

NATURAL SMOKE: COMPOSITION AND PROPERTIES

Aaron E. Wasserman and Walter Fiddler
Eastern Utilization Research and Development Division
Agricultural Research Service, USDA

Smoke is a gas, or vapor, containing a large number of chemical compounds that has become visible because some of the compounds condense on particles of dust or dissolve in droplets of water in the atmosphere.

The chemical compounds are formed from the combustion of wood which consist, essentially of 40-60% cellulose and 20-30% each of hemi-cellulose and lignin. The two sugar polymers are the source of most of the acids, furans alcohols and carbonyls while lignin is the source of most of the phenolic compounds. Goos (1952) lists 213 compounds formed by the destructive distillation of wood; many of these compounds are also formed during the oxidative combustion occurring in smoke generation. To understand the process of smoking and the reactions involved it is necessary to isolate and identify all the components in smoke and establish their relationship to odor, taste and color of the smoked product.

Several parameters of smoke generation have been studied previously and the changes in chemical composition reported. The following are examples of this work.

Type of wood

Hard woods like beech and oak produce smoke high in acids; soft woods like spruce and pine yield smoke high in carbonyls; and smoke from poplar wood contains large concentrations of phenols. Soft woods yield a smoked product with a desirable flavor, but only if the smoke is produced outside the smokehouse.

Temperature

There is considerable controversy over the effect of temperature on the composition of smoke. One study (Simon et al., 1966) shows the concentration of phenols and carbonyls increase sharply as temperature rises above 300°C, whereas another (Tilgner et al., 1962a) shows phenol concentration

maximum is reached at about 200°C in the oxidation phase and the acids increase continuously with increasing temperature. The problem lies in measuring the temperature. A thermocouple located 1 inch above the sawdust bed in a laboratory-designed generator registered a temperature approximately 300°C below that in the center of the sawdust bed (Figure 1). Furthermore, the combustion of the wood is an exothermic reaction in which localized temperatures may be greater than that of the heat source.

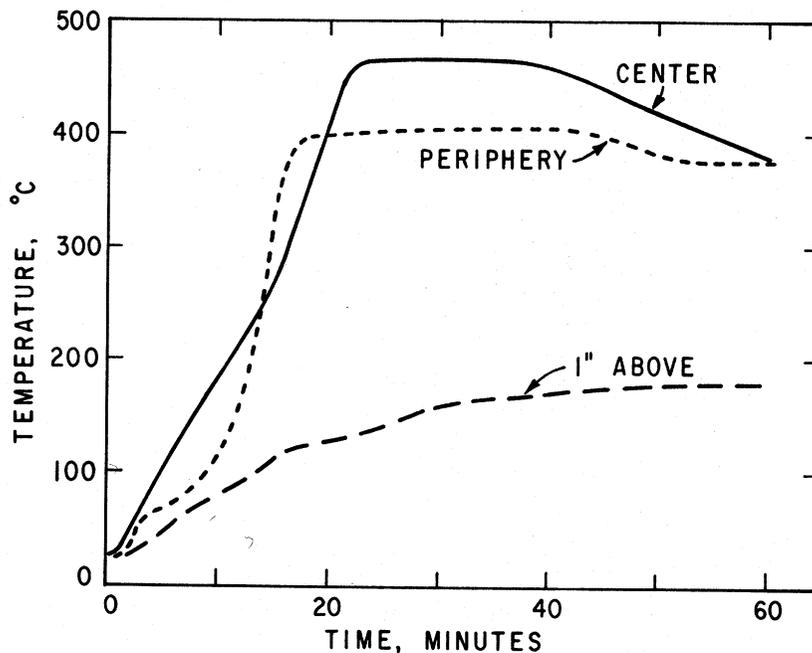


Figure 1. Temperature measured at several points in, and above, the glowing sawdust bed in a laboratory smoke generator.

Moisture

The design of the generator determines whether wet or dry sawdust can be used. With increasing moisture in the sawdust the particle size and phenol concentration decrease while

the amount of acids and carbonyls increase. Thus, the flavor of the smoked product is more acid. The color of the product produced by dry smoke is browner than the golden tone achieved with smoke from the moist sawdust (Tilgner et al., 1962b).

Conditions in the smokehouse affect the reactions of the smoke with product but little has been published on this. One study indicates that more of the smoke components are dissolved on the moist surfaces of the meat, while another project using water-filled frankfurter casings indicates a decrease in acids, carbonyls and phenols adsorbed into the casings with increasing humidity (Simon et al., 1966). At a constant humidity, increasing the smokehouse temperature led to a slight increase in carbonyls, no change in acids and a large increase in the amount of phenols taken into the water-filled links.

The above studies were done with classes of compounds which do not permit the qualitative or quantitative determination of the individual components: The use of the gas chromatograph (GC) permits the separation and isolation for identification of the individual components of a complex solution. Identifications were made on the volatile part of whole smoke and on smoke condensates using GC retention time and infrared (IR) structure comparisons to known standards (Doerr et al., 1966; Fiddler et al., 1966). A comparison of the volatiles of the whole smoke GC profile with that of the condensate is shown in Figure 2. The former contains one peak which is a mixture of gases, CO, CO₂, methane and other hydrocarbons, not found in the condensate. Peaks 3 and 5a (Figure 2), identified as furan (or propional) and 2-methyl furan, respectively, are present in greater concentration in whole smoke. The volatile and non-volatile components identified in a smoke condensate are shown in Table 1. The composition of the condensate changes on storage for several hours. Methyl alcohol reacts with formic and acetic acids in the condensates to produce the less harsh esters. Taste panel evaluations of smoke condensates (Table 2) show the preference responses to condensates of varying ages.

A study to evaluate the effect of generation parameters on the smoke components was begun by varying the O₂ concentration of the air to the heated sawdust. The peak areas/gm. sawdust consumed for 14 of the 22 components of the non-volatile fraction were compared (Figure 3). As the O₂ concentration increased from 0 to 50%, the concentration of furyl

Table 1. Composition of smoke condensate

Gases	CO, CO ₂ , CH ₄	Alcohols	Methanol
Carbonyls	Acetaldehyde	Ethanol	iso-Propanol
	Acetone	Furfuryl alcohol	
	iso-Valeraldehyde	Phenols	
	Methyl vinyl ketone	1, 2-Dimethoxybenzene	
	Diacetyl	Phenol	
	Crotonaldehyde	Guaiacol (2-methoxy-phenol)	
	Acetol	4-Methylguaiacol	
	2-Cyclopentenone	4-Ethylguaiacol	
	Furfural	4-Propylguaiacol	
	5-Methylfurfural	4-Vinyl Guaiacol	
	Cyclotene (3-methyl-cyclopent-2-en-2-of-1-one	Eugenol (4-Allylguaiacol)	
Furans		Syringol (2, 6-dimethoxy-phenol)	
	Furan	4-Methylsyringol	
	2-Methylfuran	4-Ethylsyringol	
Acids		4-Propylsyringol	
	Acetic acid	Vanillin	
Esters			
	Methyl formate		
	Methyl acetate		

Table 2. Effect of Age on Smoke Condensate Taste Compared to 2-Month Old Control

B (1 Month old) - 4.1 ^a
C (5 Hours old) - 2.8
B 3.9
C (48 Hours old) - 3.6
B 3.8
C (96 Hours old) - 3.6

^a7 Point hedonic scale: 4.0 = like as much as control.

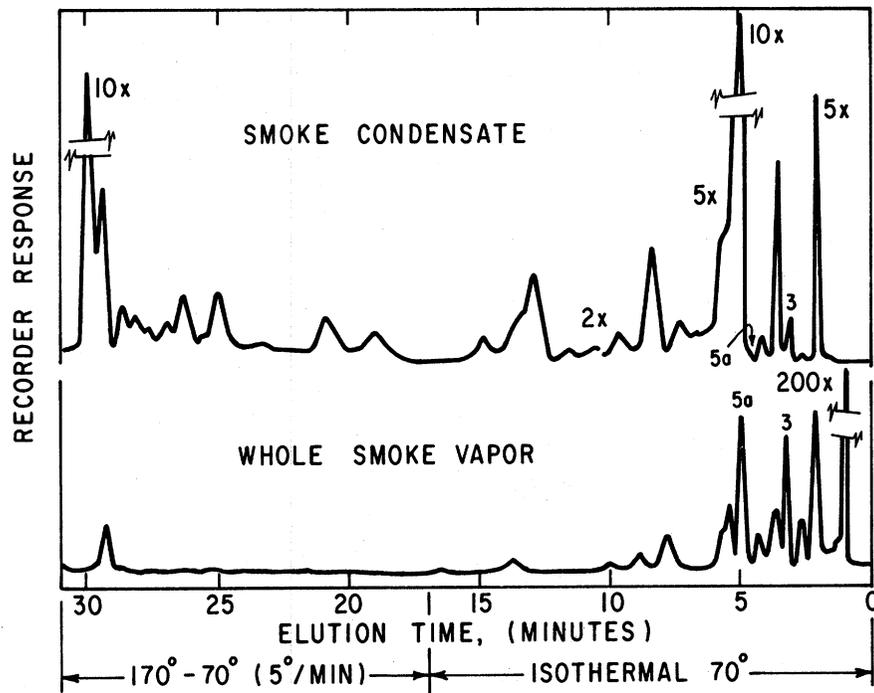


Figure 2. Comparison of the volatile components of whole smoke vapor and smoke condensate.

compounds decreased. The other major group of compounds in this fraction, the phenols, increased in 10% O₂, then decreased more rapidly than the furyl components. The taste panel could distinguish the 0 to 10% O₂ smoke condensate from the 20% O₂ (normal air) condensate but statistical differences could not be obtained between 20, 30 and 50% O₂-produced condensates. Of the panelists able to detect differences, most preferred the

normal (20% O₂) condensate. On the basis of the degree of smokiness there were no statistically significant differences among the condensates.

Further attempts to correlate chemical composition, generation parameters, and taste panel responses were halted because the condensates were distributed on the walls of the apparatus in such a manner that quantitative recoveries were not possible. This is a factor to be considered in all quantitative reports on smoke constituents.

From the present state of our knowledge it appears that smoke flavor is not due to one single chemical in the complex mixture, but is the result of blending of the flavors of a number of components. A commercial liquid smoke solution was used as the basis for this study. An ether extract of the solution was judged by the panel to give as smoky a flavor to frankfurters as the original. The extract was fractionated into three sections based on the aromas of the compounds emerging from the GC (Figure 4). The volatile material before cyclotene (Fraction A) and the higher boiling compounds after vanillin (Fraction C) did not impart a smoky flavor to frankfurters, but the middle fraction, from cyclotene to vanillin (Fraction B), was judged as smoky as the original solution. This fraction contains phenols as well as some other compounds and is not entirely comparable to the "phenolic fraction" obtained by steam distillation by other workers and claimed to be responsible for smoke flavor.

"Compounding", or mixing the known components, did not give a solution with a smoky flavor. This may be due to: (1) not having the proper ratios of the components, (2) not having identified all components, (3) important flavor components being present in concentrations too small to be detected, (4) the commercial chemicals used for compounding containing undesirable impurities. Other workers have been unsuccessful in compounding; Spanyer (1966) in Hungary identified components in wood smoke by wet chemical methods and GC. However, when the chemicals were combined in the same proportions as in the smoke solutions so that chromatographic patterns were alike the aroma and flavor of the mixtures were not the same as those of natural smoke. Spanyer (1966) admitted he could not duplicate the smoke flavor.

Since the flavor impact of a compound is not related to its concentration, the ratio of the odor and taste thresholds and the concentration in smoke may be an indicator of its importance. However, in smoking meat the possible differences

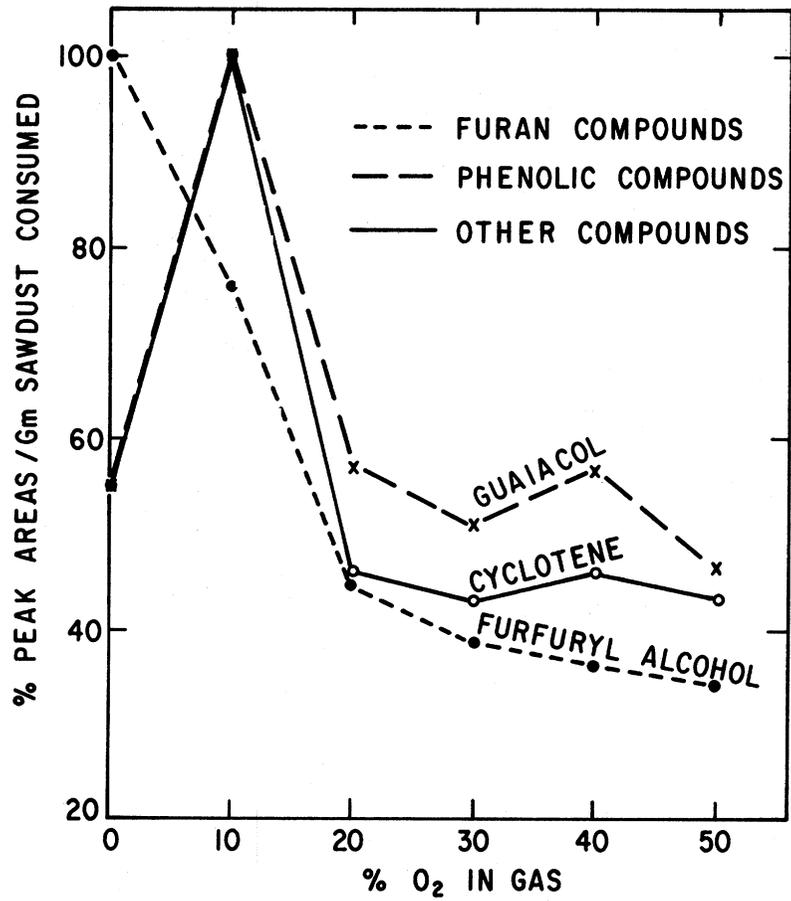


Figure 3. Variation in concentration of several smoke components with change in oxygen content of air passing through the sawdust.

in the solubility of the components in both the fat and water phases of the meat must be considered in setting up a model system. The thresholds of three smoke components, guaiacol, 4-methylguaiacol and 2,6-dimethoxyphenol (syringol), were determined in oil and water (Wasserman, 1966). The panel detected about 100 times less guaiacol than syringol in water but the levels of detection were about the same in oil. Syringol

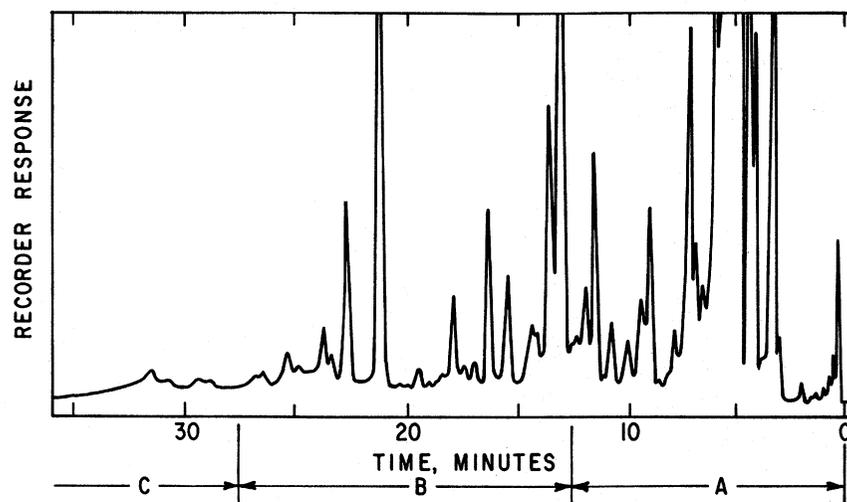


Figure 4. Separation of ether extract of smoke solution for organoleptic evaluation.

is less soluble in oil than in water so more molecules are present in the headspace. The ratios of concentration to threshold show that guaiacol, which is present in low concentration in smoke, has large flavor impact, so trace quantities may influence response to overall flavor.

Liquid smoke preparations are becoming more popular because they: (1) eliminate expense and difficulties of generating fresh smoke; (2) permit removal of harmful and undesirable components; (3) permit quality control of flavor and color. Liquid smoke solutions are of three types: (1) condensate or pyrolygneous acid; (2) smoke solutions made by dissolving smoke constituents in water, oil or other carrier; (3) artificial or imitation smokes made of mixtures of chemicals that give a smoky aroma or natural smoke solutions fortified with chemicals.

The GC profiles of several commercial smoke preparations were obtained and representative curves are shown in Figures 5 and 6. The profile of a smoke solution is shown in Figure 5, with some of the components indicated as landmarks. In the area in which the flavor fraction is located,

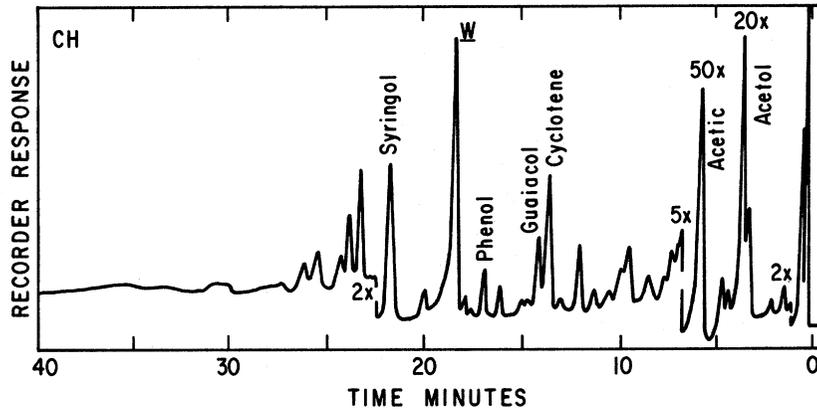


Figure 5. Gas chromatographic profile of a commercial liquid smoke preparation with some components indicated.

differences in the concentrations of the marked peaks were noted among the several commercial solutions tested. However, the frankfurters prepared from these solutions were judged to differ very little in taste. Figure 6 is the profile of an artificial smoke solution. The concentration of components is very great and their identity was not investigated.

While the smoke solutions are currently used as a dip or spray for the formed products, or incorporated into the emulsion, a new technique has been recently described in which the smoke solution has been vaporized into the smokehouse, thus creating a situation similar to the natural smoking conditions except for the presence of desirable components only. This is an interesting development and seems worthy of further analytical investigation.

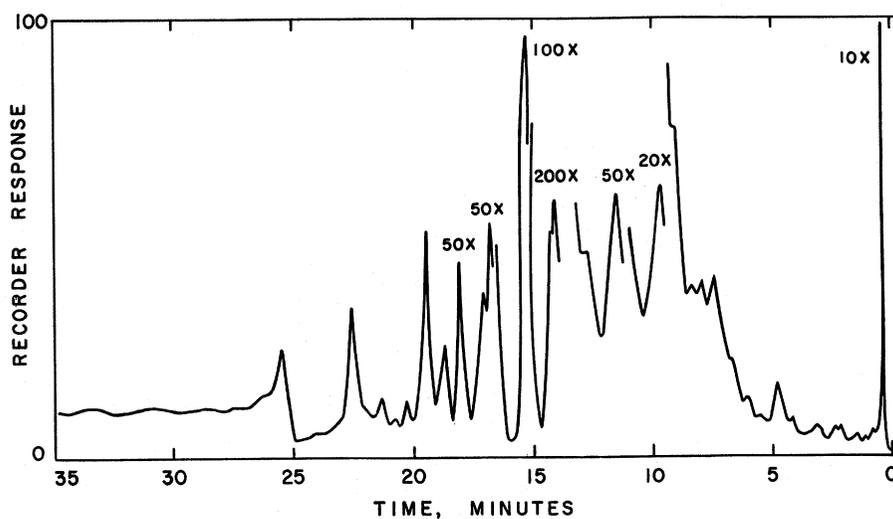


Figure 6. Gas chromatographic profile of a commercial synthetic liquid smoke preparation.

Literature Cited

1. Doerr, R. C., A. E. Wasserman and W. Fiddler. 1966. Composition of hickory sawdust smoke. Low-boiling constituents. *J. Agr. Food Chem.* 14:662.
2. Fiddler, W., R. C. Doerr, A. E. Wasserman and J. M. Salay. 1966. Composition of hickory sawdust smoke. Furans and phenols. *J. Agr. Food Chem.* 14:659.
3. Goos, A. W. The thermal decomposition of wood. In *Wood Chemistry*, (Edited by L. E. Wise and E. C. Jahn). Vol II, 2nd ed. Reinhold, N. Y. 1952. p. 826.
4. Simon, S., A. A. Rypinski and F. W. Tauber. 1966. Water-filled cellulose casings as model absorbents for wood smoke. *Food Tech.* 20:1494.
5. Spanyer, P., E. Kevei and M. Blazovich. 1966. On the problem of smoking food. VI. Components with higher boiling points in smoke condensate. *Z. Lebensm.-Untersuch. Forsch.* 133:1. (In German).

6. Tilgner, D., K. Miler, J. Prominski and D. Darnowska. 1962a. The influence of smoke production parameters upon its amount of phenolic and acidic fractions. *Tehnologija Mesa (Journal of the Yugoslav Meat Industry)*, special ed. (Advances in the Engineering of the Smoke Curing Process, II. Int. session, 1960, Gdansk, Poland), p. 18.
7. Tilgner, D., Z. Ziemba and Dju-Hak-Dju. 1962b. The quality and composition of curing smoke as influenced by water vapor. *Tehnologija Mesa (Journal of the Yugoslav Meat Industry)*, special ed. (Advances in the Engineering of the Smoke Curing Process, II. Int. session, 1960, Gdansk, Poland), p. 21.
8. Wasserman, A. E. 1966. Organoleptic evaluation of three phenols present in wood smoke. *J. Food Sci.* 31:1005.