Supporting Information

Direct Analysis of Carbonyl Compounds by Mass Spectrometry with Double-Region Atmospheric Pressure Chemical Ionization

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Contents

S-1 Optimization of mass spectrometry

Corona current, 5μA;

APCI probe temperature, 100°C;

Ion source temperature, 60°C;

Desolvation gas flow, 250L·h^{-1}.

Tandem mass spectrometry (MS/MS) experiments were carried out with collision-induced flow rate of 0.25 mL·min^{-1}.

Table S-1. Optimized parameters for direct DRAPCI-MS/MS determination of standards

Analytes	Mass (Da)	Cone (V)	Collision Energy(V)	Parent ion (m/z)	Daughter ion(m/z)
Cyclohexanone	98	18	30	99	**81**,55,41
Hexanal	100	20	10	101	**83**,55
Heptanal	114	18	10	115	**97**,69,55
Octanal	128	16	8	129	**111**,88,69

S-2 Background mass spectrum of DRAPCI

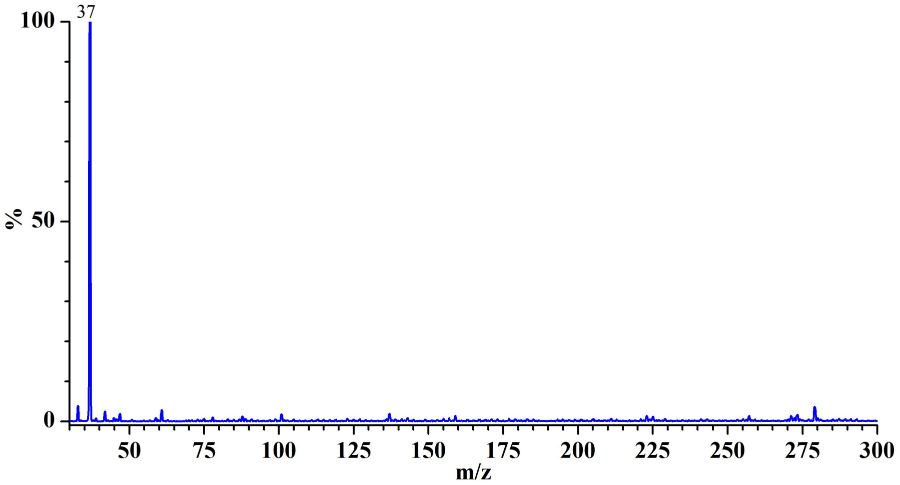

Figure S-1. Background mass spectrum of DRAPCI

S-3 Optimization of gas flow rate

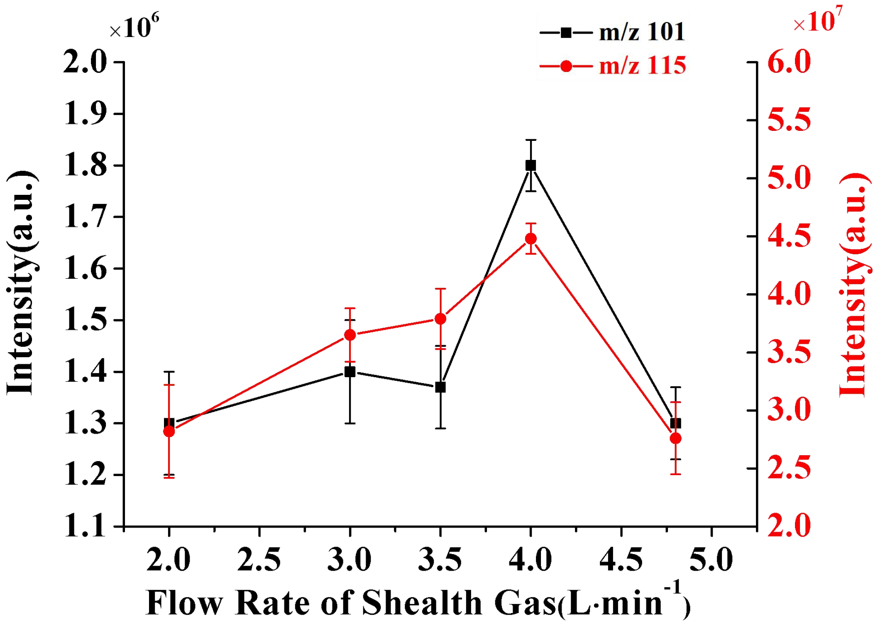

Figure S-2. Influence of flow rate of nebulizing gas on the sensitivity of mass spectrometry.

S-4 Comparison of APCI and DRAPCI in sensitivity

To determine the LODs of cyclohexanone, hexanal, heptanl, octanal in DRAPCI source, standard solution of four carbonyl compounds at concentrations of 0.5 μg·L^{-1} to 1mg·L^{-1} (12.5μg·L^{-1},25μg·L^{-1} , 50μg·L^{-1} , 100μg·L^{-1} , 250μg·L^{-1} , 500μg·L^{-1}, 1mg·L^{-1}) were analyzed in MRM mode. 10μL of standard solution vaporized in 20-mL glass vial produced the sample gas at concentration of 5 μg·m^{-3} to 400 μg·m^{-3} (5 μg·m^{-3},10 μg·m^{-3}, 20 μg·m^{-3}, 40 μg·m^{-3}, 100 μg·m^{-3}, 200 μg·m^{-3}, 400 μg·m^{-3}). In comparison, four carbonyl compounds at the same concentration were analyzed in APCI source. Each sample was analyzed 5 times. Ten consecutive analyses of the lowest concentration of the calibration curve were conducted and standard deviation (SD) were calculated; then LODs and LOQs were defined as three times of SD and ten times of SD respectively. The calibration curve (intensity versus the analyte concentration) was constructed for four carbonyl compounds.

Table S-2 Linear dynamic range, limit of detection (LOD) and limit of quantification (LOQ) of cyclohexanone, hexanal, heptanaland octanal in direct APCI-MS/MS and DRAPCI-MS/MS

Ion source	Sample	LOD[a] ($\mu g\cdot m^{-3}$)	LOQ[a] ($\mu g\cdot m^{-3}$)	Lineary Range ($\mu g\cdot m^{-3}$)	R^2	Calibration Curve
APCI	Cyclohexanone	1.27	4.23	5-400	0.995	Y=153.08X+132.2
	Hexanal	1.38	4.59	10-400	0.995	y=500.46X+82.62
	Heptanal	2.54	8.46	10-400	0.992	Y=280.82X+110.9
	Octanal	11.48	37.89	40-400	0.998	Y=34.85X+34.57
DRAPCI	Cyclohexanone	0.46	1.51	5-400	0.998	Y=232.24X+111.7
	Hexanal	0.16	0.54	10-400	0.976	Y=523.1X+69.76
	Heptanal	0.46	1.39	5-400	0.993	Y=144.56X+62.97
	Octanal	2.06	6.79	10-400	0.993	Y=40.59X+26.44

[a] Ten consecutive analyses of the lowest concentration of the calibration curve were conducted and standard deviation (SD) were calculated; then LODs and LOQs were defined as three times of SD and ten times of SD respectively.

S-5 Repeatability experiments

Repeatability was assessed by six consecutive analyses of the lowest concentration of the calibration curve. The MS detector was set in MRM mode, monitoring continuously ion transitions m/z 99→81 (for cyclohexanone), 101→83 (for hexanal), 115→97 (for heptanal) and 129→111 (for octanal).

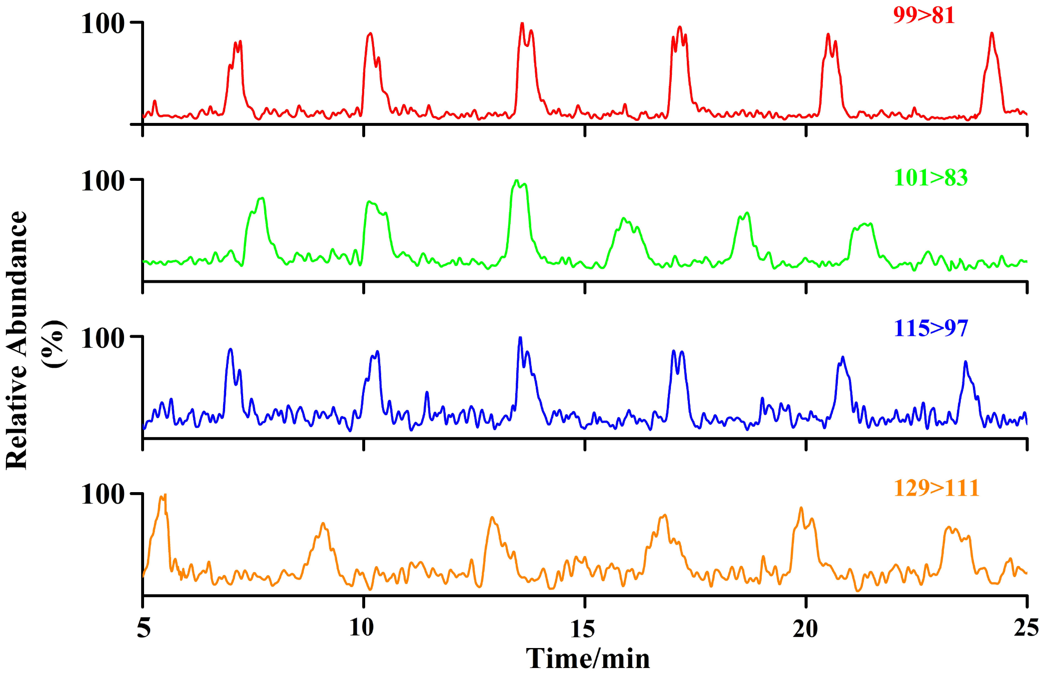

Figure S-3. The repeatability experiments were examined of six replicate injections ofthe lowest concentration of the calibration curve.

S-6 Extra Virgin Olive oil (EVOO) quantification results in DRAPCI-MS/MS and HS-SPME-GC-MS

A common analytical technique for aroma analysis is conventional gas chromatography-mass spectrometry (GC-MS). This can be combined with headspace solid-phase microextraction (HS-SPME), a rapid, simple and inexpensive extraction and concentration technique for volatile compounds. However, SPME is semiquantitative and selective with respect to compound polarity, and absolute value of the total headspace volatiles was unavailable. Volatiles measured using a SPME fiber do not necessarily reflect the actual head space composition of samples, due to discrimination of volatiles on the basis of partition coefficients and adsorption kinetics.[1] Herein, we used SPME-GC-MS to validate the DRAPCI-MS/MS quantitative results.

A. Sample preparation

Hexanal was purchased from Sigma-Aldrich. Hexanal-d_{12} used as internal standard (IS) was purchased from TRC (Canada). EVOO samples were bought in local supermarket. Standard addition (SA) is considered to be one of the most straightforward methods for elimination of the influence of interferences on the result, and the procedure is believed to adjust for interferences using minimum resources.[2] Hexanal and Hexanal-d_{12} standard solution of 1500 $mg \cdot L^{-1}$ was prepared in hexane. The final concentration of hexanal added into EVOO was 0 $mg \cdot kg^{-1}$, 0.5 $mg \cdot kg^{-1}$, 1 $mg \cdot kg^{-1}$, 3 $mg \cdot kg^{-1}$, 5$mg \cdot kg^{-1}$, 10$mg \cdot kg^{-1}$.

B. Hesadspace SPME (HS-SPME)

HS-SPME-GC-MS analysis was carried out by adding standard solution to olive oil in 20 mL screw cap vails fitted with PTFE/silicone septa. The vials were heated at 50 °C for 20 min to reach the equilibrium between the sample and the headspace.

The SPME holder (Supelco, Bellefonte, PA, USA) was used to perform the experiments. A fused silica fiber-coated with a 65 μm layer of Polydimethylsiloxane/

Divinylbenzene (PDMS/DVB; Supelco) was used to extract hexanal from EVOO.

Prior to first use, fibers were conditioned by inserting into the GC injection port and heated at 250 °C for 30 min. Subsequently, the holder needle was exposed to the headspace of sample during 20 min (extraction time) at 50 °C. The fiber was then withdrawn and removed from the vial. Fibers were immediately thermally desorbed in the GC injector for 3 min at 250 °C to prevent contamination.

C. Gas chromatography-mass spectrometry system and conditions

The GC column used was a DB-WAX capillary column (60m length × 0.25mm i.d., 0.25μm film thickness) with helium as the carrier gas. The GC interface, ion source and quadrupole (5975c, Angilent) temperature were 250 °C, 230 °C and 150 °C, respectively. The GC temperature program started at 50 °C and then raised to 250°C at a rate of 10 °C per minute, and finally was held at 250 °C for 5 min.

D. Qualification results in DRAPCI-MS/MS and HS-SPME-GC-MS

Figure S-4 displayed the full scan mass spectrum of headspace of olive oil by DRAPCI-MS, where some peaks were assigned to acetic acid (m/z 61), 2-cyclohexen-1-ol / 2-hexenal (m/z 99), hexanal (m/z 100). These compounds were also identified by HS-SPME-GC-MS.

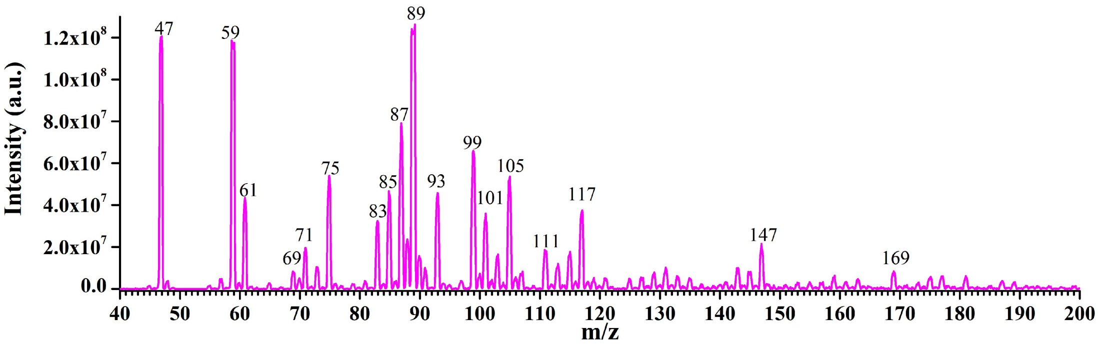

Figure S-4 Full scan mass spectrum of olive oil by DRAPCI-MS

E. Quantification results in DRAPCI-MS/MS and HS-SPME-GC-MS

Standard addition approach was employed for quantitative analysis in both DRAPCI-MS/MS and HS-SPME-GC-MS. Calibration curves were constructed by peak area ratio of analytes-to-the internal standard (Y) versus concentration of the added standard analytes (X). All data presented in this experiment were averages of three replicates. Standard deviations calculated from multiple EVOO measurements were used to estimate the limit of detection (LOD), set equal to S_0, where S_0 is the standard deviation of the analyte concentration at zero concentration[3]. The LOD of hexanal was estimated as 0.265 $mg \cdot kg^{-1}$in HS-SPME-GC-MS. The concentration of hexanal was 1.84 $mg \cdot kg^{-1}$ in EVOO using SPME-GC-MS while 3.77 $mg \cdot kg^{-1}$ in the same EVOO sample using DRAPCI-MS. The quantitative results of SPME-GC-MS were on the same order of magnitude of DRAPCI. The total analysis time of DRAPCI-MS/MS was less than 3 min while HS-SPME-GC-MS was about 1 h, indicating DRAPCI-MS/MS is a rapid, sensitive, reliable method for gas quantification.

Table S-3 Quantification results of EVOO in different instrument

Method	Calibration curve	R^2	Concentration ($mg \cdot kg^{-1}$)
HS-SPME-GC-MS	Y=0.4878x+0.8946	0.999	1.84
DRAPCI-MS/MS	Y=0.5962x+2.2485	0.998	3.77

References

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2. Andersen, J. E. T., The standard addition method revisited. *TrAC Trend Anal. Chem.* **2017,** *89*, 21-33.

3. Wu, W.; Ashley, D. L.; Watson, C. H., Determination of Nicotine and Other Minor Alkaloids in International Cigarettes by Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry. *Anal. Chem.* **2002,** *74* (19), 4878-4884.