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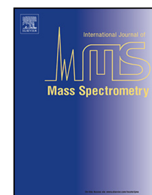

QqQ and Q-TOF liquid chromatography mass spectrometry direct aqueous analysis of herbicides and their metabolites in water

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ABSTRACT

Triple quadrupole mass spectrometry (QqQ) is the most popular and widely used technique used to analyze pesticide residues in food and environmental compartments. However, recent advances in quadrupole-time-of-flight mass spectrometry (Q-TOF) may lead to this approach becoming a useful tool for analysis of pesticide residues.

In this work, results of QqQ and Q-TOF were compared to determine their accuracy, when determining the concentration of herbicides and their metabolites in water. Double distilled and river water were therefore spiked with 18 analytes, differing in physical–chemical properties, and then directly analyzed either by QqQ and Q-TOF mass spectrometry.

Results of Q-TOF were comparable to QqQ. The latter, operating in tandem mass spectrometry, was superior in terms of compound coverage, LOQ and precision for most analytes. However, results between the two analysis methods were comparable for LOD, linearity range (4 orders of magnitude) and accuracy. Validation parameters in pure and surface water showed contrasting results. Overall, the results of this study suggest that Q-TOF may represent a valid alternative to triple quadrupole, although the specific mass spectrometer under use still plays a major role.

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1. Introduction

Sensitive and comprehensive methods for the analysis of pesticides are required considering they are generally measured at low concentrations and can involve complex matrices. In the last decade, chromatography coupled to tandem mass spectrometry has become the most popular technique used in the analysis of pesticides in food and environmental compartments [3,4,6,8,17,18,23]. Quadrupole mass analysers are extensively used mass spectrometers, due to their sensitivity, specificity, wide linear range and ease of use. In particular, liquid chromatography (LC) coupled to triple quadrupole tandem mass analysers (QqQ) is generally regarded as the most widely applied technique for multi-residue analysis of pesticides. This is principally due to its wide compound coverage and high qualitative and quantitative analytical performance [7–9,12,13,15,17,18,20,25,28]. Although QqQ provides excellent sensitivity and specificity, it also has limited structural information and does not identify non-target compounds [5,19,27]. However, quadrupole-time-of-flight (Q-TOF) tandem mass spectrometry has a broad application range, mainly for screening purposes, [5,13,14,21] overcoming the poor structural information and QqQ unsuitability for non-target compounds. Instruments that have been developed more recently, due to technological improvement in ionization sources and ion detectors, provide higher sensitivity than in the past, with a broader linear dynamic range. A number of studies, associated with the application of Q-TOF for quantitative analysis, have been published in recent years [11,16,24,29].

Therefore, both QqQ and Q-TOF approaches may be useful for the determination of pesticide residues in food and environmental compartments although with some limitations. The aim of this study is to compare two LC–MS analysers (i.e. QqQ and Q-TOF) for the direct aqueous analysis of herbicides in water. Pure water and surface water are measured, to account for possible matrix effects. The analytes targeted in this study are the most widespread classes used in Northern Italy, which have a wide range of physical–chemical properties. The analytes considered include compounds with documented risk of leaching [10,22], representing agricultural contaminants which may be found in drinking water.

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In the view of developing a fast methodology for direct analyses of pesticides in real water samples, no sample pre-treatment or pre-concentration steps have been considered, allowing a comparison between the two mass analysers. Furthermore, the diversity in chemical nature of the studied compounds would make the optimization of the pre-analytical step impractical.

2. Materials and methods

2.1. Standards and chemicals

The structures of the 18 compounds selected as target analytes are provided in Fig. 1. Standards of rimsulfuron (RIM), bensulfuron methyl (BEN), diuron (DIU), terbuthylazine (TBZ), desethyl-terbuthylazine (DET), metolachlor (MET), acetochlor (ACC), molinate (MOL), fenoxaprop-p-ethyl (FPE), fenoxaprop (FEN), pendimethalin (PEN), MCPA (MCP) and isoxaflutole (ISF) were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). Terbuthylazine-2-hydroxy (HTB) and terbuthylazine-desethyl-2-hydroxy (DHT), acetochlor-tert-oxanilic acid (ATO), acetochlor-tert-sulphonic acid (ATS) and acetochlor-sec-sulphonic acid (ASS) standards were supplied by crop protection companies. All standards were 97% pure, as minimum, and were used for both spiking and instruments calibration.

Individual stock standard solutions were prepared by weighing 10 mg of each compound, corrected for purity, into 50 mL volumetric flasks (one compound per flask) and then diluting to the mark with acetonitrile (except acetochlor metabolites, terbuthylazine metabolites and MCPA which were diluted in methanol). A mixed standard was prepared by transferring aliquots of each stock solution into a 100 mL volumetric flask and then diluting to the mark in a 80/20 (v/v) methanol/water mixture. Serial dilutions of the combined standard were prepared in 20/80 (v/v) methanol/water to create working standards in the 0.05–500 $\mu g\,L^{-1}$ concentration range. All standard solutions were stored in freezer at −18 °C and freshly prepared every 3 days.

HPLC grade methanol and acetonitrile were bought from VWR International Ltd (Poole, England), while water was milli-Q® grade. LC–MS grade formic acid (from Sigma, St. Louis, MO, USA) was used in the preparation of the LC mobile phases.

2.2. Water samples

The pure water was bi-distilled water, supplied by the Università Cattolica del Sacro Cuore internal services, while surface water was obtained from the Nure river in Pontenure, Piacenza, Italy. Surface water was filtered through a 0.45 μm cellulose membrane filter before use. Prior to use in the study, both water samples were analyzed in triplicate to exclude residues of each target analyte and to verify that the interference from the matrix was below 30% of the lower spiking level. Individual spiked samples were then prepared from 10 mL aliquots of either pure or surface water, by adding an adequate volume of combined standard solution.

2.3. QqQ analysis

A 1200 series liquid chromatograph system, equipped with a quaternary pump and an electrospray ionization system, and coupled to a G6410A triple quadrupole mass spectrometer detector (all from Agilent Technologies Santa Clara, CA, USA) were used.

Chromatographic separation was performed using a Kinetex C_{18} column (150 mm × 4.6 mm I.D., 4 μm dp) from Phenomenex (Torrance, CA, USA). Aqueous formic acid (A) and methanolic formic acid (B) (both at 0.1%, v/v) were used as mobile phase solvents. The gradient was initiated with 50% B and increased to 75% within 0.3 min, then to 86% at 2 min, to 89% at 3 min and to 95% at 6 min. The LC mobile phase temperature was set to 45 °C, the flow rate was 300 $\mu L\,min^{-1}$ until 1 min, and then 350 $\mu L\,min^{-1}$. The injection volume was 20 μL and 2 min of post-run time were adopted after a chromatographic run of 10 min.

Once optimum chromatographic conditions were determined, the tandem MS conditions were optimized for both the positive and negative ionization mode, using the ESI interface. Separate injections were carried out, for analytes acquired in positive and negative mode respectively.

Regarding source parameters, the capillary voltage was set to 4500 V, Nitrogen was used as a drying agent and the desolvation gas flow rate was 10 $L\,min^{-1}$. The drying gas temperature was 350 °C while the nebulizer was kept at 20 psi. Selected multiple reaction monitoring (MRM) based on collision induced decompositions (CID) were defined for each analyte. Mass resolution was wide (1.2 Da) for parent compound and widest (2.4 Da) for product ions; the MRM parameters are detailed in Table 1.

2.4. Q-TOF analysis

MS analyses were performed with a hybrid quadrupole-time-of-flight instrument, acquiring high-resolution MS-only spectra. A 1290 UHPLC liquid chromatograph system, equipped with a binary pump and a JetStream electrospray ionization system, and coupled to a G6540A quadrupole-time-of-flight mass spectrometer (all from Agilent Technologies, Santa Clara, CA, USA) was used.

Chromatographic separation was performed using an Agilent Zorbax Eclipse Plus C18 column (50 mm × 2.1 mm i.d., 1.8 μm dp). The LC mobile phase A consisted of water, while the mobile phase B consisted of acetonitrile. Formic acid (0.1%, v/v) was added to both mobile phase solutions. The gradient was initiated with 20% B and increased to 90% within 5 min, and then held until 7 min. The LC mobile phase temperature was set to 40 °C, and the flow rate was 200 $\mu L\,min^{-1}$. The injection volume used was 20 μL and 1 min of post time was adopted after a chromatographic run of 7 min.

MS conditions were optimized for both the positive and negative ionization mode, using the JetStream ESI interface. Separate injections were carried out for analytes acquired in positive and negative mode respectively, using the same source parameters. Regarding the latter, the capillary voltage was set to 3500 V, nitrogen was used as a drying agent and the desolvation gas flow rate was 9 $L\,min^{-1}$. The drying gas temperature was 350 °C while the nebulizer was kept at 40 psi. The sheath gas (nitrogen) was set to 11 $L\,min^{-1}$ and to 350 °C, while nozzle voltage was 800 V. The acquisition mode used was "SCAN" (MS-only), in the range from 100 to 400 m/z (scan rate 2.00 ms). For each compound, identification was based on monoisotopic accurate mass and isotopic profile, and extracted ion current was provided with a mass window of 10 mDa; the most specific ion was selected for quantitative purposes.

2.5. Methods performance

Spiked samples were prepared in triplicate at 0.1, 1.0 and 10 $\mu g\,L^{-1}$, for pure and surface water at each fortification. The lowest limit of method validation (LLMV) corresponded to the EU limit for a single compound in water intended for human consumption, as set out at EU level [2].

Individual recoveries (ratio between measured and nominal concentrations) were calculated in and used to assess accuracy (as mean recovery) and precision (as RSD). The limit of detection (LOD) was determined as the lowest concentration for which a

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