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Characterisation of Gas Phase Organic Emissions from Hot Cooking Oil in Commercial Kitchens

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Key Words

Cooking oil · Kitchens · Organic emissions · Gas chromatography/mass spectrometry

Abstract

A large quantity of oily fumes is generated in fast food and Chinese restaurants from cooking oil kept at a high temperature in the kitchens. If these oily fumes are not properly abated, they can be a major source of organic emissions in some dense urban areas with a lot of restaurants such as found in Hong Kong. In the present study, the most commonly used cooking oil, peanut oil, was kept at 260°C in an environment typical of a commercial kitchen that consisted of a two-burner stir-frying cooking range, a single-tank electric fryer, a baffle-type grease extractor and an exhaust duct. Air samples were collected at the inlet of the grease extractor and the exit of the exhaust duct. Organic material was extracted from these samples and examined by gas chromatography and gas chromatography/mass spectrometry. A new extraction protocol using a Soxhlet apparatus and freshly distilled chloroform as the solvent was established in this study. It was noticed that there was no appreciable breakdown of the oil composition at the temperature studied. The efficiency of the grease extractor was determined by obtaining the relative concentrations of gas phase organic composites at the sampling positions.

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Introduction

In a heavily urbanised city such as Hong Kong, thousands of tons of air pollutants are released into the atmosphere from different sources every year. Zhang et al. [1] studied the non-volatile organic compounds in the aerosols of Hong Kong. They collected air samples during the winter months of 1993 and analysed the samples by flash column chromatography. Their results showed that mobile combustion sources constituted 39-63% of all nonvolatile solvent-extractable organic materials and that the contribution of emissions from kitchens was also significant. Chiang et al. [2] studied the oily fumes released from heated cooking oils in Taiwanese kitchens. They reported particulates of volatile emissions from lard (at 200 and 300°C) and soybean oil (at 300°C) to be mutagenic in the Salmonella/microsomal test with S9 Mix, indicating that exposure of Taiwanese women to oily fumes may be an important risk factor for lung cancer. Chiang et al. [3] subsequently extracted aromatic amines from oily fume samples and analysed them for mutagenicity in the Salmonella/microsomal test as above. Their results indicated that exposure to oily fumes in Taiwan might be an important but controllable risk factor for bladder cancer. In the USA, Rogge et al. [4], Schauer et al. [5], Gray [6], and Hildemann et al. [7] studied fine organic aerosols in urban areas. Rogge et al. [4] reported that meat cooking operations were a major source of organic aerosol emissions

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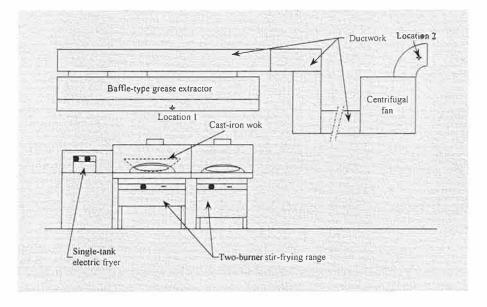


Fig. 1. The layout of a commercial kitchen.

comprising up to 21% of the primary fine organic carbon particle emissions in the Los Angeles area in the 1980s. A study [8] was recently commissioned by the US Environmental Protection Agency through the Clean Air Technology Center and the US-Mexico Border Information Center on Air Pollution to establish an emissions inventory for air pollutants from the grilling of beef and chicken on cooking devices used by street vendors. The study involved quantification of the performance of a simple aluminium mesh screen filter installed in the exhaust ductwork to remove pollutants from the cooking process. It was found that emissions of total particulate matter, total volatile organic compounds, total semi-volatile organic compounds and total hydrocarbons were basically the result of cooking meat, and that the simple screen device could substantially remove these pollutants.

In the present study, the chemical composition of gas phase organic emissions from hot cooking oil was examined. The organic components in the air samples collected were extracted in a Soxhlet apparatus using freshly distilled chloroform as the solvent for 12 h. Each extract was concentrated to 1 ml volume and was derivatised by transesterification into its methyl ester using methanol with acetyl chloride as a catalyst. The processed extracts were then examined by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). The removal efficiency of the grease extractor for gas phase organic emissions was determined by obtaining the relative concentrations of the organic compounds at the sampling positions.

Methods

Selection of Cooking Oil

The chemical composition of the organic compounds emitted from a kitchen depends on the oil used in cooking and how it reacts with meats, vegetables and sauces. In the past, animal fats (oils) were the most popular kind of cooking oil because they were easily obtained from the fresh, fatty tissue of slaughtered animals and were thus relatively cheap. However, animal fats such as lard, which is rendered from the fatty tissue of pigs, contain a relatively high concentration of cholesterol and have consequently become less popular as people have become more health conscious. Nowadays, most fast food and Chinese restaurants use peanut oil for cooking. Peanut oil contains 36-40% tri-unsaturated, 47-52% di-unsaturated and 7-11% mono-unsaturated glycerides. In terms of fatty acid composition, peanut oil contains 10-13 g C₁₆ saturated, 1.5-4 g C₁₈ saturated, 35-42 g C_{18:1} unsaturated, 39-44 g C_{18:2} unsaturated and 3-4 g C₂₂ saturated fatty acids per 100 g of oil.

Testing Procedure

A commercial-scale kitchen was used to conduct the hot cooking oil experiments. As shown in figure 1, the kitchen was equipped with a two-burner stir-frying cooking range, a single-tank electric fryer, a baffle-type grease extractor and an exhaust duct. During the experiments, the environmental conditions, including temperature and air intake, were well controlled so that the ambient pollutants would not affect the outcome of the measurements.

A cast-iron Chinese wok was placed on the stir-frying cooking range and filled with 5.8 litres of peanut oil. The oil was heated for 10 min by a gas burner to 260° C, a temperature between its smoke and flash points, as indicated in table 1. The oil temperature was then kept at 260° C and monitored by a k-type thermocouple. It was found that a continuous stream of oily fume was emitted from hot surfaces during the experiments. The organic compounds emitted were forced into the ductwork at a steady rate by switching on a large centrifugal fan driven by an AC motor. Two sampling devices, Gilian air sam-

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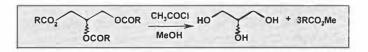
Table 1. Smoke, flash and fire points of cooking oils (extracted from Ullmann [10])

| | Free fatty acid % | Smoke point °C | Flash poiņt °C | Fire point °C |
|----------------|----------------------|-------------------|-------------------|------------------|
| Peanut oil | 0.09 | 207 | 315 | 342 |
| Peanut oil | 0.11 | 198 | 333 | 363 |
| Peanut oil | 1.00 | 160 | 290 | - |
| Cottonseed oil | 0.04 | 223 | 322 | 342 |
| Cottonseed oil | 0.18 | 185 | 318 | 357 |
| Soybean oil | 0.04 | 213 | 317 | 342 |
| Sunflower oil | 0.10 | 209 | 316 | 341 |
| Palm oil | 0.06 | 223 | 314 | 341 |

plers that were used to extract air samples into charcoal sorbent tubes at a rate of 2 1.min⁻¹ were positioned near the inlet of the grease extractor and the exit of the exhaust duct (locations 1 and 2, as shown in fig. 1). Charcoal sorbent tubes were used in the study because they were the best medium to capture the gas phase organic emission that was the focus of this study. The sampling period was set to 6 min to ensure that the amount of organic compounds in each sample was sufficient for chemical analysis. The velocities of air flowing through the opening of the grease extractor and the exhaust duct were measured by a Model KM6F22 (Kane-May Ltd., UK) precision flow meter at the start, during and at the end of each experiment to ensure isokinetic sampling. The temperature of the oily fumes was also measured using this precision dual-function flow meter. Air samples were collected at locations 1 and 2 and flow rate measurements repeated when the baffle-type grease extractor removed the organic components with circulating water plus detergent.

Gas Chromatography/Mass Spectrometry

A trial test was carried out before the main experiments to examine the degree to which tri-acylglycerides and di-acylglycerides would break down into simpler organic compounds during the heating process at a temperature of 260°C. An air sample was collected and extracted for 12 h in a Soxhlet apparatus using freshly distilled chloroform. The organic extract was concentrated and analysed by a Finnigan GCQ ion trap mass spectrometer using a 30-metre fused-silica DB5 capillary column (0.25 µm film thickness and 0.25 mm internal diameter) interfaced with an Incos data system. The GC oven was programmed for: (1) injection at 100°C, (2) isothermal hold at 100 °C for 5 min, (3) temperature ramp of 20 °C \cdot min $^{-1}$ for 2.5 min followed by isothermal hold at 150°C for 5 min, and (4) a temperature ramp of 20°C·min⁻¹ for another 5 min and then isothermal hold at 250°C for 20 min. This preliminary GC/MS analysis gave no observable peaks on the chromatogram (even after using a 24-hour hold period at high temperature) suggesting that the polarity of any organic compounds present was such that they were retained on the column. As a result, a new protocol was developed for the quantitative analysis of the samples. For each charcoal sorbent tube collected from the hot cooking oil experiments, extraction of organic composites was carried out in the Soxhlet apparatus using freshly distilled chloroform as the solvent for 12 h. After the extraction, the solution was concentrated to 1 ml and any fatty acids present were transesterified into their methyl esters using methanol with acetyl chloride as the catalyst:



The resulting reaction mixture was then analysed in a Hewlett-Packard Gas Chromatograph Series II 5890 with a flame ionisation detector under the oven conditions as above. This instrument was equipped with an injector (splitless mode) and a 30-metre fused-silica HP5 column (0.25 μ m film thickness and 0.25 mm internal diameter). The area of the peaks was used to calculate the amount of materials in the gas phase under different conditions. In order to identify the detailed chemical composition of the reaction mixture, further analyses were carried out using the Finnigan GCQ ion trap mass spectrometer with an electron impact ionisation energy of 70 eV. Mass fragmentograms of the major components were identified by using standard *n*-alkanoic acid methyl esters and confirmed by computer matches to a standard reference in the National Institute of Standards and Technology (NIST) library.

Results

The measured flow velocities through the opening of the grease extractor and the exhaust duct were 7 and $3.6 \text{ m} \cdot \text{s}^{-1}$ at locations 1 and 2, respectively. The calculated volume flow rate at both locations was $1.67 \text{ m}^3 \cdot \text{s}^{-1}$. However, it should be noted that the take-up rate of gas phase organic emission by the samplers would not be the same at the two locations because the flow velocities differed by about 50%. In order to determine the removal efficiency of the grease extractor, the second set of data was normalised by the baseline information obtained from the first set of air samples.

The organic components of the air samples, after extraction followed by transesterification, were found to contain several *n*-alkanoic acids as methyl esters by monitoring the total ion current. Figure 2 shows the mass chro-

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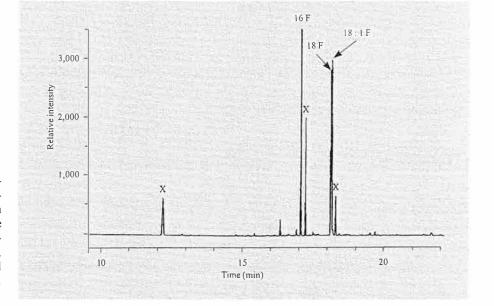


Fig. 2. Selected gas chromatogram of *n*-alkanoic acids as methyl esters at location 1. Figures on peaks refer to the carbon chain length of the homologous compounds; the letter F on peaks refers to compounds identified as methyl esters of *n*-alkanoic acids, e.g. 16 F = hexadecanoic (palmitic) acid methyl ester; 18:1 F = oleic acid methyl ester; X refers to unidentified compounds.

Table 2. The integrated area of the peaks

 obtained from the gas-chromatographic

 analyses at locations 1 and 2

| Set No. ¹ | Location | Relative area under the following peaks (organic compounds) | | | Total area under the 3 major peaks |
|-------------------------|----------|--|-------------------------------|----------------------------|---------------------------------------|
| | | C ₁₆ fatty acid | C ₁₈ fatty acid | 9,12-octadeca- dienoate | |
| 1 | 1 | 3,558 | 2,836 | 2,979 | 9,376 |
| | 2 | 4,071 | 3,525 | 3,708 | 11,304 |
| 2 | 1 | 6,078 | 5,381 | 5,752 | 17,211 |
| | 2 | 1,946 | 1,756 | 1,811 | 5,513 |

¹ Set 1 was obtained when the grease extractor was switched off, set 2 when the grease extractor was switched on.

matogram from a sample collected at location 1. Several of the chromatographic peaks eluting at retention times between 17 and 19 min were identified. Compound identification was performed by using standard *n*-alkanoic acid methyl esters and with the help of the NIST library, to make comparisons with mass fragmentation patterns of standard reference compounds. From those compound identifications, the major organic compounds were found to be the methyl esters of palmitic acid (C_{16}), linoleic acid (C_{18}) and oleic acid (C_{18}). These fatty acids derive from the tri-acylglycerides and di-acylglycerides of peanut oil. This also shows that there was no appreciable breakdown

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of the fatty acid components of the peanut oil glycerides at a temperature of 260°C.

The removal efficiency of the baffle-type grease extractor was calculated by comparing the area of integration of the peaks obtained from chromatographs at locations 1 and 2 as shown in table 2. It was found that the extractor's removal efficiency for gas phase organic emission was 73%, which is slightly higher than the estimated removal efficiency of around 60% of air-borne mass reported elsewhere [9]. It should be noted that the calculated removal efficiency is only applicable to gas phase organic emission. The organic particulate matter and those organic compos-

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ites attached to solid particulate matter were not included. It should also be noted that the size/mass distribution of the oily fumes, i.e. particulate matter versus gas phase organic emission, is complex and strongly depends on the cooking temperature and how the cooking oil reacts with other food substances. Further investigation into these topics is being carried out.

Discussion

The results in this paper represent the first part of a long-term study of the organic emissions in a Chinese cooking environment. The results provide a baseline inventory of the composition of oily fumes released from hot cooking oil. In the next stage of our study we will look into organic emissions from other food substances commonly used in Chinese cooking. The measurement protocol developed in this study will also be employed in the next stage of our analysis.

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