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RESEARCH PAPER

Flexible Device for Direct Analysis in Real Time without Grid Electrode for Mass Spectrometric Analysis

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Abstract: A flexible and simple direct analysis in real-time (DART) device was developed without grid electrode for mass spectrometer injection. It contained inert carrier gas, ionizer, heater and temperature-controller etc. By excluding the grid electrode and then reducing the structure units, the device could be easy to build up in low cost and flexible to connect with a variety of mass spectrometers. Under the optimum experimental conditions including argon carrier gas with a flow rate of 7.5 L min^{-1}, and heat tape temperature of 300 °C, the device was used to analyze benzene alcohol, linoleic acid, dichlorvos emulsion, mosquito coils, citrus peel, and sample (propranolol hydrochloride) on thin-layer plate combined with mass spectrometer. The results were accurate and showed the device was stable and reliable.

Key Words: Direct analysis in real time; Device; Mass spectrometry

1 Introduction

Direct analysis in real time (DART) was first developed by Cody group in 2005[1] as a sample injection unit of mass spectrometer. DART presented the advantages including no sample pretreatment, short analysis time, no adduct ions (M+Na, M+K) produced etc, and was applied in the analysis of harmful substances in the food[2], crops surface bacteria[3,4], fake drugs[4], packaging materials[5,6], synthetic compounds in mosquito repellent products[7], plant varieties difference[8], in which all results were obtained in real time, and no contact and no sample loss. Marinella etc[9] detected the residual harmful composition in the fruit peel directly by DART-MS, in which the limit of detection of imazalil was 1 ng. The work showed that DART-MS technique had high sample throughput, lack of cross contamination between runs, and simplicity. By using DART ionization technique, Fernandez *et al*[10] identified counterfeit artesunate tablet directly, clearly as commonly excipients of stearate and palmitate with no or little effective antimalarial artesunate composition. Without sample preparation process, ten samples could be analyzed in just two minutes. Hye *et al*[11] provided a thin layer chromatography (TLC)-DART-MS analysis method for rapid identifying chemical composition in plants. The results showed that TLC-DART-MS was a simple, rapid and efficient method for the research of chemistry component in natural product by real-time high resolution mass spectrometry data of compound components in thin layer plate. Adams *et al*[12] characterized 16 reference papers in terms of their pulp composition and pitch contaminants by DART-MS, in which the real-time mass spectrograms of bleached kraft, chemithermomechanical, and stone groundwood pulp papers were obtained without extraction, derivatization, separation, and other time- and chemical-consuming sample preparation. The result shows the DART-MS lossless test capacity. Zhang *et al*[13] identified 8 kinds of tea in situ by DART-MS without sample preparation. In addition, Borges *et al*[14] analyzed organometallic compounds and Zhao *et al*[15] analyzed small molecules in plasma using DART-MS method, showing its wide application.

However, the existing DART equipments were expensive, complex with difference interface and difficult to install for different mass spectrometer. In this study, a simple, flexible and economic DART device was developed without grid

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electrode according to the simplified DART mechanism. The device showed DART-MS ability in analytical experiments of several different samples.

2 Experimental

2.1 Instruments and reagents

The following instruments were used in this study: SolariX 70T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS, Bruker), SL-080BF ion generator (ion wind snake, sealed sensing head in a normally open state, working voltage 4.6 kV, Shenzhen Electronic Technology Co., LTD. Hao Fork), XMTD-6411 Temperature controller (PID control temperature, Shanghai Turing Instrument Ltd.), and heater band (length/width = 100 cm/3 cm fiberglass, 400 °C of heat-resistant, Jiangsu Runjiang Electric Heating Instrument Ltd).

As shown in Fig.1, a quartz glass tube (docked in the export of ion generator, total length of 230 mm and diameter of 8 mm) was used as the export of ion generator with 30 mm long, and the middle part was 150 mm long with 4 mm diameter, 2 mm diameter inserting the stilligout with 50 mm long, wall thickness was all 2 mm). A 90-mm straight glass stilligout and a stainless steel sieve (100 meshs, Shanghai Kunyuan Screen Ltd.) were also used in the experiment. Argon and nitrogen were purchased from Shanghai Shenzhong Industrial Gas Ltd.

Tangeretin (reference substance, ≥ 99%) was purchased from Shanghai Ruji Biological Technology Ltd. Linoleic acid (60%−74%), phenylethyl alcohol (CP), methanol and isopropanol (HPLC grade) were from Sinopharm Chemical Reagent Co. Ltd. Propranolol hydrochloride was purchased from Changzhou Yabang Pharmaceutical Factory. Dichlorvos emulsion with 77.5% dichlorvos was produced from Nantong Jiangshan Pesticide Chemical Industry Co., LTD. Mosquito coil with content of dimefluthrin as 0.03% was product of Zhejiang Zhengdian Industrial Co., LTD. Orange was purchased from local supermarket. Distilled water was from Guangzhou Watsons Food &Beverage Co., LTD.

2.2 Experimental method

2.2.1 Construction of apparatus

According to the principle of DART and the charge selection module in mass spectrometer, the grid electrode was removed in this device to simplify the device structure. For the convenience of constructing experimental device, a commercial ion generator was used, and heater band was wrapped on the outside of the quartz glass tube to heat the ionic gas. The established DART device structure diagram is shown in Fig.1a. The photographs of real installed device and quartz glass tube are all shown in Fig.1b and Fig.1c. The gas from cylinder passed through ionization device with 4.6 kV and ionized. The ionized gas flow was heated to the definite temperature in quartz glass tube which was wrapped by heater band. Quartz glass tube was connected closed with straight glass stilligout. The outlet of straight glass stilligout was fixed on the rotating platform and aimed at inject port of mass spectrometry. The DART-MS analysis was performed by manipulating the software of the mass spectrometer.

2.2.2 Sample preparation

Preparation of liquid samples: (1) 100 μL of formic acid

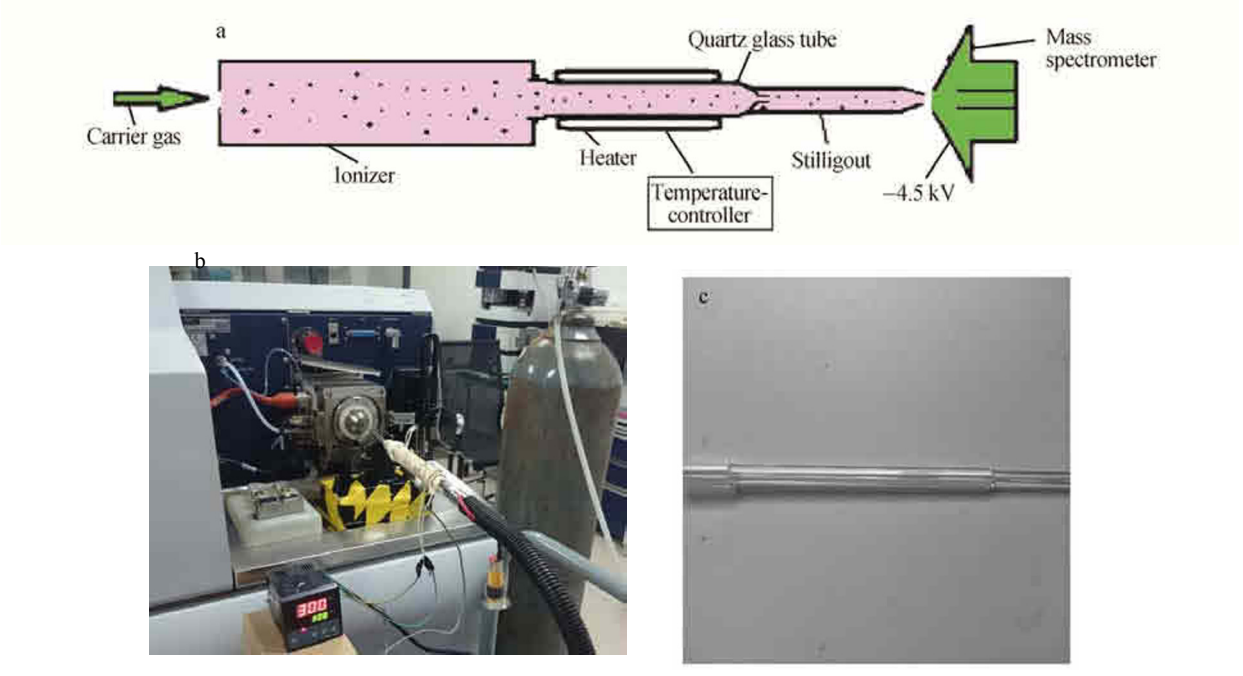

Fig.1 Structure diagram of the flexible DART device without grid electrode (a), its enlarged part (b) and silica glass tube (c)