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Pulsed micro-discharge ambient ionization mass spectrometry

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ABSTRACT

A method named pulsed micro-discharge ambient ionization mass spectrometry (PMD-AIMS) was developed for direct surface analysis with simple apparatus. In PMD-AIMS, micro-discharges is generated between a copper plate and a tungsten needle with pulsed high voltage applied, in which the analyte on the surface of copper plate is desorbed and ionized, then drawn to the inlet of the mass spectrometer. In this experiment, the tungsten needle was fabricated via an electrochemical method with sharp apex to reduce the volume of the discharge. The experimental parameters were optimized to achieve a high sensitivity and high spatial resolution for mass spectrometry imaging. LOD (S/N = 3) was determined to be 20 ng/ml for atrazine on the yam and 1 ng/ml for atrazine on the copper plate with a lateral resolution of 60 μm. The PMD-AIMS technique was further applied for the rapid detection of the residual herbicide on epidermis. The distribution of the herbicide in plant tissue was investigated with mass spectrometry imaging. The results indicate that PMD-AIMS is a sensitive analytical technique with the capability of mass spectrometry imaging.

1. Introduction

Mass spectrometry imaging (MSI) is a combination technique of mass spectrometry and visualization of molecular imaging with no specific markers, which can realize the detection of different molecules on biology tissues with a high sensitivity, and provide the spatial distribution of the target compounds [1–3]. Compared with the two traditional MSI of matrix-assisted laser desorption ionization (MALDI) [4,5] and secondary ion mass spectrometry (SIMS) [6,7], ambient ionization mass spectrometry imaging (AIMSI) has the significant advantage that it is operated in ambient air and requires minimal sample preparation [8], which means AIMSI can be applied to live samples.

In 2004, Cooks group developed the desorption electrospray ionization (DESI) [9] on the basis of electrospray ionization (ESI) [10] technology and succeeded in MSI [11,12], which is suitable for the imaging analysis of small molecules with a typical spatial resolution of 200 μm [13]. It raised a growing interest in research of ambient ionization technology worldwide. The ambient ionization (AI) technology are mainly based on the ESI or atmospheric pressure chemical ionization (APCI) [14]. There is a type of ambient ionization technique based on APCI named dielectric barrier discharge ionization (DBDI) [15], and later developed into low-temperature plasma probe (LTP) [16]. This LTP was used to identify Chinese art, and detect different chemical compositions of different seals by MSI with a spatial resolution of 250 μm [17]. Also some groups developed new AIMS techniques through combining two or more techniques. For example, Liu group developed online coupling of in-tube solid phase microextraction (IT-SPME) with direct analysis in real time mass spectrometry (DART-MS) [18]. Nie group promoted a liquid sampling atmospheric pressure afterglow microplasma ionization source [19]. DESI and DART coupled to time-of-flight mass spectrometry was developed by Fernandez group [20].

So far, AIMS has been used in many fields [21–26]. In agriculture, herbicides made a lot of contributions to the increasing of crop yield, but most herbicides are harmful to human health. According to reports, the number of people in developing countries died from herbicides poisoning is more than those died from infectious diseases [27,28]. Atrazine, as one of the triazine herbicide, has been popular in agriculture supermarket since its invention, and it still is one of the most widely used herbicides after five decades of developments [29]. Atrazine also remains easily in the soil and groundwater. It was demonstrated by scientists that atrazine scrambled sex in frogs, and it was linked tightly to prostate cancer. Atrazine was also down for the endocrine disruptor in both USA and European Union. The traditional detection for herbicides residues is using high performance liquid chromatography (HPLC), which

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requires complex pretreatment and cannot get the information of herbicides distribution on plant tissues.

Herein, we promote an ambient ionization technique named pulsed micro-discharge ambient ionization mass spectrometry (PMD-AIMS), which was developed for direct surface analysis with simple apparatus. The ion source works in ambient condition, requiring no solvent or auxiliary gas. In PMD-AIMS, micro-discharge was generated between a copper plate and a tungsten needle with pulsed high voltage applied, in which the analytes on the surface of copper plate were ionized and sampled by the mass spectrometer. Compared to the ion sources based on ESI, PMD-AIMS shows more efficiency for some non-polar compounds. Since DBDI has succeeded in direct detection of explosives on solid surfaces [30], it indicates that it is possible for PMD-AIMS to work in both positive mode and negative mode. Similar with DBDI, PMD-AIMS have simple apparatus than DART. Moreover, it can be used to analysis not only solid organic compounds but also solid metal [31]. Different from nanotip ambient ionization mass spectrometry (NAIMS) [32], we simplified the experiment device configuration that the sample plate is perpendicular to the mass spectrum inlet, so that ionized analytes on the copper plate are directly led to the mass spectrum inlet without any deflection, improving ion transmission efficiency and thus the sensitivity [33]. Limit of detection (S/N = 3) of PMD-AIMS was determined to be 20 ng/ml for atrazine on the yam and 1 ng/ml atrazine on the copper plate with a lateral resolution of 60 μm. PMD-AIMS technique was further applied to detect the residual herbicide on the epidermis and its distribution in pant tissue by MSI.

2. Experimental section

2.1. Chemicals, materials, and instrumentation

The herbicide sample of Jiujiuhong (90% atrazine WP) was purchased from Shangdong Kesai Agrochem Holdings Ltd., China. The herbicide sample of Simazine (50% Simazine WP) was purchased from Zhejiang Zhongshan Chemical Factory Ltd., China. The Propazine sample was purchased from J&K,China. Pulsed high voltage power supply with output voltage of 0–3 kV, frequency of 1 Hz to 1 kHz, and pulse width of 1–10 μs was purchased from Senyuan Ltd., China. The tungsten needle was fabricated via an electrochemical method using tungsten wire (99.9999%, purchased from Xiamen Tungsten Ltd., China) with a diameter of 100 μm. Mass spectra were obtained using a micrOTOF-Q mass spectrometer from Bruker Daltonics. All fresh vegetables, such as potato, tomato, yam, sweet potato, and carrot, were bought from the local supermarket.

2.2. Sample preparation

The atrazine sample was dissolved in pure water. A series of atrazine solutions with different concentrations of 0.01, 0.05, 0.1, 0.5, 1, 5, and 10 μg/ml were prepared, and 20 μl of each solution was deposited on the copper plate and dried. Another series of atrazine solutions at concentrations of 0.01, 0.1, 1, 10, 100, and 1000 ug/ml with volume of 20 μl deposited on epidermis of yam separately and dried. In further experiment, 20 μl atrazine solution (1000 ug/ml) was deposited on the surface of potato, yam, sweet potato, and carrot separately and dried, then plants were rinsed with water for 0, 0.5, 1, 3, 5 min, Then, their epidermis of about 1 mm thickness were cut off and fixed on quickly the copper plate using the conducting. In MSI experiment, 20 μl atrazine solution (1000 ug/ml) was deposited on the pericarp of potato, yam, sweet potato, and carrot separately, then after 2, 5, 20, 50 h a 1 mm thick-layer was cut out from the tuber and the cross section was subject for imaging. Simazine and propazine were dissolved in pure water separately, resulting in a concentration of 10 ug/ml, and 20 μl of each of them were deposited on the copper plate and dried respectively.

2.3. Pulsed micro-discharge ambient ionization source

The schematic diagram of PMD-AIMS is shown Fig. 1 A high pulsed voltage was applied to a copper plate and the tungsten needle was set to ground, which generated plasma for desorption and ionization. The distance between the plate and needle was 500 μm. Then the ions were drawn into the mass spectrometer for analysis from the glass capillary orifice (0.5 mm i.d., 6.5 mm o.d. ground potential) with the force of electric field and aerodynamics. The plasma was in line with the glass capillary orifice, because the copper plate was perpendicular to the glass capillary. The tungsten needle was fabricated via an electrochemical method [34] using tungsten wire with a diameter of 50 μm, and the tungsten needle tip formed an angle of 45° towards the copper plate surface. The copper plate serving as the anode was fixed on a 3D translation stage, and the tungsten needle was grounded as the capillary cap. The high pulsed voltage was provided by a pulse generator connected to a high pulsed power supply, and it supplied output voltage of 0–3 kV, frequency of 1 Hz - 1 kHz, and pulse width of 1–10 μs. A current diagram of the micro-discharge with a pulse

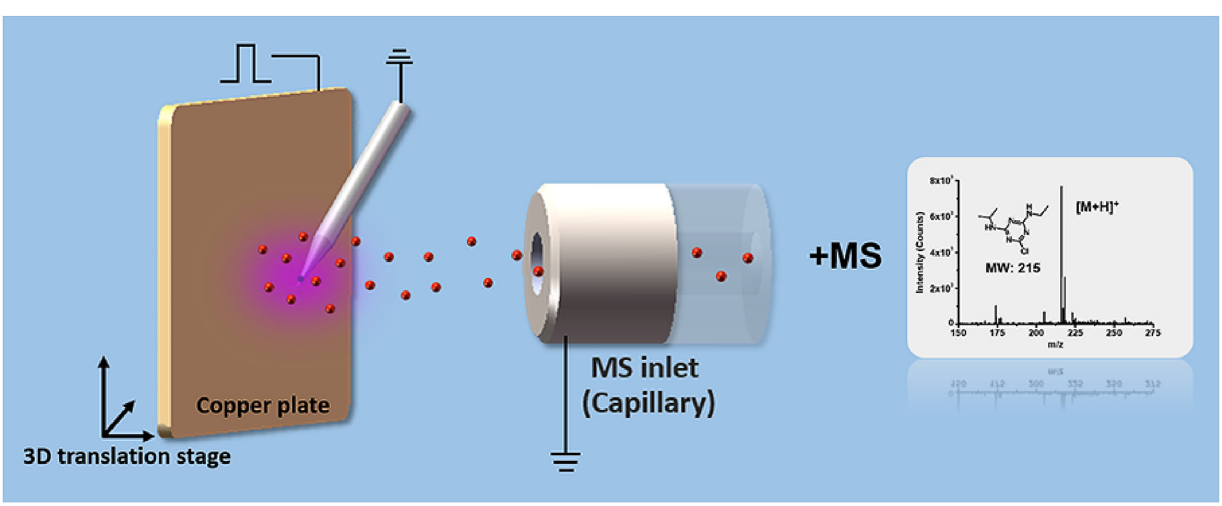

Fig. 1. Schematic diagram of PMD-AIMS.