CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 44, Issue 1, January 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin J Anal Chem, 2016, 44(1), 8–12.

RESEARCH PAPER

Preliminary study of Microfabricated Glow Discharge Plasma for Mass Spectrometry Imaging

TIAN Cai-Yan[1,2], DING Xue-Lu[1,2], YIN Jin-Wei[1,2], DUAN Yi-Xiang[1,2,3,*]

[1] College of Life Science, Sichuan University, Chengdu 610064, China
[2] Research Center of Analytical Instrumentation, Sichuan University, Chengdu 610064, China
[3] Key Laboratory of Bio-resource and Eco-environment Ministry of Education, Sichuan University, Chengdu 610064, China

Abstract: To evaluate the ability of microfabricated glow discharge plasma (MFGDP) as ion source used for mass spectrometry imaging, the different handwritings with urea added were analyzed, and the spatial distribution of stearic acid and the ramification of quercetin in a slice of winter jujube were explored. The MFGDP, independently researched and developed by our lab, acted as ion source to absorb and ionize the sample. The excited sample ions entered into mass spectrometer and then obtained the mass spectra, which were converted by special software into corresponding image. The results showed that the MFGDP source was feasible and valuable for mass spectrometry imaging. The simple device, easy operation, low temperature plasma and time saving (< 20 min) were its remarkable features and it could locate the distribution of the different substance in a sample. The factors influencing definition of image were discussed and the experimental conditions were optimized, the resolution was about 300 μm under the optimum conditions. The technique could distinguish different handwritings according to the "fingerprints" of chemical substances, and obtain commendably the distribution of different nutrients in the real sample, therefore, it provided a new method for the study of the calligraphy and painting, identification for artwork and acquisition for nutrients distribution.

Key Words: Micro-fabricated glow discharge plasma (MFGDP); Mass spectrometry; Scan; Imaging

1 Introduction

Mass spectrometry imaging (MSI) is a new method which is different from laser resonance focus, autoradiography (ARG) and immune precipitation. MSI can obtain unique and accurate image without additional tags and molecular printing. It is one of the molecular imaging techniques that achieved the image of most molecules rather than certain specific molecules. MSI became a vital method for forensic identification, food analysis, geological detection and other related fields within several decades[1–4]. In recent years, MSI was widely applied in the research of biological tissue and the clinical medicine[5–7], and good results were achieved. The spatial and chemical information of the sample were homologous in MSI, samples were scanned through X, Y two dimensions or X, Y, Z three dimensions to obtain the corresponding mass spectrometry data, which was transformed by related software into the image according to their spatial distribution where the different colors represent various components.

At present, the MSI techniques are classified into several categories according to their operation condition and the desorption mechanism: (1) the matrix assisted laser desorption ionization (MALDI)[8] and secondary ion mass spectrometry (SIMS)[9] working under vacuum condition; (2) the ionization based on spray in ambient, such as desorption electrospray ionization(DESI)[10], probe electrospray ionization (PESI)[11]; (3) the ionization techniques based on laser ablation, such as laser ablation electrospray ionization (LAESI)[12], infrared laser ablation metastable-induced chemical ionization (IR-LAMICI)[13]; (4) the ionization methods based on plasma, such as low temperature probe (LTP)[14], desorption

Received 10 October 2015; accepted 4 November 2015
*Corresponding author. Email: yduan@scu.edu.cn

DOI: 10.1016/S1872-2040(16)60894-0

atmospheric pressure chemical ionization(DAPCI)[15]etc. In the past years, the technique of MSI has become a focus with the need of medical diagnosis and geological detection, especially in the ambient condition. In general, small molecules (the molecular weight is less than 2000 Da) can be analyzed, the spatial resolution is from dozens μm to several hundred μm[16–18]. Unfortunately, the techniques based on plasma are rarely used for MSI because of their inherent limit. Microfabricated glow discharge plasma (MFGDP), independently researched and developed by our lab, has a great potential in MSI due to the small dimension and low temperature of the plasma, and with no pollution, high sensitivity, strong specificity and high flux when it acts as ion source to desorb the samples. Therefore, in our preliminary study, the MFGDP used for MSI was achieved. In the beginning, the handwritings written by ink with urea and winter jujube slice were scanned, and gained the specific outline of the handwritings and the images of stearic acid and the ramification of quercetin in a slice of winter jujube, therefore, it provided a new method which was suitable for the study of calligraphy and painting, identification for artwork and acquisition for nutrients distribution.

2 Experimental

2.1 Instruments and devices

A commercial ion trap mass spectrometer (LCQ Fleet, Thermo Fisher, San Jose, CA) with Xcalibur (version 1.4RS1) software was used as the corresponding workstation. An object stage, a two dimension electric displacement platform and a stepping motor controller were purchased from Zolix instruments CO., Ltd (Beijing China). A DC stabilized power source was purchased from Yangzhou shuanghong Co., Ltd. (Yangzhou, China). The mass flow controller (D07-19B) was purchased from Sevenstar in Beijing (China). The MFGDP acted as ion source was independently researched and developed by our lab.

2.2 Chemicals and reagents

The ink and winter jujube were purchased from a local store. Urea was purchased from Shanghai Sangon Biological Engineering Technology & Services Co., Ltd and of analytical grade. Ar (99.9%) provided by Qiao Yuan Gas Company was used as the working gas.

2.3 Materials and sample preparation

Write the "3" on a platform using a pen with ink in which contained 70 μg mL^{-1} of urea, and the scan area of the handwriting was 14 mm × 12 mm; Tissue section of 0.5 mm in thickness of winter jujube was prepared at room temperature with a scalpel, and without further treatment, it was carefully placed onto the sample stage to image.

2.4 Microfabricated glow discharge ion source and operating conditions

The detailed parameters of microglow discharge ion source were reported by Ding *et al*[19,20].

2.4.1 Operating conditions

The MFGDP generated an abnormal glow discharge with the typical plasmas, working voltage and current were around 1520 V, 11 mA, gas flow rate was 0.8 L min^{-1} controlled by a mass flow controller (D07-19B, Sevenstar, Beijing, China). The MFGDP source was mounted on a homemade stainless steel stand, about 10 mm away from the MS inlet; in between the microplasma source and MS inlet, a 3D adjustable stage served as the sample holder, keeping the samples typically 6 mm away from the plasma wake plume in the ionization area. The sample was paralleled with MS inlet (Fig.1). The speed and the sequence were controlled by a stepping motor.

2.4.2 Mass spectrometer conditions

The MFGDP combined with a commercial ion trap mass spectrometer (LCQ Fleet, Thermo Fisher, San Jose, CA) with Xcalibur (version 1.4RS1) software as the corresponding workstation, which removed the official ion source. In both positive and negative ion modes, the automatic gain control mode was off. Mass spectrometer conditions were optimized as follows: capillary temperature, 200 °C; capillary voltage, 9.5 V; tube lens, 29 V; and multipole RF DAC, 320 V. The maximum ion injection time was set to 50 ms at 3 microscans per spectrum; the rest of parameters were automatic tuning value of the mass spectrometer.

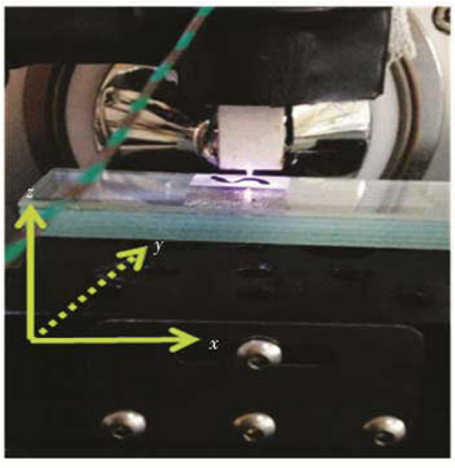

Fig.1 Work state of MFGDP mass spectrometry imaging