



Original Research Article

Paper spray ionization mass spectrometry: Study of a method for fast-screening analysis of pesticides in fruits and vegetables

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ABSTRACT

New faster and simpler methods for determination of pesticides in agricultural products are necessary as requirements for food safety are becoming increasingly stringent. One possibility is to introduce a fast, easy and low-cost screening method before liquid chromatography mass spectrometry analyses. We hereby present a systematic proof of concept study of paper spray mass spectrometry method for pesticide detection as a screening method. Two sampling approaches – wiping the surface with paper and applying the sample homogenate directly on the paper – were used. The wiping method was more extensively studied for imazalil and thiabendazole originally present in oranges. For homogenized samples three matrices – oranges, tomatoes and grapes – and five pesticides of different chemical nature and polarity – thiabendazole, aldicarb, imazalil, methomyl and methiocarb – were chosen. It has been shown that limits of detection below maximum residue levels can be achieved for both methods (e.g. imazalil and thiabendazole detection limits were found to be lower than 5 mg/kg). The methods are therefore suitable for fast screening of samples. Moreover, the wiping method was also applied for 11 samples – oranges, grapefruits, lemons, limes, mandarins, tomatoes, apples, pears, strawberries, grapes and sweet peppers – from the local supermarket to screen for different pesticides. Three positive samples for thiabendazole and imazalil and one positive sample for imazalil were found.

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1. Introduction

Pesticides are a diverse group of chemical compounds used to protect agricultural products from pests. Both pre- and postharvest applications of pesticides are used (Fenik et al., 2011; LeDoux, 2011). The overuse of pesticides may result in environmental contamination as they could be toxic, environmentally stable and mobile substances. Moreover, humans can come into contact with pesticides through the food chain, therefore being exposed to the risk of intoxication. Grapes, citrus fruits and potatoes are particularly likely to be contaminated by pesticides (Fenik et al., 2011).

To regulate the use of pesticides, maximum residue levels (MRL) – the upper legal limits of pesticide residues in foods – have been set (LeDoux, 2011). Due to the increasingly higher demands on food safety, more sensitive, reliable and faster analysis methods are constantly needed (Zhang et al., 2012).

The analysis of pesticide residues in foods can be divided into two main parts: sample pretreatment and instrumental determination. Sample pretreatment is used to eliminate possible interferences from the matrix by extracting the analyte (Zhang et al., 2012). Sample pretreatment steps mostly include homogenization, extraction (and possibly enrichment), and clean-up (Iffa et al., 2010; Zhang et al., 2012). These steps are time-consuming and require well-trained laboratory workers. Therefore, the current trend is toward reducing the need for sample pretreatment, which could save significant amounts of money and time. As analytes differ in their physicochemical properties, different instrumentation is used for quantification. Gas chromatography and high-performance liquid chromatography (LC) with different detectors are used for determination of pesticides. The role of mass spectrometry (MS) and especially tandem MS as a detector for LC has been expanding rapidly during recent years in both routine screening and in research (Fenik et al., 2011; LeDoux, 2011).

The main problem of the LC/MS technique is the complexity caused by the need to transfer different analytes from the wide range of matrices into a vacuum as ions. Therefore extensive sample pretreatment steps are necessary. The need for sample

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pretreatment is decreased with the new family of ionization techniques called ambient ionization (Alberici et al., 2010). Since 2004, over 30 new ionization methods have been reported, indicating high interest and fast development (Ifa et al., 2010).

One of these new ionization methods is paper spray ionization (PSI) (Liu et al., 2010), where the sample is first transferred onto a paper triangle with a sharp tip in front of an MS entrance. Voltage of approximately 3000–4500 V is then applied between the paper and the MS entrance, and finally the whole triangle is wetted with an eluent. As soon as this is done, the liquid starts spraying and the sample components are ionized and directed toward the MS. Paper has several advantageous characteristics for this type of ionization: well-known properties in chemical analysis, possibility of chemical modification, availability, low cost and ease of fabrication. Moreover, paper can be used as a substrate on which the sample is collected and then transported to a laboratory. Therefore, with PSI it is possible to connect the sample pretreatment and ionization into one step (Liu et al., 2010).

The mechanisms of the different processes occurring in PSI have been studied. It has been shown that a saturation limit for the amount of sample exists starting from which adding more sample does not increase the signal intensity (Yang et al., 2012b). This amount depends on the size of the paper used for PSI. The mechanism by which the liquid moves on the paper has also been studied. It was found that capillary forces and the movement of excess liquid on the paper toward the spray are responsible for the majority of the liquid's movement. Movement due to the electrophoretic forces was not found to be significant (Yang et al., 2012b). It has been found that two different ionization mechanisms work in PSI. During the first period of spraying when there is still enough eluent on the paper to form a Taylor cone, the ionization mechanism is similar to nanospray. However, after most of the eluent has been used up and visually no more spray is seen, higher electrical current is measured and spectra similar to atmospheric pressure chemical ionization (APCI) can be seen. It is therefore theorized that an electrical discharge and desorption of analyte molecules occur (Espy et al., 2012b).

It has been shown that a great variety of analytes including amino acids, peptides, proteins, herbicides, therapeutic drugs and fatty acids can be ionized with PSI. Also PSI has been applied for analyses of different matrices, such as urine and, especially, blood (Liu et al., 2010). Out of the different possible applications of PSI, the possibility of measuring therapeutic drugs from dried blood spots has gained the most attention (Espy et al., 2012a; Manicke et al., 2011a,b; Yang et al., 2012a). Moreover, when a whole piece of tissue is placed on the paper, hormones, lipids and therapeutic drugs can be identified (Wang et al., 2011). PSI can also be used in food analysis. When a cola drink was used as eluent, caffeine could be identified from the spectrum. Also, thiabendazole and imazalil could be identified from the peel of an orange with wiping method where the orange is wiped with the paper that is later used for PSI (Liu et al., 2010).

Although the possibility of screening pesticides in fruit and vegetables using PSI/MS has been envisaged and shown, systematic evaluation of this approach in terms of different pesticides and different matrices has not been carried out. Qualitative determination of only two pesticides – post-harvest pesticides imazalil and thiabendazole from oranges – has thus far been demonstrated by wiping the surface of the sample (Liu et al., 2010). The possibility of screening pre-harvest pesticides from homogenized fruit or vegetable has not been studied. The limit of detection (LoD) of pesticide determination has not been evaluated and compared to the MRL of the pesticides. The aim of this study was to demonstrate, as a proof of concept, the applicability of PSI as an efficient screening method for both post- and pre-harvest pesticide analysis prior to LC/MS.

2. Materials and methods

2.1. Equipment and parameters used

Varian 320 triple quadrupole MS model number: MS0906A002 (Varian Inc., Palo Alto, CA, USA) with nanospray housing in the positive ion mode was used for measurements. A specifically designed template was used for fabricating isosceles paper triangles with height of 10 mm and base of 5 mm. The paper triangle was placed into a holder, made from stainless steel, which was specifically fabricated to fit into the nanospray housing (see Figs. 1 and 2). The holder with the paper was placed in front of the MS inlet so that the distance between the inlet and the paper tip was approximately 5 mm. The distance from the tip of the paper triangle to the MS inlet could be reproducibly measured using a camera fitted to the nanospray housing. The nanospray housing allows for precise positioning of the paper tip in all three axes.

Capillary voltage and collision energy were optimized for every analyte with the native nanospray ion source of the same MS instrument. The emitter voltage was set to 3200 V and shield voltage to 300 V when PSI experiments were conducted. The shield is a part of the ion optics in front of the MS inlet that helps transmittance of ions into the capillary. Drying gas pressure was set to 8 psi and temperature to 150 °C. Gas pressure of 1.5 mTorr was used for fragmentation. The electron multiplier detector voltage was set to 1300 V.

2.2. The experimental protocol of recording the MS data

After fixing the triangle in the housing the sample was applied on the paper triangle. Then the voltage was applied between the triangle and the MS inlet. After applying the voltage between the paper holder and the MS-inlet, the recording of the spectrum was started and thereafter 20 µL of eluent was added using a 20 µL automatic pipette (Eppendorf AG, Hamburg, Germany). This sequence of operations enables recording of the whole spectrum and avoids partial vaporization of the eluent before the spray is initiated. Peak heights were used to calculate the signal-to-noise ratio (S/N). It must be noted that safety precautions must be taken when working with high voltage and conductive liquids. The paper holder and other inner parts of the ion source can be touched only when it has been ensured that the high voltage has been switched off.

For both sampling methods the multiple reaction monitoring and scan mode were used to record MS responses. The monitored transitions can be found in the Supplementary data. The spectra in

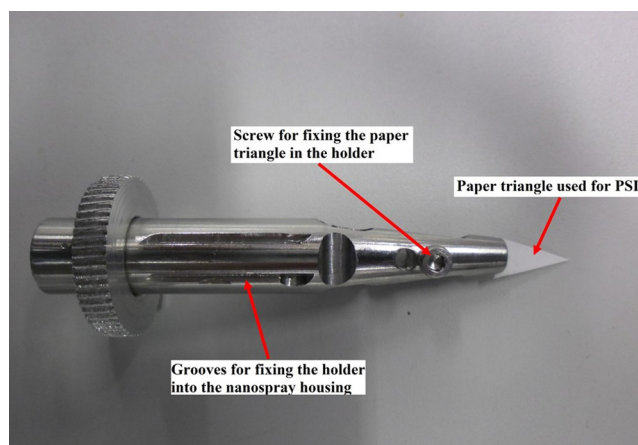


Fig. 1. Picture of the paper triangle holder with paper.

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