Flavor and Fragrance Analysis II Using Dynamic Headspace by PAL System

Application Note
Food and Cosmetics

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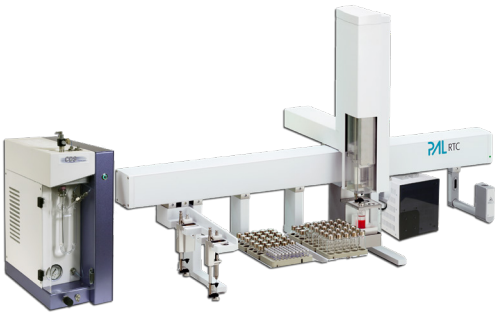
Abstract
This application note demonstrated the correlation coefficient (R^2) > 0.99 from 26 fragrance compounds analyzed by a CDS Analytical 7000C concentrator equipped with a dynamic headspace (DHS) module. This setup was mounted on a PAL RTC rail and connected to a GC/MS for compounds separation and detection.

Introduction
In the previous study, a CDS Analytical 7000C concentrator with an optional DHS module was used to perform fragrance profiling study. An average RSD = 2.8% (n=8) was observed from 26 fragrance compounds. Interestingly, the result was showing that the response factor from the DHS module is two times higher than the direct GC injection method. This application paper is a continuous study after the previous work. The experimental design focused solely on obtaining calibration curves from the same 26 fragrance compounds to show the system is qualified for quantification studies.

Experimental Setup
As previously described, the same GC sample introduction hardware was deployed as a CDS 7000C concentrator configured with a DHS module. On the automation side, the setup was connected to a CTC RTC rail. This automated system is controlled by Pal Sample Control (PSC) software with two plug-ins for the 7000C concentrator and the DHS module individually.

The DHS module was mounted on the RTC rack. A perfume sample was sealed in a 10 ml VOC vial and placed on the sample tray. During testing, the VOC vial is transported by the CTC Purge and Trap Tool, which is the robotic arm designed specifically to handle 10 ml, 20 ml and 40 ml VOC vials for purge and trap applications, into the DHS module. Once the sample was loaded into the DHS module, the dual jacketed needle inside the DHS module was lowered to pierce the top septum of the vial. Inlet purge gas flow followed to purge the sample in the headspace through a heated transfer line to be enriched in the analytical trap installed 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, 1 min 4 °C/min to 245 °C hold 20 min
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

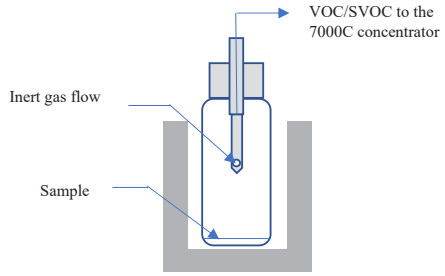


Figure 1: Sampling in the dynamic headspace module

In this experimental setup, the Full Evaporation Technique (FET) by Markelov [1] was followed. A commercially purchased perfume oil was diluted with methanol to a final 5% (v/v) concentration. A micro syringe was used to obtain 0.5 μL, 1.0 μL, 2.0 μL, 5.0 μL and 10.0 μL volume of sample from the diluted solution individually. Each aliquot was injected individually to the bottom of a clean 10 mL VOC vial and each sample vial was capped immediately after injection for future analysis.

Results

Figure 2 presented the chromatogram data from a 2.0 μL run. All fragrance peaks were numbered based on the compounds list in Table1. For each of the 26 compounds identified in the Figure 2, a calibration curve was drawn by fitting the peak areas from 5 runs (0.5 μL, 1.0 μL, 2.0 μL, 5.0 μL and 10.0 μL sample volume) with a linear polynomial. The assumption is that he response factor obtained from FET method is independent of the sample volume. To better depict the data, 26 compounds were separated into two groups based on the peak area from the 10.0 μL sample volume run. If the peak area of a specific compound from the 10.0 μL run is below 4,500,000, this compounded is considered as a high response compound. If not, it is grouped into low response compounds. Figure 3 and 4 summarized the calibration curve for high response and low response compounds.

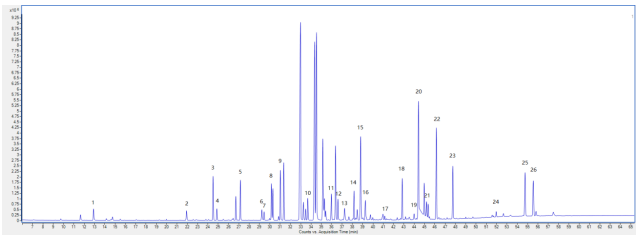


Figure 2: GC/MS chromatograph from a 2- μL perfume oil solution sample. Compound peak is numbered.

Table 1 summarized the correlation coefficient (R^2) of the linear polynomial fitting. All the R^2 values were greater than 0.99. Combining with the reproducibility data from the previous application note, the FET method was qualified for quantification studies in fragrance analysis.

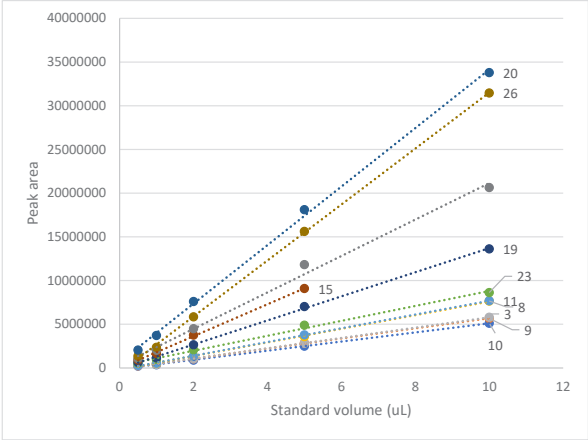


Figure 3: Calibration curves for high response compounds

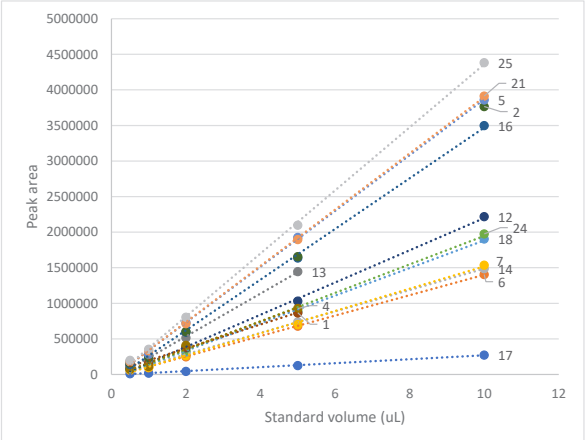


Figure 4: Calibration curves for low response compounds

Table 1: Correlation coefficients from calibration curve fitting

No.	Compound	RT (min)	R^2
1	Limonene	12.98	0.9930
2	Dihydromyrcenol	21.925	0.9918
3	Linalool	24.515	0.9981
4	Linalyl Acetate	24.88	0.9850
5	Homolinalool	27.155	0.9988
6	D-alpha-Pinene	29.205	0.9975
7	Styralyl Acetate	29.42	0.9949
8	Benzyl Ethanoate	30.28	0.9967
9	Citronellol	31.045	0.9987
10	alpha-Isomethyl Ionone	33.7	0.9980
11	Hydroxycitronellal	35.99	0.9978
12	Muguet Carbinol	36.62	0.9957
13	Cyclamen Aldehyde	37.255	0.9954
14	Isopropyl Myristate	38.225	0.9994
15	Lilial	38.87	0.9992
16	β-Cetone	39.305	0.9966
17	Bacdanol	41.115	0.9956
18	n-Hexyl salicylate	42.86	0.9955
19	γ-Undecalactone	43.97	0.9993
20	Hedione	44.49	0.9973
21	Galaxolide	45.375	0.9990
22	α-Hexylcinnamaldehyde	46.195	0.9917
23	Helional	47.75	0.9930
24	Benzyl Benzoate	51.925	0.9952
25	Ethylene Brassylate	54.755	0.9986
26	Benzyl Salicylate	55.545	0.9987

Conclusions

Dynamic headspace sampling is a highly effective GC sample introduction method. It tackles with many challenges from complex sample matrices such as foods and perfume. The FET method further simplifies the sample preparation process. Comparing to the direct GC injection, FET method shows a 2X improved sensitivity and less than 3% RSD. On the quantification side, FET is capable of yielding a calibration curve within 20X concentration range.

Reference

[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.