Flavor and Fragrance Analysis Using Dynamic Headspace by PAL System

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Application Note

Food and Cosmetics

Abstract

This application note demonstrated a fragrance profiling study by a CDS Analytical 7000C concentrator with a dynamic headspace module. This system is mounted on a PAL RTC rail and connected to a mainstream GC/MS for compounds separate and detection. The results were compared to direct GC injection to show superior response factors and recovery rates. Reproducibility study is also performed through multiple runs.

Introduction

Odor of the consumer products is one of the key factors that determine the perception and acceptance of the product, especially for the food and cosmetic industry. The flavor and fragrance profiling analysis becomes critical for these manufacturers in the quality control and assurance process. There are various sampling techniques before reaching the GC/MS for separation and detection, but the most common way is the headspace, where the volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) from the top of the sample in a sealed container were collected. If the sampling technique involves a concentration device, which is known as the analytical trap, it could be further categorized as the dynamic headspace.

Experimental Setup

A CDS 7000C concentrator and a DHS dynamic headspace module were setup on a CTC RTC rail as the automated sampling flatform. This system is controlled by Pal Sample Control (PSC) software with built-in plugs for the 7000C and DHS module. The DHS module was mounted on the RTC rack directly. A perfume sample was sealed in a headspace glass vial and placed on the sample tray. During testing, the glass vial is transported by the CTC Purge and Trap Tool, which is essentially a robotic arm designed for this setup, into the DHS module. Once the sample was loaded into the DHS module, the top septum of the vial was pierced by a dual jacketed needle, which provides both the inlet purge gas flow and the outlet sample gas flow through a heated transfer line to eventually reach the analytical trap in the 7000C concentrator. The setup is shown in Figure 1.

Instrument Parameters:

DHS Module:

Vial Station:	150 °C
Valve Oven:	300 °C
Transfer Line:	300 °C

GC/MS:

Column:	Restek Stabilwax 30 m, 0.25 mmx0.5 μm
Carrier gas:	Helium 1mL/min
GC Oven:	40 °C/min till 245 °C
MSD:	Scan 29-350 amu

7000C Concentrator:

Valve Oven:	300 °C
Transfer Line:	300 °C
Vial Volume:	10 mL
Purge Flow:	Helium, 50 mL/min 10 min
Dry Purge:	200 mL/min 2 min
Desorb:	280 °C 4 min
Bake:	290 °C 4 min
Wet Trap:	Bypassed
Analytical Trap:	Type X

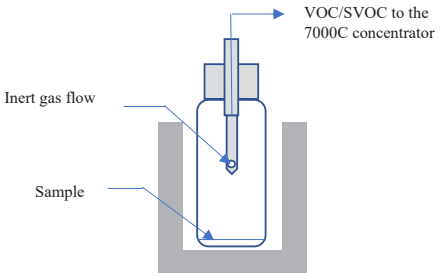

Figure 1: Sampling in the dynamic headspace module

In this experimental setup, the Full Evaporation Technique (FET) by Markelov[1] was followed. A commercially purchased perfume oil was diluted in methanol to a final 5% (v/v) concentration. A 2 μL of the diluted solution was directly injected to the GC injection port as the control. Same amount of diluted solution was injected into the bottom of a headspace vial for future dynamic headspace run.

Results

For the direct injection technique, the chromatogram from the 5% diluted perfume oil solution is shown in the top of Figure 2. As a comparison, the chromatogram by FET is depicted in the bottom of Figure 2. The fragrance compounds from the two chromatograms were identified by MS. The compound lists were identical between the two techniques and were summarized in Table 1. To test the reproducibility of the system, 8 samples were run by the FET from the DHS module. The Relative Standard Deviation (RSD) was calculated from these 8 runs. Figure 3 showed the peak area comparison for each compound in Table 1 from the two techniques. On average, the peak area from FET is 2 times higher than the peak area from direct injection. To further quantify the results, the DHS recovery rate was calculated by the following algorithm: Within each technique, the largest highest peak area from compound #20, which is hedione, is normalized to 1 by a normalization factor. This normalization factor was applied to the rest of the compound peak areas individually. Then the DHS recovery rate is calculated by the ratio of each compound's normalized peak area between the FET and the direction injection.

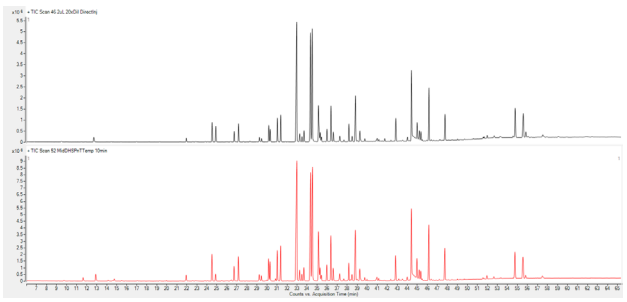

Figure 2: GC/MS chromatographs from a perfume oil solution sample. Top: 2- μL sample from direct injection. Bottom: 2- μL sample from FET by DHS module

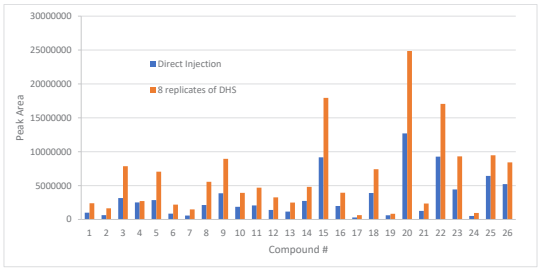

Figure 3: The peak area comparison of each identified compound between direct injection and FET. Sample volume is the same as 2 μL.

Table 1. Quantification of FET by DHS module

No.	Compound Name	RT (min)	DHS Recovery Rate (%)	RSD% n=8
1	Limonene	12.716	121.0	2.3
2	Dihydromyrcenol	21.951	133.8	3.2
3	Linalool	24.52	126.7	2.9
4	Linalyl Acetate	24.89	55.5	7.0
5	Homolinalool	27.163	126.1	2.3
6	D-α-Pinene	29.242	129.4	2.9
7	Styralyl Acetate	29.467	130.4	2.5
8	Benzyl Ethanoate	30.319	132.5	2.8
9	Citronellol	31.038	118.0	2.3
10	α-Isomethyl Ionone	33.695	106.7	2.4
11	Hydroxycitronellal	35.983	116.3	1.8
12	Muguet Carbinol	36.626	117.8	3.6
13	Cyclamen Aldehyde	37.274	109.8	2.8
14	Isopropyl Myristate	38.179	90.0	1.5
15	Lilial	38.817	99.9	1.4
16	β-Cetone	39.278	101.0	2.7
17	Bacdanol	41.164	107.7	1.9
18	n-Hexyl salicylate	42.863	97.1	1.4
19	γ-Undecalactone	44.018	69.0	4.6
20	Hedione	44.427	Normalization Factor	2.0
21	Galaxolide	45.211	95.5	1.8
22	α-Hexylcinnamaldehyde	46.168	94.0	1.2
23	Helional	47.768	107.2	1.0
24	Benzyl Benzoate	51.98	94.0	2.6
25	Ethylene Brassylate	54.772	75.2	8.4
26	Benzyl Salicylate	55.576	82.4	3.1

Conclusions

Dynamic headspace sampling is a simple and effective way to thermally extract VOC and SVOC from the sample. This technique is especially useful when dealing with complex sample matrices, such as blood, food and skincare products. Results from this application note support the statement that the CDS 7000C concentrator with DHS module on a PAL System is a reliable setup with highly reproducible data for flavor and fragrance samples.

References

1. Markelov, Michael, and John P. Guzowski Jr. "Matrix independent headspace gas chromatographic analysis. This full evaporation technique." Analytica Chimica Acta 276.2 (1993): 235-245.cal Techniques 40 CFR Parts 141 and 143 (Final Rule), Federal Register 53 (No. 33), 5142-5147 (Feb. 19, 1988)