Odorant impact and quantification of selected volatile sulfur compounds (VSC) in Swiss Tilsit cheese by headspace-solid phase microextraction-gas chromatography/pulsed flame photometric detection (HS-SPME-GC/PFPD) and olfactometry

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Introduction

Volatile sulfur compounds (VSCs) such as methanethiol, hydrogen sulfide and sulfides are key flavour compounds found in a variety of cheeses. They are mainly derived from the decomposition of the sulfur-containing amino acids cysteine and methionine. Due to their low odor thresholds, their sensory properties are very pronounced even at very low concentrations, and they can have a significant influence on cheese flavour. Gas chromatography-olfactometry (GC-O) is used to identify compounds having an odor impact. However, given their high volatility and reactivity, VSC analytics remain challenging.[1–5]

Objectives

- **Obtention of physiological information of VOCs** influencing the overall Tilsit cheese odor by GC-MS-olfactometry (GC-MS-O) on a 2-way-GC-O-system where two panelists judge a sample simultaneously
- **Quantification of target odor-impact VSCs** using GC and sulfur specific detection (pulsed flame photometric detection, GC-MS/PFPD)

Experimental

Commercial Tilsit cheese was used.

Headspace solid phase microextraction (HS-SPME) sampling

- Fiber: CAR/PDMS 85 µm 1 cm
- For GC/PFPD[6]: T= 60 °C; $t_{incubation}$= 10 min, $t_{adsorption}$= 30 min
- For GC-O: T= 60 °C; $t_{adsorption}$= 30 min

VSC determination by GC/PFPD

- Use of two internal standards (*IS*) to correct for variations
- External calibration curve for correction factor and quantification
- Analyses were conducted in triplicate

GC-Olfactometry

- Trained judges (total n= 20; two at a time) described the perceived odors and rated their intensity on a three-point-scale
- Data were processed using the Acquisniff® software[7,8] taking into account detection frequency, odor intensity and the descriptive vocabulary employed by the judges after attribution to odor families

Results

GC/PFPD

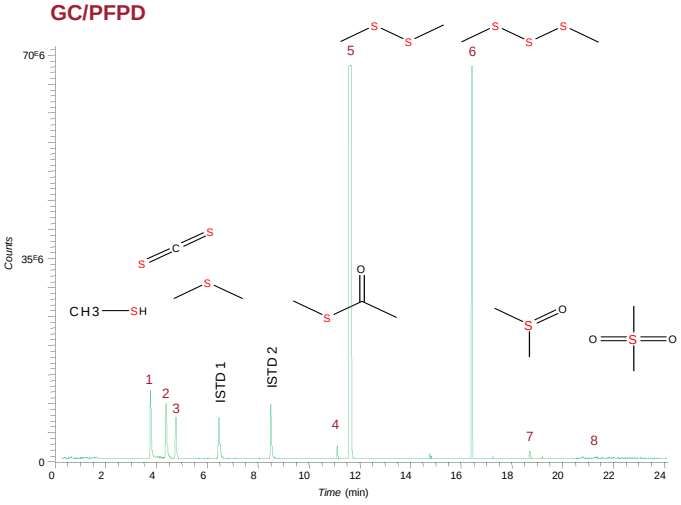

Fig. 1 PFPD signal of Tilsit headspace extracted with a CAR/PDMS 85 µm 1cm SPME fibre

Tab. 1 Quantification of target VSCs in Tilsit using two internal standards and an external calibration curve. Only molecules having an odor impact were quantified. Literature threshold values in water are indicated. It is important to consider that the oil in the cheese matrix can also strongly influence the odor threshold.

N° Fig. 1	Name	Odor characteristics (literature)[9-11]	Odor threshold In water [ppb]	Concentration [µg kg^{-1}= ppb]
1	Methanethiol	rotten cabbage, burnt rubber	1.8–2[11]	*In progress*
2	Carbone disulfide	sweet, ethereal, slightly green, sulfidy	50[11]	*n.d.*
3	Dimethyl sulfide	canned corn, cooked cabbage, asparagus	0.3–1[9]	4
4	Methyl thioacetate	sulfurous, eggy, cheese, dairy, vegetable, cabbage	50 [11]	0.1
5	Dimethyl disulfide	vegetal, cabbage, onion-like at high levels	0.16–12[10]	1.7
6	Dimethyl trisulfide	sulfurous, alliaceous, cooked, savory, meaty	0.005–0.01[10]	0.5
7	Dimethylsulfoxide	garlic	*NA*	*n.d.*
8	Dimethylsulfone	sulfurous, burnt	*NA*	*n.d.*

n.d.= not determined, *NA*= not available

GC-Olfactometry

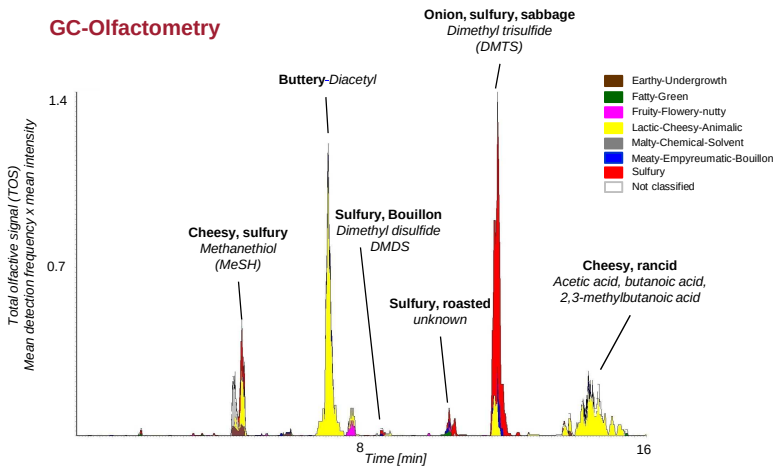

Fig. 2 Aromagram of Tilsit cheese, identified odorant main VSCs, VOCs and odor descriptors used by the judges in this study. The repartition of the mean total olfactive signal (*TOS*) into eight previously defined odor families is shown; main odor families being "lactic-cheese-animalic" and "sulfury".

Conclusion

About a dozen VSCs were detected in different concentrations: methanethiol, dimethyl sulfide, methyl thioacetate, dimethyl disulfide and dimethyl trisulfide were found at ppb levels. In addition, carbon disulfide, dimethylsulfoxide and dimethylsulfone were also identified.

GC-O revealed MeSH, DMDS and DMTS to be the main identified VSCs having an impact on the odorant profile of the tested cheese sample. However, in the employed conditions, DMDS showed a minor, MeSH a more important and only DMTS a strong odor impact. Although DMDS was found in a quantity about three times higher than DMTS, the observed difference in odor impact can be explained by DMTS having a much lower detection threshold. Other odorant VSCs seem to be below odor threshold. Further VOCs such as diacetyl and carboxylic acids were also detected. According to these results, the main VOCs influencing the cheese's overall odor are DMTS, diacetyl, MeSH and a mixture of carboxylic acids.

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