Strategies for quantification and confirmation of multi-class polar pesticides and transformation products in water by LC–MS^2 using triple quadrupole and hybrid quadrupole time-of-flight analyzers

Félix Hernández, Óscar J. Pozo, Juan V. Sancho, Francisco J. López,
José M. Marín, María Ibáñez

Liquid chromatography–tandem mass spectrometry (LC–MS^2) is an excellent technique for the determination of polar pesticides and transformation products in water. On-line trace enrichment by solid-phase extraction (SPE)-LC in combination with MS^2 satisfies most analytical demands of modern laboratories for pesticide-residue analysis, with respect to sensitivity (limits of detection and limits of quantification at sub-μg/L levels), selectivity, reliability and rapidity, and all with very little sample manipulation. However, several obstacles have to be overcome when developing SPE-LC–MS^2 multi-residue and confirmative methods. The different physicochemical characteristics and wide polarity range of pesticides and their transformation products make their simultaneous preconcentration, chromatographic separation and determination difficult. Also, for the correct confirmation of the identity of compounds, it is necessary to increase the number of monitored MS transitions, which normally leads to a loss in sensitivity. This may hamper confirmation at low concentrations in a single chromatographic run (i.e., when a second analysis is not performed).

In this article, we discuss different strategies for developing sensitive multi-residue methods for pesticides in water, able to correctly quantify and confirm compounds detected in samples. We discuss the use of different analyzers, triple quadrupole and hybrid quadrupole time-of-flight and compare their performances for screening purposes, and for the quantification and confirmation of positive samples. We present several practical cases of water samples, including some positive findings that would result in false positives if no criteria were applied for unequivocal confirmation of the identity of detected compounds.

Keywords: Confirmation; Liquid chromatography; Pesticides; Quantification; Screening methods; Tandem mass spectrometry; Time-of-flight; Transformation product; Triple quadrupole; Water

Félix Hernández*,
Óscar J. Pozo, Juan V. Sancho,
Francisco J. López,
José M. Marín, María Ibáñez
Research Institute for Pesticides
and Water, University Jaume I,
P.O. Box 224, E-12080
Castellón, Spain

*Corresponding author.
Tel.: +34 964 728100;
Fax: +34 964 728066;
E-mail: hernandf@exp.uji.es.

1. Introduction

Liquid chromatography–mass spectrometry (LC–MS) using atmospheric pressure ionization (API) interfaces has dramatically changed the analytical methods used to determine polar organic pollutants in water, as evidenced by the growing number of papers concerning the determination of polar pesticides in environmental water by LC–API-MS published in the scientific literature in the last few years. Interesting, detailed discussions on the use of LC–MS for the determination of organic pollutants, including pesticides, in water can be found in recent articles [1–4]. The great potential of LC–MS for pesticide residue analysis (PRA), focused on polar compounds, and the advantages of this technique in water analysis are widely recognized. However, several difficulties have to be overcome in qualitative and

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quantitative determination of organic compounds. The main obstacles are matrix effects that affect the ionization of the analytes and obviously the quantification, the limited resolution of quadrupole and ion-trap MS, and the limited fragmentation encountered in collision-induced dissociation (CID), this latter restricting its application to qualitative analysis [5]. Additionally, high sensitivity is required in PRA of water, and one faces a challenging variety of pesticides of quite different polarities and chemical forms (anionic, cationic and neutral).

Some of the problems associated with LC–MS methods may be reduced by improved instrumentation [e.g. tandem MS (MS^2) or time-of-flight (TOF)-MS] or improved chromatographic separation. Besides, an efficient sample clean-up is a common approach to remove interfering matrix components prior to the ionization process. For example, solid-phase extraction (SPE) with various sorbents has frequently been employed in water analysis, as a simple way of performing sample clean-up and preconcentration. Thus, most published papers dealing with PRA in water by LC–MS use preconcentration by SPE, either off-line or on-line, before injection into the LC–API-MS system, in order to reach the sensitivity required. The sample volume processed normally depends on the instrument used, the limit of detection (LOD) required and the SPE mode applied (off-line or on-line). High sample volumes (500–1000 mL) are typically used when performing the SPE step off-line and using single MS instruments [6,7], but they can be lower (50–100 mL) when on-line SPE is used [8,9]. Moreover, if an MS^2 instrument is used, the volumes processed on-line can be decreased down to 10–25 mL [10,11] or even below 5 mL [12,13] and still achieve the required LODs. The excellent sensitivity reached by LC–MS^2 with triple quadrupole (QqQ) instruments may facilitate the detection of some polar pesticides in water, without performing any preconcentration step [14,15]. On-line SPE offers the possibility of reducing the sample volume in comparison to off-line procedures without loss in sensitivity, also minimizing sample manipulation and the use of organic solvents, with the advantage of being easily automated, facilitating its application in monitoring programs.

Efficient, practical monitoring of pesticides in water would require the use of multi-residue methods focused on those compounds most widely applied in the area under investigation, although other parameters, such as toxicity, persistence in the aquatic environment and mobility (leachability), would also have to be taken into account [16,17]. The wide range of polarities of pesticides that can potentially reach the water is one of the main obstacles in the development of multi-residue methods. This problem is increased by the current interest in monitoring the transformation products (TPs) of polar pesticides in water, considered as emerging contaminants by some authors [18]. Eventually, the list of selected analytes will surely include pesticides of different polarities and a number of relevant metabolites or TPs [19]. The wide polarity range of analytes and the existence of different chemical forms in water will demand some kind of compromise to develop efficient multi-residue methods able to determine simultaneously highly polar TPs and medium polar pesticides, sacrificing sensitivity in some cases.

Different strategies could be applied for monitoring pesticides in water depending on the objectives pursued. The method requirements will differ, depending on whether it is intended simply to detect, to quantify or to confirm the presence of a possible residue. Analytical methods might be therefore classified into three categories:

(i) screening methods, which may (quickly) detect the presence of one or more compounds based on one or more common characteristics of a class of pesticides in a qualitative or semi-quantitative manner at a specified concentration limit;
(ii) quantitative (or determinative) methods, which should provide precise information concerning the amount of an analyte that may be present, but may provide only indirect information about the identity of the analyte; and,
(iii) confirmatory methods, which should confirm the identity of the analyte but may or may not have a quantitative or semi-quantitative component [20].

Screening methods are useful because they provide greater analytical efficiency and allow samples with no detectable residue to be discriminated from those with pesticide residues at any appropriate level of interest. This would allow the analytical effort to focus on quantitation and confirmation of presumptive positive samples.

From this point of view, multi-residue SPE-LC–MS^2 methods used for screening and quantification satisfy the analytical demands of sensitivity, selectivity and accuracy required nowadays in PRA, but their screening capabilities are reduced due to the need to pre-select the MS^2 transitions before acquisition (target analysis), and they cannot reveal the presence of any other pesticide residues. It is very important that MS^2 methods can also unequivocally confirm the identity of the compounds detected in water. Although MS^2 detection can be considered a very selective technique, this selectivity may be overestimated due to the great complexity of environmental samples. This might result in false positive findings, especially when low-resolution MS detection is used. In order to minimize this risk, a recent European Commission Decision [22] established interesting criteria for the confirmation of positive findings based on the collection of identification points (IPs). Thus, adequate confirmation is made in low-resolution instruments (e.g., QqQ) acquiring two MS^2 transitions