Olfactometry profile and evaluation of odour-active volatile sulphur compounds in three different Swiss Tilsit cheeses by HS-SPME-GC-MS/PFPD and HS-SPME-GC-MS-O using vocabulary-intensity-duration of elementary odours by sniffing (VIDEO-Sniff)

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Introduction

Volatile sulphur compounds (VSCs) such as methanethiol, hydrogen sulphide and sulphides are key flavour compounds found in a variety of cheeses and in general, cheeses made from raw milk have a more intense flavour than cheeses manufactured with pasteurized milk[1].

The mentioned VSCs are mainly derived from the decomposition of the sulphur-containing amino acids cysteine and methionine. Due to their low odour thresholds, their sensory properties are very pronounced even at very low concentrations, and they can have a significant influence on cheese flavour. Given their high volatility and reactivity, VSC analysis remain challenging[2–6].

Objectives

- **Determination/quantification of VSCs** in Tilsit cheese using gas chromatography and sulphur specific detection (pulsed flame photometric detection, GC-MS/PFPD)
- **Obtention of physiological information on odour quality and impact of VSCs** on the overall Tilsit cheese odour by GC-MS-olfactometry (GC-MS-O) on a 2W-GC-O-system where two panellists judge a sample simultaneously

Experimental

Commercial Tilsit cheeses were analyzed.

Headspace solid phase microextraction (HS-SPME) sampling

- For GC/PFPD[7]: T= 60 °C; $t_{extraction}$= 60 min, fibre: CAR/PDMS 85 µm 1 cm
- For GC-O[3]: T= 45 °C; $t_{extraction}$= 16 h, Fibre: DVB/CAR/PDMS 50/30 µm 2 cm

VSC determination by GC/PFPD

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

GC-Olfactometry

- Trained judges (total n = 8; two at a time) described the perceived odours and rated their intensity on a five-point-scale
- Data were processed taking into account detection frequency and odour intensity (mean olfactory signal by classes ($\overline{OSC}_{Int \times Det}$) as well as the employed descriptive vocabulary sorted into odour classes using the Acquisniff® software[8,9]

Results

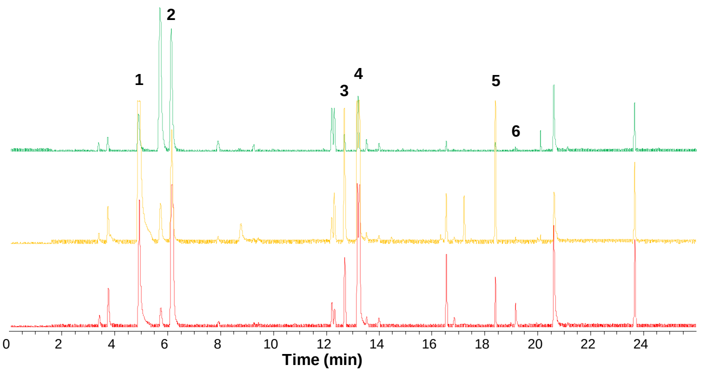

Fig. 1 PFPD signals of Tilsit cheese headspace manufactured with **raw**, **pasteurized** milk and with **higher fat content**; extracted with a CAR/PDMS 85 µm 1cm SPME fibre

Tab. 1 Quantification of the odorant VSCs found in Tilsit with a low odour threshold using one internal standard and external calibration curves

N° Fig. 1-4	Name	Odour characteristics (literature)[10]	Odour threshold In water [µg · kg^{-1}][10]	Concentration [µg · kg^{-1}]		
1	Methanethiol (MeSH)	rotten cabbage, burnt rubber	0.02	*23 ±2.1*	*307 ±19.5*	*164 ±19.2*
2	Dimethyl sulphide (DMS)	Pungent, cabagge, cooked vegetables	0.3-1	15 ±0.6	27 ±0.8	56 ± 4.9
3	Methyl thioacetate (MeSAc)	Cabbage, vegetables	50	0.3 ±0.07	2.8 ±0.13	2.6 ± 0.08
4	Dimethyl disulphide (DMDS)	Vegetal, cabbage, onion-like at high levels	0.16-1.2	1.5 ± 0.1	37 ±0.7	75 ±6.8
5	Dimethyl trisulphide (DMTS)	Sulphurous, alliaceous, cooked, savory, meaty	0.005–0.01	0.5 ±0.03	4.8 ± 0.07	4.4 ±0.22
6	Methional	Boiled potatoes	0.2	7.0 ±1.62	5.9 ±1.62	36 ±1.3

GC-Olfactometry

The OSC-aromagrams consist of eight individual aromagrams obtained by 2W-GC with eight selected panelists. Odour descriptions of the panelists were classified into ten different families (buttery-cheesy, **empyreumatic**, floral-fruity, green-fatty, malty-chemical, meaty, spicy, nutty, sulphur and earthy-undergrowth)

Pasteurized milk
Fat content: 45% FDM
Ripening time: 30-60 days
Flavour: mild, slightly acidic[11]

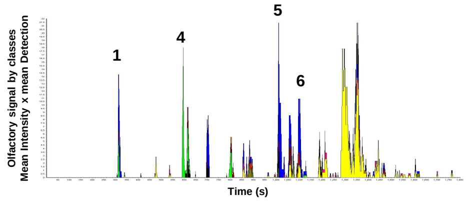

Fig. 2 Aromagrams of Tilsit cheese made from pasteurized milk

Pasteurized milk
Fat content: 55% FDM
Ripening time: 30-75 days
Flavour: mild, creamy flavour, slightly acidic[11]

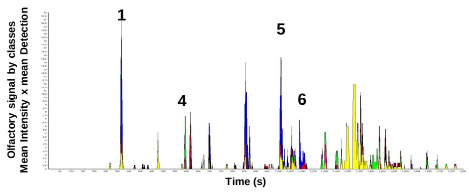

Fig. 3 Aromagrams of Tilsit cheese made from pasteurized milk with an higher fat content

Thermized mik and raw milk
Fat content: 45% FDM
Ripening time: 70-110 days
Flavour: Rich and spicy[11]

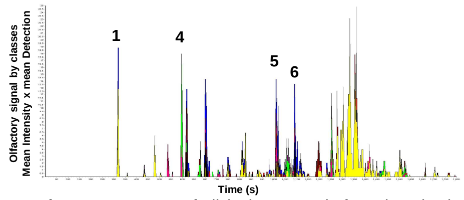

Fig. 4 Aromagrams of Tilsit cheese made from thermized and raw milk mixture

Conclusion

About a dozen VSCs were detected in different concentrations in the studied cheeses. MeSH, DMS, MeSAc, DMDS, DMTS and methional were found at ppb levels with a low odour threshold. In addition, carbon disulphide, dimethylsulfoxide and dimethylsulfone were also identified and quantified (data not shown) but due to their high odour thresholds, they were not considered. Quantification of VSCs shows a clear increase in concentrations between cheese made from pasteurized milk and cheese made from thermized/raw milk. This can be explained by a longer ripening time, but also by a wider variety of the indigenous microflora in raw milk. Tilsit containing 55% fat in dry matter (FDM) shows also a higher concentration of VSCs than cheese made with pasteurized milk for the same ripening time. A higher fat content can affect growth of the microflora, enzymatic activity, partioning and matrix effects thus influencing the concentration of VSCs [12]. GC-olfactometry revealed that MeSH, DMDS (co-elution with hexanal), DMTS and methional were the only identified VSCs found to have a strong impact on the odorant profile of the tested cheese samples. The aromagrams of the cheeses show differences, but for VSCs not as strongly as one might expect from the quantification results. The cause might be a limitation of methodology: when the concentration of a given compound widely exceeds the odour threshold, the panellist cannot rate the intensity of the perceived odour stronger than the maximum of the employed scale (1 to 5), and also detection frequency cannot exceed 100%. This is particularly the case for the most intense peaks and might explain why, despite clear differences in quantified VSC amounts, these are not directly translated in the aromagrams.

The authors thank the panellists for their participation.

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