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Travelling-wave ion mobility time-of-flight mass spectrometry as an alternative strategy for screening of multi-class pesticides in fruits and vegetables

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ABSTRACT

This paper reports a novel approach to screening multi-class pesticides by ion mobility time-of-flight mass spectrometry detection. Nitrogen was selected as mobility gas. After optimization of the different ion mobility parameters, determination of matrix effect on the drift times was conducted using different matrix extracts. The results showed that drift time values are not influenced by the matrix and also are independent of the concentration within the working range for 100 pesticides tested, making drift time a powerful additional identification tool. Based on statistics, 2% variation criteria provides a good fit for all the pesticides targeted, and could be considered as a maximum acceptable criteria associated with the drift time parameter for identification purpose. This 2% value is in agreement with already reported criteria, for instance, for GC or LC retention time in European documents. Finally, the well-known feature of mobility to separate complex mixtures was also tested to obtain purified extracted mass spectra of pesticides present in fruit extract.

1. Introduction

The use of pesticides on crops, to protect and increase agricultural production, can cause possible risks to human health. To protect consumers, authorities worldwide have set maximum residue limits and require monitoring of these compounds to guarantee the safety of foods. With over a thousand of compounds to monitor [1] in different matrices, multi residue methods using gas and liquid chromatography hyphenated with tandem mass spectrometry (GC–MS/MS and LC–MS/MS) have become the standard methodology for laboratories involved in food control [2]. In recent years, the new generation of pesticides are more polar compounds hence the number of LC amenable compounds has drastically increased. This trend is also reflected on the scope of published data for LC–MS/MS methods, from 19 pesticides in 2004 [3] to 240 analytes in 2012 [4]. Targeting this large number of compounds, with two transition acquisitions per analyte for confirmation requirement, has a direct impact on the quality of the data. In these conditions, to manage an overall cycle acquisition time offering sufficient data points per chromatographic peak, the analyst can either stretch the elution gradient or have multiple injections per sample [5]. The last option is generally preferred because most laboratories are using UHPLC (ultra high-performance liquid chromatography) offering very short chromatographic run with increased peak capacity compared to HPLC (high-performance chromatography) [6]. Furthermore, this second option only requires to efficiently distributing, between the different injection runs, the acquisition transitions with regards to an overall cycle time generating sufficient data points for quantification and identification purposes. However, the problem is only temporarily solved once new compounds have to be monitored. One way to overcome this problem, is to alleviate the quantification method by performing first a screening, then confirming and quantifying any detected pesticide by the quantitative method. Screening methods of targeted pesticides can be done in MS/MS mode [5–7] but with the introduction of benchtop high resolution mass spectrometers (HRMS), such as Time-of-Flight (ToF) and Orbitrap®, laboratories can measure accurate masses with instruments that are easier to operate. Although, the latest HRMS instruments offer improved resolution power and sensitivity, there are still some issues concerning the impact of matrix co-extracted compounds on the measurement for both

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systems [8]. Concerning ToF analysers, it is well characterized that low ion counts for the target compound [9] and or contribution from isobaric matrix peak can result, after centroid processing, to mass shifts hindering correct identification [10–12]. While for Orbitrap analysers, ion count does not influence mass accuracy, it can have an impact on the detection of the target compound due to the automatic gain control feature that is designed to avoid negative overloading effect of the trap device (C-trap). If the C-trap is receiving a large amount of ions, such as chemical background interference or matrix compounds, the gain control will lower the accumulation time. This will consequently lower the amount of ions, targeted and non-targeted, in the C-trap and impede the detection of compounds at low concentration [8–12]. Recently, the performance of both type of systems has been tested for screening of multi-residue pesticides in different matrices [13–16]. Results or these tests demonstrate that there are still some issues concerning false-negative findings caused by several reasons depending partially on the mass analyser technology. This research revealed the high efficiency of these instruments in terms of sensitivity, speed, resolution and that false-negatives reporting are not common occurring events. Nonetheless, missing the signal of an analyte is a serious limitation for screening methods, which are based here on detection of target compounds. This shortcoming could have severe consequences on human health. Identification and confirmation of a chemical residue in a complex sample is one of the most challenging task for chemists, thus any improvement that can help the analyst to gain more insight and confidence in the results in a time efficient manner should be explored. Ion Mobility Mass Spectrometry (IMMS) can separate molecules in complex mixtures. The coupling of IM with liquid chromatography (LC) and ToF MS gives a degree of orthogonality to both techniques by separating co-eluting LC compounds in mobility space before mass analysis. Hence, the overall peak capacity of the method is increased [17–19].

In this study, a new approach is proposed to multi-residue screening of pesticides by using chromatographic separation (UPLC™) in conjunction with ion mobility–mass spectrometry for pesticide identification and confirmation. At first, the optimal mobility separation conditions enabling simultaneous monitoring of pesticides covering a wide range of m/z with the mass spectrometer acquiring in full scan mode, was investigated by means of experimental design. Second, the system was tested with a hundred of pesticides in different complex matrix extracts. And last, the drift time was examined as a potential identification-point (IP) in addition to chromatographic and mass spectra data, in order to provide a higher degree of confidence in the identification process and to decrease the likelihood of false negative–positive results.

2. Material and methods

2.1. Reagents and standards

Analytical standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany) and were of purity exceeding 95%. Leucine-enkephalin used as lock-mass internal standard was from Sigma-Aldrich (Diegem, Belgium) TraceSELECT grade ammonium acetate and phosphoric acid were obtained from Sigma-Aldrich. UPLC/MS grade solvents (water, acetonitrile and methanol) were from Biosolve (The Netherlands).

Individual stock standard solutions of 1 mg/mL were prepared in acetonitrile with 0.1% of acetic acid, or methanol/water depending on the pesticide's solubility. Mix standard solutions were prepared by appropriate dilution in methanol of the stock standard solutions. All the solutions were stored in the dark at −20 °C.

The mobile phases A and B for liquid chromatography were 5 mM ammonium acetate in water/methanol (90/10; v/v) and in methanol/water (90/10; v/v), respectively. A solution of 20 mM ammonium acetate in methanol/water (90/10; v/v) was prepared and used as extraction mixture.

2.2. Sample treatment

Leek, pepper, oranges, raisins, onions and apples were purchased from organic supermarkets for the preparation of corresponding blank extracts. A methanolic extraction procedure was applied to the fruit and vegetable samples before spiking with mix standard solution [20]. Briefly, 10 g of homogenized sample was extracted with 40 mL of the extraction mixture with the help of an Ultra-Turrax® system for one minute. The crude extract was filtered and the final volume adjusted to 60 mL with the same extraction mixture. An aliquot of 3 mL was transferred to a 5 mL volumetric flask, and then spiked with 500 μL of a standard mix of 100 pesticides at 100 ng/mL. Finally the volume was adjusted to 5 mL with mobile phase A and the concentration of each pesticide in the final extract was 10 ng/mL. The crude extract was also diluted without any fortification to be used as blank matrix extract. A standard solution containing the 100 pesticides at 10 ng/mL was finally prepared.

2.3. Liquid chromatography settings

Chromatographic separation of pesticides was performed using ultra-high-pressure liquid chromatography on a Waters Acquity UPLC system (Waters, Milford, USA) and using ACQUITY™ BEH C18 column (1.7 μm; 2.1 mm × 100 mm) at 45 °C. A binary gradient was delivered at 0.45 mL/min, starting at 0.1% of mobile phase B, increasing linearly for 10 min up to 99.9%, followed by an isocratic hold for 2 min before going back to the initial percentage in 0.1 min and kept for 2.9 more minutes.

2.4. ESI–IMS–MS

The mass spectrometry detection was carried out on a Synapt G2 HDMS (Waters, Manchester, UK) using an ESI source operating in positive mode with the optimum following settings: source temperature, 120 °C; desolvation temperature, 450 °C; desolvation gas flow, 800 L/h; cone gas flow, 20 L/h; capillary voltage, 0.6 kV; cone voltage, 30 V; extraction cone voltage, 5 V.

Although, the Synapt G2 has been described in detail elsewhere [21–23] in short, this instrument is a hybrid system in the form: quadrupole-ion mobility spectrometry-orthogonal acceleration time-of-flight. The ion mobility section comprises three main travelling-wave ion guides. After ionization in the source and transport through the quadrupole, the ions arrive at the first travelling-wave ion guide that acts as an ion trap, the so-called "trap TWIG". In this region, the ions are accumulated before being released in packets and accelerated (trap-bias voltage) to the second region "IMS-TWIG" for mobility separation. In the IMS-TWIG a travelling wave is applied continuously through the cell at a given height and velocity to enhance separation through the relatively short mobility cell, filled with the chosen gas.

The mass range covered for the experiments were 50–1000 Da consequently mass spectra was acquired at 0.054 ms/scan and mobility spectra at 10.8 ms/scan with only one scan function used with trap at 4 V.

For mobility experiments, the following settings were applied after careful optimization: trap bias at 37 V, wave velocity of 750 m/s, wave height 25 V, helium gas flow at 115 mL/min and nitrogen carrier gas flow at 55 mL/min. The instrument was externally mass calibrated before each assay using phosphoric acid for m/z ranging from 50 to 800.