AP-42 Section 9.5.2
Reference 3
Report Sect. 2
Reference 6

Smoke in Food Processing

Author
Joseph A. Maga
Professor
Department of Food Science and
Human Nutrition
Colorado State University
Fort Collins, Colorado

CRC Press, Inc.
Boca Raton, Florida

Library of Congress Cataloging-in-Publication Data

Maga, Joseph A.
Smoke in food processing.

Includes bibliographies and index.
1. Meat, Smoked. 2. Fish, Smoked. I. Title.
TP371.44.M34 1988 664'.0286 87-24231
ISBN 0-8493-5155-3

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

International Standard Book Number 0-8493-5155-3

Library of Congress Card Number 87-24231
Printed in the United States

Chapter 3

SMOKE GENERATION TECHNOLOGY

I. INTRODUCTION

Through the years various ways of pyrolyzing wood to produce smoke-flavor compounds have developed. From a commercial standpoint this has evolved from the first primitive ways which probably just involved hanging meat on the ceiling of a dwelling and permitting smoke resulting from a fire that was used solely as a source of warmth to pass around and through the product. Today, the generation of smoke in many commercial operations can be quite sophisticated. Also, in most countries techniques are required that minimize environmental pollution.

Another factor that in some countries has dictated that technologically advanced smoke-generation systems be employed is the potential health concerns associated with certain rather primitive smoke-generation systems. This potential problem will be discussed in a later chapter.

The current major commercial methods of generating smoke from wood have been reviewed,[1-3] and thus at this point, only a brief summation of the six major techniques will be given. It should be noted that modern smoking operations usually pyrolyze wood in a separate chamber and then transport the generated smoke into a chamber where the food item is present. This is in contrast with more primitive techniques where smoke generation and application steps are accomplished in the same chamber.

In fact, some of the more advanced smoke-generation units are photoelectronically controlled in such a manner that the appearance of a flame in the smoldering sawdust causes the metering of a new portion of sawdust. As a result, such units can efficiently produce a smoke of uniform composition.[55]

Other researchers[56] have thoroughly studied the aerodynamic parameters that are important for the optimum mixing of air and smoke so as to obtain maximum smoke color and flavor in the food being smoked as well as to minimize smoke pollution. This information has gone into the design of smoke-processing chambers. Also, it has been found that pulsating air is more effective than a steady-flow air system.[56] In addition, computer simulations of many smoking processes have been developed[57] to predict the most efficient and economic options required to produce and utilize smoke in a wide variety of foods.

II. SMOLDERING

As the name smoldering implies, a wood source, usually in a sawdust form, is permitted to smolder by the action of a heating coil, or in some instance, in the presence of a gas flame. Through continuous gentle agitation, and in the presence of sufficient oxygen, a steady supply of sawdust and resulting smoke will be produced.

The resulting smoke is then either drawn or pushed into the actual smoking chamber and permitted to interact with the food in question. The amount of tar and other solid particles that enters the smoking chamber can be controlled to some extent by the distance the smoldering unit is from the smoking unit, with the longer the distance, the greater the opportunity for tar to settle out. Also, various baffles and filters can be placed in line to remove tar, but routine cleaning is required to remove buildups of these compounds in the system.

Smoke production or generation temperature, using the smoldering technique, can vary over a fairly wide range, dependent upon available air. If a large quantity of air is present, the actual smoldering temperature may be in excess of 800°C, but if the amount of available air is controlled, lower smoldering temperatures will result.

Smoke production temperature can also be lowered by controlling the sawdust moisture content.[2] Most small commercial operations do not normally consider wood moisture content, but wood containing approximately 30% moisture will effectively lower smoldering temperature 100 to 300° over a completely dry wood sample. This in turn reduces energy requirements and produces a smoke generally lower in polycyclic aromatic hydrocarbons (PAH), which have significant health implications.

III. FRICTION

Some processors use the friction method whereby an intact wood block is pressed against a rapidly rotating metal friction wheel. Heat produced by friction is sufficient to cause wood pyrolysis. Air is permitted to enter through the center of the friction wheel thus producing a cooling effect on the resulting smoke. The more air that is present, the lower the resulting smoke temperature. This is in direct contrast with the smoldering technique. In addition, it is a flameless method of generating smoke and the resulting wood dust falls to the bottom of the generation chamber with the smoke being directed into the smoking chamber.

If the apparatus is operated in a discontinuous fashion, such that the friction wheel is in operation for 10 sec and then rested for several minutes, smoke temperatures that are only a few degrees above ambient temperature can be achieved. However, if operated in a continuous fashion, smoke temperatures in the range of 140 to 160°C are common.

Other factors influencing smoke temperature include the amount of force applied to the wood block, the wheel speed, and the shape of the friction edges.[4-6] The actual temperature during wood pyrolysis using friction is in the neighborhood of 450 to 560°C, but rapid cooling occurs, so actual smoke temperature can be relatively low.[6]

However, Toth[4] has reported that the sensory properties resulting from friction-generated smoke, when compared to smoldering-generated smoke, contain only low amounts of volatile phenols, guaiacol, and syringol, but higher amounts of allyl- and propenyl syringol, and only about 10% of higher molecular weight compounds, which in turn adversely influence product taste and smell. Apparently, the rapid cooling associated with friction smoke generation does not permit sufficient time and/or temperature for the primary products of wood pyrolysis to undergo extensive secondary reactions, thus limiting the number of compounds formed.

IV. WET SMOKE

In the wet smoke or condensate smoke method, sawdust and superheated steam containing varying amounts of heated air are blended, causing sawdust pyrolysis. The resulting smoke has a temperature of approximately 80°C, and is moist because of condensed water from steam. This represents another flameless method, and pyrolysis normally occurs in the 300 to 400°C range. Advantages cited for the process include a short treatment time and improved smoke yield.[7-11]

V. FLUIDIZATION

With this technique, air is heated to between 300 to 400°C by means of an electric heater, and under high velocity, mixed with sawdust. Because of the resulting turbulence, the sawdust is "suspended" or fluidized. Because of the air temperature, pyrolysis occurs at approximately 350°C in around 10 sec. A cyclonic separator is used to yield smoke and charred sawdust. This procedure is also flameless, and because of the cooling effect, smoke temperature does not go much beyond ambient temperature.

Table 1
SMOKE CHARACTERISTICS OF VARIOUS SMOKE PRODUCTION TECHNIQUES

Smoke production technique	Smoke production temp (°C)	Smoke temp (°C)	Smoke characteristics
Smoldering	400—800	20	Dry, dense, contains oxygen
Friction	300—500	20	Dry, dense, much oxygen
Wet smoke	300—400	80	Moist, dense, low oxygen
Fluidization	300—400	25	Dry, dense, contains oxygen
Two stage	300—400	30	Dry, dense, contains oxygen
Carbonization	300—400	20	Dry, dense, low oxygen

VI. TWO STAGE

The two-stage procedure is a modification and extension of the fluidized technique described above. The first stage involves initial wood pyrolysis by the action of nitrogen or carbon dioxide at a temperature of 300 to 400°C on sawdust. In the second stage, the reactants of the first stage are mixed with oxygen or air heated to 200°C, and further pyrolysis occurs. The second stage promotes oxidation, condensation, and polymerization reactions thus resulting in a more complex mixture of potential flavor compounds in the smoke. Because of the dual effect, the resulting temperature is in the neighborhood of 30°C.

Factors influencing smoke composition and yield are first-stage pyrolysis temperature, amount of nitrogen or carbon dioxide during first-stage pyrolysis, and temperature of second-stage oxidation. Maximum smoke amounts were found to occur at a first-stage temperature of 400°C, with a nitrogen level of 1500 ℓ/hour, and a second oxidation temperature of 200°C.[2]

VII. CARBONIZATION

Production of smoke via carbonization requires specialized equipment in that sawdust is pressed together in a tubular casing by means of a tapered screw. As a result, most of the air associated with sawdust is eliminated. Directly at the end of the compression device is a variable temperature electrical heating element, which, because of lack of air in the compressed sawdust, causes the product to give off smoke during carbonization. This is another system that is flameless, and produces smoke that has a temperature close to ambient conditions.

Some of the general characteristics of the smoke produced by the above six techniques are summarized in Table 1. It should be noted that with the smoldering and friction methods, smoke-generation temperature is rather difficult to control, whereas with the other procedures, it is easier to generate smoke at a preselected temperature, which is usually lower than that used for the first two mentioned methods.

Also, with the smoldering methods, flames may actually be produced, which can actually combust desirable smoke-associated compounds. The other methods in turn all produce smoke without the presence of flames.

You can also note from Table 1 that only the wet smoke method results in moist smoke, while the others produce dry smoke. This in turn could influence product yield due to potentially higher food weight losses associated with the use of dry smoke. Also, a moist smoke may be more beneficial from a color standpoint.

The other major difference among the procedures outlined in Table 1 is the fact that the smokes produced have varying amounts of oxygen associated with them. This has both positive and negative aspects. Oxygen will provide for more secondary oxidation reactions to occur, thus resulting in the formation of additional flavor-associated compounds. However, certain smoke-associated compounds are sensitive to oxygen and are actually decomposed in the presence of large amounts of oxygen.

VIII. HOT VS. COLD SMOKING

The actual smoke temperature can vary quite widely dependent upon the method of generation and the ambient temperature surrounding the food item being smoked. Obviously, if high ambient temperatures are used, the food will also undergo some degree of cooking as well as absorb and react with components in smoke. On the other hand, it is possible to expose food to temperatures only slightly above room temperature and the food will still obtain a smoky character without undergoing any cooking. This is the major difference between cold smoking, which usually occurs at temperatures of 15 to 25°C,[29] while for hot smoking, temperatures in the range of 55 to 80°C are employed.[1] Foods typically cold smoked are raw ham and bacon, while typical hot smoke foods include cooked ham and frankfurters. Some processors also utilize warm smoking where the smoke and chamber temperature is between 25 and 40°C.[13]

Several reports have appeared demonstrating that hot vs. cold smoking can influence resulting phenol composition[14,15] with apparently more variation in the fat than in the lean portion of meat.[15] However, no difference due to hot or cold smoke processing relative to carbonyl content was found.[15]

From an efficiency standpoint, hot smoke becomes associated with food approximately seven times faster than cold smoke,[1] but with hot smoking, chemical changes occur primarily in the fat portion of the food. Essentially, a cold-smoked food is not cooked.

Time of smoking is another major difference between the two processes. For example, the cold smoking of a food can take up to several weeks so that the proper amount of color and/or flavor are generated in the food, whereas hot smoking may only take several hours.[30]

Cold smoking seems to be especially adaptable to most fish species.[58-60] In the case of rainbow trout[58] it was found that cold smoking for 2 hr at 30°C gave a product of equal smoke quality to that smoked for 1 hr at 80°C. With catfish and kipper, cold smoking was found to be preferable from a sensory standpoint, and in addition, better yields were obtained as compared to hot smoking of either whole fish or fillets.[59]

Some processors also practice what is called moist smoking.[12] This involves using a smoke-chamber temperature of 24 to 48°C and relative humidities in excess of 30%. The process has found application in the smoking of dry sausage and salamis.

Dark smoking is another process whereby a dense smoke is permitted to blacken the surface of the food in question.[31] As a result, the food has a strong smoky character. Smoke that has quite a bit of particulate matter associated with it, such as pine, is normally used, but the practice has to be questioned from a health standpoint, since smoke particulate matter can be high in PAH.

As can be seen in Table 2, there is no question that the composition of light and dark smoke is significantly different, thus resulting in different sensory properties. It is also apparent from Table 2 that the wood source can also influence smoke composition, and in turn its sensory properties. This concept will be expanded upon in a later chapter.

IX. ELECTROSTATIC SMOKING

As mentioned earlier, smoke is composed of two phases, namely a particulate or dispersed phase and a gaseous or dispersing phase.[32] The dispersed phase is the visable portion of smoke and is primarily composed of tars, wood resins, high-boiling phenolic-type com-

Table 2
INFLUENCE OF WOOD SOURCE AND DEGREE OF SMOKING ON RESULTING COMPOSITION

Smoke fraction	Beech smoke (light)	Beech smoke (heavy)	Oak smoke (light)	Oak smoke (heavy)
Ash and soot	8.0	8.2	21.8	23.5
Insoluble in ether	216.0	99.6	154.2	757.4
Free bases	45.3	155.8	42.0	48.0
Aldehydes and ketones	47.9	108.9	24.8	71.0
Carboxylic acids	37.3	203.6	64.3	327.5
Phenols	15.9	93.3	9.0	73.3
Neutral organic compounds	298.9	1757.0	477.6	803.6
Unknown	12.2	95.6	21.9	45.2

Adapted from Ziemba, A., *Przem. Spozyw.*, 2, 200, 1957.

Table 3
VOLATILE COMPOSITION OF UNTREATED AND ELECTROSTATICALLY FILTERED SMOKE

	mg%	
Compound class	**Untreated smoke**	**Electrostatically filtered**
Acids	211.0	150.0
Phenols	7.5	2.7
Carbonyls	347.0	192.0

pounds, and lower boiling compounds that vary with temperature and smoke concentration.[1] These particles are usually in the form of liquid droplets that form by condensation and are 0.196 to 0.346 μm in average diameter.[17-19,33] However, most of the characteristic flavor associated with wood smoke is present in the gas phase.[20]

The fact that wood smoke is a two-phase system has brought about the introduction of electrostatic smoking.[1,2,20-26,34,35,39] The procedure has found application in a continuous tunnel-type arrangement whereby the product is positioned between live electrical wires that are charged to between 20 to 60 kV. Smoke passing through this system is charged according to its phase and smoke components can then precipitate on the oppositely charged meat surface. This is usually followed by infrared radiation, which drys the product surface.[2,27]

As would be expected, the process changes the volatile composition of smoke. As seen in Table 3, electrostatically filtered smoke was found to be lower in acids, phenols, and carbonyls than untreated smoke.

Because of these differences one would predict that products smoked by the two procedures would have different sensory properties. Rusz[23] found that for a variety of smoked sausages, electrostatically filtered smoke usually gave less smoky aroma and color development than normal smoke but the sensory flavor scores were fairly similar. However, since most researchers used subjective sensory panels to evaluate the original properties of smoked foods, no clearcut decision can be made on whether or not electrostatically smoked foods are more or less acceptable than traditionally smoked foods.

Factors such as distance between wires and time of treatment are obviously two factors that can significantly influence the amount of flavor compounds deposited. For example, as seen in Table 4, wire spacing of 60 cm produced less total phenols than a traditionally smoked bacon control, while a spacing of 20 cm produced more. Thus, by varying wire spacings, one could at least theoretically obtain comparable phenol levels. Also, as seen in

Table 4
INFLUENCE OF ELECTROSTATIC PROCESSING CONDITIONS OF THE VOLATILE COMPOSITON OF BACON

Variable	Phenols[a]	Monocarbonyls[b]	Total carbonyls[b]
Traditionally smoked	3881	3.3	22
Electrostatic-20 cm wire spacing	5481	4.4	31
Electrostatic-60 cm wire spacing	3660	3.7	22
Traditionally smoked (2 hr)	3730	NR	15
Electrostatic (2 hr)	4826	NR	17
Electrostatic (1 hr)	2418	NR	10

Note: NR = not reported.

[a] mg/100 g bacon.
[b] m*M*/100 g bacon.

Adapted from Girard, J. P., Talon, R., Sirami, J., and Denoyer, C., *Sci. Aliment.*, 2, 1, 1982.

Table 4, time is influential. The 2 hr electrostatic process resulted in more phenols than the 2 hr traditional control. Therefore, an advantage of electrostatic smoking is that it is faster.

In the case of fish, it has been reported[61] that the conditions of electrostatic smoking have to be adjusted dependent upon the size and fish species being smoked. From 50 to 80% of the smoke components were found to be trapped by the skin and subcutaneous muscle. Other factors found to be important were skin density, the presence of scales, and the amount of subcutaneous fat.[62]

X. MISCELLANEOUS TECHNOLOGIES

A. Gas-Phase Smoke

Another interesting technological concept is based on utilization of only the gaseous phase of wood smoke. Generated smoke is separated by cooling and washing or filtering to recover only the gaseous phase. This usually results in a characteristic flavor but a lighter surface color can be expected, since no particulate matter is present.

B. Closed Smoking

Primarily because of concerns for environmental pollution, the closed smoking system has been developed.[2,36] In this procedure, a portion of the smoke remaining in the smoking chamber as exhaust is recycled back to the smoke-generation chamber as a partial replacement for fresh air.[28,37] This in turn has several effects. First, less total smoke is emitted into the atmosphere since it is essentially recycled. Second, since the recyled smoke is generally lower in oxygen than normal air, the smoldering temperature in the generation chamber is reduced, which in turn lowers the formation of PAH.

C. Indirect Smoking

In this process, herbs and/or spices that are going to be incorporated into a food formulation are smoked independently[45] and then just added to food, which is then usually heat processed. Obvious limitations include the fact that only low overall smoke flavor may result in the food, and smoke flavor can be localized to the spice portion of the food.

D. Liquid Smoke

In certain countries the product called liquid smoke has become quite popular. The reported

Table 5
COMPOSITION OF COMMERCIAL LIQUID SMOKES

Fraction	%
Water	11—92
Phenols	0.2—2.9
Acids	2.8—9.5
Carbonyls	2.6—4.6
Tar	1—17

Adapted from Baltes, W., Wittkowski, R., Sochtig, I., Block, H., and Toth, L., in *The Quality of Foods and Beverages*, Vol. 2, Charalambous, G. and Inglett, G., Eds., Academic Press, New York, 1981, chap. 1.

advantages of utilizing liquid smoke condensate include: (1) some flavor can be incorporated throughout a product in a uniform manner instead of having a higher concentration on the outside vs. inside as with traditional smoking, (2) it can intensify the flavor of traditionally smoked foods, (3) there is closer control on the amount of smoke flavor a product receives, (4) it can be fractionated to intensify smoke flavor and to remove potentially harmful compounds before it is used with food, (5) it has application to a wide variety of foods that traditionally are not smoked, (6) it can be used at the consumer level as well as the commercial processing level, (7) normally it represents a cost savings since wood and smoking equipment are not required as part of a food smoking plant, (8) there is less environmental pollution associated with its use, and (9) it can be applied in various ways such as spraying on the surface, dipping, and actual mixing in with the food.[1,38,46-51]

Condensed smoke can be obtained and utilized in various forms. The classical liquid smoke is smoke condensate that is dissolved in water, oil, or smoke extracts in organic solvents. In addition, smoke condensate can be adsorbed on the solids such as spices, salt, sugars, starch, or protein, thus resulting in dry or powdered forms.[64]

Freshly generated smoke that is condensed in water usually has a bright yellow color that with time darkens due to the formation of brown-colored condensation or polymerization products. These compounds, along with tarry products and polycyclic aromatic hydrocarbons (PAH), settle out with time. The resulting liquid phase can then be decanted, resulting in a liquid preparation that is low in PAH. In contrast, smoke that is condensed into water that contains solvents such as ethanol or glycol does not precipitate tars and PAH.[64]

Also, as seen in Table 5, the composition of commercial liquid smoke can vary widely, dependent upon method of manufacture.[41-44] An important compositional factor is the acidity in the resulting smoke, since this in turn can influence phenol solubility. As shown in Table 6, the solubility of most phenols increases significantly with increasing acidity. Thus, if the acidity is not high enough, some phenols may actually settle out during the prolonged storage of liquid smoke, and thus their measurement is suggested.[52]

In the case of experimentally smoked fish in a traditional manner as compared to the use of liquid smoke, it has been reported[63] that the liquid smoke treated product has less pronounced aroma and flavor. Analysis of the phenolic substances showed that the liquid smoked fish had 1.14 to 1.75 mg/100 g while the traditional product had 5.94 to 13.55 mg/100 g. Also, carbonyl and total acid levels were 22.8 and 0.59 mg/100 g, respectively, in the liquid smoke product while corresponding values for traditionally smoked fish were 23.7 and 0.69.

Table 6
INFLUENCE OF LIQUID SMOKE ACIDITY ON PHENOL SOLUBILITY

	Solubility of (%)		
Acidity (%)	Cresol	Guaiacol	2,6-Dimethoxyphenol
2	2	40	30
4	8	45	35
6	17	62	42
8	22	78	78
10	30	80	100

Adapted from Gubler, D. and Vernois, M., *Ind. Aliment. Agric.*, 89, 621, 1972.

The question may arise as to whether liquid smoke or traditional smoking was used in the production of certain smoked foods. A somewhat simple answer to this question is the measurement of a specific smoke component, usually guaiacol, in the center vs. the exterior of the food.[40,53,54] In traditional smoking one would expect a much lower concentration of quaiacol towards the center since phenol migration is not significant in traditional smoking. However, if liquid smoke had been added to the product, the guaiacol level should be fairly uniform throughout the product. Care should be taken though, since if liquid smoke were only sprayed on the product surface and then the product heated and/ or smoked, low guaiacol levels would also be present in the product center leading someone to falsely conclude the product was smoked in the traditional manner.

REFERENCES

1. **Draudt, H. N.**, The meat smoking process: a review, *Food Technol.*, 17, 1557, 1963.
2. **Klettner, P. G.**, Modern methods of smoking meat products, *Fleischwirtschaft*, 59(1), 73, 1979.
3. **Klettner, P. G.**, Technology of common smoking methods, *Fleischerei*, 29(10), 60, 1978.
4. **Toth, L.**, Influence of smokehouse technology on phenols in the smoke, *Fleischwirtschaft*, 60(8), 1472, 1980.
5. **Klettner, P. G.**, Curing smoke production with the friction smoke generator, *Fleischwirtschaft*, 55(11), 1498, 1975.
6. **Khavan, E. A., Blejus, V. G., Sandosvskii, B. F., and Voskresenskii, H. A.**, Smoke, *Rybn. Khoz.*, 47(9), 57, 1971.
7. **Zweig, K. and Schossig, H.**, Experience with the type 301 steam-type smoke generator in Bruhwurst sausage manufacture, *Fleisch*, 33(9), 173, 1979.
8. **Schuldt, P.**, Application of steam-generated smoke in cold-smoking and controlled environment smoking, *Fleischerei*, 30(12), 990, 1979.
9. **Fessman, G. and Fessman, K. D.**, Steam-generated smoke for hot and cold smoking, *Fleischerei*, 30(12), 1006, 1979.
10. **Rusz, J. and Kopslova, M.**, New method for smoking of meat and meat products, *Fleisch*, 28(12), 236, 1974.
11. **Fessman, G.**, Production and utilization of curing smoke, *Fleischerei*, 24(11), 14, 1973.
12. **Reich, W.**, Applications of modern universal cooking chambers for smoking and cooking, *Fleischerei*, 28(3), 25, 1977.
13. **Butanski, I.**, Smoke and its preserving role in meat and meat product smoking, *Khranit. Prom.*, 28(5), 8, 1979.
14. **Toth, L.**, Uptake of phenols from smokehouse smoke into meat products, *Fleischwirtschaft*, 62(11), 1398, 1982.

15. **Khlamova, R. I., Soloveva, L. I., and Petrakova, A. N.,** Content of phenolic and carbonyl compounds in cold smoked products, *Myasn. Ind. SSSR,* No. 2, 37, 1980.
16. **Ziemba, A.,** Generation of industrial curing smoke and its chemical composition, *Przem. Spozy.,* 2, 200, 1957.
17. **Foster, W. W.,** Deposition of unipolar charged aerosol particles by mutal repulsion, *Br. J. Appl. Phys.,* 10, 206, 1959.
18. **Foster, W. W.,** Attenuation of light by wood smoke, *Br. J. Appl. Phys.,* 10, 416, 1959.
19. **Foster, W. W., Simpson, T. H., and Campbell, D.,** Studies of the smoking process for foods. II. The role of smoke particles, *J. Sci. Food Agric.,* 12, 635, 1961.
20. **Foster, W. W. and Simpson, T. H.,** Studies of the smoking process for foods. I. The importance of vapours, *J. Sci. Food Agric.,* 12, 363, 1961.
21. **Hanley, J. W., Draudt, H. N., and Brockmann, M. C.,** A continuous process for smoked meat. I. Development of a process, *Food Technol.,* 9, 591, 1955.
22. **Hanley, J. W., Montgomery, G. I., Rarick, M. S., and Brockmann, M. C.,** A continuous process for smoked meats. II. Equipment design and application, *Food Technol.,* 9, 597, 1955.
23. **Rusz, J.,** Experiences with the use of electrostatically filtered smoke for smoking of meat products, *Acta Aliment. Pol.,* 3, 301, 1977.
24. **Girard, J. P., Talon, R., Sirami, J., and Denoyer, C.,** Electrostatic smoking: efficiency in relation to two technological parameters, *Sci. Aliment.,* 2, 1, 1982.
25. **Talon, R. and Girard, J. P.,** Smoking of meat products, *Viandes Produits Carnes,* 1(4), 16, 1980.
26. **Kleitz, R.,** Smoking equipment used in the fish industry of the German Democratic Republic, and possibilities for its mechanization, *Lebensm. Ind.,* 26, 257, 1979.
27. **Pigott, G. M. and Tillisy, M.,** Short time high quality (STHQ) smoking and dehydration, *Proc. 6th Int. Conf. Food Sci. Technol.,* 1, 193, 1983.
28. **Huch, R.,** Means of restricting emissions from plants for smoked foods, *Wasser Luft Betr.,* 20(12), 669, 1976.
29. **Corretti, K.,** Raw sausage and meat products. II. Raw meat products. Smoking and storage of uncooked cured meat, *Fleischwirtschaft,* 55(11), 1504, 1975.
30. **Toth, L.,** Influence of smoking technology on smoke components in meat products, *Fleischwirtschaft,* 62(2), 172, 1982.
31. **Shaposhnikov, Y. K., Khvan, E. A., Stepanova, M. I., and Kondakova, L. V.,** The chemical composition of a smoking medium, *Rybn. Khoz.,* No. 9, 75, 1972.
32. **Proskura, Y. D.,** Conditioning of smoking smoke, *Rybn Khoz.,* 47(10), 55, 1971.
33. **Rusanov, V. V., Lapshin, I. I., and Kuchumov, A. M.,** Study of smoking medium particles by electron microscopy, *Rybn. Khoz.,* No. 5, 67, 1975.
34. **Hardy, R. and McGill, A. S.,** Smoking of foods: methods and some toxicological aspects, *Proc. Biochem.,* 14(11), 2, 1979.
35. **Khan, E. A.,** Physico-chemical properties of wood smoke, *Tr. Vses. Nauchno-Issled. Inst. Morsk. Rybn. Khoz. Okeanogr.,* 73, 102, 1970.
36. **Abaseev, V. K., Kvasov, A. A., and Shaposhnikov, Y. K.,** Catalytic additional combustion of residual smoke gases from fish smoking, *Rybn. Khoz.,* No. 11, 66, 1973.
37. **Sadovskii, B. F., Khvan, E. A., Radakova, T. N., and Bazarov, A. P.,** The thermal regime of smoke formation in smoke generators, *Rybn. Khoz.,* No. 3, 80, 1974.
38. **Golovanev, V. F. and Bolshakov, A. S.,** Effect of cooking and smoking methods on the quality of textured products, *Izv. Vyssh. Uchebn. Zaved. Pishch. Tekhnol.,* No. 3, 71, 1978.
39. **Alexander, A.,** Electrostatic principles applied to smoking technology, *Food Flavor Ingred. Pkg. Proces.,* 1(5), 31, 1980.
40. **Baltes, W., Wittkowski, R., Sochtig, I., Block, H., and Toth, L.,** Ingredients of smoke and smoke flavor, in *The Quality of Foods and Beverages,* Vol. 2, Charalambous G. and Inglett, G., Eds., Academic Press, New York, 1981, chap. 1.
41. **Hollenbeck, C. M.,** Novel concepts in technology and design of machinery for production and application of smoke in the food industry, *Pure Appl. Chem.,* 49, 1687, 1977.
42. **Wistreich, H. E.,** Smoking of meats, Proc. Meat Ind. Res. Conf., Chicago, 1977, 37.
43. **Baichev, I. and Stefanov, Y.,** Application of liquid smoke for the production of cooked ham, *Proc. Eur. Meet. Meat Res. Workers.,* No. 25, 12.13:945, 1979.
44. **Wesley, P.,** Liquid smoke stays brine-soluble, *Food Prod. Dev.,* 16(2), 30, 1982.
45. **Keller, G. and Gunther, H. O.,** Investigations into aroma compounds of seasonings treated with liquid smoke, *Fleischwirtschaft,* 56(4), 564, 1976.
46. **Potthast, K.,** Using liquid smoke for surface treatment of meat products, *Fleischwirtschaft,* 63(10), 1558, 1983.
47. **Schneck, J. C.,** Liquid smoke application to cured meat, *Proc. Annu. Rec. Meat Conf. Am. Meat Sci. Assoc.,* 101, 1982.

48. **Hsu, L. A.**, Technology of smoking meat products, *Boletin Inst. Technol. Aliment. Brazil*, No. 52, 1, 1977.
49. **Gubler, D. and Vernois, M.**, New smoking techniques, *Ind. Aliment. Agric.*, 89, 621, 1972.
50. **Wechel, L.**, Optimum smoking methods, *Fleischwirtschaft*, 62(10), 1264, 1982.
51. **Hsu, L. A. and Sink, J. D.**, Color of meat products with liquid smoke products, *Coletanea Inst. Technol. Aliment.*, 8, 271, 1977.
52. **Rusanov, V. V.**, Spectrophotometric determination of phenols in smoking liquids, *Izv. Vyssh. Uchebn. Zaved. Pishch. Tekhnol.*, No. 1, 50, 1976.
53. **Baltes, W., Wilcopolski, K., and Lehmann, B.**, Detection of liquid smoke preparations in sausages, *Lebensm. Gerichtl. Chemie*, 33(4), 73, 1979.
54. **Baltes, W. and Bange, J.**, The detection of liquid smoke aromas smoke flavorings in foodstuffs, *Acta Aliment. Pol.*, 3, 325, 1977.
55. **Pionov, I. T., Marinosyan, O., Kuyumdzhiev, K. N., Nenchev. N. R., and Khodikyan, N.**, Smoke generator with automatic regulation of smoke formation, *Proc. Eur. Meet. Meat Res. Workers*, 31, 725, 1985.
56. **Brazhnikov, A. M., Kamenskii, S. N., Malova, N. D., Babanov, I. G., Sukhanova, S. I., and Minaev, A. I.**, Distribution of air in thermal chambers for processing cold smoked sausages, *Myasn. Ind. SSSR*, 4, 39, 1985.
57. **Lange, W. G. K.**, Calculation method of smoking technology, *Fleischerei*, 37(2), 88, 1986.
58. **Simmonds, C. K., Avery, K. W. J., and Higgo, D.**, Smoking of rainbow trout, *Annu. Rep. Fish. Ind. Res. Inst. Cape Town*, 38, 8, 1984.
59. **Simmonds, C. K. and Avery, K. W. J.**, Smoked and canned catfish and Kurper, *Annu. Rep. Fish Ind. Res. Inst. Cape Town*, 38, 8, 1984.
60. **Maharova, N. A., Goncharova, A. M., Pasternak, V. E., and Kosinova, R. N.**, Pilot plant experiments with smokeless cold smoking of fish, *Rybn. Khoz.*, 4, 56, 1985.
61. **Kurko, V. I. and Mezenova, O. Y.**, Determination of completeness of precipitation of smoking preparation during electrostatic smoking of fish, *Rybn. Khoz.*, 9, 58, 1985.
62. **Kurko, V. I. and Mezenova, O. Y.**, Diffusion of phenolic compounds into fish during smokeless electric smoking, *Rybn. Khoz.*, 7, 70, 1985.
63. **Makarova, N. A., Goncharova, A. M., and Tatarenko, L. Y.**, Microbiological study of cold smoked fish during storage, *Rybn. Khoz.*, 1, 70, 1985.
64. **Toth, L. and Potthast, K.**, Chemical aspects of the smoking of meat and meat products, *Adv. Food Res.*, 29, 87, 1984.

Chapter 4

FLAVOR CHEMISTRY OF WOOD SMOKE

I. INTRODUCTION

If a general population who is familiar with smoked foods were asked what they liked best about smoked foods, the majority would undoubtedly answer that is was the unique flavor. Thus, it is imperative that the flavor composition of wood smoke be understood so that uniform optimum flavor can result.

Numerous researchers have devoted a great deal of time and effort attempting to actually identify, and in a few cases quantitate, the compounds that are present in wood smoke. Considering the relatively few number of constituents present in most woods, this would seem to be a rather simple and straightforward task, but as anyone who has been exposed to flavor chemistry knows, the organoleptic properties of most products are far from simple.

Wood smoke is no exception, and this is compounded by the fact that numerous other factors typified by wood moisture content and temperature of smoke generation can also dramatically influence wood-smoke chemical composition. In addition, certain compounds apparently only serve as intermediates in the formation of more stable forms of compounds. Also, in most model systems involving smoke generation not in the presence of food, one is usually only concerned with volatile compounds that may or may not have distinctive odor properties at low concentrations. This in turn does not account for the fact that certain nonvolatile compounds may also make significant contributions to flavor. These facts are further complicated when food is actually exposed to volatiles and particulate matter found in smoke because these compounds in turn can chemically react with certain food components to form an entirely new generation of flavor compounds.

Fortunately for the flavor chemist, the identification of compounds present in wood smoke has been made somewhat easier through the use of combined gas chromatography/mass spectrometry. Most of the over 400 volatiles identified to date in smoke and its by-products have used this technique. For your information, most of the compounds identified to date have been summarized in Table 1.* This list includes 48 acids, 22 alcohols, 131 carbonyls, 22 esters, 46 furans, 16 lactones, 75 phenols, and 50 miscellaneous compounds. As always, when compiling an extensive list of this type, oversights may exist. In any event, it should be fairly apparent that what most people consider to be something relatively simple, in actuality can be quite complex.

It should also be noted that just because a compound has been identified as being present in smoke does not necessarily mean that it makes any contribution to the overall or certain specific sensory properties of the resulting product. Aside from its presence, one needs to know the following before the contribution of a compound to flavor can be fully evaluated: the quantity present; its odor threshold or minimum concentration required to be perceived; the specific odor properties or descriptions of the compound in question over a wide concentration range; potential synergistic odor properties of the compound with similar compounds in a homologous series, stability to temperature, light, and oxygen; and possible chemical interaction with other compounds. If one were to consider all of these factors in evaluation of the 400-plus compounds listed in Table 1, a great deal of time and effort would result. Therefore, it is not surprising that to date the individual compounds that are totally responsible for the characteristic flavor and aroma of wood smoke have not been completely and positively identified.

---

* Tables appear following text.

This becomes even more frustrating when one realizes that the compounds responsible for the characteristic flavor associated with different wood sources has not even been resolved. Therefore, in general, flavor chemists currently conclude that the overall characteristic flavor of wood smoke is probably due to the contribution of compounds from several compound classes, each of which contribute certain portions to the overall sensory properties of wood smoke.

At this point, perhaps we should discuss in some detail the classes of compounds that are thought to contribute most to the flavor and odor properties of wood smoke.

II. IMPORTANT FLAVOR COMPOUND CLASSES

A. Phenols

Historically numerous researchers[2,3,5,7,9-11,17,19,25,29,31,40,42] have concluded that phenols, as a compound class, are the primary contributors to wood-smoke aroma. However, other groups dispute this claim[1,4,8,11-16,18,20] since they have found other classes of compounds that also produce typical smoke aroma properties. Probably the primary reason for this conflict is the fact that for the most part, rather primitive and thus usually incomplete fractionation procedures have been utilized to recover what is normally called the phenolic fraction, which actually contains other compound classes which also can have potent sensory properties. This classical isolation procedure is shown in Table 2. If the fractions named in Table 2 are subjected to gas chromatography, one can readily see the problem, since several types of compound classes are present in each fraction, and if the sensory properties of each named fraction are evaluated, erroneous conclusions can be made. What is actually needed in this area are more sophisticated forms of separation to insure the purity of each fraction.

Structurally, phenols are aromatic hydrocarbons composed of benzene to which varying numbers of hydroxy groups are attached. In addition, phenolic compounds can have other functional groups such as aldehydes, ketones, acids, and esters. Simple phenols, when dissolved in water, display acidic properties while in alkaline conditions they are solubilized by dissociation to form phenolates. Increasing the number of hydroxy groups present on the benzene ring causes the resulting phenol to be quite reactive with metals and sensitive to light and oxygen. A monohydroxyphenol has a boiling point of 183°C whereas the addition of a second hydroxy group increases the boiling point to 270°C.[73] Ether forms of phenols are insoluble on water and can be converted to phenol ketones at low temperature or can form condensation products by reacting with aldehydes.

Not considering wood type or combustion conditions, there is no question that phenols can be produced at relatively high levels in wood smoke. The major ones found by Kornreich and Issenberg[3] are shown in Table 3, and as can be seen, the concentration of phenols in whole smoke can be 10 to 60 times that in the vapor phase of some smoke products. Thus, type of smoke application utilized would in turn influence phenolic concentration, and thus in turn, product flavor. For example, Ishiwater et al.,[12] in surveying 15 different samples of commercial smoke flavors, found a total phenolic range of from less than 0.001 to 1.06 mg/mℓ.

Lustre and Issenberg[5] demonstrated that not all phenolic compounds produced in wood smoke end up as such in smoked foods. These include the compounds 2,6-dimethoxy-4-vinylphenol, 2,6-dimethoxy-4-*cis* and *trans* propenylphenol, propiosyringone, coniferaldyhyde, and sinapaldehyde. This is interesting in light of the fact that especially the last two compounds are present in wood smoke at fairly significant levels. Because their structures contain carbonyl groups and an activated double bond, they are prone to addition reactions, and thus, the authors concluded that they can react with meat proteins to form other compounds. However, another research group[11] did find sinapaldehyde in a variety of smoke foods, thereby indicating that apparently some of the compound can be associated with certain smoked foods in the unreacted state.

It should also be noted that with storage, the amount of individual free phenols can decrease dramatically. Data supporting this are summarized in Table 4. It was clearly shown that volatility was not a contributing factor. Probable covalent binding of quinones, resulting from the oxidation of phenols to reactive protein groups probably resulted.

Another factor to consider relative to phenols in foods is their degree of penetration into smoked foods. As would be expected, there is preferential adsorption on outer surfaces. Bratzler et al.,[50] in working with a smoked bologna emulsion, clearly demonstrated this. A portion of their data is summarized in Table 5.

Consideration should also be given to the fact that the fat content of a smoked food can influence the amount of individual phenol compound recovered. For example, Issenberg et al.,[51] in working with model systems, demonstrated, as can be seen in Table 6, that for some phenols, percent recovery was lower in water than from a lipid system, whereas for some compounds it was essentially the same (guaiacol), while for others, higher recovery was recorded for the lipid system. Thus, depending upon the levels of individual phenols and the amount of fat in the food, the amount of total measured phenols can vary.

In the unique case of utilizing fire-charred wood barrels for the storage and aging of distilled spirits, one should also consider the fact that compounds formed during the partial thermal destruction of wood can then be dissolved and adsorbed into the final product. In the case of phenolic compounds, Maga[68] has identified 28 such compounds. These are summarized in Table 7 and as can be seen, all of the phenols are common compounds relative to wood smoke. In addition, a series of 13 phenolic acids, some of which are chemically quite active, was also identified.

1. Sensory Properties

Numerous researchers have attempted to evaluate the role of individual, as well as the composite phenol fraction, to the sensory properties of wood smoke. As can be seen in Table 8, certain phenols can have fairly low taste and odor thresholds, but as pointed out by Wasserman,[52] one should also consider the actual amount of compound present. Therefore, if you look at what Wasserman[52] calculated to be the flavor index, by far the most important phenol was 4-methyl-guaiacol. It can also be seen that certain phenols had lower odor thresholds in a water system, whereas, others were more sensitive in an oil system, thus making it difficult to make generalizations as to the overall odiferous properties of phenols in a smoked food.

Wasserman[52] also asked a taste panel of approximately 20 people to describe the odor and taste properties of the three phenols shown in Table 9, and as can be seen, the major response for all three compounds was smoky, with the second major response being phenolic. The third major response varied dependent upon the sensory properties being evaluated. In the case of odor it was sweet, while for taste it was bitter. The compound found to have the most smoky odor sensation was 2,6-dimethoxyphenol.

Since phenols are significant contributors to smoke aroma, data have been reported[73] indicating that phenols of medium volatility are the most important. For example, the flavor properties of phenol fractions distilled from a liquid smoke were characterized as follows: the low-boiling fraction (60 to 90°C) composed primarily of phenol, cresols, guaiacol, and methyl-, and ethylguaiacol had a hot and bitter taste; the medium fraction that distilled over at 91 to 132°C and contained *cis*- and *trans*-isoeugenol, syringol, and methylsyringol had a pure and characteristic smoke flavor; the high-boiling phenol fraction (133 to 200°C) had an acid, chemical property that was judged of poor quality.

This in turn probably points out a void in the published data relative to the sensory properties of phenols, in that their odor has been described in somewhat general terms, and usually these compounds are only evaluated in relatively concentrated forms. This is exemplified by a portion of the data reported by Kim et al.[4] as summarized in Table 10. Here you can see general sensory terms such as pungent, cresolic, and burnt. Similar data have been reported by Baltes and Sochtig.[43] Contrast the rather general sensory descriptions for phenols in Table 10 with the very detailed descriptions for some of the same compounds in Table 11. You can also note in Table 11 the approximately tenfold differences in optimum sensory concentrations for these compounds. A most useful study would be to describe the odor properties of increasing concentrations of each individual compound and then to evaluate the potential synergistic effect by combining some of the more interesting compounds.

Some data based upon the lines of the above suggestions have been reported.[73] The sensory properties of increasing concentrations of individual phenols were characterized by a panel and as seen in Table 12, the concentrations of each phenol that produced an optimum response was varied with dimethylphenol being needed in the lowest concentration and isoeugenol in the highest. Also, all compounds showed smoke-like properties along with other sensations. Data of these type can serve as the basis for the formation of imitation smokes.

The fact that phenols are important to overall whole smoke aroma should not be considered to be the only class of compounds involved was nicely demonstrated by Fujimaki et al.[29] Some of their data are shown in Table 13. They fractionated whole smoke condensate and then evaluated the sensory effect of adding these fractions back to the phenolic fraction, and as can be seen, the combination of at least three fractions produced the best results. However, it should be noted that the two different combinations of three fractions produced the best results although their aroma descriptions were different. Thus it would appear that depending on the overall characteristic, and perhaps intensity, of smoke aroma desired, different fractions are involved.

Olsen[42] also fractionated a commercial liquid smoke preparation and with the aid of a sensory panel concluded that the phenol fraction was important but not complete from a sensory standpoint. These data are summarized in Table 14. It can also be seen that normally objectionable tastes such as chemical and acidulous can be associated with certain fractions but were not apparent in the composite sample.

In an interesting study, Daun[53] isolated the phenolic fraction from both the vapor and particulate phases of wood smoke and through dilution determined, with the aid of a sensory panel, their recognition threshold and most desirable concentration for both odor and taste sensations. These data are summarized in Table 15. For both odor and taste the recognition threshold was lower in the particulate phase as compared to the vapor phase, thus indicating that either a higher level or more potent phenols were associated with the particulate phase. Because of this, the most desirable concentration for both odor and taste was also lower in the particulate phase, in turn indicating that if smoke containing a particulate phase is being used, a smaller amount of smoke is required to achieve an optimum level of smoke odor and taste.

2. *Formation Pathways*

It has been clearly demonstrated by Fiddler et al.[41] that a large number of phenols can result from the key thermal degradation product of lignin, ferulic acid, which in turn can form another key intermediate, 4-vinylguaiacol. The conversion of ferulic acid to 4-vinylguaiacol is presented in Table 16. Maximum numbers of by-products result in the presence of air, although some by-products will also form in the presence of nitrogen. Some of the typical by-products isolated from the thermal degradation of ferulic acid are shown in Table 17 and those that are thought to form from 4-vinylguaiacol are shown in Table 18. Some of these by-products in turn can undergo further chemical reaction to form other compounds.

In an earlier chapter it was shown that lignin is composed of repeating phenol units having three-carbon sidechains. Also, lignin from softwoods has fewer methoxy groups than lignin from hardwoods which accounts for the different range of phenols found in smoke generated from these different types of woods. However, lignin is not the only source of phenols since they can also be derived from cellulose via the conversion at high temperature of aliphatic compounds to aromatic compounds.[73] Also, phenols can result from the thermal degradation of amylopectin which is a component of hemicellulose.

One should also not forget that spices and their thermal decomposition can be a source of phenols in smoked foods. Some of the common spices used with smoked foods and the phenols associated with each are summarized in Table 19, and as can be seen, a wide range of phenols are associated with these spices.

B. Furans

Furans represent a class of five-membered oxygen-containing heterocyclic compounds that most probably result from the dehydration of glucose which in turn is an intermediate of the thermal dehydration of cellulose. Other furans such as furfuraldehyde can be formed from pentosans which are degradation products of hemicellulose. Furfuraldehyde in turn can condense to form numerous analogs that possess aromas such as sweet, fruity, and grassy.[73] The major six-membered ring oxygen-containing heterocyclic compound found in smoked foods is maltol.

Kim et al.[4] feel that furans also contribute to the overall sensory properties of wood smoke in that they tend to soften the heavy smoky aromas usually associated with phenolic compounds. Some of the odor properties associated with a portion of the furans isolated from wood smoke are summarized in Table 20. Radecki et al.[17] have also reported that a furan fraction isolated by the steam distillation of a commercial liquid smoke, in which six furans were identified, possesses a sweet, fragrant, and floral aroma, which also was felt to soften heavy smoky aromas. Numerous furans were also identified by Maga[68] in charred oak and are summarized in Table 21.

C. Carbonyls

Carbonyls are also thought to contribute to the overall sensory properties of wood smoke. For example, Fiddler et al.[1] isolated a polyfunctional carbonyl subfraction from wood smoke that possesses a caramel or burnt sugar aroma which the author felt modified the flavor of phenols.

Some of the carbonyls isolated by Kim et al.[4] from wood smoke were found to have unique aroma properties, as can be seen by viewing Table 22. Most had an odor described as grassy, which the authors contributed little to overall aroma, but no data were provided to substantiate this claim.

Most carbonyls are thought to originate through the thermal decomposition and rearrangement of cellulose and hemicellulose via classical carbohydrate degradation schemes.[4] However, in going back to Table 1 of this chapter, it should be noted that the carbonyl class represented the largest number of compounds identified to date from wood smoke. Since this general class represents a diverse group of structural compounds, more effort should be made to more completely understand their importance to wood-smoke aroma.

A carbonyl of potential concern is the compound formaldehyde, due to its toxicity. It has been found at levels of up to 200 mg/100 g of wood in smoke and at a concentration of up to 50 mg/kg in smoked meats.[73]

Certain ketoalcohols can also act as aliphatic intermediates for the formation of heterocyclic hydroxyfurans and alicyclic compounds such as cyclopentanones which possess unique and potent burnt maple aromas.

D. Others

Two other groups of flavor compounds that have received relatively little attention as to their potential role in wood-smoke flavor chemistry are the lactones and pyrazines. As can be seen in Table 23, a rather extensive group of lactones has been identified by Kim et al.[4] and all possessed aroma properties that can be considered to be characteristic[71] and beneficial to wood smoke aroma. The lactone fraction had a yield of 29.2 mg% with approximately half (14.5 mg%) being due to the compound 2,4-dimethyl-2-butenalide, with the compound 2-ethyl-4-methyl-2-butenalide contributing 8.1 mg%. They postulated that lactones in wood smoke are primarily derived from the thermal degradation of cellulose and hemicellulose via the intermediates butyrolactone and 2-butenolide. These compounds in turn form hydroxyacids. For example, the dehydration of α-hydroxybutric acid results in the formation of γ-butyrolactone, while the dehydration of α-crotonic acid produces 2-butenolide. These end-products in turn can serve as intramolecular esters needed for the conversion of aliphatic compounds to aromatic ones.

Several reports have appeared identifying pyrazines in wood smoke or charred wood. Pyrazines are characterized as heterocyclic nitrogen-containing compounds that are primarily thermally produced and possess potent and unique sensory properties.[65-67] Kim et al.[4] found the compounds pyrazine, methylpyrazine, and 2,5- (or 2,6-) dimethylpyrazine at a combined level of 1 mg% in the basic fraction of wood smoke. Since wood contains a nitrogen source, it is possible that a large number of these compounds are actually present in wood smoke.

Recently, Maga[68] reported on the volatile composition of fire-charred white oak (*Quercus alba*). Charred oak was fractionated into basic, carbonyl, phenolic, and neutral portions and their sensory contribution and chemical composition determined. Based on a 10-point intensity scale, with 1 being bland and 10 intense, a sensory panel concluded that the basic fraction, whose composition is shown in Table 21, had an intensity rating of 7.8, which was followed by the carbonyl, neutral, and phenolic fractions at 7.2, 6.8, and 6.2, respectively. Thus, based on both seonsory and objective data centering on pyrazines, he concluded that in the case of charred white oak, pyrazines are important sensory contributors and probably find their way into alcoholic beverages that are subsequently stored in charred oak casks. Pyrazine composition in wood smoke as influenced by wood source will be discussed in a later section.

In addition, numerous types of up to five-carbon aliphatics such as hydrocarbons, alcohols, and acids are present in smoke and some smoked foods. Of special interest is the toxicologically active compound methanol which is primarily derived from the methoxy groups of lignin. However, upon oxidation it can either form formaldehyde, which also presents toxicological concerns, or formic acid.[73]

III. WOOD SOURCE

It is a well-accepted fact that the type of wood used for a smoke source can significantly influence the organoleptic properties of the resulting smoke. Because of availability, cost, and numerous other factors, many types of wood have historically been used. In general, it can be stated that wood from broad-leaved trees produces a more acceptable smoke than smoke derived from needle-leaved trees. However, this may not always be the case. As can be seen in Table 24, pine was judged to produced a better smoke than fir, while some broad-leaved woods produced as inferior a smoke as fir.

Jodai[28] evaluated the effect of pyrolignous acid extraction from charcoal derived from cherry, oak, and pine using a variety of solvents including benzene, butyl acetate, hexane, petroleum ether, ethyl ether, and trichloroethylene. Benzene and butyl acetate were found to be the most efficient solvents with cherry and oak-derived charcoal giving acceptable-smelling products. The compounds that were thought to contribute most to a desirable product were cresol, 2,6-dimethoxyphenol, methyl ethyl ketone, and 3-methyl-2-butanone. However, pine-aroma extract was found to be unacceptable with all solvents.

Probably the most extensive study centering on the influence of wood source on resulting aroma acceptability and composition was conducted by Fujimaki et al.[29] Wood sources that were utilized included two oak species (*Queretis acuta* and *Q. seriata*), cherry, bamboo, pine, and cedar. Some condensate generated from each wood source was distilled and further fractionated into basic, carbonyl, noncarbonyl, and phenolic acid portions. The sensory and chemical composition of each fraction was then evaluated. As can be seen in Table 25, the total and individual amounts of volatile materials varied significantly among wood sources. For example, cedar had approximately half the amount of total volatiles as the other wood sources, most of which were composed of acids. The amount of phenolic material was fairly constant in all wood sources, while the carbonyl, noncarbonyl, acid, and basic fractions varied dependent upon wood type. Interestingly, *Q. acuta* and cherry had proportionately high yields of the basic fraction, which exhibited a strong burnt aroma. The overall flavors of the smoke condensates were reported to be distinctly different with *Q. acuta* having a strong burnt flavor with some sweetness; *Q. seriata* having a heavy, sweet smoke which was judged to be best of all woods evaluated; bamboo also had a pleasant smoke flavor; pine and cedar had pungent phenolic and poor fragrance sensory properties; while cherry was variable with some samples possessing oak-like properties while others were more pine-like.

Through organoleptic evaluation, the authors reported that the phenolic fraction had a good characteristic smoky aroma that was monotonous while the phenolic/carbonyl fractions had a better fragrant smoke aroma. The combination of the phenolic and neutral fractions had a very good aroma that was described as possessing a complex and fragrant property. The most pleasant aroma resulted from the combination of phenolic, neutral, and basic fractions. This product was thought to closely approximate the original smoke aroma, but without an acid odor. Thus, the authors concluded that although the phenolic fraction of wood smoke is an important contributor to smoke aroma, other fractions tend to complement and add complexity to smoke aroma.

Gas chromatographic analysis of the major volatile compounds associated with the whole flavor concentrate showed no major differences, however, when each fraction was chromatographically evaluated, differences were apparent among wood sources in that certain minor constituents were either present or absent. Thus, even though the same major compounds were apparently present in all woods, flavor differences were apparently due to differences in the relative amounts of these compounds. A specific example of this was the fact that syringol and some of its substituted forms were present in broad-leaved wood sources but absent in needle-leaved woods. Also, the ratio of guaiacol and its derivatives, as compared to phenol, cresols, and xylenols, appeared to be different in the smoke of broad- and narrow-leaved tree woods. Actual compositional differences of the compounds identified from the various wood sources are shown in Table 26.

Baltes et al.[64] also presented some interesting similar data, which are summarized in Table 27 showing that relative to phenols the major difference between hardwood and softwood is the higher proportion of 4-methylguaiacol and the lower proportion of syringol, 4-methylsyringol, and 4-propenylsyringol in softwood as compared to hardwood. Based on this fact, Baltes et al.[64] proposed that it is possible to determine if hardwood or softwood was used as a wood smoke source simply by determining the proportion of syringol to guaiacol and its derivatives.

In comparing the carbonyl composition of smoke derived from either alder or fir, Borys[30] found that fir contained more aliphatic ketones, cyclic ketones, and aromatic carbonyl compounds than alder. However, the potential sensory significance of this was not discussed. In the case of fir-wood smoke, a total of 39 compounds were identified while 28 compounds were found in alder wood smoke. Khvan et al.[56] also found major volatile compound differences in smoke as dictated by wood source. Smoke from oak was found to contain more volatile acids, neutral, and basic compounds compared to pine-derived smoke. However, due to the larger amount of resin present in pine, more phenols were found in pine smoke.

Lee and Song[57] compared various chemical and sensory properties of oak and chestnut smokes. One factor that would tend to indicate differences between the two woods was pH. Oak smoke had a pH of 2.20 while the pH of the chestnut smoke was 2.65. However, when these two smokes were incorporated into a sausage, a taste panel showed no statistical difference between the two. The actual volatile composition of the two smokes was not evaluated.

Ziemba[72] reported that smoke from oak wood contained more organic acids than beech wood and thus was inferior to beech. His data comparing the smoke composition of these woods when used for light and heavy smoking are summarized in Table 28.

In general, it has been reported[39] that woods such as beech and oak, which are considered to be hardwoods, produce smoke that is high in acids, while softwoods, such as pine and spruce, have high levels of carbonyls in their smoke. Also, poplar is quite high in phenols. Data supporting this observation are summarized in Table 29.

Several research groups have evaluated the influence of wood type on the resulting sensory properties of smoked fish products. In one study, softwoods such as fir and red cedar produced a resinous flavor in smoked herring,[58] however, other workers[55] found that sprats smoked with pine were better than those using beech wood.

An extensive study with smoked white fish, using 12 wood sources, was conducted by Lantz and Vaisey.[59] Using a 61-member taste panel, the data in Table 30 were tabulated. They found that red maple, red oak, trembling aspen, white ash, balsam, poplar, and birch gave better-flavored fish. Beech and white oak only gave moderately acceptable products, while hard maple and hickory were only marginally acceptable and diamond willow and burr oak resulted in objectionable products. Actual chemical analyses on volatile compound differences among the woods were not performed. It is of interest to note that hickory wood was not rated very highly for fish since in the U.S. it is thought to be one of the most acceptable woods for the smoke processing of red meats. The sensory and/or chemical reasons for this difference should be investigated. Perhaps because of differences in protein content or composition between fish and red meats, different types or amounts of flavor compounds are formed.

Solanki et al.[60] smoked eel, also using various wood sources and noted the resulting color, odor, and flavor. As can be seen in Table 31, overall, the best wood source was a blend of one part coconut husk and one part teak sawdust. Using teak sawdust also produced an attractive color, but the odor and flavor were acrid and unpleasant. The use of sajad, acacia, and mango sawdust produced a resinous odor and flavor. In contrast, coconut husk has a good odor and flavor, but the resulting color was a pale yellow. Therefore, by blending wood sources they were able to optimize sensory properties. This concept of blending woods has not been investigated extensively, but it would appear that with certain smoked foods, a very complex combination of sensory properties could be achieved, thereby adding another dimension to the acceptability of smoked foods.

As mentioned earlier, numerous wood and related by-products have commercially been used as a smoke source, and there is no question that their resulting flavors can vary widely. Some of these sources include mahogany, numerous fruit tree woods, corn cobs, prunings from grape vines, and more recently, mesquite wood.

Recently, Maga and Fapojuwo[69] and Maga and Chen[70] reported upon the sensory and volatile pyrazine composition of various wood smoke sources. Smoke generated from apple, chestnut, cherry, hard maple, hickory, mesquite, and red and white oaks were fractionated into carbonyl, neutral, and basic and phenolic units. Equal concentrations of each were dissolved in water and presented to a sensory panel for aroma intensity evaluation using a 10-point scale with 1 being slight and 10 strong. As seen in Table 32, it is clearly demonstrated that the fraction possessing the strongest aroma intensity is dependent upon wood source. For example, in the case of mesquite, the phenolic fraction appears to be most important whereas with apple, the basic fraction has the strongest intensity. These data would support the concept of blending wood smoke sources to obtain complex aroma properties as discussed above.

A series of eight pyrazine compounds including pyrazine, 2-methoxy-3-ethylpyrazine, 2-ethoxy-3-ethylpyrazine, 2-propyl-3,6-dimethylpyrazine, 2-butyl-3,5-dimethylpyrazine, 2-butyl-3,6-dimethylpyrazine, 2-acetyl-3-methylpyrazine, and 2-acetyl-3,5-dimethylpyrazine were identified in the smoke generated from 17 different wood sources[70] and as seen in Table 33, the total pyrazine content ranged from a low of 10.33 mg/100 g of redwood to 41.03 mg/100 g of hickory. There did not appear to be any obvious differences between hardwoods and softwoods. Also, total and individual pyrazine levels were not found to be correlated with wood nitrogen content, which has to be assumed to be the nitrogen source, nor to the levels of cellulose, hemicellulose, or lignin present. Again, the authors concluded that based on both the amounts and types of pyrazines found, they can contribute to overall smoke aroma.

IV. GENERATION CONDITIONS

One would assume that if variables in the combustion process such as temperature, moisture, and air levels are manipulated, the amount of flavor-producing compounds can vary, thus in turn influencing the overall sensory properties of the resulting smoke. Numerous studies have demonstrated this, but just a few typical ones will be cited.

A. Temperature

Relative to temperature, data presented by Porter et al.[18] as summarized in Table 34 are fairly typical of what happens to the quantities of flavor compound classes. As can be seen, there is an increase as temperature increases, and then a general decline at higher temperatures.

Daun[53] generated smoke at higher temperatures than the above study and although the actual 14 phenolic compounds were not identified even though they were reported gas chromatographically, general increases and decreases were evident for these compounds as temperature was increased from 400 to 600°C. In turn, this had a significant influence on the vapor phase recognition threshold and most desirable concentration for both their odor and taste properties. This information is summarized in Table 35. As can be seen, the smoke product at 400°C apparently was more concentrated in flavor compounds than at the other two temperatures since both its odor and taste thresholds and most desirable concentrations were lower.

The amount of phenolic material generated at still higher temperatures has been reported by Toth,[27] and as can be seen in Table 36, the same general trend of an increase with gradual decline at the highest temperature is evident. Baltes et al.[64] also reported that maximum phenol, carbonyl, and acid yields occurred at approximately 600°C. They also stated that double-valanced phenols, such as pyrocatechin, are especially stable at high temperatures, therefore increasing their relative amount at the expense of thermally less-stable compounds.

Simon et al.[61] looked at compound compositional change associated with small smoke temperature generation increases and they found, as can be seen in Table 37, the actual weight percent of acids and phenols decreased with increasing temperature, while carbonyl content increased. However, the total number of volatiles increased by a factor of 4.5 over the 115°C temperature range evaluated. Since the relative amounts of acids and phenols were decreasing with increasing temperature, it becomes apparent that the relative amount of carbonyls increased significantly.

If the actual content of individual phenols is looked at relative to smoke generation temperature, some interesting facts appear. For example, in Table 38 it can be seen that for the compound phenol, temperature makes little difference in the amount formed, but for syringol an increase of 200°C from 450 to 650°C resulted in almost a fourfold increase. Thus, it would appear that at least in a theoretical sense one can encourage the generation of certain phenolics by adjusting generation temperature.

Borys et al.[24] attempted to mathematically and chemically evaluate various combustion conditions, including temperature, on the resulting volatiles. Their initial assumption was that combustion rate was dependent upon combustion temperature and air flow rate relative to the equation:

$$Y = A + B\,(T \times u)$$

where Y = combustion rate, A = constant dependent on wood particle size, B = constant dependent on wood moisture content, T = combustion temperature, and u = air flow rate.

Based on their experimental smoking conditions, very high correlation coefficients were found for this formula. Later work reported by Klossowska[62] also used the same mathematical approach and she concluded that the logarithm of the wood combustion rate is a linear function of the combustion temperature and the logarithm of the air flow rate. In addition, she concluded that the temperature of the combustion zone is limited to the rate of air flow by a functional relationship representing a Gaussian curve.

In evaluating variables that influence the types and amounts of pyrazines formed during wood smoke generation, Maga and Chen[70] reported that the concentration of eight pyrazines increased from 41.03 mg/100 g dry weight wood when hickory sawdust was thermally degraded at 290°C to a total of 59.05 mg/100 g when a temperature of 450°C was used.

One should remember however that as pointed out by Wasserman and Fiddler,[39] the actual measurement of temperature at the combustion site is somewhat difficult. For example, they found that the temperature 1 in. above a smoldering sawdust bed was as much as 300°C lower than in the center of the bed. In addition, wood combustion is an exothermic reaction, and therefore, localized sites may have temperatures that are far greater than the composite temperature or temperature of the heat source.

B. Air

The amount of air present during smoke generation is another factor that can apparently influence the resulting flavor component composition. As an example, Wasserman and Fiddler[39] varied oxygen composition from 0 to 59% of the gas mixture used during smoke generation and saw some major differences in the volatile composition of several measured compounds as a result. These data are shown in Table 39. Normal air has an oxygen content of 20%. In general, they found that as percent oxygen increased, furans, typified by the compound furfuryl alcohol, decreased, thus demonstrating that oxygen is not prerequisite for the formation of furans. Interestingly, phenolic compounds (guaiacol) and carbonyls (cyclotene) increased significantly at 10% oxygen, but then also fell off as oxygen content increased.

With the aid of a sensory panel, Wasserman and Fiddler[39] concluded that the sensory smoke properties of condensates derived from 0 to 10% oxygen could be statistically differentiated from 20% oxygen, but no statistical differences were noted when 20, 30, and 50% oxygen-produced condensates were compared. Thus, at least in this study, smoke condensate produced with normal amounts of oxygen was found to be quite acceptable. The question is raised, however, if this result is due only to the fact that this produced the most normal sensation and that lower levels of oxygen produced different and perhaps therefore not as agreeable condensates.

A sensory panel was also used by Daun[53] to compare the sensory properties of the vapor phase of smoke produced in the presence of low (500 ℓ/hr) and high (2500 ℓ/hr) air flow. As seen in Table 40, smaller amounts of the smoke produced with low air supply were needed for odor recognition threshold and most desirable odor concentration as compared to the high air level. This would be in general agreement with the Wasserman and Fiddler[39] study which found higher amounts of certain flavor-producing compounds at lower oxygen levels. However, when taste was considered, the smoke produced with high air levels required less to be most desirable, perhaps indicating that a wider variety of compounds or compound concentration was a factor that should be considered.

The presence or absence of air significantly influenced the amount of pyrazines formed in hickory smoke.[70] With air, the total amount was 41.03 mg/100 g of wood, however, when air was excluded during smoldering, the total pyrazine content increased to 51.33 mg/100 g. In all probability, the lack of air minimized formation of certain classes of unstable compounds thus resulting in larger amounts of more stable pyrazines.

C. Wood Moisture Content

One would also assume that initial wood moisture content could possibly alter the type and amount of volatile compounds in smoke, and this in turn would influence overall sensory properties. Data published by Gorbatov et al.[63] clearly support this concept. As shown in Table 41, lower moisture wood tended to produce higher amounts of phenols, acids, and carbonyls, but these data should be interpreted carefully since it can be seen that the total amount of condensate also varied. If the data were calculated on the same amount of condensate yield, the middle moisture samples would have proportionately more volatiles. Interestingly, the middle moisture samples were those that were judged to have the most acceptable sensory properties. Since the formation of certain flavor compounds is moisture dependent, more research should be devoted to determine which specific compounds are preferentially formed in low and high moisture-containing foods during smoking.

Recently, Maga and Chen[70] followed the rate of pyrazine formation as influenced by hickory wood moisture content at the time of smoldering at 290°C. Through moisture additions, they generated hickory smoke from sawdust that had either 4, 20, or 30% moisture. No significant differences in total pyrazine contents were noted when the sawdust had 20 or 30% moisture, but pyrazine concentration doubled when the moisture content was at 4%. Thus, if one were interested in maximizing the generation of pyrazines in wood smoke, one should use a fairly dry wood source for smoke generation.

D. Wood Particle Size

The actual size of the wood particle being used as a smoke source can indirectly influence resulting smoke flavor in that, as pointed out by Borys et al.,[24] the larger the particle, the higher the air flow rate required to obtain the same combustion rate as a smaller particle. Thus, if air flow is not altered according to particle size, combustion rates will differ, which in turn will influence final smoke composition. Again, this is an area that deserves further research in that most naturally occurring sawdust a wide range in particle size can exist, thereby possibly leading to variations in volatiles produced.

V. SMOKING PROCEDURE

As discussed in an earlier chapter, numerous smoking procedures exist, some of which claim that superior sensory properties result. This in turn would indicate that some unique aspect of the process, probably including some or all of the factors discussed above, results in the formation of more or a wider range of flavor compounds.

Data typical of this contrast are presented in Table 42 where the chemical and volatile composition of sawdust smoke and friction smoke are compared. It can be seen that both the steam volatile and nonsteam volatile fractions of friction smoke are more acidic both in pH and in percent total acids. In addition, friction smoke contained four more steam volatile acids and approximately eight times more carbonyls than sawdust smoke. Overall, friction smoke contained more steam volatiles that are known to be important to smoke flavor than sawdust smoke. However, these differences may be due in part to the fact that friction smoke was concentrated, since it only contained 71% moisture, whereas sawdust smoke contained 87% moisture.

Even more dramatic is the comparison of hot vs. cold smoking of a product relative to the number and amount of phenols present. Data of these type are seen in Table 43. As you can see, guaiacol, maltol, and phenol were only found in measurable quantities in the cold smoking process which had approximately three times more eugenol than the hot process. In contrast, the hot process contained major amounts of acetovanillone and acetosyringone, which were hardly present in the cold process. Differences as dramatic as this undoubtedly account for significant differences in resulting product-sensory properties. Thus, it becomes very obvious that the smoking process employed can play a major role in influencing the resulting sensory properties of the product involved.

VI. STORAGE

In the generation and utilization of liquid smoke, research has demonstrated that chemical changes that occur with time can alter the sensory properties of smoke. This has potential significance with the long-term storage of liquid smoke. This fact is summarized in Table 44. As can be seen, the newest smoke (5 hr old) had the lowest sensory score, but with time, the score gradually improved. They postulated that with time, methyl alcohol can react with formic and acetic acids to form less harsh-flavored esters.

Doerr et al.[14] actually followed the formation of methyl acetate and methyl formate in liquid smoke stored at 25°C over a period of approximately 30 days, and as seen in Table 45, the amount of methyl formate formed reached equilibrium in approximately 70 hr, whereas the level of methyl acetate was still gradually increasing after 700 hr. Undoubtedly, other chemical changes can occur during liquid smoke storage that can either result in the loss of desirable or undesirable compounds with the formation of other flavor-related compounds. More study in this area is also encouraged, especially with long-term storage.

Table 1
COMPOUNDS IDENTIFIED IN WOOD SMOKE

Acids	**Ref.**
Formic (methanoic)	18,22,33,36,48
Acetic (ethanoic)	4,6,12,16,18,22,24,25,29,32,33,36,37,39,43,48
Glycolic (hydroxyethanoic)	48
Propionic (propanoic)	4,6,12,16,18,20,22,24,29,32,33,36,37,43,48
Isobutyric (2-methylpropanoic)	4,18,20,29,32,33,37,48
Acrylic (propenoic)	48
Methacrylic (methylpropenoic)	20,48
Butyric (butanoic)	4,6,16,18,20,22,24,29,32,33,36,37,48
α-Methylbutyric	48
Isovaleric (3-methylbutanoic)	4,16,18,20,29,32,33,37,38
Crotonic (2-butenoic)	33,36,48
trans Crotonic (*trans* 2-butenoic)	4,29,32,37
cis Crotonic (*cis* 2-butenoic)	4,29,37
3-Butenoic	48
Tiglic (2-methyl-2-butenoic)	1,6,33,36,48
Angelic (*cis* 2-methyl-2-butenoic)	20,37,48
trans 2-methyl-2-butenoic	4,20,32,37
Valeric (pentanoic)	4,6,16,18,20,24,29,32,33,36,37,48
α-Methylvaleric (2-methylpentanoic)	48
3-Methylpentanoic	20
Isocaproic (4-methylpentanoic)	16,20,37,48
4-Methyl-2-pentenoic	48
2-Pentenoic	4,48
3-Pentenoic	48
Levulinic (4-oxopentanoic)	6,48
Caproic (hexanoic)	16,18,20,24,32,37,48
Enanthic (heptanoic)	18,32,33,37,48
5-Heptenoic	48
Caprylic (octanoic)	18,20,32,37,48
Dehydroxycaprylic	48
Pelargonic (nonanoic)	18,32,48
Capric (decanoic)	18,32,48
Lauric (dedecanoic)	37
Myristic (tetradecanoic)	32,34,37
Pentacecylic (pentadecanoic)	32
Palmitic (hexadecanoic)	32,34,37,48
Stearic (octadecanoic)	48
Oleic (9-octadecanoic)	48
Arachidic (eicosanoic)	48
Behinic (docosanoic)	48
Benzoic	20,33,37
Salicylic (*O*-hydroxybenzoic)	30,46
3-Methoxy-4-hydroxybenzoic	44
Sorbic (2-4-hexadienoic)	33
Vanillic (4-hydroxy-3-methoxybenzoic)	41
Abietinic	48
Pimaric	48
Lignoceric	48
Alcohols	
Methyl (methanol)	4,13,14,36,39,48
Ethyl (ethanol)	4,13,14,20,39,43,46,48
Propyl (1-propanol)	48
Isopropyl (2-propanol)	14,39,48

Table 1 (continued)
COMPOUNDS IDENTIFIED IN WOOD SMOKE

	Ref.
Isobutyl (2-methyl-1-propanol)	48
Allyl (2-propen-1-ol)	4,13,48
Propan-2-on-1-ol	4
Amyl (2-methyl-2-butanol)	4
Isoamyl (3-methyl-2-butanol)	34,48
Butan-2-on-1-ol	4
Butan-3-on-2-ol	4
2-Buten-1-ol	48
Pentan-2-on-1-ol	4
Pentan-3-on-2-ol	4
1-Penten-3-ol	35
1-Nonanol	30
Phenylethylalcohol	4,34
Cyclohexanol	48
Benzylalcohol	4,43
p-Hydroxybenzylalcohol	46
Fenchyl (6-fenchanol)	48
Isofenchyl (iso-6-fenchanol)	48
Carbonyls	
Methanal	13,15,18,48
Ethanal	13—15,18,20,36,39,48
Hydroxyethanal	48
Phenylethanal	34,35
2-Pyrroaldehyde	43
Propanal	13—15,18,20,48
2-Propanal (Acrolein)	15
2-Methylpropanal	13,15
2,2-Dimethylpropanal	48
2-Methylpropenal	13
Acetone (2-propanone)	4,13—15,18,20,39,48
Acetylacetone	30
3-Methylacetylacetone	30
1-Hydroxypropanone (acetol)	6,14,24,25,30,39,48
2-Hydroxypropanone	30
Acetoxypropanone	48
1,3′-Dimethoxy-4-phenyl-1-propanone	30
1,3′-Dimethoxy-4-phenyl-2-propanone	30
1,5′-Dimethoxy-4-phenyl-2-propanone	30
α-Methyl-β-ethylpropenal	48
Butanal	13,15,18
2-Butenal	13—15,18,39,48
3-Methylbutanal	14,15,18,34,39,48
2-Methyl-2-butenal	15,20,46,48
2-Butanone	4,13,15,18,46
3-Methyl-2-butanone	15,28
1-Hydroxy-2-butanone	6
3-Hydroxy-2-butanone	30
1-Phenyl-2-butanone	30
3,3-Dimethyl-2-butanone	15
Diacetyl (2,3-butanedione)	4,13—15,20,30,36,39,48
Pentanal	13,15,18,48
α-Methylpentanal	15
2-Methyl-2-pentenal	43
2-Pentanone	4,15,18,30,48

Table 1 (continued)
COMPOUNDS IDENTIFIED IN WOOD SMOKE

Carbonyls	Ref.
3-Pentanone	15,48
4-Hydroxy-2-pentanone	48
4-Hydroxy-4-methyl-2-pentanone	37
2-Methyl-3-pentanone	48
2,4-Dimethylpentanone	30
Pentadiene	46
Methylpentadiene	46
2,3-Pentanedione	20,35,48
4-Pentanedienal	30
2,4-Pentanedienal	43
Hexanal	35
2-Hexenal	35
2-Hexanone	15,30
3-Hexanone	15,48
5-Methyl-2-hexanone	30
2-Methyl-3-hexanone	30
3-Hexen-2-one	48
5-Hexen-2-one	30
2,4-Hexadienal	37
2,4-Hexanedione	4
2,5-Hexanedione	6,30,43
3-Methyl-2,5-hexanedione	30
2-Heptanone	30
4-Heptanone	30,37,48
3,6-Octanedione	48
Methyl ethyl ketone	20,28,30
Methyl isopropyl ketone	30,43
Methyl isopropenyl ketone	20
Methyl butyl ketone	43
Methyl vinyl ketone	14,39
Butyl methyl ketone	48
Allyl methyl ketone	4
1-Cyclohexyl methyl ketone	37
Cyclic ketone	4
Acetophenone (methyl phenyl ketone)	4,20,43
m-Methylacetophenone	4
p-Methylacetophenone	4
Acetosyringone(4′-hydroxy-3′,5′-dimethoxyacetophenone)	21,23,26,27,45
Propiosyringone(4′hydroxy-3′,5′dimethoxypropioacetophenone)	21,23
4′-Hydroxy-3′-methoxyacetophenone	23
Benzaldehyde	4,20,30
Salicyaldehyde (2-hydroxybenzaldehyde)	21,46
Anisaldehyde (4-hydroxybenzaldehyde)	30,43,45,46
Dihydroxybenzaldehyde	45
1,2-Dihydroxy-3-methylbenzaldehyde	42
2-Hydroxy-3-methoxybenzaldehyde	30
4-Hydroxy-2-methoxybenzaldehyde	30
4-Hydroxy-3-methoxybenzaldehyde (vanillin)	3,5,6,21,23—27,30,37,39,41,43—46
4-Hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde)	3,11,21,23,26,27,30,44—46
3,5-Dimethoxybenzaldehyde	44
Sinapaldehyde (3-(4′-hydroxy-3′,5′dimethoxyphenyl)-2-propenal)	11,21,23,25
Coniferaldyhyde (3-(4′-Hydroxy-3′-methoxyphenyl)-2-propenal)	21,23

Table 1 (continued)
COMPOUNDS IDENTIFIED IN WOOD SMOKE

Carbonyls	**Ref.**
3-(4′-Hydroxy-3′,5′-dimethoxyphenyl)-1-propanal	45
3-(4′-Hydroxy-3′-methoxyphenyl)-1-propanal	45
Cyclopentanone	4,29,30,43,48
Methylcyclopentanone	4,48
Dimethylcyclopentanone	48
Trimethylcyclopentanone	48
3,3,5-Trimethylcyclopentanone	48
1,2-Cyclopentanediol	48
3-Methyl-1,2,4-cyclopentanetrione	37
3-Methylcyclopenta-1,2-dione	4
3-Ethylcyclopenta-1,2-dione	4
3,4-Dimethylcyclopenta-1,2-dione	4
2-Cyclopentenone	4,25,39,43,46,48
2-Methyl-2-cyclopentenone	4,6,29,48
4-Methyl-2-cyclopentenone	4,48
5-Methyl-2-cyclopentenone	4
2-Ethyl-1-cyclopentenone	4
3-Ethyl-2-cyclopentenone	4
2-Ethyl-3-methyl-2-cyclopentenone	4
2-Ethyl-4-methyl-2-cyclopentenone	4
2-Ethyl-5-methyl-2-cyclopentenone	4
3-Ethyl-2-methyl-2-cyclopentenone	4
2,3-Dimethyl-2-cyclopentenone	4,6,29,43
2,4-Dimethyl-2-cyclopentenone	4
2,5-Dimethyl-2-cyclopentenone	4
3,4-Dimethyl-2-cyclopentenone	4
3,5-Dimethyl-2-cyclopentenone	4
2,3,4-Trimethyl-2-cyclopentenone	4
2,3,5-Trimethyl-2-cyclopentenone	4
3-*n*-Propyl-2-cyclopentenone	4
3-Isopropyl-2-cyclopentenone	48
3-Methyl-2-cyclopenten-2-ol-1-one	1,4,20,29,43,44
3,4-Dimethyl-2-cyclopenten-2-ol-1-one	1,4,6
3-Ethyl-2-cyclopenten-2-ol-1-one	1,4,6
2-Hydroxy-3-methylcyclopent-2-ene-1-one (cyclotene)	2,3,5,6,8,21,23,25,26,30,37,39,43,46,48
Cyclohexanone	4,43,48
2,4,4-Trimethylcyclohexanone	48
2-Cyclohexenone	20,43
2,4-Dimethyl-4-cyclohexenone	48
1-Methyl-2-cyclohexen-5-one	48
5,5-Dimethyl-1,3-cyclohexanedione	30
Cyclohexanecarboxaldehyde	48
Cyclohexanepropionaldehyde	48
Esters	
Methyl formate	13,14,20,39,48
Methyl acetate	13,14,39,48
Methyl propionate	48
Methyl butyrate	4,48
Methyl isobutyrate	48
Methyl crotonate	48
Methyl valerate	48
Methyl caproate	48
Methyl enanthate	48
Methyl myristate	34,35
Methyl palmitate	35

Table 1 (continued)
COMPOUNDS IDENTIFIED IN WOOD SMOKE

Esters	Ref.
Methyl acrylate	20
Ethyl myristate	34
Ethyl benzoate	20
Cresyl acetate	20
Hydroxy-2-butanone acetate	4,6,48
Hydroxy-2-propanone propionate	48
Salicylic acid methyl ester	46
4-Methoxybenzoic acid methyl ester	43
4-Hydroxy-4-methoxybenzoic acid methyl ester	45
4-Hydroxy-3,5-dimethoxybenzoic acid methyl ester	45
3-Methoxy-4-hydroxyphenylacetic acid methyl ester	45
Furans	
Furfuryl alcohol	2,21,25,30,33—37,39,43,46,48
2-Furfuryl methyl alcohol	37
Furan	13,14,20,39,46,48
2-Methylfuran	20,36,39,46
2,5-Dimethylfuran	46,48
2,4-Dimethylfuran	43
2-Ethylfuran	17,20
2-Acetylfuran	17,20,29,43,46
Propylfuran	48
2-Isopropylfuran	43
2-Propenylfuran	43
2-Acetyl-5-methylfuran	43
2,5-Dimethyl-3-acetylfuran	43
Amylfuran	48
2,3,5-Trimethylfuran	48
2-Vinylfuran	46
2-Vinyl-3-methylfuran	46
Benzofuran	43,46,48
2-Methylbenzofuran	20,37,43,46
Dimethylbenzofuran	20,37
Dibenzofuran	46
Bis-(furfuryl)-2-furan	43
2,3-Dimethyl-5-ethylfuran	17
3,4-Dimethyl-5-ethylfuran	17
2-Ethyl-2,3-dihydro-5-methylfuran	48
2,5-Tetrahydrodimethylfuran	48
2-Methyltetrahydrofuran-3-one	4
2,5-Dimethyltetrahydrofuran-3-one	1,4,6
2-Acetyltetrahydrofuran-3-one	4
2-Furoic acid	48
4-Methyl-2-furoic acid	48
Methyl-2-furoate	4,48
Furfuryl methyl ether	4,37
2-Furfuryl methyl ketone	4,6,37,48
3-Furfuryl methyl ketone	37
2-Furfuryl propyl ketone	30
2-Furfuryl butyl ketone	30
2-(5-Methylfuryl)-methyl ketone	4
2-Furfural	4,6,12,20,21,24,25,29,30,33,35,36,39,43,46,48
3-Furfural	30,46
4-Methylfurfural	17,30
5-Methylfurfural	4,6,12,14,17,20,21,24,25,29,30,33—35,39,43,46,48

Table 1 (continued)
COMPOUNDS IDENTIFIED IN WOOD SMOKE

	Ref.
2-Methyl-3-furfural	30,48
3-Methyl-2-furfural	30,48
5-Hydroxymethyl-2-furfural	6,43,48
2,5-Difurfuryledine-1-cyclopentanone	48
Lactones	
γ-Butyrolactone	4,6,48
β-Angelica lactone	6
γ-Crotonolactone	6
γ-Hydroxyvalerolactone	48
δ-Hydxroxyvalerolactone	48
α-Hydroxy-γ-hydroxyvalerolactone	48
2-Butenolide	4
2-Methyl-2-butenolide	4
4-Methyl-2-butenolide	4
2,3-Dimethyl-2-butenolide	4
2,4-Dimethyl-2-butenolide	4
3,4-Dimethyl-2-butenolide	4
2,3,4-Trimethyl-2-butenolide	4
4-Ethyl-2-methyl-2-butenolide	4
4-Ethylidiene-2-methyl-2-butenolide	4
Methylvinyl-2-butenolide	4
Phenols	
Phenol	1—6,10,12,17,19—21,23,25—27,29,32—35,37—40,42—46,48
o-Cresol (2-methylphenol)	4,6,12,17,20,21,23,27—29,32—35,37.38,40,43—48
m-Cresol (2-methylphenol)	4—6,10,12,17,20,21,23,25—27,29,32—35,37,38,40,42—46,48
p-Cresol (4-methylphenol)	4—6,10,12,17,20,21,23,26,27,29,32—35,37,38,40,43—46,48
2-Ethylphenol	20,23,33,43,45,46,48
3-Ethylphenol	20,27,43,45
4-Ethylphenol	1,6,20,27,42—46
2-Ethyl-5-methylphenol	4
3-Ethyl-5-methylphenol	4,20
2,3-Xylenol (2,3-dimethylphenol)	4,20,23,32—35,37,43—45,48
2,4-Xylenol (2,4-dimethylphenol)	1,4,6,20,23,29,32—35,43,45,46,48
2,5-Xylenol (2,5-dimethylphenol)	6,20,37,43,45
2,6-Xylenol (2,6-dimethylphenol)	4,11,20,23,27,43,45,46
3,4-Xylenol (3,4-dimethylphenol)	1,6,7,17,23,39,43—46
3,5-Xylenol (3,5-dimethylphenol)	4,12,23,29,37,44,45,48
Diethylphenol	43,44,46
2,3,5-Trimethylphenol	4,20,23,27,37,43,45,46
2,3,6-Trimethylphenol	45
2,4,6-Trimethylphenol	44—46
4-Propylphenol	27,45
4-Isopropylphenol	33,43,44,46
2-Methyl-5-isopropylphenol	43,46
4-Butylphenol	20,37
2-Isobutylphenol	46
2-Allylphenol	45
3-Allylphenol	45
4-Allylphenol	45
4-Vinylphenol	23,44,45

Table 1 (continued)
COMPOUNDS IDENTIFIED IN WOOD SMOKE

Phenols	Ref.
3-Methoxyphenol	20
4-Methoxyphenol	44
Dimethoxyphenol	45
Methoxyethylphenol	45
3,4-Dimethoxyphenol	43
Syringol (2,6-dimethoxyphenol)	3—6,9,12,17,20,21,23—25,27—29,31—34,37—40,42—46,48
4-Methylsyringol (2,6-dimethoxy-4-ethylphenol)	3,4,6,9,12,17,20,21,23—25,27,29,31,32,34,35,37,39,40,42—46,48
4-Ethylsyringol (2-dimethoxy-4-ethylphenol)	3,4,6,9,11,17,20,21,23,25,29,32,34,35—37,39,40,42—46,48
4-Propylsyringol (2,6-dimethoxy-4-propylphenol)	4,6,20,23,25,37,39,40,44—46
4-Isopropylsyringol (2,6-dimethoxy-4-isopropylphenol)	20
4-Propenylsyringol (2,6-dimethoxy-4-propenylphenol)	4,20,38,42,43,46
4-*trans* Propenylsyringol (2,6-dimethoxy-4-*trans* propenylphenol	21,23,45
4-*cis* Propneylsyringol (2,6-dimethoxy-4-*cis* propenylphenol)	21,23,44,45
4-Allysyringol (2,6-dimethoxy-4-allylphenol)	5,8,17,20,21,23,24,26,27,37,38,42,44—46
4-Vinylsyringol (2,6-dimethoxy-4-vinylphenol)	21,23,46
4-Isobutylsyringol (2,6-dimethoxy-4-isobutylphenol)	44
2,4-Dimethoxy-4-allylphenol	42
1,2-Dihydroxy-4-methylphenol	42
2-Methoxy-4-acetic acid phenol	44
3-Methoxy-4-propan-2-one phenol	44
Acetophenol	37
4-Isopropylacetophenol	37
4-Hydroxy-3-methoxyacetophenol	37
3,4-Dimethoxycetophenone	44
2-Acetovanillone (4′-hydroxy-3′-methoxyacetophenone)	4—6,11,21,26,27,33,41,45,46
Guaiacol (2-methoxyphenol)	1—4,6,10,12,19—21,23,25—27,29,31—35,37—48
4-Methylguaiacol (2-methoxy-4-methylphenol)	3—6,10,11,17,19—21,23—25,27,29,31—35,37,39—47
6-Methylguaiacol (2-methoxy-6-methylphenol)	45,48
5-Methylguaiacol (2-methoxy-5-methylphenol)	45
3-Methylguaiacol (2-methoxy-3-methylphenol)	4,27,45
4-Ethylguaiacol (2-methoxy-4-ethylphenol)	4—7,17,20,21,23,25,29,31—35,37,39—46,48
4-Propylguaiacol (2-methoxy-4-propylphenol)	4,6,20,23,25,32—35,37,39,40,43—45,48
4-Isopropylguaiacol (2-methoxy-4-isopropylphenol)	20
4-Vinylguaiacol (2-methoxy-4-vinylphenol)	4,6,20,21,23,25,32—35,37,39,41,44—46,48
5-Vinylguaiacol (2-methoxy-5-vinylphenol)	7,17
3-5-Dimethylguaiacol (2-methoxy-3,5-dimethylphenol)	48
Eugenol (2-methoxy-4-allylphenol)	4,6,7,17,20,21,23,25—27,32—34,37,49,40,42—46
trans-Isoeugenol (2-methoxy-4-*trans*-propenylphenol)	3,5,6,11,20,21,23,24,26,27,32—35,37,40,42—46,48
cis-Isoeugenol (2-methoxy-4-*cis*-propenylphenol)	5,6,21,23,27,37,43,44,45
Pyrocatechol (2,3-benzenediol)	4,37,44
3-Methylpyroacatechol	4,27,37,45
4-Methylpyrocatechol	4,27,37,44
5-Methylpyrocatechol	44
4-Ethylpyrocatechol	4
3-Methoxypyrocatechol	4,6,27,45
Resorcinol (1,3-dihyroxybenzene)	20,46
4-Ethylresorcinol	27,45

Table 1 (continued)
COMPOUNDS IDENTIFIED IN WOOD SMOKE

Miscellaneous	Ref.
Methylamine	48
Dimethylamine	48
Trimethylamine	48
Pyrazine	4
Methylpyrazine	4
2,5-Dimethylpyrazine	4
Pyrrole	33
2-Acetylpyrrole	43,46
2-Formlypyrrole	4
α-Methyl pyrryl ketone	4
α-Ethyl pyrryl ketone	4
Pyridine	48
4-Hydroxy-6-methyl-2,4-pyran-2-one	37
Maltol (3-hydroxy-2-methylpyrone)	1,3,6,21,23,36,30,33,37,45,48
Dimethoxymethane	48
Dimethoxyethane	48
Methoxybenzene	43
Thymol	43
Ethanediol	48
1-Naphthol	44
Toluene	13,20
Styrene	20
Benzene	13,20,48
Ethylbenzene	4
5-Propyl-1,2,3-benzentriol	48
1,2-Dimethoxybenzene (veratrol)	4,20,25,39,43
1,2-Dimethoxy-4-methylbenzene (methylveratrol)	4,20,43,48
1,2-Dimethoxy-4-ethylbenzene (ethylveratrol)	4
1,4-Dimethoxybenzene	20,43
n-Pentadecane	32
2,6,10,14-Tetramethylpentadecane	32,33
1-Indanone	4,30,43,46
2-Methyl-1-indanone	4
3-Methyl-1-indanone	4
6-Methyl-1-indanone	4
Indene	20,37,46
3-Methylindene	20,46
Trimethylindene	46
2,3-Dihydroindene	46
Dimethylindene	20,46
Naphthalene	20,46,48
1-Methylnaphthalene	46
2-Methylnapthalene	20,46
2-Ethylnaphthalene	46
Trimethylnaphthalene	46
Methylethylnaphthalene	46
Methylvinylnaphthalene	46
Allylnaphthalene	44
6-Methyl-1,2-dihydronaphthalene	46
Methyldihydronaphthalene	46

Table 2
TYPICAL FRACTIONATION SCHEME FOR WOOD SMOKE VOLATILES

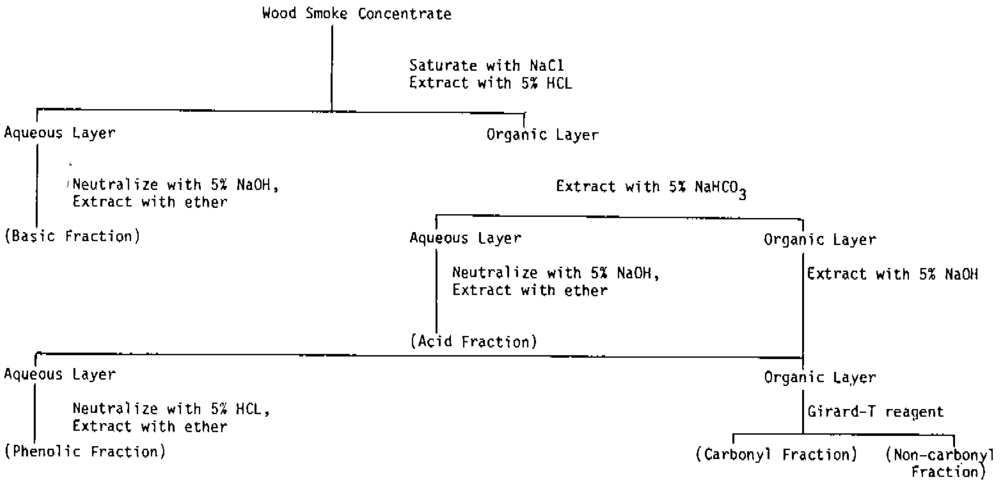


Table 3
CONCENTRATIONS OF MAJOR PHENOLS IN WOOD SMOKE

Compound	Whole smoke (mg/ℓ)	Vapor phase (mg/ℓ)
Phenol	59	5.9
Guaiacol	417	32.1
4-Methylguaiacol	333	13.6
Syringol	392	6.5
Total	1201	58.1

Adapted from Kornreich, M. R. and Issenberg, P., *J. Agric. Food Chem.*, 20, 1109, 1972.

Table 4
% LOSS OF PHENOLS WITH 40 DAYS STORAGE AT −4°C FROM SMOKED COD

Compound	% Remaining
Vanillin	0
2,3-Dimethylphenol	0
Eugenol	0
4-Ethylguaiacol	13
3,4-Dimethylphenol	24
4-Methylguaiacol	34
4-Ethylphenol	44
Isoeugenol	51
3,5-Dimethylphenol	54
Guaiacol	55
2,6-Dimethoxyphenol	63
Phenol	67
m-/p-Cresol	69

Adapted from McWeeny, D. J., *Food Chem.*, 9, 89, 1982.

Table 5
TOTAL PHENOL (mg/100 g) DISTRIBUTION IN A SMOKED BOLOGNA EMULSION

Layer	Concentration
Outer 1.6 mm	3.70
Next 1.6 mm	2.04
Next 1.6 mm	1.41
Next 1.6 mm	1.02
Next 1.6 mm	0.78
Next 1.6 mm	0.43
Next 1.6 mm	0.26
Inner 1.6 mm	0.12
Raw emulsion	0.00

Adpated from Bratzler, L. J., Spooner, M. E., Weatherspoon, J. B., and Maxey, J. A., *J. Food Sci.*, 34, 146, 1969.

Table 6
INFLUENCE OF MEDIA ON PHENOL RECOVERY

Compound	Recovery from water (%)	Recovery from lipid (%)
Phenol	81	89
Guaiacol	80	80
Methylguaiacol	77	84
Syringol	99	92

Adapted from Issenberg, P., Kornreich, M. R., and Lustre, A. O., *J. Food Sci.*, 36, 107, 1971.

Table 7
PHENOLICS IDENTIFIED IN CHARRED OAK

Phenols	Phenolic acids
Phenol	Benzoic acid
o-Cresol	*p*-Hydroxybenzoic acid
m-Cresol	2,3-Dihydroxybenzoic acid
p-Cresol	3,5-Dihydroxybenzoic acid
p-Cresol	2,6-Dihydroxybenzoic acid
Guaiacol	2,3,4-Trihydroxybenzoic acid
2,4-Dimethylphenol	3-Methoxy-4-hydroxybenzoic
2,6-Dimethylphenol	2-Methoxy-4-hydroxybenzoic
2,6-Dimethoxy-4-methylphenol	2,3-Dimethoxybenzoic acid
2,6-Dimethoxy-4-ethylphenol	3,4-Dihydroxycinnamic acid
Acetoxyringone	Phenylacetic acid
Eugenol	Phenylbutric acid
p-Hydroxybenzyl alcohol	*m*-Hydroxyphenylacetic acid

Adapted from Maga, J. A., *Progress in Flavour Research*, Adda, J., Ed., Elsevier, Amsterdam, 1985, 409.

Table 8
THE FLAVOR THRESHOLD (ppm) AND FLAVOR INDEX[a] IN WATER AND OIL OF SEVERAL IMPORTANT SMOKE ASSOCIATED PHENOLS

	Water				Oil	
Compound	Taste threshold	Taste index	Odor threshold	Odor index	Odor threshold	Odor index
Guaiacol	0.013	6,400	0.021	4,600	0.07	1,000
4-Methylguaiacol	0.065	90,000	0.09	58,800	0.40	18,000
2,6-Dimethoxyphenol	1.65	1,400	1.85	1,200	0.34	7,000

[a] Concentration in smoke condensate ÷ mean odor threshold concentration.

Adapted from Wasserman, A. E., *J. Food Sci.*, 31, 1005, 1966.

Table 9
SENSORY CHARACTERIZATION OF SEVERAL PHENOLS ASSOCIATED WITH WOOD SMOKE

	% characterizing compound as					
	Taste			Odor		
Compound	Smoky	Phenolic	Bitter	Smoky	Phenolic	Sweet
2,6-Dimethoxyphenol	46.5	34.0	17.0	71.5	31.5	—
Guaiacol	58.6	33.5	9.5	53.5	37.5	5.2
4-Methylguaiacol	43.2	36.3	26.0	51.8	35.5	13.8

Adapted from Wasserman, A. E., *J. Food Sci.*, 31, 1005, 1966.

Table 10
ODOR DESCRIPTIONS OF VARIOUS PHENOLS ISOLATED FROM WOOD SMOKE

Compounds	Description
Phenol	Pungent
o-Cresol	Pungent
m- and *p*-Cresol	Pungent
2,3-Xylenol	Pungent
2,4-Xylenol	Pungent
2,6-Xylenol	Cresolic
3,4-Xylenol	Cresolic
3,5-Xylenol	Cresolic
2-Ethyl-5-methylphenol	Cresolic
3-Ethyl-5-methylphenol	Cresolic
2,3,5-Trimethylphenol	Cresolic
Guaiacol	Sweet, smoky, somewhat pungent
3-Methylguaiacol	Weak, phenolic
4-Methylguaiacol	Sweet, smoky
4-Ethylguaiacol	Sweet, smoky
4-Allyguaiacol	Woody
2,6-Dimethoxyphenol	Smoky
2,6-Dimethoxy-4-methylphenol	Mild, heavy, burnt
2,6-Dimethoxy-4-ethylphenol	Mild, heavy, burnt
2,6-Dimethoxy-4-propylphenol	Mild, heavy, burnt
4,6-Dimethoxy-4-propenylphenol	Mild, heavy, burnt
Pyrocatechol	Heavy, sweet, burnt
3-Methylpyrocatechol	Heavy, sweet, burnt
4-Methylpyrocatechol	Heavy, sweet, burnt
4-Ethylpyrocatechol	Heavy, sweet, burnt

Adapted from Kim, K., Kurata, T., and Fujimaki, M., *Agric. Biol. Chem.*, 38, 53, 1974.

Table 11
SENSORY DESCRIPTIONS OF VARIOUS SMOKE-ASSOCIATED PHENOLS

Compound	**Optimum sensory concentration (mg/100 mℓ)**	**Odor description**	**Flavor description**
Dimethylphenol	0.9	Phenolic, like ink, aromatic, sweet	Phenolic, sharp, charred sweet, dry
4-Methylguaiacol	1.9	Sweet, like vanilla, fruity, like cinnamon, somewhat smoky, pleasantly sharp, phenol tones	Sweet, like vanilla, caramel-like, aromatic, pleasant smoke tones, burning
Guaiacol	3.75	Phenolic, smoky, aromatic, sharp, sweet	Phenolic, sharp, spicy smoked-sausage-aromatic, sweet, dry
Syringol	7.50	Smoky, spicy, aromatic, smoked-sausage, phenolic, sharp, sweet	Phenolic, smoky, freshly charred wood, like whiskey, dry, sharp
o-Cresol	7.5	Phenolic, sweet-fruity, aromatic, like caramel, smoked-sausage	Sweet, sharp, unpleasant smoky, burning
Isoeugenol	9.8	Sweet-fruity, like vanilla, like rhubarb, phenolic	Sweet-fruity, mild smoke, dry, sharp

Adapted from Baltes, W., Wittkowski, R., Sochtig, I., Block, H., and Toth, L., *The Quality of Food and Beverages*, Vol. 2, Charalambous, G. and Inglett, G., Eds., Academic Press, New York, 1981, 1.

Table 12
SENSORY PROPERTIES OF INDIVIDUAL PHENOLS

Phenol	**Optimum concentration (mg/100 mℓ H_2O)**	**Sensory description**	
		Odor	**Taste**
Dimethylphenol	0.90	Phenolic, ink, aromatic, sweet	Phenolic, hot, sweet, dry
4-Methylguaiacol	1.90	Sweet, vanilla-like, fruity, like cinnamon, smoky	Sweet, vanilla-like, caramel-like, aromatic, pleasant smoke
Cyclotene	1.90	Like hydrolyzed vegetable protein, smoked ham, spicy, aromatic, like clove	Like hydroxyzed vegetable protein, like smoked ham, sweet, hot
Guaiacol	3.75	Phenolic, smoky, aromatic, hot, sweet	Phenolic, hot spicy, smoked ham, sweet, dry
o-Cresol	7.50	Phenolic, sweet, fruity, aromatic, caramel-like, like smoked ham	Sweet, hot, unpleasant, smoky, burning
Isoeugenol	9.80	Like hydrolyzed vegetable protein, ham, spicy, aromatic like clove	Like hydrolyzed vegetable protein, like smoked ham, sweet, hot

Adapted from Toth, L. and Potthast, K., *Adv. Food Res.*, 29, 87, 1984.

Table 13
EFFECT OF SMOKE FRACTION ADDITIONS ON RESULTING AROMA PROPERTIES

Fraction additions	Aroma description	Aroma quality
Phenolic only	Montonous, smoky	Good
Phenolic + carbonyl	Smoky, with fragrance	Better
Phenolic + carbonyl + noncarbonyl	Smoky, with fragrance	Best
Phenolic + neutral + basic	Burnt, smoky	Best

Adapted from Fujimaki, M., Kim, K., and Kurata, T., *Agric. Biol. Chem.*, 38, 45, 1974.

Table 14
SENSORY INTENSITIES OF LIQUID SMOKE FRACTIONS

	Fraction					
Taste property	**1**	**2**	**3**	**4**	**5**	**6**
Smoke taste intensity	6	7	3	11	4	10
Tarry taste intensity	3	1	2	0	6	1
Chemical taste intensity	1	1	3	0	1	0
Acidulous taste intensity	1	2	3	0	0	0

Note: Intensity scale: 0 = below threshold; 11 = highest value; (1) distilled at 67 to 90°C; (2) distilled at 91 to 132°C; (3) distilled at 133 to 200°C; (4) phenol subfraction; (5) terpene subfraction; and (6) whole liquid smoke.

Adapted from Olsen, C. Z., *Proc. Eur. Meet. Meat Res. Workers*, No. 22, F7:1, 1976.

Table 15
ODOR AND TASTE RECOGNITION THRESHOLDS (ppm) AND MOST DESIRABLE CONCENTRATIONS (ppm) OF THE PHENOLIC FRACTION ISOLATED FROM THE VAPOR AND PARTICULATE PHASES OF WOOD SMOKE

Odor

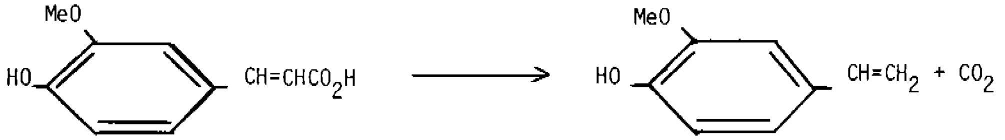
Recognition threshold		Most desirable concentration	
Vapor	**Particulate**	**Vapor**	**Particulate**
10.4	7.8	20.8	16.7

Taste

Recognition threshold		Most desirable concentration	
Vapor	**Particulate**	**Vapor**	**Particulate**
2.3	1.4	15.6	8.3

Adapated from Daun, H., *Lebensm. Wiss. Technol.*, 5, 102, 1972.

Table 16
CONVERSION OF FERULIC ACID TO 4-VINYLGUAIACOL



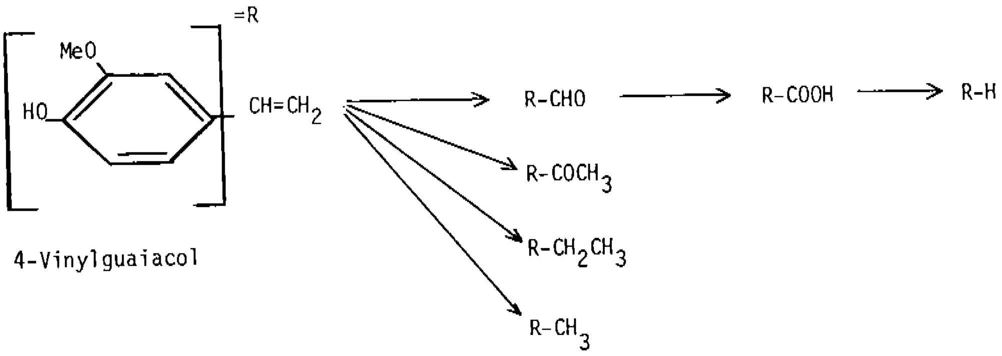
Adapted from Fiddler, W., Parker, W. E., Wasserman, A. E., and Doerr, R. C., *J. Agric. Food Chem.*, 15, 757, 1967.

Table 17
THERMAL DECOMPOSITION PRODUCTS OF FERULIC ACID

Guaiacol
4-Methylguaiacol
4-Ethylguaiacol
4-Vinylguaiacol
cis-Isoeugenol
Vanillin
Acetovanillone

Adapted from Fiddler, W., Parker, W. E., Wasserman, A. E., and Doerr, R. C., *J. Agric. Food Chem.*, 15, 757, 1967.

Table 18
CONVERSION OF 4-VINYLGUAIACOL TO VARIOUS BY-PRODUCTS



Adapted from Fiddler, W., Parker, W. E., Wasserman, A. E., and Doerr, R. C., *J. Agric. Food Chem.*, 15, 757, 1967.

Table 19
PHENOLS ASSOCIATED WITH VARIOUS SPICES

Spice	Phenols
Cinnamon	Phenol *O*-Cresol 2-Vinylphenol 4-Allylphenol Guaiacol 4-Ethyl-2-methoxyphenol Eugenol Methyleugenol Acetyleugenol
Thyme	2-Isopropyl-5-methylphenol 5-Isopropyl-2-methylphenol
Pepper	Eugenol Methyleugenol
Nutmeg	Eugenol Methyleugenol Methoxyeugenol Isoeugenol Methylisoeugenol
Marjoram	5-Isopropyl-2-methylphenol 4-Allylphenol Eugenol
Cloves	4-Allylphenol Eugenol Acetoeugenol

Adapted from Baltes, W. and Sochtig, I., *Z. Lebensm. Unters. Fursch.*, 169, 17, 1979.

Table 20
ODOR DESCRIPTIONS OF CERTAIN FURANS ISOLATED FROM WOOD SMOKE

Compound	Odor description
Furfural	Sweet, bread-like, caramel-like
5-Methylfurfural	Sweet-spicy, warm, slightly caramel-like
2-Furylmethylketone	Powerful, balsamic, sweet
2-(5-Methylfuryl)-methylketone	Sweet, fragrant
Methyl furoate	Grassy, acetophenone-like

Adapted from Kim, K., Kurata, T., and Fujimaki, M., *Agric. Biol. Chem.*, 38, 53, 1974.

Table 21
VOLATILES IDENTIFIED IN THE BASIC FRACTION OF FIRE-CHARRED WHITE OAK

Pyrazines

Pyrazine
2-Methyl-3-isopropylpyrazine
2-Methoxy-3-ethylpyrazine
2-Methoxy-3-methylpyrazine
2-Methoxy-3-propylpyrazine
2-Acetylpyrazine
2-Acetyl-3-methylpyrazine
2-Acetyl-3,5-dimethylpyrazine
2-Methyl-5-acetylfuran

Furans

2,5-Dihydrofuran
3-Methyl-2,3-dihydrofuran
3-Methyl-2,5-dihydrofuran
3-Methyl-2(5H)-furanone
5-Methyl-2(5H)-furanone
2,5-Dimethylfuran
3,4-Dimethylfuran
2,3,4-Trimethylfuran
2,5-Diethylfuran
2-Furancarboxaldehyde
2-Methyl-5-ethylfuran
2-Furanylethanone

Miscellaneous

3,5-Dimethylpyrazole
Dimethylmelamine
2-Isopropylfuran
4-Propenyl-2,3-dihydrofuran
2-Methyl-5-isopropylfuran
2-Propyl-5-methylfuran
2-Furfuryl alcohol
5-Methyl-2-oxo-2,3-dihydrofuran
2-Acetyl-3-hydroxyfuran
2,5-Dimethyl-3-ethylfuran
2-Methoxy-3-isobutyl-5-methylpyrazine

Pyridines

2-Methylpyridine
2-Ethylpyridine
3-Methoxypyridine
2-Ethyltetrahydropyridine
2-Propyltetrahydropyridine

Pyrans

3,4-Dihydropyran
4H-Pyran-2-one
2H-4-Hydroxy-6-methylpyran-2-one

Adapted from Maga, J. A. and Fapojuwo, O. O., *J. Sensory Stud.*, 1, 9, 1986.

Table 22
AROMA DESCRIPTION OF CERTAIN CARBONYLS ISOLATED FROM WOOD SMOKE

Compound	Odor description
2-Cyclopentenone	Grassy, potato-like
3-Methyl-2-cyclopentenone	Somewhat sweet, grassy
2,3-Dimethyl-2-cyclopentenone	Grassy, bitter
2,4-Dimethyl-2-cyclopentenone	Somewhat grassy
2,5-Dimethyl-2-cyclopentenone	Somewhat grassy
3,4-Dimethyl-2-cyclopentenone	Somewhat grassy
3,5-Dimethyl-2-cyclopentenone	Somewhat grassy
3-Ethyl-2-cyclopentenone	Grassy
2-Ethyl-3-methyl-2-cyclopentenone	Mild, medicine-like
2-Ethyl-4-methyl-2-cyclopentenone	Grassy

Adapted from Kim, K., Kurata, T., and Fujimaki, M., *Agric. Biol. Chem.*, 38, 53, 1974.

Table 23
ODOR DESCRIPTIONS OF CERTAIN LACTONES IDENTIFIED IN WOOD SMOKE

Compound	Odor description
γ-Butyrolactone	Somewhat bitter, burnt
2-Methyl-2-butenolide	Sweet, burnt, caramel-like
4-Methyl-2-butenolide	Smoky, burnt
2,3-Dimethyl-2-butenolide	Spicy, vanilla-like
2,4-Dimethyl-2-butenolide	Sweet, burnt
3,4-Dimethyl-2-butenolide	Weak, sour, smoky
2,3,4-Trimethyl-2-butenolide	Weak, burnt, caramel-like
2-Ethyl-4-methyl-2-butenolide	Burnt, woody
4-Ethylidene-2-methyl-2-butenolide	Sweet, caramel-like

Adapted from Kim, K., Kurata, T., and Fujimaki, M., *Agric. Biol. Chem.*, 38, 53, 1974.

Table 24
ACCEPTABILITY OF SMOKE VS. WOOD SOURCE

Good woods:	Beech
	Oak
	Maple
Fair woods:	Pine
	Birch
Poor woods:	Alder
	Lime
	Aspen
	Fir

Adapted from Tilgner, D. J., *Fleischwirtschaft*, 10, 751, 1958.

Table 25
YIELD (mg %) OF TOTAL AND INDIVIDUAL AROMA FRACTIONS AS INFLUENCED BY WOOD SOURCE

	Aroma fraction					
Wood	**Total**	**Phenolic**	**Carbonyl**	**Noncarbonyl**	**Acid**	**Basic**
Oak *(Queretis seriata)*	1860	151	117	99	1140	48
Oak *(Q. acuta)*	1600	225	323	310	820	80
Cherry	1490	101	111	60	660	108
Bamboo	1180	144	86	211	610	40
Pine	1180	166	53	24	640	33
Cedar	890	122	90	73	520	40

Adapted from Fujimaki, M., Kim., K., and Kurata, T., *Agric. Biol. Chem.*, 38, 45, 1974.

Table 26
RELATIVE SMOKE COMPOUND COMPOSITION AS INFLUENCED BY WOOD SOURCE

	% of peak area					
Compound	***Queretis acuta***	***Q. seriata***	**Cherry**	**Bamboo**	**Pine**	**Cedar**
Acetic acid	56	28	9	17	74	10
Propionic acid	13	32	35	50	9	36
Isobutyric acid	3	4	7	3	1	7
n-Butyric acid	1	10	13	15	<0.1	17
Isovaleric acid	<0.1	1	2	1	<0.1	3
cis-Crotonic acid	0.3	<0.1	0.3	<0.1	0.3	2.5
n-Valeric acid	<0.1	1	1	1	—	1
trans-Crotonic acid	0.7	0.7	1.3	0.4	0.2	1.2
Guaiacol	45	40	30	36	26	24
4-Methylguaiacol	12	12	9	7	10	11
4-Ethylguaiacol	2	2	1	2	1	2
o-Cresol	24	23	39	40	40	45
p-Cresol	10	10	13	9	15	16
3,5-Xylenol	4	4	4	3	1	2
3,4-Xylenol	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Syringol	4	4	4	3	4	0
4-Methylsyringol	2	1	1	<0.5	1	0
4-Ethylsyringol	0	<0.5	0	0	0	0
Cyclopentanone	3	4	3	11	1	3
2-Methyl-2-cyclopentenone	10	11	13	7	10	11
Furfural	38	38	37	41	49	27
2-Acetylfuran	8	11	9	11	6	9
3-Methyl-2-cyclopentenone	1	1	2	1	3	2
2,3-Dimethyl-2-cyclopentenone	2	2	4	2	2	2
5-Methylfurfural	24	22	22	12	17	31

Adapted from Fujimaki, M., Kim., K., and Kurata, T., *Agric. Biol. Chem.*, 38, 45, 1974.

Table 27
DIFFERENCES BETWEEN THE PHENOLIC COMPOSITION OF HARDWOOD AND SOFTWOOD

	Relative % in	
Compound	**Hardwood**	**Softwood**
Phenol	4	4
o-Cresol	2	2
m-Cresol	2	2
p-Cresol	2	1
Guaiacol	8	10
Pyrocatechol	6	8
4-Methylguaiacol	7	10
4-Methylpyrocatechol	2	4
4-Methylresorcinol	3	4
4-Ethylguaiacol	3	5
Syringol	12	3
4-Vinylguaiacol	3	5
4-Allylguaiacol	2	4
4-Methylsyringol	9	3
4-Ethylsyringol	11	11
4-Vinylsyringol	3	1
4-Allylsyringol	3	1
4-Propenylsyringol	10	2

Adapted from Baltes, W., Wittkowski, R., Sochtig, I., Block, H., and Toth, L., *The Quality of Food and Beverages*, Vol. 2, Charalambous, G. and Inglett, G., Eds., Academic Press, New York, 1981, 1.

Table 28
COMPOSITION OF LIGHT AND HEAVY BEECH AND OAK SMOKES

	Composition in mg/m^3 smoke			
Smoke component	**Light beech**	**Light oak**	**Heavy beech**	**Heavy oak**
Ash and soot	7.95	21.77	8.24	23.50
Ether insolubles	216.0	154.16	99.58	754.40
Free bases	45.3	41.96	155.76	48.01
Aldehydes and ketones	47.9	24.75	108.65	70.95
Carboxylic acids	37.28	64.32	203.6	327.5
Phenols	15.91	8.97	93.31	73.27
Neutral organic compounds	298.96	477.60	1757.02	803.64

Adapted from Ziemba, A., *Przem. Spozyw.*, 2, 200, 1957.

Table 29
SMOKE COMPOSITION FROM DIFFERENT WOOD SPECIES

	g/100 g sawdust					
Class/compound	**Spruce**	**Pine**	**Acacia**	**Oak**	**Beech**	**White beech**
Monocarbonyls	3.06	3.10	1.70	2.40	1.77	2.50
Oxy- and dicarbonyls	6.30	6.12	1.86	1.98	3.60	4.95
Formaldehyde	0.21	0.20	0.11	0.14	0.15	0.16
Acetaldehyde	1.15	1.00	0.81	0.63	0.66	0.65
Acetone	0.69	0.54	0.64	0.37	0.74	0.69
Furfural	0.21	0.18	0.24	0.35	0.18	0.26
NaOH reducing substances	7.83	7.40	4.56	4.68	6.94	9.75
Reductants	0.21	0.29	0.13	0.17	0.16	0.32
Dehydroreductants	2.10	1.80	1.56	0.66	1.32	2.16
Total acids	3.07	3.17	2.94	3.56	4.06	6.79
pH	3.8	4.7	4.3	4.0	4.8	4.1
Esters	8.08	11.16	8.48	10.47	6.69	10.35
Phenols	0.29	0.29	0.36	0.16	0.14	0.32

Adapted from Toth, L. and Potthast, K., *Adv. Food Res.*, 29, 87, 1984.

Table 30
INFLUENCE OF WOOD SOURCE ON SMOKED WHITEFISH ACCEPTABILITY

Wood	Sensory hedonic score[a]	Panel comments
Red maple	6.49	Good blend of salty, sweet, smoky
Red oak	6.42	Good; slight sour and burnt
Trembling aspen	6.24	Good; slower flavor impact, sweet
White ash	6.08	Good; slight medicinal
Balsam poplar	6.05	Slower impact; sweet, mild
Birch	5.98	Good; sweet, smoky blend; medicinal
Beech	5.91	Good; flat taste; slightly burnt
White oak	5.82	Fair; slight medicinal, bitter
Hard maple	5.32	Dominant sweet-sour taste
Hickory	5.24	Salt and smoky flavor, poorly blended
Diamond willow	4.70	Strong, fruity, sweet, medicinal, astringent
Burr oak	3.77	Unacceptable; strong medicinal, gasoline-like taste

[a] Maximum = 9.00.

Adapted from Lantz, A. W. and Vaisey, M., *J. Fish Res. Board Can.*, 27, 1201, 1970.

Table 31
INFLUENCE OF WOOD SOURCE ON THE SENSORY PROPERTIES OF SMOKED EEL

Wood	Eel color	Eel odor	Eel flavor
Teak sawdust	Rich red	Acrid	Slightly unpalatable
Teak wood chips	Pale yellow	Acrid	Unpalatable
Sajar sawdust	Reddish yellow	Acrid	Slightly unpalatable
Acacia sawdust	Rich red	Very acrid	Bitter, unpalatable
Mango sawdust	Reddish yellow	Very acrid	Tarry, unpleasant
Coconut husk	Pale yellow	Pleasant	Very palatable
75% coconut husk + 25% teak sawdust	Rich yellow	Pleasant	Palatable
50% coconut husk + 50% teak sawdust	Rich yellow	Pleasant	Palatable
25% coconut husk + 75% teak sawdust	Rich red	Mildly pleasant	Slightly acrid

Adapted from Solanki, K. K., Kandoran, M. K., and Venkataraman, R., *Fish Technol.*, 7, 169, 1970.

Table 32
AROMA INTENSITY RATINGS OF VARIOUS WOOD SMOKE FRACTIONS

Wood source	Carbonyl	Neutral	Basic	Phenolic
Apple	4.02	2.28	5.32	3.40
Chestnut	3.86	1.82	3.44	3.21
Cherry	5.40	4.13	4.61	3.59
Hard maple	4.23	2.75	3.15	3.59
Hickory	4.32	3.40	3.57	4.96
Mesquite	3.15	2.54	2.80	5.83
Red oak	6.03	2.92	4.07	3.17
White oak	5.46	2.63	3.52	3.44

Adapted from Maga, J. A. and Fapojuwo, O. O., *J. Sensory Stud.*, 1, 9, 1986.

Table 33
PYRAZINE CONTENT OF VARIOUS WOOD SMOKE SOURCES

Wood	mg total pyrazines/ 100 g dry wt wood
Redwood	10.33
Chestnut	10.59
Douglas fir (heartwood)	14.08
White oak	17.05
Aspen	17.16
Walnut	17.51
Douglas fir (sapwood)	20.07
Cherry	20.48
Eastern cedar	22.05
Hard maple	22.32
Apple	23.24
Red oak	23.84
Red alder	24.03
Birch	26.28
Lodgepole pine (bark)	29.57
Lodgepole pine (wood)	35.59
Hickory	41.03

Adapted from Maga, J. A. and Chen, Z., *Flavour Fragrance J.*, 1, 37, 1985.

Table 34
INFLUENCE OF SMOLDERING TEMPERATURE ON THE AMOUNTS OF PHENOLS, CARBONYLS, AND ACIDS IN WOOD SMOKE

Smoldering temperature (°C)	Phenols (μg phenol/mℓ)	Carbonyls (mg acetaldehyde/mℓ)	Acids (meq acid/mℓ)
252	88	20.0	0.082
287	91	20.2	0.077
322	153	27.3	0.121
355	197	31.2	0.104
386	165	37.2	0.112

Adapted from Porter, R. W., Bratzler, L. J., and Pearson, A. M., *J. Food Sci.*, 30, 615, 1965.

Table 35
INFLUENCE OF SMOLDERING TEMPERATURE ON THE RECOGNITION THRESHOLD (ppm) AND MOST DESIRABLE CONCENTRATION (ppm) OF VAPOR-PHASE WOOD SMOKE

Smoldering temperature (°C)	Recognition threshold		Most desirable concentration	
	Odor	Taste	Odor	Taste
400	10.4	2.3	20.8	15.6
500	20.8	4.1	41.7	27.1
600	18.7	6.2	37.5	25.2

Adapted from Daun, H., *Lebensm. Wiss. Technol.*, 5, 102, 1972.

Table 36
INFLUENCE OF SMOLDERING TEMPERATURE ON THE PHENOL CONTENT OF BEECHWOOD SMOKE

Smoldering temperature (°C)	Phenol content (mg/100 g)
400	350
450—500	800
500—600	2960
700—800	2810
900—1050	1945

Adapted from Toth, L., *Fleischwirtschaft*, 60, 728, 1980.

Table 37
CHANGE IN VOLATILE COMPOSITION AND CONTENT WITH INCREASING SMOKE GENERATION TEMPERATURE

Generator temperature (°C)	Acids (wt %)	Phenols (wt %)	Carbonyls (wt %)	Total (mg/100 mℓ)
300	41	2.3	57	147
315	40	1.7	59	214
343	32	1.7	66	437
385	27	1.6	72	503
415	24	1.5	74	634

Adapted from Simon, S., Rypinski, A. A., and Tauber, F. W., *Food Technol.*, 20, 1494, 1966.

Table 38
INFLUENCE OF SMOKE GENERATION TEMPERATURE ON THE CONTENT OF CERTAIN PHENOLS

Generation temperature (°C)	mg/100 g			
	Phenol	Guaiacol	Benzocatechol	Syringol
450	20	60	35	85
550	30	85	60	150
650	55	125	135	260
750	20	115	135	215
850	25	100	125	175

Adapted from Toth, L., *Fleischwirtschaft*, 60, 1472, 1980.

Table 39
INFLUENCE OF % OXYGEN IN THE GAS USED FOR SMOLDERING vs. VOLATILE COMPONENT COMPOSITION

	% peak area/g sawdust consumed		
% oxygen in gas	**Furfuryl alcohol**	**Cyclotene**	**Guaiacol**
0	100	55	55
10	75	100	100
20	44	45	55
30	40	43	50
40	38	46	55
50	36	45	48

Adapted from Wasserman, A. E. and Fiddler, W., Proc. Meat Ind. Res. Conf., Chicago, 1969, 163

Table 40
INFLUENCE OF AIR AMOUNT ON THE SENSORY PROPERTIES OF SMOKE VAPOR

	Recognition threshold (ppm)		Most desirable concentration (ppm)	
Air amount	**Odor**	**Taste**	**Odor**	**Taste**
Low	7.4	1.4	15.6	17.7
High	8.3	1.3	16.7	8.3

Adapted from Daun, H., *Lebensm. Wiss. Technol.*, 5, 102, 1972.

Table 41
INFLUENCE OF WOOD MOISTURE CONTENT ON RESULTING CHEMICAL COMPOSITION AND SENSORY PROPERTIES

	Yield/100 g sawdust				
Moisture content (%)	**Condensate (g)**	**Phenols (mg)**	**Acids (mg)**	**Formaldehyde (mg)**	**Sensory quality**
1.8	28.2	236	3293	122	Unsatisfactory
21.5	41.5	136	3288	81	Good
24.5	43.5	100	3003	78	Good
31.2	32.8	33	890	—	Almost satisfactory

Adapted from Gorbatov, V. M., Krylova, N. N., Volovinskaya, V. P., Lyaskouskaya, Y. N., Bazarova, K. I., Khlamova, R. I., and Yakovleva, G. Y., *Food Technol.*, 25, 71, 1971.

Table 42
CHEMICAL COMPARISON OF SAWDUST SMOKE AND FRICTION SMOKE

	Sawdust smoke		Friction smoke	
Property	Steam volatile	Nonsteam volatile	Steam volatile	Nonsteam volatile
pH	4.00	4.20	3.18	3.00
% total acids	1.28	0.183	4.98	0.209
% total carbonyls	0.627	0.164	4.78	2.79
% total phenols	0.068	0.007	0.217	0.067
% total volatiles	1.35	0.354	9.98	3.07
% moisture	86.7		70.6	

Adapted from Husaini, S. A. and Cooper, G. E., *Food Technol.*, 11, 499, 1957.

Table 43
PHENOLIC DIFFERENCES BETWEEN HOT AND COLD SMOKING

	mg/kg	
Compound	Hot smoke	Cold smoke
Cyclotene	Trace	Trace
Guaiacol	Trace	1.90
Maltol	Trace	10.15
Phenol	Trace	2.35
m, p-Cresol	Trace	Trace
Eugenol	12.23	34.80
Isoeugenol	Trace	Trace
2,6-Dimethoxy-4-alkylphenol	Trace	Trace
Vanillin	Trace	Trace
Acetovanillone	17.65	Trace
Syringaldehyde	75.25	42.80
Acetosyringone	59.45	Trace

Adapted from Potthast, K., *Acta Aliment. Pol.*, 3, 189, 1977.

Table 44
EFFECT OF SMOKE AGE AS COMPARED TO A 2-MONTH-OLD CONTROL

Age	Score (7 point hedonic)
2 month	4.0
1 month	4.1
96 hr	3.6
48 hr	3.6
5 hr	2.8

Adapted from Wasserman, A. E. and Fiddler, W., Proc. Meat Ind. Res. Conf., Chicago, 1969, 163.

Table 45
INFLUENCE OF STORAGE ON METHYL ACETATE AND FORMATE LEVELS

	Concentration (molarity)	
Storage time (hr)	Methyl acetate	Methyl formate
0	0	0.001
100	0.010	0.009
200	0.027	0.010
300	0.036	0.011
400	0.037	0.009
500	0.038	0.009
600	0.039	0.010
700	0.041	0.010

Adapted from Doerr, R. C., Wasserman, A. E., and Fiddler, W., *J. Agric. Food Chem.*, 14, 662, 1966.

REFERENCES

1. **Fiddler, W., Wasserman, A. E., and Doerr, R. C.,** A smoke flavor fraction of a liquid smoke solution, *J. Agric. Food Chem.*, 18, 934, 1970.
2. **Knowles, M. E., Gilbert, J., and McWeeny, D. J.,** Phenols in smoked cured meats. Phenolic composition of commercial liquid smoke preparations and derived bacon, *J. Sci. Food Agric.*, 26, 189, 1975.
3. **Kornreich, M. R. and Issenberg, P.,** Determination of phenolic wood smoke components as trimethylsillyl esters, *J. Agric. Food Chem.*, 20, 1109, 1972.
4. **Kim, K., Kurata, T., and Fujimaki, M.,** Identification of flavor constitutents in carbonyl, non-carbonyl, neutral and basic fractions of aqueous smoke condensates, *Agric. Biol. Chem.*, 38, 53, 1974.
5. **Lustre, A. O. and Issenberg, P.,** Phenolic components of smoked meat products, *J. Agric. Food Chem.*, 18, 1056, 1970.
6. **Fiddler, W., Doerr, R. C., and Wasserman, A. E.,** Composition of an ether-soluble fraction of a liquid smoke solution, *J. Agric. Food Chem.*, 18, 310, 1970.
7. **Radecki, A., Lamparczyk, H., Grzybowski, J., Halkiewicz, J., Bednarek, P., Boltrukiewicz, J., and Rapicki, W.,** Analysis of a commercial smoke-curing agent. III. Separation and identification of components of low-boiling phenolic fractions, *Bromatol. Chem. Toksykol.*, 9, 327, 1976.
8. **Radecki, A., Grzybowski, J., Halkiewicz, J., Lamparcyzk, H., Bednarek, P., Boltrukiewicz, J., and Rapicki, W.,** Analysis of a commercial smoke preparation. IV. Separation and identification of some components significantly influencing the organoleptic and preserving properties of the preparation, *Bromatol. Chem. Toksykol.*, 9, 461, 1976.
9. **Radecki, A., Bednarek, P., Boltrukiewicz, J., Cacha, R., Rapicki, W., Grzybowski, J., Halkiewicz, J., and Lamparczyk, H.,** Analysis of a commercial smoke-curing agent. I. Separation and identification of high-boiling phenolic fractions, *Bromatol. Chem. Toksykol.*, 8, 179, 1975.
10. **Radecki, A., Halkiewicz, J., Lamparczyk, H., Grzybowski, J., Bednarek, P., Boltrukiewicz, J., Cacha, R., and Rapicki, W.,** Analysis of a commercial smoke-curing agent. II. Separation and identification of some constitutents of the low-boiling phenolic fraction, *Bromatol. Chem. Toksykol.*, 8, 185, 1975.
11. **Radecki, A. and Grzybowski, J.,** Method for determination of phenolic compounds in smoked products, *Bromatol. Chem. Toksykol.*, 14, 129, 1981.
12. **Ishiwata, H., Watanabe, H., Watanabe, M., Hayashi, T., Hara, Y., Kato, S., and Tanimura, A.,** Chemical compositions of smoke flavour, *Bull. Natl. Inst. Hygienic Sci.*, 94, 112, 1976.
13. **Hoff, J. E. and Kapsalopoulou, A. J.,** Low-boiling components of wood smoke. Identification by means of syringe reactions, *J. Gas Chromatogr.*, 2, 296, 1964.
14. **Doerr, R. C., Wasserman, A. E., and Fiddler, W.,** Composition of hickory sawdust smoke. Low-boiling constituents, *J. Agric. Food Chem.*, 14, 662, 1966.

15. **Love, S. and Bratzler, L. J.**, Tentative identification of carbonyl compounds in wood smoke by gas chromatography, *J. Food Sci.*, 31, 218, 1966.
16. **Hamid, H. A. and Saffle, R. L.**, Isolation and identification of the volatile fatty acids present in hickory sawdust smoke, *J. Food Sci.*, 30, 697, 1965.
17. **Radecki, A., Grzybowski, J., Halkiewicz, J., and Lamparczyk, H.**, Isolation and identification of some components of the lower-boiling fraction of a commercial smoke flavoring, *Acta Aliment. Pol.*, 3, 203, 1977.
18. **Porter, R. W., Bratzler, L. J., and Pearson, A. M.**, Fractionation and study of compounds in wood smoke, *J. Food Sci.*, 30, 615, 1965.
19. **Luten, J. B., Ritskes, J. M., and Weseman, J. M.**, Determination of phenol, guaiacol and 4-methylguaiacol in wood smoke and smoked fish products by gas-liquid chromatography, *Z. Lebensm. Unters. Forsch.*, 168, 289, 1979.
20. **Hurza, D. E., van Praag, M., and Heinsohn, H.**, Isolation and identification of the components of tar of hickory wood smoke, *J. Agric. Food Chem.*, 22, 123, 1974.
21. **Lustre, A. O. and Issenberg, P.**, Volatile components of hardwood sawdust smoke, *J. Agric. Food Chem.*, 17, 1387, 1969.
22. **Husaini, S. A. and Cooper, G. E.**, Fractionation of wood smoke and the comparison of chemical composition of sawdust and friction smokes, *Food Technol.*, 11, 499, 1957.
23. **van Chuyen, N. and Kato, H.**, Recent studies on smoke flavor. II, *Nippon Shokuhin Kogyo Gakkai Shi*, 30, 722, 1983.
24. **Borys, A., Flossowska, B., Obiedzinski, M., and Olkiewicz, M.**, Influence of combustion conditions on the composition of carbonylic, carboxylic, polynucelar hydrocarbons and phenolic compounds present in wood smoke, *Acta Aliment. Pol.*, 3, 335, 1977.
25. **Fiddler, W., Doerr, R. C., Wasserman, A. E., and Salay, J. M.**, Composition of hickory sawdust smoke. Furans and phenols, *J. Agric. Food Chem.*, 14. 659, 1966.
26. **Potthast, K.**, Determination of phenols in smoked meat products, *Acta Ailment. Pol.*, 3, 189, 1977.
27. **Toth, L.**, Separation and analysis of phenol fractions from smokehouse smoke. II. Separation, purification and analysis of phenol fractions, *Fleischwirtschaft*, 60, 728, 1980.
28. **Jodai, S.**, Studies of smoke perfume. I. Organic solvent extracts of pyroligneous acid, *J. Food Sci. Technol.*, 15, 335, 1968.
29. **Fujimaki, M., Kim, K., and Kurata, T.**, Analysis and comparison of flavor constituents in aqueous smoke condensates from various woods, *Agric. Biol. Chem.*, 38, 45, 1974.
30. **Borys, A.**, Composition of carbonyl fraction in smoke from selected types of wood, *Rocz. Inst. Przem. Miesnego Tluszezowego*, 15, 157, 1978.
31. **Kasahara, K. and Nishibori, K.**, Volatile components of smoked salmon. I, *Bull. Jpn. Soc. Sci. Fish.*, 45, 1543, 1979.
32. **Kasahara, K. and Nishibori, K.**, Volatile components of smoked salmon. II. The relationship between flavors of smoked salmon and smoke tar, *Bull. Jpn. Soc. Sci. Fish.*, 45, 1547, 1979.
33. **Kasahara, K. and Nishibori, K.**, Volatile components of smoked cuttlefish and octopus, *Bull. Jpn. Soc. Sci. Fish*, 49, 913, 1983.
34. **Kasahara, K. and Nishibori, K.**, Volatile components of smoked herring, *Bull. Jpn. Soc. Sci. Fish.*, 47, 783, 1981.
35. **Kasahara, K. and Nishibori, K.**, Volatile components of smoked sardine, *Bull. Jpn. Soc. Sci. Fish.*, 47, 113, 1981.
36. **Kasahara, K. and Nishibori, K.**, Volatile carbonyls and acids of smoked sardines, *Bull. Jpn. Soc. Sci. Fish.*, 48, 691, 1982.
37. **Borys, A.**, Chemical composition of the Bieszczadzki refined liquid smoke preparation, *Rocz. Inst. Przem. Miesnego Tluszczowego*, 16, 95, 1979.
38. **Toth, L.**, Influence of smokehouse technology on phenols in the smoke, *Fleischwirtschaft*, 60, 1472, 1980.
39. **Wasserman, A. E. and Fiddler, W.**, Natural smoke: composition and properties, Proc. Meat Ind. Res. Conf., Chicago, 1969, 163.
40. **Baltes, W. and Sochtig, I.**, Detection by glass capillary gas chromatography of addition of smoke flavor condensate to sausages, *Z. Lebensm. Unters. Forsch.*, 169, 17, 1979.
41. **Fiddler, W., Parker, W. E., Wasserman, A. E., and Doerr, R. C.**, Thermal decomposition of ferulic acid, *J. Agric. Food Chem.*, 15, 757, 1967.
42. **Olsen, C. Z.**, Chemical composition and application of smoke flavor, *Proc. Eur. Meet. Meat Res. Workers*, No. 22, F7:1, 1976.
43. **Baltes, W. and Sochtig, I.**, Low molecular weight ingredients of smoke flavor preparations, *Z. Lebensm. Unters. Forsch.*, 169, 9, 1979.
44. **Borys, A., Obiedzinski, M., and Olkiewicz, M.**, Identification of phenolic compounds in a polish smoke flavor extract, *Proc. Eur. Meet. Meat. Res. Workers*, No. 22, F8:1, 1976.

45. **Wittkowski, R., Toth, L., and Baltes, W.,** Separation and analysis of phenol fractions from smokehouse smoke. III. Separation and identification of mono- and di-hydroxycompounds, *Z. Lebensm. Unters. Forsch.*, 173, 445, 1981.
46. **Baltes, W., Block, H., and Mevissen, L.,** Studies of high molecular weight tars from smoke aroma condensates, *Z. Lebensm. Unters. Forsch.*, 175, 130, 1982.
47. **Lapshin, I. I. and Rodina, T. G.,** The role of phenols in the MINCH liquid smoke separation for treatment of fish, *Rybn. Khoz.*, No. 2, 75, 1974.
48. **Goos, A. W.,** The thermal decomposition of wood, *Wood Chemistry,* Vol. 2, 2nd ed., Reinhold, New York, 1952.
49. **McWeeny, D. J.,** Reactions of some food additives during storage, *Food Chem.*, 9, 89, 1982.
50. **Bratzler, L. J., Spooner, M. E., Weatherspoon, J. B., and Maxey, J. A.,** Smoke flavor as related to phenol, carbonyl and acid content of bologna, *J. Food Sci.*, 34, 146, 1969.
51. **Issenberg, P., Kornreich, M. R., and Lustre, A. O.,** Recovery of phenolic wood smoke components from smoked foods and model systems, *J. Food Sci.*, 36, 107, 1971.
52. **Wasserman, A. E.,** Organoleptic evaluation of three phenols present in wood smoke, *J. Food Sci.*, 31, 1005, 1966.
53. **Daun, H.,** Sensory properties of phenolic compounds isolated from curing smoke as influenced by its generation parameters, *Lebensm. Wiss. Technol.*, 5, 102, 1972.
54. **Maga, J. A.,** Pyrazines in foods. An update, *CRC Crit. Rev. Food Sci. Nutr.*, 16, 1, 1982.
55. **Tilgner, D. J.,** Analysis and use of smoke from various kinds of wood, *Fleischwirtschaft,* 10, 751, 1958.
56. **Khvan, E. A., Shaposhnikov, Y. K., Radakova, T. N., Alsufev, V. A., and Kondakova, L. V.,** Study of the chemical composition of smoke evolved by different types of wood, *Rybn. Khoz.*, No. 5, 62, 1975.
57. **Lee, J. M. and Song, K. W.,** Effects of conventional smoking and liquid smoke treatment on the quality of pork sausages, *Korean J. An. Sci.*, 17, 511, 1975.
58. **Sidaway, E. P.,** A comparison of some British Columbia softwoods for smoking fish, *Fish. Res. Board Can. Prog. Rep. Pac. Coast Stn.*, 59, 12, 1944.
59. **Lantz, A. W. and Vaisey, M.,** Flavor effects of different woods on whitefish smoked in a kiln with controlled temperature, humidity, and air velocity, *J. Fish. Res. Board Can.*, 27, 1201, 1970.
60. **Solanki, K. K., Kandoran, M. K., and Venkataraman, R.,** Studies on smoking of eel fillets, *Fish Technol.*, 7, 169, 1970.
61. **Simon, S., Rypinski, A. A., and Tauber, F. W.,** Water-filled cellulose casings as model absorbents for wood smoke, *Food Technol.*, 20, 1494, 1966.
62. **Klossowska, B. M.,** Wood destruction rate versus combustion conditions in the process of generating wood smoke — a mathematical approach, *Acta Ailment. Pol.*, 7, 283, 1981.
63. **Gorbatov, V. M., Krylova, N. N., Volovinskaya, V. P., Lyaskovskaya, Y. N., Bazarova, K. I., Khlamova, R. I., and Yakovleva, G. Y.,** Liquid smokes for use in cure meats, *Food Technol.*, 25, 71, 1971.
64. **Baltes, W., Wittkowski, R., Sochtig, I., Block, H., and Toth, L.,** Ingredients of smoke and smoke flavor preparations, in *The Quality of Foods and Beverages,* Vol. 2, Charalambous, G. and Inglett, G., Eds., Academic Press, New York, 1981, 1.
65. **Maga, J. A. and Sizer, C. E.,** Pyrazines in foods. A review, *J. Agric. Food Chem.*, 21, 22, 1973.
66. **Maga, J. A. and Sizer, C. E.,** Pyrazines in foods, *CRC Crit. Rev. Food Technol.*, 4, 39, 1973.
67. **Maga, J. A.,** Pyrazines in foods. An update, *CRC Crit. Rev. Food Sci. Nutr.*, 16, 1, 1982.
68. **Maga, J. A.,** Flavor contribution of wood in alcoholic beverages, in *Progress in Flavour Research,* Adda, J., Ed., Elsevier, Amsterdam, 1985, 409.
69. **Maga, J. A. and Fapojuwo, O. O.,** Aroma intensities of various wood smoke fractions, *J. Sensory Stud.*, 1, 9, 1986.
70. **Maga, J. A. and Chen, Z.,** Pyrazine composition of wood smoke as influenced by wood source and smoke generation variables, *Flavour Fragrance J.*, 1, 37, 1985.
71. **Maga, J. A.,** Lactones in foods, *CRC Crit. Rev. Food Sci. Nutr.*, 8, 1, 1976.
72. **Ziemba, A.,** Generation of industrial curing smoke and its chemical composition, *Przem. Spozyw.*, 2, 200, 1957.
73. **Toth, L. and Potthast, K.,** Chemical aspects of the smoking of meat and meat products, *Adv. Food Res.*, 29, 87, 1984.

Chapter 10

POTENTIAL HEALTH CONCERNS ASSOCIATED WITH SMOKE

I. INTRODUCTION

Up until now we have primarily talked about the positive aspects of wood smoke. However, in all fairness, we should also look at the reported negative aspects of wood smoke relative to human health. Since we are talking of humans, one must realize that moral and legal limitations make this an extremely difficult area to gather scientific evidence from well-designed studies. Therefore, mainly inferences have been made from animal studies and human death rate statistics. One can argue that humans have been consuming smoked foods for literally centuries and anyone would have an extremely difficult time in proving beyond a doubt that man has significantly threatened his life because of this practice.

However, based on the chemistry of certain compounds that can be formed in smoke, namely polycyclic aromatic hydrocarbons (PAH) and nitrosamines, a rational approach would be to minimize the ingestion of such compounds not especially by decreasing the amount of smoked foods consumed, but by reducing the levels of such compounds in our total commercial and home-processed food supply.

It should be noted that certain countries have established maximum limits for these compounds in commercial foods, but little if anything is done to educate the general public as to how these compounds can be reduced in home processed and prepared foods.

Human nature is unique in that a commercial food processing operation can quickly receive condemnation for marketing food that contains potentially harmful compounds, but no publicity or outrage is voiced to the individual or entire society who produces these same compounds in their homes. For example, PAH can be generated from various sources, and thus, can enter our food supply via several routes. PAH can be thermally produced by both high temperature pyrolysis and from the incomplete combustion of materials containing carbon and hydrogen. Various forms of air pollution can be a significant source of PAH. In addition, PAH are naturally associated with petroleum and coal tar products which can also be environmental pollutants, thus resulting in contaminated food supplies.

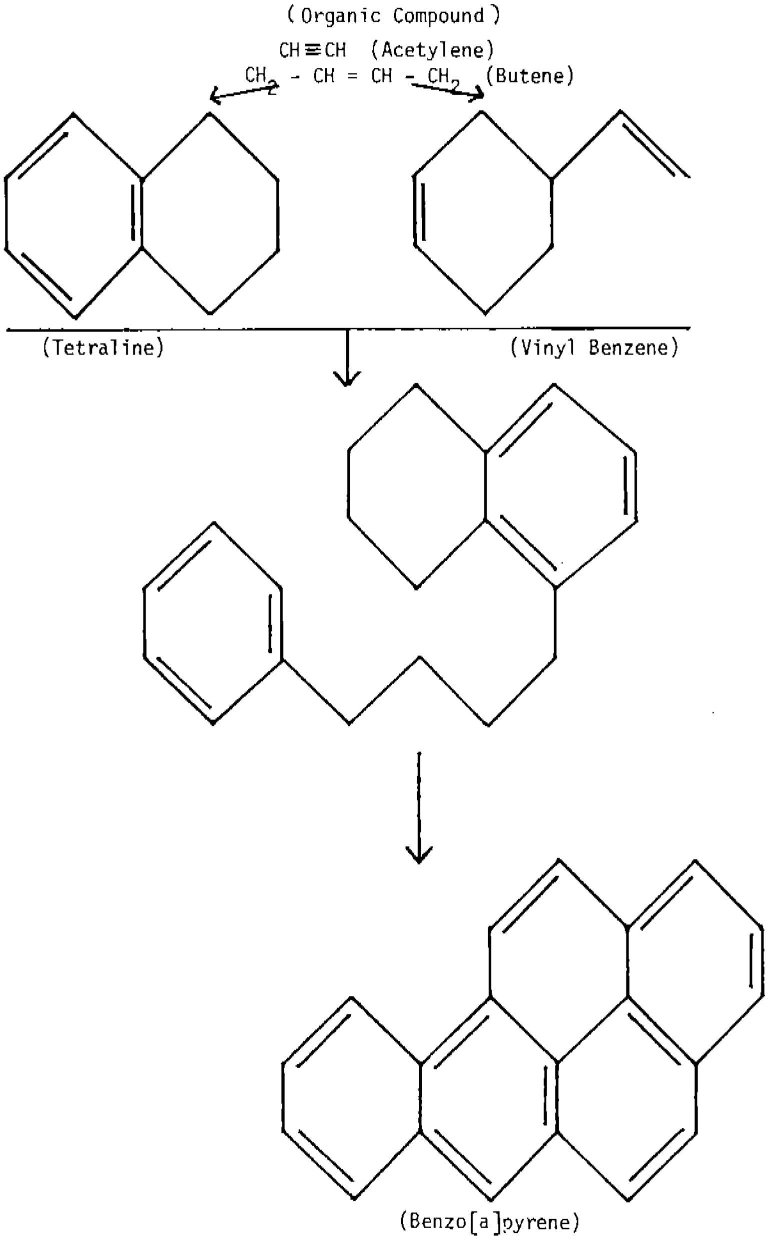
Health hazards associated with smoke, soot, and tar products were apparent long before the compounds responsible were known. For example, skin cancer was considered to be an occupational hazard of chimney sweeps centuries ago but the actual cause was not realized until the 1930s. Researchers discovered that PAH isolated from combustion residues were carcinogenic in animal tests.[40] The problem is compounded by the fact that apparently PAH is not acutely toxic and thus time is required for symptoms to develop.

Relative to the general thermal formation of PAH, it is generally thought that during the pyrolysis of organic matter the compound acetylene is a key intermediate, as outlined in Table 1. Since acetylene can be derived from many forms of organic starting materials, it is then not surprising that the occurrence of PAH is widespread. In fact, it has been shown, as seen in Table 2, that a relatively simple compound, such as glucose, can produce benzo[a]pyrene when pyrolyzed, and as structure complexity increases, so does the amount of PAH formed. Thus, in the heating or smoking of a food, which contains a vast number of potential reactants, PAH formation is a standard fact of life.

II. SMOKING METHODS VS. PAH CONCENTRATION

PAH is composed of multiple fuzed benzene rings and at least on a theoretical basis hundreds of such compounds can exist. To date, 40 to 60 such compounds have actually

Table 1
PYROSYNTHESIS OF BENZO[A]PYRENE



Adapted from Badger, G., Kimber, R., and Spotswood, T., *Nature*, 187, 663, 1960.

been identified although up to 100 have actually been detected. Some of the more common PAH are listed in Table 3.

Since it has been known for quite some time that some PAH act as potent chemical carcinogens (Table 4), their presence in food is of major concern. Smoked foods are a special area of concern since it has been well documented that smoke generation conditions can dramatically influence the level of resulting PAH in the smoke and consequently, in smoked foods.[1-21] At this point, certain of these studies will be discussed.

Table 2
BENZO[A]PYRENE GENERATION FROM THE PYROLYSIS (840°C) OF VARIOUS ORGANICS

Compound pyrolyzed	μg benzo[a]pyrene/kg pyrolyzate
Glucose	48
Stearic acid	1200
β-Sitosterol	3750

Adapted from Schmeltz, I. and Hoffman, D., *Carcinogenesis*, Vol. 1, Frendenttal, R. I. and Jones, P. W., Eds., Raven Press, New York, 1976.

Table 3
COMMON FOOD PAH

Indene
Methylindene
Ethylindene
Naphthalene
Methylnaphthalene
Dimethylnaphthalene
Ethylnaphthalene
Naphthylene
Napthene
Ethylnaphthalene
Methylnaphthylene
Trimethylnaphthalene
Fluorene
Methylfluorene
Phenanthrene
Anthracene
2-Methylanthracene
9-Methylanthracene
Methylphenanthrene
Pyrene
Dimethylanthracene
Dimethylphenanthrene
1-Methylpyrene
11-H-benzo[a]fluorene
Fluoranthene
Benzo[a]anthracene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[j]fluoranthene
1,2-Benzpyrene
3,4-Benzyprene
Perylene
7,12-Dimethylbenz[a]anthracene
Methylchloroanthrene
Indenopyrene
Benzo[g,h,i]perylene
Anthranthrene
Dibenzo[a,c]anthracene
Dibenzo[a,j]anthracene
Dibenzo[a,h]anthracene
Coronene
3,4,9,10-Dibenzpyrene
Benzo[c]phenanthrene
Dibenzo[a,h]pyrene
Dibenzo[a,i]pyrene
Dibenzo[e,l]pyrene
Cholanthrene

In the case of a frankfurter-type product, Simon et al.[1] demonstrated that the type of casing used during the smoking process could significantly influence benzo[a]pyrene concentrations in the resulting product. As seen in Table 5, sheep casing apparently permitted the passage of PAH into the product while the synthetic cellulose casing retarded PAH penetration. Also, as would be expected, increased smoking time increased product PAH concentrations. Apparently, the structure of the cellulose casing was such that the rather large molecular weight PAH could not effectively pass into the product. Thus, based on these data, the use of certain natural casings should be discouraged with smoked foods.

Rusz et al.[2] clearly demonstrated that electrostatic precipitators operating at a voltage of 10 kV and a temperature of 75 to 80°C were quite effective in removing PAH from smoke streams. Lenges[3] also promoted the use of electrostatic precipitators for PAH reduction.

Toth and Blaas[4] reported on numerous smoke-processing techniques that can significantly lower PAH levels. They noted a linear increase in benzo[a]pyrene concentration as smoke

Table 4
DEGREE OF CARCINOGENICITY AMONG CERTAIN PAH

Compound	Degree of carcinogenicity
7,12-Dimethylbenz[a]anthracene	+ + + +
3-Methylcholanthrene	+ + + +
Benzo[a]pyrene	+ + +
Dibenz[a,h]anthracene	+ + +
Dibenzo[a,i]pyrene	+ + +
Benzo[a]phenanthrene	+ + +
Benzo[y]anthracene	+
Indeno[1,2,3-c,d]pyrene	+
Benzo[b]fluoranthene	+
Pyrene	−
Benzo[a]fluorene	−

Note: + + + + extremely carcinogenic; + + + very carcinogenic; + + carcinogenic; + somewhat carcinogenic; − not carcinogenic.

Adapted from Toth, L. and Potthast, K., *Adv. Food Res.*, 29, 87, 1984.

Table 5
INFLUENCE OF CASING TYPE AND SMOKING TIME ON BENZO[A]PYRENE LEVELS (ppb) IN SMOKED FRANKFURTERS

	Smoking time (min)	
Type of casing	5	10
Sheep	4.0	13.0
Cellulose	1.6	1.6

Adapted from Simon, S., Rypinski, A. A., Tauber, F. W., Pencyla, R. M., and Westerberg, D. O., *J. Agric. Food Chem.*, 17, 1128, 1969.

generation temperature was increased from 400 to 1000°C. At the higher temperatures, primarily four- and five-membered PAH compounds were formed. Thus, it appears that smoke generation temperature is the key factor influencing PAH formation. They[4] demonstrated that when smoke generation temperature was 400°C, smoked meat had 0.4 ppb PAH, while if smoke generation temperature was reduced to 300°C, PAH levels in the meat fell to 0.09 ppb. Other significant factors resulting in reductions of smoke-generated PAH included cooling, which reduced PAH levels 25%, washing which resulted in a 20 to 30% reduction, increasing distance from the smoke generator — 40%, and filtering smoke for a 90% reduction. As would be expected, they[4] also reported that more PAH was deposited on food during hot smoking vs. cold smoking and a very high buildup of PAH during the dark smoking of food was observed due to soot buildup on the product surface. Raja et al.[18] and Potthast[19] have also clearly demonstrated that moistening the wood source during smoking effectively lowers smoke generation temperature, and thus, also PAH levels.

Table 6
INFLUENCE OF SMOKE GENERATION TEMPERATURE (°C) ON PAH FORMATION (μg/100 g OF WOOD)

	Smoke generation temperature			
Compound	**400**	**600**	**800**	**1000**
Benzo[a]pyrene	8	10	15	18
3,4-Benzofluoranthene	9	12	18	22
Pyrene	35	60	80	115
Fluoranthene	70	100	135	175
Total	122	182	248	330

Adapted from Lenges, J., *Rev. Ferment. Ind. Aliment.*, 27, 53, 1972.

A recent study has shown that at least in the case of benzo[a]pyrene, commercial smoking units represented by smoldering in open or closed systems, friction smoke, and steam smoke generation all produced frankfurters that had 0.1 to 0.7 ppb.[155]

Another study[156] has shown that the benzo[a]pyrene levels in European smoked meat products has changed very little over the 10-year period from 1975 to 1984 perhaps indicating that equipment design and operation is such that little more can be done to reduce or totally eliminate PAH from smoked meats. However, they did report that in the case of black-smoked products, approximately 40% of all samples exceeded the suggested 1 ppb benzo[a]pyrene level with one such product having 570 ppb present. Recent analysis of liquid smoke preparations have also found acceptable levels of benzo[a]pyrene present.[157]

The potential problem of only measuring benzo[a]pyrene content as influenced by smoke generation temperature as an indicator of total PAH is clearly shown in Table 6. It can be seen that several PAH compounds are present at significantly higher levels than benzo[a]pyrene, and at higher generation temperatures these compounds are actually formed at a faster rate than benzo[a]pyrene.

Similar results were obtained for alder chip smoke in that benzo[a]pyrene was found at a very low concentration (less than 1 ppb) whereas PAH derivatives of methylphenanthrenes were found at levels ranging from 3.1 to 43.1 ppm and isomeric forms of pentamethylphenanthrenes were present at levels ranging from 24.9 to 99.8 ppm.[154] Thus, if one applied the general rule that smoke or food containing less than 1 ppb benzo[a]pyrene is satisfactory, one is not absolutely sure as to its overall safety.

Toth and Blaas[5] also found that the total quantity of potentially harmful PAH in smoked meats was five to ten times the amount of benzo[a]pyrene detected. In light of this, the question arises if the German law permitting a maximum of 1 ppb benzo[a]pyrene in smoked foods is actually strict enough. Granted, the law is a good one, but perhaps it needs to be expanded to include other PAH.

With smoked poultry, Raja et al.[18] demonstrated that a restricted air supply and moistened wood shavings used as a smoke source produced a product lower in benzpyrene than smoking for the same time but with unlimited air and dry wood. Conditions such as these are usually not difficult to control in a commercial smoking operation, but one must wonder how many noncommercial smokers are operated with these parameters in mind. For example, Fritz and Soos[36] surveyed a wide range of commercially produced German smoked meats and found an average benzo[a]pyrene content of 0.43 μg/kg of product whereas artisanal smoked meats had an average of 0.76 μg/kg. In contrast, they found that Hungarian commercially smoked meats had an average of 0.60 μg/kg while Hungarian home smoked meats had 0.74 μg/kg.

They[36] also measured the benzo[a]pyrene level in smoked meats traditionally prepared by using soft wood as the smoke source by a Slovenian minority known to have a higher incidence of stomach cancer than the general population and these products were found to contain on the average 4.16 μg/kg.

As mentioned elsewhere, the filtration of smoke can significantly lower PAH concentration. For example, Steinig and Schreiber[11] evaluated the effectiveness of various types of metal (perforated sheets, steel wool, and expanded metal) and fiberglass filters. The fiberglass filters were found to be more effective, but more wood was needed to produce the equivalent amount of smoke as when no filter was used. Also, although more effective, the fiberglass filters could not be effectively cleaned to be reused whereas the metal filters could be reused upon cleaning.

Direct and indirect smoking conditions relative to resulting benzo[a]pyrene concentration in smoked fish was evaluated by Steinig.[9] It was found that the direct method gave levels greater than 1 ppb whereas indirect smoking produced products that had less than 1 ppb.

Toth and Blaas[5] examined benzo[a]pyrene levels in cold-, hot-, and black-smoked meats and found quite a range in levels with the black-smoked meats having the highest amounts. Traditional cold-smoked meats had an average of 0.6 ppb with a high of 1.6 ppb while hot-smoked products averaged 0.4 ppb with a high of 1.1 ppb. Since the cold-smoked meats were smoked for a longer period of time, they had higher levels than the hot-smoked products. In contrast, the black-smoked products ranged from 0.3 to 55 ppb.

Dikun et al.[20] demonstrated with fish products that using liquid smoke produced lower benzpyrene levels (1 to 1.2 μg/kg of fish) than by smoking using two commercial smoking units whose levels ranged from 1.6 to 39.0 μg/kg and averaged 9.7 μg/kg. Similar results with liquid smoke were reported by Ruchkovskii et al.[48] Thus, if product quality can be maintained, good quality liquid smoke can be used to minimize PAH.

Larsson[47] evaluted PAH types and amounts in Swedish commercially smoked fish as influenced by wood source. Either alder or spruce/juniper was used. Surprisingly, fish smoked over alder had a higher total PAH concentration (439 μg/kg of fish) than for spruce/juniper (271 μg/kg). However, there was a greater proportion of higher molecular weight PAH associated with the spruce/juniper wood source.

It is interesting to note that most commercial food smoking operations have routinely adopted many or all of the above steps to minimize PAH buildup in smoked foods, but the individual who is smoking foods for his own personal use usually smokes in a rather primitive manner, which in turn can lead to high PAH concentrations.

In light of the German maximum limit of 1 ppb 3,4-benzopyrene in smoked foods, Potthast[40] has summarized data obtained from several research groups on the influence of smoking method on resulting 3,4-benzopyrene content. A portion of his data is shown in Table 7, and as can be seen, overall, the method resulting in the lowest level is the wet smoke procedure. In contrast, either hot or cold dark smoking and the smoldering smoke method produced samples that had relatively high 3,4-benzopyrene amounts. Obviously, not all samples evaluated for each method had equal amounts of 3,4-benzopyrene as can be seen by the range of values found for each method, thus demonstrating that not only is the method of smoking important but the operator of the smoking unit also apparently plays an important role since these were commercial samples that were evaluated.

Potthast[7,15] has perhaps best summarized optimum smoke generation conditions required to minimize PAH. Since PAH generation is temperature dependent, he suggests generating smoke below 400°C, removing particulate matter through filtration or by means of a cold trap, wrapping products to be smoked in synthetic casings that are impermeable to PAH, using spatial separation of the product being smoked from the smoke source, and reducing the smoking time of products that have high surface-to-weight ratios.

Relative to filtration of smoke as a means of reducing PAH content, Potthast et al.[12] have

Table 7
INFLUENCE OF SMOKING METHOD ON RESULTING 3,4-BENZOPYRENE CONTENT IN COMMERCIAL SMOKED MEAT PRODUCTS

Smoking method	3,4-Benzopyrene (μg/kg)
Smoldering smoke	0—36.23
Wet smoke	0.09—0.77
Friction smoke	0.01—4.56
Hot smoke	
Lightly smoked	0—2.08
Dark smoked	0.22—36.23
Cold smoke	
Lightly smoked	0.10—3.16
Dark smoked	0.10—56.04

Adapted from Potthast, K., *Fleischwirtschaft*, 58, 38, 1978.

shown that the technique can reduce PAH levels up to 97% while cooling generated smoke can result in up to a 35% reduction. Also, the washing of smoke after generation can reduce PAH by 35%. Fedonin et al.[192] have also demonstrated the effectiveness of filtering smoke.

Another potential method for reducing the PAH level in smoked foods in through the use of smoke-flavored seasonings.[34] These seasonings were found to contain up to 20 μg/kg of benzopyrene, but when used at a maximum dose of 5 g of seasoning per kilogram of meat product, the resulting benzopyrene content was below the German 1 ppb standard.

Also to be added to the list is the use of hardwoods instead of softwoods for smoke generation, and in the case of smoking fish, removal of the skin since fish smoked without skin contained an average of 1 to 39 μ/kg of benzopyrene whereas the same fish smoked with the skin on contained 8.55 μg/kg.[55] Obviously, rapid hot smoking and black smoking result in high PAH levels[4] as does smoke generation with an open flame.

As discussed elsewhere, food lipid content is another factor that can contribute to PAH formation during smoking, and thus where possible, the lipid content of the food being smoked should be kept to a minimum. This appears to be especially true for smoked fish.

III. PAH IN WOOD SMOKE

Since PAH can be associated with wood smoke, numerous researchers have attempted to separate, identify, and quantitate such compounds. For example, Obiedzinski and Borys[23] detected 27 PAH while Potthast[17] identified 25 PAH compounds in smoke condensates. The major PAH in smoke appears to be phenanthrene[17,24] and closely related compounds. The same observation was noted earlier by Rhee and Bratzler,[22] and as can be seen in Table 8, whole smoke had approximately twice the PAH as the vapor phase thus again reinforcing the concept that the level of smoke particulate matter permitted to reach a food surface should be minimized.

The other major research area has been to evaluate PAH composition of liquid smoke since, in theory, techniques described in the previous section are available to reduce PAH levels. For example, as seen in Table 9, a tar recovered from a liquid smoke preparation

Table 8
PAH COMPOSITION IN WHOLE AND VAPOR PHASE WOOD SMOKE

Compound	Whole smoke	Vapor phase
Phenanthrene	51.5[a]	28.4
1,2-Benzanthracene	7.0	4.3
Fluoranthene	5.7	4.2
Pyrene	5.5	4.1
Anthracene	3.8	1.9
Chrysene	2.6	0.3
3,4-Benzopyrene	1.2	0.4
1,2-Benzopyrene	0.9	Trace
Total	78.2	43.6

[a] μg/4.5 kg of hard maple sawdust smoldered at 750 to 800°C.

Adapted from Rhee, K. S. and Bratzler, L. J., *J. Food Sci.*, 33, 626, 1968.

Table 9
PAH COMPOSITION OF A TAR RECOVERED FROM LIQUID SMOKE

Compound	Quantity (ppb)
Pyrene	51,745
Chrysene	48,590
Floranthene	46,260
Benzo[k]fluoranthene	24,710
Benzo[a]pyrene	15,933
Dibenz[a,h]anthracene	14,238
Benzo[g,h,i]perylene	13,058
Benzo[e]pyrene	11,660
Perylene	4,400
Dibenz[a,j]anthracene	3,516

Adapted from Obiedzinski, M., *Acta Aliment. Pol.*, 3, 183, 1977.

had large amounts of PAH present,[25] demonstrating that significant amounts of PAH can be effectively removed from liquid smokes.

However, it is not appropriate to assume that liquid smoke preparations are totally free of PAH. For example, Potthast[26] evaluated 12 commercial liquid smoke products and found from less than 0.05 to 2600 μg/ℓ of benzo[a]pyrene, while White et al.[27] found trace amounts of some three- and four-ring PAH compounds in 3 of 7 commercial liquid smokes they evaluated. In addition, from 25 to 3800 ppb of benzo[a]pyrene was found in the resinous condensates that eventually settled out of these liquid smokes during storage. Therefore, if someone were attempting to be economical and utilize all the material in a liquid smoke container, certain batches of smoke-flavored food could be high in PAH.

Two recent studies have clearly demonstrated that smoke source can dramatically influence both PAH levels and types of compounds present in smoke. In an interesting study evaluating the PAH composition found in various types of commercial briquets,[158] it was found that coal- and wood-base charcoal briquets contained numerous types of PAH ranging up to 13,000 ppb while lava stone and pressed sawdust briquets had no detectable PAH. A portion of these data is summarized in Table 10, and as can be seen, isomeric forms were not positively identified. This study was initiated to determine whether the alleged use of petroleum pitch, coal tar pitch, and high-boiling petroleum distillers as binders in preparing cooking briquets was apparent relative to PAH composition. Three different coal-based briquets had from 36 to 50 individual PAH that ranged from 5400 to 7100 ppb. In the case of three wood-derived briquets, 30 to 53 individual PAH compounds were identified with total concentrations ranging from 2500 to 13,000 ppb. It is of interest to note that benzo[a]pyrene was not found in any samples.

In another study,[159] the PAH composition of mesquite wood smoke and hickory wood smoke were compared. As seen in Table 11, a total of 31 such compounds having a composite composition of 1250 mg/kg of wood were found in the mesquite smoke vs. 22 compounds having a total concentration of 688 mg/kg in the condensed hickory smoke. This is quite interesting in light of the fact of the dramatic growth in certain parts of the U.S. of mesquite-grilled foods. Mesquite is a dense wood that is especially noted for its high smoldering temperature which in turn can significantly encourage PAH formation. The reason for the high thermal degradation temperature associated with mesquite is probably the fact that mesquite was found to be composed of 64% lignin whereas hickory used in the study had only 17.7% lignin[159] and as discussed in an earlier chapter, lignin is the last major wood component to thermally degrade.

IV. PAH IN FOODS

It is not the intention of this section to provide an inclusive listing of every study that has reported upon the presence of PAH in foods. Suffice it to say that literally many hundreds of such studies are in the literature, and most of these data have already been reviewed.[28-49]

At this point it should also be noted that mutagenic effects and PAH content are not unique to smoked foods but are apparently inherent to most heat-processed foods. Method and degree of heat processing, as well as food composition, seem to be important factors.[50-65] The fact that cooking increases PAH levels is clearly evident from the data shown in Table 12.

As can be seen in Table 13, the types of foods in which PAH have been found is as diverse as food itself. If it has been heat processed, it probably contains some amount of PAH. Also, the direct drying of foods with fossil fuels seems to be a major PAH source in products such as malt[66] and certain cereals.[67] For example, Fritz[67] found that when cereals were dried using fuel oil as the heat source, the 3,4-benzopyrene content in the cereals increased 140 to 250% over using natural gas. When lignite briquets were used, amounts increased 220 to 530% and when raw lignite was used, the 3,4-benzopyrene content increased 830 to 900%.

Lawrence and Das[143] measured PAH in various commercial puffed breakfast cereals, and as seen in Table 14, they all had detectable levels with rice being the lowest and wheat the highest. These products are interesting in that they probably have both environmental PAH as well as PAH formed during processing. In the case of puffed rice only one PAH was detected whereas the other cereals had up to four such compounds.

Similar types of data for barley malt were reported by Lawrence and Weber,[65] but as seen in Table 15, the total PAH content among the three commercial sources varied dramatically from 2.2 to 237.9 μg/kg. Undoubtedly the PAH in malt would carry over into the final alcoholic beverage.

The charcoal broiling of meats presents a unique situation whereby heat, smoke, and lipid

Table 10
PAH COMPOSITION (ppb) OF VARIOUS COMMERCIAL CHARCOAL BRIQUETS

	Briquet source					
Compound	**Coal**	**Coal**	**Coal**	**Wood**	**Wood**	**Wood**
Naphthalene	587	102	22	450	735	73
Benzo[b]thiophene	127	—	—	—	—	—
Dimethylbenzofuran	40	—	—	—	—	—
Dimethylbenzofuran	185	—	—	—	—	—
Dimethylbenzofuran	35	—	—	—	—	—
Methylbenzo[b]thiophene	15	—	—	—	—	—
Methylnaphthalene	484	109	52	472	323	82
Methylbenzo[b]thiophene	33	—	—	—	—	—
Methylnaphthalene	405	140	63	360	132	78
Biphenyl	211	91	40	402	161	86
Dimethylbenzo[b]thiophene	21	—	—	—	—	—
Ethylnaphthalene	78	30	18	138	72	49
Ethylnaphthalene	—	—	—	—	—	21
Dimethylnaphthalene	226	69	20	163	132	—
Dimethylnaphthalene	110	226	169	129	465	—
Dimethylnaphthalene	471	83	22	208	232	—
Dimethylnaphthalene	31	—	—	162	—	—
Dimethylnaphthalene	155	—	—	112	—	—
Acenaphthene	41	—	—	—	68	—
Methylbiphenyl	167	79	26	90	228	—
Methylbiphenyl	104	—	—	75	30	—
Dibenzofuran	728	109	140	943	228	174
Methylethylnaphthalene	—	—	—	72	—	—
Trimethylnaphthalene	30	109	11	70	27	—
Trimethylnaphthalene	28	143	85	142	91	—
Trimethylnaphthalene	56	47	81	559	46	—
Trimethylnaphthalene	55	—	184	—	82	—
Trimethylnaphthalene	30	185	714	—	73	—
Trimethylnaphthalene	150	137	—	463	47	—
Trimethylnaphthalene	198	—	—	—	—	—
Fluorene	95	20	52	129	43	62
Trimethylnaphthalene	402	—	—	—	—	—
Dimethylbiphenyl	43	—	—	—	—	—
Methyldibenzofuran	320	263	147	536	169	—
Xanthene	360	90	162	—	338	—
Tetramethylnaphthalene	70	110	—	200	—	—
Isobutylnaphthalene	30	—	—	—	—	—
Methylfluorene	133	50	96	247	38	63
Methylfluorene	55	—	—	370	42	85
Methylfluorene	101	—	—	209	—	—
Tetramethylnaphthalene	30	—	—	279	211	—
Tetramethylnaphthalene	157	—	—	—	—	—
Dibenzothiophene	75	—	—	—	—	—
Phenanthrene	145	141	74	815	338	259
Anthracene	86	40	—	215	—	57
Phenylindole	50	—	—	—	—	31
Phenylnaphthalene	27	—	92	161	56	25
Dimethylphenanthrene	36	25	37	61	38	150
Fluoranthene	20	35	—	257	—	150
Pyrene	23	55	37	160	26	98
Trimethylphenanthrene	29	—	148	—	—	—
Chrysene	30	114	162	139	—	83

Table 10 (continued)
PAH COMPOSITION (ppb) OF VARIOUS COMMERCIAL CHARCOAL BRIQUETS

Compound	Briquet source					
	Coal	Coal	Coal	Wood	Wood	Wood
Tetramethylnaphthalene	—	—	70	—	—	—
Tetramethylnaphthalene	—	81	287	—	—	—
Tetramethylnaphthalene	—	219	—	—	—	—
Methylphenanthrene	—	94	92	279	—	—
Methylphenanthrene	—	89	81	214	—	—
Methylphenanthrene	—	91	81	279	—	—
Methylphenanthrene	—	141	225	190	—	—
Dimethylphenanthrene	—	122	214	110	21	214
Dimethylphenanthrene	—	20	19	—	—	—
Trimethylphenanthrene	—	—	37	621	—	—
Tetramethylphenanthrene	—	164	—	—	—	—
Tetramethylphenanthrene	—	1,675	1,718	113	43	—
Benz[a]anthracene	—	—	96	—	—	—
Perylene	—	51	—	—	—	—
Methyldibenzofuran	—	—	—	643	127	250
Methyldibenzofuran	—	—	—	250	85	53
Methyldibenzofuran	—	—	—	365	—	39
Methyldibenzofuran	—	—	—	—	—	42
Benzo[h]quinoline	—	—	—	—	34	—
Phenylindole	—	—	—	—	—	36
Phenylindole	—	—	—	—	—	35
Methylphenanthizene	—	—	—	—	47	—
Methylphenanthizene	—	—	—	—	42	—
Dimethylphenanthrene	—	—	—	108	34	—
Dimethylphenanthrene	—	—	—	123	—	—
Dimethylphenanthrene	—	—	—	139	—	—
Dimethylphenanthrene	—	—	—	150	—	—
Benzonaphthofuran	—	—	—	150	—	—
Methylfluoranthene	—	—	—	90	—	53
Methylfluoranthene	—	—	—	27	—	—
Methylfluoranthene	—	—	—	135	—	—
Methylfluoranthene	—	—	—	134	—	—
Benzo[c]phenanthrene	—	—	—	—	—	21
Benzo[a]anthracene	—	—	—	—	—	34
Dimethylbenzo[c]-phenanthrene	—	—	—	33	—	—
Total	7,118	5,349	5,574	12,969	5,057	2,509

Adapted from Kushwaha, S. C., Clarkson, S. G., and Mehkeri, K. A., *J. Food Saf.*, 7, 177, 1985.

pyrolysis products can all contribute to the production of PAH. In the mid-1960s reports started to appear which pointed out that this type of food preparation can lead to significant amounts of PAH production. In one of the first studies[50] it was reported that a well-done 1.1-kg steak grilled over charcoal contained 8 μg/kg of benzo[a]pyrene which is equivalent to the amount generated by smoking 600 cigarettes. Other studies[52,58] demonstrated that PAH levels were most closely related to the amount of fat originally present in the grilled food, the closeness of the food to the heat source, and the exposure time of the food to the heat source. In a similar study,[61] it was found that many home and camping food preparation techniques can result in relatively large amounts of PAH. For example, the grilling of

Table 11
PAH COMPOSITION OF MESQUITE AND HICKORY WOOD SMOKE

Compound	μg/kg in Mesquite	μg/kg in Hickory
Pyrene	155	104
Benzo[a]pyrene	74	41
Benzo[e]pyrene	36	20
1-Methylpyrene	27	18
Dibenzo[a,e]pyrene	4	ND
Dibenzo[a,i]pyrene	3	ND
Dibenzo[a,h]pyrene	3	ND
Dibenzo[a,l]pyrene	2	ND
Indeno[1,2,3-c,d]pyrene	53	24
Fluoranthene	162	94
Benzo[b]fluoranthene	34	22
Benzo[j]fluoranthene	24	11
Benzo[k]fluoranthene	35	14
Benzo[a]fluorene	66	24
Benzo[b]fluorene	31	17
Anthanthrene	22	7
Anthracene	47	31
Benzo[a]anthracene	60	38
2-Methylanthracene	11	4
9-Methylanthracene	3	1
Dibenzo[a,c]anthracene	5	ND
Dibenzo[a,h]anthracene	2	ND
9,10-Diphenylanthracene	3	ND
Phenanthrene	204	114
1-Methylphenanthrene	17	7
2-Methylphenanthrene	21	15
3,6-Dimethylphenanthrene	6	ND
Chrysene + triphenylene	72	49
Picene	7	ND
Perylene	14	4
Benzo[g,h,i]perylene	47	29
Total	1250	688

Note: ND = not detected.

Adapted from Maga, J. A., *J. Agric. Food Chem.*, 34, 249, 1986.

frankfurters in the flames of a log fire produced 212 μg/kg of benzo[a]pyrene whereas when grilling was carried out over the embers, the level dropped to 7.7 μg/kg. As can be seen in Table 16, the method cooking frankfurters dramatically influenced PAH concentration. For example, using the open flames of a log fire produced the highest PAH levels with the PAH concentration dropping by a factor of 10 if cooking was done using just the embers from the same fire. Surprisingly, using pine cones, which contain a large amount of resinous material, as a fuel source was not as detrimental as expected. A small amount of PAH was found if charcoal was used whereas an increase in PAH was not seen with electric oven or pan frying.

Recently, Lawrence and Das[193] determined the PAH content of four commercial brands of charbroiled hamburgers, and as seen in Table 17, the total measured PAH content ranged from 1.51 to 28.1 μg/kg. The actual identities of the hamburger brands were not given, but

Table 12
INFLUENCE OF COOKING ON THE PAH COMPOSITION (ppb) OF FISH

PAH	Raw	Cooked
Anthrace	0.14	1.25
Pyrene	0.77	4.22
Benzo[a]anthracene	0.08	0.29
Benzo[b]fluoranthene	0.36	1.08
Benzo[k]fluoranthene	0.06	0.27
Benzo[a]pyrene	0.05	0.54
Benzo[e]pyrene	0.16	0.89
Benzo[g,h,i]perylene	0.04	0.93
Total	1.66	9.47

Adapted from Obana, H., Hori, S., Tanaka, R., and Kashimoto, T., *J. Food Hyg. Soc. Jpn.*, 25, 35, 1984.

Table 13
FOODS IN WHICH PAH HAVE BEEN IDENTIFIED

- Fruits and vegetables
  - Citrus
  - Fruit
  - Cabbage
  - Endive
  - Kale
  - Leeks
  - Lettuce
  - Potatoes
  - Spinach
  - Tomatoes
- Dairy products
  - Butter
  - Smoked cheese
  - Coffee whitener
  - Infant milk formula
  - Margarine
  - Milk
  - Milk powder
- Cereal products
  - Bran cereals
  - Puffed cereals
  - Malt
  - Rice
  - Rye
  - Wheat
  - Toast
- Legumes
  - Cottonseed
  - Peanuts
  - Soybeans
- Drinks
  - Alcoholic beverages
  - Coffee
  - Mineral water
- Cooking oils
  - Corn oil
  - Coconut oil
  - Cottonseed oil
  - Olive oil
  - Palm oil
  - Palm kernel oil
  - Peanut oil
  - Rape oil
  - Soy oil
  - Sunflower oil
- Meat products
  - Bacon
  - Charbroiled meats
  - Frankfurters
  - Ham
  - Sausages
  - Smoked meats
  - Smoked poultry
- Fish and seafood products
  - Canned shrimp
  - Frozen shrimp
  - Lobster
  - Lobster paste
  - Oysters
  - Scallops
  - Shellfish
  - Smoked fish
  - Smoked mussels
  - Smoked oysters
- Miscellaneous
  - Copra
  - Eggs
  - Olives
  - Sugar

Table 14
PAH DISTRIBUTION AND CONTENT (μg/kg) IN COMMERCIAL PUFFED CEREALS

PAH	Rice	Corn	Oats	Wheat
F	1.2	1.2	1.9	3.2
B[a]A	ND	ND	0.16	ND
DMBA	ND	ND	ND	ND
B[b]F	ND	0.05	0.08	0.09
B[k]F	ND	0.02	ND	0.04
B[a]P	ND	0.03	ND	0.04
Total	1.2	1.30	2.14	3.37

Note: ND = not detected.

Adapted from Lawrence, J. F. and Das, B. S., *Int. J. Environ. Anal. Chem.*, 24, 113, 1986.

Table 15
PAH COMPOSITION (μg/kg) OF COMMERCIAL BARLEY MALT

	Sample		
PAH	A	B	C
NDMA	T	13	150
FL	0.8	2.6	26
PY	1.1	3.2	48
B[b]FL	0.1	0.1	0.5
DMP	0.1	0.2	6.2
B[a]A	0.1	0.2	4.2
Per	T	0.1	0.4
B[a]P	T	T	0.3
D[a,c]A	T	T	0.4
D[a,h]A	T	T	1.2
Pi	T	T	0.3
IP	T	T	0.4
Total	2.2	16.5	237.9

Note: T = trace.

Adapted from Lawrence, J. F. and Weber, D. F., *J. Agric. Food Chem.*, 32, 794, 1984.

it is apparent from these data that dramatic differences exist. It is not known if the actual time and method of preparation or differences in fat content was the primary factor responsible for these differences, but apparently one of the four companies is aware of the significance of PAH and is controlling their process/product sufficiently to produce a hamburger with low PAH.

In another study, Lawrence and Weber[64] compared PAH in commercially prepared charbroiled vs. fried hamburgers, and as seen in Table 18, the charbroiled products had a greater

Table 16
INFLUENCE OF COOKING TECHNIQUE ON PAH CONCENTRATION (μg/kg) in FRANKFURTERS

	Concentration		
Technique	Minimum	Maximum	Average
Log fire	2.8	171	41.4
Log fire embers	ND	16.3	4.3
Pine cone fire	2.2	21.6	12.9
Charcoal fire	ND	0.8	0.2
Electric oven	ND	ND	ND
Pan frying	ND	ND	ND

Note: ND = not detected.

Adapted from Larsson, B. K., Sahlberg, G. P., Eriksson, A. T., and Busk, L. A., *J. Agric. Food Chem.*, 31, 867, 1983.

Table 17
PAH DISTRIBUTION AND CONTENT (μg/kg) IN COMMERCIAL CHARBROILED HAMBURGERS

	Brand			
PAH	A	B	C	D
F	0.73	6.2	15.4	14.7
B[a]A	0.29	2.7	4.9	5.8
DMBA	0.09	1.5	ND	1.7
B[b]F	0.23	1.9	2.1	3.6
B[k]F	0.10	1.2	ND	1.2
D[ah]A	0.07	1.2	ND	1.2
Total	1.51	14.46	23.6	28.1

Note: ND = not detected.

Adapted from Lawrence, J. F. and Das, B. S., *Int. J. Environ. Anal. Chem.*, 24, 113, 1986.

number and concentration of PAH than the fried hamburgers. In light of this, it would be interesting to know if certain of the major hamburger chains who openly advertise that their product is flame broiled are aware of the consequences relative to PAH of this method of preparation.

It should be remembered that PAH can be found in a wide cross section of our food supply because of environmental contamination. A classical example is the presence of such compounds in raw shellfish[64] and the distribution of PAH in wheat[65] where the bran portion was found to contain up to ten times more total PAH than in the endosperm. This should be a factor to consider in the promotion of bran-based breakfast cereals. Data of these type are summarized in Table 19 and 20. Also, any food that undergoes heating during refining and/or processing can be expected to contain PAH. For example, as seen in Table 21, the toasting of bread can result in the formation of increased levels of benzo[a]pyrene.

Table 18
PAH CONTENT (μg/kg) OF COMMERCIALLY CHARBROILED AND FRIED HAMBURGERS

PAH	Charbroiled A	Charbroiled B	Fried A	Fried B
FL	6.2	5.9	0.1	0.4
PY	14	19	0.4	0.5
B[b]FL	0.5	1.7	T	T
DMP	T	0.6	T	0.1
B[a]A	2.1	2.8	0.1	0.2
Per	0.9	1.1	T	T
B[a]P	1.5	2.9	T	0.1
D[a,c]A	1.0	0.6	T	T
D[a,h]A	2.1	1.3	T	T
Pi	1.0	1.6	T	T
IP	3.6	5.8	T	T
AN	1.1	0.8	T	T
D[a,e]P	0.4	0.7	T	T
D[a,h]P	0.3	0.4	T	T
Total	34.7	45.2	0.6	1.3

Note: T = trace.

Adapted from Lawrence, J. F. and Weber, D. F., *J. Agric. Food Chem.*, 31, 18, 1983.

Table 19
PAH CONTENT OF MILLED WHEAT FRACTIONS AND BREAKFAST CEREALS

Product	PAH content (μg/kg)
Mill fractions	
Whole wheat	9.7
Wheat bran	55.2
Wheat flour	5.1
Breakfast cereals	
Wheat bran	59.5
Puffed wheat	20.3
Whole wheat	18.6
Whole grain oats	6.9
Corn bran	6.7
Flaked milled corn	5.7

Adapted from Lawrence, J. F. and Weber, D. F., *J. Agric. Food Chem.*, 32, 794, 1984.

It should be remembered that nonheat-treated foods can also contain PAH most probably through the effect of environmental contamination, some of which can be smoke discharged from a food smoking operation. For example, the PAH content of lettuce grown at different locations as well as in the open air as compared to a greenhouse situation varied from 4.8 to 94 μg/kg fresh lettuce weight.[185] The lower values were associated with lettuce grown

Table 20
PAH DISTRIBUTION AND CONTENT (μg/kg) IN COMMERCIAL BRAN CEREALS

	Brand					
PAH	A	B	C	D	E	F
F	0.46	1.4	1.5	1.6	1.8	1.3
B[a]A	0.07	ND	0.02	0.06	0.16	0.11
DMBA	0.04	ND	ND	ND	ND	ND
B[b]F	0.06	ND	0.09	0.11	ND	0.63
B[k]F	0.03	ND	0.03	0.05	0.04	0.06
B[a]P	ND	0.02	0.03	0.11	ND	0.07
Total	0.66	1.42	1.67	1.93	2.00	2.17

Note: ND = not detected.

Adapted from Lawrence, J. F. and Das, B. S., *Int. J. Environ. Anal. Chem.*, 24, 113, 1986.

Table 21
THE BENZO[A]PYRENE CONTENT (μg/kg) OF TOASTED BREAD

Product	Benzo[a]pyrene content
Untoasted bread	0.23
Toasted bread — 3 min	0.39
Toasted bread — 5 min	0.56

Adapted from Lintas, C. and DeMatthaeis, M. C., *Food Cosmet. Toxicol.*, 17, 325, 1979.

Table 22
BENZO[A]PYRENE LEVELS IN SOME DUTCH FOODS

Foods	Median (μg/kg)
Potatoes, vegetables, meat, and egg products	0.4
Smoked meat products	0.25
Smoked fish	0.5
Tea leaves	0.8
Tea extract	0.01
Instant coffee	0.09
Endive	1.1
Milk	0.03

Adapted from Vaessen, H. A. M. G., Schuller, P. L., Jekel, A. A., and Wilbers, A. A. M. M., *Toxicol. Environ. Chem.*, 7, 297, 1984.

under glass and the authors concluded that PAH in lettuce resulted primarily from the deposition of PAH-containing particles present in ambient air.

Vegetable oils and fats represent another food group that has usually low PAH levels, but in these foods there is potential concern due to the widespread and relatively high consumption of these products.[186] Usually the major PAH source is combustion-associated

Table 23
ESTIMATED DUTCH MAXIMUM DAILY DIETARY PAH INTAKE (μg)

Compound	Intake
Fluoranthene	10.4
Pyrene	5.1
Chrysene	5.0
Benzo[b,j,k]fluoranthene	1.7
Benzo[g,h,i]perylene	0.9
Benzo[a]pyrene	0.5
Indeno[1,2,3-c,d]pyrene	0.3

Adapted from Vaessen, H. A. M. G., Schuller, P. L., Jekel, A. A., and Wilbers, A. A. M. M., *Toxicol. Environ. Chem.*, 7, 297, 1984.

atmospheric contamination of the raw material source during its growth cycle. In the case of butter for example, contaminated forage or feed is consumed by cattle and the PAH is transmitted to the milk and eventually concentrated in the resulting butter. They[186] also found that crude coconut oil had a PAH concentration of 4600 μg/kg due to the fact that the copra starting material was dried using a heat source that produced smoke. However, a sample of commercially deodorized coconut oil had a PAH level of 92 μg/kg. The authors postulated that the deodorization by steam distillation of this oil source is quite effective in removing PAH-type compounds. When the types of PAH in the two products were compared, it was found that the deodorized oil had a lower concentration of the lower molecular weight PAH due to its distillation during processing.

The Dutch have conducted surveys as to the PAH content of their food supply and as seen in Tables 22 and 23, a wide range of foods were considered with maximum daily PAH amounts from an average diet being 23.9 μg/kg.

V. METHODS OF PAH ANALYSIS

Since certain countries have set maximum limits on the amounts of PAH that can be associated with food, it is imperative that simple, fast, and accurate analytical techniques are available for the routine analysis of foods. Also, these techniques must function over a wide range of food compositional properties (liquids to solids, high to low fat, protein, and carbohydrate).

Historically, procedures were developed that measured only one specific PAH, usually benz[a]pyrene. However, in light of present PAH knowledge, one would have to question this practice, especially in light of the fact that many other PAH compounds may be present in much higher concentrations than this one specific PAH. Also, the carcinogenic properties of other PAH compounds may actually be many times more significant than that of benz[a]pyrene. The general problems with PAH isolation and quantitation have been well reviewed.[68,69]

One general problem with most analytical techniques is the recovery effectiveness of the compound(s) in question over a wide concentration range. In the case of PAH, data as shown in Table 24 are typical. Utilizing high performance liquid chromatography (HPLC) in conjunction with fluorescence detection, Lawrence and Das[193] showed that at relatively low concentrations some PAH have low recovery rates whereas with other PAH, recovery rates are lowered as concentration increases.

Table 24
RECOVERY RATES (%) OF PAH AS INFLUENCED BY CONCENTRATION

	Level added (μg/kg)		
PAH	**1.0**	**5.0**	**25.0**
B[a]A	70.7	50.8	69.8
B[b]F	49.6	57.5	79.0
B[a]P	81.2	92.5	92.3
D[a,i]P	78.6	56.4	20.6

Adapted from Lawrence, J. F. and Das, B. S., *Int. J. Environ. Anal. Chem.*, 24, 113, 1986.

Table 25
RECOVERY RATES (%) OF PAH AT RELATIVELY LOW CONCENTRATIONS

	Level added (μg/kg)		
PAH	**1.0**	**2.0**	**4.0**
FL	119	111	99
PY	106	142	120
B[a]A	103	98	95
DMP	97	96	88
Pi	93	96	91
IP	92	86	86
DPA	89	82	86
D[a,c]A	88	79	71
D[a,c]P	78	74	77
B[b]FL	76	77	83
D[a,i]P	71	82	90
D[a,h]P	70	77	71
D[a,h]A	61	57	60
B[a]P	38	48	50
Per	28	36	44
An	24	34	45

Adapted from Lawrence, J. F. and Weber, D. F., *J. Agric. Food Chem.*, 32, 789, 1984.

Utilizing a similar technique, Lawrence and Weber[64] reported, as seen in Table 25, that some PAH can give recovery rates substantially above 100% even at relatively low concentrations, and thus to accurately quantitate all PAH in each specific food system, one should determine individual PAH recovery rates of the spiked food over the concentration range that is normally expected in that food. Once these specific recovery rates are known, initial data can be factored to obtain a more accurate quantitative picture.

Another potential problem is the fact that since certain PAH may be present in only trace amounts, care must be taken in selecting an analytical technique that is sensitive at low concentrations specifically to the compound(s) in question. As shown in Table 26, the limits

Table 26
PAH DETECTION LIMITS USING HPLC VS. GC

	Detection limit (pg)	
PAH	HPLC	GC
F	18.4	30
B[a]A	13.6	30
DMBA	12.0	30
B[b]F	12.3	30
B[a]P	12.5	60
D[a,h]A	15.6	60
D[a,i]P	264.4	300

Adapted from Lawrence, J. F. and Das, B. S., *Int. J. Environ. Anal. Chem.*, 24, 113, 1986.

of detection are currently lower for HPLC for all PAH evaluated as compared to gas chromatography (GC). This is the primary reason that most prefer HPLC over GC for the composite analysis of PAH.

The problem of potential contamination from solvents and environmental sources during the purification of PAH prior to actual analysis was recently clearly demonstrated by Grimmer and Naujack.[194] At the nanogram range of PAH with which they were working, solvents, glassware, and laboratory air were major sources of contamination. Considering these factors, they were still able to demonstrate the presence of basic nitrogen-containing aromatic compound (N-PAC) which are known to also be carcinogenic in ham.

It can safely be stated that any sensitive and accurate technique currently used for total PAH quantitation is lengthy and tedious. In addition, it usually involves multiple techniques which in turn causes questions as to absolute quantitation due to potential losses during transfer, etc. Some of the general steps usually involved include saponification of the food sample and subsequent solvent extraction, concentration steps involving liquid-liquid partition and column chromatography, separation procedures such as TLC, GC, or HPLC, and final quantitation by ultraviolet, fluorescence, flame ionization, or mass spectrometry. Thus, the total procedure is not only time consuming but usually involves rather expensive equipment.

Howard et al.[70,71] utilized thin-layer chromatography (TLC) to separate and quantitate PAH. Numerous similar procedures have been reported.[72-76] In general, TLC is relatively simple but if a complex mixture of PAH is present, complete separation of all compounds can be somewhat difficult which in turn hinders positive compound identification and quantitation. In addition, care must be taken to prevent PAH photodegradation during separation.

Gas-liquid chromatography (GLC) has also found application for PAH analysis[77-80,89] but difficulty in separating isomeric PAH forms, the need for relatively expensive capillary columns and selective detectors or the need to form derivatives does not make GLC an all inclusive method for PAH analysis. Also, elution times as long as 2 hr are needed for complete elutions.[160]

Most of the more recently published procedures for PAH analysis have utilized HPLC techniques.[64,65,81-88,193,195-197] Although the general method is far from simple, it appears to lend itself to the effective separation and quantitation of a wide variety of PAH compounds.

All of the above techniques have direct application to the analysis of foods but another major analytical concern involves the biological monitoring of humans who may be exposed to PAH in a food smoking operation, for example. Becher and Bjorseth[87] described the extraction of PAH and its metabolites from human urine followed by subsequent HPLC analysis using selective and sensitive fluorescence detection methods.

VI. PAH METABOLISM

Considering the fact that all adults and most children have been exposed to PAH from various dietary and environmental sources, one should ask the question as to metabolically what happens to PAH when ingested. Through much research it has been demonstrated that a series of closely associated enzymes are capable of breaking down PAH in animal cells, but that an alteration in the balance of these enzyme activities can dramatically alter resulting types and amounts of PAH metabolites.[90]

The key enzyme appears to be aryl hydrocarbon hydroxylase[91] which is actually a complex of enzymes[92] in which cytochrome P-450 plays a major role. By this enzymatic action PAH can be converted to phenol and numerous dihydrodihydroxy derivatives, which in turn can either enzymatically or chemically be converted to conjugated sulfates, glucuronides, and mercapturic acids. Another enzyme, epoxide hydrase, is important in converting PAH epoxides to dihydrodiols.[93] In addition, PAH that have methyl groups as ring components are important metabolically since they yield hydroxy-methyl derivatives.[94] Thus, most if not all humans have the general capability to metabolically handle PAH, but the unanswered questions deal with how much and for how long can the human effectively metabolize PAH before they can cause significant metabolic harm.

The scientific literature has also caused some confusion due to the fact that the development of arylhydroxylase activity is apparently dependent upon the location of administering PAH.[40] For example, if given intratracheally, PAH is eliminated in less than a day whereas if it is administered subcutaneously, it is still detectable 6 months later. It has also been shown[40] that in experimental animals, higher resulting tumor rates are associated with subcutaneous injection as compared to intratracheal administration. In addition, the dose/effect response was more negative with subcutaneous injection since 500 times the quantity needed to produce skin cancer was required to produce cancer in the respiratory tract. From these data some would conclude that PAH ingestion is not as dangerous as epicutaneous or subcutaneous application, but this is a narrow and potentially misleading assumption. If enough PAH is present in the diet, there is no doubt that the risk for cancer is increased.

The concentration of PAH in certain workplace environments can exceed by factors of more than 1000 the PAH concentration in normal atmosphere.[87] This should be a cause for health concern but some argue from a metabolic standpoint that this may not sound as bad as it is since only a small portion of PAH found in the environment is bioavailable due to the fact that PAH is adsorbed to particles. Also, some argue that man may be less sensitive than experimental animals with respect to PAH-induced cancer.

From a metabolic standpoint there is potential concern that certain of the PAH metabolically oxidized products are potentially more of a health concern than nonoxidized PAH. Also to be considered is the fact that hydroxylated PAH may induce the development of carcinomas before there is the opportunity for these compounds to be detoxified via activated glucuronic acid from the body.[40]

Sound scientific metabolic study, especially utilizing humans, is difficult in determining the potential interaction of both carcinogenic and noncarcinogenic PAH compounds with other toxic and nontoxic compounds. For example, certain noncarcinogenic PAH have a cocarcinogenic effect when combined with certain benzopyrenes whereas other PAH have been reported to inhibit carcinogenesis.[40]

It has also been reported[40] that the metabolic resorbability of certain PAH is improved by the consumption of caffeine. The obvious question arising from this observation is does a heavy coffee or tea drinker who also consumes foods high in PAH have a higher cancer risk than a person who does not consume caffeine-containing drinks? Other potential PAH/diet constituent interactions probably exist but research in this area is still lacking.

Sullivan[187] discussed the potential for free radicals to serve as intermediates in the metabolism of PAH. For example, with benzo[a]pyrene, at least four different types of free radicals have been observed as influenced by reaction conditions. The simplest free radical form involves a one-electron reduction or a one-electron oxidation resulting in the formation of an anion or cation radical. Also, another free radical species can form when benzo[a]pyrene is heated above its melting point. In addition, numerous oxygenated free radicals such as 6-oxybenzo[a]pyrene have been identified.[187] From a biological standpoint, clear evidence for biological involvement of the anion form has been proposed. From a smoke generation standpoint, the melting of benzo[a]pyrene is especially interesting. Cavalieri and Rogan[199] demonstrated that the one-electron oxidation radical form can cause PAH carcinogenesis by the direct application of PAH to rat mammary gland.

Cation radicals have been shown[187] to react with certain nucleophiles at position 6. Also, the benzo[a]pyrene cation radical is quenched by numerous nitrogenous compounds and antioxidants. In addition, this radical has been shown[187] to result in adduct formation with DNA. Oxy radicals also bind strongly with DNA and compounds such as caffeine.

VII. PAH STABILITY

Primarily from a pollution concern, research has been conducted to determine the stability of PAH once they are emitted into the ecosystem. For example, Thomas et al.[95] demonstrated that PAH are closely associated with soot particles and as such do not appear to be present in air in their free form. However, Korfmacher et al.[96] have reported that once absorbed onto coal fly ash, PAH vary in their susceptibility to photodecompose. They found that benzo[a]pyrene, pyrene, and anthracene all were efficiently photolyzed in liquid solution but were highly resistant to photodegradation when absorbed onto ash. In contrast, phenanthrene and fluoranthene were resistant to photodecomposition both in liquid and ash systems. The relationship of these observations to food systems is not known, and thus, would serve as an interesting study to determine the stability of various PAH in food systems as influenced by such factors as solids content, packaging, and exposure to light with time.

Jager[97] reported that PAH emitted into the atmosphere are quickly degraded by several pathways including photooxidation, reaction with atmospheric oxidants, and reactions with other chemical pollutants such as nitrogen oxides and nitric acid.

Cimberle et al.[99] have also noted that photodecomposition of PAH is an important pathway for their decomposition, with time of year relative to the amount and intensity of sunshine being important factors to consider. Thus, during cloudy days their decomposition may be quite low thereby making them more of an environmental concern.

As pointed out by Seifert,[98] PAH decomposition can also be a potential problem during their analysis. He found a 50% reduction in benzo[a]pyrene after a few minutes of separation on TLC. Thus, if analytical precautions are not taken, there is the potential to grossly underestimate PAH levels in food systems. The stability of other PAH compounds during analysis should also be investigated.

In contrast, Gunther and Westlake[198] reported that when certain PAH were applied at a rate of 10 ppm to the surfaces of mature oranges still on the tree, a persistance of up to 175 days resulted indicating that at least on oranges, PAH is not completely photooxidized in short periods of time. A portion of their data is summarized in Table 27.

PAH contamination of certain ecosystems has resulted in the detection of PAH in raw shellfish such as mussels and oysters.[100-103] Thus, if these products are smoked and found to contain PAH, one cannot be sure of the portion, if any, of PAH which results from the

Table 27
DEGRADATION AND PERSISTANCE OF PAH (10 ppm) WHEN APPLIED TO ORANGES

	Half-life (days)	
PAH	**Degradation**	**Persistence**
B[a]P	1	175
B[ai]P	1.5	12
B[a,h]A	2	125
An	1.5	175

Adapted from Gunther, F. A. and Westlake, W. E., *Residue Rev.*, 17, 81, 1967.

Table 28
PAH AMOUNTS IN CONTAMINATED OYSTERS

Compound	Exposure time (days)	Depuration time (days)	Concentration in oyster (μg/g)
Anthracene	2	0	5.6
	2	7	1.2
	8	7	0.4
	8	23	0.1
Fluoranthene	2	0	5.0
	2	7	1.7
	8	7	1.4
	8	23	0.4
Benz[a]anthracene	2	0	2.8
	2	7	1.9
	8	7	1.0
	8	23	0.3
Benzo[a]pyrene	2	0	0.36
	2	7	0.40
	8	7	0.20
	8	23	0.12

Adapted from Lee, R. F., Gardner, W. S., Anderson, J. W., Blaylock, J. W., and Barwell-Clarke, J., *Environ. Sci. Technol.*, 12, 832, 1978.

smoking process. Apparently, PAH are relatively stable in live shellfish since in a study reported by Lee et al., oysters that were intentionally exposed to anthracene, fluoranthene, benz[a]anthracene, and benzo[a]pyrene for up to 8 days and then subjected for up to 23 days of depuration or purging still had measurable PAH levels. These data are summarized in Table 28.

VIII. NITROSAMINES

Nitrosamines are a class of compounds that can be formed by the action of nitrite on secondary and tertiary amines, and are powerful biological agents many of which have been shown to be carcinogenic.[104] They have been identified in a wide variety of foods[105-135] but most research has centered around their presence in cured and smoked meat products since the intentional addition of nitrate/nitrite and spices to these products is a common practice.[136-138] However, as pointed out by White,[139] cured meat products only account for approximately one sixth of the nitrate consumed in the U.S., while vegetables account for over four fifths. Also, two thirds of the nitrite that reaches the gut comes from saliva while cured meats account for the other third.

To make matters more interesting relative to nitrosamine formation in smoked foods, Walker et al.[140] demonstrated that phenols can actually catalyze nitrosamine formation in model systems. Thus, it can be assumed that in the presence of nitrite, phenols present in wood smoke can form nitrosamines. They also demonstrated that this same reaction can lead to high results during certain nitrosamine analyses.

In light of the above information, the utilization of liquid smoke preparations in a brine that contains nitrite has to be seriously questioned since nitro- and nitrosophenols can form under these conditions.

In a more recent study, Mandagere et al.[141] actually reacted wood smoke condensate with combinations of nitrite and cysteamine, cysteine, or cystine. Small amounts of certain nitrosamines were found in all systems, but the combination of wood smoke, nitrite, and cysteamine produced significant amounts of nitrosamines.

Kalve and Kann[142] also reported upon the formation of various nitrogen oxides from wood smoke that could enter into nitrosamine formation. Smoke generation temperature was the primary factor governing the amounts of nitrogen oxides formed with the higher the temperature, the greater the oxide levels.

Recently, the influence of phenol and 2,6-dimethoxyphenol (syringol), two common wood smoke components, on the rates of *N*-nitrosomorpholine, *N*-nitrosopyarolidine, and *N*-nitrosopyrrolidine production has shown that syringol significantly increased the production of all three whereas phenol had no influence on *N*-nitrosomorpholine levels but dramatically increased *N*-nitrosopyrrolidine production by approximately 350%. Thus, it would appear that smoke high in certain phenols may have either beneficial or negative effects relative to nitrosoamine formation.

Two recently discovered nitroso compounds are *N*-nitrosothiazolidine and *N*-nitrosothiazolidine-4-carboxylic acid[163,171-179] which have been most closely associated with cured, smoked foods such as cured meats and bacon. The reasons these two specific compounds are of potential concern are that *N*-nitrosothiazolidine has been indicated as being genotoxic in microbial and hepatocellular test systems[180] while *N*-nitrosothiazolidine-4-carboxylic acid has shown to induce diabetes in experimental animals.[175] This latter compound thus has been implicated as the compound responsible for the high levels of juvenile diabetes associated with mothers who consumed large amounts of smoked meats during pregnancy.[175] Sen et al.[179] reported that fried bacon that had been commercially directly smoked had levels of *N*-nitrosothiazolidine-4-carboxylic acid of up to 13,700 ppb when fried.

The levels of nitrosamines in commercial bacon have been measured[181-184] and in the most recent study[184] the average amounts in milligrams per kilogram of *N*-nitrosodimethylamine in the rasher and fried-out fat were 4.0 and 5.3; 0.7 and 1.5 for *N*-nitrosopiperidine; 17 and 32 for *N*-nitrosopyrrolidine; and 8.9 and 3.4 for *N*-nitrosothiazolidine. From these data they concluded that the average daily intake of *N*-nitrosopyrrolidine from fried bacon was 76 ng per person. Also, they found that many consumers of bacon use the fried-out fat for other cooking purposes which would further elevate their intake of nitrosamines.

The reader is directed to an excellent series of papers[164-170] that cover nitrosamine formation, analysis, and safety issues in smoked and heated foods.

IX. TOXICOLOGICAL PROPERTIES OF WOOD SMOKE

Several Polish groups have reported on the toxicological properties of commercial liquid smokes.[143-145] Based on standard procedures, Kozlowski et al.[143] determined that the LD_{50} doses for their liquid smoke were 2750 mg/kg of mouse body weight, 3750 mg/kg of rat body weight, 192 mg/kg of cat body weight, and greater than 5000 mg/kg of pig body weight. Histopathological analysis of organs revealed no difference from control groups not fed liquid smoke.

Fitko et al.[144] fed Polish large white swine daily doses of 200, 600, 1000, or 1400 mg/kg of body weight of liquid smoke while Swiss albino mice and Wistar rats received diets containing 0.1, 0.5, 1.0, and 2.0% liquid smoke for 3 months. In the case of pigs, pathological changes in the digestive tract, liver, kidneys, and lungs were apparent but biochemical and hematological blood changes were not observed. In both pigs and rodents, increasing amounts of liquid smoke in the diet decreased body weight gains even though feed consumption increased thus indicating that liquid smoke adversely influenced digestion and/or absorption.

Fitko et al.[145] also determined LD_{50} values in mice and rats administered liquid smoke. The LD_{50} for female mice was 2420 mg/kg while for male mice it was 2700 mg/kg of body weight. In the case of female rats, an LD_{50} of 3550 mg/kg was calculated while for male rats it was 4010 mg/kg. In the animals that died, gross pathological changes were observed including hyperemia and hemorrhages in the stomach and duodenal mucosa, and hyperemia and edema of the kidneys and liver. In test animals that did not die, the higher doses of liquid smoke caused parenchymatous and fatty degeneration of liver and kidneys and acute to subacute catarrhal inflammation of the stomach and small intestine mucosa. The authors concluded that liquid smoke demonstrated low acute toxicity and the physiological changes associated with high dosages were typical to those of similar compounds. However, because of the potential wide differences in composition and concentration of liquid smoke preparations, these studies should not be taken as average LD_{50} values for smoke in general.

X. MUTAGENIC PROPERTIES OF WOOD SMOKE

Most scientists now believe that compounds that can be shown to possess bacterial mutagenic activity have a potential cause for concern in our diet. However, the question as to whether all compounds that are demonstrated to be mutagenic are also carcinogenic is still being debated. In any event, a few studies have appeared reporting on the mutagenic properties of wood smoke although more studies have appeared on the mutagenic properties of individual phenols,[146-150] which can be the major components of wood smoke. For the most part, individual phenols have given negative results relative to mutagenic activity.

One relatively recent study has reported upon the mutagenic properties of phenolic smoke fractions and their isolated phenols.[151] They found no mutagenic activity, at five concentrations up to 5000 μg per plate, associated with phenol, cresols, 2,4-dimethylphenol, benzcatechine, syringol, eugenol, vanillin, and guaiacol. However, when smokehouse smoke was condensed and fractionated, certain phenolic fractions did give an increase in the number of revertants. The authors postulated that apparently there can be small amounts of mutagenic impurities in wood smoke that give a positive test for mutagen formation. At this point the specific compounds responsible are not known. However, as pointed out by Haugen and Peak,[152] complex mixtures of aromatic compounds can actually suppress mutagenic activity, thus possibly resulting in erroneous conclusions. Since so little work relative to smoke has been reported in this area, more well-designed experiments are required in order to resolve this very important issue.

Obviously it would be difficult to obtain direct evidence positively correlating the consumption of smoked foods to specific forms of cancer, but general data, such as the fact that stomach and colon cancer occurrences are higher in countries or populations that have significant ingestion levels of PAH,[153] strongly point to the fact that since most smoked foods contain various types and amounts of PAH, these foods can serve as one source as precursors for cancer.

In actual animal studies utilizing mice and rats, Kozlowski et al.[143] reported on the influence of smoke extract consumption on inducing carcinomas and teratogenic effects. They calculated that a human population would consume approximately 0.10 mg of smoke extract per 1 kg of body weight while in their animal studies consumption was in the range of 16 to 21 mg of extract per kilogram body weight. No signs of neoplastic or mutagenic activity were noted in the test animals.

REFERENCES

1. **Simon, S., Rypinski, A. A., Tauber, F. W., Pencyla, R. M., and Westerberg, D. O.,** Effect of cellulose casing on the absorption of polycyclic hydrocarbons in wood smoke by absorbents, *J. Agric. Food Chem.*, 17, 1128, 1969.
2. **Rusz, J., Kopalova, M., and Pelikanova, K.,** Effect of some factors on 3,4-benzpyrene content of smoke for smoking food, *Prum. Potravin*, 22, 106, 1971.
3. **Lenges, J.,** Smoking of meat products, *Rev. Ferment. Ind. Aliment.*, 27, 53, 1972.
4. **Toth, L. and Blaas, W.,** The effect of smoking technology on the content of carcinogenic hydrocarbons in smoked meat products. II. Effect of smoldering temperature of wood and of cooling, washing and filtering of smoke, *Fleischwirtschaft*, 52, 1419, 1972.
5. **Toth, L. and Blaas, W.,** The effect of smoking technology on the content of carcinogenic hydrocarbons in smoked meat products. I. Effect of various smoking methods, *Fleischwirtschaft*, 52, 1121, 1972.
6. **Kersken, H.,** Smoking today, *Fleischwirtschaft*, 54, 1721, 1974.
7. **Potthast, K.,** Problems of smoking meat and meat products, *Fleischwirtschaft*, 55, 1492, 1975.
8. **Prihavec, D. and Polic, M.,** Basic characteristics of manufacture of a smoke concentrate; the properties of this concentrate, *Tehnol. Mesa*, 17, 349, 1976.
9. **Steinig, J.,** Benzo[a]pyrene contents of smoked fish in relation to smoking procedure, *Z. Lebensm. Unter. Forsch.*, 162, 235, 1976.
10. **Lenges, J., Vo Thi, N. B., and Declerck, D.,** Effect of smoking technology on the contamination of smoked fish with 3,4-benzopyrene, *Rev. Ferment. Ind. Aliment.*, 31, 97, 1976.
11. **Steinig, J. and Schreiber, W.,** Minimization of the 3,4-benzopyrene content of smoked fish products by modification of the smoking process, *Inf. Fleischwirtschaft*, 24, 126, 1977.
12. **Potthast, K., Eigner, G., and Eichner, R.,** Reduction of content of polycyclic hydrocarbons in smoked meat products, *Ber. Landwirtscha.*, 55, 817, 1977.
13. **Hamm, R.,** Analysis of smoke and food, *Fleischwirtschaft*, 57, 92, 1977.
14. **Borys, A., Klossowska, B., Obiedzinski, M., and Olkiewicz, M.,** Influence of combustion conditions on the composition of carbonylic, carboxylic, polynuclear hydrocarbons, and phenolic compounds present in wood smoke, *Acta Aliment. Pol.*, 3, 335, 1977.
15. **Potthast, K.,** Smoking procedures and their effect on 3,4-benzpyrene and other smoke components in smoked meat products, *Fleischwirtschaft*, 58, 371, 1978.
16. **Hardy, R. and McGill, A. S.,** Smoking of foods: methods and some toxicological aspects, *Process Biochem.*, 14(11), 2, 1979.
17. **Potthast, K.,** The influence of smoking technology on the composition of polycyclic hydrocarbons in smoked meat products, smoke condensates and in waste gases from smoking plants, *Fleischwirtschaft*, 59, 1515, 1979.
18. **Raja, K. C. M., Mahendraker, N. S., and Morrjani, M. N.,** Benzpyrene in smoked poultry, *J. Food Sci. Technol. India*, 17, 156, 1980.
19. **Potthast, K.,** Dark smoking at high smokehouse temperature, *Fleischwirtschaft*, 61, 1630, 1981.
20. **Dikun, P. P., Kostenko, L. D., Shendrikova, L. D., Emshanova, A. V., and Nikitin, B. N.,** Contents of 3,4-benzpyrene in fish processed by various smoking technologies, *Rybn. Khoz.*, 5, 78, 1981.
21. **Sirami, J.,** Application of smoking processes, *Viandes Produits Carnes*, 2(6), 8, 1981.
22. **Rhee, K. S. and Bratzler, L. J.,** Polycyclic hydrocarbon composition of wood smoke, *J. Food Sci.*, 33, 626, 1968.
23. **Obiedzinski, M. and Borys, A.,** Identification of polynuclear aromatic hydrocarbons in wood smoke, *Acta Aliment. Pol.*, 3, 169, 1977.

24. **Colmsjo, A. L., Zebuhr, Y. U., and Ostman, C. E.**, Polycyclic aromatic compounds in curing smoke, *Z. Lebensm. Unters. Forsch.*, 179, 308, 1984.
25. **Obiedzinski, M.**, Determination of polycyclic aromatic hydrocarbons in wood smoke, *Acta Aliment. Pol.*, 3, 183, 1977.
26. **Potthast, K.**, The composition of smoking preparations, *Fleischwirtschaft*, 54, 183, 1974.
27. **White, R. H., Howard, J. W., and Barnes, C. J.**, Determination of polycyclic aromatic hydrocarbons in liquid smoke flavors, *J. Agric. Food Chem.*, 19, 143, 1971.
28. **Toth, L.**, Carcinogenic substances in smoked meat products, *Fleischwirtschaft*, 49, 1611, 1969.
29. **Tilgner, D. J.**, Carcinogenic hydrocarbons in food, *Gordian*, 71, 2, 1971.
30. **Luks, D. and Lenges, J.**, Some analytical and practical aspects of the contamination of smoked meat products by carcinogenic compounds, *Rev. Ferment. Ind. Aliment.*, 28, 111, 1973.
31. **Hamm, R.**, Polycyclic carcinogenic compounds in meat products and toxic trace elements in meat, *Med. Weter.*, 29, 708, 1973.
32. **Filipovic, J. and Karakas, R.**, The impact of smoking and the content of carcinogens in meat products, *Hrana Ishrana*, 14, 447, 1973.
33. **Gilbert, J. and Knowles, M. E.**, The chemistry of smoked foods: a review, *J. Food Technol.*, 10, 245, 1975.
34. **Henning, W.**, How dangerous are smoke-flavored seasonings?, *Ernaehrungswirtschaft*, 3, 108, 1976.
35. **Polic, M.**, The chemistry of smoke and smoke concentrates: the effect and importance of individual components for the meat products, *Tehnol. Mesa*, 17, 345, 1976.
36. **Fritz, W. and Soos, K.**, Studies on the content of carcinogenic hydrocarbons in smoked foods in the German Democratic Republic and in Hungary, *Nahrung*, 21, 951, 1977.
37. **Walker, E. A.**, Some facts and legislation concerning polycyclic aromatic hydrocarbons in smoked foods, *Pure Appl. Chem.*, 49, 1673, 1977.
38. **Bories, G., Tchimbakala, A., and Tchimbakala, E.**, A survey of food contamination by 3,4-benzpyrene, *Ann. Nutr. Aliment.*, 32, 811, 1978.
39. **Potthast, K.**, The occurrence of 3,4-benzpyrene in smoked meat products, seasonings and other foods, *Fleischerei*, 29(5), 67, 1978.
40. **Potthast, K.**, The problem of 3,4-benzopyrene in smoked meat products, *Fleischwirtschaft*, 58, 38, 1978.
41. **Mossanda, K., Poncelet, F., Fouassin, A., and Mercier, M.**, Detection of mutagenic polycyclic aromatic hydrocarbons in African smoked fish, *Food Cosmet. Toxicol.*, 17, 141, 1979.
42. **Binnemann, P. H.**, Benso[a]pyrene contents of meat products, *Z. Lebensm. Unters. Forsch.*, 169, 447, 1979.
43. **Schober, B.**, Smoke components and their effects, *Lebensm. Ind.*, 26, 262, 1979.
44. **Mossanda, K.**, Polycyclic aromatic hydrocarbons in smoked fish from central Africa, *Rev. Ferment. Ind. Aliment.*, 35, 132, 1980.
45. **Potthast, K.**, Recent figures for benzo[a]pyrene contents in meat products, *Fleischwirtschaft*, 60, 1941, 1980.
46. **Nistor, C., Raileanu, L., Pacular, T., Ichim, I., Mancas, D., Stoleru, F., Sinpetru, L., and Lamasanu, F.**, Contamination of smoked foods with polycyclic aromatic hydrocarbons, *Igiena*, 29, 345, 1980.
47. **Larsson, B. K.**, Polycyclic aromatic hydrocarbons in smoked fish, *Z. Lebensm. Unters. Forsch.*, 174, 101, 1982.
48. **Ruchkovskii, B. S., Tikhtin, L. A., and Palyura, A. N.**, Contents of benzo[a]pyrene in sausage products, *Vopr. Pitan.*, 1, 62, 1982.
49. **Afolabi, O. A., Adesulu, E. A., and Oke, O. L.**, Polynuclear aromatic hydrocarbons in some Nigerian preserved freshwater fish species, *J. Agric. Food Chem.*, 31, 1083, 1983.
50. **Lijinsky, W. and Shubik, P.**, Benzo[a]pyrene and other polynuclear hydrocarbons in charcoal-broiled meat, *Science*, 145, 53, 1964.
51. **Lijinsky, W. and Shubik, P.**, Polynuclear hydrocarbon carcinogens in cooked meat and smoked food, *Ind. Med. Surg.*, 34, 152, 1965.
52. **Lijinsky, W. and Ross, A. E.**, Production of carcinogenic polynuclear hydrocarbons in the cooking of food, *Food Cosmet. Toxicol.*, 5, 343, 1967.
53. **Tilgner, D. J. and Daun, H.**, Polycyclic aromatic hydrocarbons in smoked food, *Residue Rev.*, 27, 19, 1969.
54. **Caurie, M., Lee, T. C., Salomon, M., and Chichester, C. O.**, Hot smoke fish curing, *J. Natl. Sci. Counc. Sri Lanka*, 2, 77, 1974.
55. **Engst, R. and Fritz, W.**, Food-hygenic toxicological evaluation of the occurrence of carcinogenic hydrocarbons in smoked products, *Acta Aliment. Pol.*, 3, 255, 1977.
56. **Yamazaki, H., Minami, J., Ichiakwa, T., and Kondo, M.**, Analysis of polycyclic aromatic hydrocarbons in raw and broiled fishes, *J. Food Hyg. Soc. Jpn.*, 18, 368, 1977.
57. **Lintas, C. and DeMatthaeis, M. C.**, Determination of benzo[a]pyrene in smoked, cooked and toasted food products, *Food Cosmet. Toxicol.*, 17, 325, 1979.

58. **Doremire, M. E., Harmon, G. E., and Pratt, D. E.,** 3,4-benzopyrene in charcoal grilled meats, *J. Food Sci.*, 44, 622, 1979.
59. **Heddeghem, A., Giel, W., and Moor, H.,** Polycyclic aromatic hydrocarbons in smoked and grilled foods, *Meded. Fac. Landbouwwet. Rijksuniv. Gent*, 44, 1221, 1979.
60. **Newburg, D. S. and Concon, J. M.,** Malonaldehyde concentrations in food are affected by cooking conditions, *J. Food Sci.*, 45, 1681, 1980.
61. **Larsson, B. K., Sahlberg, G. P., Eriksson, A. T., and Busk, L. A.,** Polycyclic aromatic hydrocarbons in grilled foods, *J. Agric. Food Chem.*, 31, 867, 1983.
62. **Fretheim, K.,** Polycyclic aromatic hydrocarbons in grilled meat products — a review, *Food Chem.*, 10, 129, 1983.
63. **Bjeldanes, L. F., Morris, M. M., Timourian, H., and Hatch, F. T.,** Effects of meat composition and cooking conditions on mutagen formation in fried ground beef, *J. Agric. Food Chem.*, 31, 18, 1983.
64. **Lawrence, J. F. and Weber, D. F.,** Determination of polycyclic aromatic hydrocarbons in some Canadian commercial fish, shellfish, and meat products by liquid chromatography with confirmation by capillary gas chromatography-mass spectrometry, *J. Agric. Food Chem.*, 32, 789, 1984.
65. **Lawrence, J. F. and Weber, D. F.,** Determination of polycyclic aromatic hydrocarbons in Canadian samples of processed vegetable and dairy products by liquid chromatography with fluorescence detection, *J. Agric. Food Chem.*, 32, 794, 1984.
66. **Ondrisekova, M. and Sedova, V.,** Study of phenolic compounds in smoked malt ordered by Japanese customers, *Kvasny Prum.*, 27(3), 58, 1981.
67. **Fritz, W.,** Formation of carcinogenic hydrocarbons during thermal treatment of foods. VI. Investigation of the contamination of cereals resulting from smoke drying, *Nahrung*, 18, 83, 1974.
68. **Haenni, E. O.,** Analytical control of polycyclic aromatic hydrocarbons in food and food additives, *Residue Rev.*, 24, 41, 1968.
69. **Grimmer, G.,** Analysis of polycyclic aromatic hydrocarbons, *Landwirtsch. Forsch.*, 35, 683, 1979.
70. **Howard, J. W., Teague, R. T., White, R. H., and Fry, B. E.,** Extraction and estimation of polycyclic aromatic hydrocarbons in smoked foods. I. General method, *J. Assoc. Off. Anal. Chem.*, 49, 595, 1966.
71. **Howard, J. W., White, R. T., Fry, B. E., and Turicchi, E. W.,** Extraction and estimation of polycyclic aromatic hydrocarbons in smoked foods. IV. Benzo[a]pyrene, *J. Assoc. Off. Anal. Chem.*, 49, 611, 1966.
72. **Rijk, M. A. H. and Battum, D.,** A rapid method for determining benz[a]pyrene in smoke aroma, *Dtsch. Lebensm. Rundsch.*, 69, 75, 1973.
73. **Kedzierski, B. and Kubacki, S. J.,** A modification of the Howard method of benzo[a]pyrene determination in foods, *Acta Aliment. Pol.*, 3, 175, 1977.
74. **Shiraishi, Y. and Shirotori, T.,** Determination of polycyclic aromatic hydrocarbons in foods. VII. Separation and determination of benzo[a]pyrene and benzo[k]fluoranthene, *J. Food Hyg. Soc. Jpn.*, 20, 345, 1979.
75. **Mossanda, K.,** Polycyclic aromatic hydrocarbons in smoked fish from central Africa. I. Development of a qualitative and quantitative analytical method, *Rev. Ferment. Ind. Aliment.*, 35, 99, 1980.
76. **Segredos, A. N., Sinha-Roy, D., and Jan, E.,** A contribution to the determination of polycyclic aromatic hydrocarbons in smoked foodstuffs via caffeine complexes, *Dtsch. Lebensm. Rundsch.*, 77, 33, 1981.
77. **Grimmer, G. and Bohnke, H.,** Polycyclic aromatic hydrocarbon profile analysis of high-protein foods, oils and fats by gas chromatography, *J. Assoc. Off. Anal. Chem.*, 58, 725, 1975.
78. **Potthast, K.,** Polycyclic aromatic hydrocarbons in smoked meat products. An application of a new method, *Acta Aliment. Pol.*, 3, 195, 1977.
79. **Radecki, A., Lamparczyk, H., Grzybowski, J., and Halkiewicz, J.,** Separation of polycyclic aromatic hydrocarbons and determination of benzo[a]pyrene in liquid smoke preparations, *J. Chromatogr.*, 150, 527, 1978.
80. **Tanner, R. L. and Fajer, R.,** Determination of nitro-polynuclear aromatics in ambient aerosol samples, *Int. J. Environ. Anal. Chem.*, 14, 231, 1983.
81. **Guerrero, H., Bichl, E. R., and Kenner, C. T.,** High-pressure liquid chromatography of benzo[a]pyrene and benzo[ghi]perylene in oil-contaminated shellfish, *J. Assoc. Off. Anal. Chem.*, 59, 989, 1976.
82. **Toussaint, G. and Walker, E. A.,** Use of high-performance liquid chromatography as a clean-up procedure in analysis of polycylic aromatic hydrocarbons in alcoholic beverages, *J. Chromatogr.*, 171, 448, 1979.
83. **Crosby, N. T., Hung, D. C., Philp, L. A., and Patel, I.,** Determination of polynuclear aromatic hydrocarbons in food, water and smoke using high-performance liquid chromatography, *Analyst*, 106, 135, 1981.
84. **Gertz, C.,** Improved method for the quantitative separation of 3,4-benzpyrene(benzo[a]pyrene) from food, *Z. Lebensm. Unters. Forsch.*, 173, 208, 1981.
85. **Joe, F. L., Salemme, J., and Fazio, T.,** High performance liquid chromatography with fluorescence and ultraviolet detection of polynuclear aromatic hydrocarbons in barley malt, *J. Assoc. Off. Anal. Chem.*, 65, 1395, 1982.

86. **Nielsen, T.**, Isolation of polycyclic aromatic hydrocarbons and nitro derivatives in complex mixtures by liquid chromatography, *Anal. Chem.*, 55, 286, 1983.
87. **Becher, G. and Bjorseth, A.**, Determination of exposure to polycyclic aromatic hydrocarbons by analysis of human urine, *Cancer Lett.*, 17, 301, 1983.
88. **Balya, D. R. and Danchik, R. S.**, Chromatographic techniques for characterization of coal tar pitch volatiles, *Am. Ind. Hyg. Assoc. J.*, 45, 260, 1984.
89. **Radecki, A., Lamparczyk, H., Halkiewicz, J., and Grzybowski, J.**, Studies on determination of benzo[a]pyrene in smoke flavorings, *Acta Aliment. Pol.*, 3, 209, 1977.
90. **Brookes, P.**, Mutagenicity of polycyclic aromatic hydrocarbons, *Mutation Res.*, 39, 257, 1977.
91. **Gelboin, H. V., Wiebel, F. J., and Kinoshita, N.**, Aryl hydrocarbon hydroxylase regulation and role in polycyclic hydrocarbon action, *Chemical Carcinogenesis, Part A*, Marcel Dekker, New York, 1974, 309.
92. **Huberman, E., Yamasaki, H., and Sachs, L.**, Independent regulation of two types of aryl hydrocarbons benzo[a]pyrene hydroxylase in mammalian cells, *Int. J. Cancer*, 18, 76, 1976.
93. **Oesch, F.**, Mammalian epoxide hydrases: inducible enzymes cytolysing the inactivation of carbinogenic and cytotoxic metabolites derived from aromatic and definite compounds, *Xenobiotica*, 3, 305, 1973.
94. **Sims, P.**, The metabolism of 7- and 12-methylbenz[a]anthracene and their derivatives, *Biochem. J.*, 105, 591, 1967.
95. **Thomas, J. F., Mukai, M., and Tebbens, B. D.**, Fate of airborne benzo[a]pyrene, *Environ. Sci. Technol.*, 2, 33, 1968.
96. **Korfmacher, W. A., Wehry, E. L., Mamantov, G., and Natusch, D. F. S.**, Resistance to photochemical degradation of polycyclic aromatic hydrocarbons vapor-absorbed on coal fly ash, *Environ. Sci. Technol.*, 14, 1094, 1980.
97. **Jager, J.**, Detection and characterization of nitro derivatives of some polycyclic aromatic hydrocarbons by fluorescence quenching after thin-layer chromatography: application to air pollution analysis, *J. Chromatogr.*, 152, 575, 1978.
98. **Seifert, B.**, Stability of benzo[a]pyrene on silica gel plates for high-performance thin-layer chromatography, *J. Chromatogr.*, 131, 417, 1977.
99. **Cimberle, M. R., Bottino, P., and Valerio, F.**, Decomposition of benzo[a]pyrene deposited on glass fiber filters and exposed to sunlight, *Chemosphere*, 12, 317, 1983.
100. **Iosifidou, H. G., Kilikidis, S. D., and Kamarianos, A. P.**, Analysis for polycyclic aromatic hydrocarbons in mussels *(Myticus galloprovincialis)* from the Thermaikos Gulf, Greece, *Bull. Environ. Contam. Toxicol.*, 28, 535, 1982.
101. **Xoaa, S., Picard-Berube, M., and Gouygou, J. P.**, Polynuclear aromatic hydrocarbons in mussels from the estuary and northwestern Gulf of St. Lawrence, Canada, *Bull. Environ. Contam. Toxicol.*, 31, 41, 1983.
102. **Mix, M. C. and Schaffer, R. L.**, Concentrations of unsubstituted polynuclear aromatic hydrocarbons in bay mussels *(Mytilus edulis)* from Oregon, U.S.A., *Marine Environ. Res.*, 9, 193, 1983.
103. **Lee, R. F., Gardner, W. S., Anderson, J. W., Blaylock, J. W., and Barwell-Clarke, J.**, Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures, *Environ. Sci. Technol.*, 12, 832, 1978.
104. **Magee, P. N.**, Toxicity of nitrosamines: their possible human health hazards, *Food Cosmet. Toxicol.*, 9, 207, 1971.
105. **Ceh, L. and Ender, F.**, A sensitive method for the colorimetric determination of volatile nitrosamines in food products and air, *Food Cosmet. Toxicol.*, 16, 117, 1978.
106. **Dikun, P. P.**, Group evaluation of volatile and nonvolatile N-nitroso compounds in foodstuffs, *IARC (Int. Agency Res. Cancer) Sci. Publ.*, 14, 57, 1976.
107. **Dikun, P. P., Romanova, L. E., Shendrikova, I. A., Reim, N. D., and Yunusova, Z. Y.**, Contents of *N*-nitrosamines in fish and some types of fish preserves, *Rybn. Khoz.*, 8, 69, 1980.
108. **Nieper, L. and Etzel, V.**, Nitrate content in smoked fish muscle, *Arch. Lebensmittelhyg.*, 34, 149, 1983.
109. **Sen, N. P. and Dalpe, C.**, A simple thin-layer chromatographic technique for the semi-quantitative determination of volatile nitrosamines in alcoholic beverages, *Analyst*, 97, 216, 1972.
110. **Spiegelhalder, B., Eisenbrand, G., and Preussmann, R.**, Contamination of beer with trace quantities of *N*-nitrosodimethylamine, *Food Cosmet. Toxicol.*, 17, 29, 1979.
111. **Walker, E. A., Castegnaro, M., Garren, L., Toussaint, G., and Kowalski, B.**, Intake of volatile nitrosamines from consumption of alcohols, *J. Natl. Cancer Inst.*, 63, 947, 1979.
112. **Slack, P. T. and Wainwright, T.**, Hordenine as the precursor of NDMA in malt, *J. Inst. Brew.*, 87, 259, 1981.
113. **Hotchkiss, J. H., Havery, D. C., and Fazio, T.**, Rapid method for estimation of *N*-nitrosodimethylamine in malt beverages, *J. Assoc. Off. Anal. Chem.*, 64, 929, 1981.
114. **Lance, D. G., Barrett, P. A., Kavanagh, T. E., and Clarke, B. J.**, Methods for the determination of volatile nitrosamines in malt, wort and beer, *J. Inst. Brew.*, 87, 19, 1981.

115. **Havery, D. C., Hotchkiss, J. H., and Fazio, T.**, Nitrosamines in malt and malt beverages, *J. Food Sci.*, 46, 501, 1981.
116. **Tauts, O. V. and Kaive, R. E.**, Causes of *N*-nitrosodimethylamine formation in beer, *Tallinna Polutehnilise Inst. Toim.*, No. 537, 38, 1982.
117. **Huxel, E. T., Scanlan, R. A., and Libbey, L. M.**, Formation of *N*-nitrosopyrrolidine from pyrrolidine ring containing compounds at elevated temperatures, *J. Agric. Food Chem.*, 22, 698, 1974.
118. **Telling, G. M., Bryce, T. A., and Althorpe, J.**, Use of vacuum distillation and gas chromatography-mass spectrometry for determination of low levels of volatile nitrosamines in meat products, *J. Agric. Food Chem.*, 19, 937, 1971.
119. **Sen, N. P.**, The evidence for the presence of dimethylnitrosamine in meat products, *Food Cosmet. Toxicol.*, 10, 219, 1972.
120. **Crosby, N. T., Foreman, J. K., Palframan, J. F., and Sawyer, R.**, Estimation of steam-volatile *N*-nitrosamines in foods at the 1 μg/kg level, *Nature*, 238, 342, 1972.
121. **Wasserman, A. E., Fiddler, W., Doerr, R. C., Osman, S. F., and Dooley, C. J.**, Dimethylnitrosamine in frankfurters, *Food Cosmet. Toxicol.*, 10, 681, 1972.
122. **Panalaks, T., Lyengar, J. R., and Sen, N. P.**, Nitrate, nitrite, and dimethyl-nitrosamine in cured meat products, *J. Assoc. Off. Anal. Chem.*, 56, 621, 1973.
123. **Bills, D. D., Hildrum, K. I., Scanlan, R. A., and Libbey, L. M.**, Potential precursors of *N*-nitrosopyrrolidine in bacon and other fried foods, *J. Agric. Food Chem.*, 21, 876, 1973.
124. **Gough, T. A., Goodhead, K., and Walters, C. L.**, Distribution of some volatile nitrosamines in cooked bacon, *J. Sci. Food Agric.*, 27, 181, 1976.
125. **Patterson, R. L. S., Taylor, A. A., Mottram, D. S., and Gough, T. A.**, Localized occurrence of *N*-nitrosopyrrolidine in fried bacon, *J. Sci. Food Agric.*, 27, 257, 1976.
126. **Sen, N. P., Seaman, S., and Miles, W. F.**, Volatile nitrosamines in various cured meat products: effect of cooking and recent trends, *J. Agric. Food Chem.*, 27, 1354, 1979.
127. Nitrite Safety Council, A survey of nitrosamines in sausages and dry-cured meat products, *Food Technol.*, 45, 1980.
128. **Hotchkiss, J. H., Libbey, L. M., and Scanlan, R. A.**, Confirmation of low μg/kg amounts of volatile *N*-nitrosamines in foods by low resolution mass spectrometry, *J. Assoc. Off. Anal. Chem.*, 63, 74, 1980.
129. **Hauser, E., Gruber, E., and Mihalik, K.**, Nitrosamine formation in bacon. Effect of formaldehyde, *Proc. Eur. Meet. Meat Res. Workers*, 27, Vol. II, 480, 1981.
130. **Greenfield, E. L., Vasco, G. A., Legette, L., and Malanoski, A.**, Screening procedure for detection of volatile *N*-nitrosamines in cooked bacon by one-trap mineral oil vacuum distillation and thermal energy analyzer, *J. Assoc. Off. Anal. Chem.*, 65, 1316, 1982.
131. **Greenfield, E. L., Smith, W. J., and Malanoski, A. J.**, Mineral oil vacuum distillation method for nitrosamines in fried bacon, with thermal energy analyzer: collaborative study, *J. Assoc. Off. Anal. Chem.*, 65, 1319, 1982.
132. **Kimoto, W. I., Pensabene, J. W., and Fiddler, W.**, Isolation and identification of *N*-nitrosothiazolidine in fried bacon, *J. Agric. Food Chem.*, 30, 757, 1982.
133. **Pensabene, J. W., Miller, A. J., Greenfield, E. L., and Fiddler, W.**, Rapid dry column method for determination of *N*-nitrosopyrrolidine in fried bacon, *J. Assoc. Off. Anal. Chem.*, 65, 151, 1982.
134. **Havery, D. C., Kline, D. A., Miletta, E. M., Joe, F. L., and Fazio, T.**, Survey of food products for volatile *N*-nitrosamines, *J. Assoc. Off. Anal. Chem.*, 59, 540, 1976.
135. **Sen, N. P. and Seaman, S.**, Volatile *N*-nitrosamines in dried foods, *J. Assoc. Off. Anal. Chem.*, 64, 1238, 1981.
136. **Sen, N. P., Miles, W. F., Donaldson, B., Panalaks, T., and Lyengar, J. R.**, Formation of nitrosamines in a meat curing mixture, *Nature*, 245, 104, 1973.
137. **Sen, N. P., Donaldson, B., Charbonneau, C., and Miles, W. F.**, Effect of additives on the formation of nitrosamines in meat curing mixtures containing spices and nitrite, *J. Agric. Food Chem.*, 22, 1125, 1974.
138. **Gough, T. A. and Goodhead, K.**, Occurrence of volatile nitrosamines in spice premixes, *J. Sci. Food Agric.*, 26, 1473, 1975.
139. **White, J. W.**, Relative significance of dietary sources of nitrate and nitrite, *J. Agric. Food Chem.*, 23, 886, 1975.
140. **Walker, E. A., Pignatelli, B., and Friesen, M.**, The role of phenols in catalysis of nitrosamine formation, *J. Sci. Food Agric.*, 33, 81, 1982.
141. **Mandagere, A. K., Gray, J. I., Skrypec, D. J., Booren, A. M., and Pearson, A. M.**, Role of woodsmoke in *N*-nitrosothiazolidine formation in bacon, *J. Food Sci.*, 49, 658, 1984.
142. **Kalve, R. E. and Kann, Y. M.**, Formation of nitrogen oxides during production of curing smoke, *Tallinna Polutehnilise Inst. Toim.*, No. 489, 15, 1980.
143. **Kozlowski, Z. P.**, Investigations on the chemical, toxicological and biological properties of the Polish smoke extract, *Proc. Eur. Meet. Meat Res. Workers*, 15, 516, 1969.

144. **Fitko, R., Markiewicz, K., Markiewicz, Z., Szuperski, T., and Krzymowska, H.**, The zootechnical indexes and pathological changes in animals after smoke flavouring application in subacute toxicity test, *Acta Aliment. Pol.*, 3, 269, 1977.

145. **Fitko, R., Grabowski, J., Krzymowska, H., Markiewicz, K., and Szuperski, T.**, The acute toxicity of smoke flavouring, *Acta Aliment. Pol.*, 3, 275, 1977.

146. **Florin, F., Rutberg, L., Curvall, M., and Enzall, C. R.**, Screening of tobacco smoke constituents for mutagenicity using the Ames test, *Toxicology*, 15, 219, 1980.

147. **Gilbert, P., Rondelet, J., Poncelet, F., and Mercier, M.**, Mutagenicity of *p*-nitrosophenol, *Food Cosmet. Toxicol.*, 18, 523, 1980.

148. **Gocke, E., Kind, M. T., Eckhardt, K., and Wild, D.**, Mutagenicity of cosmetics ingredients licensed by the European communities, *Mutation Res.*, 90, 91, 1981.

149. **McCann, J., Choi, E., Yamasaki, E., and Ames, B. N.**, Detection of carcinogens as mutagens in the salmonella microsome test: assay of 300 chemicals, *Proc. Natl. Acad. Sci. U.S.A.*, 72, 5135, 1975.

150. **Shahin, M. M., Bugaut, A., Gilard, P., and Kalopissis, G.**, Studies on the mutagenicity of resorcinol and hydroxy-3-(*p*-amino) anilino-6 *N*[*p*-aminophenol] benzoquinone-monoimine-1,4 in *Salmonella typhimurium, Mutation Res.*, 78, 213, 1980.

151. **Pool, B. L. and Lin, P. Z.**, Mutagenicity testing in the *Salmonella typhimurium* assay of phenolic compounds and phenolic fractions obtained from smokehouse smoke condensates, *Food Chem. Toxicol.*, 20, 383, 1982.

152. **Haugen, D. A. and Peak, M. J.**, Mixtures of polycyclic aromatic compounds inhibit mutagenesis in the salmonella/microsome assay by inhibition of metabolic activation, *Mutation Res.*, 116, 257, 1983.

153. **Toth, L. and Potthast, K.**, Chemical aspects of the smoking of meat and meat products, *Adv. Food Res.*, 29, 87, 1984.

154. **Colmsjo, A. L., Zebuhr, Y. U., and Ostman, C. E.**, Polycyclic aromatic compounds in curing smoke, *Z. Lebensm. Unters. Forsch.*, 179, 308, 1984.

155. **Muller, W. D.**, Filling and smoking frankfurter-type sausages, *Fleischwirtschaft*, 65, 287, 1985.

156. **Wigand, W. and Jahr, D.**, Benzo[a]pyrene content of smoked meat products, *Fleischwirtschaft*, 65, 980, 1985.

157. **Uherova, R., Dubravicky, J., Smirnov, V., and Hrivnak, J.**, Hygienic aspects of liquid smoke, *Proc. Eur. Meet. Meat Res. Workers*, 31, 516, 1985.

158. **Kushwaha, S. C., Clarkson, S. G., and Mehkeri, K. A.**, Polycyclic aromatic hydrocarbons in barbecue briquets, *J. Food Saf.*, 7, 177, 1985.

159. **Maga, J. A.**, Polycyclic aromatic hydrocarbon (PAH) composition of mesquite *(Prosopis fuliflora)* smoke and grilled beef, *J. Agric. Food Chem.*, 34, 249, 1986.

160. **Vaessen, H. A. M. G., Schuller, P. L., Jekel, A. A., and Wilbers, A. A. M. M.**, Polycyclic aromatic hydrocarbons in selected foods; analysis and occurrence, *Toxicol. Environ. Chem.*, 7, 297, 1984.

161. **Gilbert, J., Knowles, M. E., and McWeeny, D. J.**, Formation of C- and S-nitroso compounds and their further reactions, *J. Sci. Food Agric.*, 26, 1785, 1975.

162. **Virk, M. S. and Issenberg, P.**, Nitrosation of phenol and 2,6-dimethyoxyphenol and its effect on nitrosamine formation, *J. Agric. Food Chem.*, 33, 1082, 1985.

163. **Massey, R. C., Crews, C., Dennis, M. J., McWeeney, D., Startin, J. R., and Knowles, M. E.**, Identification of a major new involatile *N*-nitroso compound in smoked bacon, *Anal. Chim. Acta*, 174, 327, 1985.

164. **Hotchkiss, J. H. and Vecchio, A. J.**, Nitrosamines in fried-out bacon fat and its use as a cooking oil, *Food Technol.*, 38(1), 67, 1985.

165. **Skrypec, D. J., Gray, J. I., Mandagere, A. K., Booren, A. M., Pearson, A. M., and Cuppett, S. L.**, Effect of bacon composition and processing on *N*-nitrosamine formation, *Food Technol.*, 38(1), 74, 1985.

166. **Havery, D. C. and Fazio, T.**, Human exposure to nitrosamines from foods, *Food Technol.*, 38(1), 80, 1985.

167. **Sen, N. P., Seaman, S. W., and Baddoo, P. A.**, *N*-nitrosothiazolidine and nonvolative *N*-nitroso compounds in foods, *Food Technol.*, 38(1), 84, 1985.

168. **Wagner, D. A. and Tannenbaum, S. R.**, In-vivo formation of *N*-nitroso compounds, *Food Technol.*, 38(1), 89, 1985.

169. **Pensabene, J. W. and Fiddler, W.**, Formation and inhibition of *N*-nitrosothiazolidine in bacon, *Food Technol.*, 38(1), 91, 1985.

170. **Scanlan, R. A. and Reyes, F. G.**, An update on analytical techniques for *N*-nitrosamines, *Food Technol.*, 38(1), 95, 1985.

171. **Kimoto, W. I., Pensabene, J. W., and Fiddler, W.**, The isolation and identification of *N*-nitrosothiazolidine in fried bacon, *J. Agric. Food Chem.*, 30, 757, 1982.

172. **Pensabene, J. W. and Fiddler, W.**, *N*-nitrosothiazolidine in cured meat products, *J. Food Sci.*, 48, 1870, 1983.

173. **Sen, N. P., Seaman, S. W., and Baddoo, P.,** *N*-nitrosothiazolidine and nonvolatile *N*-nitroso compounds in foods, *Food Technol.*, 38(1), 84, 1985.
174. **Mandagere, A. K., Gray, J. I., Skrypec, D. J., Booren, A. M., and Pearson, A. M.,** Role of woodsmoke in *N*-nitrosothiazolidine formation in bacon, *J. Food Sci.*, 49, 658, 1984.
175. **Helgason, T., Ewen, S. W. P., Jaffray, B., Stowers, J. M., Outram, J. R., and Pollock, J. R. A.,** *N*-nitrosamines in smoked meats and their relation to diabetes, *IARC (Int. Agency Res. Cancer) Sci. Publ.*, 57, 911, 1984.
176. **Pensabene, J. W. and Fiddler, W.,** Factors affecting the *N*-nitrosothiazolidine content of bacon, *J. Food Sci.*, 48, 1452, 1983.
177. **Pensabene, J. W. and Fiddler, W.,** Formation and inhibition of *N*-nitrosothiazolidine in bacon, *Food Technol.*, 38(1), 91, 1985.
178. **Tricker, A. R., Perkins, M. J., Massey, R. C., Bishop, L., Key, P. E., and McWeeny, D. J.,** Incidence of some non-volatile *N*-nitroso compounds in cured meats, *Food Additives Contaminants*, 1, 245, 1984.
179. **Sen, N. P., Baddoo, P. A., and Seaman, S. W.,** *N*-nitrosothiazolidine and *N*-nitrosothiazolidine-4-carboxylic acid in smoked meats and fish, *J. Food Sci.*, 51, 821, 1986.
180. **Loury, D. J., Byard, J. L., and Shibamoto, T.,** Genotoxicity of *N*-nitrosothiazolidine in microbial and hepatocellular test systems, *Food Chem. Toxicol.*, 22, 1013, 1984.
181. National Research Council, *The Health Effects of Nitrate, Nitrite and N-nitroso Compounds*, National Academy Press, Washington, D.C., 1981.
182. **McCutcheon, J. W.,** Nitrosamines in bacon: a case study of balancing risks, *Public Health Rep.*, 99, 360, 1984.
183. **Havery, D. C. and Fazio, T.,** Human exposure to nitrosamines from foods, *Food Technol.*, 39(1), 80, 1985.
184. **Vecchio, A. J., Hotchkiss, J. H., and Bisogni, C. A.,** *N*-nitrosamine ingestion from consumer-cooked bacon, *J. Food Sci.*, 51, 754, 1986.
185. **Wickstrom, K., Pyysalo, H., Plaami-Heikkila, S., and Tuominen, J.,** Polycyclic aromatic compounds (PAC) in leaf lettuce, *Z. Lebensm. Unters. Forsch.*, 183, 182, 1986.
186. **Hopia, A., Pyysalo, H., and Wickstrom, K.,** Margarines, butter and vegetable oils as sources of polycyclic aromatic hydrocarbons, *J. Am. Oil Chem. Soc.*, 63, 889, 1986.
187. **Sullivan, P. D.,** Free radicals of benzo[a]pyrene and derivatives, *Environ. Health Perspect.*, 64, 283, 1985.
188. **Obana, H., Hori, S., Tanaka, R., and Kashimoto, T.,** Dietary intakes of polycyclic aromatic hydrocarbons, *J. Food Hyg. Soc. Jpn.*, 25, 35, 1984.
189. **Yamazaki, H., Minami, J., Ichikawa, T., and Kondo, M.,** Analysis of polycyclic aromatic hydrocarbons in raw and broiled fishes, *J. Food Hyg. Soc. Jpn.*, 18, 368, 1977.
190. **Badger, G., Kimber, R., and Spotswood, T.,** Polycyclic aromatic hydrocarbons for the pyrolysis of various organic compounds, *Nature*, 187, 663, 1960.
191. **Schmeltz, I. and Hoffmann, D.,** *Carcinogenesis*, Vol. 1, Frendenttal, R. I. and Jones, P. W., Eds., Raven Press, New York, 1976.
192. **Fedonin, V. F., Kuznetsov, V. V., Bershova, T. M., and Basmanov, P. I.,** Content of benz[a]pyrene in dispersed smoking medium in relation to aerosol particle size, *Myasn. Ind. SSSR*, 12, 35, 1978.
193. **Lawrence, J. F. and Das, B. S.,** Determination of nanogram/kilogram levels of polycyclic aromatic hydrocarbons in foods by HPLC with fluorescence detection, *Int. J. Environ. Anal. Chem.*, 24, 113, 1986.
194. **Grimmer, G. and Naujack, K. W.,** Gas chromatographic profile analysis of basic nitrogen-containing aromatic compounds (azaarenes) in high protein foods, *J. Assoc. Off. Anal. Chem.*, 69, 537, 1986.
195. **Arashidani, K., Yoshikawa, M., and Kodama, Y.,** A simplified analysis of polynuclear aromatic hydrocarbons in soil and sediment by high performance liquid chromatography, *Eisei Kagaku*, 31, 24, 1985.
196. **Tsuji, I., Koide, K., Moriyama, H., Tanabe, K., and Matsushita, H.,** Analysis of polynuclear aromatic hydrocarbons in shellfishes, seabottom sediments and sea water by high performance liquid chromatography, *J. Food Hyg. Soc. Jpn.*, 26, 50, 1985.
197. **Friocourt, M. P., Bodennec, G., and Berthou, F.,** Determination of polyaromatic hydrocarbons in scallops *(Pecten maximus)* by UV fluorescence and HPLC combined with UV and fluorescence detectors, *Bull. Environ. Contam. Toxicol.*, 34, 228, 1985.
198. **Gunther, F. A. and Westlake, W. E.,** Residue behavior of polynuclear hydrocarbons on and in oranges, *Residue Rev.*, 17, 81, 1967.
199. **Cavalieri, E. and Rogan, E.,** Role of radical cations in aromatic hydrocarbon carcinogenesis, *Environ. Health Perspect.*, 64, 69, 1985.