

Formation of Polycyclic Aromatic Hydrocarbons during Processing of Duck Meat

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The effects of various processing methods, steaming, roasting, smoking, charcoal grilling, and liquid smoke flavoring (LSF), on the formation of polycyclic aromatic hydrocarbons (PAHs) in duck breast steak were studied. The various PAHs in the duck samples were analyzed by gas chromatography with ion-trap detection. Results showed that with processing time from 0.5 to 1.5 h, charcoal grilling of duck samples with skin contained the highest amount of total PAHs, followed by charcoal grilling of duck samples without skin, smoking, steaming, and LSF. For carcinogenic PAHs, smoking contained the highest amount, followed by charcoal grilling and roasting. No carcinogenic PAHs were observed for steaming and LSF-treated duck samples. Also, the highest amounts of both total and carcinogenic PAHs were found after smoking duck samples for 3 h.

Keywords: *Polycyclic aromatic hydrocarbons; formation; processing; duck meat; GC-MS*

INTRODUCTION

In today's world the environmental pollution has become a major problem for public health. Many pollutants are widely distributed in nature, of which polycyclic aromatic hydrocarbons (PAHs) represent an important class of such compounds because of their carcinogenicity, mutagenicity, and cytotoxicity (Josephson, 1981; Haugen et al., 1986; Davis et al., 1987; Pyysalo et al., 1987). Although more than one hundred PAHs were found in nature, only 16 were selected as "priority pollutants" according to the U.S. Environmental Protection Agency (EPA). Of these 16 PAHs, benzo[*a*]pyrene was reported to be the most carcinogenic (IARC, 1983, 1987). Also, it has been reported that PAHs containing four or more rings are more susceptible to inducing malignant tumors than those containing two or three rings (Grimmer, 1983). The formation of PAHs can be attributed to incomplete combustion of wood or gasoline, or food processing such as grilling and smoking. Although the exact mechanism of PAHs formation was not well understood, some authors postulated that they might be formed through free radical reaction, intramolecular addition or polymerization of small molecules (Pitts, 1983; Perez et al., 1986; U.S. EPA, 1987).

Many reports have demonstrated that carcinogenic PAHs can be formed through grilling and smoking of foods (Lijinsky and Ross, 1967; Doremire et al., 1979; Afolabi et al., 1983; Maga, 1986; Nico et al., 1987; Gomaa et al., 1993; Chen et al., 1996). The formation of various PAHs profiles during smoking can be dependent upon temperature, time, smoke composition, moisture content of wood and the presence of oxygen (Fretheim et al., 1980). More than 400 components have been isolated from smoke, including 48 acids, 22 alcohols, 131 carbonyl compounds, 22 esters, 46 furans, 16 lactones, 75 phenols, and 50 other compounds (Maga, 1988). Although the formation of phenolic compounds can have antioxidant activities, the formation of byproducts such as PAHs during smoking can also be detrimental to human health. To remedy this problem some processors used liquid smoke flavorings (LSF) instead to lower carcinogenic PAHs (Gomaa et al., 1993; Yabiku

et al., 1993). The advantages of using LSF are as follows (Pearson and Tauber, 1984): (1) during manufacture of LSF, the PAHs in the smoke can be removed by setting and filtration; (2) the LSF concentration can be properly controlled so that the quality of final product can be more uniform; (3) air pollution can be minimized because LSF was manufactured in the plant; (4) the capital cost of using LSF is lower than that of traditional wood smoking; (5) the utilization of LSF is very handy because meat can be either soaked or sprayed. It has also been reported that smoked meat products processed with LSF had smaller concentration of total PAHs than those processed with natural wood smoke (Simko et al., 1992; Gomaa et al., 1993).

In the past decade many methods have been developed to isolate, separate and quantitate the various PAHs in foods. The most common method for the isolation of PAHs from foods usually involves saponification of lipids by methanolic KOH, followed by liquid-liquid partition and liquid-solid chromatography (Joe et al., 1982, 1984; Kolarovic and Traitler, 1982; Takatsuki et al., 1985; Hopia et al., 1986; Karlesky et al., 1986; Chen et al., 1996). Of the various isolation methods, the soxhlet extraction of PAHs followed by purification with a Sep-Pak Florisil Cartridge was reported to be able to remove more impurities than the sonication method (Chen et al., 1996). For separation methods, the HPLC technique permitted both a better resolution and a shorter analysis time of PAHs than those of GC (Castello and Gerino, 1993; Chiu et al., 1996). However, with gas chromatography and ion-trap detection (GC-ITD) it is possible to obtain higher sensitivity than that of HPLC (Castello and Gerino, 1993). In addition, the application of GC-ITD could distinguish the various PAHs in foods readily through reconstructed ion chromatogram even in the presence of PAH-like impurities (Johnston et al., 1994; Chiu et al., 1996).

Duck meat is an important food commodity in Taiwan, and the consumption of duck meat has increased steadily in recent years. The major processed duck meat products in Taiwan include boiled salted-duck, charcoal grilled duck, roasted duck, and smoked duck. Due to the fact that the PAHs formation can be correlated well to the processing methods such as

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roasting, grilling, and smoking, the formation of PAH profiles as affected by various processing methods has to be investigated. The purposes of this study were to determine the effects of steaming, roasting, grilling, smoking, and LSF on PAHs formation in duck breast steak by employing the GC-ITD technique.

MATERIALS AND METHODS

Materials. Sixteen PAH standards, including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*g,h,i*]perylene, and indeno[1,2,3-*c,d*]pyrene was purchased from Accustandard Co. (New Haven, CT). The purity of each standard was approximately 98% as reported by the manufacture. Each standard was dissolved in methylene chloride/methanol (50/50, v/v) for a concentration of 200 ppm. Reagents including potassium hydroxide and anhydrous sodium sulfate were purchased from Sigma Co. (St. Louis, MO). Solvents used for extraction of PAHs, including methanol, *n*-hexane, and methylene chloride, were analytical grade, and were from Merck Co. (Darmstadt, Germany). Sixty pieces of duck breast steak of approximately 300 gm each were purchased from a duck meat export company in Taipei, Taiwan. Liquid smoke flavorings (30 mL) were obtained from a local company in Taipei, Taiwan. Charcoal was from a local charcoal shop in Taipei, Taiwan. Wood, which contains hickory, was from J. Rettenmaier & Sonne Co. (Ellwangen-Holzmuhle, Germany). Nylon/LLDPE plastic bags were from SIN-HO Co. (Hsinchuang, Taiwan). The Sep-Pak Florisil cartridge containing 960 mg of packing material was from Millipore Co. (Bedford, MA).

Instrumentation. The GC instrument consisted of a Varian Model 3400 gas chromatograph with a Varian 1077 split/splitless injector and a Saturn III ion-trap mass spectrometer (Palo Alto, CA). An MA4A grinder used to grind samples was from CHIN-TEN Co. (Taipei, Taiwan). The N-1 rotary evaporator was from Eyela Co. (Tokyo, Japan). The smoke house (CS700EL mode) was from Kerres Smoke-Air Co. (Sulzbach, Germany). The all-purpose oven (Varzoplus 611 mode), which can be used for steaming or roasting, was from Palux Co. (Bad Mergentheim, Germany). The vacuum packaging machine (GK123D) was from Chien-Long Machinery Co. (Taipei, Taiwan). The separatory funnel shaker (VS-6 type) was from Shiang-Tai Machinery Co. (Taipei, Taiwan). The freeze-dryer (FD24 model) was from Chin-Ming Co. (Taipei, Taiwan).

Processing of Duck Meat. Before processing, two pieces of duck breast steak were randomly selected to determine if there was any PAH present in untreated samples.

(1) *Steaming.* Six pieces of duck breast steak were trimmed to obtain a uniform size and shape of each. After cleaning, the duck breast steaks were placed in an all-purpose oven for steaming for 0.5, 1.0, and 1.5 h at 100 °C. Two pieces of samples were randomly collected at the same time following each steaming treatment, and a total of six pieces were collected for cooling and the subsequent PAHs analyses. After cooling, all samples were vacuum-packed in nylon/LLDPE plastic bags and stored at -20 °C until analyzed by GC-MS.

(2) *Roasting.* Six pieces of duck breast steak were trimmed to obtain a uniform size and shape of each. After cleaning, the duck breast steak were placed in an all-purpose oven for roasting for 30, 40, and 50 min at 200 °C. Two pieces of samples were randomly collected at the same time following each roasting treatment, and a total of six pieces were collected for cooling and the subsequent PAHs analyses. After cooling, all samples were vacuum-packed in nylon/LLDPE plastic bags and stored at -20 °C until analyzed by GC-MS.

(3) *Smoking.* Ten pieces of duck breast steak were trimmed to obtain a uniform size and shape of each. After cleaning, the duck breast steak were blown by hot air (50 °C) for 1 h to remove excess water. The smoking wood which contains hickory chip was tempered to contain 10-15% moisture. Samples were hung vertically and smoked for 0.5, 1.0, 1.5, 2.0,

and 3.0 h at 60 °C in a smoke house. The distance from smoke generation source to product surface was approximately 1 m. Two pieces of samples were randomly collected at the same time following each smoking treatment, and a total of ten pieces were collected for steaming, cooling, and the subsequent PAHs analyses. After smoking all samples were steamed at 70 °C for 30 min. Then the samples were vacuum-packed in nylon/LLDPE plastic bags after cooling and stored at -20 °C until analyzed by GC-MS.

(4) *Liquid Smoke Flavoring (LSF).* Two pieces of duck breast steak were trimmed to obtain a uniform size and shape of each. After cleaning, the duck breast steak were immersed in 30 mL LSF for 24 h, followed by blowing with hot air (50 °C) for 1 h. After cooling, samples were vacuum-packed in nylon/LLDPE plastic bags and stored at -20 °C until analyzed by GC-MS.

(5) *Charcoal Grilling.* Twelve pieces of duck breast steak were trimmed to obtain a uniform size and shape of each. Then the duck samples were divided into two sets of six pieces each, and skin was removed for one set. Before hanging, approximately 2 kg of charcoal was placed in the bottom of the oven, and 100 mL of gasoline was poured onto charcoal to start fire for 5 min. After cleaning of duck samples and ceasing of charcoal fire, six duck breast steaks with skin and six without skin were hung in a bomb oven. The distance between samples and charcoal was about 1 m. Samples were grilled for 0.5, 1.0, and 1.5 h. Two pieces of duck samples with skin and two without skin were randomly collected at the same time following each grilling treatment, and a total of twelve pieces were collected for cooling and the subsequent PAHs analyses. After cooling, all samples were vacuum-packed in nylon/LLDPE plastic bags and stored at -20 °C until analyzed by GC-MS.

Extraction of PAHs from Duck Meat. A method based on that described by Joe et al. (1984), Takatsuki et al. (1985), and Chen et al. (1996) was used. 30 g of duck breast steak was cut into approximately 90 pieces of 0.5 cm³ each, ground, and freeze-dried before placement in a round filter paper. The paper was placed in the center of a Soxhlet extractor. A 500-mL round bottom flask, to which 200 mL of methanol and 25 mL of 50% aqueous potassium hydroxide were added for extraction of PAHs and saponification of lipid, was connected to the bottom of the Soxhlet extractor. After reflux for 3 h, the alkaline mixture was cooled to 40 °C, and 150 mL of *n*-hexane was added with occasional swirling. Then the solution was poured into a 500-mL separatory funnel containing 150 mL of water. The flask was rinsed twice with 10 mL of methanol, and the rinses were added to the separatory funnel, which was then shaken vigorously and allowed to stand to form aqueous and organic layers. The aqueous layer was extracted twice with 150 and 100 mL of hexane, and the hexane extracts were all combined, washed with 100 mL of water three times, and dried over anhydrous sodium sulfate. The dried hexane extract was poured into a 500-mL flask and concentrated to 1 mL by a rotary evaporator. The 1 mL concentrate was poured into a Sep-Pak Florisil cartridge, which had been previously conditioned with 10 mL methylene chloride and 20 mL of hexane. 10 mL of hexane followed by 8 mL of hexane/methylene chloride (1:1, v/v) were passed through the cartridge. The eluate was collected, evaporated to dryness, and the residue was dissolved in 1 mL of methanol/methylene chloride (1:1, v/v). The solution was filtered through a 0.2- μ m membrane filter and stored in a vial filled with nitrogen gas for GC-MS analysis.

Extraction of PAHs from Liquid Smoke Flavoring (LSF). The extraction and purification of PAHs from LSF was carried out as described by Black et al. (1979) and Gomaa et al. (1993).

GC-MS Analysis of PAHs in Duck Meat. A DB-5 capillary column (30 m \times 0.32 mm i.d.) with 0.25- μ m film thickness was used. Helium was used as a carrier gas with a flow rate at 1.0 mL/min. Both injector and transfer line temperatures were 280 °C with split flow rate at 30 mL/min. Column temperature was maintained at 70 °C for 1 min, heated to 150 °C at 10 °C/min and then 280 °C at 4 °C/min, and held at 280 °C for 14 min. The PAHs in the duck breast

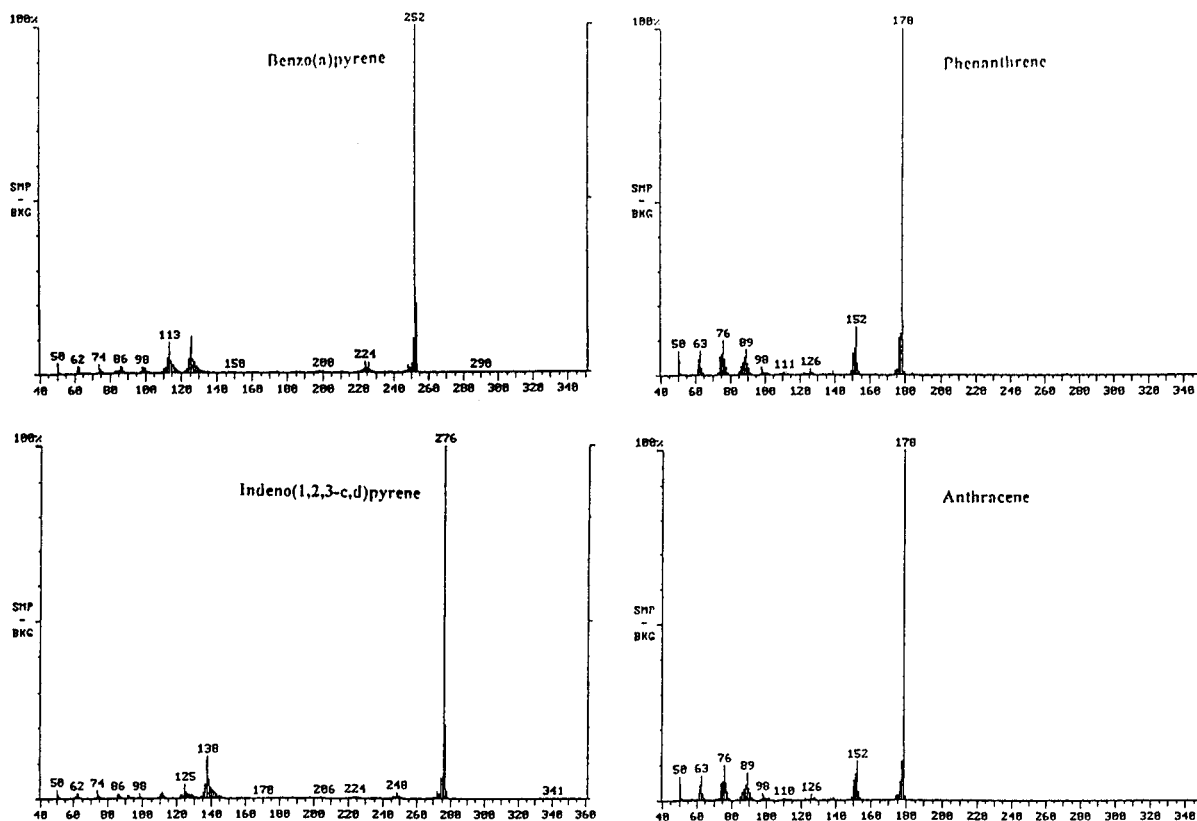


Figure 1. MS spectra of phenanthrene, anthracene, benzo[*a*]pyrene, and indeno[1,2,3-*c,d*]pyrene detected by ion-trap MS.

steak were identified by (1) comparison of retention time of unknown peaks with reference standards on the reconstructed ion chromatogram, and (2) comparison of mass spectra of unknown peaks with those in NIST Mass Spectral Database by means of library search. Positive confirmations required a retention time match of $\pm 0.5\%$ and a match of relative intensity of the three most characteristic ions $\pm 15\%$. A Varian Saturn III ion-trap spectrometer in the electron impact ionization mode with a scan range of 50–350 amu, 1 s/scan, a 55.5-min acquisition time and a 5-min filament/multiplier delay was used. The instrument was autotuned to give a multiplier voltage of 1350 V with a target value of 20 000. Compound perfluorotributylamine was used for mass calibration at *m/z* 69, 131, 264, 414, 502, and 614. A mixture of 16 PAHs standards containing 200 ppm each was prepared and diluted to 20 times with methylene chloride/methanol (50/50, v/v), and the injection volume was 1 μL . Each PAH in the sample was quantified using the absolute calibration method. Four concentrations of each PAH ranging from 0.5 ppb to 20 ppm, were injected onto GC, and the calibration curve for each standard was obtained by plotting concentration against area of the base ion. The regression equation and correlation coefficient (r^2) were calculated. The recovery was obtained by adding a 50 μL (0.5 μg) mixture of 16 PAHs to a duck sample, and extraction was performed by the Soxhlet method as described earlier. After quantification, the recovery data were also subjected to analysis of variance (PROC ANOVA) and Duncan's multiple range test procedures for statistical analysis (SAS, 1985). Each PAH in the sample was quantified using the following formula:

$$W_s \text{ (ppb)} = \frac{A_s \text{ (ng}/\mu\text{L}) \times 1000 \mu\text{L}}{30 \text{ g} \times a \times R}$$

where W_s is the PAH concentration in the sample, A_s is the concentration relative to peak area of PAH in the injection volume (1 μL), a is the slope of the regression line, and R is the recovery of PAH. Duplicate analyses were conducted and mean values determined. The detection limit for each PAH was determined based on the minimum injected quantity that produces correct library search identification within the first three search hits.

RESULTS AND DISCUSSION

Analysis of PAHs in Duck Samples. Many methods have been developed to analyze PAHs in meat products (Doremire et al., 1979; Joe et al., 1984; Lawrence and Weber, 1984a; Takatsuki et al., 1985; Gomaa et al., 1993; Yabiku et al., 1993; Wise et al., 1993; Chen et al., 1996). In this study Soxhlet method was adopted for extraction of PAHs (Joe et al., 1984; Takatsuki et al., 1985; Chen et al., 1996), and separation and detection of PAHs were conducted by GC-ITD (Castello and Gerbino, 1993; Johnston et al., 1994). The presence of many PAH-like impurities such as glycerides and aliphatic hydrocarbons in meat products posed a major problem for PAH identification (Chiu et al., 1996). These impurities were further confirmed by means of standard NIST library search programs. Based on the total ion chromatogram, the presence of impurities may interfere with identification of various PAHs in duck samples by comparison of retention time of unknown peaks with reference standards. However, with reconstructed ion chromatograms the various PAHs in duck samples could be readily distinguished. Nevertheless, some PAHs such as benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]pyrene were tentatively identified because the mass spectra only partially fit those in NIST database by means of library search. Figure 1 shows the mass spectra of some PAHs standards, including phenanthrene, anthracene, benzo[*a*]pyrene, and indeno[1,2,3-*c,d*]pyrene. The major base ion of each PAH standard was selected for preparing the standard calibration curve. The following base ions were used: naphthalene, *m/z* 128; acenaphthylene, *m/z* 152; acenaphthene, *m/z* 153; fluorene, *m/z* 165; phenanthrene, *m/z* 178; anthracene, *m/z* 178; fluoranthene, *m/z* 202; pyrene, *m/z* 202; benzo[*a*]anthracene, *m/z* 228; chrysene, *m/z* 228; benzo[*b*]fluoranthene, *m/z* 252; benzo[*k*]fluoranthene, *m/z* 252; benzo[*a*]pyrene, *m/z* 252;

Table 1. Detection Limits and Recoveries of 16 Priority PAHs by GC-ITD

| compound | detection limit (pg) ^a | recovery (%) ^b |
|----------------------------------|-----------------------------------|---------------------------|
| naphthalene | 10.0 | 62.6 (5.6) ^c |
| acenaphthylene | 5.0 | 66.8 (6.9) |
| acenaphthene | 5.0 | 83.2 (4.7) |
| fluorene | 5.0 | 80.6 (5.8) |
| phenanthrene | 5.0 | 85.3 (16.1) |
| anthracene | 10.0 | 89.5 (4.3) |
| fluoranthene | 5.0 | 81.2 (9.0) |
| pyrene | 5.0 | 88.3 (3.9) |
| benzo[<i>a</i>]anthracene | 25.0 | 75.8 (6.9) |
| chrysene | 10.0 | 90.6 (4.2) |
| benzo[<i>b</i>]fluoranthene | 10.0 | 76.7 (8.6) |
| benzo[<i>k</i>]fluoranthene | 25.0 | 69.2 (10.5) |
| benzo[<i>a</i>]pyrene | 25.0 | 79.6 (7.9) |
| dibenzo[<i>a,h</i>]perylene | 50.0 | 65.4 (9.2) |
| benzo[<i>g,h,i</i>]perylene | 25.0 | 68.5 (8.3) |
| indeno[1,2,3- <i>c,d</i>]pyrene | 25.0 | 61.7 (9.3) |

^a The minimum injected quantity that produces correct library identification within first three search hits. ^b Mean of duplicate analyses. ^c Values in parentheses represent coefficient of variation (%).

indeno[1,2,3-*c,d*]pyrene, *m/z* 276; dibenzo[*a,h*]anthracene, *m/z* 278; and benzo[*g,h,i*]perylene, *m/z* 276. The linearity responses were high, and the linear calibration better than 0.90 were observed for most PAHs.

Table 1 shows the detection limits and recoveries of 16 PAHs using GC-ITD. The detection limits and recoveries ranged from 5.0 to 50.0 pg and 61.7% to 90.6%, respectively. The coefficient of variation for the recoveries was between 3.85% and 10.48%. The detection limits were slightly higher than those reported by Castello and Gerbino (1993), mainly because of difference in setting of target value. The high target value could lower detection limit, however, it also decreased the clarity and thus affected the interpretation of mass spectra. The recoveries were somewhat lower than those reported by Chiu et al. (1996), probably because of different types of meat samples used. It has been well established that the presence of impurities in meat samples such as aliphatic hydrocarbons, fatty acids, phenols and polycyclic organic compounds can greatly reduce the extraction efficiency of PAHs (Wise et al., 1977; Natusch and Tomkins, 1978; Chen et al., 1996). Thus, the amounts and varieties of impurities in untreated duck and smoked chicken samples could account for the recovery differences. In addition, some PAHs such as naphthalene, acenaphthylene, dibenzo[*g,h,i*]anthracene and benzo[*g,h,i*]perylene might undergo partial loss during extraction and purification (Karlesky et al., 1986; Dong et al., 1993; Chen et al., 1996), which in turn resulted in low recoveries for these PAHs. Figures 2 and 3 show the total and reconstructed ion chromatograms of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, and indeno[1,2,3-*c,d*]pyrene in smoked duck breast steak detected by GC-ITD. No PAHs were detected in untreated duck samples.

Steaming. Table 2 shows the effect of steaming (100 °C) on the formation of PAHs in duck breast steak. The heating time was selected based on how well duck breast steak was done. After steaming for 0.5 h, the duck breast steak was well done, and several PAHs, including naphthalene (0.7 ppb), acenaphthylene (0.3 ppb), acenaphthene (0.3 ppb), fluorene (1.2 ppb), phenanthrene (1.3 ppb), and pyrene (0.6 ppb) were detected. In general the PAHs concentrations increased along

with increasing steaming time with the exception of acenaphthylene, acenaphthene and fluorene. After steaming for 1.5 h, the duck breast became somewhat hard, and levels of naphthalene, phenanthrene and pyrene increased from 0.7, 1.3, and 0.6 ppb to 2.0, 4.0, and 1.2 ppb, respectively. However, no significant difference ($p > 0.05$) was observed for acenaphthylene, acenaphthene and fluorene during steaming. In a similar study, Obana et al. (1984) determined PAHs levels in fish and found that the sum of eight PAHs increased from 1.7 to 9.5 ppb during cooking of fish in water.

Roasting. Table 3 shows the effect of roasting (200 °C) on the PAHs formation in duck breast steak. Duck breast steak was well done after roasting for 40 min, and eleven PAHs, including naphthalene (43.6 ppb), acenaphthylene (5.6 ppb), acenaphthene (5.1 ppb), fluorene (7.0 ppb), phenanthrene (16.8 ppb), anthracene (3.9 ppb), fluoranthene (4.3 ppb), pyrene (13.0 ppb), benzo[*a*]anthracene (4.8 ppb), chrysene (0.9 ppb), and benzo[*b*]fluoranthene (10.5 ppb) were detected. The concentration changes of PAHs followed the same trend as steaming with the exception of acenaphthylene, acenaphthene, fluorene, anthracene, pyrene, benzo[*a*]anthracene, chrysene, and benzo[*b*]fluoranthene, and no significant difference ($p > 0.05$) was observed for these PAHs during roasting. After roasting for 50 min, naphthalene was present at highest concentration (52.7 ppb), followed by phenanthrene (16.0 ppb), pyrene (13.0 ppb), benzo[*b*]fluoranthene (10.0 ppb), fluoranthene (8.7 ppb), fluorene (6.9 ppb), acenaphthylene (5.8 ppb), benzo[*a*]anthracene (5.0 ppb), acenaphthene (5.0 ppb), anthracene (3.6 ppb), and chrysene (0.9 ppb). This result implied that roasting can induce more PAHs formation than steaming. The formation of PAHs during roasting may be due to some food components, such as fatty acid, triglyceride and cholesterol, which may transform to form PAHs under high-temperature heating (Halaby and Fagerson, 1970). Similar result was observed by Lawrence and Weber (1984b), who investigated PAHs in Canadian samples of milk powder and found that the total carcinogenic PAHs were present at 8.1 ppb, which can be attributed to the effect of direct heating. Nico (1987) analyzed 55 commercial coffee beans and found that benzo[*a*]pyrene was less than 0.5 ppb. However, the benzo[*a*]pyrene level increased to 2 ppb in coffee prepared from roasted coffee bean. This result further demonstrated that roasting can accelerate PAH formation, and the amount formed can be dependent upon time and temperature. In another study no carcinogenic PAHs such as benzo[*a*]pyrene were observed in grilled products mainly because electric heat was employed (Lijinsky and Ross, 1967). Masuda et al. (1966) also reported that heating food by gas can induce more PAH formation than roasting by electric heat.

Smoking. Table 4 shows the effect of smoking on the formation of PAHs in duck breast steak. In most cases, the PAH levels in duck breast steak increased along with smoking time with the exception of indeno[1,2,3-*c,d*]pyrene, which showed no significant difference ($p > 0.05$) during smoking. After smoking for 3 h, 14 PAHs were detected, and anthracene was present at highest concentration (122.4 ppb), followed by fluoranthene (91.4 ppb), naphthalene (86.1 ppb), phenanthrene (56.5 ppb), pyrene (52.1 ppb), benzo[*a*]anthracene (17.8 ppb), fluorene (17.8 ppb), chrysene (16.4 ppb), acenaphthylene (16.0 ppb), benzo[*b*]fluoranthene (15.8 ppb), benzo[*a*]pyrene (13.9 ppb), acenaphthene (8.2 ppb), benzo[*k*]fluoranthene (7.4 ppb), and indeno[1,2,3-*c,d*]-

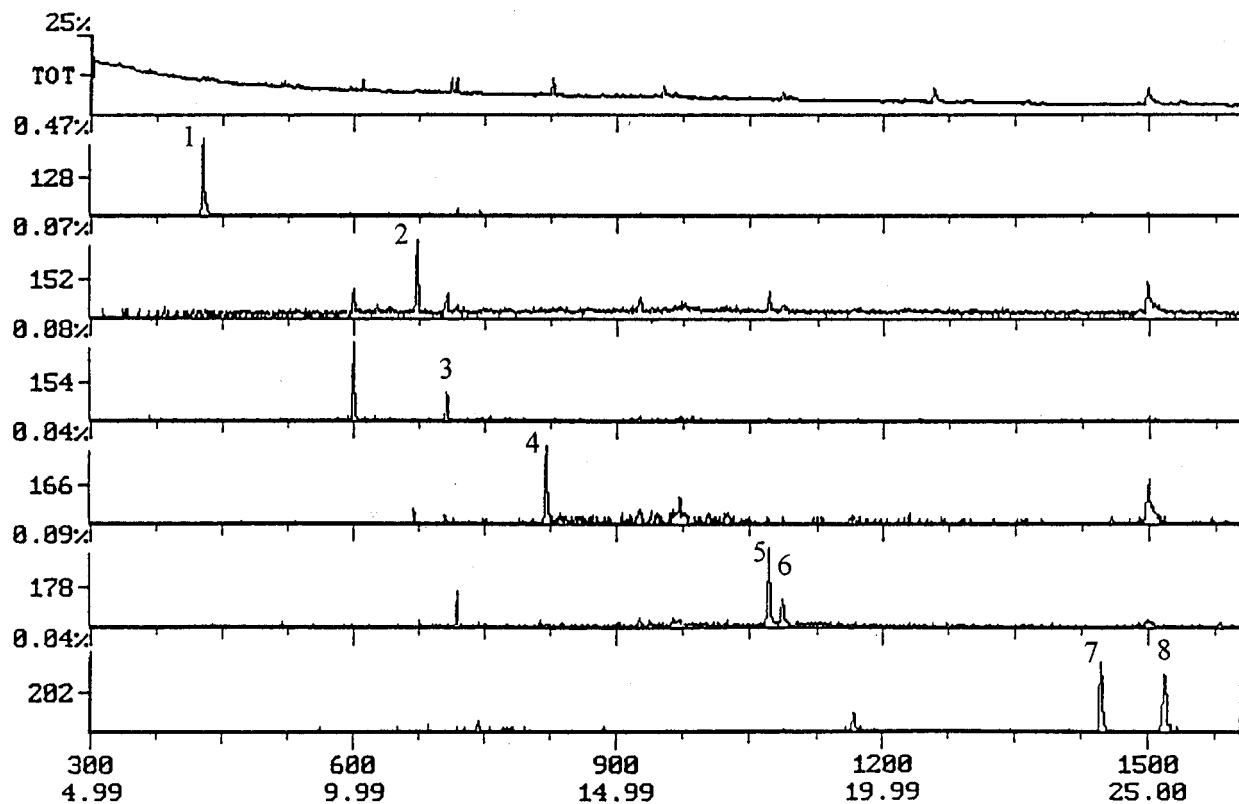


Figure 2. Total and reconstructed ion chromatograms of naphthalene (peak 1), acenaphthylene (peak 2), acenaphthene (peak 3), fluorene (peak 4), phenanthrene (peak 5), anthracene (peak 6), fluoranthene (peak 7), and pyrene (peak 8) in smoked duck breast steak detected by ion-trap MS.

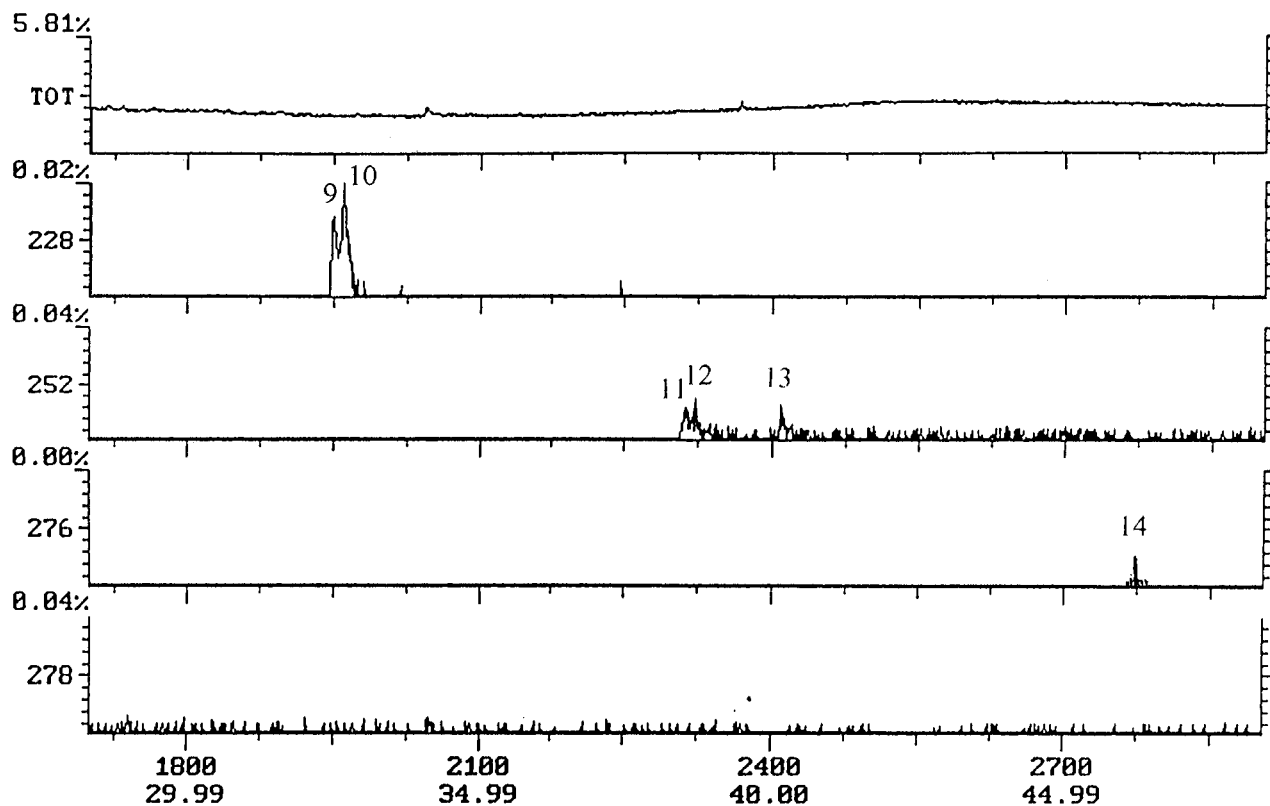


Figure 3. Total and reconstructed ion chromatograms of benzo[*a*]anthracene (peak 9), chrysene (peak 10), benzo[*b*]fluoranthene (peak 11), benzo[*k*]fluoranthene (peak 12), benzo[*a*]pyrene (peak 13), and indeno[1,2,3-*c,d*]pyrene (peak 14) in smoked duck breast steak detected by ion-trap MS.

pyrene (5.1 ppb). The total PAHs concentrations increased from 18.7 to 52.6 ppb during smoking for 0.5–3.0 h. Similar results were observed by Simon et al. (1969), who reported that the benzo[*a*]pyrene level

increased from 4 to 13 ppb during smoking of Frankfurt sausage for 5–10 min. Toth and Blaas (1972a,b) further reported that the higher smoking temperature, the more formation of PAHs. Afolabi et al. (1983), who deter-

Table 2. Changes of PAHs Concentrations (ppb)^a in Duck Breast Steak during Steaming for 0.5, 1.0, and 1.5 h

| compound | steaming time (h) | | |
|--------------------------------------|---------------------------------------|------------------------|------------------------|
| | 0.5 | 1.0 | 1.5 |
| naphthalene | 0.7 ^{1,d} (0.8) ^f | 2.2 ² (1.3) | 2.0 ² (1.5) |
| acenaphthylene | 0.3 ¹ (0.5) | 0.3 ¹ (0.6) | 0.2 ¹ (0.3) |
| acenaphthene | 0.3 ¹ (0.7) | 0.2 ¹ (1.0) | 0.2 ¹ (0.8) |
| fluorene | 1.2 ¹ (1.2) | 1.1 ¹ (1.0) | 1.0 ¹ (1.1) |
| phenanthrene | 1.3 ¹ (1.3) | 3.6 ² (2.4) | 4.0 ² (2.8) |
| anthracene | ND ^c | ND | ND |
| fluoranthene | ND | ND | ND |
| pyrene | 0.6 ¹ (0.5) | 1.2 ² (1.3) | 1.2 ² (1.8) |
| benzo[a]anthracene ^b | ND | ND | ND |
| chrysene | ND | ND | ND |
| benzo[b]fluoranthene ^{b,e} | ND | ND | ND |
| benzo[k]fluoranthene ^e | ND | ND | ND |
| benzo[a]pyrene ^{b,e} | ND | ND | ND |
| indeno[1,2,3-c,d]pyrene ^b | ND | ND | ND |
| dibenzo[a,h]anthracene ^b | ND | ND | ND |
| benzo[g,h,i]perylene | ND | ND | ND |
| total PAHs | 4.4 | 8.6 | 8.6 |
| carcinogenic PAHs | ND | ND | ND |

^a Mean of duplicate analyses. ^b Carcinogenic PAH. ^c ND, not detected at a limit of 5–50 pg. ^d Numbers tagged with superscript 1 and 2 in the same row are significantly different ($p < 0.05$). ^e Tentatively identified. ^f Values in parentheses represent coefficient of variation (%).

Table 3. Changes of PAH Concentrations (ppb)^a in Duck Breast Steak during Roasting for 30, 40, and 50 min

| compound | roasting time (min) | | |
|--------------------------------------|--|-------------------------|-------------------------|
| | 30 | 40 | 50 |
| naphthalene | 24.9 ^{1,d} (5.8) ^f | 43.6 ² (8.3) | 52.7 ³ (9.8) |
| acenaphthylene | 4.1 ¹ (1.7) | 5.6 ¹ (2.3) | 5.8 ¹ (2.1) |
| acenaphthene | 4.7 ¹ (1.5) | 5.1 ¹ (1.1) | 5.0 ¹ (1.3) |
| fluorene | 6.1 ¹ (1.9) | 7.0 ¹ (2.1) | 6.9 ¹ (2.3) |
| phenanthrene | 13.1 ¹ (3.7) | 16.8 ² (7.2) | 16.0 ² (6.8) |
| anthracene | 3.8 ¹ (1.1) | 3.9 ¹ (0.9) | 3.6 ¹ (1.3) |
| fluoranthene | 3.8 ¹ (1.2) | 4.3 ¹ (1.4) | 8.7 ² (3.6) |
| pyrene | 12.4 ¹ (5.7) | 13.0 ¹ (6.3) | 13.0 ¹ (4.9) |
| benzo[a]anthracene ^b | 4.5 ¹ (0.8) | 4.8 ¹ (1.3) | 5.0 ¹ (1.0) |
| chrysene | 1.2 ¹ (1.1) | 0.9 ¹ (0.7) | 0.9 ¹ (1.2) |
| benzo[b]fluoranthene ^{b,e} | 9.9 ¹ (4.7) | 10.5 ¹ (6.2) | 10.0 ¹ (5.8) |
| benzo[k]fluoranthene ^e | ND ^c | ND | ND |
| benzo[a]pyrene ^{b,e} | ND | ND | ND |
| indeno[1,2,3-c,d]pyrene ^b | ND | ND | ND |
| dibenzo[a,h]anthracene ^b | ND | ND | ND |
| benzo[g,h,i]perylene | ND | ND | ND |
| total PAHs | 88.5 | 115.5 | 127.6 |
| carcinogenic PAHs | 14.4 | 15.3 | 15.0 |

^a Mean of duplicate analyses. ^b Carcinogenic PAH. ^c ND, not detected at a limit of 25–50 pg. ^d Numbers tagged with superscript 1–3 in the same row are significantly different ($p < 0.05$). ^e Tentatively identified. ^f Values in parentheses represent coefficient of variation (%).

mined PAHs in several traditional smoked meat products, also observed the same result. In general, the carcinogenic PAHs levels in traditionally smoked products was 2–10 times higher than those in other products. Also, the PAHs were formed at a higher concentration by cold smoking than that by hot smoking, mainly because the processing time of the former was longer, which in turn resulted in the accumulation of PAHs (Toth and Blaas, 1972a,b; Potthast, 1979). In our study the PAHs concentrations were much higher than those in other reports, probably because of long smoking time used. The wide variations in PAH concentrations can be directly related to the smoking conditions, which include the type of generator, temperature of combustion, degree of smoking, time of smoking and fat content of products (Draudt, 1963; Malanoski et al., 1968; Gomaa et al., 1993). In general, the higher smoking

temperature, the more formation of benzo[a]pyrene. In Germany the maximum allowable amount of benzo[a]pyrene in foods is 1 ppb, which is more strict than that set by FAO/WHO in 1987, which stated that benzo[a]pyrene in foods should not exceed 10 ppb. Nevertheless, some more carcinogenic PAHs such as benzo[a]anthracene, benzo[b]fluoranthene, and indeno[1,2,3-c,d]pyrene were also formed during smoking. Thus it is necessary to set a new safety standard for these carcinogenic PAHs in foods.

Liquid Smoke Flavoring (LSF). Table 5 shows the PAHs levels in LSF and LSF-treated duck breast steak. Eleven PAHs, including naphthalene (15.2 ppb), acenaphthylene (8.4 ppb), acenaphthene (9.4 ppb), fluorene (12.9 ppb), phenanthrene (8.3 ppb), anthracene (8.8 ppb), fluoranthene (7.2 ppb), pyrene (5.9 ppb), benzo[a]anthracene (1.4 ppb), chrysene (4.4 ppb), and benzo[k]fluoranthene were detected in LSF. After treatment with LSF, only three PAHs, naphthalene, fluorene, and benzo[k]fluoranthene were all present with a concentration at 0.1 ppb. This result demonstrated that the application of LSF could reduce the PAHs levels greatly. The reduction of PAHs content by LSF can be attributed to the sorption of flavor compounds from foods by packaging materials such as polyethylene (Kwapong and Hotchkiss, 1987; Arora et al., 1991; Nielsen et al., 1991; Simko and Brunckova, 1993; Simko et al., 1994). Simko and Brunckova (1993) further postulated that the PAHs migrated from the strongly polar medium into the nonpolar medium, where van der Waals disperse forces had the decisive influence in the sorption of nonpolar PAHs into packaging material. Nevertheless, many studies showed that commercial LSF may contain residual PAHs. White et al. (1971) analyzed seven LSF, and three PAHs containing three or four rings were detected. Yabiku et al. (1993) analyzed eleven commercial LSF and detected seven PAHs, of which benzo[a]pyrene concentration ranged from 0.1 to 336.6 ppb. This concentration apparently greatly exceeded the safety standard of benzo[a]pyrene (10 ppb) set by FAO/WHO. Gomaa et al. (1993) analyzed 18 commercial LSF and found the total PAHs concentrations ranged from 6.3 to 43.7 ppb, with the carcinogenic PAHs ranged from 0.3 to 10.2 ppb. In another study Henning (1976) pointed out that the maximum concentration of LSF which can be used in meat was 0.5%. Thus, if benzo[a]pyrene was present at a concentration of 20 ppb in LSF, the actual amount of benzo[a]pyrene in meat should be 0.1 ppb (20 ppb \times 0.5%), which is well below the safety standard set by FAO/WHO.

Charcoal Grilling. To determine the effect of fat content on PAHs formation in duck breast steak, duck samples with and without skin were investigated. Duck breast steak with skin was found to contain moisture 55.92%, crude protein 19.53%, crude fat 22.18%, and ash 2.32%, while duck without skin was found to contain moisture 55.88%, crude protein 32.23%, crude fat 10.85%, and ash 3.17%. Table 6 shows the effect of charcoal grilling on PAHs formation in duck breast steak with skin. After grilling for 0.5 h, duck breast steak possesses golden-yellow appearance and is ready to eat, and all 16 PAHs with the exception of dibenzo[a,h]anthracene and benzo[g,h,i]perylene were found. After grilling for 1.5 h, naphthalene was present at highest concentration (73.8 ppb), followed by phenanthrene (55.3 ppb), pyrene (47.1 ppb), fluoranthene (29.9 ppb), chrysene (29.7 ppb), anthracene (10.9 ppb), acenaphthylene (10.6 ppb), benzo[b]fluoranthene (8.3 ppb),

Table 4. Changes of PAH Concentrations (ppb)^a in Duck Breast Steak during Smoking for 0.5, 1.0, 1.5, 2.0, and 3.0 h

| compound | smoking time (h) | | | | |
|--------------------------------------|--|-------------------------|--------------------------|--------------------------|---------------------------|
| | 0.5 | 1.0 | 1.5 | 2.0 | 3.0 |
| naphthalene | 47.8 ^{1,d} (9.6) ^g | 50.2 ¹ (8.9) | 58.4 ² (11.5) | 65.1 ³ (13.6) | 86.1 ⁴ (17.2) |
| acenaphthylene | 9.8 ¹ (5.8) | 11.7 ¹ (4.7) | 11.0 ¹ (6.1) | 13.5 ¹ (5.2) | 16.0 ² (9.3) |
| acenaphthene | 6.1 ¹ (2.3) | 6.5 ¹ (1.9) | 6.3 ¹ (2.0) | 6.6 ¹ (1.7) | 8.2 ² (5.6) |
| fluorene | 11.0 ¹ (5.3) | 11.2 ¹ (4.8) | 11.8 ¹ (6.0) | 12.2 ¹ (4.5) | 17.7 ² (8.7) |
| phenanthrene | 29.1 ¹ (10.3) | 32.0 ¹ (9.5) | 32.8 ¹ (8.6) | 34.3 ¹ (7.5) | 56.5 ² (13.8) |
| anthracene | 10.3 ¹ (6.1) | 10.6 ¹ (4.8) | 10.9 ¹ (5.7) | 77.5 ² (9.6) | 122.4 ³ (20.5) |
| fluoranthene | 13.0 ¹ (4.9) | 14.2 ¹ (5.2) | 15.2 ¹ (3.9) | 23.6 ² (8.2) | 91.4 ³ (12.7) |
| pyrene | 5.8 ¹ (6.0) | 10.4 ² (7.2) | 16.9 ³ (5.8) | 30.7 ⁴ (10.1) | 52.1 ⁵ (9.5) |
| benzo[a]anthracene ^b | 5.3 ¹ (3.7) | 6.4 ¹ (2.5) | 13.3 ² (6.8) | 13.5 ² (5.7) | 17.8 ³ (8.6) |
| chrysene | 1.3 ¹ (1.0) | 5.7 ² (2.8) | 5.7 ² (2.3) | 6.9 ² (3.1) | 16.4 ³ (7.4) |
| benzo[b]fluoranthene ^{b,e} | 1.9 ¹ (1.3) | 2.4 ¹ (1.0) | 8.2 ² (4.5) | 12.6 ³ (7.6) | 15.8 ⁴ (10.3) |
| benzo[k]fluoranthene ^e | 1.6 ¹ (2.1) | 1.6 ¹ (1.8) | 2.3 ¹ (1.6) | 5.7 ² (4.8) | 7.4 ³ (5.9) |
| benzo[a]pyrene ^{b,e} | 6.9 ¹ (3.2) | 6.9 ¹ (2.9) | 9.0 ² (5.3) | 10.6 ² (4.6) | 13.9 ³ (7.8) |
| indeno[1,2,3-c,d]pyrene ^b | 4.7 ¹ (2.1) | 4.7 ¹ (1.9) | 4.7 ¹ (1.5) | 4.8 ¹ (2.3) | 5.1 ¹ (1.2) |
| dibenzo[a,h]anthracene ^b | ND ^c | ND | ND | ND | ND |
| benzo[g,h,i]perylene | ND | ND | ND | ND | ND |
| total PAHs | 154.6 | 174.5 | 206.5 | 317.6 | 526.8 |
| carcinogenic PAHs | 18.8 | 20.4 | 35.2 | 41.5 | 52.6 |

^a Mean of duplicate analyses. ^b Carcinogenic PAH. ^c ND, not detected at a limit of 25 pg. ^d Numbers tagged with superscripts 1–4 in the same row are significantly different ($p < 0.05$). ^e Tentatively identified. ^f Values in parentheses represent coefficient of variation (%).

Table 5. Amounts of PAHs (ppb)^a in Liquid Smoke Flavorings (LSF) and LSF-Treated Duck Breast Steak

| compound | LSF | LSF-treated duck steak |
|--------------------------------------|-------------------------|------------------------|
| naphthalene | 15.2 (5.3) ^e | 0.1 (1.2) |
| acenaphthylene | 8.4 (2.8) | ND ^c |
| acenaphthene | 9.4 (3.2) | ND |
| fluorene | 12.9 (6.1) | 0.1 (0.8) |
| phenanthrene | 8.3 (3.8) | ND |
| anthracene | 8.8 (1.9) | ND |
| fluoranthene | 7.2 (4.5) | ND |
| pyrene | 5.9 (5.6) | ND |
| benzo[a]anthracene ^b | 1.4 (2.5) | ND |
| chrysene | 4.4 (1.8) | ND |
| benzo[b]fluoranthene ^{b,e} | ND | ND |
| benzo[k]fluoranthene ^e | 5.4 (3.0) | 0.1 (1.0) |
| benzo[a]pyrene ^{b,e} | ND | ND |
| indeno[1,2,3-c,d]pyrene ^b | ND | ND |
| dibenzo[a,h]anthracene ^b | ND | ND |
| benzo[g,h,i]perylene | ND | ND |
| total PAHs | 87.3 | 0.3 |
| carcinogenic PAHs | 1.4 | 0.0 |

^a Mean of duplicate analyses. ^b Carcinogenic PAH. ^c ND, not detected at a limit of 5–50 pg. ^d Tentatively identified. ^e Values in parentheses represent coefficient of variation (%).

fluorene (8.3 ppb), benzo[k]fluoranthene (6.9 ppb), acenaphthene (5.7 ppb), benzo[a]anthracene (5.5 ppb), benzo[a]pyrene (5.0 ppb), and indeno[1,2,3-c,d]pyrene (2.7 ppb). The total PAHs concentrations increased from 151.4 to 299.7 ppb during grilling of duck breast steak (with skin) for 0.5–1.5 h. For carcinogenic PAHs, it increased from 10.2 to 16.0 ppb during grilling. Table 7 shows the effect of charcoal grilling on PAHs formation in duck breast steak (without skin). After grilling for 30 min, the texture of duck breast steak becomes hard. As grilling time increased to 1 h, the appearance of duck sample gradually turns black. Like duck breast steak with skin, all 16 PAHs with the exception of dibenzo[a,h]anthracene and benzo[g,h,i]perylene were detected during grilling. After grilling for 1.5 h, naphthalene was present at highest concentration (58.8 ppb), followed by phenanthrene (58.6 ppb), chrysene (38.0 ppb), pyrene (31.6 ppb), fluoranthene (26.3 ppb), benzo[a]anthracene (22.3 ppb), acenaphthylene (19.0 ppb), fluorene (14.4 ppb), anthracene (13.3 ppb), benzo[b]fluoranthene (11.1 ppb), benzo[a]pyrene (8.5 ppb), benzo[k]fluoranthene (6.7 ppb), acenaphthene (5.6 ppb), and indeno[1,2,3-c,d]pyrene (5.2 ppb). It was also found that during grilling,

Table 6. Changes of PAH Concentrations (ppb)^a in Duck Breast Steak (with Skin) during Grilling for 0.5, 1.0, and 1.5 h

| compound | grilling time (h) | | |
|--------------------------------------|--|--------------------------|--------------------------|
| | 0.5 | 1.0 | 1.5 |
| naphthalene | 36.3 ^{1,d} (8.1) ^f | 42.7 ² (13.5) | 73.8 ³ (10.9) |
| acenaphthylene | 6.0 ¹ (3.1) | 6.7 ¹ (2.5) | 10.6 ² (5.8) |
| acenaphthene | 5.2 ¹ (1.6) | 5.4 ¹ (0.9) | 5.7 ¹ (1.2) |
| fluorene | 7.2 ¹ (3.4) | 7.7 ¹ (2.7) | 8.3 ¹ (1.9) |
| phenanthrene | 24.9 ¹ (6.3) | 29.1 ² (9.2) | 55.3 ³ (15.3) |
| anthracene | 7.3 ¹ (4.2) | 9.5 ² (6.3) | 10.9 ² (5.8) |
| fluoranthene | 22.4 ¹ (10.1) | 26.4 ² (13.8) | 29.9 ² (9.7) |
| pyrene | 21.5 ¹ (8.6) | 48.8 ² (14.5) | 47.1 ² (12.7) |
| benzo[a]anthracene ^b | 1.6 ¹ (2.5) | 2.6 ¹ (1.3) | 5.5 ² (5.2) |
| chrysene | 5.9 ¹ (3.8) | 6.6 ¹ (5.0) | 29.7 ² (9.7) |
| benzo[b]fluoranthene ^{b,e} | 4.2 ¹ (1.8) | 3.4 ¹ (2.4) | 8.3 ² (5.6) |
| benzo[k]fluoranthene ^e | 2.8 ¹ (3.0) | 3.2 ¹ (2.5) | 6.9 ² (6.3) |
| benzo[a]pyrene ^{b,e} | 3.7 ¹ (2.3) | 5.0 ¹ (1.6) | 5.0 ¹ (2.1) |
| indeno[1,2,3-c,d]pyrene ^b | 2.4 ¹ (1.9) | 2.6 ¹ (1.5) | 2.7 ¹ (2.0) |
| dibenzo[a,h]anthracene ^b | ND ^c | ND | ND |
| benzo[g,h,i]perylene | ND | ND | ND |
| total PAHs | 151.4 | 199.7 | 299.7 |
| carcinogenic PAHs | 11.9 | 13.6 | 21.5 |

^a Mean of duplicate analyses. ^b Carcinogenic PAH. ^c ND, not detected at a limit of 25 pg. ^d Numbers tagged with superscript 1–3 in the same row are significantly different ($p < 0.05$). ^e Tentatively identified. ^f Values in parentheses represent coefficient of variation (%).

duck breast steak without skin contained higher amounts of total PAHs as well as carcinogenic PAHs than those of duck breast steak with skin. This result seems to be contradictory to some reports by Lijinsky and Ross (1967), Engst and Fritz (1977), and Doremire et al. (1979). Doremire et al. (1979) reported that the amount of benzo[a]pyrene is directly proportional to fat content during charcoal grilling. Engst and Fritz (1977) also reported that benzo[a]pyrene was formed at a higher concentration in fish with skin than that without skin. In our study the charcoal grilling method used was different from the others, and thus the contamination of meat by PAHs, could be reduced. This can be explained as follows: During grilling, the fat drippings did not fall on the charcoal, and hence, the PAHs formed did not come up with smoke, and thus the adherence of PAHs to the meat surface might not be possible. To prevent formation of PAHs during charcoal grilling, the direct contact of meat with the cooking flame or grilling

Table 7. Changes of PAH Concentrations (ppb)^a in Duck Breast Steak (without Skin) during Grilling for 0.5, 1.0, and 1.5 h

| compound | grilling time (h) | | |
|---|--|--------------------------|--------------------------|
| | 0.5 | 1.0 | 1.5 |
| naphthalene | 21.0 ^{1,d} (8.7) ^f | 57.3 ² (15.2) | 58.8 ² (13.8) |
| acenaphthylene | 7.5 ¹ (10.3) | 12.9 ² (13.6) | 19.0 ³ (9.8) |
| acenaphthene | 4.7 ¹ (2.7) | 5.3 ¹ (1.5) | 5.6 ¹ (2.1) |
| fluorene | 7.5 ¹ (3.4) | 11.5 ² (6.2) | 14.4 ³ (6.8) |
| phenanthrene | 24.9 ¹ (9.5) | 48.4 ² (13.2) | 58.6 ³ (16.7) |
| anthracene | 9.4 ¹ (7.3) | 11.7 ² (8.5) | 13.3 ² (6.3) |
| fluoranthene | 19.7 ¹ (9.8) | 26.9 ² (13.5) | 26.3 ² (12.1) |
| pyrene | 24.0 ¹ (7.8) | 31.6 ² (11.6) | 31.6 ² (12.0) |
| benzo[<i>a</i>]anthracene ^b | 2.4 ¹ (1.3) | 10.5 ² (6.3) | 22.3 ³ (9.8) |
| chrysene | 30.8 ¹ (10.3) | 29.4 ¹ (8.9) | 38.0 ² (15.6) |
| benzo[<i>b</i>]fluoranthene ^{b,e} | 10.0 ¹ (7.2) | 10.4 ¹ (6.5) | 11.1 ¹ (8.0) |
| benzo[<i>k</i>]fluoranthene ^e | 5.8 ¹ (3.2) | 6.5 ¹ (1.9) | 6.7 ¹ (2.3) |
| benzo[<i>a</i>]pyrene ^{b,e} | 9.2 ¹ (4.7) | 8.4 ¹ (3.2) | 8.5 ¹ (2.9) |
| indeno[1,2,3- <i>c,d</i>]pyrene ^b | 5.2 ¹ (3.8) | 5.2 ¹ (2.5) | 5.2 ¹ (1.7) |
| dibenzo[<i>a,h</i>]anthracene ^b | ND ^c | ND | ND |
| benzo[<i>g,h,i</i>]perylene | ND | ND | ND |
| total PAHs | 182.1 | 276.0 | 319.4 |
| carcinogenic PAHs | 26.8 | 34.5 | 47.1 |

^a Mean of duplicate analyses. ^b Carcinogenic PAH. ^c ND, not detected at a limit of 25 pg. ^d Numbers tagged with superscript 1–3 in the same row are significantly different ($p < 0.05$). ^e Tentatively identified. ^f Values in parentheses represent coefficient of variation (%).

at high temperature should be avoided. The formation of PAHs during charcoal grilling at high temperature may be due to the incomplete combustion of charcoal or transformation of some food components such as triglyceride and cholesterol. Also, during charcoal grilling at high temperature, the fat drippings fall on the hot coals were pyrolyzed, producing benzo[*a*]pyrene and other PAHs which were subsequently deposited onto the surface of the meat. In contrast, with electric grilling only minor amount of PAHs and no carcinogenic PAHs were observed (Masuda et al., 1996; Lijinsky and Ross, 1967). In another study Lijinsky and Shubik (1964) further reported that the charcoal grilled well-done beef steak contained 8 ppb benzo[*a*]pyrene. Thus, the potential hazard of charcoal grilled meat to human health cannot be ignored.

Comparison of PAH Levels by Various Processing Treatments. Table 8 shows the amounts of the total PAHs and carcinogenic PAHs in duck breast steak by various processing methods. With processing time from 0.5 to 1.5 h, charcoal grilling of duck samples with skin contained the highest amount of total PAHs, followed by charcoal grilling of duck without skin, smoking, roasting, steaming, and LSF. For carcinogenic PAHs, the trend is the same with the exception that smoking contained the highest amount. Also, the highest amounts of total and carcinogenic PAHs were observed after smoking of duck samples for 3.0 h. From Table 8 it may be concluded that steaming and LSF were the most appropriate methods to process duck meat because no carcinogenic PAHs were detected. The total and carcinogenic PAHs concentrations of grilled and smoked samples shown in this study were somewhat higher than those from the commercial meat products as reported by the other researchers (Gomma et al., 1993; Yabiku et al., 1993; Chen et al., 1996). These authors found that in smoked or grilled meat samples the total PAHs concentrations did not exceed 150 ppb. This difference may be attributed to the fact that some PAHs are susceptible to oxygen and light degradations, and thus, the PAHs concentrations can undergo graduate loss during storage of commercial

Table 8. Total PAH and Carcinogenic PAH Contents (ppb) in Duck Breast Steak by Various Processing Methods

| | time (h) | total PAHs | carcinogenic PAHs ^a |
|--|----------|------------|--------------------------------|
| steaming | 0.5 | 4.4 | ND ^b |
| | 1.0 | 8.6 | ND |
| | 1.5 | 8.6 | ND |
| roasting | 0.5 | 88.5 | 14.4 |
| | 0.6 | 115.5 | 15.3 |
| | 0.8 | 127.6 | 15.0 |
| smoking | 0.5 | 154.6 | 18.8 |
| | 1.0 | 174.5 | 20.4 |
| | 1.5 | 206.5 | 35.2 |
| | 2.0 | 317.6 | 41.5 |
| | 3.0 | 526.8 | 52.6 |
| charcoal grilling of duck with skin | 0.5 | 151.4 | 11.9 |
| | 1.0 | 199.7 | 13.6 |
| | 1.5 | 299.7 | 21.5 |
| charcoal grilling of duck without skin | 0.5 | 182.1 | 26.8 |
| | 1.0 | 276.0 | 34.5 |
| | 1.5 | 319.4 | 47.1 |
| liquid smoke flavoring (LSF) | | 87.3 | 1.4 |
| LSF-treated duck breast steak | | 0.3 | ND |

^a Carcinogenic PAHs include benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, and dibenzo[*a,h*]anthracene. ^b ND, not detected at a limit of 50 pg.

meat products. Nevertheless, we have to point out here that the PAHs contents observed in this study may not be identical to those in real commercial processed meat products, mainly because only several duck samples were selected for PAHs determination for each treatment and the processing conditions may be different. Thus, further research is necessary to determine PAHs content change during commercial production of duck meat. In addition, with the exception of benzo[*a*]pyrene, both FAO and WHO should include some more PAHs such as benzo[*a*]anthracene and benzo[*b*]fluoranthene as reference toxic compounds in foods, because both are carcinogenic and are present in significant amount in smoked and grilled duck meat.

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