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Determination of Polycyclic Aromatic Hydrocarbons in Fumes from Fried Chicken Legs

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The amount and variety of polycyclic aromatic hydrocarbons (PAHs) in fumes during frying of chicken legs in edible oils were determined using a modified smoke collection device and a GC-MS technique. Chicken legs were fried in soybean oil, canola oil, or sunflower oil at 163 °C for 1−4 h. Results showed that most smoke (99%) was collected in the condensation apparatus, whereas the rest (1%) was adsorbed onto adsorption wool. A large proportion of PAHs in the smoke were detected in adsorption wool, whereas a small portion was found in the condensation apparatus. Canola oil generated the largest content (500.9 g for a frying time of 4 h) of smoke, followed by soybean oil, and sunflower oil. A similar trend was observed for PAH formation in fumes, with the exception that soybean oil produced a higher level than canola oil.

KEYWORDS: Fume; polycyclic aromatic hydrocarbon; edible oil; frying; GC-MS

INTRODUCTION

Epidemiological study has shown that lung cancer ranked first among female cancers in Taiwan and China (*1*−*3*). One of the major factors has been attributed to the smoke produced in the kitchen during cooking (*4*−*6*). It has been well documented that the smoke contained many mutagenic and carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs) and lipid degradation products (*6*−*9*).

Teschke et al. (*7*) reported that the nitro-containing PAHs were detected in kitchen air. Vainiotalo and Matveinen (*10*) also found that several carcinogenic compounds such as naphthalene were present in restaurant air. A large amount of benzo[*a*]pyrene and dibenzo[*a*,*h*]anthracene was formed in the fumes when soybean oil was heated at 265 °C for 2−4 h (*8*). In addition, the highly carcinogenic benzo[*a*] anthracene, benzo[*a*]pyrene, and dibenzo[*a*,*h*]anthracene were also detected in the smoke when lard, soybean oil, and peanut oil were heated at 250 °C for 30 min (*6*).

The composition and amount of PAHs in fumes could be affected by many factors such as variety of foods, smoke collection device, analytical technique, and heating time and temperature (*9*). However, little is known regarding PAH formation in fumes from foods cooked in a variety of edible oils. Most authors used filter paper for collection of smoke (*4*, *6*, *8*, *10*, *11*), which may decrease adsorption efficiency because a large volume of steam produced during the frying of food may interfere with the adsorption of fumes. Thus, in this study we tried to develop a new smoke collection device for maximum adsorption of smoke by incorporating both adsorption wool and glass beads instead of filter paper. Also, the positive identification of PAHs in the smoke should be carried out using a more advanced technique such as GC-MS. The objectives of this study were to modify the current smoke collection methods and use a GC-MS technique for the determination of PAHs in fumes during the frying of chicken legs in soybean oil, sunflower oil, and canola oil.

MATERIALS AND METHODS

Materials. Soybean oil was purchased from Chia-Hsing Food Co. (Taichung, Taiwan), sunflower oil was from President Co. (Tainan, Taiwan), and canola oil was from Tung-Mau Co. (Yuanlin, Taiwan). Chicken legs were bought from a local supermarket in Taipei. Flavoring powder, composed of modified starch, gum, spicy powder, and vegetable powder, was from Yuan-Yil Co. (Taoyuan, Taiwan). Flavoring liquid was made by mixing flavoring powder and water at a ratio of 1:10. A batter composed of flour, salt, and gum was made by mixing flavoring powder and water at a ratio of 1:4. Glass beads were obtained from Jeng-Mei Co. (Taipei, Taiwan). Adsorption wool, a polypropylene ester type of adsorbent, was from Taiwan Filter Technology Co. (Taipei, Taiwan).

Frying and Adsorption Apparatus. The frying and adsorption device (**Figure 1**) consisted of four parts: (A) frying tank and cover; (B) condensation apparatus and a glass bottle containing 600 g of round glass beads with a diameter of ∼0.4 cm each and a cooling tube; (C) vacuum pump; and (D) cooler. Six liters of oil with or without chicken legs was poured into the frying tank, which was closed tightly with a cover. The inner surface of the cover was filled with adsorption wool (32 × 30 cm). One temperature detection hole and four smoke-out holes were on the surface of the cover. For the condensation apparatus, a smoke inlet was connected to the cover of the frying tank and guided to the bottom using PVC tubes, whereas an air outlet was connected to a vacuum pump. A 1-L glass bottle containing beads was immersed in circulating water (3 ± 2 °C) in the tank. The aspiration rate was 15

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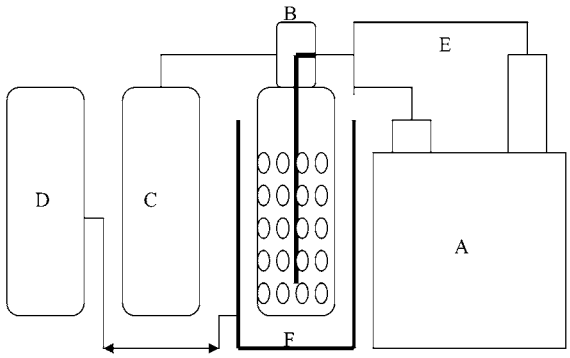

Figure 1. Frying and adsorption apparatus: (A) frying tank and cover; (B) condensation apparatus containing a glass bottle and a cooling tube; (C) vacuum pump; (D) cooler; (E) PVC tube connecting the cover and cooling tube; (F) tank containing ice water.

L/min. The adsorption wool and glass bottle were replaced every 2 h to maintain the efficiency of adsorption of the smoke. The smoke was collected and concentrations were calculated using the following steps: (1) The adsorption wool was cut into small pieces of ~1 cm square each, divided into two portions, and placed into two extraction thimbles (45 × 150 mm) separately and then refluxed with 300 mL of acetone for 20 h using two Soxhlet extractors. The extracts were combined and concentrated to 1 mL. After evaporation to almost dryness, the residue was dissolved in 10 mL of acetone. The solution was transferred to a brown vial and stored at −70 °C for GC-MS analysis of PAHs. The amount of smoke adsorbed onto the adsorption wool was calculated by the weight difference of the wool before and after heating or frying for 1, 2, and 4 h. (2) The smoke condensate was collected by pouring both the liquid in the glass bottle and glass beads into a Büchner funnel connected to a filtration flask. After 1 min of suction, the total amount of condensate was calculated on the basis of the weight difference of the flask. One hundred grams of condensate was collected and concentrated to 1.0 mL. After evaporation to almost dryness with nitrogen, the residue was dissolved in 2 mL of acetone. The solution was transferred to a brown vial and stored at −70 °C for GC-MS analysis of PAHs. (3) The smoke adsorbed onto the glass beads was calculated as the weight of residual liquid on the glass beads, which was obtained by subtracting the total amount of condensate from the weight of the beads-containing glass bottle gained after heating or frying for 1, 2, or 4 h. The glass beads were placed in a flask containing 250 mL of acetone and sonicated for 60 min, after which the solution was concentrated to 1.0 mL and evaporated to almost dryness with nitrogen. The residue was then dissolved in 2 mL of acetone and transferred to a brown vial for GC-MS analysis of PAHs.

A total of 420 chicken legs with an average weight of 160 ± 15 g was divided into six portions of 70 each. The proximate analysis of chicken legs was performed using an AOAC method (*12*). Initially 70 chicken legs were immersed in a flavoring liquid (12 L) for 12 h at refrigerated temperature. The flavoring liquid was made by mixing flavoring powder and water at a ratio of 1:10, whereas a batter was made by mixing flavoring powder and water at 1:4. Prior to frying, five chicken legs were immersed in the batter for ~2 s and then coated with powder. The chicken legs were then poured into a tank containing 6 L of oil and fried at 163 °C for 11 min, which is the standard processing condition for most fast-food restaurants. Chicken legs were selected as reference sample because they are a popular food commodity in Taiwan's market. After frying, chicken samples were collected and another five chicken legs were fried again after heating time of the oil reached 30 min with a temperature maintained at 163 °C. As five chicken legs were fried every 30 min, a total of 10, 20, and 40 chicken samples were used for heating times of 1, 2, and 4 h, respectively. Three edible oils, soybean oil, sunflower oil, and canola oil were used, and duplicate experiments were performed. For control treatment, soybean oil alone was heated following the same procedure as described above.

Reagent. Sixteen PAH standards and internal standard 2-methylphenanthrene (2-mpa) were obtained from Supelco Inc. (Bellefonte, PA). Chemicals including benzene, glacial acetic acid, TBA reagent, petroleum ether, sulfuric acid (98%), potassium iodide, chloroform, isopropyl alcohol, methanol, sodium hydroxide, boric acid, and soluble starch were from Merck Co. (Taipei, Taiwan). Solvent acetone used for GC-MS was of pesticide grade and was from Mallinckrodt Laboratory Chemicals (Phillipsburg, NJ).

Table 1. Q1 Ratio of 16 PAHs

PAH	target ion	qualifier ion	Q1 ratio
naphthalene	128.0	126.0	0.1340
acenaphthylene	152.0	150.0	0.0494
acenaphthene	154.0	154.0	0.0557
fluorene	166.0	165.0	0.0109
phenanthrene	178.0	176.0	0.0518
anthracene	178.0	176.0	0.0535
fluoranthene	202.0	200.0	0.0484
pyrene	202.0	200.0	0.0478
benz[*a*]anthracene	228.0	226.0	0.0379
chrysene	228.0	226.0	0.0346
benzo[*b*]fluoranthene	252.0	252.0	0.0436
benzo[*k*]fluoranthene	252.0	252.0	0.0451
benzo[*a*]pyrene	252.0	252.0	0.0430
dibenz[*a*,*h*]anthracene	278.0	276.0	0.0363
indeno[1,2,3-*cd*]pyrene	276.0	274.0	0.0490
benzo[*g*,*h*,*i*]perylene	276.0	274.0	0.0422

Table 2. Linear Equation and R^2 of the Calibration Curves of 16 PAHs

PAH	linear equation	R^2
naphthalene	$y = 1.6243x - 0.3331$	0.9863
acenaphthylene	$y = 1.8927x - 0.5482$	0.9855
acenaphthene	$y = 1.1379x - 0.2484$	0.9854
fluorene	$y = 1.3257x - 0.3551$	0.9858
phenanthrene	$y = 1.9749x - 0.4544$	0.9857
anthracene	$y = 2.0275x - 0.5152$	0.9847
fluoranthene	$y = 2.2586x - 0.5941$	0.9846
pyrene	$y = 2.3381x - 0.5957$	0.9961
benz[*a*]anthracene	$y = 2.2980x - 0.8633$	0.9896
chrysene	$y = 2.2844x - 0.6641$	0.9862
benzo[*b*]fluoranthene	$y = 2.3717x - 0.6794$	0.9909
benzo[*k*]fluoranthene	$y = 2.6838x - 0.6168$	0.9880
benzo[*a*]pyrene	$y = 2.4581x - 1.0114$	0.9894
indeno[1,2,3-*cd*]pyrene	$y = 1.1361x - 0.0672$	0.9916
dibenz[*a*,*h*]anthracene	$y = 2.0173x - 0.4847$	0.9927
benzo[*g*,*h*,*i*]perylene	$y = 1.2554x - 0.0835$	0.9936

Determination of Moisture, Crude Protein, Crude Fat, and Ash of Chicken Legs. The proximate analysis of chicken legs was performed using an AOAC method (*12*). The moisture, ash, crude fat, and crude protein contents of chicken legs were measured according to AOAC methods 950.14, 920.153, 985.15, and 992.15, respectively.

Determination of Peroxide Value, Acid Value, and TBARs in Edible Oil. The peroxide value (POV) and acid value of edible oils were measured according to AOAC methods 965.33 and 925.41, respectively (*12*). The value of TBARs was determined using a method described by Hoyland and Taylor (*13*).

Determination of Fatty Acid Composition in Food Lipids. The fatty acid composition in food lipids was analyzed on the basis of the method described by Lu et al. (*14*).

Determination of Extraction Recovery of PAHs. A PAH stock solution containing naphthalene (353 ppm), acenaphthylene (400 ppm), acenaphthene (310 ppm), fluorene (360 ppm), phenanthrene (316 ppm), anthracene (336 ppm), fluoranthene (382 ppm), pyrene (347 ppm), benzo[*a*]anthracene (308 ppm), chrysene (352 ppm), benzo[*b*]fluoranthene (200 ppm), benzo[*k*]fluoranthene (220 ppm), benzo[*a*]pyrene (336 ppm), dibenzo[*a*,*h*]anthracene (157 ppm), benzo[*g*,*h*,*i*]perylene (40 ppm), and indeno[1,2,3-*c*,*d*]pyrene (40 ppm) was prepared by dissolving an appropriate amount of each PAH in acetone. Two milliliters of PAH solution was mixed with adsorption wool (32 × 30 cm) in pieces and 600 g of glass beads separately, whereas 10 mL of PAH solution was mixed with 100 mL of water. Then the various PAHs were analyzed

Table 3. Composition of Chicken Legs before and after Battering

composition	fresh	after battering[a]
moisture (%)	72.71 ± 2.81	73.76 ± 2.09
crude fat (%)	7.16 ± 1.49	6.13 ± 0.66
crude protein (%)	20.09 ± 0.69	19.25 ± 0.61
ash (%)	0.80 ± 0.11	0.78 ± 0.10
carbohydrate (%)	0.04 ± 0.02	0.02 ± 0.01

[a] Mean ± standard deviation of triplicate analyses.

Table 4. Properties of Commercial Edible Oils during Frying of Chicken Legs

oil	heating time[a] (h)	chicken legs	AV[b] (mg of KOH/g of oil)	POV[b] (mequiv/kg of oil)	TBARs[b]
soybean	0	0	0.04 ± 0.02a[c]	1.03 ± 0.07a	10.60 ± 0.72a
	1	10	0.10 ± 0.02b	11.30 ± 1.25b	26.60 ± 1.25b
	2	20	0.12 ± 0.02b	15.93 ± 3.62c	28.70 ± 1.11b
	4	40	0.26 ± 0.04c	35.41 ± 4.81d	40.17 ± 1.68c
canola	0	0	0.05 ± 0.01a	1.83 ± 0.17a	11.23 ± 0.78a
	1	10	0.10 ± 0.01b	10.51 ± 0.52b	32.03 ± 3.12b
	2	20	0.12 ± 0.01b	14.66 ± 1.26c	35.00 ± 3.06b
	4	40	0.22 ± 0.01c	33.87 ± 0.96d	45.30 ± 2.52c
sunflower	0	0	0.07 ± 0.02a	1.04 ± 0.09a	12.00 ± 1.59a
	1	10	0.12 ± 0.01b	7.71 ± 0.48b	24.43 ± 2.00b
	2	20	0.13 ± 0.01b	19.37 ± 0.97c	29.13 ± 1.16c
	4	40	0.23 ± 0.02c	22.68 ± 1.50d	31.23 ± 0.25d

[a] Heating temperature was 163 °C. [b] Mean ± standard deviation of triplicate analyses. AV, acid value; POV, peroxide value; TBARs, thiobarbituric acid reactive substance. [c] Values within a column in the same oil followed by different letters are significantly different ($p < 0.05$).

by GC-MS using the same extraction procedure for adsorption wool, condensate, and glass beads as described above.

Determination of PAHs in the Smoke. A method described by Chen and Chen (*9*) was used to determine the various PAHs in the smoke. An HP 6890 gas chromatography system coupled with a model 5973 mass selective detector was used. An HP-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness) with an He carrier gas flow rate (1.0 mL/min) and a split ratio of 30:1 was used. The injector temperature was 290 °C, and the column temperature was programmed from 70 to 250 °C at 10 °C/min, then raised to 290 °C at 5 °C/min, and maintained at 290 °C for 10 min. The injection volume was 1.0 μL. The various PAHs were identified by comparing unknown peaks with reference standards and cochromatography with added standards. Also, a GC-MS/selected ion monitoring (SIM) mode was used to identify the unknown PAHs by comparing the Q1 ratio of unknown peaks with those of reference standards. The Q1 ratio was defined as the ratio of the area of the qualifier ion to that of the corresponding target ion (**Table 1**), and the value should be <20% for positive confirmation.

Each PAH was quantified using an internal standard. Five concentrations (5,10, 20, 40, and 100%) of PAH stock solutions and 20 μL of internal standard 2-mpa (50 ppm) were mixed. The standard curve of each PAH was prepared by plotting the abundance ratio of each PAH to 2-mpa against the concentration ratio. The regression equation and correlation coefficient (r^2) were calculated (**Table 2**). The PAH content (micrograms per gram) in the smoke was calculated using the following formula:

$$\text{PAH } (\mu\text{g/g of smoke}) = \frac{\frac{\text{A/RRF}}{A_i} \times W_i \times \text{volume} \times \text{dilution factor} \div \text{recovery}}{W_s}$$

RRF is the relative response factor $(A/A_i) \times (W/Wi)$, A is the peak area of PAH, A_i is the peak area of the internal standard, W_i is the concentration of internal standard (ppm), W_s is the weight of smoke (g), volume refers to 2 mL each for glass beads and condensate and 10 mL for adsorption wool, and the dilution factor is 1 for both adsorption wool and glass beads (the dilution factor of condensate is the weight of condensate gained after adsorption/100).

Statistical Analysis. Duplicate experiments were performed, and the various PAHs were analyzed twice. The data were subjected to analysis of variance and Duncan's multiple-range tests using SAS (*15*).

RESULTS AND DISCUSSION

Table 3 shows the basic composition of chicken legs before and after battering. On the basis of the mean value of triplicate analyses, the fresh chicken legs were found to contain 72.71% moisture, 7.16% crude fat, 20.09% crude protein, 0.8% ash, and 0.04% carbohydrate. Only minor differences were observed for the same composition of chicken legs after battering.

Table 4 shows the properties of three commercial edible oils during the frying of chicken legs. Initially low acid values (AV), peroxide values (POV), and thiobarbituric acid reactive substance (TBARs) values were present for all three oils. An increased trend was found for AV, POV, and TBARs along with increasing heating time for soybean oil, sunflower oil, and canola oil. However, there was no significant difference ($p > 0.05$) for AV and TBARs when soybean oil was heated for 1 or 2 h. In contrast, the sharp increase of POV indicated that a large amount of hydroperoxide was formed. As heating time reached 4 h, a pronounced increase of AV, POV, and TBARs occurred for soybean oil. This result implied that after prolonged heating, the quality of soybean oil deteriorated. Both sunflower oil and canola oil exhibited similar changes of AV, POV, and TBARs. However, with the same heating time (4 h), canola oil showed the largest increase of TBARs, followed by soybean oil and sunflower oil. This is probably because canola oil contained a much higher amount of linolenic acid (6.75%) and should be more susceptible to hydroperoxide degradation after extensive heating when compared to soybean oil (5.30%) or

Table 5. Yield of Smoke from Three Edible Oils during Heating and Frying

adsorption device	heating time (h)	smoke[a] (g)			
		soybean oil[b] (heating)	soybean oil[c] (frying)	sunflower oil[c] (frying)	canola oil[c] (frying)
wool	1	0.0099 ± 0.0014aA	0.9905 ± 0.0308aB[b]	0.9601 ± 0.0107aB	1.0791 ± 0.0112aB
	2	0.0299 ± 0.0024bA	2.0746 ± 0.0305bB	1.9640 ± 0.0106bB	2.2603 ± 0.0102bC
	4	0.0794 ± 0.0102cA	4.0444 ± 0.0484cC	3.7842 ± 0.0115cB	4.1914 ± 0.0124cD
glass beads	1	0.00	2.18 ± 0.14aA	2.14 ± 0.09aA	2.08 ± 0.08aA
	2	1.31 ± 0.12aA	2.33 ± 0.20aB	2.15 ± 0.18aB	2.20 ± 0.19aB
	4	3.03 ± 0.20bA	4.20 ± 0.13bB	4.15 ± 0.06bB	4.18 ± 0.18bB
condensate	1	ND[d]	144.13 ± 1.39aB	130.43 ± 2.28aA	135.50 ± 7.35aAB
	2	ND	227.87 ± 4.83bA	224.83 ± 5.87bA	245.00 ± 8.72bB
	4	ND	472.67 ± 8.36cB	437.16 ± 6.14cA	492.53 ± 6.67cC

[a] Mean ± standard deviation of duplicate analyses. Values a–c within a column or A–C within a row are significantly different ($p < 0.05$). [b] Only soybean oil was used for control treatment. [c] Chicken legs in edible oils were used. [d] Not detected.

Table 6. Extraction Recovery of 16 PAHs Spiked onto the Wool, Bead, and Condensate

PAH	recovery[a] (%)		
	wool	glass bead	condensate
naphthalene	92.79 ± 3.02	100.57 ± 8.05	92.04 ± 0.09
acenaphthylene	91.86 ± 2.08	98.62 ± 4.02	90.07 ± 0.04
acenaphthene	95.00 ± 1.21	95.61 ± 2.12	93.27 ± 0.23
fluorene	96.81 ± 3.01	97.64 ± 7.66	96.06 ± 0.06
phenanthrene	96.86 ± 2.18	98.35 ± 5.07	90.13 ± 0.04
anthracene	90.81 ± 2.73	96.67 ± 4.10	92.02 ± 0.11
fluoranthene	96.11 ± 1.17	100.02 ± 3.03	91.08 ± 0.03
pyrene	92.72 ± 4.23	93.57 ± 4.04	92.12 ± 0.03
benz[*a*]anthracene	90.52 ± 0.35	95.33 ± 2.04	92.13 ± 0.04
chysene	91.70 ± 1.63	94.21 ± 5.19	92.07 ± 0.04
benzo[*b*]fluoranthene	82.01 ± 10.13	88.72 ± 10.03	88.05 ± 0.07
benzo[*k*]fluoranthene	82.42 ± 10.05	85.69 ± 11.05	88.13 ± 0.04
benzo[*a*]pyrene	93.35 ± 1.07	100.33 ± 2.02	94.11 ± 0.01
dibenz[*a*,*h*]anthracene	92.48 ± 2.12	99.21 ± 1.13	94.08 ± 0.03
benzo[*g*,*h*,*i*]perylene	90.55 ± 2.47	90.56 ± 3.72	92.02 ± 0.11
indeno[1,2,3-*cd*]pyrene	90.35 ± 1.25	95.45 ± 2.15	92.97 ± 0.18
av	91.65	95.66	91.90

[a] Mean ± standard deviation of triplicate analyses.

sunflower oil (0.50%). For hydroperoxide formation, soybean oil increased more than canola oil, which could be attributed to a much higher content of linoleic acid for the former (54.85%) than the latter (19.85%). Liu and White (*16*) further demonstrated that the quality of frying oil correlated well to the amount of linolenic acid in the oil. **Table 5** shows the yield (grams) of smoke from the three edible oils during heating and frying. When soybean oil was heated alone, glass beads were found to contain a higher yield of smoke than wool. Interestingly, no smoke was detected in the condensate, revealing that most fumes were adsorbed onto glass beads in the absence of food sample. The amount of smoke formed followed an increased order for the increase of heating time. When chicken legs were fried in soybean oil, the smoke was generated at a much greater content than when soybean oil was heated alone. For instance, with a heating time of 2 h, small contents of 0.0299 and 1.31 g of smoke from soybean oil were found for adsorption wool and glass beads, respectively. On the contrary, with the same frying time, high yields of 2.0746 and 2.33 g of smoke were produced for adsorption wool and glass beads, respectively. Obviously the large volume of water (72.7%) and complex components of chicken legs would account for this phenomenon. In addition, most smoke generated during frying was collected in the condensate because of the production of a great level of steam during frying. For adsorption wool and condensate, canola oil produced the largest yield of smoke, followed by soybean oil and sunflower oil, when chicken legs were fried for 4 h. This result further demonstrated that linolenic acid played a more important role in smoke formation than linoleic acid or oleic acid. Nevertheless, this outcome seemed to be contradictory to a report by Chen and Chen (*9*), who found that soybean oil formed a slightly higher amount of smoke than canola oil when both were heated alone at 220 °C for 2 h. This could be explained by the difference in smoke collection device and heating with or without food commodity. A Rancimat oil stability analyzer was used as a model system for heating oil, and Tenax was used as adsorbent for adsorption of smoke by Chen and Chen (*9*), which are not applicable in our experiment because smoke formation accompanied by a large volume of steam during frying would substantially decrease the adsorption efficiency. In a similar study Wu and Yen (*11*) used filter paper to adsorb smoke and reported that canola oil generated a higher level of smoke than soybean oil or sunflower oil.

Table 6 shows the extraction recovery of 16 PAHs spiked onto the wool, glass beads, and condensate. Several authors have used cyclohexane to extract PAHs in the smoke (*10*, *17*). Other authors used acetone for extraction of PAHs (*4*, *6*, *8*); however, no recovery was reported. In this study we also used acetone to extract PAHs in the smoke and a high recovery was obtained. The average recoveries of 16 PAHs for wool, glass beads, and condensate were 91.65, 95.66, and 91.90%, respectively. The lowest recovery for adsorption wool is probably due to a long reflux time and high extraction temperature (65 °C), which in turn resulted in a significant loss of PAHs. Likewise, a low recovery was found for the condensate, which could be attributed to the long concentration time due to the presence of a large amount of water. No concentration step was applied to the glass beads, and thus a higher recovery was achieved.

Table 7 shows the PAH concentration (micrograms per gram of smoke) in the smoke from soybean oil during the frying of

Table 7. Concentration of PAHs in the Smoke from Soybean Oil during Frying

PAH	concn (μg/g of smoke) at heating time of								
	1 h			2 h			4 h		
	wool	beads	condensate	wool	bead	condensate	wool	beads	condensate
naphthalene	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND
acenaphthylene	22.93 ± 0.28	2.08 ± 1.32	0.20 ± 0.03	19.50 ± 0.47	2.89 ± 1.04	0.23 ± 0.03	20.24 ± 1.46	2.80 ± 0.61	0.24 ± 0.08
acenaphthene	74.24 ± 0.28	16.06 ± 1.32	0.62 ± 0.03	54.04 ± 0.47	20.03 ± 1.04	0.68 ± 0.03	43.94 ± 1.46	17.22 ± 0.61	0.53 ± 0.08
fluorene	65.68 ± 0.09	22.71 ± 0.99	0.58 ± 0.01	53.08 ± 1.35	24.81 ± 2.30	0.55 ± 0.06	47.31 ± 1.63	22.85 ± 1.13	0.53 ± 0.06
phenanthrene	75.86 ± 1.04	10.44 ± 1.82	0.61 ± 0.04	77.55 ± 1.52	14.76 ± 3.70	0.82 ± 0.02	70.30 ± 2.42	17.70 ± 1.44	0.75 ± 0.06
anthracene	51.51 ± 2.92	14.91 ± 1.65	0.41 ± 0.06	42.45 ± 1.47	19.46 ± 0.67	0.51 ± 0.02	43.94 ± 1.31	16.80 ± 2.79	0.58 ± 0.03
fluoranthene	86.50 ± 1.71	10.48 ± 1.87	0.47 ± 0.06	83.25 ± 1.45	18.40 ± 2.42	0.81 ± 0.03	79.20 ± 3.72	20.03 ± 1.21	0.52 ± 0.09
pyrene	83.35 ± 1.99	ND	0.54 ± 0.05	66.44 ± 1.19	16.77 ± 0.70	0.84 ± 0.02	63.98 ± 2.87	14.67 ± 1.11	0.62 ± 0.14
benz[*a*]anthracene	54.96 ± 1.69	5.96 ± 0.66	0.44 ± 0.07	46.38 ± 2.33	17.31 ± 0.66	0.61 ± 0.03	48.04 ± 3.90	21.35 ± 0.08	0.61 ± 0.06
chrysene	49.00 ± 1.61	2.98 ± 0.33	0.39 ± 0.14	43.42 ± 2.64	9.21 ± 0.27	0.55 ± 0.03	35.28 ± 1.76	10.86 ± 0.78	0.48 ± 0.02
benzo[*b*]fluoranthene	4.04 ± 1.28	ND	0.05 ± 0.01	3.54 ± 0.28	ND	0.05 ± 0.02	4.65 ± 0.62	0.86 ± 0.27	0.07 ± 0.02
benzo[*k*]fluoranthene	2.80 ± 0.29	ND	0.02 ± 0.01	2.55 ± 0.27	ND	0.05 ± 0.02	5.70 ± 0.97	0.47 ± 0.11	0.05 ± 0.02
benzo[*a*]pyrene	24.00 ± 0.30	ND	0.17 ± 0.02	17.17 ± 1.09	ND	0.22 ± 0.03	18.15 ± 1.80	5.26 ± 0.76	0.17 ± 0.01
indeno[1,2,3-*cd*]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
benzo[*g*,*h*,*i*]perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
dibenz[*a*,*h*]anthracene	23.44 ± 0.39	ND	0.18 ± 0.01	17.17 ± 3.83	5.72 ± 0.06	0.35 ± 0.03	31.49 ± 1.06	8.52 ± 160.44	0.36 ± 0.05
total	595.38	83.54	4.47	507.04	146.46	6.04	491.97	156.58	5.26

[a] Mean ± standard deviation of duplicate analyses. [b] Not detected.

Table 8. Concentration of PAHs in the Smoke from Sunflower Oil during Frying

	concn[a] (μg/g of smoke) at heating time of								
	1 h			2 h			4 h		
PAH	wool	beads	condensate	wool	beads	condensate	wool	beads	condensate
naphthalene	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND
acenaphthylene	21.57 ± 5.09	4.49 ± 0.38	0.22 ± 0.02	30.20 ± 2.69	9.51 ± 0.40	0.31 ± 0.09	24.55 ± 0.79	8.16 ± 1.94	0.25 ± 0.02
acenaphthene	22.60 ± 0.90	5.68 ± 0.55	0.18 ± 0.02	22.15 ± 0.16	11.91 ± 0.33	0.25 ± 0.05	19.66 ± 0.61	9.27 ± 0.14	0.22 ± 0.04
fluorene	13.08 ± 2.25	ND	0.12 ± 0.01	13.07 ± 0.71	2.44 ± 0.49	0.14 ± 0.06	11.25 ± 1.56	2.62 ± 0.10	0.15 ± 0.01
phenanthrene	59.54 ± 3.65	4.86 ± 0.40	0.54 ± 0.02	45.29 ± 1.18	10.93 ± 0.99	0.59 ± 0.12	39.71 ± 2.64	6.51 ± 0.69	0.37 ± 0.02
anthracene	44.10 ± 1.17	3.57 ± 0.23	0.42 ± 0.05	41.56 ± 3.19	5.93 ± 0.27	0.57 ± 0.02	50.67 ± 3.31	5.48 ± 0.88	0.47 ± 0.08
fluoranthene	25.01 ± 0.63	7.42 ± 0.27	0.23 ± 0.05	22.84 ± 1.62	15.00 ± 0.22	0.29 ± 0.02	23.16 ± 0.68	13.16 ± 0.12	0.27 ± 0.06
pyrene	69.56 ± 1.45	5.43 ± 1.07	0.53 ± 0.09	48.72 ± 3.15	10.49 ± 1.77	0.67 ± 0.04	30.20 ± 0.28	7.44 ± 0.20	0.35 ± 0.02
benz[*a*]anthracene	31.82 ± 0.58	3.97 ± 1.65	0.28 ± 0.06	38.02 ± 0.58	8.68 ± 0.52	0.38 ± 0.02	32.34 ± 3.53	9.08 ± 0.45	0.38 ± 0.04
chrysene	22.91 ± 2.57	3.50 ± 0.99	0.21 ± 0.06	28.14 ± 0.35	7.27 ± 0.72	0.31 ± 0.04	27.05 ± 2.90	5.40 ± 0.76	0.31 ± 0.01
benzo[*b*]fluoranthene	ND	ND	ND	9.31 ± 0.92	ND	0.09 ± 0.01	11.19 ± 1.42	0.28 ± 0.11	0.22 ± 0.01
benzo[*k*]fluoranthene	ND	ND	ND	12.44 ± 0.53	ND	0.11 ± 0.01	16.02 ± 0.40	1.45 ± 0.69	0.08 ± 0.01
benzo[*a*]pyrene	3.08 ± 2.07	ND	0.07 ± 0.03	6.84 ± 0.46	ND	0.09 ± 0.04	8.86 ± 0.13	2.00 ± 0.46	0.12 ± 0.02
indeno[1,2,3-*cd*]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
benzo[*g*,*h*,*i*]perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
dibenz[*a*,*h*]anthracene	12.71 ± 2.57	ND	0.14 ± 0.04	13.05 ± 0.60	6.69 ± 0.18	0.19 ± 0.02	14.77 ± 1.03	5.87 ± 1.24	0.16 ± 0.01
total	325.98	38.93	2.94	331.64	88.85	3.99	309.44	76.70	3.34

[a] Mean ± standard deviation of duplicate analyses. [b] Not detected.

Table 9. Concentration of PAHs in the Smoke from Canola Oil during Frying

	concn[a] (μg/g of smoke) at heating time of								
	1 h			2 h			4 h		
PAH	wool	beads	condensate	wool	beads	condensate	wool	beads	condensate
naphthalene	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND
acenaphthylene	20.62 ± 0.87	3.29 ± 1.44	0.19 ± 0.03	25.06 ± 0.50	7.25 ± 1.78	0.31 ± 0.02	42.35 ± 1.53	8.72 ± 1.45	0.44 ± 0.01
acenaphthene	44.27 ± 0.15	6.79 ± 0.66	0.39 ± 0.09	33.79 ± 1.36	10.08 ± 0.77	0.37 ± 0.09	40.42 ± 1.85	10.82 ± 0.15	0.36 ± 0.01
fluorene	54.65 ± 0.69	ND	0.53 ± 0.07	52.56 ± 1.29	ND	0.61 ± 0.07	41.80 ± 1.73	ND	0.42 ± 0.02
phenanthrene	44.68 ± 0.72	19.17 ± 1.47	0.43 ± 0.09	36.50 ± 0.88	20.26 ± 1.42	0.40 ± 0.07	38.54 ± 0.54	17.56 ± 0.12	0.36 ± 0.02
anthracene	46.38 ± 1.33	18.13 ± 2.37	0.51 ± 0.01	48.78 ± 0.95	26.29 ± 1.02	0.47 ± 0.03	43.78 ± 1.42	22.11 ± 0.74	0.46 ± 0.03
fluoranthene	43.82 ± 0.19	19.86 ± 0.95	0.39 ± 0.07	37.92 ± 1.32	26.78 ± 1.55	0.40 ± 0.05	36.68 ± 1.11	18.61 ± 1.28	0.37 ± 0.02
pyrene	57.66 ± 0.13	ND	0.55 ± 0.05	51.21 ± 0.21	ND	0.71 ± 0.07	48.90 ± 0.27	2.88 ± 0.21	0.45 ± 0.01
benz[*a*]anthracene	52.07 ± 0.69	7.11 ± 1.18	0.45 ± 0.14	38.08 ± 1.03	12.85 ± 0.12	0.38 ± 0.05	41.17 ± 1.87	9.62 ± 0.67	0.39 ± 0.03
chrysene	48.14 ± 0.63	ND	0.52 ± 0.10	47.06 ± 0.62	1.01 ± 0.05	0.18 ± 0.04	44.34 ± 0.47	1.36 ± 0.91	0.17 ± 0.05
benzo[*b*]fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND
benzo[*k*]fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND
benzo[*a*]pyrene	20.90 ± 0.26	2.47 ± 3.13	0.19 ± 0.06	15.54 ± 0.34	1.01 ± 0.06	0.17 ± 0.02	15.57 ± 1.60	3.07 ± 0.09	0.16 ± 0.02
indeno[1,2,3-*cd*]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
benzo[*g*,*h*,*i*]perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
dibenz[*a*,*h*]anthracene	20.90 ± 1.89		0.18 ± 0.03	18.71 ± 0.07	4.49 ± 0.07	0.26 ± 0.01	23.53 ± 1.40	6.26 ± 0.57	0.21 ± 0.02
total	454.08	76.83	4.33	405.21	110.03	4.26	417.09	101.00	3.78

[a] Mean ± standard deviation of duplicate analyses. [b] Not detected.

chicken legs. Adsorption wool was found to contain the highest content of PAHs, followed by glass beads and condensate. Unlike glass beads, the total amount of PAHs for adsorption wool and condensate did not show an increased order for the increase of heating time. This is probably because chicken legs contain a large volume of water, which could be evaporated to form steam that would then be adsorbed onto adsorption wool or condensed to form liquid during frying. The dilution effect of water would thus affect the PAH concentration. In addition, the weight variation of chicken legs may also cause this difference. With a frying time of 1 h, 13 PAHs were detected in both adsorption wool and condensate, whereas 8 PAHs were present on glass beads. The same trend was observed for frying times of 2 and 4 h, with the exception that 9 and 13 PAHs occurred for glass beads, respectively. It is apparent that after extensive heating, some more varieties of PAHs were formed and adsorbed onto glass beads.

For the three most carcinogenic PAHs, benzo[*a*]anthracene was present in highest level, followed by dibenzo[*a*,*h*]anthracene and benzo[*a*]pyrene. A similar result was reported by Li (*8*), who found that dibenzo[*a*,*h*]anthracene was formed at a larger amount than benzo[*a*]pyrene when soybean oil was heated at 265 °C for 2−4 h. However, in another study Chiang (*6*) reported that benzo[*a*]pyrene was produced at a higher content than benzo[*a*]anthracene and dibenzo[*a*,*h*]anthracene during heating of soybean oil at 250 °C for 30 min. As stated before, the amount and variety of PAHs generated in fumes could depend on many factors such as heating method, time and temperature, variety of edible oil, smoke collection device, and heating with or without food samples.

Chiang et al. (*6*) used a glass fiber filter paper and a vacuum pump to collect fumes from cooking oil. The same smoke collection device was also used by Qu et al. (*4*) and Wu et al. (*11*). However, this device may not be applicable to our study because chicken legs contain a high amount of water, which can form steam during frying and thus decrease the adsorption efficiency of filter paper. Therefore, in our experiment both adsorption wool and condensation apparatus were employed.

Tables 8 and **9** show the concentration (micrograms per gram of smoke) of PAHs in the smoke from sunflower oil and canola oil, respectively, during frying. A similar outcome was shown as in **Table 5**; that is, adsorption wool possessed the highest efficiency to adsorb smoke, followed by glass beads and condensate. However, the variety of PAHs formed was different from soybean oil. After 1 h of frying in sunflower oil, 11 PAHs were found for both adsorption wool and condensate, whereas 8 PAHs occurred for glass beads. With frying times of 2 and 4 h, 10 and 13 PAHs were present for glass beads, respectively, whereas 13 PAHs were found for both adsorption wool and condensate.

By comparison of the results shown above, a high proportion of total PAHs was adsorbed onto adsorption wool, which amounted to 75.3−87.1, 78.1−88.6, and 78.0−84.8%, respectively, for soybean oil, sunflower oil, and canola oil. Conversely, a low percentage of total PAHs was found for condensate, which ranged from 0.65 to 0.92%, from 0.80 to 0.86%, and from 0.72 to 0.82% for soybean oil, sunflower oil, and canola oil, respectively. For glass beads, the proportions of total PAHs were 12.2−23.9, 10.6−20.9, and 14.4−21.2%, respectively, for soybean oil, sunflower oil, and canola oil. Although most PAHs were adsorbed onto adsorption wool, the amount of PAHs in glass beads and condensate could not be ignored. Thus, both glass beads and condensate should be taken into consideration for smoke collection in order to avoid quantitation error of PAHs. In contrast to the result for smoke formation, soybean oil produced a higher level of PAHs than canola oil. This may be explained as follows: In addition to PAHs, it has been well established that the smoke contained many carcinogenic lipid degradation products such as 2-butene, *trans*,*trans*-2,4-decadienal, and benzaldehyde (*9*, *11*). It was postulated that *trans*,*trans*-2,4-decadienal may react with 2-butene to form 4-pentyl-2,3-dimethylbenzoic acid, which in turn results in the formation of PAHs such as 2,3-dimethyl-4-pentyl-1-carboxylnaphthalene through further reaction with 2-butene (*9*). As linoleic acid and linolenic acid were probable precursors for these lipid degradation products, soybean oil should be more susceptible to PAH formation than canola oil because the former is abundant in both fatty acids (*9*). Also, the presence of other toxic compounds in the smoke such as heterocyclic amines may cause this variation (*18*). It has been well documented that heterocyclic amines can be formed through heating of four precursors: amino acids, creatine, creatinine, and sugar (*19*). However, it is also possible that the lipid degradation products may facilitate the formation of pyridine or pyrazine compounds through Maillard reaction, which in turn results in the formation of heterocyclic amines (*20*). Further research is necessary to study the formation mechanism of PAH derivatives in the smoke.

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