Evaluation of monolithic sorptive extraction (MMSE) as an alternative aroma extraction technique

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Introduction

A precondition in finding relations between results from aroma and sensory analysis is that the prepared aroma extract resembles the aroma of the actual product. In this study we compared the extraction capability of the well known sample preparation techniques of Large Volume Static Headspace (LVSH) and Headspace Sorptive Extraction (HSSE) with a relative new extraction technology called Monolithic Material Sorptive Extraction (MMSE). Based on sensory evaluation of the obtained extracts of strawberry flavored milk it was shown that the extract obtained from MMSE resembles the aroma of the original strawberry flavored milk the best. The intraday reproducibility (CV %) and linearity (r^2) for the components investigated varied between 3.3 and 5.5% and 0.94 and 0.99, respectively.

What is MMSE?

MMSE makes use of a new generation media for adsorption and extraction developed by using silica monolith technology. Based on this silica monolith technology an innovative hybrid adsorbent of silica and activated carbon (or graphite carbon) having a large surface area bonded with octadecyl silane (C_{18},ODS) was manufactured (**Figure 1 and 2**). The ODS bonded hybrid medium application showed adsorption capabilities to a wide variety of compounds. It was also reported that an advantage of MMSE is a large surface area, a high recovery and a short extraction and conditioning time [**1,2**].

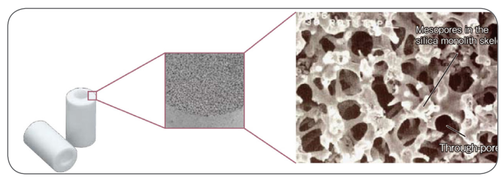

Figure 1.
Illustration of the silica monolith material.

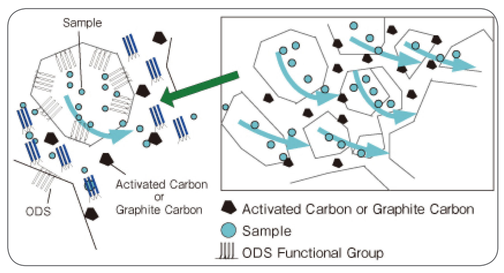

Figure 2. Adsorption on MMSE.

Experimental set up

Strawberry flavoured milk

Semi-skimmed milk was fortified with a mixture of 7 aroma components (**Table 1**) to obtain a strawberry flavoured milk.

#	Component	Concentration in Milk (µg/l)
1	Propanoic acid, 2-methyl, ethyl ester	300
2	Butanoic acid ethyl ester	800
3	Butanoic acid, 2-methyl, ethyl ester	800
4	Hexanoic acid, ethyl ester	600
5	(Z)-3-hexen-1-ol acetate	500
6	(Z)-3-hexen-1-ol	800
7	(E) Hex-2-en-1-ol (E)	200

Table 1.
Used aroma mixture and final milkconcentrations.

LVSH

LVSH was performed using a LVSH device. An amount of 25 ml of the strawberry flavoured milk was transferred to a glass tube and closed with a plunger (total headspace volume 150 ml). The sample was cooled to 7°C. After 30 minutes the plunger was moved down and the volatiles were collected on a TENAX tube.

HSSE

HSSE was performed by using a 20 ml headspace vial equipped with a headspace insert. An amount of 3.33 ml of the strawberry flavoured milk was added and a pre-conditioned twister was put in the headspace insert. Extraction was performed during 30 minutes at 7°C.

MMSE

An amount of 3.33 ml of the strawberry flavored milk was transferred to a 20 ml vial. Via a special holder the MMSE device was exposed to the volatiles in the headspace (30 minutes, 7°C).

GC/MS

All collected samples were thermally desorbed by programming a TDU from 30° to 250°C (holding time 10 minutes) at 60°C/min. After cryofocussing in a CIS4 at -20°C the CIS4 was heated to 250°C at 12°C/s. The components of interest were transferred (solvent vent mode) to a Wax 58 (FFAP) CB column (25m x 0.25mm I.D., 0.25 µm film thickness). The oven was programmed from 40°C (hold time 2 min.) to 275°C (hold time 2 min.) at 15°C/min. Helium was used as a carrier gas (flow rate 1.5 ml/min). The mass spectrometer (EI) was operated in the SIM mode. Two selective ions per component were used for identification and quantification.

Collection of volatiles

After decoupling the mass spectrometer, the volatile components were collected at the end of the analytical column in 0.66 ml of milk that was cooled at 0°C.

Determination of intraday repeatability and linearity for the MMSE technique

Repeatability was measured by determining the peak area of measuring five times the concentration of the middle calibration point. For all components a 5-point calibration curve was prepared in concentration ranges as described in **Table 2**. d_{12}-hexanal was used as an internal standard.

Component	Upper limit concentration range in Milk(µg/l)
Propanoic acid, 2-methyl, ethyl ester	160
Butanoic acid ethyl ester	320
Butanoic acid, 2-methyl, ethyl ester	320
Hexanoic acid, ethyl ester	320
(Z)-3-hexen-1-ol acetate	266
(Z)-3-hexen-1-ol	6400
(E) Hex-2-en-1-ol	1600

Table 2.
Upper limits for used concentration ranges.

Sensory evaluation

A sensory panel (N=11) evaluated the original milk sample and the samples collected at the end of the column. The panelist were asked to describe the differences between samples and give an indication about the size of the difference.

Results

The strawberry flavoured milk was extracted by the LVSH, HSSE and MMSE technique and analytically compared based on GC/MS data (**Figure 3**). The results show that aroma extracts prepared with the LVSH and MMSE technique result in comparable aroma profiles.

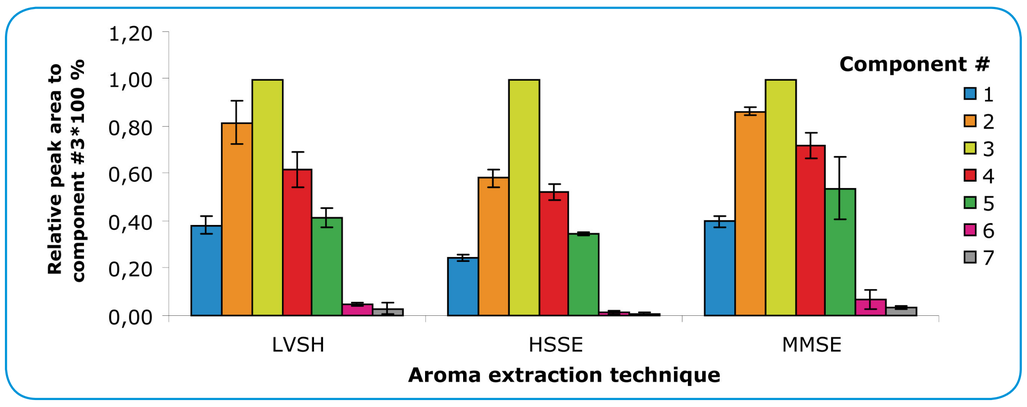

Figure 3. Comparison of the LVSH, HSSE and MMSE technique based on GC/MS analysis. For decoding the components see table 1.

After thermal desorption the extracted aroma components were collected in cooled semi-skimmed milk and sensorially compared to the original milk sample (also purged with the gas coming from the column outlet). The aim was to determine which extraction technique best resembles the aroma of the strawberry milk sample. **Table 3** shows the result of this sensory comparison. The results show clearly that the aroma extract of MMSE technique most resembles the aroma of the original strawberry flavoured milk.

Description of difference compared to reference	Number of panelists HHSE	MMSE	LVSH
No	0	1	1
Small	2	4	1
Reasonable	3	6	2
Large	2	0	7
Very Large	4	0	0

Table 3.
Results of the comparison of the aroma of strawberry milk (purged with gas coming from the GC-column outlet) and the aroma extracts prepared with the HHSE, MMSE and LVSH technique.

The sensory panel was also asked which extract has an aroma that is the most comparable to the original strawberry flavoured milk. 9 out of 11 panelists answered that the aroma of MMSE mimics the best the aroma of the original strawberry flavoured milk.

For the MMSE technique the intraday reproducibility and linearity was further investigated. **Table 4** presents the results of this study. The observed intraday reproducibility and linearity are in line with values normally found for the investigated concentration range.

Component	RSD(%)	r^2
Propanoic acid, 2-methyl, ethyl ester	3,31	0,95
Butanoic acid ethyl ester	4,13	1,00
Butanoic acid, 2-methyl, ethyl ester	2,26	1,00
Hexanoic acid, ethyl ester	0,83	0,98
(Z)-3-hexen-1-ol acetate	2,32	1,00
(Z)-3-hexen-1-ol	4,75	0,99
(E) Hex-2-en-1-ol	5,45	0,99

Table 4.
Results of intraday reproducibility (RSD %) and linearity (r^2) of the MMSE technique.

Conclusions

A comparison of aroma extraction techniques showed that an aroma extract prepared with MMSE best resembles the extract of strawberry flavoured milk. Consequently, for the investigated matrix and aroma, the MMSE technique is therefore very powerful in finding relations between analytical and sensory data.
Linearity and reproducibility of the MMSE showed good results indicating that MMSE is useful for quantitative analysis of aroma components.

References

[1] A novel approach for aroma components analysis using a monolithic hybrid adsorbent as a new generation medium."MonoTrap", **Atsushi Sato, Katsuhiko Sotomaru, Manami Takeda**, Poster 40th International Symposium on Essential Oils, 2009
[2] Headspace enrichment of bergamot and mandarin juices by means of Monolithic Material Sorptive Extraction (MMSE), **Rosaria Costa, Paola Dugo, Giovanni Dugo and Luigi Mondello**, Poster 34th International Symposium on Capillary Chromatography', 2010

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