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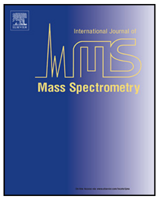

Method development for directly screening pesticide residues in foodstuffs using ambient microfabricated glow discharge plasma (MFGDP) desorption/ionization mass spectrometry

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ABSTRACT

An innovative method for directly screening pesticide residues in foodstuffs was developed using ambient microfabricated glow discharge plasma (MFGDP) desorption/ionization mass spectrometry. The capability of qualitative and quantitative analysis with MFGDP–MS at atmospheric pressure on agrochemicals has been demonstrated. Nine multi-class compounds (ametryn, amitraz, buprofezin, dimethoate, diphenylamine, imazalil, isoproturon, malathion, parathion-ethyl) were examined in spiked solutions, in extracts of fruits and vegetables, and in unprocessed samples. In the standard solutions of the nine pesticides, the application of MFGDP-MS for the detection of organophosphorus, organochlorine and organonitrogen compounds was demonstrated. Limits of detection (LODs) at levels down to 0.13 ng g^{-1} mm^{-2} of the spiked extracts of tomato, green pepper, and orange (collected by “QuEChERS”) were obtained, with RSDs of 3.48–13.46%. In the direct analysis of unspiked peels and extracts of apple, celery and grapes, the residues of diphenylamine, dimethoate and malathion were successfully analyzed by tandem mass spectrometry (MS/MS). The distribution of diphenylamine in apples was obtained by scanning the various unprocessed parts of the apple piece-by-piece in depth directly. Thus, an MFGDP–MS, having a small size and operating at a low temperature, made it possible to directly and accurately screen for pesticide residues in fruits and vegetables *in situ*.

1. Introduction

During the long history of farming, over 800 different compounds have been applied to crops as insecticides, fungicides and herbicides world-wide [1]. As with the use of fertilizer, pesticides are used to ameliorate harvests. However, the excessive use of pesticides has been shown to be hazardous to human health but also detrimental to the environment generally even at relatively low levels. It's imperative to employ pesticides responsibly in modern agriculture and related industries. Therefore, maximum residue levels (MRLs) have been established by various governments such as China, the United States, and the European Union, constraining the safe amount of various pesticide residues on or in foodstuffs. There has been an ever-increasing societal attention and scientific interests in the efficient detecting and quantifying of trace levels of pesticides in foodstuffs.

Pesticides can be categorized in different classes depending on their primary compositions, such as organophosphorus, organochlorine, organonitrogen and so on. Since the residues of these classes are at various levels, the accurate analysis of pesticides is a great present challenge for analytical chemists. Among the methods developed in the past decades, gas chromatography coupled to mass spectrometry and gas chromatography tandem mass spectrometry (GC–MS and GC–MS/MS) [2,3] as well as liquid chromatography mass spectrometry and liquid chromatography tandem mass spectrometry (LC–MS and LC–MS/MS) [4,5] are the most widely used due to their outstanding qualitative and quantitative capabilities. The advantages of chromatography technology and mass spectrometry technology are such that some countries such as China and the United States use GC–MS (or GC–MS/MS) and LC–MS (or LC–MS/MS) as the standard means of agrochemical residue detection [6,7]. To reduce the matrix effect, LC and GC extraction technologies, such as liquid-liquid microextraction chromatography [8], liquid-liquid extraction (LLE) [9], supercritical fluid extraction [10,11], microwave-assisted extraction (MAE) [12], ultrasound-assisted extraction [13,14], solid-phase microextraction (SPME) [15], matrix solid-phase dispersion

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(MSPD) [16], dispersive solid-phase extraction (DSPE) [17], and colorimetry [18], *etc.*, have been introduced. However, these GC–MS and LC–MS based methods (or GC–MS/MS and LC–MS/MS) are usually time consuming because of complicated pretreatment and separation processes, especially when a large batch of samples must be analyzed. In light of this, reliable and fast *in situ* screening methods useable without prior sample preparation are urgently needed in order to deal with foodstuffs in a timely manner. Ambient mass spectrometry is a candidate for solving this problem.

Ambient mass spectrometry is a booming field of MS techniques with the introduction of various ambient desorption/ionization sources over the past two decades. It is defined as mass spectrometric analysis with minimal or no sample pretreatment, so as to allow for the direct injection and ionization of samples in an ambient environment [19]. These instruments are smaller because the vacuum systems ordinarily necessary for ion sources are eliminated. Sampling directly can also provide quicker results. Simultaneously, these processes retain the sensitivity and accuracy of mass spectrometry using all kinds of mass analyzers. Therefore, ambient mass spectrometry with manifold desorption/ionization technologies have been applied to bioanalysis, detection of pharmaceuticals and drugs, foodstuffs, explosives and so forth ever since desorption electrospray ionization (DESI) [20] technology was described in 2004. In some reviews [21,22], ambient desorption/ionization technologies have been typically classified by desorption mechanisms, for instance: spray droplet assisted desorption, laser desorption/ablation techniques and plasma-based techniques. Plasma-based ambient sources are the subjects of much current intensive investigations. There have been direct analysis in real time (DART) [23], dielectric barrier discharge ionization (DBDI) [24], atmospheric pressure glow discharge desorption ionization (APGDI) [25], microhollow cathode discharge microplasma [26], microwave induced plasma desorption/ionization (MIPI) [27] and so on. In contrast to spray techniques, plasma-based sources employ various modes of electro-discharge instead of charged droplets to generate a plasma gas that contains radicals, excited/metastable state atoms, and electrons [28]. Since the discharge performs differently, the sample introduction system, the plasma temperature and the power consumption are diverse. Therefore, there are various methods using plasma-based ambient MS techniques in public safety and forensic trace analysis of different chemicals in a complex matrix. Methods such as direct analysis in real time (DART) [29], low-temperature plasma (LTP) [30,31], and atmospheric-pressure solids analysis probe (ASAP) [32] have been used to detect agrochemicals and/or their degradations products in fruit and vegetable samples using a quadrupole, a time of flight (TOF) or an ion trap mass spectrometer, all with limited success hitherto.

Herein, we present a new tool for the fast and sensitive analysis of pesticides using a microfabricated glow discharge plasma for ambient desorption/ionization mass spectrometry (MFGDP–MS). MFGDP generates a stable plasma at room temperature using direct current with either argon or helium, and possesses good performance while ignoring the shapes and the condition of the sample surfaces [33]. Due to the low temperature of the plasma flame, there is no heating damage to the sample surface during analysis. This small volume, low power microplasma tool can provide effective detection of pesticides with a high sensitivity and an excellent repeatability. In this article, we develop an innovative method based on MFGDP–MS to directly analyze diverse classes of pesticides and/or their degradation products in different fruits and vegetables. The reliability of this new MFGDP–MS method in detecting organophosphorus, organochlorine, organonitrogen compounds was evaluated. Qualitative and quantitative analyses were carried out on standard solutions of 9 pesticides, and extractions of three kinds of fruits and vegetables spiked with these 9 compounds. The LODs were 0.13–3.09 ng g^{-1} mm^{-2} in different fruit and vegetable extractions with RSDs of 3.48–13.46%. In addition, the MFGDP–MS method was also used to analyze real fruits and vegetables without any sample pretreatment by scanning on the sample surfaces directly. Particularly, a mapping work of the diphenylamine distribution in apples was done piece-by-piece in depth with this newly developed MFGDP–MS method. This mapping demonstrated the capability of the method for directly screening pesticides in real fruit and vegetable samples with a high throughput.

2. Materials and methods

2.1. Chemicals and reagents

HPLC grade methanol and acetonitrile were purchased from Kermel (Tianjin, China) and Guanghua Sci-Tech (Guangzhou, China) respectively and used directly without any further purification. Pesticide analytical standards were purchased from the Agro-Environmental Protection Institute, Ministry of Agriculture (AEPI, Tianjin, China) and Shanghai Pesticide Research Institute (SPRI, Shanghai, China). Individual pesticide stock solutions (10.0–50.0 mg mL^{-1}) and diluted working solutions (1.0–10.0 mg mL^{-1}) were all prepared in methanol or acetonitrile and stored at −20 °C. Primary–secondary amine (PSA) bond elut was obtained from Varian, Inc. (Palo Alto, CA, USA). Inorganic salts like sodium chloride and anhydrous magnesium sulfate were purchased from Kermel (Tianjin, China) and Guanghua Sci-Tech (Guangzhou, China). The discharge gases, helium (99.999%) and argon (99.9%), were provided by Qiaoyuan Gas Company (Chengdu, China). Ultrapurified water (18 MΩ cm^{-3}) was produced using an Ultra-pure water purification system.

2.2. Procedure of sample extractions of agrichemicals from fruits and vegetables

Fruit and vegetable samples (apples, oranges, tomatoes, green peppers, grapes and celery) were purchased from a local market. Peels and extractions of fruit and vegetable were directly analyzed using MFGDP–MS. The extractions were collected by the standard treatment process of "QuEChERS" (Quick, Easy, Cheap, Effective, Rugged and Safe) [34]. "QuEChERS" is a rapid foodstuff pretreatment technique developed in 2003. This process has become popular since then because of its simple procedures and low hazards. The main steps of the procedure were: the vegetable or fruit, without cleaning or any other treatment, was homogenized in a high speed blender. A 15.00 g sample was added to a 200 mL PTFE centrifuge tube. After the addition of 15.0 mL of acetonitrile, the tube was vigorously shaken by hand for 1.0 min. The centrifuge tube was again vigorously shaken for 1.0 min after the addition of 6.00 g $MgSO_4$ and 1.50 g NaCl. The extraction was stratified preliminarily and centrifuged at 4000 rpm for 1.0 min in order to effect clean separation of the organic phase. A pipette was used to transfer 5.0 mL of the supernatant (the acetonitrile phase) into a 15 mL PTFE centrifuge tube containing 750.0 mg of $MgSO_4$ and 250.0 mg of PSA. After being vigorously shaken for 20 s the tube was centrifuged (4000 rpm) for 1.0 min. The equivalent 1.0 g sample per milliliter extraction in 100% acetonitrile was obtained.

2.3. Microfabricated glow discharge plasma mass spectrometry

A commercial ion trap mass spectrometer (LCQ Fleet, Thermal Fisher, San Jose, CA) was used in this study. Data were acquired using the instrument software (Xcalibur version 1.4SR1). The analysis was done in the positive-ion mode and all spectra were

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