VOLATILE AND LESS VOLATILE COMPONENTS IN SPANISH SMOKED SAUSAGE STUDIED BY SPME AND GC/MS. ROLE OF THE CASING IN THE SMOKING PROCESS.

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Background

Smoke causes several changes in meat derived products in colour, texture, odour, flavour and preservation[1]. Wood smoke contains higher proportions of carbonylic and carboxylic derivatives than of phenolic derivatives[2]. Paprika dry fermented sausages are manufactured smoked in many cases. The smoking is usually carried out by means of wood smoke; this process has the risk of potential contamination with Polycyclic Aromatic Hydrocarbons.

Objectives

This paper has as its objective the study of the volatile and less volatile components of smoked dry fermented paprika sausages and of their casing by means of Solid Phase Microextraction followed by Gas Chromatography/Mass Spectrometry. The study allows us to know what smoke components are present in the head space of the smoked meat product and which of them has reacted with meat product components. At the same time the role of the casing in relation to the diffusion of the smoke components towards the interior of the meat product has been studied. In addition the effectiveness of the methodology used in relation to others is tested.

Methods

Samples. Commercial smoked dry fermented paprika sausages were acquired in a local supermarket. The casing was separated from the meat product and both were chopped manually; samples of 1g of chopped casing, or of chopped meat product without casing were weighed into 4mL Screw Top amber vials (Supelco), and sealed with hole cap PTFE/silicone septums for the generation of headspace.

Headspace SPME. Vials containing 1g of sample (meat product or casing) were introduced into a water bath maintained at a constant temperature. The fiber used was Polyacrylate (85 µm film thickness acquired from Supelco). A temperature of 50 ºC for the formation of the headspace and a time of 60 minutes for adsorption of the volatile components onto the fiber were chosen.

Gas Chromatography/Mass Spectrometry. Fibers with the volatile compounds adsorbed onto them were injected into a Hewlett-Packard gas chromatograph model HP 6890 Series, equipped with a Mass Selective Detector 5973 and a Hewlett-Packard Vectra XM Series 4 computer. The column used was a fused-silica capillary column acquired from Hewlett Packard (60 m long x 0.25 mm inner diameter x 0.25 µm film thickness), coated with a non-polar stationary phase (HP-5MS, 5% phenyl methyl siloxane). The operating conditions were the following: the oven temperature was set initially at 45 ºC (0.50 min hold), increased to 250 ºC at 4 ºC/min (20 min hold); the temperatures of the ion source and the quadrupole mass analyzer were kept at 230 and 150 ºC, respectively; helium was used as carrier gas at a pressure of 16.5 psi; injector and detector temperatures were held at 220 and 280 ºC, respectively; splitless mode was used for injection with a purge time of 5 minutes. The fiber was maintained in the injection port for 10 minutes. Mass spectra were recorded at an ionization energy of 70 eV. Some components were tentatively identified by their retention times, by their mass spectra, by comparing their mass spectra with those in a commercial library (Wiley 138.L, Mass Spectral Database, Wiley 1990) and many others by using standards. The semiquantification presented here was based on arbitrary units of peak area counts of the molecular ion peak of the compounds multiplied by 10^{-5}.

Results and discussion

The number of detected components is higher than three hundred and much greater than that found by other authors in similar products, using other methodologies[3,4]. The reproducibility of this technique is very high for compounds eluting after eight minutes. Due to the high number of compounds present in the head space of this product, many of them elute together and, for this reason, their accurate quantification is not possible.

Among the detected components are: acids from two to eighteen carbon atoms; aliphatic and aromatic aldehydes; linear and cyclic aliphatic ketones as well as aromatic ketones; a very high number of lactones (furanones and pyranones), in relation to the number found by other authors in similar products[3,4]; some alcohols, both aliphatic and aromatic; esters; alkyl-arylethers coming from the smoke; a very high number of phenol derivatives, including phenol, guaiacol and syringol and a large number of their alkyl-derivatives; some nitrogen-derivatives, including compounds such as 5-methyl-2,4-imidazolidinedione, not detected before in this type of products, and whose formation can be attributed to *Lactobacillus*[5]; sulphur-derivatives and terpenes coming from garlic and spices used in the manufacture of the product; and a very high number of aliphatic and aromatic hydrocarbons coming from the smoke.

A very big difference between the proportions and concentrations of the several components in the smoke and those found in the head space of this meat product has been observed. There are many main smoke components that are not present in the head space of the smoked product, indicating that they probably have reacted with meat product components. These are basically carbonylic derivatives. So, furancarboxaldehyde, which is one of the main components of many smokes has not been detected in the meat product. Smoke carbonyl derivatives are thought responsible for the change in colour and texture of the meat product by means of reactions similar to Maillard. However the head space of the meat product contains most of the smoke phenolic derivatives in proportions, to a certain degree, similar to those in the smoke, showing them to be less reactive than carbonyl derivatives; they are important contributors, together with others, to the odour and flavour of this product.

Finally, from the comparison of the head space composition of the casing and of the interior of the meat product, and without taking into account the matrix effect, it could be deduced that some smoke components diffuse without difficulty through the casing and they are at similar concentrations in both casing and interior of meat product. Others are at lower concentrations in the head space of the interior of the meat product than in the casing; this could indicate that either these compounds have reacted with meat product components or that they had difficulty crossing the casing. Finally, it has been found that other compounds only appear in the head space of the casing. Hydrocarbons belong to the two latter groups, and it could be inferred that these compounds either do not pass through the casing or have difficulty; this fact is of great interest from the food safety point of view. Table 1 gives the relative concentrations, expressed in arbitrary area counts, of some smoke components, among which are some polycyclic aromatic hydrocarbons, in the head space of casing and in the interior of the meat product; these data were obtained from the quantification of the molecular ion peak of the mass spectra of these components.

Conclusions

This methodology has a good reproducibility and has allowed us to detect a very high number of compounds, some not detected before in similar meat products. The high number of lactones and the presence of some nitrogenated compounds such as 5-methyl-2,4-imidazolidinedione, produced by *Lactobacillus* is noteworthy. The absence of some smoke carbonyl derivatives such as furancarboxaldehyde has been observed, however there is a significant number of smoke phenol derivatives. In addition, some polycyclic aromatic hydrocarbons present in the head space of the casing have not been detected in the head space of the interior of the meat product and others have been detected but in smaller proportions.

Pertinent Literature

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Table1. Retention time, molecular weight and concentration of some components in the head space of 1g of casing and of the interior of the meat product expressed in arbitrary units of counts area of the molecular ion peak $.10^{-5}$ together with the standard deviation

RT	Compound	MW	Casing	Interior
20.52	Cyclotene	112	25.9(2.1)	20.4(1.2)
24.17	Ethylcyclopentenolone	126	4.3(0.2)	3.4(0.1)
27.09	4-Methylguaiacol	138	91.6(6.4)	87.7(5.2)
33.25	4-Propylguaiacol	166	8.4(0.4)	2.8(0.1)
26.89	Naphthalene	128	19.9(1.9)	8.1(0.3)
36.18	Acenaphthylene	152	19.6(1.8)	0.3(0.1)
40.26	Fluorene	166	6.5(0.4)	nd
45.86	Phenanthrene	178	16.2(1.5)	0.9(0.1)