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Off-flavour Analysis in Food Using a Simple and Rapid SPME-GC/TQMS Method with Dedicated Off-flavour Database

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Introduction

Flavour is one of the most critical sensory characteristic of food. Off-flavours not only negatively impact consumers' acceptability but more importantly, may indicate safety risks. Various analytical techniques for the analysis of off-flavour in specific samples have been described.[1] For a generic method applicable to a wide range of samples, speed and ease of use are important criteria. Solid phase micro-extraction (SPME) is a sampling technique that matches these criteria. In SPME, the thin layer of polymeric stationary phase coating (fibre) can be directly exposed to the sample or positioned in the headspace. When sampling is performed in the headspace, there is flexibility in the physical nature of sample matrix analysed.
This study describes a GC/TQMS method coupled to SPME for targeted identification and semi-quantitation of off-flavour compounds from food samples of different physical natures. Using the unique off-flavour analyser system (Shimadzu Corporation, Japan) containing a database of off-flavour compounds and optimised instrumental parameters, simple and rapid screening was possible.

Methods and Materials

This study was carried out on a gas chromatography triple quadrupole system, GCMS-TQ8040 (Shimadzu Corporation, Japan) coupled to the AOC-6000 autosampler containing the SPME modules (Shimadzu Corporation, Japan) (Figure 1). Further details on the instrumental conditions can be found in Table 1. The whole process from SPME sampling was fully automated using the AOC-6000 autosampler.

Figure 1 GCMS-TQ8040 system with AOC-6000 autosampler

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Four different types of food were studied for the off-flavour molecules generated during spoilage. They represented samples of different physical properties, ranging from liquid (milk and watermelon juice), to semi-solid (cream cheese) and solid (lettuce). Food spoilage was induced by storing them at room temperature for 3 days. These were compared to control samples that were stored at 4 °C. One millilitre each of milk and watermelon juice, 2.0 g of cream cheese and 1.0 g lettuce samples were separately transferred into headspace vials for analyses of the off-flavour molecular composition.
The concentrations of compounds in each samples were calculated using the in-built calibration curves. The fold change analysis for each group of food samples was carried out using the MetaboAnalyst 3.0 software.[2]

Table 1. Instrumental conditions used in study

Parameter	Setting
AOC-6000 autosampler	
SPME fibre	: Divinylbenzene/carboxen/polydimethylsiloxane 50/30 µm, 23Ga
Conditioning Temperature	: 270 °C
Incubation Temperature	: 80 °C
Incubation Time	: 5 min
Agitator Speed	: 250 rpm
Sample Extract Time	: 30 min
Sample Desorb Time	: 2 min
Gas Chromatograph	
Column	: InertCap Pure-Wax (30 m × 0.25 mm × 0.25 µm)
Injector Port Temperature	: 250 °C
Injection Mode	: Split (1:5)
Carrier gas	: Helium
Flow Control Mode	: Pressure
Pressure	: 83.5 kPa
Column Oven Temperature	: 50 °C (5 min) → 10 °C/min to 250 °C (10 min)
Mass Spectrometer	
Ion Source Temperature	: 200 °C
Operation Mode	: Scan/MRM
Scan Range	: m/z 42 - 500
MRM Transitions	: Included in Off-flavour Analyzer

Results

The MRM method successfully identified off-flavor compounds in food samples. An example of MRM chromatograms for flavor compounds detected in control and spoilt food (milk sample) are shown in Figure 2. The top 10 compounds that were elevated in each type of rancid sample are shown in Table 2

Watermelon Juice

34 compounds associated with off-flavour were increased in spoilt samples (Figure 3 (a)). The compound which increased by the largest extent was acetic acid, which resulted from the fermentation of sugars.

Milk

Spoilage resulted in elevated concentrations of 31 compounds related to off flavour (Figure 3 (b)). Short chain fatty acids, butyric acid, caproic acid and caprylic acid, were likely degradation products of triglycerides in milk. Microbial metabolism or light-induced degradation of sulphur-containing amino acids are possible causes for the elevated levels of dimethyl disulphide. Similarly, microbial activities are known to produce indole from tryptophan metabolism.

Cream Cheese

13 compounds were found to be elevated by at least 1.5 fold in spoilt samples (Figure 3 (c)). Levels of short chain fatty acid, isobutyric acid and isovaleric acid were markedly elevated possibly due to the lipase-mediated breakdown of triglycerides.

Lettuce

47 compounds were significantly higher in spoilt samples compared to control samples while 8 compounds were of lower concentrations (Figure 3 (d)). Key molecules such as 2-ethyl-1-hexanol and p-ethylguaiacol are products of microbial metabolism. Ethyl acetate and acetic acid possibly originated from microbial fermentation processes.

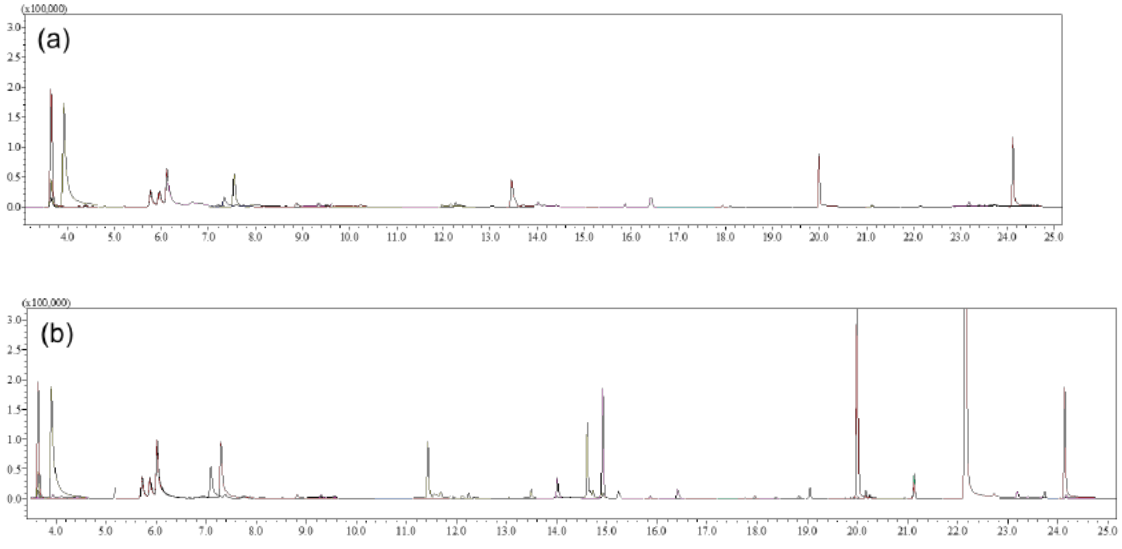

Figure 2. The MRM chromatograms for flavour compounds detected for milk samples, (a) control sample stored at 4 °C for 3 days and (b) spoilt sample stored at room temperature for 3 days

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Table 2. Top 10 compounds that were elevated in each type of rancid sample

Milk		Watermelon Juice		Cream Cheese		Lettuce	
Compound	[Rancid] / [Control]	Compound	[Rancid] / [Control]	Compound	[Rancid] / [Control]	Compound	[Rancid] / [Control]
Butyric acid	11253.0	Acetic acid	53761.0	Isobutyric acid	586.3	2-Ethyl-1-hexanol	42985.0
Caproic acid	7780.7	Caprylic acid	7880.6	Isovaleric acid	561.7	2,3-Xylenol	14972.0
2-Nonanol	1285.3	Caproic acid	7359.5	n-Dodecanal	125.0	L-Menthol	14604.0
1-Dodecanol	595.3	Ethyl acetate	3152.6	n-Hexyl acetate	79.3	p-Ethylguaiacol	10810.0
3-Heptanone	123.7	Eugenol	584.3	Indole	79.3	p-Ethylphenol	10680.0
Acetophenone	104.7	Benzyl alcohol	537.5	1-Dodecanol	75.7	Phenol	8483.3
n-Decanal	97.3	Linalool	447.9	2-Nonenal	73.3	α-Terpineol	6688.3
n-Butyl-acetate	52.0	1-Dodecanol	385.9	Linalool	13.7	Butyl-cellosolve	2728.7
γ-Decalactone	33.3	2-Nonanone	215.3	2-Phenylethanol	7.3	1-Undecanol	2650.8
p-Ethylphenol	20.5	Phenylacetic acid	211.9	1-Methoxy-2-propyl acetate	3.3	Ethyl acetate	1290.9

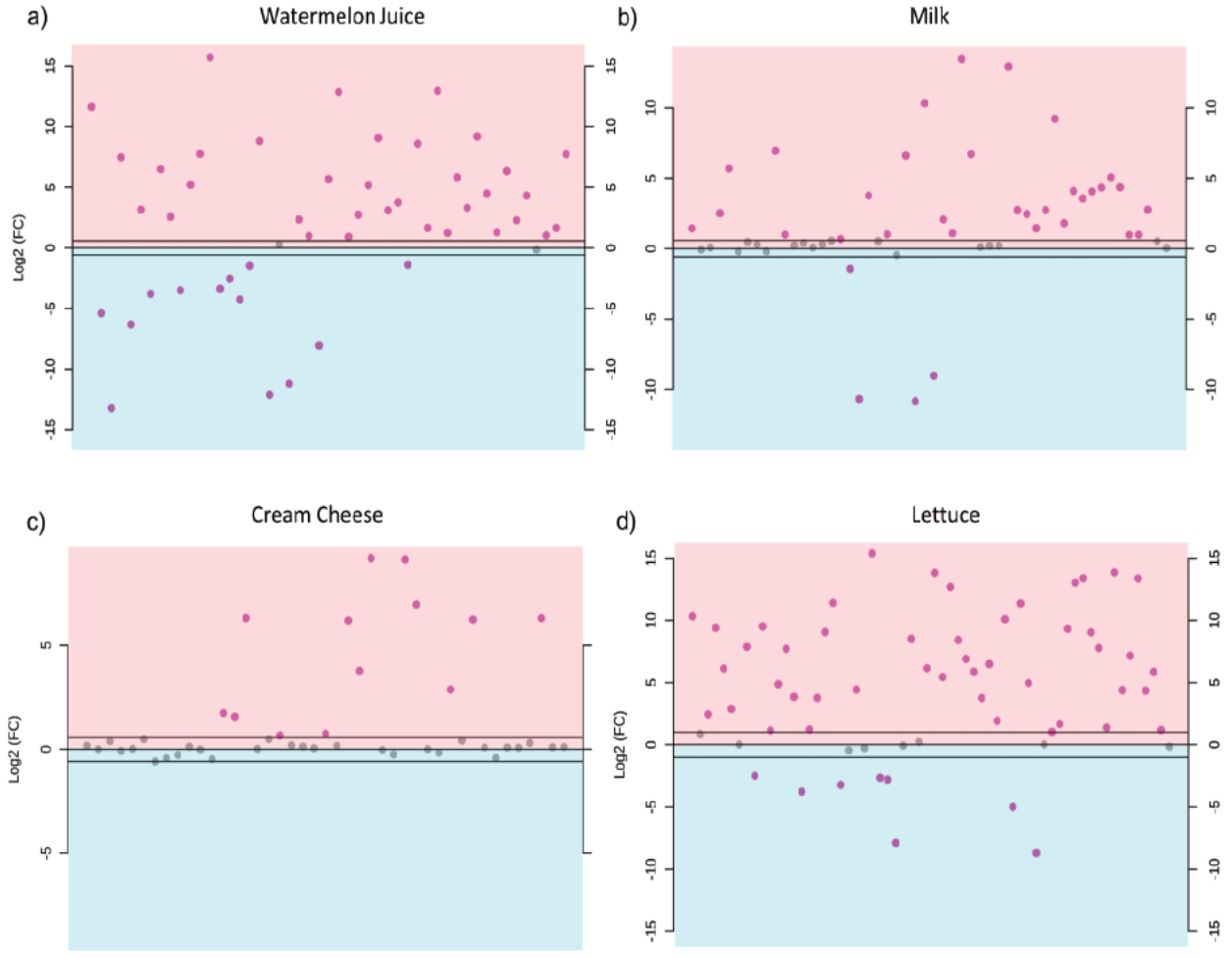

Figure 3. Fold change plot of [rancid]/[control] for (a) watermelon juice, (b) milk, (c) cream cheese and (d) lettuce. Red regions indicate area where [spoilt] is higher than [control] and the blue regions indicate area where [spoilt] is lower than [control]. Pink-coloured dots indicate compounds that have exceeded the 1.5 fold threshold.

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Conclusion

The SPME-GC/TQMS method in this study successfully detected off-flavour molecules in rancid food samples using the off-flavour database. The flexibility of the SPME method in analyses of food samples of varying physical natures was demonstrated. Successful screening of discriminating off-flavour molecules in test samples facilitated further investigation of cause and understanding of biochemical changes associated with food spoilage.

References

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