

Review

Last trends in pesticide residue determination by liquid chromatography–mass spectrometry



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ABSTRACT

Liquid chromatography–mass spectrometry (LC–MS) is as an excellent analytical tool in the determination of pesticides. Multiresidue analysis of these compounds at trace levels is one of the oldest analytical schemes within environmental and food safety. However, the issue of “pesticide residue determination” is still a hot topic for the analytical community. This review discusses current approaches and recent advances in using LC–MS for pesticide identification and quantification. We outline how MS has influenced the sample preparation process. We critically assess and compare various mass spectrometers, highlighting their strengths and limitations. We, then, review the main applications of LC–MS in pesticide residue determination in the past three years. We also look at the implications for the future of the field.

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1. Introduction

Synthetic pesticides are used in agriculture throughout the world since the middle of the 20th century to avoid pest in plants and animals [1,2]. Any environmental and food sample is susceptible to contain pesticide residues because they are widely dispersed from their application areas, reaching environment and food chain [3]. As a result, people are exposed to pesticide residues at low concentrations through the environment, their diets, etc. Scientists are interested about the health effects because they are

not clearly understood yet. Moreover, new alarms regarding the prevalence and effects of these compounds in the environment, and concerns of synergies between them have recently emerged [2,4,5].

Consequently, in the 70s and 80s, the European Union (EU) established strict regulations banning many pesticides [6,7]. Since that moment, new groups of these substances coined as “currently used” or “modern” pesticides have been introduced in the market replacing the oldest ones [2].

In case of environmental samples, EU adopted the Water Framework Directive 2000/60/EU [8]. The adopted Decision No 2455/2001/EC [9], which amends Directive 2000/60/EC [8], has established a list of 33 priority substances in the field of water policy, the third part of which are pesticides. Previously, another

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directive, 98/83/EC [10], had set limits for pesticides in water intended for human consumption (100 ng/L for individual pesticides and 500 ng/L for the sum of all pesticides) [11].

For food samples, pesticide residues have been regulated by several legislative authorities throughout the world, basically concerned with the quality, efficacy and safety in the use of pesticides, however, there is not a global harmonized legislation [12]. EU has set through maximum residue levels (MRL) (European Commission, 1999) [13]. In general, the MRLs are in the range of 0.01–10 mg/kg, depending on the combination commodity and pesticide. The lowest is characteristic of banned compounds because is considered as the minimum limit of detection (LODs) achievable. A value of zero is considered below the LOD because of the slight inaccuracies in the measurement methods available [12].

The analysis of pesticide residues represents a basic instrument not only for the protection of human health, but also for trade and official control purposes [12]. Despite of multiresidue analysis of these compounds at trace levels has been carried out since the 70s [14], analysis of pesticides still remains a challenge because different chemical classes are present at low concentrations in complex matrices. Therefore, it is necessary to continue developing multi-residue analytical methods with higher recoveries and lower limits of detection [11] as well as incorporating the ultimate innovations to them.

Nowadays, liquid chromatography–mass spectrometry (LC–MS) is preferred over gas chromatography (GC) because currently used pesticides are quite polar, thermally labile or not easily vaporized [14], and consequently, worst detected by GC. Therefore, LC–MS has become one of the most powerful analytical tool for organic compound analysis at sub $\mu\text{g/L}$ level providing the sensitivity, selectivity, and specificity needed to meet EU legislation for the analysis of pesticides in water and food samples [15,16]. As a demonstration of the growing interest of this topic, Fig. 1, summarizes the number of articles published from 2009 to 2013 shorted from the ISI Web of Science and the SCOPUS using the keywords “Pesticides” and “liquid chromatography–mass spectrometry”. The number of articles increases year after year. Furthermore, the number of recent review articles dealing with this subject [1,12,17–25] can add elements to the evidence already pointed out in Fig. 1. This review offers a critical overview of the current workflow within pesticide residue analysis by LC–MS because the many reviews that treat this topic are more general and focus not only on LC–MS but on a sort of techniques. Special attention is paid to provide comprehensive coverage of ultimate innovations in the field. Finally, possible future trends and developments in this area are briefly discussed.

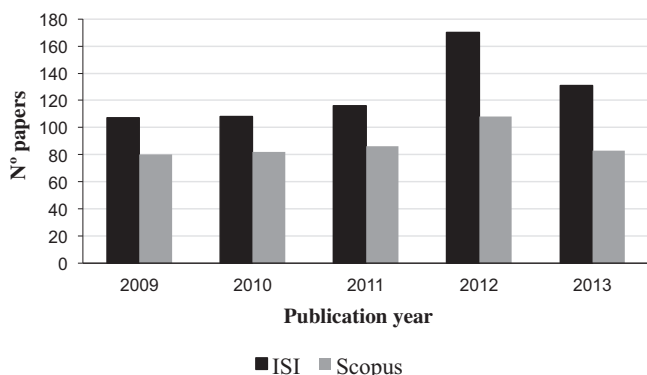


Fig. 1. Pesticide residues and liquid chromatography–mass spectrometry.

2. Analysis

Table 1 includes a summary of the most significant studies regarding LC–MS for pesticide residue determination. These reports are classified according to the mass analyzer and to the matrix and show the number of pesticides, the matrix selected, the sample preparation procedure, the separation setup and the determination with an insight in sensitivity.

2.1. Extraction procedures

Sample preparation step is necessary to isolate and concentrate pesticide residues. These procedures often take up most of the total analysis time, contributing highly to its total cost, and greatly influencing its reliability and accuracy [65]. Extraction and purification of pesticides has evolved a lot since the first multiresidue extraction scheme proposed by Mills [66]. Many of these analyses are made on food and other perishable products. Therefore, method rapidity, or at least, method feasibility in a reasonable time is important. The first methods developed, even though they were milestones in the analysis of organic contaminants, were long, tedious, consumed large amount of sample and organic solvents and required a sophisticated purification involving solvent partition and column chromatography clean-up that could require several days [67].

Fig. 2 provides an outline of the evolution of extraction methods parallel to the increase in the specificity of detection systems. MS, particularly when combined with LC has been architect of a chemist's dream: to reduce the sample preparation. For economic reasons and practicality and thanks to selectivity and specificity of MS, extraction tends to be generic. This means that these procedures are able to extract the widest number of organic contaminants, not only pesticides, to later identify them unequivocally by LC–MS [65].

Nowadays, among the different analytical methods developed, solid-phase extraction (SPE) in combination with LC is the most applied technique for the extraction of pesticide residues in water [68]. On-line SPE is considered the elegant alternative (includes automation and miniaturization) and solid-phase microextraction (SPME) the environmental friendly (requires little quantity of water samples and is almost solvent free) but both are less used. With the aim of offering a clear idea of the current situation, of 9 studies in water presented in Table 1, 6 were performed using conventional SPE, 1 using a variant of the SPME (in-tube SPME), 1 applying a liquid–liquid microextraction procedure (LLME), based on supramolecular solvents (SUSME), and finally, other just made direct injection.

Similarly, the determination of pesticide residues in solid samples is mostly afforded by the QuEChERS “Quick, Easy, Cheap, Effective, Rugged, and Safe” method [69]. It provides a versatile platform of many different protocols, depending on the type of pesticide (influence of pH, degradability), the type of matrix (fatty, acidic or especially complex), the purpose of the analysis, etc. Of 40 studies collected in Table 1, 40% apply some kind of QuEChERS protocol. The other studies on matrices different to water are based on an array of techniques that can be used alone or combined. These alternative techniques include liquid–liquid (LLE) [31,33,48,55,56,58,59], membrane assisted (MASE) [5], matrix solid phase dispersion (MSPD) [35,41], turbulent flow chromatography [36], microwave-assisted (MAE) [38], pressurized liquid (PLE) [39], SPME [39], stir bar sorptive (SBSE) [51], SPE [54] and high throughput planar SPE (HTpSPE) [47] extractions or just dilution of the sample and direct injection [44].

LC–MS has made possible that sample preparation directs toward simple, miniaturized and environmental friendly methods (according to the principles of Green Chemistry). This

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