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ANALYSIS OF SMOKE AND SMOKED FOODS

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Abstract - After a review on the chemical classes of compounds present in smoke and smoked foods and on the desirable and undesirable effects of these compounds, the influence of the smoking technology on the composition and the amount of the fractions of polycyclic aromatic hydrocarbons (PAH) and phenolic compounds in smoke and smoked foods is briefly described. The importance of profound knowledge on the composition and the effect of liquid smokes (smoke condensates) and other ingredients for smoke flavouring is pointed out. The procedures for isolation and determination of PAH present in smoke and smoked foods, particularly in smoked meat products, are discussed. A new method for the clean up of the PAH fraction, developed by Potthast, reduces time and costs of the assay remarkably. Furthermore, procedures for isolation and determination of phenols are discussed. A new method for the isolation of phenols from smoked meat products was developed by Potthast; this procedure needs less time and is easier to carry out than the earlier methods. Now reliable and time-saving methods for isolation and identification of PAH and phenols are available. The exact identification of single components, however, is expensive and time-consuming. The quality control could be only simplified if further research would lead to some few "key substances" the concentration of which could give sufficient information on quality and toxicological properties of smoked products.

INTRODUCTION

Wood smoke, which is used for smoking of foods, contains a tremendous number of compounds formed by the pyrolysis of wood constituents such as cellulose, hemicellulose and lignin. More than 300 substances could be detected but many more may exist. Many of these smoke components can be found in smoked foods. The most important classes of chemical compounds detected in smoke and liquid smoke preparations are phenols (14, 25, 31, 39, 46, 51, 59, 80, 83, 97), carbonyls (14, 17, 25, 30, 39, 46, 59, 69, 95, 97), acids (14, 17, 25, 30, 39, 46, 59, 95, 97), furans (14, 25, 39, 46), alcohols and esters (25, 39, 46, 59), lactones (14, 25, 46) and polycyclic aromatic hydrocarbons (12, 15, 16, 31, 32, 39, 60, 66, 72, 73, 79, 81, 86, 101, 103, 105, 106, 107, 108). Presently the approximate numbers of identified components of the several chemical classes of compounds present in smoke are as follow (25, 46, 72): 45 phenolic compounds, more than 70 carbonyls such as ketons and aldehydes, 20 acids, 11 furans, 13 alcohols and esters, 13 lactones and 27 polycyclic aromatic hydrocarbons.

*Abbreviations: CYH: cyclohexane; DMF: dimethylformamide; GC: gaschromatography; MS: massspectrometry; PAH: polycyclic aromatic hydrocarbons; TC: thinlayer-chromatography;

The desirable effects of smoking on foods are flavoring, preservation and coloring; undesirable effects are contamination with toxic components of smoke and some destruction of essential amino acids of food proteins. Such desirable and detrimental effects were attributed to certain classes of components of smoke or liquid smokes. So, the typical aroma of smoked foods seem to be due mainly to the effect of certain phenols (3, 5, 6, 15, 23, 25, 31, 58, 64, 65, 68, 80, 112, 113); carbonyls and acids are supposed to cause at least differences in the flavour of smoked foods (5, 15, 23). The entoxidative effect of curing smoke and liquid smoke preparations is caused mainly by the presence of certain phenols (54, 57, 75). The characteristic golden-brown colour of smoked foods seems to be an effect of carbonyl compounds present in wood smoke which are thought to undergo non-enzymic browning with the amino groups of protein in the food matrix (4, 25, 85, 89, 116, 117); a similar colouring effect is also caused by the carbonyls of liquid smokes (35, 56). These browning reactions of the Maillard type have, of course, also an undesirable influence because they destroy essential amino acids. The amount of essential amino acids such as lysine in smoked meat products is lowered by smoking and by flavoring with liquid smokes (4, 40, 55, 85). As to the toxic components of curing smoke and smoke condensates, the polycyclic aromatic hydrocarbons (PAH)* such as benzo (a)-pyrene have received particular attention (11, 25, 32, 79, 108) because some of these compounds are cancerogenic. However, also certain phenols are supposed to be toxic because of a cocancerogenic effect in the presence of PAH (24, 42, 43, 44, 110, 111).

From the results published it becomes clear that those desirable and detrimental effects of smoking of foods cannot be attributed to certain classes of chemical compounds such as phenols, carbonyls, PAH etc., but only to certain individual members of these classes. Therefore, the determination of the bulk of phenols, carbonyls, PAH etc. might be only of some use for a rough quality control of smoked products or liquid smokes (93, 96, 102) but is not suitable for the toxicological evaluation and for exact studies on the effect os smoke on foods and its dependence on smoking technology (93, 102). Consequently, analytical procedures are necessary which render it possible to detect as many members of the different classes of chemical smoke components as possible. If it is known which of all these components are most important for the different effects of smoking, the analysis could be confined to such particular components and therefore, be simplified. But this is still a dream of the future.

Many of such compounds, which have to be determinded, are present in ppm or even ppb concentrations only. Everybody, who is familiar with the analysis of fat-containing foods knows, that the crucial point of each analysis of such small amounts is the isolation of the particular class of compounds from the food without the presence of interfering substances. The purified fraction obtained by this way has to be separated into the individual components, usually by TC or GC. For the identification of these components more or less sophisticated methods are available which are mostly basing on spectrometric techniques such as UV, IR, spectrofluorimetry, MS or NMR.

This lecture is concerned with the analysis of PAH and phenols aonly. The

analysis of carbonyls, acids and other classes of smoke components will not be discussed because we have not much experience with the analysis of these compounds in our laboratory. There are also no contributions to this symposium concerning the analysis of compounds others than phenols and PAH. But from the reactions of smoke carbonyls with food proteins it becomes evident that the analysis of this fraction is of particular importance for a better understanding of the effect of smoke on foods.

Particular attention should be payed to the analysis of liquid smokes and other smoked ingredients for two reasons. 1. By the use of such ingredients the smoke components are not only located in the surface layer as in the case of the conventional smoking but in the whole product, 2. the composition of liquid smokes or smoked ingredients might be different from the obtained after normal smoking. The use of such ingredients should not be permitted if they are not well defined in terms of their chemical composition.

POLYCYCLIC HYDROCARBONS

A. General Remarks

As certain PAH are known to be cancerogenic, the public interest in food safety has prompted numerous studies on their occurence in smoked foods (12, 20, 21, 25). It should be mentioned that a number of PAH are not cancerogenic but show either a cocancerogenic or an antagonistic effect (18, 74, 77). Therefore, it seems to be necessary to determine possibly all PAH present in smoke. This is also important for answering the question whether benzo (a)-pyrene or any other PAH is a reliable indicator for the total amount of cancerogenic PAH in smoke.

As to the smoking of meats and fish the influence of smoking technology on the PAH content of smoke, liquid smokes and smoked products is of particular interest. It was found that the composition of curing smoke can be influenced in a relatively simple way. So, smoke generated at lower temperatures (300 - 400 °C) imparts to the meat products a good flavour but contains less PAH than smoke generated at higher temperatures (10, 64, 100, 101, 107). Filtration or cooling of smoke also lower the PAH contration without a detrimental effect on the flavouring properties (16, 96, 99, 105). All processes which cause a removal of the larger smoke particles (soot), cause a reduction in the amount of benzo (a)-pyrene and other PAH (79). By the use of such smokes for the production of liquid smokes and also by certain treatments of smoke condensates, it is possible to produce preparations containing no or very small amounts of PAH (47, 53, 79, 101). However, such liquid smokes often show a lack of the desirable flavour components such as phenols (31, 78). Generally it can be said that the PAH content of commercial preparations of liquid smoke varies over a very wide range.

After treatment with wood smoke, the PAH are located in the surface layer of the product. Removal of the surface reduces essentially the PAH in the smoked product (16, 105). The benz (a)-pyrene content of sausages can be drastically reduced by the use of certain casings which retain the PAH but not the flavouring components of smoke (12, 16, 94, 105). More recently, however, artifical casings are in commercial use, which retain also the

aroma components and, therefore, prevent a smoke aromatization of the product. In such cases a smoke-flavouring of the sausage mixture by addition of certain ingredients such as smoked spices or smoked salt, smoked bacon or smoke condensates is necessary.

It should be mentioned that in the Federal Republic of Germany the benzo (a) -pyrene content of smoked meat products may not exceed 1 ppb. This seems to be the only legal regulation in any country which is limiting the content of a PAH in a food product.

B. Analysis of Polycyclic Hydrocarbons

The methods for PAH analysis of smoked foods mainly involve liquid-solid or liquid-liquid extraction of the previously ground material (22, 27, 62, 104). In addition, extraction procedures are used in which the smoked products are subjected tc prior alkaline disintegration (11, 88). These procedures have, for the most part, the disadvantages of being expensive in terms of time and of the amount of materials needed: especially expensive are the ultra-pure extraction reagents. Another disadvantage of these procedures is the fact that the residue after the extraction must be further purified by column chromatography.

As an example of this type of techniques the extraction procedure recommended by Grimmer (26, 29) should be briefly described (Fig. 1). The PAH of the smoked food are extracted by liquid-liquid chromatography using methanol and cyclohexane (CYH). As most foods contain water, first the water is extracted with methanol. During this treatment only small amounts of PAH are dissolved in the alcohol, which have to be extracted by repeated shaking with CYH. The residue is then repeatedly extracted with CYH which dissolves the lipids as well as the PAH. The combined CYH extracts are shaken with dimethylformamide (DMF) as long as all fluorescent substances are transferred into the DMF phase. After addition of water this phase is again extracted with CYH until the DMF phase does not fluoresce. The CYH phase is evaporated and purified on silica gel. This purified extract is analyzed by TC or GC. In the case that the material contains much fat, the partition between DMF and CYH has to be repeated several times because fat and fat-accompanying compounds disturb the chromatographic analysis.

An alkaline disintegration instead of the extraction with methanol is recommended for the analysis of materials which contain, besides fats and proteins, considerable amounts of unsaponificable, fat-accompanying substances (Fig. 2). During treatment of foods with boiling alcoholic potassium hydroxide fats and proteins are hydrolized. The potassium salts of the amino acids and fatty acids formed are insoluble in CYH. Therefore, during extraction of the alkaline hydrolysate with CYH only the unsaponifiable compounds such as cholesterol, PAH and other neutral compounds are transferred into the phase of the organic solvent. This phase is purified by extraction with DMF. After dilution with water the PAH dissolved in the DMF phase con be extracted with CYH. This extract has to be purified by removing the impurities with silica gel.

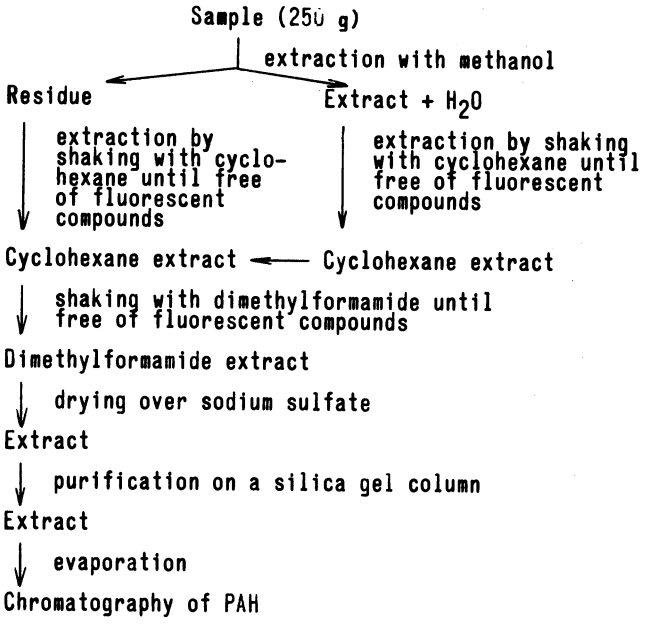

Fig. 1. Isolation of PAH from meat products by liquid-liquid extraction of the untreated sample

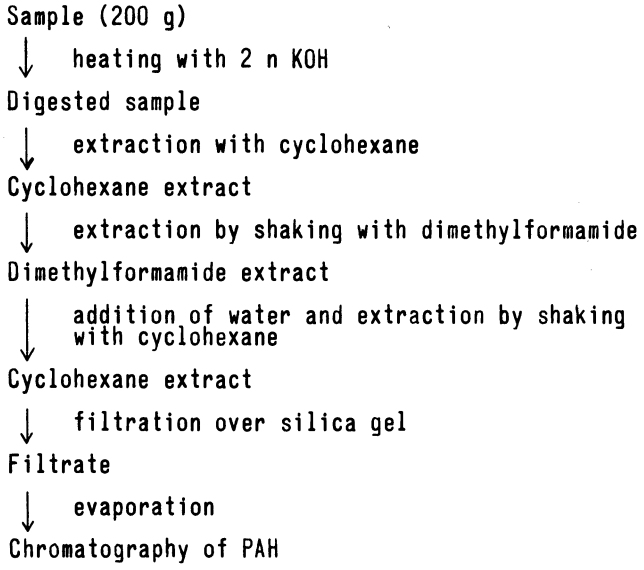

Fig. 2. Isolation of PAH from meat products by liquid-liquid extraction after alkaline hydrolisis of the sample

The extract obtained by these procedures usually contain some impurities which interfere with the analysis of PAH. Therefore, Grimmer (26, 29) recommends a chromatographic purification using Sephadex LH 20 columns. For this purpose the extracts have to be evaporated to dryness and to be dissolved with isopropyl alcohol. This solution is put into a sephadex column from which different fractions of PAH are eluated. The single fractions are separately analyzed.

Howard et al. (13, 36, 37, 38, 115) used a similar extraction procedure as Grimmer but they recommend the use of dimethylsulfoxide instead of DMF. Both techniques need a great amount of ultra-pure solvents. Kędzierski and

Kubacki (95) modified the Howard method by omitting the purification with dimethylsulfoxide, changing the sequence of analytical steps and replacing TC by column chromatography on cellulose acetate. This modification reduces the time for analysis and simplifies the procedure. Obiedziński (71) and Radecki et al. (84) also modified the Howard method for the determination of PAH in liquid smokes, using purification of the extracts on fluorisil columns.

In all the methods described the isolation of PAH starts with a partition process basing on the fact that PAH are more soluble in CYH than in water. In the procedure of Rhee et al. (87) which is similar to the methods of Grimmer and Howard, the sample is dried by mixing it with sodium sulfate before extraction with CYH and methanol. By this treatment the lipids and the PAH become easier extractable. It is a great disadvantage of these techniques, however, that also a considerable amount of fats and similar compounds are extracted. The clean-up would be much easier if those interfering compounds could be removed just at the beginning of the procedure. This problem could be solved by a new method, developed by Potthast (82) in our laboratory. The process is based on the observation that the PAH are more soluble in propylene carbonate than in any other organic solvent and that extraction of the PAH from smoked meat products with this solvent yields a fat-free extract; this is particularly advantageous for the rapid purification and preparation of extracts. Therefore, the procedure is much less time-consuming and less expensive than the methods mentioned above.

In this procedure (Fig. 3) the smoked meat product is mixed with chloroform, which extracts the fats, and with sodium sulfate which binds the water. After mixing this mixture with celite the lipids besome uniformly distributed over the surface of the adsorbent, thus facilitating the extraction of PAH. Then the chloroform is removed by using a vacuum drying cabinet at 40°C. This dry material is extracted in a column by elution with propylene carbonate. The eluate is shaken with sodium hydroxyde in order to hydrolyze the propylene carbonate to propylene glycol. The PAH are extracted from the alkaline solution of propylene glycol by shaking with light petroleum. After evaporation of this extract the PAH can be immediately analyzed. With this procedure a recovery of benzo(a)-pyrene of 95 - 100 percent from meat products was achieved. The time requirement for the extraction and further preparation is estimated to be about 4 hr, thus in comparison with earlier methods the time is greatly reduced. In addition, the method provides the advantage of a relatively problem-free technique and of a small expenditure for solvents. The successfull application of this method for the analysis of smoked meat products is reported by Potthast (80).

For the analysis of the extract, which is obtained by one of the procedures mentioned, the PAH can be separated by column chromatography or TC. In the column chromatography at normal and at high pressure the separation occurs continuously, i.e. by combining the column with the flow cuvette of a photometer (28, 41, 48, 49, 50, 73, 76, 98, 118, 119). In the case of the TC, the bands of PAH can be directly evaluated by in-situ analysis, measuring the remission or transmission of light at a defined wave length (60, 88, 92, 104) or by careful removal of the material, which contains the bands from the plates, evaluation of this material with organic solvents and analyzing

the evaluate by UV or fluorescence spectrometry (19, 37, 67, 69, 114). In these procedures the UV or fluorescence spectra are used for identification of the PAH (33, 34, 42, 109) in addition to the retention time or R_f values.

Sample (200 g)
↓ + chloroform + sodium sulfate + celite
Drying at reduced pressure
↓ extraction by elution with propylene carbonate
Propylene carbonate eluate
↓ saponification with NaOH
Watery solution
↓ extraction by shaking with petroleum ether
Petroleum ether extract
↓ filtration over calcium chloride + celite + florisil
Filtrate
↓ evaporation to 1 ml or less
Chromatography of PAH

Fig. 3. Isolation of PAH from meat products by solid-liquid extraction

More recently the application of the GC to the analysis of PAH is recommended (26, 28, 29, 73). In this case, however, the PAH are identified by means of the retention time only; a more reliable identification can be reached by combination of GC with mass spectrometry (MS); but the coupling of GC with MS fulfills the requirements of an extract identification only if the GC provides a sufficient separation of the PAH because many PAH with the same molecular might exist. So, benzo(a)-, benzo(b)-, benzo(j)- and benzo(k)--fluoranthene, perylene, benzo(e)- and benzo(a)-pyrene have the same molecular weight of 252.

Packed columns (7, 26, 28, 29, 91) as well as capillary columns (28, 70) are recommended for the GC of PAH. The length of the packed columns should be at least 10 m in order to provide sufficient separation (26, 29). The hydrocarbons OV 1, OV 17, OV 101 or SE 30 are proved to be suitable as stationary phase.

There is no doubt that the capillary columns provide better separation effects than packed columns. This is mainly due to the fact that during coating of support for packed columns adsorption effects cannot be completely prevented. Consequently, during GC of PAH a broadening of peaks occurs which lowers the sensitivity of the method considerably. By suitable coating the capillary columns can be completely depolarized and, therefore, adsorption effects can be prevented. The results are narrow peaks of well separated PAH which can be recorded within a few seconds. So, the GC with capillary columns is more sensitive; amounts of 10^{-10} g PAH can be detected without difficulty (81).

PHENOLIC COMPOUNDS

A. General Remarks

As it was mentioned in the introduction, the phenols of smoke contribute essentially to the typical flavour of smoked foods. Apparently certain phenolic compounds such as guaiacol, syringol and eugenol play a predominant role in this flavouring effect of smoke (80). However, an addition of such phenols to meat products does by far not give a smoke flavour which is comparable to the effect of freshly developed wood smoke (24, 31, 44). This observation makes it clear that the proper analysis of all phenols and other flavouring constituents of smoke and smoked products is necessary in order to understand the chemical nature of the aroma of smoked foods.

The amount and composition of phenols in curing smoke are strongly influenced by the temperature of smoke generation (31) and by smoking technology (80). The phenol composition of liquid smokes shows an extremely wide variation (31). During the normal smoking process, the phenols penetrate into the product to a depth of a few mm only (31); but if liquid smoke preparations or other smoked ingredients are added to the sausage mixture, phenols are found also in the center of the product. Based on this fact, Baltes and Bange (1) developed a method for the identification of liquid smokes in foods.

As we showed for meat products smoked with different techniques in our laboratory, an increasing amount of phenols is not necessarily connected with an increasing concentration of PAH (31). A similar observation on smoked herring is reported by Lenges et al. (61). But in the case of liquid smokes we found an increasing PAH content with rising content of phenolic compounds (31).

B. Analysis of Phenolic Compounds

The analysis of phenols begins with the extraction of the phenolic compounds from the food. In alkaline solution phenols form salts which are not soluble in organic solvents; in this way the phenols can be separated from fats. However, the instability of phenols in alkaline solutions and the possibility of its oxidation under such conditions are disadvantageous. Nevertheless, this type of procedure for the extraction of phenols from foods is described in text books as well as in papers (52, 64) and is in common use.

In this procedure triglycerides and neutral fat-accompanying substances are extracted from the food with peroxide-free diethylether under strongly alkaline conditions (pH 12 - 13). Then the phenols can be extracted from the acidified watery phase also with diethylether; but besides the phenols also organic acids present in smoked foods are extracted. For removal of these acids the ether phase has to be shaken with a watery alkaline solution and to be adjusted to pH 7 by CO_2 gas. At this pH the organic acids are present as anions whereas the phenols are not dissociated and can be, therefore, extracted with diethylether.

Potthast (80) replaced the suspect alkaline treatment and the extraction procedure by a steam distillation of the phenolic compounds at high boiling

point (130 - 170 °C). The advantages of this methods are the good recovery of phenolic compounds and the simplicity of technique which allows a much faster isolation of phenols than the methods used before.

The determination of the isolated phenols is usually carried out by GC. The phenols are volatile at relatively low temperatures; they can be separated as such on polar phases or as esterified phenols such as trimethylsilyl derivatives on unpolar phases. Similar to the separation of the PAH also for the separation of phenols packed columns (2, 8, 64) or capillary columns (2, 9, 52) are used. Besides of the retention times, coupling of GC with MS is used for the identification of phenols. Liquid chromatography or TC do not seem to be of importance in the analysis of phenols although such methods might have some advantages with regard to the identification of phenols.

In conclusion it can be stated that now adequate, reliable and timesaving methods for the isolation and determination of PAH and phenols are available. The identification of the single components of PAH and phenolic fractions need sophisticated methods with expensive instrumentation. Much more research will be necessary to find out whether the concentration of some key substances can offer sufficient information on the sensoric and toxicological quality of smoked foods and liquid smoke preparations. If such key substances are known, the quality control of smoked products in industry and food inspection could be essentially simplified.

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