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Analysis of Aroma Compounds in Edible Oils by Direct Thermal Desorption GC/MS using Slitted Microvials

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Abstract
This application note describes the direct thermal desorption of desirable and undesirable aroma compounds from edible oils. The oil sample is placed in a microvial from where it is directly thermally desorbed using a GERSTEL Thermal Desorption Unit (TDU). Volatile compounds are transferred to the GC/MS system while leaving the non-volatile oil matrix behind in the microvial, preventing it from reaching and contaminating the GC inlet and the GC column. Different designs of microvials were evaluated for effectiveness of analyte transfer. Microvials with a slit at 1 cm from the bottom were found to be the best suited providing efficient and repeatable analyte transfer and sensitive determination of a wide range of compounds.

Introduction

The determination of aroma compounds in edible oils (olive oil, sunflower oil, fish oil etc.) is important for manufacturers and vendors of these products. Especially off-flavors derived from unsaturated fatty acid degradation such as, for example, hexanal, 2-(E)-nonenal and 2,4-(E,E)-decadienal are of interest. These compounds can compromise the taste and therefore the quality of a product even in the ng/g concentration range [1,2,3,4]. Sensitive and fast analysis methods, ideally combined with simple sample preparation, are needed. In 2008, GERSTEL developed a sensitive analysis method employing dynamic headspace sampling [5]. At that time direct thermal desorption from standard microvials placed in TDU thermal desorption tubes was also tested. Although the technique performed well for volatile analytes, the resulting sensitivity for high boiling compounds (e.g. 2,4-decadienal) was not satisfactory. In this project we returned to the microvial approach and evaluated different microvial designs to improve the transfer of high boiling compounds while maintaining the excellent performance for the volatile fraction.

Experimental

Instrumentation. Thermal desorption of oil samples placed in microvials in thermal desorption tubes was conducted in the GERSTEL Thermal Desorption Unit (TDU). Analytes were refocused in a GERSTEL Cooled Injection System (CIS 4), PTV-type inlet, at low temperatures before being transferred to the GC column. A 7890/5975 GC/MS system from Agilent Technologies was used for separation and detection of the analytes of interest. Thermal desorption tubes containing the samples were delivered to the TDU automatically using a GERSTEL MultiPurpose Sampler (MPS) (figure 1).

Figure 1. GC/MS system for thermal desorption of edible oils. GERSTEL Thermal Desorption Unit (TDU) mounted on a Cooled Injection System (CIS), PTV-type inlet and an Agilent GC 7890 / MSD 5977.

Materials. Standard empty TDU tubes with single notch were used (p/n 013010-100-00) for thermal desorption. Oil samples were placed in standard microvials (p/n 014756-002-00) or newly designed microvials respectively. All new designs were produced manually from standard microvials by either cutting off the top part or by cutting a slit at a defined height from the bottom (figure 2). The microvials with a slit at 1 cm from the bottom are now commercially available from GERSTEL (p/n 014756-601-00).

Figure 2. Different microvial designs (from left to right): standard, slit at 1.5 cm from bottom, slit at 1 cm from bottom, cut at 1.5 cm from bottom, cut at 1 cm from bottom. For this study all slitted and cut microvials were produced manually. Currently the left and middle microvials are commercially available (p/n 014756-002-00 and 014756-601-00).

Sample Preparation. Edible oil was spiked with the analytes listed in table 1 in the concentration range between 10 and 1000 ng/g. A set of 30 mg samples of the oil were weighed into individual microvials and placed in thermal desorption tubes. Each tube was capped with a transport adapter (figure 3) and placed in the autosampler tray for later desorption.

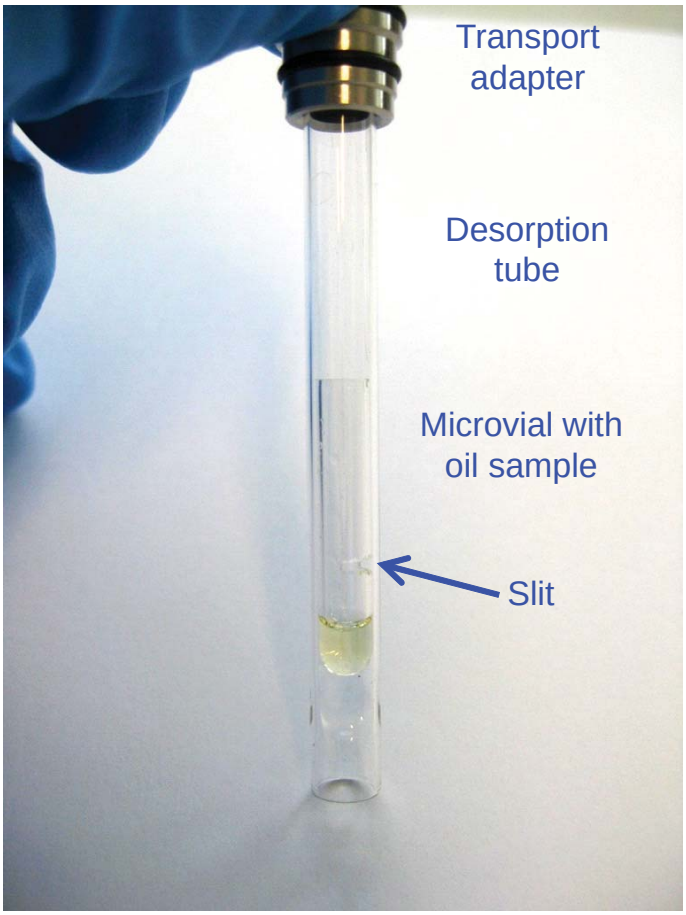

Figure 3. A 30 mg sample of edible oil placed in a microvial with slit at 1 cm inside a TDU tube.

Analysis Conditions

TDU: Solvent venting
30°C; 200°C/min; 90°C (15 min)
PTV: Glassbead liner,
0.2 min solvent vent (30 mL/min)
split 3:1
-70°C; 12°C/s; 280°C (30 min)
Column: 15 m ZB-FFAP (Phenomenex)
d_i = 0.25 mm d_f = 0.25 µm
Pneumatics: He, constant flow = 1.3 mL/min
Oven: 35°C (1 min); 4°C/min;
120°C (5 min); 50°C/min; 250°C (8 min)
MSD: SIM, cf. table 1

Table 1. Analytes spiked into edible oil. Retention times, quantifier- and qualifier m/z.

Compound	RT [min]	Quant. [m/z]	Qual. [m/z]
3-Methylbutanal	1,194	58	57; 86
Hexanal	2,304	56	72; 82
4-Heptanone	2,787	71	114; 43
2-Ethylpyrazine	6,851	107	80; 53
Dimethyltrisulfide	7,540	126	79; 47
2-Ethyl-3,5-dimethylpyrazine	9,797	135	136; 108
Methional	9,992	104	76; 48
2-(E)-Nonenal	12,217	83	70; 96
2,3-Dimethoxytoluene	15,477	152	137; 109
2,4-(E,E)-Nonadienal	16,641	81	138; 95
2-Methylpentanoic acid	18,533	74	87; 43
2,4-(E,E)-Decadienal	19,431	81	152; 95
gamma-Decalactone	28,107	128	100; 85

Measurements. Several 30 mg samples of spiked oil were desorbed in different types of microvials and the analyte peak areas compared. The best performing microvial design was selected. Subsequently, 10 oil samples of 30 mg each were prepared in microvials of the selected design and individually desorbed in the TDU in order to determine the repeatability.

Results and Discussion

The concept of thermal extraction of aroma compounds from edible oils employing microvials is feasible (figure 4). The microvial prevents contamination of the analysis system by high boiling matrix compounds while allowing effective transfer of analytes onto the analytical column. After sample processing the microvial can be disposed of and the desorption tube is ready to take up the next sample.

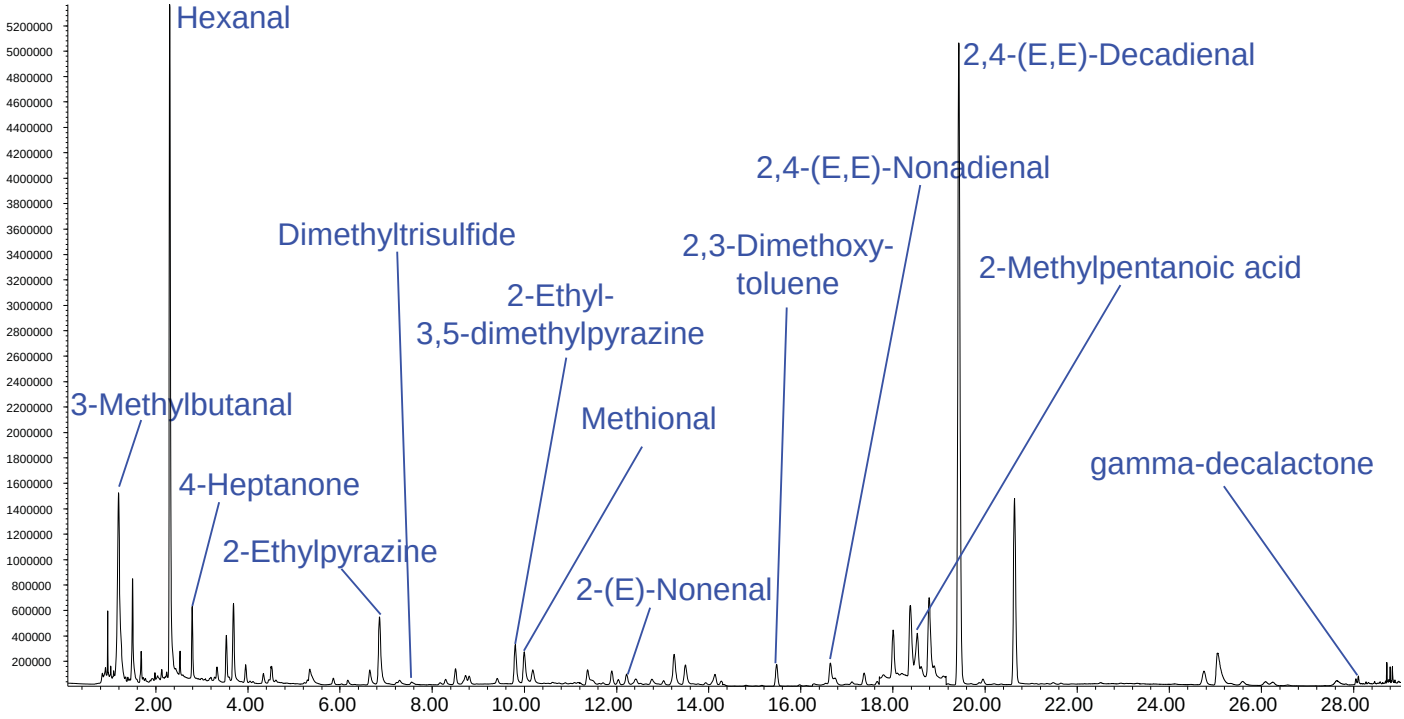

Figure 4. SIM chromatogram resulting from thermal desorption of a spiked edible oil inside a microvial with slit placed 1 cm from bottom.

In this study the performance of different microvial designs was investigated. A relatively short desorption time of 15 min was chosen to clearly reveal differences. It turned out that microvials with the slit placed at a height of 1 cm from the bottom were the most effective for analyte transfer (figure 5) - especially for high boiling compounds (e.g. gamma-decalactone).

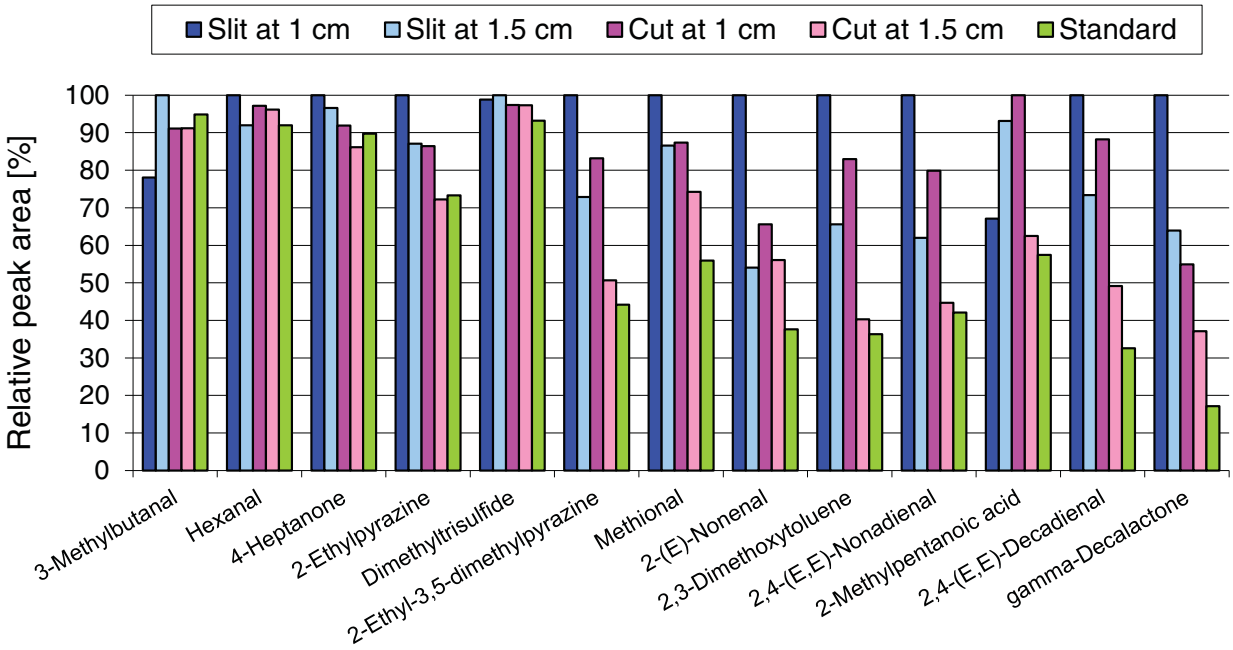

Figure 5. Comparison of analyte transfer from different types of microvials. Peak areas are normalized to the largest observed peak for the respective compound.

Figure 6 shows the desorption gas flow path for different microvial designs. It is reasonable to assume that the vapor phase directly above the sample surface would be more efficiently purged when using the slit design than when using the standard microvial, in which one relies mainly on analyte diffusion through a stagnant vapor phase volume due to the extended distance between the sample surface and the purge flow path. In other words, the microvials with slit enable faster more efficient compound transfer from the sample to the analysis system. A different effect seems to be responsible for the improved transfer of 2-methylpentanoic acid when using the microvial cut at 1 cm. Probably the reduced glass surface area in the analyte transfer path is beneficial for transfer of active compounds such as acids.

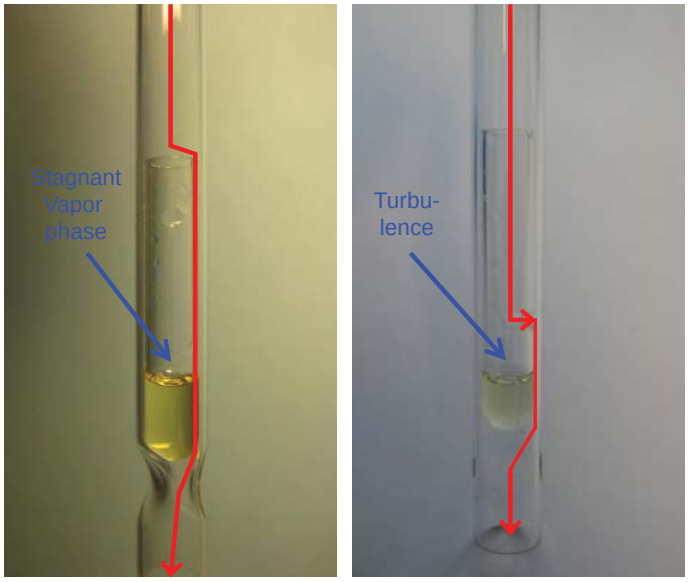

Figure 6. Illustration of the gas flow path during thermal desorption from a standard microvial (left) and a slitted microvial (right). The purge efficiency directly above the sample surface is obviously higher when using the slitted microvial enabling more effective analyte transfer.

Relative standard deviations for 10 repeat measurements with the 1 cm slitted microvial were between 7.2 and 16.8% with a median of 9.7% (figure 7). This is highly acceptable considering the complex matrix, the low concentrations and the straightforward sample preparation. A longer desorption time would likely improve the relative standard deviations further.

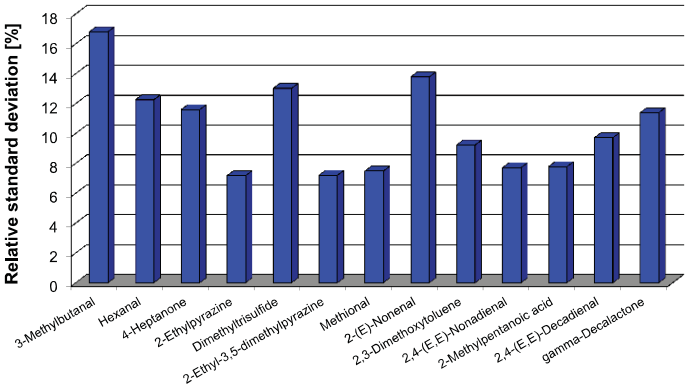

Figure 7. Relative peak area standard deviations resulting from thermal desorption of edible oil samples (n=10) in slitted microvials (1 cm from bottom).

Conclusions

- Aroma compounds can be determined in edible oil in the ng/g concentration range by direct thermal desorption from a slitted microvial.
- Introduction of liquid samples to the microvials is easily performed using a pipette and is the only required sample preparation step.
- The microvial design with the slit at 1 cm distance from the bottom was found to deliver the best performance and is now commercially available from GERSTEL (p/n 014756-601-00).
- Slitted microvials can be beneficial for the determination of volatile and semi-volatile compounds in other liquid, pasty or solid materials.

References

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