POLYCYCLIC AROMATIC HYDROCARBONS (PAH) AND PHENOLIC SUBSTANCES IN COLD SMOKED SAUSAGES DEPENDING ON SMOKING CONDITIONS USING SMOLDERING SMOKE

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Abstract – The contents of polycyclic aromatic hydrocarbons (PAH) and phenolic substances in minisalamis were investigated depending on cold smoking conditions (smoldering smoke). For the 24 smoking experiments three different smoke densities (light, medium, and intensive smoke) and ventilator velocities (750, 1500, and 3000 rpm) as well as wood chips with four different moisture contents (12, 19, 24, and 30%) were tested. During the smoking process, the concentrations of O_2, CO, and CO_2, the humidity and the temperature in the smoking chamber as well as the smoke generation temperature were determined. The chemical analysis included benzo[a]pyrene and PAH4 as well as the phenolic substances guaiacol, 4-methylguaiacol, syringol, eugenol, and trans-isoeugenol. The smoke density had a significant influence on the PAH contents. Sufficient amounts of phenolic substances were detected in all of the experiments.

Key Words – GC/MS, glow smoke, minisalamis

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) consist of two or more condensed aromatic carbon rings and are formed during the incomplete combustion of organic material. About 660 different compounds belong to the PAH group [1], some of them showing carcinogenic properties [2]. Due to the carcinogenic properties the Scientific Committee on Food (SCF) recommended that the contents of the PAHs in food should be “as low as reasonably achievable” in adherence with the so-called ALARA-principle [3]. Furthermore, the Codex Alimentarius Commission recommended investigations to identify optimal smoking conditions to minimize the PAH contents [4].

In a previous study [5] it was shown that a minimization of the PAH compounds in hot smoked sausages is possible using glow smoke. The most important parameter influencing the PAH contents was the smoke generation temperature, yet also the ventilator velocity had a noticeable influence on the PAH contents. Reduction in the content of PAH compounds did not necessarily lead to a decrease in the amounts of phenolic substances.

The main objective of this study was to investigate the correlations between the PAH contents and the phenolic substances in raw sausages depending on cold smoking conditions using smoldering smoke. Within the group of PAH compounds the investigations focused on benzo[a]pyrene (BaP) and the sum content of BaP, chrysene (CHR), benzo[a]anthracene (BaA), and benzo[b]fluoranthene (BbF) (PAH4). New maximum levels for PAH4 in smoked meat products of 30 µg/kg (1/9/2012 to 31/08/2014) and, later, 12 µg/kg were established in Commission Regulation (EU) No 835/2011. Within the group of phenolic substances the dominant compounds guaiacol, 4-methylguaiacol, syringol, eugenol, and trans-isoeugenol were analyzed. The smoking experiments were performed with minisalamis, having the advantage of a large surface/mass ratio and a short ripening period. The same smoking time was selected for the 24 smoking experiments.

II. MATERIALS AND METHODS

The minisalamis were made of 77% frozen pork, 19% frozen back fat, 2.4% salt (containing 0.4% sodium nitrite ($NaNO_2$)), 0.4% glucose, 0.4% spice mix, and at least 3 x 10^9 bacteria per kg. Due to the growth of undesirable microorganisms in less smoked minisalamis, the content of starter cultures was increased to a min. of 10^{10} bacteria per kg, and 0.4 – 0.5% glucono delta-lactone (GDL) were added. Sheep casings (diameter: 18 – 20 mm) made from the sub-mucosa of the small intestine were used. The volume of a salami chub was 35 cm³. A batch weighed approx. 8 kg and was used for two smoking experiments (first experiment=a; second experiment=b) and as matrix blank.

Before smoking, the minisalamis were fermented for 2 d in a climatic chamber at a temperature of 22°C and a relative humidity (RH) of 94 to 92%, respectively. On the third day they were smoked in a T 1900 Ratio smoking chamber combined with a smoke generator RZ 325 from Fessmann at 22°C for 30 min, using beech wood chips (size: 4.0 – 12.0 mm). The smoke generator was able to produce three different smoke densities: intensive, medium, and light smoke. The ventilator velocity in the smoking chamber was also variable between 750, 1500, and 3000 rpm. The smoking time was set to 30 min for each smoking experiment. The moisture of wood chips was not changed for experiments 1a,b to 9a,b and averaged out at about 12%. For the experiments 10a,b to 12a,b the moisture of the wood chips was adjusted by adding water. Changes in smoke density, ventilator velocity, and the moisture of the wood chips resulted in 24 experiments (Table 1). After two additional days of drying at 20°C and a RH of 55 to 60%, about 1 kg of the minisalamis were homogenized with eatable casings in a 5 L bowl chopper and stored in the dark at -18°C until chemical analysis.

The measurement of the smoke generation temperature and the gas concentrations as well as the analytical method used for the determination of the PAH contents and the phenolic compounds are described elsewhere [5].

Table 1. Parameters of the smoking experiments.

Exp.	Smoke density	Ventilator velocity [rpm]	Moisture of wood [%]
1a/b*	intensive	3000	11.7/12.0
2a/b	intensive	1500	11.7/12.9
3a/b	intensive	750	12.0/11.9
4a/b	medium	3000	10.7/11.5
5a/b	medium	1500	11.7/11.6
6a/b	medium	750	12.2/12.6
7a/b	light	3000	11.9/12.0
8a/b	light	1500	12.1/12.2
9a/b	light	750	11.5/12.2
10a/b	intensive	3000	18.3/19.7
11a/b	intensive	3000	24.4/24.0
12a°/b	intensive	3000	29.8/29.5

* Smoking experiment 1b was interrupted after 27 min
° Exp. 12a failed (maximum temperature: 370°C).

III. RESULTS AND DISCUSSION

The smoke density influenced the smoke generation temperature whereas the ventilator velocities did not show an obvious dependency. Intensive smoke resulted in the highest and light smoke in the lowest smoke generation temperature maxima (T_{max}) and mean smoke generation temperatures (T_{mean}) (intensive: T_{max}: 845°C, T_{mean}: 598°C; medium: T_{max}: 680°C, T_{mean}: 434°C; light: T_{max}: 514°C, T_{mean}: 324°C). Consequently, the contents of BaP and PAH4 were higher for intensive smoke (BaP: 0.5 µg/kg; PAH4: 3.0 µg/kg; N=6), than for medium (BaP: 0.3 µg/kg; PAH4: 2.1 µg/kg; N=6) and light (BaP: 0.2 µg/kg; PAH4: 1.8 µg/kg; N=6) smoke, respectively (Fig. 1).

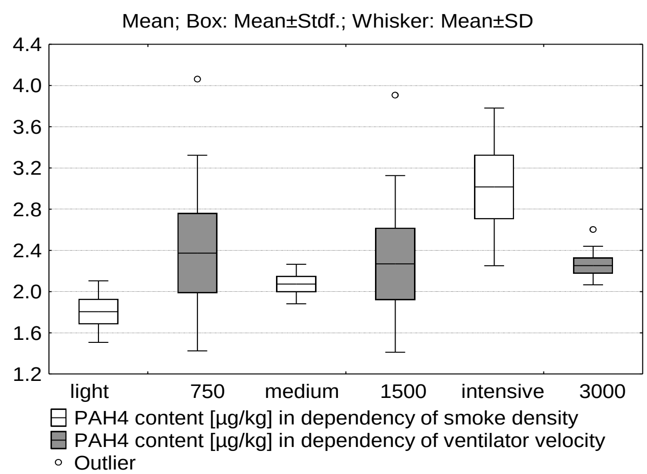

Figure 1. Content of PAH4 [µg/kg] depending on smoke density and ventilator velocity.

The different ventilator velocities did not influence the BaP and PAH4 contents. The mean BaP and PAH4 contents for the ventilator velocities 750, 1500, and 3000 rpm were very similar to each other (BaP: 0.3 µg/kg, PAH4: 2.3 – 2.4 µg/kg; N=6). However, the standard deviations of the BaP and PAH4 contents were significantly lower for a ventilator velocity of 3000 rpm than for 1500 and 750 rpm (Fig. 1). Non-smoked minisalamis were also analyzed (BaP: 0.1 µg/kg; PAH4: 1.4 µg/kg; N=13). A differentiation between the first and the second smoking experiment showed that the mean smoke generation temperatures of the first experiment were always lower than those of the second experiment. Yet the BaP and PAH4 contents were higher in the first experiment than in the second one. Consequently, the higher PAH contents detected in the first smoking experiment compared to the second experiment could not be explained by higher smoke generation temperatures. It should be noted that the CO-concentrations in the smoking chamber showed the same tendency as the PAH contents: For the experiments 1a,b to 7a,b the CO maximum concentrations of the first smoking experiment were on average about 6% higher than the CO maximum concentrations of the second experiment. For the experiments 8a,b and 9a,b the CO maximum concentrations of the first and the second experiment were very similar to each other (about 3000 ppm), and the PAH4 content (8a: 1.9 µg/kg, 8b: 1.6 µg/kg; 9a: 1.6 µg/kg, 9b: 1.5 µg/kg) was not much higher than that of the non-smoked salamis (1.4 µg/kg). The higher CO maximum concentrations of the first experiments, 1a to 7a, indicated a less complete combustion of the wood chips compared to the second experiment. The conditions of a less complete combustion possibly favor the formation of PAHs. The ratios between the maxima of the CO and CO_2 concentrations were on average 0.8 for intensive, 0.7 for medium, and 0.5 for light smoke. There were no differences in these ratios between the first and the second smoking experiment, but the mean smoke generation temperature in the second experiment was on average 54°C higher for intensive smoke, 48°C higher for medium smoke, and 83°C higher for light smoke. The temperature profiles of the first and the second smoking experiment were different. The first experiment resulted in higher PAH contents, but the mean smoke generation temperatures were lower. On the other hand, in the first smoking experiments a longer time period was needed to reach a constant temperature level than in the second experiments.

The influence of the moisture of the wood chips was also investigated applying a constant smoke density (intensive smoke) and ventilator velocity (3000 rpm). Higher moisture of the wood chips resulted in lower mean smoke generation temperatures. But an increase in the moisture of the wood chips from 12 to 24% also resulted in higher PAH4 contents in a linear relationship (experiment 1a, 10a and 11a: BaP 0.4–0.5 µg/kg (R^2=0.99), PAH4 2.6–3.3 µg/kg (R^2=0.99); experiment 1b, 10b and 11b: BaP 0.3–0.5 µg/kg (R^2=0.98), PAH4 2.3–3.1 µg/kg (R^2=0.98)). Sufficient smoking with wood chips at a moisture of 30% was not possible.

The highest sum content of the five phenolic compounds (76.2 mg/kg) was detected in intensively smoked sausages when applying a ventilator velocity of 750 rpm, the lowest contents with an identical moisture level of the wood chips (12%) were detected in lightly smoked sausages (29.6 mg/kg; ventilator velocity: 3000 rpm).

Guaiacol was the main compound of the five analyzed phenolic compounds, showing contents between 8.8 mg/kg (light smoke; 3000 rpm) and 24.5 mg/kg (intensive smoke; 750 rpm).

The ventilator velocity influenced the content of phenolic compounds in the intensively smoked minisalamis. The sum content of the five phenolic compounds increased from 45.8 mg/kg at a ventilator velocity of 3000 rpm to 74.6 mg/kg at a ventilator velocity of 750 rpm. The content of medium smoked sausages showed no dependency on different ventilator velocities. The highest sum content of phenolic compounds in lightly smoked sausages was analyzed in minisalamis smoked at a ventilator velocity of 1500 rpm (60.9 mg/kg). The lowest content was detected in lightly smoked sausages when applying a ventilator velocity of 3000 rpm (35.3 mg/kg).

The smoke density showed a great influence on the maximum of the smoke generation temperature. The phenolic content of the minisalamis, smoked at a ventilator velocity of 3000 rpm and 1500 rpm showed no direct correlation to the smoke density. In contrast, the sum content of phenolic compounds in the minisalamis smoked at 750 rpm decreased from 74.6 mg/kg (intensive smoke) to 59.5 mg/kg (medium smoke) and up to 50.6 mg/kg (light smoke).

The moisture of the wood chips influenced the maximum of the smoke generation temperature. The contents of phenolic compounds in minisalamis, which were smoked with moistened wood chips, also showed a dependency on the different wood moisture. The sum content of phenolic compounds increased from 41.2 mg/kg (original wood moisture: 11.7%; maximum of the smoke generation temperature: 827°C) to 68.2

mg/kg (wood moisture: 29.5%; maximum of the smoke generation temperature: 544°C).

A correlation between the sum content of the five phenolic compounds and the content of PAH4 was only observable for the experiments applying wood chips with a different moisture content. The PAH4 content of the smoked minisalamis with the highest phenolic content were about 3.1 µg/kg. Therefore, the desired objective of lowering the PAH content without lowering the content of phenolic compounds was not achieved by moistening the wood chips.

IV. CONCLUSION

In all of the smoking experiments, minisalamis with a low PAH content (BaP: 0.1 to 0.7 µg/kg; PAH4: 1.5 to 4.1 µg/kg) were produced. A minimization of the PAH compounds in cold smoked sausages is possible using smoldering smoke. The most important parameter influencing the PAH content is the smoke generation temperature, which is influenced by the smoke density. Therefore, accurate control of the smoke generation temperature to avoid a smoke generation temperature above 800°C and to achieve mean smoke generation temperatures below 600°C is a promising approach for lowering the PAH contents in cold smoked sausages.

The minimization of the low PAH contents in cold smoked minisalamis is limited as the lowest observed PAH contents in smoked sausages were nearly at the same level as in the unsmoked sausages. The reason for this contamination, which cannot be attributed to PAH-containing spices, is probably contamination by air, in which the PAHs occur ubiquitously in the climatic chamber, since all samples (the smoked, as well as the unsmoked minisalamis) are stored in the chamber for about four days. This kind of contamination cannot be excluded, consequently, the PAH contents at this low level are the limitation for the minimization strategies for PAHs in cold smoked raw sausages.

An increase in the wood chip moisture content also does not seem to be a reasonable approach for reducing the PAH contents in cold smoked sausages using smoldering smoke. This was counter-productive, because smoking using wood chips with a higher moisture content led to higher PAH contents. A preheating of the smoke generator can also slightly lower the formation of PAH, compared to a cold smoke generator.

For PAH minimization strategies it does not seem to be necessary to consider the contents of phenolic compounds as in all smoking experiments sufficient amounts of phenolic compounds were detectable.

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REFERENCES

1. Sander, L.C., & Wise, S.A. (1997). Polycyclic Aromatic Hydrocarbon Structure Index. NIST Special Publication 922 (revised 2011), Gaithersburg: National Institute of Standards and Technology. http://www.nist.gov/mml/analytical/organic/sp922page.cfm.
2. IARC (2010). Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol 92, International Agency for Research on Cancer, Lyon, France. http://monographs.iarc.fr/ENG/Monographs/vol92/mono92.pdf.
3. SCF, Scientific Committee on Food (2002). Opinion of the Scientific Committee on Food on the Risks to Human Health of Polycyclic Aromatic Hydrocarbons in Food. http://ec.europa.eu/food/food/chemicalsafety/contaminants/out153_en.pdf.
4. CAC (2008), Codex Alimentarius Commission. Proposed Draft Code of Practice for the Reduction of Contamination of Food with Polycyclic Aromatic Hydrocarbons (PAH) from Smoking and Direct Drying Processes: ftp://ftp.fao.org/codex/alinorm08/al31_41e.pdf.
5. Pöhlmann, M., Hitzel, A., Schwägele, F., Speer, K., & Jira, W. (2012). Contents of polycyclic aromatic hydrocarbons (PAH) and phenolic substances in Frankfurter-type sausages depending on smoking conditions using glow smoke. Meat Science, 90, 176-184.
6. Commission Regulation (EU) No 835/2011 of 19 August 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in foodstuffs. Official Journal of the European Union L 215:4-8.