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Highlights of Mass Spectrometric Methodologies in Environmental Pollution

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1. Introduction

1.1 The integrated pest management (IMP)

Phytodrugs or, more commonly, pesticides are chemical devices of both natural and synthetic origin playing an important role in crop protection. International agencies presiding environmental control have recently issued many directives to avoid pollution due, among others, to chemical treatment of fields by agricultural farms. The role of chemical analysis through the many platforms available by applying modern mass spectrometric methods, has become, therefore, of primary importance either for the control of the health of our planet and for the welfare of many developing and undeveloped countries.

The state-of-the-art of agriculture chains in the world could be represented by a survey published by Botswana scientists on the knowledge and perception of pests, diseases and pest management practices by local vegetable farmers (Obopile et al., 2008). The results showed that pesticides were used and that seven out of twenty-four of them are considered extremely or highly hazardous by the World Health Organisation. Conversely, it is well known that worldwide starving requires a wider distribution of goods, many of them coming from agriculture. Integrated pest management (IPM) represents the only reliable approach helping producers in preserving their crops, therefore training on efficient and safe use of pesticides is needed to minimise their use. Comprehensive studies for each particular problem posed by pest infections are also vital for an environmental friendly approach to the unavoidable use of pesticides (El-Bouhssini et al., 2009; Gennaro et al., 2003).

Mass spectrometry is an affordable chemical method suitable, for its specificity and sensitivity, to deal with identification and assay of molecules in complex mixtures. The method has been implemented in the last years in its sampling, ionizing and analyzing facilities thus allowing molecules from few to million Daltons to be detected. Hyphenation with chromatographic devices helps in the analyses of complex mixtures, whereas parallel and concomitant detection of the separated analytes with other systems such as ultra violet (UV) spectroscopy, pulsed flame photometric (PFPD) (Amiray & Jing, 1998; De Nino et al., 2003) and electrochemical (EC) (Kullman & Matsumara, 1996; Garrido-Frenich et al., 2001) detectors are determinant in many applications. The evaluation of organophosphates in oranges carried out by GC/MS/PFPD allowed an easy assignment of the analytes in extracted mass chromatogram (A, figure 1).

Fig. 1. (A) extracted mass chromatogram typical of the PFPD-identified pesticides (chlorpyrifos-methyl, m/z 125, 286, 288; malathion, m/z 125 and 173; parathion, m/z 109 and 291; chlorpyrifos-ethyl, m/z 314 and 316; and ronnel, m/z 125 and 285); (B) reconstructed mass chromatogram from the EI full-scan spectrum; and (C) PFPD chromatogram obtained for organophosphate standard mixture with -1.85 min offset.

1.2 An overview on the mass spectrometric methodologies

A mass spectrometer is a comprehensive “laboratory” where any class of molecule can be analyzed and fully characterized. A peculiarity of the methodology is represented by the chance of performing quantitative analysis direct from complex mixtures with, or without, a preliminary sample fractionation. Mass spectrometry is based on the identification of ionic species either pre-existent or generated by suitable ionization devices. Electron ionization (EI) has been the first method to be exploited and is still determinant in many analytical laboratory practises. It is based on the action accelerated electrons on gaseous neutral molecules (equation 1)

The very simple equation 1 describes how a neutral molecule M can be perturbed by an electron beam causing the formation of the molecular radical species. The minimum amount of energy required for the process is represented by the ionization energy of a given species (Table 1)

Compound	I.E. (eV)	PA (kJ/mol)
Benzene	9.24	750.4
Cyclohexane	9.88	686.9
Cyclohexene	8.95	784.5
1,3-hexadiene;	8.54	769,1

Table 1. value of ionization energy of some typical hydrocarbons

An acceleration energy of 70eV on the average is normally used because it is well above that required by the removal of one electron from a typical organic molecule and it is higher enough to guarantee the efficiency of the process.

The stability of the molecular radical cations thus formed was an important issue of early MS applications since the information on the composition of the analyte could be lost. Chemical ionization (CI) methods were therefore introduced which were based on the proton exchange between the gaseous analyte and an appropriate plasma. The proton affinity (PA, table 1) value provides information on the energetics of ion dissociation. Atmospheric pressure chemical ionization (APCI) source, now available in many commercial instruments, is based on the same principles and has become more popular than CI because it does not require sample evaporation.

Fig. 2. Schematic of desorption ionization mechanism

A breakthrough in mass spectrometry was represented by the introduction of methods which directly ionize sample solutions after spraying in an electric field (ESI) or deposited on suitable tags and exposed to ion, atom and laser light bombardment (SIMS, FAB, MALDI). Combination of these methods will be addressed in an appropriate chapter. The kinetic energy transferred from the impinging species to the samples, in the desorption ionization methods, is used by the system to drive any kind of chemical reactions, which brings about the formation of protonated/deprotonated species as well ion clusters and electron radical species that are released in the gas phase and analyzed by a suitable mass spectrometer.

2. Liquid chromatography-mass spectrometry (LC-MS)

2.1 Sample preparation

Many environmental samples cannot be analyzed without preliminary sample preparation because they are too dilute or the matrix is too complex. Thus, despite advances in the development of highly efficient analytical instrumentation for their final determination, sample pretreatment remains an important part of obtaining accurate quantitative results. Consequently, the development of an appropriate sample preparation procedure involving extraction, enrichment, and cleanup steps becomes mandatory to obtain a final extract

concentrated on target analytes and as free as possible of matrix compounds. However, the complex sample matrix may contain abundant quantities of chlorophyll, lipids, sterols and other components that can interfere with good sample analysis. The fundamental assumption underlying any methodology for determining residues is that it should guarantee true and precise results at appropriately low limits of detection for a wide spectrum of analytes. Many choices have been proposed for pretreatment and/or extraction of pesticide residues in foods. In most of these the extraction procedure usually involves sample homogenization with an organic solvent, alone or mixed with water or pH-adjusted water, using a homogenizer, blender, or sonicator. In addition to these classical extraction techniques, other more recent approaches, for example QuEChERS, supercritical fluid extraction (SFE), pressurized-liquid extraction (PLE), microwave-assisted extraction (MAE), matrix solid-phase dispersion (MSPD), solid-phase extraction (SPE), solid-phase microextraction (SPME), and stir-bar-sorptive extraction (SBSE), have resulted in new possibilities in sample treatment and advantages such as a substantial reduction of the extraction time and incorporation into on-line flow-analysis systems. Each technique has its advantages and disadvantages and the choice should depend on the analytical problem. All of this extraction and preparation techniques will be discussed in another chapter of the book.

2.2 Sample introduction

LC is complementary to GC, because it permits the analysis of thermally labile, non-volatile, and highly polar compounds. In the past the application of LC in pesticides analysis was usually focused on groups of compounds or single compounds for which no suitable conditions were available for GC analysis. But now LC is particularly adapted to multiresidue analysis of pesticides over a wide range of polarity, including their transformation products, without the need to derivatize any compound. With the trend towards biodegradable pesticides, which are generally more polar than the old ones, LC is becoming the preferred analytical method for most insecticides and their metabolites. The majority of LC-MS is conducted on MS/MS instruments with enhanced selectivity; therefore extensive cleanup is less crucial when compared with analysis by GC-MS and there is a growing trend toward LC-MS analysis without cleanup. Any cleanup of food extracts is still usually performed off-line before LC-MS, whereas the use of online trace enrichment has been successfully used for the determination of pesticide residue in water. SPME, in-tube SPME, and SBSE have all been used as sample introduction devices for LC-MS. These facts together with the ability to cover wide range of physico-chemical properties of pesticides including GC non-amenable analytes predetermine LC the leading approach.

2.3 Chromatography

LC has a variety of separation modes and mobile phases for optimizing a separation. In GC the separation mechanism is based on the interactions between the stationary phase and the solute. In LC the separation mechanisms appear more complicated because of the many primary and secondary interactions between the stationary phase, the mobile phase, and the solute. As mass selectivity does not completely eliminate isobaric interferences and matrix affects that may affect the relative response of analytes. Although separation of all analytes is not considered necessary for detection of pesticide residues due to the high selectivity provided by MS/MS, ion suppression is observed either from coelution with other analytes or, more likely, coeluting matrix components. Also the use of stable isotope dilution assay by inserting labelled analogues of the analytes as internal standard (Di Donna et al., 2007;

Mazzotti et al., 2009). Stationary phases are usually classified according to the separation mechanisms. To a first approximation these are: (i) adsorption chromatography using silica, alumina, or silica modified by polar groups; (ii) reverse-phase chromatography, using alkyl- or phenyl-bonded silicas, apolar copolymers, or carbonaceous sorbents; (iii) ion-exchange chromatography using sorbents containing ion-exchanger groups at their surface and (iv) size-exclusion chromatography. The most important and widely used separation technique for pesticides is LC on reversed-phase (RP) columns. The mobile phase is important to obtain a good chromatographic separation, but it also affects the analyte ionization and the sensitivity of the mass spectrometer. For example, analyte charge should be suppressed by manipulation of the mobile-phase pH for optimum retention but this can have a detrimental affect on MS response. Contrary to conditions for RP LC retention, for optimized electrospray (ES) ionization, the pH should be adjusted to promote the charged state of the analyte over its neutral species as ionization takes place in the liquid phase. Methanol-water (Leandro et al., 2006; Mickov et al., 2003) and MeCN-water (Di Donna et al., 2007; Mazzotti et al., 2009) mixtures with addition of ammonium acetate (Leandro et al., 2006; Chueng & Wilson, 2006) were mostly utilized as mobile phases at gradient elution conditions. Methanol and/or MeCN are used as organic modifiers, methanol is preferred over MeCN for several reasons.

2.4 Liquid chromatography-mass spectrometry (LC/MS) applications

The different advantages of LC coupled to MS in the field of pesticide residue determination in environmental samples have been addressed (Malik et al., 2010). Moreover, the additional benefits of using MS/MS in terms of increased selectivity and sensitivity have also been discussed. These characteristics, together with the easy compatibility of LC with aqueous samples and the ability to perform most of the analysis without derivatization, make LC-MS/MS the best technique currently available for the determination of polar and ionic pesticides. Although the majority of the methods developed for their application to fruits and vegetables depend usually on the change in the extraction procedures, however in this section the application and the development of the LC-MS methods will be discussed. Quantification of pesticides with LC-MS depends on multiple parameters, such as the choice of the analytical column, mobile phase, flow rate, ionization and acquisition conditions. One of the main problems in the quantitative determination of pesticide residues is that its extraction easily carries away interferences (sugars, cellulose, lipids, etc.) in the final extract. Therefore, quantitative analysis can be severely affected by matrix effects, the most common being the suppression or enhancement of analyte ionization in the mass spectrometer, which lead to unacceptable results if no correction is being made. Signal suppression or enhancement is related to the ionization procedure rather than the analyzer used (Ferrer & Fernández-Alba, 2005) and depends on the type of pesticides being analyzed and the type of matrix. This effect is more important when using electrospray interfaces, and the effect is more intense under positive ionization mode. The extent of suppression or enhancement of the signal is typically 0–30% but in some cases, it can be total (Klein & Alder, 2003; Jansson et al., 2004). For this reason, procedures optimized with standards in pure solvent by adjusting MS parameters can lead to wrong conclusions. To evaluate signal suppression, it is a good practice to perform a matrix-matched calibration (standards in identical or similar matrix than sample to be analyzed) or to use appropriate labeled surrogate and internal standards or application of an efficient clean-up step. Also it should be taken into account that the mobile phase is important to obtain a good chromatographic separation, but it also

affects the analyte ionization and the sensitivity of the mass spectrometer (Andreu & Picò , 2005; Medana et al., 2005). Chromatographic separation of ionic compounds can be achieved by different retention mechanisms, mainly, ionexchange and ion-pair reversed-phase liquid chromatography (IP-RPLC). Ion pairing, with the corresponding counter-ions, has been done for acidic and basic analytes (Sancho et al., 2005). For the former, the ammonium cation is the weakest ion-pairing agent, while tri- and di-alkylamines are the stronger ones, and for the latter, perfluorinated organic acids serve as anionic counter-ions (Castro et al., 2001; Sancho et al., 2005). The type and quantity of organic modifier added to the eluent, has to be a compromise between improvement of separation and minimization of suppression of the atmospheric pressure ionization (API) techniques. In the contrary the ion-exchange approach is not very suited to the electrospray interface (ESI) due to the use of buffers with high ionic strength (Castro et al., 2001).

The analysis of pesticides residue may be targeted or non-targeted but always using a multi-residue procedure as generic and simple as possible, reducing to the maximum the clean up steps. The multi-residue methods reported in the literature are very different depending on the food substrate. It is not always necessary to extract pesticides from liquid samples, such as juice and wine, with organic solvents because the pesticides are already dissolved in them and can be directly injected in the LC-MS system (Goto et al., 2005). Goto et al., have been developed an analysis method for N-methyl carbamate pesticides in juice and wine that only required sample dilution with ultra-pure water, and LC-ESI-MS/MS determination by direct sample injection into a short column. However, other authors prefer the use of an extraction procedure (Wu et al., 2002), they improved the determination of polar pesticides in water and wine by coupling automated in-tube SPME to LC-ESI-MS. In-tube SPME conditions were optimized by selecting the appropriate extraction parameters, specially the stationary phases used for SPME.

Target analysis is a conventional analysis based on developing a method with standards prior to analysis and monitoring real samples that do not detect compounds not defined in it. The trend within the target analysis is the development of large-scale multiresidue methods (able to determine more than 100 compounds). These methods applied LC-MS/MS, using QqQ, QLT and TOF-MS. LC-MS/MS using QqQ has as a serious limitation the number of compounds that can be simultaneously determined (up to 100–150 depending on the scan speed/dwell time). For example, it has been developed a multi-residue method for the screening, quantification and confirmation of 52 pesticides and metabolites in four fruit and vegetable matrices (Hernández et al., 2006). LC-ToF-MS can be used for the quantitative analysis of pesticides in fruits and vegetables and reports the usefulness of this technique to obtain structural information for unequivocal identification of target compounds provided by elemental composition formula information. A new study were presented by Sage et al. (2002) comparing, the quantitative performance of ToF-MS and LC-MS/MS with MRM for 15 pesticide residues in fruit extracts. This comparative study was concluded that MRM detection is a more sensitive technique than full scan QTOF, allowing lower limits of detection, although LC-ToF-MS could also be used to quantify pesticide residues. This technique provided elevated spectral resolution allowing exact mass measurement and full mass spectral sensitivity for low level analyte detection. The application of TOF or hybrid quadrupole time of flight (QTOF), is increased in the last few years. This increased use is either for metabolite identification studies, for analyte confirmation in positive samples, or for screening methods, based on the high resolution power and accurate mass measurement capabilities of this technique, both in MS or,

preferably, in MS/MS mode in the case of the hybrid QTOF. LC-QTOF-MS is more selective because the accurate mass measurement of product ions allows to remove ambiguities. Soler et al. compare four LC-MS systems, equipped with single quadrupole, QqQ, QIT and QTOF to evaluate the performance for the analysis of carbofuran and its metabolites. Although quantitative results were best with QqQ, but QTOF was the most selective technique because the accurate mass of product ions allowed ambiguities to be removed (Soler et al., 2006). The recently introduced hybrid QLT instrument has also been used to perform MS/MS. This instrument retains classical QqQ modes for quantitative and qualitative analysis (SRM mode and neutral loss scan) and combines them with sensitive ion trap scan modes for the confirmation of analytes or characterization of unknowns, including enhanced product ion mode, time delayed fragmentation, and MS³ with an ion accumulation capacity higher than a conventional three dimensional ion trap analyzer. The QqLIT analyzer can provide an improved sensitivity in these MS/MS studies and up to 200 compounds can be analyzed in a unique LC-MS/MS run, with 2 SRM transitions (Garcia-Reyes et al., 2007). The working modes (enhanced product ion and MS³) are useful for the unambiguous confirmation of pesticides with poor fragmentation at low concentration levels, which cannot be easily confirmed by QqQ instruments due to the high SRM ratio between the two transitions (or absence of the second transition) for confirmatory purposes.

Another important issue on pesticide control to ensure food safety, which is still a challenge for the analyst, is the identification of non-target pesticides and metabolites. The non-target analysis offers the possibility of identifying unexpected pesticides, transformation products and/or impurities, or even untargeted compounds that can be toxic. This analysis is more complicated because it requires the identification of unknown compounds. The high resolving power of mass spectrometric techniques, such as TOF-MS, has been applied successfully to this field (Thurman et al., 2005a, 2005b). There are two reports that describe an interesting identification scheme, using a combination of LC-MS/TOF and LC-MS QIT with searching of empirical formulas generated through accurate mass and a ChemIndex or MerckIndex databases. This scheme has been applied to investigate imazalil and prochloraz, the main degradation product of imazalil, and a non-previously reported prochloraz degradation product in citrus fruits extract (Thurman et al., 2005a) and to discover unknown pesticides in tomato skin (Thurman, 2005b). This identification was accomplished basically by combining the information provided by LC-TOF-MS accurate mass analysis with that deduced from the fragmentation pathway of the parent compound and carried out by LC-ion trap MSⁿ experiments (typically MS/MS or MS³). To conclude this section, the acquisition of better sensitivity and selectivity of target analytes detection, tandem mass spectrometry (MS/MS) is a generally the preferred option for quantitation purposes. The use of LC-MS/MS with triple quadrupole (QqQ) instruments in multiple reaction monitoring (MRM) mode is so far the more appropriate technique for target analysis. It provides excellent sensitivity and selectivity. This technique is now becoming a well-established approach in the field, as demonstrated by the number of published papers. Also the use of LC-QqTOF-MS is at present one of the most advanced and efficient approaches for screening and identification of non-target pesticides and their metabolites in food.

3. Application of spray desorption methods

Recently, a new family of MS techniques has been developed, allows ions to be created under ambient conditions and then collected and analyzed by MS (Cooks et al., 2006).

Ambient mass spectrometry is the ability to record mass spectra on ordinary samples, in their native environment, without sample preparation or pre-separation by creating ions outside the instrument. Desorption electrospray ionization (DESI, Figure 3) is an ambient ionization technique that can be used in mass spectrometry for chemical analysis. It is an atmospheric pressure ion source that ionizes gases, liquids and solids in open air under ambient conditions (Takats et al., 2004). DESI is a combination of electrospray (ESI) and desorption ionization (DI) methods. In the DESI process, a spray of charged micro-droplets from a pneumatically-assisted electrospray needle is directed towards the object or analyte of interest in the ambient environment and allowed to impact the surface, giving desorption of the analyte into the gas phase and subsequent ionization.

Fig. 3. Schematic configuration of DESI source

DESI approach has been applied in food analysis, in particular 16 different compounds belonging to different classes of agrochemicals (insecticides, herbicides, and fungicides) have been selected as representative of different class of pesticides (García-Reyes et al., 2009). For evaluate the goodness of DESI approach two different approach were performed, direct DESI-MS/MS analysis of fruit peels and DESI analysis of foodstuff extracts, the latter was obtained using the conventional sample treatment protocol used worldwide for pesticide analysis. Identification and confirmation capabilities and sensitivity were examined in detail using different spray solvents, and the optimized method was applied to a wide range of samples obtained by local store. Very low LOD values were obtained under MS/MS experiments, for example, in the case of the ametryn, one of the selected agrochemical choice the LOD is $0.1 \mu\text{gL}^{-1}$. Ion suppression due to matrix effects, which are common in electrospray mass spectrometry, were observed but can be reduced with appropriate dilutions, since the sensitivity and LODs obtained (in the micrograms per kilogram range in fruit and vegetable matrixes) were satisfactory even after dilution of the food extracts. With DESI approach, it becomes possible to perform direct analysis of market samples without any further treatment. Therefore the accurate trace quantitation in complex are more attainable using DESI-MS with isotopically labeled standards. Ambient electric discharge provides high density of charged molecules, and metastable neutral species (such as $\text{HO} \cdot$, $\text{O} \cdot$, $\text{NO} \cdot$, etc.), showing attractive attribution for primary ion production.

Low-Temperature Plasma (LTP, Figure 4) is a plasma based technique that operated on the base of the ambient discharge and/or plasma to make the energetic species as the ionization reagents. LTP is obtained by using helium gas as the working medium, and a large number of electrons and positive ions, resulting in the generation of helium atoms at excited energy levels. Besides the metastable helium atoms, the electrons and positive ions can be used as

the carrier of energy and charges for the secondary ionization of the targeted analytes. Because gases (such as moist air, nitrogen gas, helium gas, etc.) can be introduced into the electric field as the discharge medium, the gaseous samples (e.g., air, volatile organic compounds) can be directly analyzed by this technique, showing potential applications for sensitive detecting nonpolar compounds without tedious sample pretreatment. In the LTP stage, gas is supplied continuously between the two electrodes, and plays an important role to maintain discharge, to cool the electrode, and to provide reagent ions.

Fig. 4. Schematic configuration of LTP probe

In the LTP probe experiments, the probe is used to directly desorb and ionize the analytes from aqueous solutions. To demonstrate this feature, a glass dish containing 150 mL of deionized water was spiked with atrazine (agricultural herbicide) resulting in a 1 ppm aqueous solution. The solution was placed near the MS inlet, and the LTP probe (He discharge gas) was used to direct the plasma over the liquid surface. The MS spectrum gives a signal at m/z 216 which can be assigned at protonated atrazine, that is confirmed by MS² spectrum. The linear dynamic range for atrazine in this case for deionized water varies from 1 ppb to 1 ppm (Harper et al., 2008). LTP-MS has been utilized for the detection of pesticide residues in food. Different multi-class agricultural chemicals were considered (ametryn, amitraz, atrazine, buprofezin, DEET, diphenylamine, ethoxyquin, imazalil, isofenphos-methyl, isoproturon, malathion, parathion-ethyl and terbuthylazine). The experiments were performed directly on fruit peels as well as on fruit/vegetable extracts. Most of the agrochemicals examined displayed remarkable sensitivity in the positive ion mode, giving limits of detection (LOD) for the direct measurement in the low picogram range. The semi-quantitative screening, with LTP-MS, of agrochemicals in foodstuffs were performed using fruit and vegetable extracts (Wiley et al., 2010). DESI works best with polar analytes that are easy to protonate or deprotonate, although analytes of low polarity are accessible to a certain extent, this was the rationale for developing DAPCI. In order to improve the efficiency of ambient MS in the regime of low-polarity compounds, desorption atmospheric pressure photoionization (DAPPI, Figure 5) has been developed. DAPPI represents the adaptation of APPI for the ambient analysis of surfaces analogous to the conversion of APCI to DAPCI. In DAPPI, a heated jet of solvent vapor and nebulizer gas desorbs solid analytes from the surface. A krypton discharge lamp is directed toward the sample so as to irradiate the vapor phase immediately above the surface with UV photons of 10 eV where ionization of the analyte occurs. Like DESI and DAPCI, DAPPI uses a standard API interface to collect the ions (Haapala et al., 2007).

Fig. 5. Schematic configuration of DAPPI source

DAPPI has been used to study a set of harmful compounds typically found in environmental or food samples, DAPPI-MS spectra has recorded in both positive and negative ion modes. The analytes include five polycyclic aromatic hydrocarbons (PAHs) and one N-PAH (acridine), one brominated flame retardant (tetrabromobisphenol A, TBBPA), and nine pesticides. Two authentic samples, orange peel and a spiked soil sample were analyzed by DAPPI-MS in order to demonstrate the suitability of the technique for the analysis of environmental or food samples. The PAHs are neutral non-polar compounds, while the TBBPA and the pesticides are slightly acidic or basic. Limits of detection (LODs, signal-to-noise (S/N) ratio > 3) were determined for all the compounds using a characteristic ion identified from the mass spectrum. If multiple analyte ions were observed in the mass spectrum of a single analyte, the most intense ion was selected as the characteristic ion to be measured. The analysis was carried out in full scan MS mode and the LOD values are averages of four separate sample spots. For the PAH compounds the LODs were determined in positive ion mode and they ranged from 0.1 to 1 ng. The LODs were observed to decrease as the size of the molecule increased. This is expected since the number of delocalized p-electrons increases with increasing molecule size, thus leading to a lower ionization energy. The LODs for the pesticides determined in positive ion mode ranged from 30 to 300 pg. There were no significant differences between the LODs of different pesticides, which is thought to be because of their similar physical and chemical properties, i.e. functional groups containing oxygen and nitrogen (Luosujärvi et al., 2010).

Direct analysis in real time (DART, Figure 6) is another different atmospheric pressure ion source that instantaneously ionizes gases, liquids and solids in open air under ambient conditions. In the DART method, an electrical potential is applied to a gas with a high ionization potential (typically nitrogen or helium) to form a plasma of excited-state atoms and ions, and these desorb low-molecular weight molecules from the surface of a sample (Cody et al., 2005). The cold plasma passes through a second chamber where a second perforated electrode can remove cations from the gas stream that is subsequently heated and passed through a final grid electrode removing oppositely charged species. The ionizing neutral gas may either be directed towards the sampling orifice of an API interface, or analogous to DESI, may hit the sample surface at an angle suitable for its reflection into the entrance of the mass spectrometer.

DART has been applied in several fields, This includes the typical safety-related and forensic usages of ambient MS like detection of explosives, warfare agents, or pharmaceuticals and drugs of abuse. DART is used for the routine rapid analysis of highly

insoluble polycyclic aromatic compounds. Direct analysis of such compounds as solid samples under solvent-free conditions shows that DART is a powerful analytical platform capable of providing high-throughput analysis for these complex samples, and no special sample pre-treatment or instrument setup are required (Domin et al., 2010). Ambient mass spectrometry has been used for the analysis of strobilurin residues in wheat, (DART) ion source coupled with a time-of-flight mass spectrometer (TOF MS), permitted a direct screen of the occurrence of target fungicides in treated grains in less than 1 min. For quantification purpose by DART-TOF MS, an ethyl acetate extract had to be prepared, with the use of a prochloraz as internal standard. The performance characteristics obtained by repeated analyses of extract, spiked at 50 μgkg^{-1} with six strobilurins (azoxystrobin, picoxystrobin, dimoxystrobin, kresoxim-methyl, pyraclostrobin, and trifloxystrobin), were in the following range: recoveries 78-92%, repeatability (RSD) 8-15%, linearity $R^2 = 0.9900-0.9978$. The analysis of wheat with incurred strobilurin residues demonstrated good trueness of data generated by the DART-TOF MS method; the results were in a good agreement with those obtained by the conventional approach (Schurek et al., 2008).

Fig. 6. Schematic configuration of DART source

4. Gas-chromatography mass spectrometry (GC/MS) applications

4.1 Introduction

Considerable efforts have been made to validate analytical methods that allow researchers to obtain reproducible data in the effective sample preparation, separation, identification, and precise quantification of pesticide analytes at the lowest possible level. The trend in the development of new analytical techniques is to simplify the operating procedure, and especially in the improvement and development of new methods by instrumental point of view. This section aims to explore the different gaschromatography-mass spectrometry (GC-MS) methods, both mass spectrometry (MS) and tandem mass spectrometry (MS/MS), developed in recent years for the determination and quantification of pesticides in food, water, soil and air samples. One of the innovations that led in recent years a significant improvement in the analysis of pollutants has been the coupling of fast gaschromatography (fast GC) with different MS devices. In fact, the fast GC-MS allows to process a greater number of analysis while maintaining the same sensitivity and efficiency compared to the GC-MS. Regarding the methods of ionization, the most used are EI and CI while recently is finding a growing use of the application negative chemical ionization (NCI) in MS detection. The most important development in the analysis of pollutants is undoubtedly due to the use of innovative MS analyzers. Indeed, the advent of devices such as ion trap (IT), triple quadrupole (QqQ), time of flight (TOF), and particularly their combinations has attracted the attention of researchers towards the application to the analysis of trace contaminants

and in particular to the multi-residual analysis. The applications of the latest analyzers allow the determination of pollutants in different modes mainly depending on the sensitivity and specificity to be achieved: full-scan, selected ion monitoring (SIM) or selected ion storage (SIS), MS/MS, multiple reaction monitoring (MRM) and selected reaction monitoring (SRM). In the following section it will be discussed the recent applications of GC-MS analysis of the major classes of pesticides: organochlorine, organophosphorus, carbamates, pyrethroids, triazines, and the multi-residual analysis.

4.2 Organochlorine pesticides

A simple and fast analysis of five organochlorine pesticides (OCPs), heptachlor (HTC), aldrin (ALD), dieldrin (DEN), endosulfan-I (EDSI) and endosulfan-II (EDS-II), in aqueous samples was carried out by Tsai et al., (2009) by using the dispersive liquid-liquid microextraction with little solvent consumption (DLLME-LSC) technique for the samples preparation and subsequent gas chromatography/mass spectrometry analysis. The developed procedures were applied to the determination of targeted OCPs in tap water, reservoir water, river water, and sea water. The MS was operated in the selected ion monitoring (SIM) mode for determination of target compounds selecting three ions of each compound. In another approach, the analysis of three chloroacetanilide herbicides, acetochlor, metolachlor and butachlor, in the same matrix was performed with the analytical GC-MS in SIM mode (Xu et al., 2007). The extraction technique developed was the direct immersion solid-phase microextraction (DI-SPME) by means of a PDMS fiber which showed a high affinity for all the three analytes. The SIM technique was also used for determination of nine OCPs in vegetables by single-drop microextraction (SDME) coupled with GC-MS. A solution of p-xylene and acetone (8:2, v/v) was used as organic phase extraction which was subsequently injected for GC-MS analysis (Zhang et al., 2008). The analysis of eighteen organochloride pesticides from complex water samples by ion trap GC-MS in SIM mode was performed with the same single-drop microextraction (SDME) technique (Cortada et al., 2009). The SDME method has been studied by experimental design that allowed the optimization of variables such drop volume, aqueous sample volume, agitation speed, ionic strength and extraction time. A high-level linearity was obtained for the calculated calibration curves for all target analytes. By another method seventeen organichlorine pesticides were analyzed and quantified in air samples by gas chromatography-negative chemical ionization-mass spectrometry (GC-NCI-MS) operating under SIM mode (Yang et al., 2008). The sampling was performed every month within a year from two different urban and suburban sites and extraction was obtained by collecting the atmospheric OCPs on quartz fibre filter (QFF) and polyurethane foam (PUF) using accelerated-solvent extraction (ASE) and subsequent neutral silica solid phase extraction (SPE).

The first application of the triple quadrupole tandem mass spectrometry for analysis of organochlorine pesticides in oils and fats was realized by Patel et al., (2005). GC-MS analysis is preceded by gel permeation chromatography which provides the removal of lipids. For each of nineteen studied organochlorine compounds, MRM analysis was performed by choosing as the precursor ion the base peak in full-scan spectrum. In some cases were used, in addition to the base peak, even ion masses of lower intensity in order to minimize the matrix effect. Each segment contained a minimum of two and a maximum of four transitions (i.e. one or two analytes per segment). In table 2 are reported the MRM optimization parameters of some studied compounds.

Pesticide	First transition m/z	Second transition m/z	Quantification ions
α -HCH	219 > 147	219 > 183	183
Hexachlorobenzene	284 > 214	284 > 249	249
β -, χ -, δ -HCH	181 > 145	219 > 183	183
Heptachlor	272 > 237	274 > 239	237
Aldrin	263 > 191	293 > 257	191+149
Oxychlordane	187 > 123	185 > 149	123+149
cis-, trans- Chlordane	373 > 264	373 > 266	266
Endosulfan	241 > 206	195 > 125	206
p,p'DDE	246 > 176	318 > 246	176
Dieldrin	263 > 193	277 > 241	193+241
Endrin	263 > 191	281 > 245	191+245
β -Endosulfan	241 > 206	195 > 160	160+206
p,p'-, o,p'-DDT; p,p'-TDE	235 > 165	235 > 199	165

Table 2. MRM optimization parameters in some organochlorine compounds.

The GC-MS/MS triple quadrupole analysis of organochlorine pesticides showed a higher selectivity and allowed the univocal identification and quantification of all the target analytes at low ppb levels in a single analysis. For this reasons a large number of studies applied the same technique. For example, gas chromatography-triple quadrupole tandem mass spectrometry analysis was recently developed for determination of seventeen organochlorine pesticides in fish feed (Nardelli et al., 2010). The best compromise between sensitivity and selectivity was obtained choosing one precursor and two daughters in multiple reaction monitoring (MRM) mode. The GC-MS/MS analysis showed very low LOD and LOQ values. This method was applied successfully to the monitoring of 37 fish feed samples which showed the natural presence of four pesticides (p,p'-DDE, p,p'-DDD, α -endosulfan and endosulfan sulphate), and HCB was used as internal standard, at a concentration, expressed as sum of isomers, lower than legal limit (50 $\mu\text{g kg}^{-1}$).

A simple method for determination of nineteen organochlorine pesticides in soil using gas chromatography-tandem mass spectrometry was developed from Rashida et al., (2010). A QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method, based on two steps, was used for extraction and clean-up procedure. The MS/MS method included two transitions for each analyte which allowed simultaneous quantification and confirmation of any residues detected.

4.3 Organophosphorus pesticides

Since the prohibition of the first-generation organochlorine pesticides, organophosphorus pesticides have been increasingly important in the global agrochemical industry. The chemical-biological and slow degradation properties together with unscrupulous and extensive uses of this class of pesticides have led to the occurrence of several cases of environmental pollution and food contamination. Basheer et al., (2007) developed a simple binary solvent-based two-phase hollow fiber membrane (HFM)-protected liquid-phase microextraction (BN-LPME) technique followed by analysis under GC/MS selective ion monitoring mode. This method was compared with a classical SPME procedure and both techniques were applied in water samples to determine the presence of six moderately polar

organophosphorus pesticides (OPPs): triethylphosphorothioate, thionazin, sulfotep, phorate, disulfoton, methyl parathion and ethyl parathion. The first sample preparation method was a hollow polypropylene fiber-protected liquid-phase microextraction with a 1:1 mixture of toluene:hexane as extraction solvent over a period of 35 min. The second technique was a direct immersion solid phase micro-extraction (DI-SPME) procedure using a PDMS-DVB fiber and an extraction time of 35 min with stirring. The fiber was desorbed in the injection-port of the GC for 3 minutes at 250 °C. The organophosphorus compounds studied and extracted with both previously cited procedures were quantitatively determined by GC-MS in SIM mode. Linearity, repeatability, relative recoveries and limits of detection (LODs) were investigated under optimized conditions. BN-LPME combined with GC/MS analysis provided repeatability (R.S.D.s $\leq 12\%$), linearity ($r^2 \leq 0.994$) and LODs in the range of 0.3–11.4 ng L⁻¹. SPME combined with GC/MS analysis provided repeatability (R.S.D.s $\leq 13\%$), linearity ($r^2 \leq 0.966$) and LODs in the range of 3.1–120.5 ng L⁻¹. The BN-LPME and SPME procedures with GC/MS in SIM mode were applied to the detection of OPPs in domestic wastewater samples and no OPPs were detected in the real samples analyzed. One of the most important pesticide that is used to control the attack of the olive fruit fly, is the phosmet, a non-systemic organophosphorus insecticide. The determination of phosmet residues and its metabolites (phosmet-oxon, phthalimide, N-hydroxymethylphthalimide, and phthalic acid) in olive fruits was developed using matrix solid-phase dispersion (MSPD), and gas chromatography-mass spectrometry (GC/MS). All analytes were determined in selective ion monitoring (SIM). For each compound, at least, a target ion and three qualifying ions were chosen on the basis of their abundance and selectivity. The method showed suitable linearity with correlation coefficients higher than 0.8919 for all the compounds. The LOD values obtained ranged between 0.005 mg kg⁻¹ and 0.060 mg kg⁻¹. The limit of quantifications were between 0.070 mg kg⁻¹ and 0.15 mg kg⁻¹ and resulted below the MRL set by legislation for phosmet. The analysis of real olive samples showed that phosmet concentrations were always lower than the maximum limits set by legislation (Cunha et al., 2007).

The first work was reported using the triple quadrupole for the determination of organophosphorus, has been presented by Qu et al., (2010). This method allowed the determination of twenty organophosphorus pesticides in leek using a modified QuEChERS method for sample preparation. Microwave extraction was used and it offers great reduction of the interference from the sulfur compounds contained in the leeks. The extract was then centrifuged and injected into the GC for GC-QqQ-MS/MS acquiring the data in selected reaction monitoring (SRM) mode. Precursor ion, obtained by the mass spectrum acquired in full scan mode in the range m/z 40–400, was chosen in order to have high m/z ratio (increase in selectivity) and abundance (increase in sensitivity). Selected precursor ion was fragmented by collision-induced (CID) with argon with an energy of 5 to 20 eV, resulting in a spectrum containing the ions produced. In table 3 are reported the data of some organophosphorous studied. This work was clearly demonstrated the selectivity of QqQ analyser which proved to be efficient in the determination of organophosphorous pesticides the vegetables with sulphur-containing compounds.

4.4 Carbamates pesticides

This important class of pesticides have been used extensively since the 1950s, and are widely used since they have high effectiveness and many different biological activities and uses. They are currently used instead of other class of pesticides due to their lower environmental persistence. Since carbamates are thermally unstable, most of the work in the literature were

Pesticide name	Precursor ion (m/z)	Product ion, m/z (collision energy, eV)
Dichlorvos	185	109 (15), 93(15)
Dimethoate	125	47 (15), 93(10)
Fenchlorphos	285	270 (15), 240(15)
Malathion	173	127 (5), 99(15)
Chlorpyrifos	314	258 (12), 286(10)
Parathion	291	109 (15), 137(10)
Trithion	342	157 (10), 199(10)

Table 3. SRM optimization parameters in some organophosphorous studied

performed by liquid chromatography. Nevertheless, several works have been performed using gas chromatography and trying to control as much as possible their termolability. In fact Carabias-Martnez et al., (2005) conducted a chromatographic study of seven carbamates pesticides (aldicarb, carbetamide, propoxur, carbofuran, carbaryl, methiocarb, and pirimicarb) in water by gas chromatography-mass spectrometry (GC-MS) and by both solid-phase extraction (SPE) and solid-phase microextraction (SPME). The same analytical technique was used to determine five carbamate pesticides in water samples using liquid-phase microextraction (LPME) followed by on-column derivatization and gas chromatography-mass spectrometric (GC-MS) in SIM mode analysis (Zhang et al., 2006). For selected-ion monitoring (SIM) mode, one characteristic fragment ion was monitored in addition to the molecular ion of each compound. Single-drop microextraction (SDME) followed by selected ion monitoring gas chromatography-mass spectrometry detection was used for the determination of eight carbamate pesticides (thiofanox, carbofuran, pirimicarb, methiocarb, carbaryl, propoxur, desmedipham and phenmedipham) in water samples (Saraji & Esteki, 2008). In this work were used and compared two different procedures of sample introduction: SDME followed by cool on-column injection without derivatization, and SDME followed by in-microvial derivatization with acetic anhydride and splitless injection. The first method allowed the detection of examined carbamates at concentrations greater than 30 ng L⁻¹, but the main advantages of this method were that it avoids the use of derivatization reagents, reduced analysis times, and reduced the sample manipulation. The SDME followed by in-microvial derivatization with acetic anhydride reached lower values of detection within the range 3–35 ng L⁻¹. However, this technique required longer analysis times and more sample manipulation. Another approche by using ion trap gas chromatography-tandem mass spectrometry (GC-MS/MS) following a low-density extraction solvent-based solvent terminated dispersive liquid-liquid microextraction (ST-DLLME) was developed for the highly sensitive determination of four carbamate pesticides in the water samples (Chena et al., 2010). There is no available at present, studies on the determination of carbamates pesticides using triple quadrupole GC-MS tandem mass spectrometry.

4.5 Other pesticides

Pyrethroids are an important class of pesticides used in many types of agricultural crops as insecticides. Their widespread use is due to high stability and the wide spectrum of action that they present. An efficient methodology has been developed for the determination of pyrethroid insecticide residues in vegetable oils by using combined solid-phases extraction

and gas-chromatography/tandem mass spectrometry (GC-IT-MS/MS) analysis (Esteve-Turrillas et al., 2005). This method has been proposed in order to be used in different arrays as olive, sunflower, corn and soybean oils. Since pyrethroids can also be found in the waters, it was proposed a rapid analytical method for the determination of fourteen pyrethroids in water samples, some of which are critical to water quality (Feo et al., 2010). The method is based on ultrasound-assisted emulsification-extraction (UAEE) with chloroform as extraction solvent followed by gas chromatography-negative ion chemical ionization mass spectrometry (GC-NCI-MS) analysis. Bifenthrin, cyfluthrin, λ -cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, fenvalerate, fenpropathrin, τ -fluvalinate, permethrin, phenothrin, resmethrin, tetramethrin and tralomethrin are the studied compounds. The GC-NCI-MS analysis was achieved in SIM mode using ammonia as reagent gas. Optimization of NCI analysis was performed by developing the parameters of source temperature and system pressure for each compound. It was noted that the NCI mass spectrum of pyrethroids was generally characterized by intensive peaks obtained by loss of the ester substituents that forms stabilized carboxylate ions. Since the information on the diastereoisomer composition of pyrethroid standards was not available, the peaks corresponding to the different diastereoisomers of a single pyrethroid were integrated as sum for the building of the calibration curves. Another family of pesticides that are ubiquitous environmental pollutants are triazines compounds. Triazines, particularly simazine and atrazine, are important herbicides toxic and rather persistent in living systems, soil, and aquatic media. Determination of seven s-triazine herbicides in aquatic media was achieved by immersed solvent microextraction (SME) and gas chromatography-mass spectrometric in SIM mode analysis (Bagheri & Khalilian, 2005). For each compound the MS detection was operated using SIM mode based on the selection of two mass peaks of the highest intensity. For the analysis of triazines in aqueous samples, the same limits of concentration required by the EU and EPA legislation were obtained from Nagaraju & Huang (2007). The proposed method was based on a dispersive liquid-liquid microextraction technique (DLLME) coupled with gas chromatography ion trap mass spectrometric detection. Comparing with solid-phase microextraction (SPME) and hollow fiber protected liquid-phase microextraction (HFP-LPME); the DLLME method developed was a very simple and rapid, requiring less than 3 min. For determination of triazines in the selected-ion storage (SIS) mode, were selected for each compound the most abundant characteristic ions and two characteristic fragment ions, as showed in table 4.

Herbicide	m/z selected for SIS mass detection	Herbicide	m/z selected for SIS mass detection
Simazine (SMZ)	201,186,173 (100, 85, 42)	Bebuthilazine (SBZ)	229, 214, 200 (7.5, 15, 100)
Atrazine (ATZ)	215, 200, 173 (35, 100, 30)	Desmetryn (DMN)	213, 198, 171 (100, 84, 33)
Propazine (PPZ)	229, 214, 172 (30, 100, 58)	Simetryn (SMN)	213,198, 170 (100, 17, 35)
Secbumeton (SBN)	225, 210, 196 (25, 43, 100)	Prometryn (PMN)	241, 226, 184 (74, 65, 100)

Table 4. SIS optimization parameters for the analysis of triazines in aqueous samples.

The method was applied to the analysis of river and tap water samples, but in the real samples studied no triazine was found. A relatively high solubility in water is shown by acidic herbicide compounds that are often toxic and harmful to health. Their GC monitoring in different environmental matrices cannot be done without any prior derivatization. A derivatization step with N-methyl-N-(tert-butyldimethylsilyl) trifluoroacetamide (MTBSTFA), was needed to carry out the analysis of nine acidic herbicides in water samples by a gas chromatograph coupled to an ion-trap mass spectrometer (Rodríguez et al., 2005).

4.6 Multiresidue analysis

The possibilities of analysis by GC interfaced to a triple quadrupole or gas chromatography time-of-flight mass spectrometry determination, have made multiresidue analysis, by itself provides a particularly sensitive as the simultaneous determination of numerous different analytes, accurate and extremely advantages in terms of time, and economically from a perspective of accuracy and precision of analytical data. Most of the developed analytical methods using the triple quadrupole focused on food matrices. In a relatively, recent work Garrido-Frenich et al., (2007) developed a new multiresidue method for the simultaneous determination of 100 pesticide residues in olive oil. The analysis was carried out in only 19 minutes by gas chromatography coupled to tandem mass spectrometry using a triple quadrupole mass analyzer. In this work two extraction processes were also tested, and an evaluation of the stability and sensitivity of the chromatographic system has been performed for the tested extraction procedures. The quantitative analysis were performed using caffeine, as internal standard, and in selection reaction monitoring mode, acquiring two or three MS/MS fragmentation reactions for each compound. Two of the most common MS/MS analyzers used in pesticide residue analysis are the ion trap (IT) and the triple quadrupole (QqQ) analyzer. IT and QqQ analyzers are representative of MS/MS in time and MS/MS in space, respectively. Garrido-Frenich et al., (2008) verified the comparison between these two MS/MS approaches, evaluating the obtained performances of GC coupled to the two different analyzers (GC-QqQ-MS/MS and GC-IT-MS/MS) for pesticide residue analysis in food matrices such as cucumber (high water content) and egg (high fat content). The analysis were tested for both systems on 19 pesticides, including organochlorine, organophosphorus and pyrethroid pesticides. Two suitable extraction procedures based on the QuEChERS extraction were developed. Both the extracts were submitted to the QqQ mass spectrometric analysis operating in SRM mode and to the MS/MS analysis by ion trap mass analyzer. The QqQ and IT performance was similar in cucumber and egg matrices. However, QqQ provided better sensitivity in egg working in selected reaction monitoring (SRM). At the conclusion of this work MS data and intra-day precision were found similar in QqQ and IT, whereas inter-day precision was found significantly worse in QqQ.

Further evidence of the good obtained results in terms of linearity and sensitivity of gas chromatography-triple quadrupole mass spectrometry method for the determination of pesticide residues in food matrices can be found in another work carried out by Garrido-Frenich et al., (2006a). In this case, were determined some organophosphorus and organochlorine pesticide (thionazin, isofenphos, famfur, p,p'-DDT, mirex, γ -lindane) in meat by GC-MS/MS. In perspective of the importance of determining the presence of trace residues in food and improving the analytical techniques in terms of time and accuracy, the same research group worked to the development of multi-residue methods (MRMs) in fruits and vegetables (Garrido-Frenich et al., 2005; Vidal et al., 2006; Bolaños et al., 2007; Moreno et

al., 2008). In those methods a screening of an extremely large number of multiclass pesticide residues, such as organochlorine (OCPs), organophosphorus (OPPs), carbamates, pyrethroids, triazoles and dicarboximides, was developed and validated. The methods provided for the use of gas chromatography coupled to a triple quadrupole mass analyzer (GC/ QqQ-MS/MS) using the selected reaction monitoring (SRM) mode. In some cases, the SIM mode was also applied simultaneously. The MS/MS conditions were fixed for each compound, trying to select as precursor ion the highest m/z ratio (greater selectivity) and abundance (greater sensitivity). The same approach was applied to choose the product ions used in the quantitative analysis. According to the validation data and performance characteristics as well as the high sample throughput and low cost, the proposed method is selected for routine application. The same authors proposed the application of the same methodology to the multiresidue determination of organochlorine and organophosphorus pesticides in muscle of chicken, pork and lamb (Garrido-Frenich et al., 2006b). The proposed analytical methodology was applied to the analysis of the pesticides in 10 chicken, 10 pork and 10 lamb samples. Only three OCPs, α -endosulfan, endosulfan sulfate and dichloran were detected in three different lamb samples, while α -endosulfan was detected in only one pork sample, at concentration levels lower than the LOQ values.

In another work carried out by Walorczyk & Gnusowski (2006) a comparison between performances of low-pressure gas chromatography (LPGC- MS) and GC-MS, both with triple quadrupole mass spectrometry, operating in scan, SIM and MS/MS mode was tested. For the screening method step; 78 different target pesticides residues (OPPs, OCPs, pyrethroids, and others) were tested in vegetable matrices and 12 target pesticides in the quantitative method. The study showed that LP-GC-MS technique deeply reduced the analysis time and had a greater ability to the correct identification of pesticides at lower levels since the peaks were improved in both size and shape than conventional GC-MS analysis. It was also found to be superior to the conventional GC with respect to obtained linearity, accuracy and precision parameters. This allowed the presumption that LP-GC based methods, especially those utilizing highly sensitive and specific MS/MS detection mode, might be of practical value in application areas requiring reliable determination at very low concentration levels. Determination of multiclass pesticides in wastewater, surface, and ground water samples (from the Valencia region, Spain) was developed using gas chromatography coupled to mass spectrometry with a triple quadrupole analyzer (Pitarch et al., 2007). The method was applied to the analysis of more than 50 compounds: 19 organochlorine and organophosphorus insecticides, 6 herbicides, 7 polychlorinated biphenyls, 16 polycyclic aromatics hydrocarbons, 2 brominated diphenyl ethers, 3 octyl/nonyl phenols and pentachlorobenzene. They were analyzed in (EI)MS/MS or in negative chemical ionization mode (NCI)MS. The system operated in MS/MS (SRM) mode using argon as collision gas. NCI was tested only for OC pesticides as this ionization mode with the aim to improve the sensitivity in comparison to EI. In negative chemical ionization (NCI), the QqQ system operated in SIR (selected ion recording) mode, using methane as reagent gas. Quantification of samples was carried out by using calibration curves prepared with standards containing five isotopically labeled standards as surrogates. Two MS/MS transitions were acquired for each analyte.

The use of the TOF analyzer has been recently proposed in the complex matrices analysis for its ability to improve the selectivity by narrowing the m/z window, giving better separation of the target compounds from coeluting compounds. The quantification of almost one hundred pesticides in fruit-based baby food, pear and lettuce samples by gas

chromatography-exact mass time-of-flight mass spectrometry (GC-TOF-MS) has been developed by Leandro et al., (2007). The mass accuracy of the TOF instrument improved with increasing concentration of the analytes of interest and was more critical for analytes with low m/z values. A method was developed using programmed temperature vaporiser injection-low-pressure gas chromatography-high-resolution time-of-flight mass spectrometry (PTV-LP-GC-HR-TOF-MS) for the analysis of multiclass pesticide residues in apple-based baby food (Cajka et al., 2008). A comprehensive GC $\times$ GC-TOFMS method was optimized for separation of 51 pesticides in grape matrices (Banerjee et al., 2008). The sample preparation was performed using ethyl acetate and subsequent cleaning by DSPE with PSA. A combination of a non-polar and a polar capillary column connected in series allowed chromatographic separation of pesticides studied, thus solving the co-elution problems as observed in full scan one-dimensional GC-MS analysis, and improving the limit of detection by 2–12 times. The same analytical procedure based on comprehensive two-dimensional gas chromatography (GC $\times$ GC) coupled with time-of-flight mass spectrometry (TOF-MS) was used for the simultaneous determination of 97 organic contaminants at trace concentration in river water (Matamoros et al., 2010).

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The book offers a professional look on the recent achievements and emerging trends in pesticides analysis, including pesticides identification and characterization. The 20 chapters are organized in three sections. The first book section addresses issues associated with pesticides classification, pesticides properties and environmental risks, and pesticides safe management, and provides a general overview on the advanced chromatographic and sensors- and biosensors-based methods for pesticides determination. The second book section is specially devoted to the chromatographic pesticides quantification, including sample preparation. The basic principles of the modern extraction techniques, such as: accelerated solvent extraction, supercritical fluid extraction, microwave assisted extraction, solid phase extraction, solid phase microextraction, matrix solid phase dispersion extraction, cloud point extraction, and QuEChERS are comprehensively described and critically evaluated. The third book section describes some alternative analytical approaches to the conventional methods of pesticides determination. These include voltammetric techniques making use of electrochemical sensors and biosensors, and solid-phase spectrometry combined with flow-injection analysis applying flow-based optosensors.

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