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A simple desorption atmospheric pressure chemical ionization method for enhanced non-volatile sample analysis

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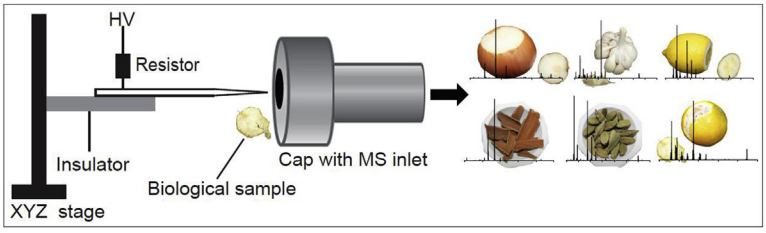
HIGHLIGHTS

- A desorption APCI method has been optimized for the analysis of nonvolatile and volatile compounds.
- Arcing, spark discharge and the erosion of the needle tip can be avoided using resistor in positive ion mode.
- DC corona discharge is better than AC corona discharge for dry sample desorption and ionization.
- Miniaturized sample size (0.5 μL) is important in many filed of applications.
- Biological samples can be analyzed with minimum sample pretreatment.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a simple desorption atmospheric pressure chemical ionization (SDAPCI) source is studied and optimized for analyzing a wide variety of samples such as nonvolatile, volatile and biological samples. In this ion source, the heated mass inlet was used for sample desorption, and a solid needle was used to produce a corona discharge for ionization. The utilization of any additional gas or heater is not required in SDAPCI. Due to its high sensitivity, only a small amount of sample is needed. Sample loading and the consequent mass spectrometry analysis process could be easy and fast, which was demonstrated by the analyses of different types of samples ranging from non-volatile to volatile compounds. High-throughput analysis can be performed by SDAPCI source with minimum or no sample preparation.

1. Introduction

Thermal desorption is one of the most attractive methods for the analysis of volatile, semi-volatile and non-volatile analytes in different field of research such as environmental monitoring, homeland security, breath analysis and aroma profiling. In a typical thermal desorption process, heat is applied to free analyte molecules from liquid phase or solid phase samples. This process is used for the analysis of volatile compounds in gas chromatography (GC) [1]. Another example is the use of thermal desorption in ion mobility spectroscopy for the detection of non-volatile compounds such as drugs and explosives [2]. Thermal desorption has also been used in a wide variety of ambient ion sources such as atmospheric pressure chemical ionization (APCI) [3-5], aerodynamic assisted

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thermal desorption [6], direct analysis in real time (DART) [7], dielectric barrier discharge (DBD) thermal desorption [8-11], thermal desorption low temperature plasma [12], flash desorption mass spectrometry [13], atmospheric pressure thermal ionization [14], thermal desorption flame induced APCI [15], thermal assisted atmospheric pressure glow discharge [16], thermal desorption electrospray ionization (ESI) [17-18], and etc.

Inlet ionization [19] is another type of ambient ionization mass spectrometry. By loading samples into the heated inlet, this technique is simple, since no high voltage or laser is required for the analysis of liquid samples. The mechanism of ion formation is believed to be induced by the high temperature of the heated ion transport tube, vacuum and the minimum cone voltage. This inlet ionization process is also related to vacuum and thermal desorption. Matrix-assisted ionization in vacuum (MAIV) [20-21] is a variant of the inlet ionization, in which the sample is sublimed by a matrix. This ionization process is believed to be assisted by vacuum and the minimum cone voltage, available by default, on a mass spectrometer.

The nanotip ambient ionization mass spectrometry (NAIMS) has recently been developed to avoid spark or arc discharge within the ionization source by using 1 MΩ resistors, and NAIMS has been applied to perform imaging mass spectrometry [22]. In some cases, analyte fragmentation is prominent and the sensitivity of NAIMS is not sufficient for high-resolution imaging due to the reduced desorption area and the long distance between the ion transport tube and the nanotip. Actually, a small portion of ions could enter the inlet of a mass spectrometer, when the sample is introduced from a remote ionization source to the inlet of a mass spectrometer. Thus, a lower MS sensitivity is observed when the ion source is far from the inlet of a mass spectrometer.

To improve MS sensitivity, simple desorption atmospheric pressure chemical ionization (SDAPCI) source has been optimized in order to detect trace-level explosives, pharmaceutical ingredients from intact tablets and volatile compounds from different food products in both positive and negative ion modes. The optimization of SDAPCI source includes the application of a 10 GΩ resistor, the minimum distance of discharge electrodes, and etc. A 10 GΩ resistor is fixed between APCI nanotip needle and the high voltage power supply to avoid spark or arc discharge in positive ion mode. The utilization of an extra heater is not required for the ion trap mass spectrometer. Any gas or syringe pump is also not needed or used in a SDAPCI experiment. Air contains N_2, O_2, NH_4, and water near the discharging region of the needle. The mechanism of SDAPCI is similar to conventional APCI and inlet ionization methods. The high voltage is applied to a sharp solid needle to create corona discharge. This discharge is responsible to produce reactant primary ion such as H_3O^+ as a proton source from ambient air. This proton is suitable for analytes with high proton affinities. The primary ion is formed after applying a high voltage between the needle tip and the ion transport tube. Two sample loading methods have been used in this study. For dry samples, they could be loaded on the cap of the MS inlet. For some liquid samples, a small amount of sample was held in a gel loading tip, and then placed between the APCI needle and the heated cap of the MS inlet. After ion-molecule reaction, molecular ion is formed and transferred into the MS inlet for further MS analyses.

Low sample consumption and high throughput are the main advantages of SDAPCI, which are important in different fields of applications such as medical, forensic and biological sciences. Only 0.5 μL liquid samples or a piece of biological sample without sample preparation can be introduced and analyzed within a short time. The rapid analyses of nonvolatile, volatile, dry and biological samples using SDAPCI were demonstrated in this study.

1.1. Mass spectrometer

A Bruker HCT ion trap mass spectrometer (Bruker Daltonics Inc. Bremen, Freie Hansestadt Bremen, Germany) was used and mass spectra were recorded in both positive and negative ion mode for all experiments. Experimental conditions were as follows: discharge current for negative ion mode, 2400 nanoamp; discharge current for positive ion mode with resistors, 20 nanoamp; nitrogen drying gas flow rate, 10 L/min; capillary temperature, 180 °C; multipole RF amplitude (V_{p-p}), 300 V. The normal scan mode was optimized and used, and the ion trap mass range was set from 50 to 500 Th in both positive and negative ion mode. The maximum ion injection time was optimized and set to 1 ms. Inner diameter of the ion transport tube was 0.55 mm. The q value of the ion trap was set at 0.35 when performing MS/MS.

1.2. Description of the ion source

Fig. 1 shows the experimental setup of SDAPCI-MS for the analysis of non-volatile, volatile and biological sample. The ion source is economical compared to other plasma-based ion sources. No extra gas (He, Ar, N_2 or CO_2) or extra heater is used in all experiments. An acupuncture needle is used and connected with an insulating strand. The strand is made of stainless steel and insulator. An ionization voltage of 1.5 kV was applied to the solid needle via the 10 GΩ resistor in positive ion mode. A distance of 0.5 mm was maintained between the corona needle and the cap of the MS inlet. An ionization voltage of 2.8–3 kV (current: ~2400 nanoamp) was applied in negative ion mode without the use of resistors. The stand is connected to a XYZ stage for position optimization. Diameter of the acupuncture needle at the tip was ~700 nm with an outer diameter of ~140 μm. Direct current (DC) was used in both positive and negative ion modes in all experiments. Volatile samples were introduced using headspace method for high-throughput analysis.

1.3. Chemical and biological samples

All chemicals (methanol, dichloromethane, acetonitrile, ethanol, dimethyl sulfoxide, benzene, formic acid, toluene, benzonitrile, acetaminophen, acetone, acetophenone, dimethylformamide, octyl

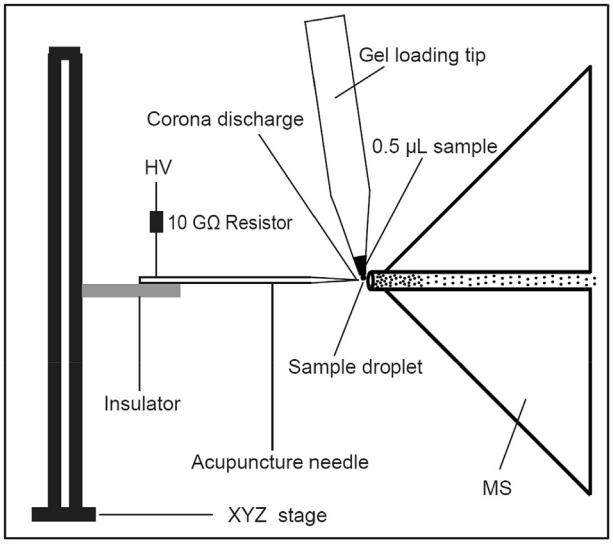

Fig. 1. Schematic setup of the simple desorption atmospheric pressure chemical ionization source with MS.