

Supplementary Information

Plasma-based Ambient Sampling/Ionization/Transmission Integrated Source for Mass Spectrometry

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Gas dynamic simulation

The finite element method (FEM) software package Comsol Multiphysics ver. 4.3a (Comsol AB, Stockholm, Sweden)²⁰ was used, and exact geometries of pin-to-funnel sleeve were considered for the simulation. In this way, the focusing effect of the funnel from atmospheric pressure to primary vacuum can be well simulated.

Preparation of mouse brain sections

The animal experiments were performed according to the Guide for the Care and Use of Laboratory Animals (NIH, No. 3040-2, revised 1999, Bethesda, MD) and approved by the Animal Care and Use Committee of the Chinese Academy of Sciences. A male Kunming mouse weighing 23 g was provided by the Experimental Animal Center of Peking University. The mouse was euthanized with intraperitoneal injection of ethyl carbamate followed by cervical dislocation. The brain was quickly removed from the skull and frozen in liquid nitrogen immediately, prior to storage at -80 °C. For cryosectioning, the frozen mouse brain was affixed to the cryomicrotome chuck (CM1950, Leica Biosystems Nussloch GmbH, Nussloch, Germany) using ice slush made from saline solution.

The brain sections were cut at thickness of 5-50 μm . Serial brain sections were alternately thaw mounted onto aluminum foil and ITO (indium tin oxide) coated conductive glass slides and directly used for AMS analysis in 3 min without any pretreatment.

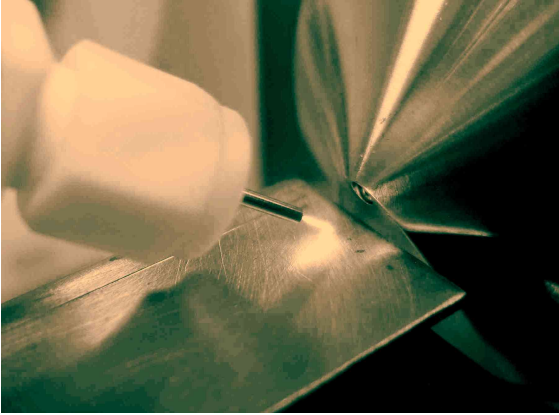
[21] W. Wissdorf, L. Pohler, S. Klee, D. Muller and T. Benter, *J. Am. Soc. Mass. Spectrom.*, 2012, **23**, 397-406.

Table S1. Ambient Sampling/Ionization Techniques Utilizing Plasma

source	discharge type	temperature at sample surface (°C)	discharge gas	flow rate (L/min)	voltage and power (used in demonstration)
DART ²	CD-GD	250-350 ^a	He, N ₂	1.0	dc, 1–5 kV
DAPCI ³	CD	N/A	N ₂	2.5	dc, 3–6 kV
LTP probe ⁵	N/A	30	He, Ar, N ₂ , air	<0.4	ac, 2-5 kHz, 2.5-5 kV, <3 W
DBDI ¹¹	N/A	N/A	He, Ar, N ₂ , air	<0.2	ac, 20.3 kHz, 3.5-4.5 kV, 5-30 W
FAPA ⁶	GD-AD	200	He	0.9-1.5	dc, -500 to -700 V, 3-20 W
PADI ¹²	GD	N/A	He	>0.7	rf, 13.56 MHz, 300 V, <5 W
DCBI ⁸	CD	room temp.-450 ^a	He	0.1-1.5	dc, 1–5 kV
Microplasma in MHCD	glow-type microdischarge	>120	He	0.3	dc, -300 to -350 V
MIPDI ⁹	N/A	>30	He, Ar	0.5-2.0	N/A
PASIT	CD-GD	30-300	He, Ar, N ₂ , air	<0.1	dc, 2-4 kV, <4 W

^a Additional heating is applied.

(a)



(b)

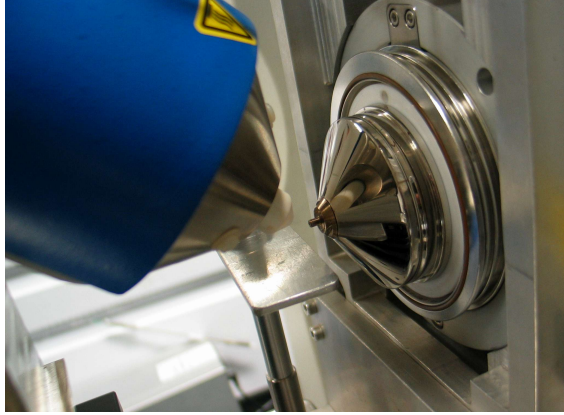


Figure S1. Photograph of two DC plasma-based sources with the pin-to-plate geometry: (a) APGD source similar to the previously reported one, (b) commercial DART source.

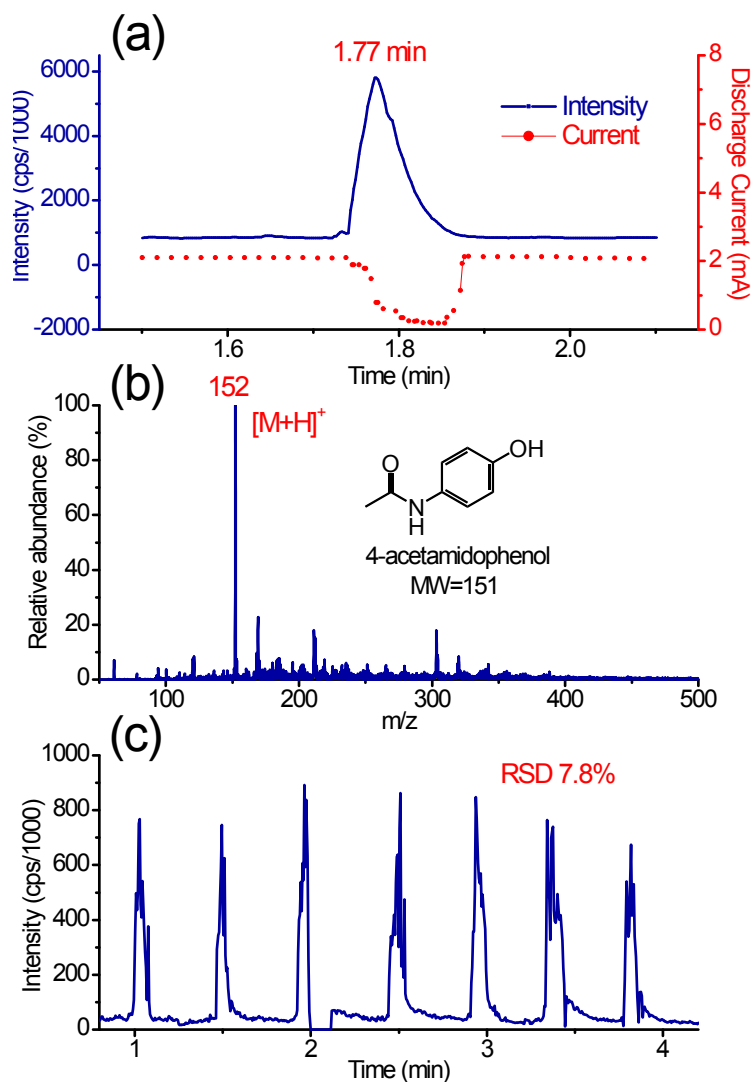


Figure S2. (a) Behavior of the TIC intensity and discharge current during the PASIT process of direct insertion sampling. The discharge current decreases after sample insertion, while the ion signal intensity immediately increases and reaches its maximum value. Analysis of 15 nmol of acetaminophen deposited on filter paper acquired in positive ion mode using the PASIT probe with argon as discharge gas: (b) mass spectra, (c) EIC at m/z 152, recorded during septuplicate PASIT-MS analysis. Relative standard deviation of ion current peak area is approx. 8%. Operating conditions (unless otherwise stated): distance between electrodes, 5 mm; discharge voltage, 2.6 kV; Ar gas flow, 0.2 L/min.

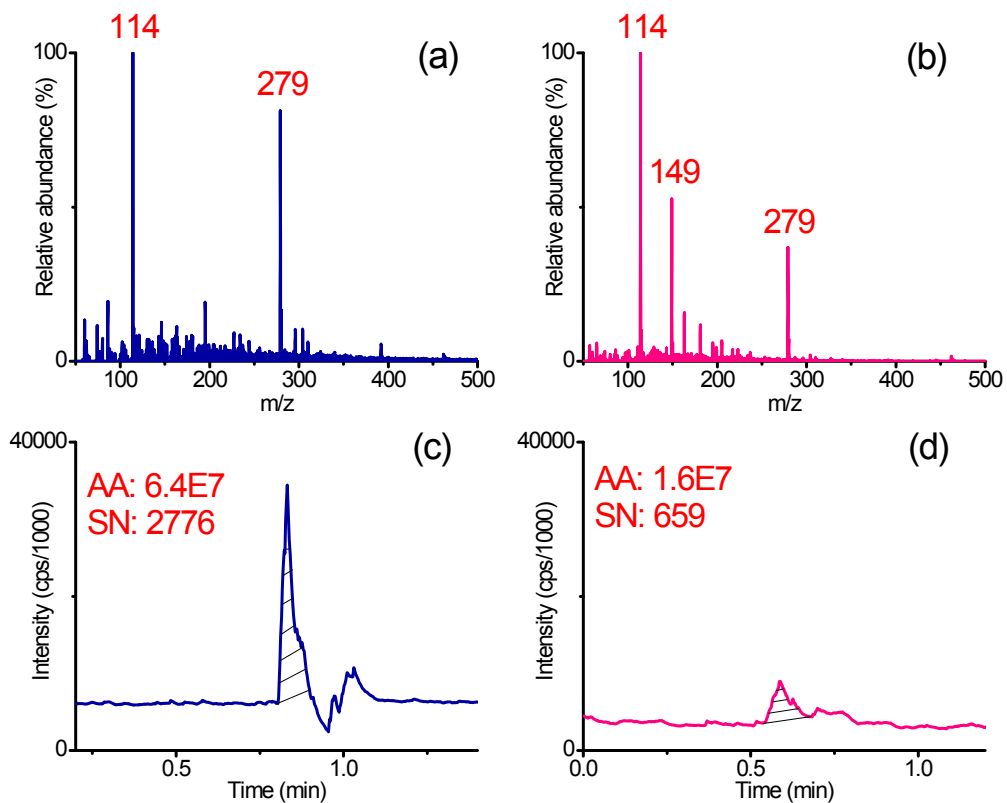


Figure S3. Mass spectra and TIC of (a and c) pin-to-funnel PASIT and (b and d) pin-to-plate source in MS analysis of blank test sample. The average and RSD of the baseline in c and d were 6.1E6, 1.8% and 3.6E6, 8.2%, respectively. The S/N from PASIT is improved by nearly a factor of three with funnel sleeve compared with pin-to-plate devices, while under both conditions the mass spectra are similar especially for the dominant species.

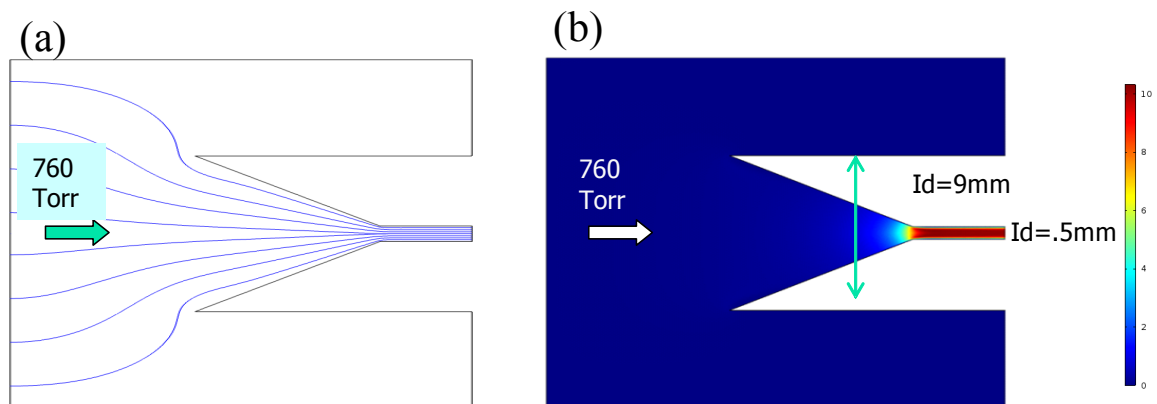


Figure S4. Gas dynamic simulations of the focusing effect of the funnel sleeve in atmospheric pressure prior to primary vacuum: (a) gas stream line, (b) contour maps of flow speed.

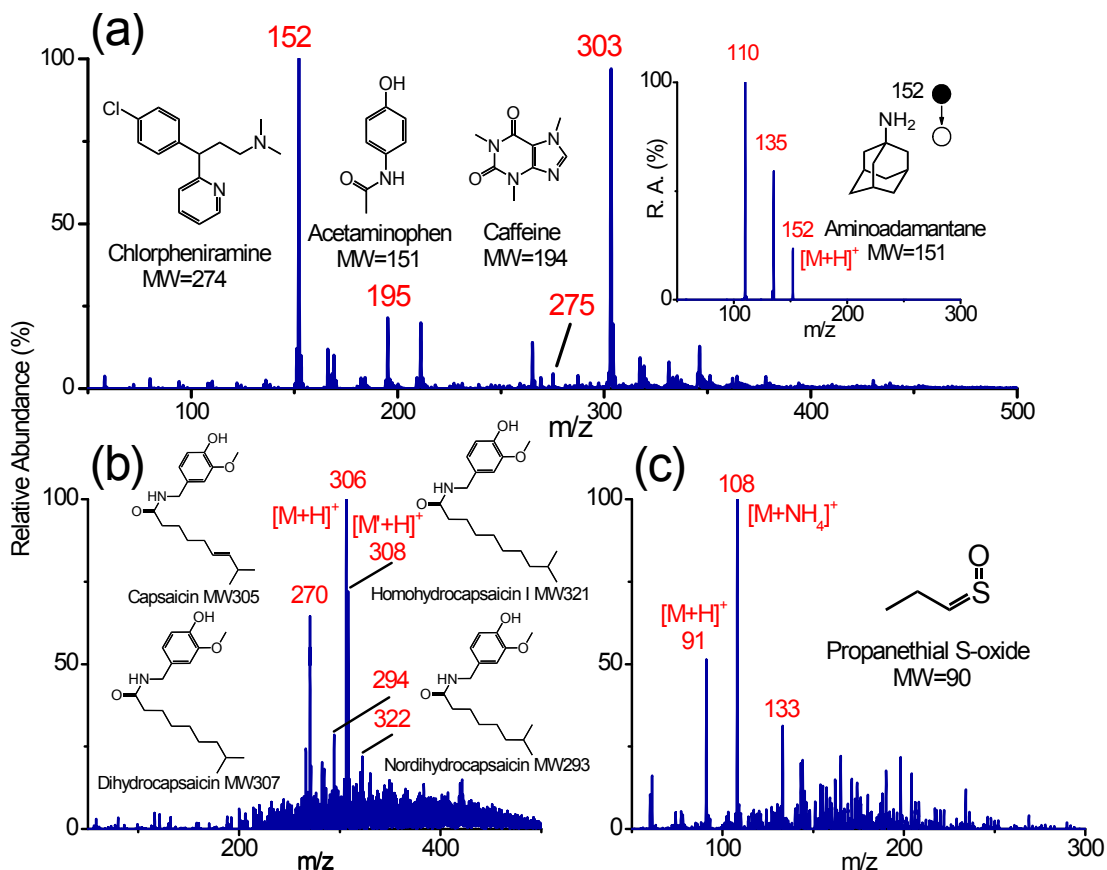


Figure S5. Direct analysis of drug tablets and plant tissues: (a) a Duoduo compound tablet mainly containing three actives paracetamol (250 mg), amantadine hydrochloride (100 mg), and caffeine (15 mg), (b) capsaicin in pepper membrane(white part holding the seeds), (c) propanethial S-oxide in freshly cut onion. Parts a, b and c are on different scales.

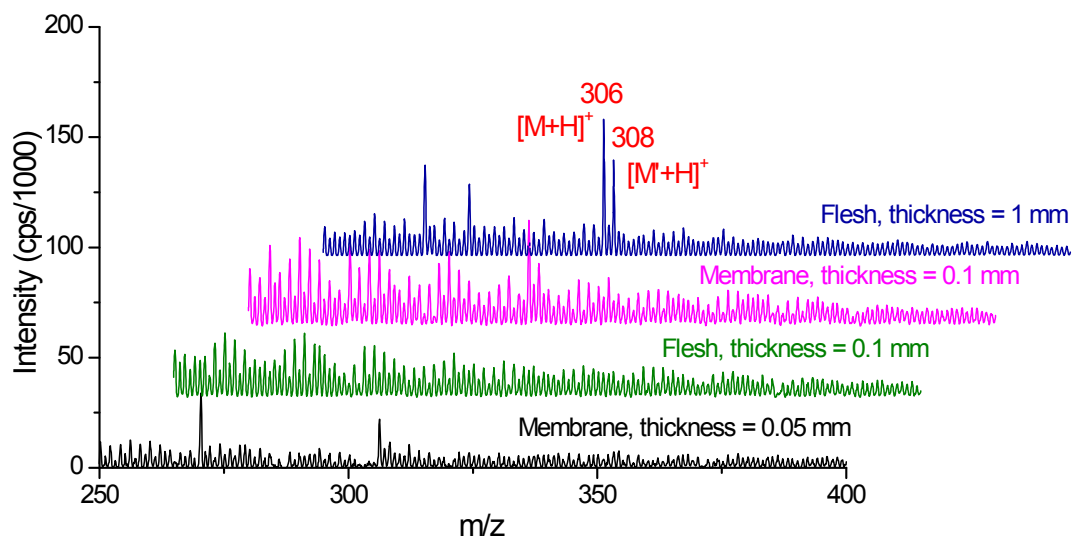


Figure S6. Representative PASIT-MS spectra from hot pepper's flesh and membrane at varying thicknesses.