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Analysis of Liquid Smoke and Smoked Meat Volatiles by Headspace Gas Chromatography

R. Wittkowski,* W. Baltes

Institut für Lebensmittelchemie, Technische Universität Berlin, D-1000 Berlin 12, Germany

W. G. Jennings

Department of Food Science and Technology, University of California, Davis, California 95616, USA

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ABSTRACT

Headspace samples of smoked sausages and bacon were analyzed and compared with headspace samples of a commercial liquid smoke flavoring, in efforts to determine components contributing to the aroma of smoked foods. Sensitivities were enhanced by methods permitting GC and GC/MS analysis of large headspace volumes without additional heat treatments or concentration steps. A series of monoterpene hydrocarbons dominated the volatiles of smoked meat products, but were not detected as components of the liquid smoke.

INTRODUCTION

Early man developed smoke treatments in his efforts to inhibit spoilage and enhance the keeping qualities of foodstuffs. Such treatments are still widely used, but their primary purpose today is to impart a smoke flavor to the finished product. There have been many attempts to isolate and identify these flavor components (Husaini & Cooper, 1957; Spanyer *et al.*, 1960; Foster & Simpson, 1961; Toth & Wittkowski, 1985), but our knowledge is

* Present address: Max von Pettenkofer-Institut, Bundesgesundheitsant, Postfach 33 00 13, D-1000 Berlin 33, Germany.

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still incomplete. Phenols have been the subject of several recent investigations (Baltes & Söchtig, 1979; Toth, 1982; Toth & Wittkowski, 1985; Wittkowski, 1985), probably because their presence is usually associated with the desirable technological effects of these curing treatments; in some cases the smoke flavor has been attributed to the presence of these materials (Wasserman, 1966; Fujimaki *et al.*, 1974; Baltes & Söchtig, 1979), and sometimes to a single component. A previous investigation (Toth & Wittkowski, 1985), however, indicated that an array of phenols was necessary to produce a qualitatively desirable smoke flavor in foodstuffs. Attempts to duplicate the flavor of smoked ham or smoked sausage with various mixtures of phenols have been unsuccessful. In addition, it remains unclear whether the more important flavor compounds are simply smoke constituents entrapped by the food, or whether they result from chemical reactions between smoke components and food ingredients.

In attempts to clarify the contribution of smoke components to the flavor of smoked meat and smoked sausage, headspace compositions were studied, using techniques that avoided the usual sample preparation procedures.

MATERIALS AND METHODS

Gas chromatography

Both a Hewlett–Packard 5710A, equipped with FID, interfaced to a Hewlett–Packard 3392A integrator, and a Varian 3700 interfaced to the data processor of a Hewlett–Packard 5880A gas chromatograph, were used to generate these data. Both instruments were retrofitted with on-column injectors. The type of fused silica open tubular column and chromatographic conditions are specified in Fig. 1. GC/MS analyses reported here were performed on a Finnigan 4000, directly interfaced to a 30 m × 0·25 mm DB-1 column.

Syringes

Injections of less than 1 ml employed a 500 μl gastight syringe (J&W Scientific), and larger size injections were made with a 10 ml gastight syringe (Hamilton). Both syringes were fitted with needles of deactivated fused silica tubing, 0·15 mm id × 0·2 mm od, 20–30 cm long.

Samples and sampling

The samples of smoked meats were purchased retail in a Berlin market; liquid smoke was a commercial preparation from a Davis supermarket.

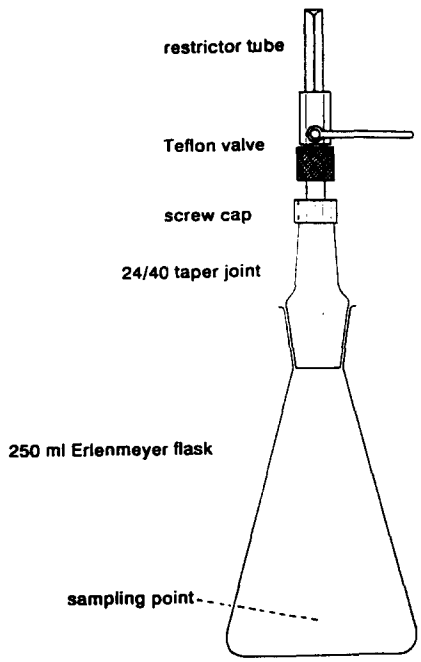

Fig. 1. Sampling device for large headspace volumes.

Larger samples and larger containers are necessary to permit the withdrawal of large headspace volumes without affecting the relative concentrations of individual volatiles in that headspace sample. The bottoms were removed from 2 ml screw-capped vials, which were then fused to 24/40 standard taper joints (inner) with the threaded end exposed. With the restrictor tube-fitted stainless steel-Teflon valve closures (an integral part of the 2 ml sample vials; J & W No. 3202000) attached, these were used to seal the 250 ml Erlenmeyer flasks used as sample containers (Fig. 1).

Samples were withdrawn following sample equilibration (below), by inserting the fused silica needle of the 10 ml sampling syringe into the restrictor tube, opening the valve, and further inserting the needle until the tip was 1 cm above the sample surface. Samples were withdrawn (and later injected) at a speed of 1 ml/2 min.

Prior to injection, a section of the inlet end of the fused silica column was immersed in a Dewar flask containing liquid nitrogen (Takeoka & Jennings, 1984) and the carrier gas flow was interrupted. Dry ice-acetone proved unsatisfactory as a coolant, due to break-through of some low molecular weight components. The injection of these large sample volumes was facilitated by dissipation of the column head pressure prior to injection. During injection, the tip of the syringe needle within the column was immediately in front of that section immersed in the coolant. Following injection, the needle was retracted until the tip was visible in the restrictor

tube, the valve was closed, the syringe completely withdrawn, and the carrier gas line returned to full pressure. After a 5 min delay, the Dewar flask was removed and the program initiated.

RESULTS AND DISCUSSION

Sampling and injection procedures

These were evaluated by comparing the standard deviations of peak areas of seven monoterpene hydrocarbons (described later) in five 5 ml headspace injections of Landjäger (a hard, salami-type German wurst) at two rates of sampling and injection (Table 1).

A rate of 1 ml/2 min yielded smaller standard deviations than did a rate of 2 ml/1 min.

The influence of sample size on the response linearity of each of the seven monoterpene hydrocarbons was evaluated by injections of 1, 3, 5, 8 and 10 ml samples, at both the faster and slower rates of sample withdrawal and sample injection. The results again support the slower rate of sampling and injection. The linear regression values for the terpenes are also listed in Table 1.

Analysis of liquid smoke samples

Headspace injections of 500 μl of a liquid smoke sample were analyzed by use of liquid nitrogen as coolant. Lacking sub-ambient capability, the

TABLE 1
Standard Deviations and Linear Regression Values of the GC-Response for the Fast and Slow Sampling and Injection Procedure

Compound	*Standard deviation (%)*		*Linear regression*	
	Fast	*Slow*	*Fast*	*Slow*
α-Pinene	10·2	4·2	0·961 8	0·999 8
Sabinene	10·5	4·8	0·966 6	0·999 8
Myrcene	10·0	7·4	0·970 8	0·999 9
α-Phellandrene	5·9	10·1	0·969 8	0·995 7
3-Carene	10·8	5·0	0·968 2	0·999 9
β-Phellandrene	13·8	6·2	0·969 8	0·999 9
Limonene	10·9	5·9	0·969 4	0·999 9

beneficial effects of lower oven temperatures were estimated by cooling the oven with dry ice to an initial temperature of −10°C. While not reproducible, the increase in solute partition ratios resulted in enhanced resolution of lower boiling solutes and facilitated their mass spectrometric identification.

An alternative approach was the use of thicker film columns. However, the very thick film, while increasing solute partition ratios and enhancing the separation of lower molecular weight solutes, also reduces the inner diameter of the column to a point that insertion of the fused silica needle becomes difficult; the stationary phase film can be disrupted, and needle breakage can also result. The problem was alleviated by coupling a retention gap to the column. The use of this combination, even with a thin film column, has turned out to be beneficial in terms of sharpening the solute bands when injecting large headspace volumes.

Analysis of smoked meat samples

Figure 2 compares headspace chromatograms of liquid smoke and several smoked meat products.

Among the major components are several monoterpene hydrocarbons dominated by alpha pinene, sabinene, 3-carene and limonene. Lesser concentrations of alpha- and beta-phellandrene, myrcene and beta-pinene are also present. The chromatogram of the 'Berliner Schinkenknacker' is characterized by the same monoterpenes that occur in 'Landjäger', which occur in roughly the same proportion. All were identified on the basis of retention indices and mass spectra. The mass spectrum of the peak preceding alpha pinene is also indicative of a monoterpene hydrocarbon, but its identity has not yet been established. These same components also occur in the smoked bacon, but the relative amounts are different. The results obtained by low temperature GCMS are listed in Table 2 and give an overview to the qualitative headspace composition of liquid smoke, smoked bacon, and 'Landjäger'.

Because the identification of the light volatiles in particular was tentatively performed, we cannot claim the results to be representative. Nevertheless, they indicate some generalities, which can be summarized as follows:

1. Only 2-propanone, 3-methylbutanal, benzene and furan were present in all three samples.
2. The occurrence and diversity of light volatile and polar compounds is much bigger in the headspace of liquid smoke than in smoked meat products.

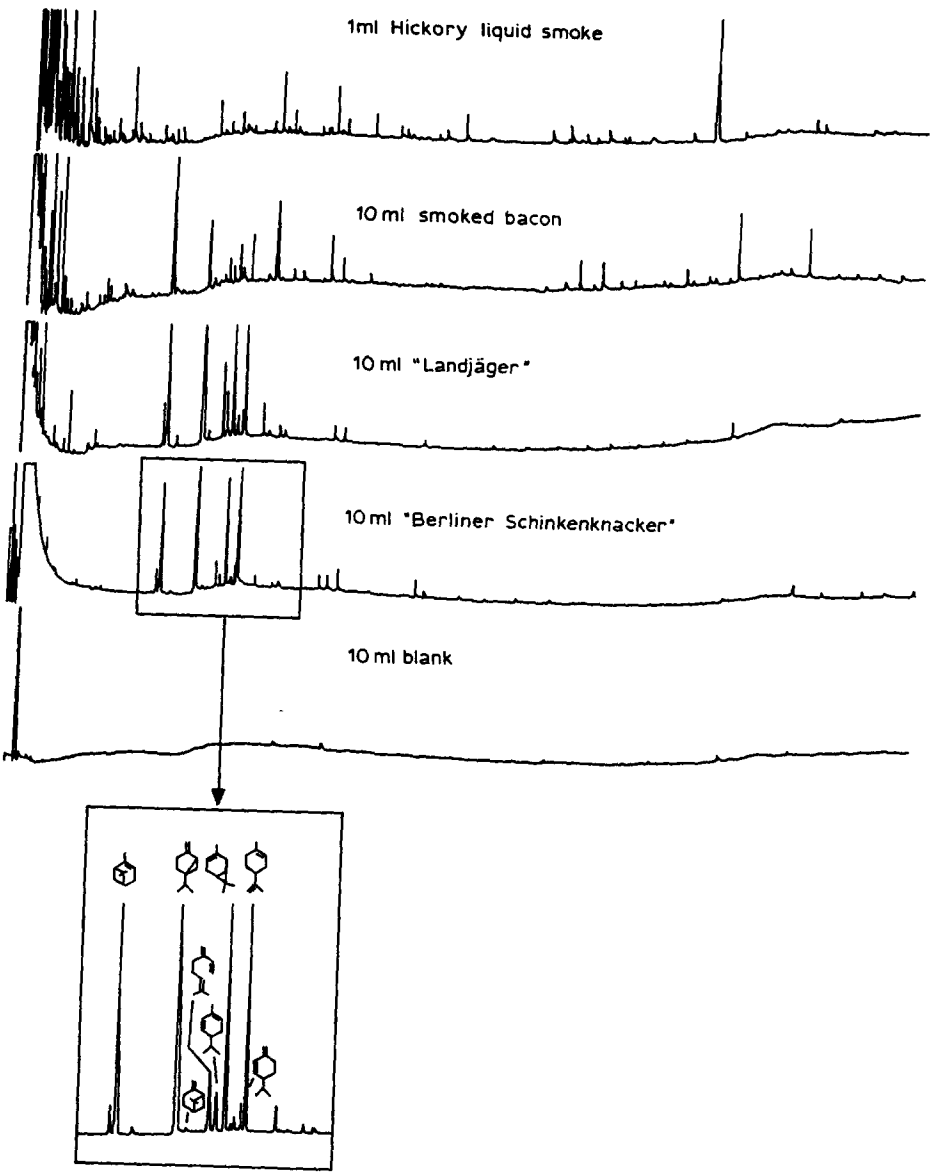

Fig. 2. Headspace gas chromatograms of a liquid smoke preparation and several smoked meat products (30 m × 0·25 DB-1 fused silica, d_f 0·25 μm; temp. program: 25°C for 10 min, then 2°C/min to 200°C).

TABLE 2

Qualitative Comparison of the Headspace Compositions of Liquid Smoke, 'Landjäger', and Smoked Bacon ('+' indicates 'detectable', '−' indicates 'not detectable')

(a) Alcohols, aldehydes and ketones.

Compound	*Liquid smoke*	*'Landjäger'*	*Smoked bacon*
Ethanol	−	+	+
3-Methyl-1-butanol	−	−	+
1-Hydroxy-2-propanone	+	−	−
2-Propanone	+	+	+
2-Methylpropanol	+	−	+
2,3-Butandione	+	+	−
Butanal	+	−	−
2-Butenal	+	−	−
trans-But-2-enal	+	−	−
3-Methyl-2-butanone	+	−	−
3-Methyl-3-buten-2-one	+	−	−
2-Pentanone	+	−	−
2,3-Pentandione	+	−	−
2-Butanone	+	−	+
2-Methyl-2-propenal	+	−	−
3-Methylbutanal	+	+	+
3-Hexanone	+	−	−
2-Hexanone	+	+	−
4-Heptanone	+	−	−
1-Cyclopropyl-1-propanone	+	−	−
2-Methyl-2-butenal	+	−	−
2-Methyl-3-pentanone	+	−	−
Cyclopentanone	+	−	+
3-Methyl-3-penten-2-one	+	−	−
Benzaldehyde	+	−	−
1-Phenyl-1-pentanone	+	−	−
3-Phenyl-2-propanal	+	−	−
3-Methylcyclopentanone	−	−	+

TABLE 2—*contd.*

(b) Esters.

Compound	*Liquid smoke*	*'Landjäger'*	*Smoked bacon*
Methylformate	+	−	−
Methylacetate	+	−	−
Methylisopropionate	+	−	−
Ethylacetate	+	+	−
Methylpropionate	+	−	−
2-Propenylacetate	+	−	−
Methyl-2-methylpropionate	+	−	−
Methylbutyrate	+	+	−
Ethylpropionate	−	−	+
Propylacetate	+	−	−
Ethylbutyrate	−	+	−
Ethyl-2-methylpropionate	−	+	−
Methylvalerate	+	−	−

(c) Heterocycles.

Compound	*Liquid smoke*	*'Landjäger'*	*Smoked bacon*
Furan	+	+	+
2-Methylfuran	−	+	+
2,5-Dimethylfuran	+	−	−
4-Methyl-2,3-dihydrofuran	+	−	−
2-Furfural	+	−	−
Methylfuranoate	+	−	−
Benzofuran	+	−	−
2,7-Dimethylbenzofuran	+	−	−
Tetrahydrofuran	+	−	−
2,5-Dihydrofuran	+	−	−

TABLE 2—*contd.*

(d) Hydrocarbons.

Compound	*Liquid smoke*	*'Landjäger'*	*Smoked bacon*
Pentane	−	−	+
Hexane	−	+	+
2-Methylhexane	−	−	+
3-Methylhexane	−	−	+
Heptane	−	−	+
Octane	−	−	+
Benzene	+	+	+
Toluene	+	−	+
Ethylbenzene	+	−	−
1,2-Dimethylbenzene	+	−	−
1,4-Dimethylbenzene	+	−	−
Timethylbenzene	+	−	−
unknown Terpene	−	+	+
α-Pinene	−	+	+
β-Pinene	−	+	+
Sabinene	−	+	+
3-Carene	−	+	+
α-Phellandrene	−	+	+
β-Phellandrene	−	+	−
Limonene	−	+	+
Myrcene	−	+	+

(e) Others.

Compound	*Liquid smoke*	*'Landjäger'*	*Smoked bacon*
Dimethyldisulfide	+	−	−
1-Methoxy-4-methyl-benzene	+	−	−
Guaiacol	+	−	−
1-Propenyloxybutane	+	−	−
Diethylether	−	+	+

3. The volatiles of smoked meat products are dominated by a high proportion of hydrocarbons.
4. The gas chromatograms of smoked bacon and 'Landjäger' were dominated by a series of terpenes, substances, which could not be detected in the headspace of the liquid smoke preparation although the latter includes some other hydrocarbon compounds.
5. The hydrocarbons found in the headspace of liquid smoke were exclusively aromatic compounds.

The point most noteworthy is that terpenes have not been previously reported in smoked foods. They could originate either from wood smoke or from spices used in the sausages, but the fact that they are also present in smoked (unspiced) bacon would seem to favor wood smoke as their source. Terpenes were also reported by Nikitin (1955), who postulated that they were reaction products formed by wood combustion. While no terpenes were detected in liquid smoke, this latter product is the aqueous supernatant from bubbling smoke through water. The apolar terpenes would be expected to partition toward the oily residues that are discarded in the manufacturing process.

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