https://doi.org/10.5194/acp-2022-326
Preprint. Discussion started: 13 May 2022

Atmospheric Chemistry and Physics Discussions

Technical note: Identification and quantification of gaseous and particulate organic compounds from cooking fumes by comprehensive two-dimensional gas chromatography-mass spectrometry

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https://doi.org/10.5194/acp-2022-326
Preprint. Discussion started: 13 May 2022

Abstract

As a significant source of indoor and outdoor pollutants, cooking fumes have a great impact on air quality and human health. However, the limited identification and quantification techniques hinder the comprehensive understanding of the complex cooking fumes with wide volatility and polarity. Herein we applied thermal desorption comprehensive two-dimensional gas chromatography-mass spectrometer (TD-GCxGC-MS) for synchronous analysis of gaseous and particulate organics emitted from cooking fumes. With a systematic 4-step qualitative procedure and precise quantitative and semi-quantitative method, 170 and 352 compounds from C2 (acetic acids) - C30 (squalene) occupying 95% and 90% of the total ion current for gaseous and particulate samples were identified and quantified. For most compounds, the correlation coefficient (R^2)is >0.9, and the relative standard deviation (RSD, n=5) of three concentration levels (low, medium, high) is within 10%. For the semi-quantification, the total uncertainty is ~27%. Compared with gas chromatography-mass spectrometer (GC-MS) and proton transfer time-of-flight mass spectrometer (PTR-ToF-MS), TD-GCxGC-MS detects more compounds, especially the diagnostic tracers related to cooking oil and matierial, and additives added during cooking and secondary products transformed from carbonyls and acids. Hence, TD-GCxGC-MS provides plenty of perspectives to analyze the primary emission and secondary formation from cooking at a molecular level.

1. Introduction

Cooking has been proven to be a significant source of indoor and outdoor pollutants in urban and rural areas. (He et al., 2004;Ni et al., 2016;See and Balasubramanian, 2008;Xiao et al., 2015)It has been reported that cooking emissions contribute to approximately 7% of the total fine particulate matter ($PM_{2.5}$, diameter less than or equal to 2.5 μm) mass and 10-30% of organic aerosol (OA) in China, and 20% of the $PM_{2.5}$ mass in Los Angeles.(He et al., 2004;Schauer and Cass, 2000;Wang et al., 2009) Due to the complexity of Chinese cooking, e.g. a large diversity of oils, food material, and ingredients, cooking emits more than 600 volatile organic compounds and various particulate components, which has been the main source of air pollutants in the indoor environment of nonsmokers' residential buildings.(Cheng et al., 2016;Huang et al., 2020;Klein et al., 2016b;Liu et al.,

https://doi.org/10.5194/acp-2022-326
Preprint. Discussion started: 13 May 2022

2017;Wang et al., 2018)

Since cooking emission is a major contributor to personal PM exposure, the adverse health effects of exposure to the cooking emissions, e.g. cardiac, pulmonary, dermal, and renal toxic effects have been widely studied. However, these studies mainly focus on the effects of particle size, surface, and concentration but toxic components contained therein. (Chowdhury et al., 2012;Sharma and Jain, 2019;Sjaastad and Svendsen, 2008;Zhao et al., 2015)Ultrafine particles emitted from cooking fumes are reported to cause oxidative stress in lung cells and enhance lung inflammation and allergic reaction. (Alessandrini et al., 2006;Beck-Speier et al., 2005)The International Agency for Research on Cancer (IARC) classifies high temperature frying emissions as “possible human carcinogens”(IARC, 2006). But besides a few pieces of research focused on the toxicity of polyaromatic hydrocarbons (PAHs) in cooking fumes, the toxicity of other components is severe due to the limited qualitative analysis of cooking fumes.(Wong et al., 2011)

Cooking organic aerosol (COA), which consists of both primary and secondary organic aerosol (POA and SOA), could take up as much as 84% of the total $PM_{2.5}$ mass in mega city of China.(Zhang et al., 2021) Previous studies have analyzed the composition of primary COA, and only 10~20% of the total primary COA mass are identified.(Zhao et al., 2007b, a;He et al., 2004) Different cooking types are reported to generate particles of different sizes and chemical compositions.(Torkmahalleh et al., 2012;Oeder et al., 2012;Zhao et al., 2019) Fatty acids, which are mainly generated from the hydrolysis and pyrolysis of triglycerides, account for 70~90% of the total identified OA mass.(Zhao et al., 2007b, a) Further, the formation of secondary organic aerosols from cooking emissions has been proved to be strongly correlated with the cooking styles due to the dictinct chemical composition of volatile, intermediate-volatility and semi-volatile organic compounds (VOCs, IVOCs, and SVOCs, respectively).(Fullana et al., 2004a, b;Katragadda et al., 2010;Torkmahalleh et al., 2017)

Limited identification and quantification of both gaseous and particulate organic compounds hinder the cognition of adverse health effects and SOA formation from cooking fumes. Gas chromatography-mass spectrometry (GC-MS) was widely used in the analysis of both gaseous and particulate organics emitted from cooking.(Fullana et al., 2004b;Katragadda et al., 2010;Zhao et al., 2007b, a) Due to the relatively poor separation property of GC-MS, and the complexity of cooking emissions, only a small fraction of the organics with authentic standards, e.g. alkanes, PAHs, aldehydes, and acids, can be identified and quantified. The specified gaseous and particulate organics only account for ~25% of NMHC and 10~20% of bulk organic particle mass, respectively. (Schauer et al., 2002;Zhao et al., 2007b, a)Besides, the analysis of gaseous organics mainly focused on VOCs.(Schauer et al., 2002;Fullana et al., 2004a, b;Katragadda et al., 2010) IVOCs, which were reported to be an important precursor of SOA, were seldom studied.

Comprehensive two-dimensional gas chromatography-mass spectrometry (GCxGC-MS) applies two columns with opposite polarities connected in series to gain extended separation capabilities. Slices of the analyte eluted from the first column (typically a non-polar column) are concentrated and then injected into the second column (typically a polar column), hence an enhanced signal-to-noise ratio and promoted sensitivity is attained. The slicing procedure is known as “modulation”. Besides, the similar 2-D retention time with similar MS spectra of homologs helps to classify compounds into different chemical classes. Herein, we first apply GCxGC-MS to analyze both the gaseous (especially IVOCs) and particulate organics emitted from deep-fried chickens, which is a widely accepted and typical dish with high emission factors and complex organic compostitions. Our results indicate that GCxGC-MS is a powerful tool for the identification and quantification of cooking emissions.

2. Sample collection and analysis

Chicken nuggets was fried with corn oil in a sealed pan. A pure nitrogen flow passed through the pan to bring out the emission into the dilution system. The detailed cooking procedures could be found in the previous work.(Zhang et al., 2021) The gaseous and particulate samples were collected through a homemade sampler. Cooking fumes pass through the inert silylated steel pipe with a total flow rate of 10 L/min to a quartz 47 mm filter (Whatman®- Sigma-Aldrich), which was used to collect particles, and then split into two flows, one passes through an adsorption tube (Gerstel 6 mm OD, 4.5 mm ID glass tube filled with ~290 mg Tenax TA) at a flow rate of 0.5 L/min for the collection of gaseous samples. The adsorption tubes were pre-conditioned at 300°C for 2 h, and the quartz filters were pre-conditioned at 550°C for 6h before sampling to remove all the contaminations. All the samples were stored at -20°C until being analyzed.

The Tenax TA samples (gaseous organics) were directly analyzed by a thermal desorption (Gerstel, TDS-C506) comprehensive two-dimensional gas chromatography-mass spectrometer (Shimadzu, GCMS-TQ8050) (TD-GC×GC-MS) system equipped with a Zoex ZX2 cryogenic modulator (Houston,TX). The quartz filters were cut into 4 mm round pieces and deposited into empty tubes (Gerstel 6 mm OD, 4.5 mm ID glass tube) to be analyzed by the TD- GC×GC -MS system. Organics were thermally desorbed from the tube inside a Gerstel thermal desorption unit (Thermal desorption system, TDS3, Gerstel) at a splitless flow mode with a helium flow of 50 mL/min. During the thermal desorption, the temperature of the TDS3 was ramped from 30 to 280 ℃ at a rate of 60 ℃ /min and isothermally held at 280 ℃ for 5 minutes. Organics desorbed from each tube were enriched by a Gerstel cooled injection system (CIS4) filled with Tenax TA at 20 ℃. After the thermal desorption, organics enriched by the CIS were thermally injected into GC-MS with a constant column flow (helium) of 1.2 mL/min and a split ratio of 15 by heating the CIS from 20 to 320 ℃ at a rate of 12 ℃/s followed by an isothermally hold at 320 ℃ for 10 minutes. The column (primary: Shimadzu SH-Rtx-5 MS, 30 m × 0.25 mm × 0.25 μm, secondary: BPX-50, 2.7 m × 0.10 mm × 0.10 μm) temperature was ramped from 60 ℃ to 320 ℃ at a rate of 5 ℃/min followed by an isothermal hold for 5 minutes. The GC×GC modulation period was 6s and the hot pulse time was 350ms. The MS was operated in scanning mode from m/z 33 to 500 at an electron ionization of 70 eV.

To gain a better separation, organics desorbed from Tenax-TA tubes were not directly injected into GCXGC-MS but re-absorbed by a cooled injection system (CIS). The CIS was normally equipped with a quartz tube and the re-absorption temperature was set at -90 ℃. With such a condition all compounds including solvents maintain in CIS. However, the cooking samples usually contain lots of water which might influence the resolving capability of the column and the vaporization of organics while heating the CIS. To remove water in cooking samples before organics being introduced into the column, the quartz tube in CIS was specially filled with a few Tenax-TA and the re-absorption temperature was set at 20 ℃ in our experiments.

3. Identification and quantification of gas- and particle-phase organics from cooking emissions

Compounds with similar structures show similarities in physicochemical properties. This facilitates the identification and grouping of resolved compounds. Homologs, a series of compounds differing from each other by a repeating unit, such as a methylene bridge $-CH_2-$, show similar 2-D retention time and 1-D retention time of equal difference in chromatographic behaviors and exhibit same MS fragments and similar peak abundance ratios. Based on these properties, four steps were applied to identify and group the organics emitted from cooking fumes.

Three standard mixtures of 112 organics including 27 alkanes (C7-C30 n-alkanes and 1 cycloalkane), 1 alkene, 7 one-ring aromatics, 16 PAHs, 7 alkanols, 2 alkenols, 7 phenols 8 aldehydes, 8 ketones, 4 acids, 17 esters, 2 amides, and 6 other compounds were applied to identify the organics (see Table S1). Chemicals exhibiting similar retention times and mass spectrum were identified as the same compounds. The homologs of the known compounds were grouped based on their routine chromatographic and MS behaviors. An example of the identification of n-alkanoic acids (blobs circled in yellow) is shown in Figure 1. Since n-alkanoic acids exhibit the same *m/z* 60, 73, 87 patterns, a selected ion chromatogram (SIC) of *m/z* 60 can extract them from a mixture of thousands of blobs. Combined with properties of similar 2-D retention time of around 1.10s and an identical increase in 1-D retention time as carbon number rises, they are soon identified as acetic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, and hexadecanoic acid in the order of 1-D time. Other classes such as alkanes, aromatics, alkanols, esters, amides, etc. can also be identified in this way.

The National Institute of Standard Technology (NIST) library (NIST 17) was utilized to match the remaining unknown chemicals. Searching results of a reversed mass spectrum match similarity (R.Match) >750 are opted for further identification. Compared to mass spectrum match similarity (Match), R.Match applies the spectrum in the NIST library to match the spectrum in samples, which can eliminate the interference of backgrounds and co-elute compounds from samples and obtain a more reliable searching result. Isomers such as *o,m.p*-xylenes, and ethylbenzene possessing similar MS spectra should be further distinguished by retention index (RI). Assuming the retention indices of n-alkanes (C_n) are n*100 (i.e. retention index of C_{10} is 1000), the RI of compound A elutes between C_n and C_{n+1} can be calculated as the following formula:

$$\mathrm{RI(A)} = (\frac{t_A - t_{C_n}}{t_{C_{n+1}} - t_{C_n}} + n) * 100$$

where t_A, t_{C_n} and $t_{C_{n+1}}$ are 1-D retention time of compound A, $C_{n,}$ and C_{n+1}, respectively.

Considering the first column of our system is SH-Rtx-5 MS, experimental RIs of semi-standard non-polar in NIST 17 are utilized. For instance, judging from the experimental RIs of ethylbenzene, *p*-xylene and *o*-xylene are 855,865 and 887 in NIST 17, three blobs of RI 847,856 and 877 in our system correspond to the three compounds, respectively. For those blobs of the high area but poor match results on R.Match or RIs, their mass spectra are further compared to the mass spectra of blobs around them (isomers) or having the same 2-D retention time (homologs). If a similar m/z pattern is found between those blobs, the unmatched blobs would be marked as isomers of the matched blob and grouped in the same classes, otherwise unresolved complex mixtures (UCMs).In total, 170 and 352 compounds were identified in the gaseous and particulate samples from deep-fried chicken, respectively.

The authentic standard mixture of 112 compounds was used to quantify the organic compounds identified in cooking fume. To gain better reproducibility, an internal standard method was utilized in the quantification of chemicals. In our system, internal standards need to be injected into the Tenax-TA tube after sampling. The solvent (dichloromethane) of internal standards would dissolve samples adsorbed on Tenax-TA and take organics, especially volatile compounds, away to split vent during desorption. The addition of a large volume of internal standard (5 uL) can cause a big uncertainty for the quantification of volatile compounds, while a small volume (1 uL) would introduce a large human error caused by manual addition. Hence, an external standard method without adding extra internal standards is applied. For the injection of authentic standards, the mixture was injected into a pre-conditioned Tenax-TA tube, and before analysis a flow rate of 0.5 L/min nitrogen gas opposite to the desorbing direction at room temperature was applied to the tube for 5 min, to reduce the influence of solvents on volatile compounds. A serious of volumes of standards mixture (1, 2, 5 uL) were tested to optimized the injection amount. Finnaly, 2 uL was chosen to give consideration to the influence of both human error of manual injection and solvent effects on volatile compounds. The linear range, slope, intercept and R^2 for standard curve and the relative standard deviation (RSD, n=5) of low, medium and high concentrations are listed in Table S1. For most compounds, the R^2 is above 0.9 and RSD (n=5) is within 10%.

For those compounds without authentic standard mixture, surrogate standard was usually uned. Alam et al. utilize n-alkanes C_n as surrogate standard to quantify compounds owning the same carbon number n in the quantification of organics in diesel exhaust and an uncertainty of 24% was

https://doi.org/10.5194/acp-2022-326
Preprint. Discussion started: 13 May 2022

observed.(Alam et al., 2018) Zhao et al also utilize C_n as a surrogate standard to quantify compounds belonging to bin B_n in the quantification of organics in the atmosphere. (Zhao et al., 2014)Hydrocarbons are the main compounds in their samples, which might exhibit similar ionization behavior and generate indiscriminate MS signals to n-alkanes. However, lots of aldehydes and acids generated during cooking might have a significantly different performance during ionization to n-alkanes. Thus, we utilize both compounds of the same classes and n-alkanes as surrogate standards to quantify organics from cooking fumes. A few standards were applied to test the uncertainty of both methods and the results are listed in Table S2. For all polar compounds besides amides, a better estimation result is obtained when compounds of the same classes were applied than n-alkanes. Thus compounds of the same classes were applied to calculate the concentrations of compounds with authentic standards in our experiment and this method has a total uncertainty of 27%.

4. Typical characteristics of two-dimensional chromatograms of cooking emissions

TD-GCxGC-MS fully identified organics from cooking fumes at a molecular level. To better analyze the data, we summarize the typical characteristics of two-dimensional chromatograms of cooking emissions and list the problems and solutions encountered in qualitative and quantitative analysis of the data.

The GCxGC chromatograms of gaseous and particulate organics emitted from fried chicken fumes are shown in **Fig. 2 and 3**, respectively. The concentrations of identified compounds are listed in Table S3. Compounds with a wide range of volatilities and functionality from C2 polar acids to C30 weak-polar hydrocarbons were divided into 8 group sets and 22 classes. Judging from **Fig.1-2**, aliphatic hydrocarbons including alkanes, alkenes, alkynes, and cylco-alkanes distribute at the bottom of GCxGC chromatogram (2^{nd} RT < 1.0 s). Among aliphatic hydrocarbons, the relatively polar cyclo-alkanes overlap with oxygenated compounds (especially alkanols) and one-ring aromatics (2^{nd} RT~ 1.0 s). While saturated ketones, acids, and aldehydes elute right above them at 2^{nd} RT of 1.0~1.5 s, olefinic ones elute at a higher range of 1.5~2.0s as they own stronger polarity. Compounds distribute above 2.0 s are mainly esters, amides and PAHs. Other compounds especially

N-compounds can distribute anywhere in the chromatogram as they usually are N-substituted compounds with the similar polarity of various non-N-substituted ones.

Since the columns we used have poor separation capacity for volatile compounds such as hexane and heptane, compounds more volatile than hexane were not detectable in our experiments. Strong break-through represents in the gaseous sample for hexane and heptane as the thermo-modulator used was an electronic refrigerator with a cooling limit of -74 ℃, which cannot freeze and concentrate hexane and heptane well (Figure **S1**). Hence, other methods are more suitable for the quantification of hexane and heptane than ours and their concentrations are listed in Table S3 but not discussed later.(Schauer et al., 2002) As the least volatile compound detected in particulate samples was squalene, the missing of compounds less volatile than eicosane (C20) in gaseous samples were more likely due to their undetectable low concentrations in the gas-phase. Compounds less volatile/ more polar than squalene may have not evaporated from quartz filters or traped by Tenax-TA utilized in CIS. In addition, some lactams in particulate samples wrapped around (i.e. the 2-D retention time of the compounds are larger than the modulation time 6s and the blobs locate at a weak-polar area, Figure S1). These blobs are very broad in the second dimension but most compounds besides hexahydropyrrolo[1,2-a]pyrazine-1,4-dione don't overlap with weak-polar compounds. Hence the wrap-around effects do not influence the quantification of most compounds. And the TIC response of hexahydropyrrolo[1,2-a]pyrazine-1,4-dione was carefully calculated by deducing the contribution made by the co-elute heptadecane. In coordination with the work by Zhao et.al, fatty acids are predominant in particulate samples, of which the blobs are so large that cover several other compounds such as hexadecanamide and 9(*Z*)-octadecenenitrile. Compounds with authentic standards like hexadecanamide can be quantified with quantifier ions which are seldom influenced by the overlapped fatty acids, while compounds without authentic standards are quantified using TIC response deduced from the response of its quantifier ion and the ratio of quantifier to TIC in the NIST library.

5. Molecular composition of gaseous and particulat organics from fried chicken fumes

The GCxGC chromatogram of gaseous organics emitting from fried chicken fumes is shown in

Fig. 2 and the detailed classification and concentrations are listed in Table 1. Previous analysis of diesel exhaust and diesel fuel samples by GCxGC-MS showed that compounds of the same class distribute separately from other classes as most of the organics are hydrocarbons, which makes it possible to separate different classes of compounds by simply mapping the blobs in GCxGC chromatogram into a group but handling each blob individually.(Alam et al., 2019;Alam et al., 2018) However, lots of polar chemicals, such as aldehydes, ketones, acids, and amides, overlap in the GCxGC chromatogram as shown in **Fig. 2**, which can hardly be distinguished by GC-MS, especially those with a minor amount. Hence, a powerful separation tool like GCxGC combined with a systematic qualitative procedure is critical for the analysis of cooking fumes. As gaseous organics distribute between C6~C20, indicating a full cover of gaseous cooking fumes (less volatile than hexanes) was obtained by our TD-GCxGC-MS method. And 170 organics of 8 group sets and 17 classes, which occupy 95% of the total ion current for gaseous cooking fumes (except for the blooding of Tenax-TA shown in Figure S1) were identified and quantified.

The total concentration of gaseous organics was 2414.3 μg/m^3. Different from vehicle emissions, only 19.1% of the total gaseous cooking fumes were hydrocarbons and the main constituent was alkanes (339.3 μg/m^3), which is comparable to the hydrocarbons emitted from Hunan cuisine (494.3 μg/m^3), Home cooking (487.2 μg/m^3) and Shandong cuisine (257.5 μg/m^3) but much lower than Barbecue (3494 μg/m^3).(Cheng et al., 2016) The predominant alkanes are ten times higher than aromatics and they are mainly VOCs ($C^* > 3.2 \times 10^6$ μg/m^3). To be noticed, though only three compounds were identified in alkenes, D-limonene with a concentration of 11.6 μg/m^3 in corn oil sample was only found in several vegetable oils (it will be discussed in other work), which might be a tracer for the use of cooking oil and could be further applied as a parameter for the estimation of cooking emission as oil was reported to be a key influence factor.

Similar to the results obtained from PTR-ToF-MS (fried chicken using sunflower oil) and GC-MS (canola oil heated at 180°C), aldehydes including both olefinic aldehydes (20.2%) and saturated aldehydes (10.6%), mainly generated from the hydrolysis of fatty acids in foods and oil, were the main organics in cooking fumes. (Liu et al., 2018;Klein et al., 2016a;Klein et al., 2016b;Schauer et al., 2002;Fullana et al., 2004a, b)But a ratio of acids to aldehydes (0.938) in our work comparable to GC-MS (0.991) but much higher than PTR-ToF-MS (0.045) was detected.(Klein et al., 2016b;Fullana et al., 2004a) The relatively poor protonation and ionization

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Preprint. Discussion started: 13 May 2022

capability of acids might lead to the inaccurate quantification of acids by PTR-ToF-MS. Ketones, which cannot be clarified with aldehydes by PTR-ToF-MS, took up 3.8% of the total gaseous cooking fume, which is similar to that from fried vegetables (4.5%) by GC-MS. (Fullana et al., 2004a)As short-chain aldehydes and acids are the products of the pyrolysis and oxidation of triglycerides in oil, their concentrations are influenced by the oil and cooking temperature. The concentration of relative aldehydes distribute as the sequence of alkenals (41%), alkanals (28%) and alkadienals (28%), which is coincident with fact that oleic acid was much lower than linoleic acid and palmitic acid in particulate samples. Hence, the relative intensity of aldehydes combined with the distribution of the fatty acids in oil and particulate samples might be an indicator for the influence of cooking conditions on the cooking fumes emission.

Other oxygenated compounds, such as alkanols and ethers, and N-compounds were not detected by GC-MS before. But the percentage for other oxygenated compounds and N-compounds in our work (14.8% and 1.5%) were also comparable to that of PTR-ToF-MS (11.5% and <3%). (Klein et al., 2016b)With limited measurements for these compounds, they are seldomly discussed in the analysis of cooking emissions and their generation and transformation are still unclear compared to carbonyls and acids. The identification and quantification by our methods offer a tool for further research on such compounds, especially for the relatively high 1-octen-3ol (58.9 μg/m^3), 1-pentanol (47.1 μg/m^3), 2,4-dimethyl cyclohexanol (29.9 μg/m^3), 3,4-dimethycyclohexanol (23.8 μg/m^3) and 1-nitropetane (19.2 μg/m^3), etc.

As the distributions and amounts show a good agreement with the work by other methods, our work with TD-GCxGC-MS largely extends the measurement range of GC-MS and makes up the weakness of PTR-ToF-MS on the identification of isomers. While TD-GCxGC-MS help PTR-ToF-MS to identify more compounds and provide accumulated concentrations of organics, PTR-ToF-MS provides more dynamic information during cooking. Simultaneous quantification of a wider range of gaseous organics by GCxGC-MS can help build a more comprehensive cooking emission inventory to better estimate the SOA formation. In addition, the precise quantification provides powerful messages for PTR-ToF-MS to identify isomers, pick up tracers for gaseous cooking fumes and observe their fromation and transformation in the gas phase. And we can further focus on the effects of cooking conditions on the generation of such organics and their contribution to the SOA formation. Thus, TD-GCxGC-MS is a powerful tool for the analysis of complex gaseous cooking fumes with lots of polar compounds.

352 compounds of a full range from acetic acid (C2) to aqualenes (C30) were detected in particulate samples. Though 90% of the total ion current for particulate cooking fumes were identified and quantified, it was an incomplete detection occupying 5~10% of the total organics as most organics in particulate sample are non-volatile compounds. Compared to the gaseous sample, a wider distribution of volatility and polarity was observed in particulate sample and the percentage of S/IVOCs with relatively lower volatility ($C^* < 3.2 \times 10^6$ μg/m^3) was higher. Due to the extremely large concentration of fatty acids, other compounds, though with a large number, took only a small proportion.

Fatty acids including alkanoic acids and alkenoic acids are predominant in fumes emitted from fried chicken, accounting for 82.6% of the total quantified particulate organics. This is consistent with our previous work on western-style fast food cooking (78%) and Chinese cooking (73~85%).(Zhao et al., 2007b, a)Linoleic acid (37.9%), palmitic acid (29.1%), and oleic acid (2.94%), which are the main fatty acids in corn oil, were also the most abundant organics in particulate fumes. However, a typical composition and chemical constant show that the ratio for linoleic acid, palmitic acid, and oleic acid is 57.0 : 27.5 : 12.2.(Kuang) This reverse of saturated fatty acids to unsaturated fatty acids in particulate samples and oil might be caused by the relative more active C=C bond in linoleic acid and oleic acid during frying chickens. Meanwhile, a higher percentage of olefinic aldehydes from the pyrolysis of unsaturated fatty acids was also observed in gaseous samples.

Besides acids, a high percentage of cholesterols (9.38%), the principal sterol synthesized by all animals, were detected, indicating that chickens are consumed during deep-frying. Sugars with several hydroxyl groups, which could hardly be detected by GC-MS, were observed with a proportion of 0.01% in our experiments. The amounts might be underestimated by our semi-quantification using n-alkanes as surrogates, as sugars bind stronger with columns and have weaker MS responses than n-alkanes. Sugars are supposed to be generated from the pyrolysis of starch coated on chicken. Other oxygenated compounds such as alkanols and phenols were also detected in particulate sample with a percentage of 1.30%. The unexpected detection of chemicals correlated with foods being cooked proves that the TD-GCxGC-MS method can be applied to analyze the detailed mutual reaction of oils, foods, and additives during cooking.

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Hydrocarbons took up only 1.53% of the total identified organics, but an odd-to-even carbon preference at the carbon number of n-alkanes above C20 was observed. This is also correlated with the vegetable oil used. Squalene (130.3 μg/m^3), an intermediate metabolite in the synthesis of cholesterol, also proves the consuming of chickens. The toxic PAHs were found minor in the particulate samples, especially the 3-rings and 4-rings aromatics were identified but with a concentration far below the low level of our standards, which cannot be quantified properly. It indicates that a targeted MS/MS method is more proper for the quantification of PAHs.(Chen et al., 2019)

The most abundant aldehydes in gaseous organics shared only a small proportion (0.13%) in particulate samples. In contrast, the content of ketones (0.78) and N-compounds (1.02%) increased. The reverse might be ascribed to the aqueous Maillard reaction between carbonyls and amines in cooking emitting particles of high heat and humidity, which exhibits a faster rate for aldehydes to ketones and generates N-compounds (imines).(Wong et al., 2019;Yang et al., 2022) 56 Esters and 55 amides, which were generated from esterification and amidation of fatty acids, occupied 0.42% and 2.38% of the total identified mass. The observation of N-compounds, amides, and esters, which were found minor in gas phase, also provides evidence on the possible aqueous reaction pathway in particulate phase and TD-GCxGC-MS might be a powerful tool to deduce the transformation of carbonyls and acids into aerosols.

Compared to the previous GC-MS method, our TD-GCxGC-MS method detects hundreds more compounds. Although the identified total mass increased only a little due to the extremely high amounts of fatty acids, previously not noticed amides and N-compounds might help reveal the transformation of carbonyls and acids towards secondary organic aerosols in the particulate phase. Moreover, the thermal desorption instrument desorbs organics on filters directly, which eliminates the complex and toxic extraction procedure and decreases the loss of samples. The consistent injection mode for both gaseous and particulate samples also simplifies the identification and quantification of all samples, realizing the synchronous measurements of gaseous and particulate organics.

6. Conclusion

For the analysis of cooking fumes with wide volatility and polarity, we offered a TD-GCxGC-MS method to realize the synchronous measurements of gaseous and particulate organics without further post-processing after sampling. With a systematic 4-step qualitative procedure and precise quantitative and semi-quantitative method, 170 and 352 compounds from C2 (acetic acid) - C30 (squalene) occupying 95% and 90% of the total ion current for gaseous and particulate samples were identified and quantified. The composition and proportion of both samples showed consistency with the results from other methods such as GC-MS and PTR-ToF-MS. However, TD-GCxGC-MS fully identified organics from cooking fumes, which might find new tracers and reveal an unknown process. The dominant gaseous organics were acids and aldehydes while particulate ones were fatty acids. Besides, oil, food, and additives correlating compounds were unexpectedly observed, indicating that TD-GCxGC-MS has a unique advantage in the analysis of cooking fumes. Moreover, numerous N-compounds, esters, and amides were identified in particulate samples, providing a powerful tool to deduce the transformation of carbonyls and acids towards secondary organic aerosols. Hence, with the strong resolving capability, TD-GCxGC-MS provides plenty of perspectives for the analysis of cooking fumes.

Acknowledgments

The work was funded by National Natural Science Foundation of China (No. 41977179, 91844301), the special fund of State Key Joint Labotatory of Environment Simulation and Pollution Control (No. 22Y01SSPCP). We greatly thank Mengxue Tong for the sample collection.

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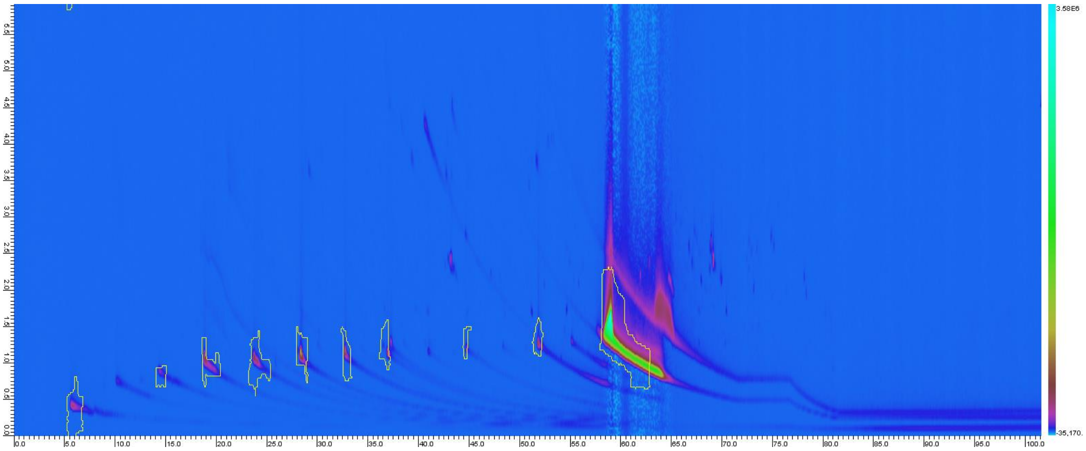
Figures Caption

Figure 1. Chromatographic behaviors of n-alkanoic acid in the GCxGC chromatograms. (SIC of m/z 60 of the particulate sample)

Figure 2. GCxGC chromatogram of gaseous organics emitting from fried chicken fumes.

Figure 3. GCxGC chromatogram of particulate organics emitting from fried chicken fumes.



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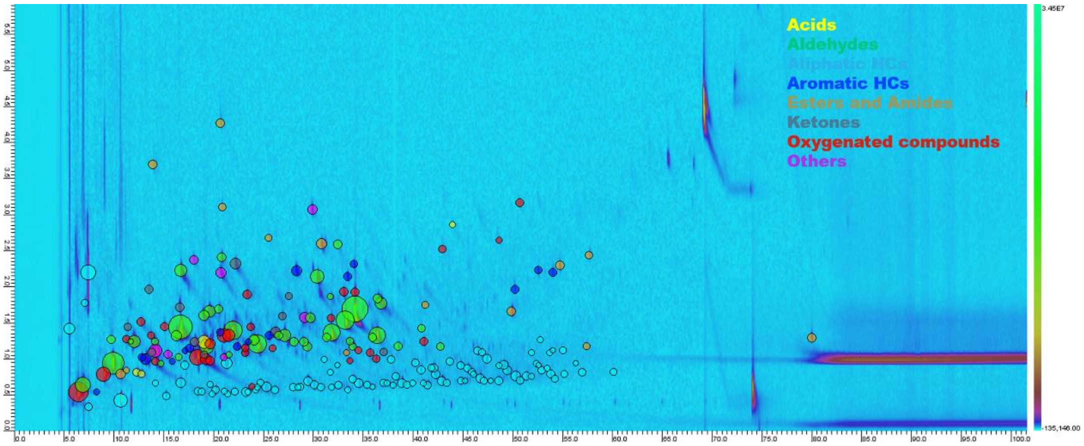

Figure 2. GCxGC chromatogram of gaseous organics emitting from fried chicken fumes.

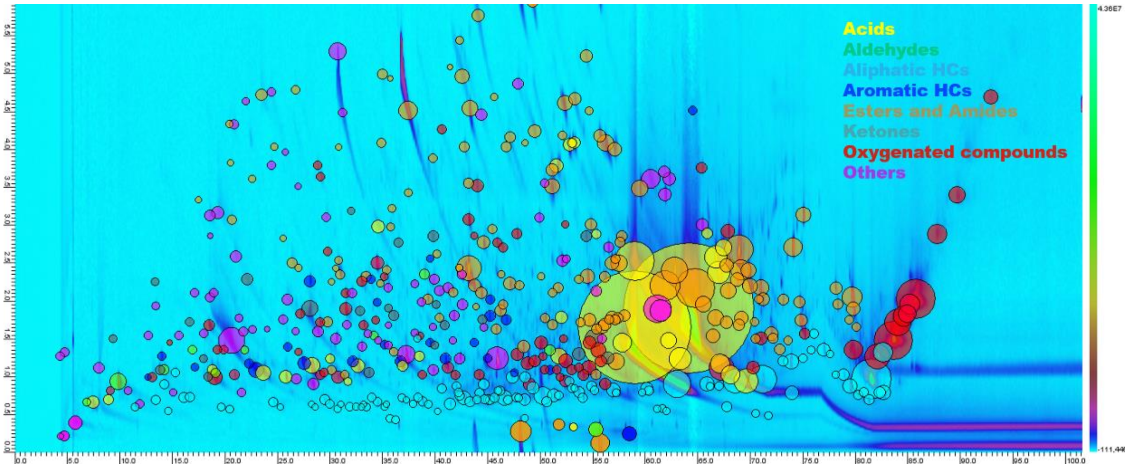

Figure 3. GCxGC chromatogram of particulate organics emitting from fried chicken fumes.

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Tables

Table 1. Concentrations and percentage mass contribution of gaseous organics emitting from fried chicken in groups.

Table 2. Concentrations and percentage mass contribution of particulate organics emitting from fried chicken in groups.

Table 1. Concentrations and percentage mass contribution of gaseous organics emitting from fried chicken in groups.

Group set	**Class**	**Number of compounds**	**Concentration ($\mu g/m^3$)**	**Percentage%**
acids	alkanoic acids	26	696.85	28.9%
aldehydes	olefinic aldehydes	4	486.75	20.2%
	saturated aldehydes	10	256.97	10.6%
Aliphatic hydrocarbons	alkanes	18	339.31	14.1%
	alkenes	3	62.17	2.6%
	alkynes	7	19.85	0.8%
Aromatic hydrocarbons	aromatics	10	33.20	1.4%
	PAHs	15	6.72	0.3%
esters and amides	esters	5	16.58	0.7%
ketones	olefinic ketones	22	60.88	2.5%
	saturated ketones	6	30.95	1.3%
others	N-compounds	3	36.13	1.5%
	others	14	11.91	0.5%
oxygenated compounds	alkanols	3	223.95	9.3%
	alkenols	15	65.59	2.7%
	oxygenated compounds	7	66.47	2.8%

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541 **Table 2.** Concentrations and percentage mass contribution of particulate organics emitting from fried
542 chicken in groups.

Group set	**Class**	**Number of compounds**	**Concentration (μg/m^3)**	**Percentage%**
acids	alkanoic acids	49	10549.49	36.17%
	alkenoic acids	13	13541.20	46.43%
aldehydes	olefinic aldehydes	17	12.06	0.04%
	saturated aldehydes	16	24.81	0.09%
Aliphatic hydrocarbons	alkanes	15	198.84	0.68%
	alkenes	6	182.21	0.62%
	alkynes	3	4.21	0.01%
Aromatic hydrocarbons	aromatics	20	51.31	0.18%
	PAHs	7	8.79	0.03%
esters and amides	esters	56	122.80	0.42%
	olefinic amides	51	337.72	1.16%
	saturated amides	4	354.93	1.22%
ketones	olefinic ketones	14	60.76	0.21%
	saturated ketones	7	166.98	0.57%
others	N-compounds	10	296.98	1.02%
	others	6	137.71	0.47%
oxygenated compounds	alkanols	4	165.63	0.57%
	alkenols	4	89.74	0.31%
	cholesterols	5	2734.75	9.38%
	oxygenated compounds	26	111.00	0.38%
	phenols	16	11.79	0.04%
	sugars	3	3.36	0.01%

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