Studies of smoke composition and deposition from primary products in comparison to wood smoldering

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Introduction

Smoking food has been used for preservation for centuries and can be considered as a cultural asset, due to unique taste-giving properties. In addition to traditional smoking, the use of liquid smoke has become established in the last decades. The advantages as regenerated smoke are well known and described[1]. Various primary products are approved for use in the European Union[2], but there are still concerns expressed by the European Food Safety Authority - using the example of primary smoke *Pure Smoke® R714* (SF-001), the concerns relate to the presence of small amounts of 2-(5*H*)-Furanone[3]. The present work is intended to compare various technologies by smoke composition.

Composition of smoke and resulting properties

The goals of smoking food can essentially be divided into three areas: extending shelf life, improving or giving unique taste and as a processing aid to influence the structure and processability of substrates[4–6].

While there are many approaches and studies in the area of shelf life extension and process decoration in the food industry (here of course also with reference to smoking), the area of taste and aroma has only been rudimentarily investigated. There are a few works on the composition of smoke condensates[7–9], some of which also specifically derive odor and taste properties depending on specific substance concentrations[10]. It is the goal of this study to gain further insight in smoke composition and its deposition on surfaces with focus on regenerated and wood-based smoking.

Condensation of smoke to obtain liquid smoke

The production of the liquid smokes registered as primary smokes are described in the registration documents. These are essentially pyrolysis processes that aim either to produce liquid smoke directly by total condensation (calciner process) or complex processes have been developed with separation of pyrolysis products. Liquid smokes are then obtained by reformulation of end products from several process streams.

In order to compare conventional methods of smoke production with that of liquid smoking, it is necessary to obtain the corresponding smoke samples in a chamber after generation/ atomization using the setup shown in Fig. 1.

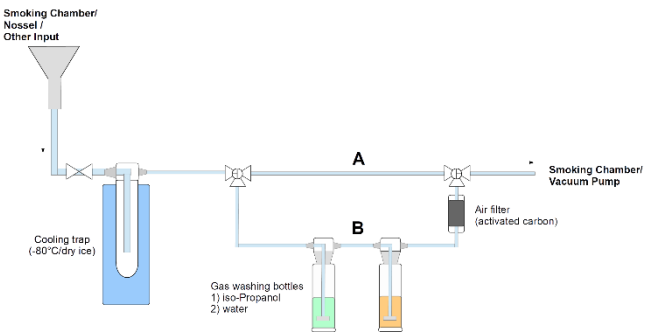

Figure 1. Experimental setup for the condensation of generated smoke using a cold trap (way A) and additional washing bottles filled with *iso*-Propanol and water (way B). The smoke is taken from a suitable place in the smoker or smoldering chamber and passed over condensate traps using a slight negative pressure.

Standard smoking processes (30 min for Liquid Smoking and 55 min for wood-based smoking) were carried out to obtain the smoke condensates. For the observation of treated surfaces the smoking chamber was also equipped with test substrates made of different materials in order to be able to examine the deposited components.

Analysis of smoke condensates

The yield of the condensates that can be obtained through the cold trap differs significantly. The duration of condensate capture was based on the standard smoking time - around 20 mL of liquid smoke and around 5 mL of smoke from chip smoldering could be condensed here. The washing bottles (each initially filled with 250mL *iso*-propanol or water) were used to adsorb smoke components that could not be directly condensed, resulting solutions are illustrated in Fig. 2.

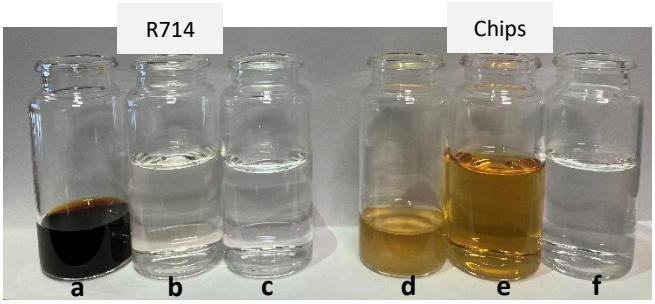

Figure 2: Collected condensates and washing solutions from the experiments with R714 (cooling trap (a), washing bottles with *iso*-Propanol (b) and water (c)) and beech wood chips (cooling trap (d), washing bottles with *iso*-Propanol (e) and water (f)).

a) Visual results

While the analyzes for approving the smoke aromas are essentially based on GC-MS analysis, a new method for non-destructive investigation using *High Performance Liquid Chromatography* (HPLC) was developed and used for the deeper analysis of the condensates. The method developed is based on a solvent gradient (water/ acetonitrile) on a C_{18}-column and is suitable for separating and quantifying the essential compounds described.

It is clearly noticeable that the R714 condensate is significantly more intense colored than the chip-based one (Fig. 2a vs. Fig 2d), while this effect is reversed, especially with the **iso**-propanol washing solutions. The stronger coloring of the R714 condensate (Fig. 2a) can be attributed to the significantly higher concentration, the stronger coloring of the *iso*-propanol solution from chip smoldering is due to the heat of the smoke - here the cooling capacity of the cold trap is not sufficient and more components are adsorptively bound in the washing solution.

b) Cooling Trap Results

Table 1 shows the specific concentrations of selected substances in the condensates examined (primary smoke *Pure Smoke® R714* vs. smoke from beech wood chips). The selection was based on the substances described in the literature as being responsible for the positive properties like taste[10], supplemented by suspected genotoxins like Furfural and 2-(5*H*)-Furanone.

The liquid smoke *Pure Smoke® R714* contains comparable amounts of 2-(5*H*)-Furanone as can be found in conventional smoke. Due to the fact that concentration is significantly higher than in the condensate derived from wood smoldering a correction factor must be applied. Based on the substances responsible for the desired properties, a correction factor of approximately 15 can be derived for the substances shown. This means that the furanone contamination is in a similar magnitude, while in the case of traditional smoking the contamination from furfural, which is classified as carcinogenic, is immense. Furfural is an allowed flavour compound in the EU[11].

Table 1. Concentration of selected compounds of the smoke condensate (cooling trap) samples. [x] - substances with relevance for taste and shelf-life extension[5,10].

Substance	**Chips** c [mg/mL]	**R714**^{normalized*} c [mg/mL]
2-(5*H*)-Furanone	0.07	0.14 +100%
Furfural	1.60	0.06 -96%
Vanilin[x]	0.17	0.02 -88%
Syringol[x]	4.69	2.79 -40%
Guaiacol[x]	0.25	0.13 -50%
4-Methyl-Syringol[x]	0.74	1.68 -126%
4-Methyl-Guaiacol[x]	0.17	0.08 -54%

**The normalization was carried out by forming the sums of the substances marked with [x] - for R714 this results in 73.55 mg/ mL and for the chips condensate 4.69 mg/ mL. The resulting correction factor is therefore 15.7.*

The simple setting up of the correction factor is only intended to take into account the fact that there is a significant difference in the concentrations of smoke active ingredients. It has been reported that the actual conditions are even more complex. For example, *para*-alkyl-substituted phenols have a significant taste and odor giving effect even in very low concentrations[10]. In our studies 4-Ethylguaicaol can be detected in concentrations of approx. 3.50 mg/ mL, while there is no evidence in the condensate of conventional smoke succeed. This means that the correction factor used above may be even higher, to verify this, further work is necessary. In summary, 2-(5*H*)-Furanone is present in both smoke condensates in equal amounts, based on smoking performance in traditional and liquid smoking.

c) Wash Bottle Results

As it can be seen in Figure 2 and mentioned before, there are major differences in the contents of the non-condensed materials. On the one hand visually, but on the other hand also after HPLC analysis.

In the case of the liquid smoke R714, the measurements of the wash bottle filled with water did not show further organic materials. Small amounts of furfural and 2-(5*H*)-Furanone can be detected in the *iso*-propanol fraction (see SI for chromatograms). Other substances cannot be clearly detected. These results are due to the fact that R714 is already a purified smoke condensate. It is interesting that 2-(5*H*)-Furanone and Furfural can apparently be removed by vacuum treatment after atomization.

As it can be seen from Figure 2e, the *iso*-propanol fraction of the chip derived smoke has significantly more ingredients – this can be confirmed with HPLC both in the phenol range (which is responsible for the sensory effect) and in the range of polar and low-boiling substances like Furfural und 2-(5*H*)-Furanone. Since no direct quantification is currently possible, Table 2 provides an overview of the peak area proportions of the reliably detected compounds.

Table 2. Overview of the determined peak area proportions of 2-(5*H*)-Furanone, Furfural and Vanillin in the chromatograms of the condensates and wash bottle solutions of the chip based smoke (see SI for chromatograms).

			2-(5*H*)-Furanone	Furfural	Vanilin
Chips	Cooling trap	Area [%]	0.9	15.6	3.4
	Wash Bottle *Iso*-Propanol	Area [%]	0.2	23.7	1.5
	Wash Bottle water	Area [%]	n.d.	> 0	n.d.

In contrast to the findings from the studies on R714, there is also an enrichment of Furfural here - this substance can be traced down to the aqueous solution. Accordingly, the total condensate of the smoking chips contains significantly more furfural and furanone than quantified in the cold trap condensate. This behavior is due to the higher temperature of the smoke, which is why the cooling capacity must be increased in subsequent experiments.

Analysis of smoked substrates

As already mentioned, various sample substrates were also smoked during the condensation experiments - neutral substrates (cotton wool) with collagen casings turned out to be the most suitable. The samples were extracted extensively with acetone and the evaporated extracts were examined using the same HPLC method like used for the liquid smoke characterization. Interestingly, Guaiacol and Syringol could be detected on the substrates smoked with R714, whereas this was not found in case of conventional smoking.

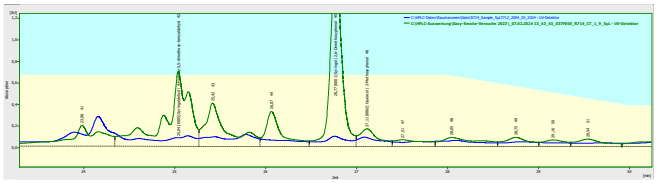

Figure 3. Extract of the chromatograms of R714 (green) and the extract of the samples smoked with R714 (blue).

However, the ratios of deposited substances are different to the composition of the condensate (see Figure 3). This finding is the first report that the reaction of smokes leads to different compositions on the surface. It underlines the fact that the composition of smokes, or even its primary condensates, is not sufficient to evaluate the safety of smoked foods. An intensive investigation is necessary for a discussion of what actually is deposited on food - both for liquid smoke, but also for conventional methods. This discussion cannot be conducted without considering the physical and chemical processes on the

substrate surface. It should be mentioned that in the samples of conventionally smoked substrates Furfural can be detected as deposited and unreacted from smoke.

Conclusion

We were able to condense smoke from a conventional smoking process and then feed it to a newly developed analysis method using HPLC. Our studies have not been dedicated to the analysis of PAHs and tars. The goal was a comparative, non-destructive analysis of smoke components. This revealed opportunities to better understand liquid smoke and further optimize it for the benefit of consumers and processors. It has been shown that conventional smoking methods also emit significant amounts of 2-(5*H*)-Furanone, as well as other compounds with genotoxic relevance. Our studies indicate that conventional smoking deposits more substances of concern.

With this work, we wanted to demonstrate that the current focus on liquid smoke for consumer protection needs to be compared with its alternatives.

The structured analysis of smoke aromas is far from complete and offers enormous possibilities for targeted product design, but this requires an objective discussion and a scientific approach.

Supporting Information

Please find selected chromatograms at the end of this document, for further information please contact the authors Dr. Alexander Scholte (Head of R&D | ascholte@pf-food.de) or Dr. Frank Höfer (CEO | fhoefer@pf-food.de).

Literature

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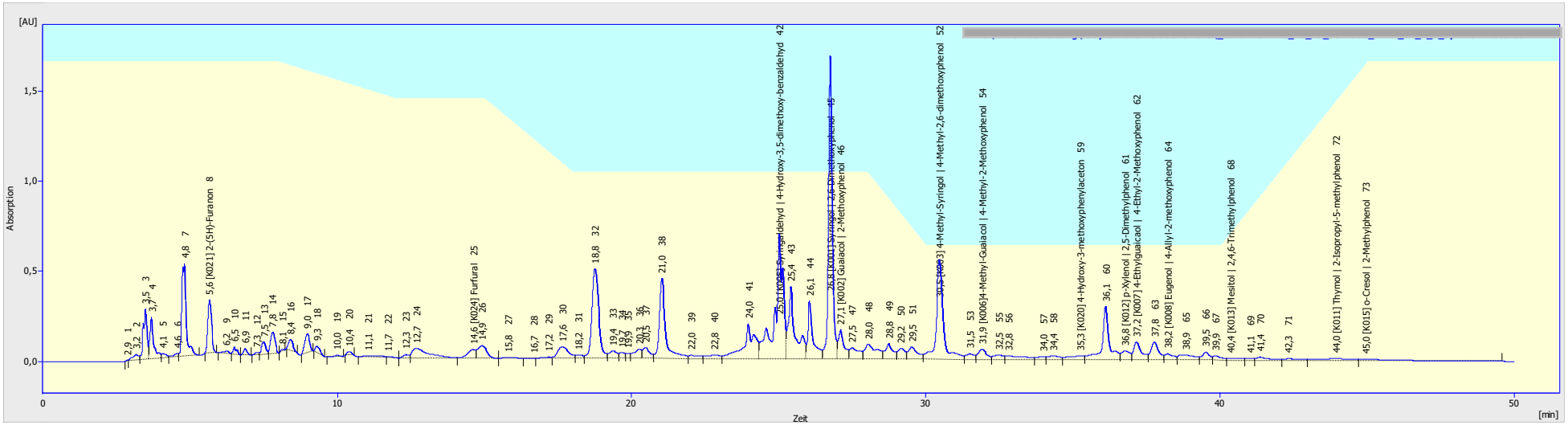

Figure S1: Chromatogram of R714 / Liquid smoke – Cooling Trap condensate.

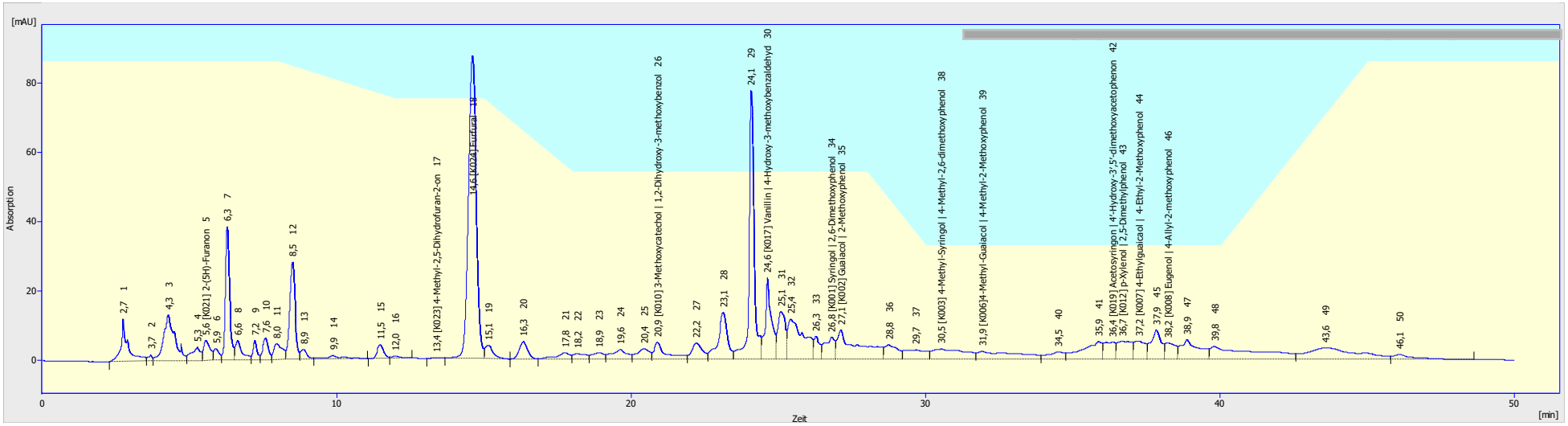

Figure S2: Chromatogram of smoke condensate from wood chips – Cooling Trap condensate.

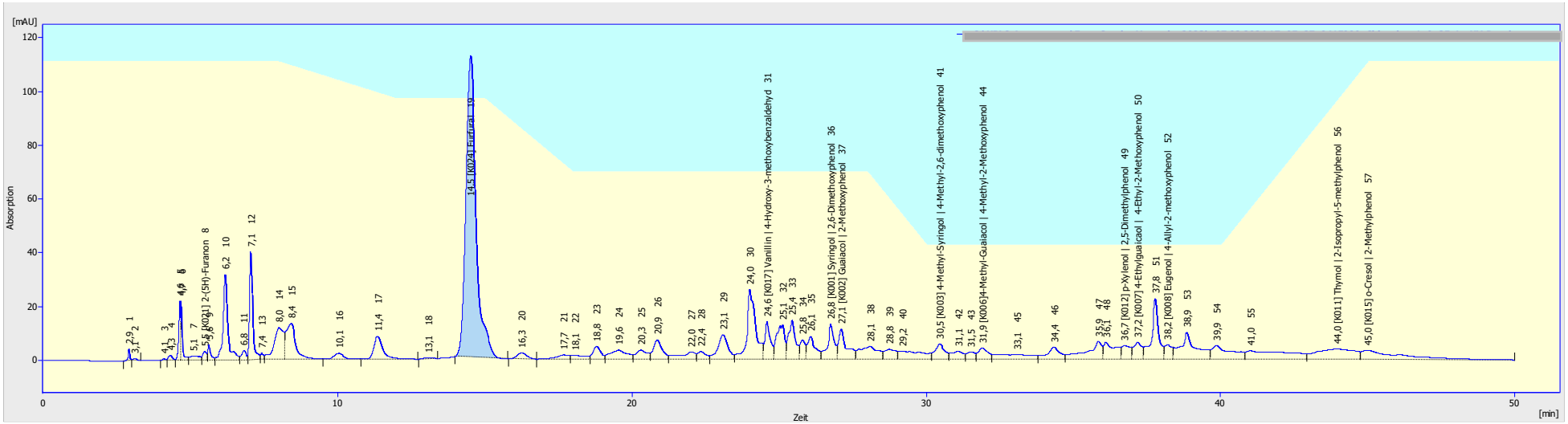

Figure S3: Chromatogram of *iso*-Propanol-filled wash bottle (wood-based smoking).

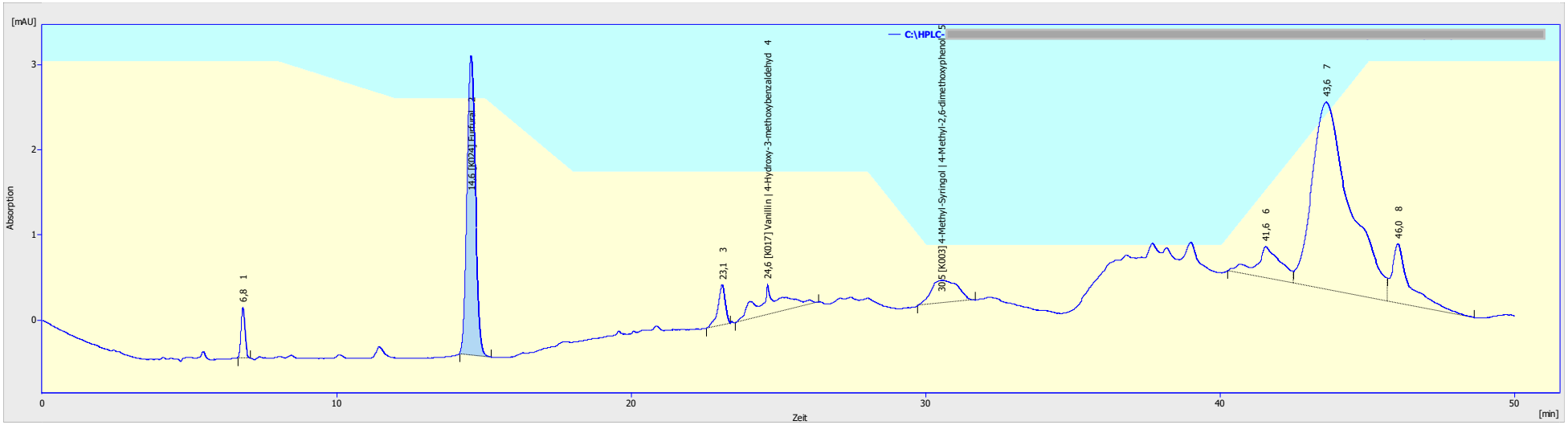

Figure S 4: Chromatogram of water-filled wash bottle (wood-based smoking).

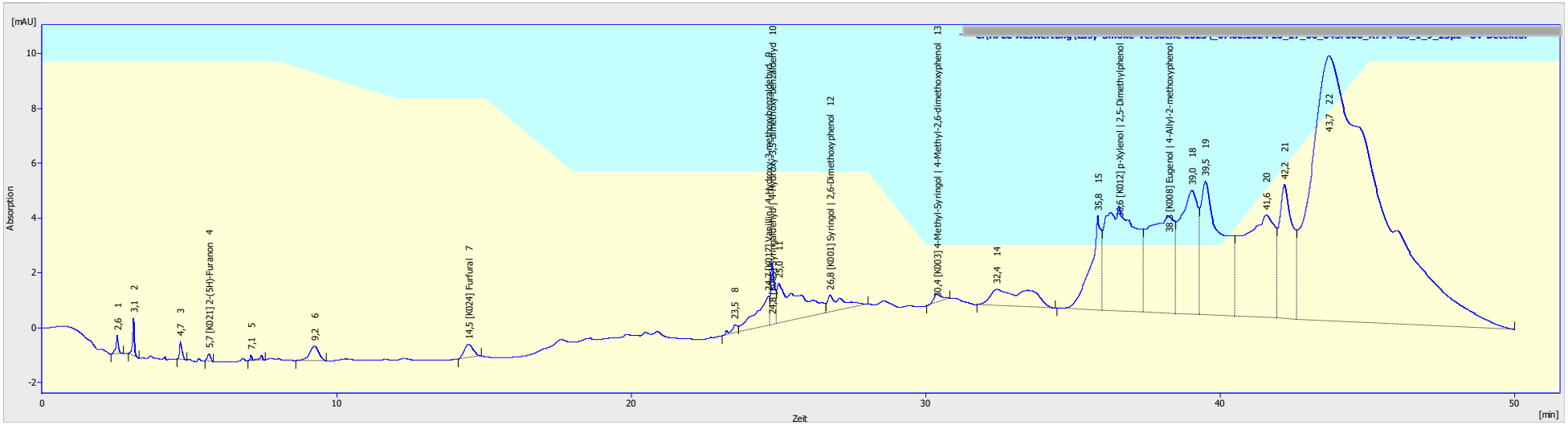

Figure S 5: Chromatogram of *iso*-Propanol-filled wash bottle (R714 / Liquid smoke).

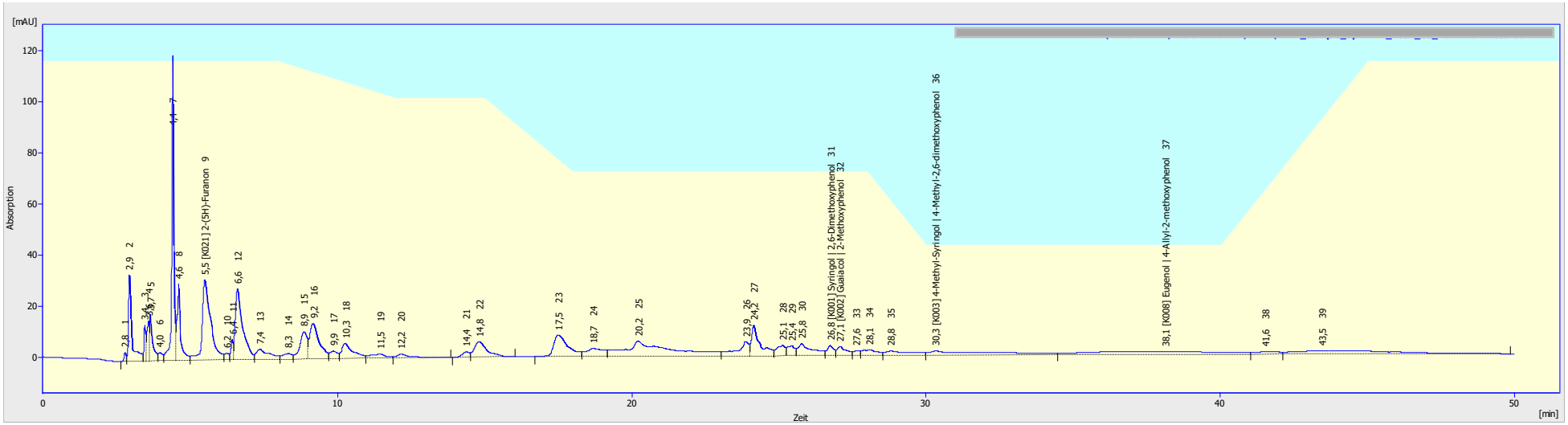

Figure S 6: Chromatogram of extracted samples (R714 / Liquid smoke).

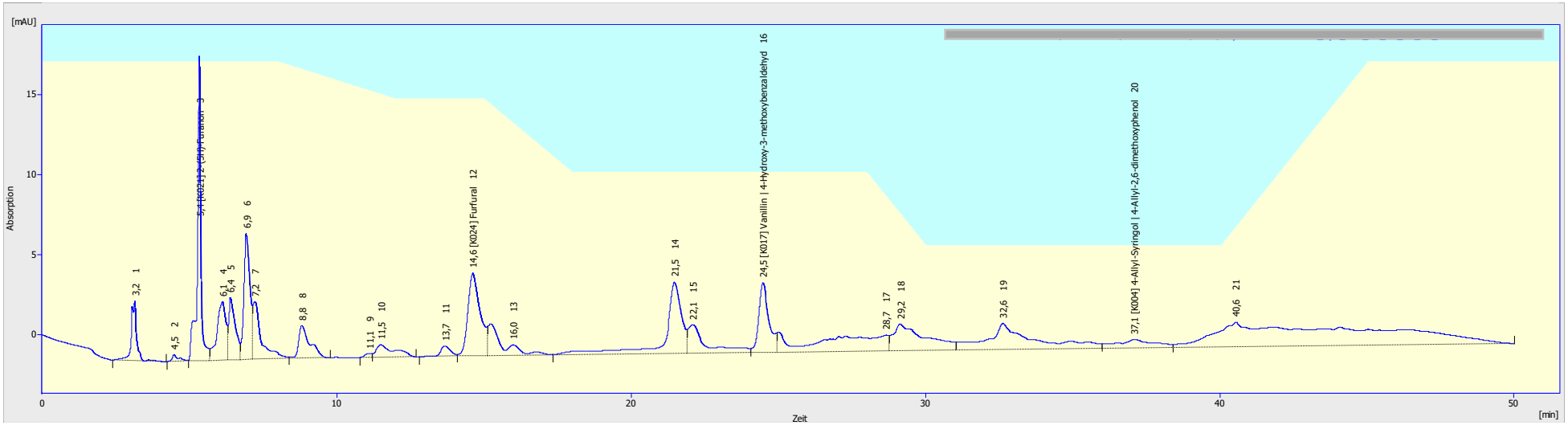

Figure S 7: Chromatogram of extracted samples (wood-based smoking).