounds 11 and 12 (structures in Fig. 2), making their identification feasible only in combination with GC-MS analysis.

DPs of relevant pesticides

Triazines

Dealkylation and dechlorination of triazines occur simultaneously. Dechlorination occurs more rapidly with the dealkylated metabolites. In terms of the chlorinated and dechlorinated compounds detected, degradation pathways are similar in the three available methods. The main difference is that TiO₂/UV and O₃/UV methods cause greater direct dechlorination of triazines than FR or ozonation which may be attributed to photolysis rather than the attack of hydroxyl radicals. Dethylatrazine, deisopropylatrazine, and chlorodiamino-s-triazine have been reported as ozonation products with respective amounts of 36%, 16%, and 3% of the original atrazine unaccounted for after 10 min of treatment [28]. When a UV light source was coupled to the ozonation process, simazine degradation increased; the main degradation products were 2,4-diamino-6-hydroxy-s-triazine (36%), 2-amino-4,6-dihydroxy-s-triazine (13%), and cyanuric acid (10%) after 120 min of treatment [29]. After 11.5 h Cl release, in FR atrazine oxidation, accounted for 40% representing dechlorinated intermediates while chlorodiamino-s-triazine and 4-acetamide-6-amino-2-chloro-s-tri-

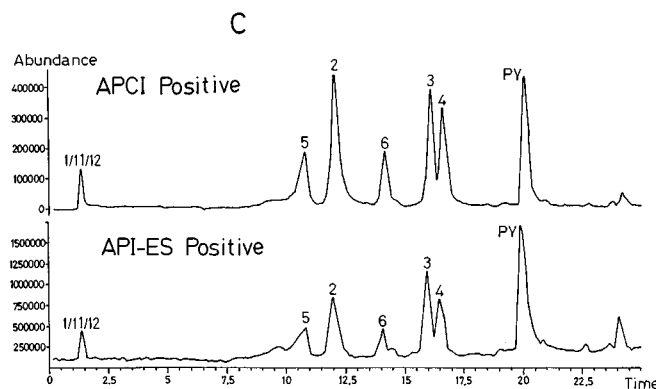


Figure 6. LC-MS chromatograms in APCI and ISP modes corresponding to a solution of Pyrimethanil treated water sample after 12 h of TiO₂ photocatalytic treatment (peak numbers correspond to Fig. 2) (from Ref. [22]).

azine roughly represented the sum of chloro-s-triazines by-products (60%) [30].

After 12h of TiO₂/UV treatment, chlorodiamino-s-triazine, 2,4-diamino-6-hydroxy-s-triazine, 2-amino-4,6-dihydroxy-s-triazine, and cyanuric acid reached 12%, 8%, 25%, and 25%, respectively, but were completely converted into cyanuric acid in 70 h of treatment [31].

No system could break the triazine ring; cyanuric acid was the most oxidized intermediate identified.

Organophosphorus pesticides

Oxon derivatives appear to be the first products formed during AOPs since the difference between those intermediates and the parent compounds is only the substitution of sulphur by oxygen in the P=S bond. There is breakdown of the molecule also by solvolysis of the ester bond [32]. Total mineralization of the organophosphorus pesticides can be achieved within short reaction times (less than 2 hours).

Photo-FR oxidation of methyl parathion gives rise to 4-nitrophenol (15%) and dimethyl phosphate (30%) as the main degradation products. Methyl paraoxon has been identified at trace level [33].

Total mineralization of fenitrothion by TiO₂/UV proceeds through several intermediates: 3-methyl-4nitro-phenol, 3-methyl-4-nitroanisole, 2-methylhydroquinone, 2-methyl-1,4-benzoquinone, phosphonic acid dimethylester, and phosphorothioic acid trimethyl ester. The relative importance of these by-products has not been assessed [16].

Ozonation of methyl parathion leads to the release of paraoxon, 4-nitrophenol, 2,4-dinitrophenol, picric acid, and phosphoric acid in the aqueous medium [34]. Again those intermediates have not been qualified.

Halogen containing pesticides

Metolachlor yielded a great number of transient organic intermediates under photo-FR treatment [33]. All by-products but one still bore the chlorine atom, while the photo-FR treatment of alachlor, a pesticide with a very similar structure as metolachlor, led only to one dechlorinated DP:

2-hydroxy-2,6'-diethyl-N-photocatalytic degradation of alachlor [35]. Similarly, the ozonolysis of bromacil, a brominated herbicide yielded two debrominated products [36]. Few data exist on the abilities of AOPs to eliminate organochlorine pesticides from waste waters. Ozone is said to have no effect on lindane and DDTs [37,38], while dicofol and tetradifon are readily degraded by ozone treatment [36]. Lindane can be eliminated by UV/TiO₂ treatment, but several toxic isomers are formed as intermediate products [39].

Acknowledgements

This study was supported by Project PETRI No. PEN96-459. The authors are grateful to Dr. Chiste Yusuf for his valuable comments.

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