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Fragrance Profiling of Consumer Products using a Fully Automated Dynamic Headspace System

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Abstract

Accurate qualitative and quantitative analysis of perfumed or flavored products is essential to the flavor and fragrance industry. Especially when unknown samples need to be analyzed traditional methods of GC analysis often lead to only vague results and often require time consuming and cumbersome sample preparation techniques such as solvent extraction (liquid/liquid, Soxhlet, Likens-Nickerson).

The technique of dynamic headspace requires minimal sample preparation, and significantly reduces overall analysis time while also improving data quality. In this work, the dynamic headspace technique is applied to different types of consumer products. The analysis of neat perfume oil is compared with that of consumer products containing the same oil.

Introduction

For consumers the odor of a product is a very important parameter for the overall perception and acceptance. Therefore it is always of interest to have the analytical means to control and/or analyze the volatile fraction of these products.

Currently, the most commonly used methods for analyzing fragrances from market products are the SPME technique and SDE (simultaneous distillation/extraction). These techniques both have certain disadvantages. The SDE technique is quite time-consuming and also some polar and/or semi-volatile compounds can be lost during sample preparation. Using the SPME technique, the time factor is improved, however often the selectivity and limited capacity of the phase results in a "distortion" of the results when compared to the actual concentration levels of individual fragrance compounds in the product.

In this paper, we present the application of DHS (dynamic headspace) as a sample preparation technique for fragrance analysis in consumer products and compare the results obtained with the "conventional" technique of SDE.

Experimental

Instrumentation

Analyses were performed using a 7890 GC equipped with a 5975 Mass Selective Detector (Agilent Technologies), Thermal Desorption Unit (TDU, Gerstel), PTV inlet (CIS 4, Gerstel) and MPS 2 with DHS option (Gerstel).

The GERSTEL Dynamic Headspace System (DHS) is an accessory for the MultiPurpose Sampler (MPS 2) that enables dynamic purging of the headspace above a sample combined with trapping of purged analytes on an adsorbent trap. In this work, a low volume aliquot of the sample is placed into an empty headspace vial, which is thermostatted to 80°C allowing the fragrance compounds to vaporize while leaving most of the low volatile matrix behind. The technique of introducing a small volume of sample and vaporizing the analytes in the headspace vial completely, without having to rely on establishing equilibrium between two phases, is called "FET" or full evaporation technique [1, 2]. Analytes in the purged headspace are trapped onto a 2 cm adsorbent bed in a compact glass tube. The tube is then placed into the Thermal Desorption Unit (TDU) and the analytes thermally desorbed and introduced into the gas chromatograph. The analytes are focused in the Cooled Injection System (CIS 4) inlet to improve peak shape and increase sensitivity. Figure 2 shows a schematic of the trapping and desorption process.

Figure 1: GERSTEL MPS 2 with DHS on an Agilent Technologies 7890 GC.

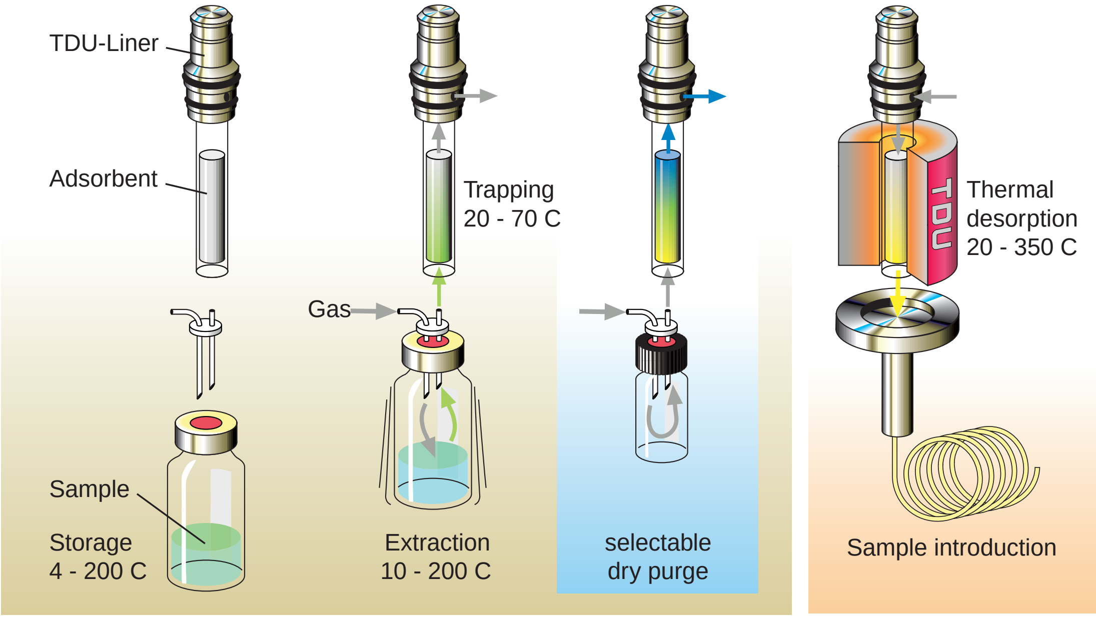

Figure 2: Schematic View of DHS Process.

Analysis conditions

Trap	Tenax TA
DHS	20 °C trap temperature 80 °C incubation temperature 500 mL purge volume 50 mL/min purge flow
TDU	solvent venting 20 °C (3 min); 100 °C/min to 250 °C (5 min)
PTV	Tenax TA liner, 0.2 min solvent vent (30 mL/min) split 10:1 20 °C; 12 °C/s to 280 °C (5 min)
Column	30 m Stabilwax (Restek) d_i = 0.25 mm d_f = 0.25 µm
Pneumatics	He, constant flow = 1 mL/min
Oven	40 °C (1 min); 3 °C/min to 240 °C (20 min)
MSD	Scan, 29 - 350 amu

Sample Preparation

1 g of liquid or solid sample and methanol, depending on the expected fragrance concentration in the sample, were added to a vial and thoroughly mixed. 8 µL of the liquid phase were then transferred into an empty 10 mL screw cap headspace vial.

Results and Discussion

In order to have comparable results, a fragrance of known composition was created and incorporated into a shower gel. Sample preparation of this gel was subsequently performed with Likens-Nickerson extractions using hexane or alternatively frigene as solvent.

Table 1 shows compound recoveries from the extractions and the DHS run compared with the fragrance formulation normalized to 100 %.

Table 1: Comparison of recoveries of fragrance compounds using different extraction methods.

No.	Compound	Likens-N. Hexane [%]	Likens-N. Frigene [%]	DHS [%]
1	Ethyl Butyrate	40	120	80
2	Limonene	53	67	82
3	Hexyl Acetate	50	90	90
4	Allyl Caproate	60	100	101
5	Dihydromyrcenol	62	73	100
6	Linalool	83	100	92
7	Agrumex	96	108	97
8	α-Terpineol	75	100	90
9	Styrallyl Acetate	117	150	99
10	Benzyl Acetate	100	120	85
11	Florol	36	32	98
12	Dihydrojasmone	150	200	95
13	DMBC Butyrate	143	179	101
14	ß-Ionone	167	135	90
15	cis-Jasmone	125	115	95
17	Lilial	183	117	49
18	Bacdanol	130	120	83
19	Hydroxycitronellol	n.d.	n.d.	109
20	Aldehyde C-14	75	150	105
21	Hedione	67	50	95
22	Galaxolide 50 IPM	150	125	81
23	Hexylcinnamic Aldehyde	100	60	85
24	Helional	69	52	37
25	Coumarin	80	93	86
26	Ethylvanillin	trace	60	133
27	Musk T 93	3	3	78
28	Frambinone	n.d.	n.d.	49

In general the results obtained using the DHS technique were closer to the original composition of the fragrance than those obtained by the extractions. The overlay-chromatogram in figure 3 demonstrates good correlation between sample and fragrance, but also gives some hints as to the composition of the matrix.

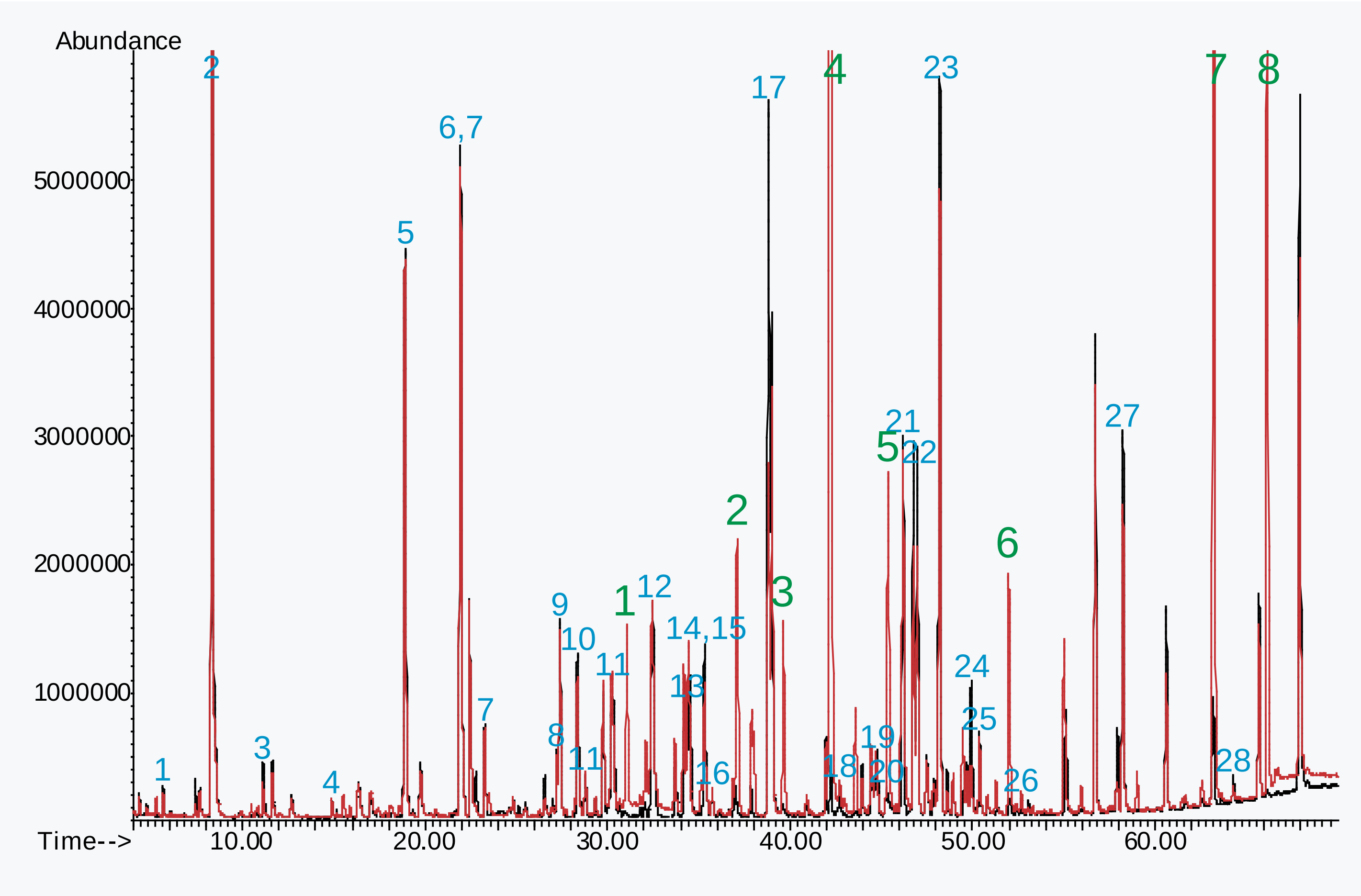

Figure 3: Overlay of fragrance standard trace (black) and shower gel trace (red). Blue annotations mark fragrance compounds (see tables), green annotations mark matrix compounds: 1. methyl laurate, 2. n-dodecanol, 3. caprylic acid, 4. 2-phenoxyethanol, 5. lauryl ethoxylate, 6. lauric acid, 7. methyl p-hydroxybenzoate, 8. N-propyl p-hydroxybenzoate.

The main reason for this is that the DHS technique results in quantitative and exhaustive extraction of the small amounts of sample, i.e. complete extraction of all fragrance compounds present in the samples. This is a big advantage compared with standard extraction techniques (SDE/SPME), which yield lower, and in some cases significantly lower, recovery for less volatile compounds such as ethylvanillin, coumarin and some musk compounds. Using DHS, both volatile and less volatile compounds are extracted from the product matrices with high recovery making it much easier to achieve the correct analysis result in terms of overall composition of the fragrance.

In the next step, the experiment was extended to handling more challenging matrices. Since we know that a nearly quantitative extraction of the fragrance compounds is in principle possible, we looked into the area of the stability of a fragrance formulation or of individual compounds depending on matrix composition. To investigate this, different consumer products, in addition to the shower gel, were formulated using the very same fragrance. These were a soap bar, a candle, an antiperspirant spray and a hair dye product. It was expected, that the fragrance that was originally designed for use in a shower gel would not be completely stable in other matrices. These products were analyzed by DHS and the results obtained were compared to the original composition of the fragrance (Table 2).

Table 2: Comparison of recoveries of fragrance compounds from different matrices.

No.	Compound	Shower Gel [%]	Bar Soap [%]	Candle Wax [%]	AT Spray [%]	Hair Color [%]
1	Ethyl Butyrate	80	n.d.	n.d.	51	n.d.
2	Limonene	82	10	32	64	20
3	Hexyl Acetate	90	n.d.	22	55	n.d.
4	Allyl Caproate	101	n.d.	31	71	n.d.
5	Dihydromyrcenol	100	96	48	74	24
6	Linalool	92	92	39	63	24
7	Agrumex	97	99	51	73	23
8	α-Terpineol	90	104	39	65	21
9	Styrallyl Acetate	99	54	40	65	n.d.
10	Benzyl Acetate	85	5	35	53	n.d.
11	Florol	98	108	52	55	34
12	Dihydrojasmone	95	105	43	49	19
13	DMBC Butyrate	101	110	56	87	24
14	ß-Ionone	90	120	35	49	24
15	cis-Jasmone	95	112	47	46	n.d.
16	Clonal	96	99	46	74	n.d.
17	Lilial	49	60	32	1	trace
18	Bacdanol	83	95	34	n.d.	28
19	Hydroxycitronellol	109	72	44	26	23
20	Aldehyde C-14	105	11	56	70	n.d.
21	Hedione	95	99	48	28	4
22	Galaxolide 50 IPM	81	122	75	56	24
23	Hexylcinnamic Aldehyde	85	105	22	57	5
24	Helional	37	n.d.	27	38	n.d.
25	Coumarin	86	100	43	27	n.d.
26	Ethylvanillin	133	29	31	n.d.	11
27	Musk T 93	78	10	72	28	n.d.
28	Frambinone	49	41	28	n.d.	12

Figure 4 shows the results for the soap bar. The most volatile part of the fragrance formulation (compounds 1-4) was lost probably due to the high processing temperature when incorporating the fragrance into the soap. In addition limonene (2) is known not to be stabile in soaps. Benzyl acetate (10) was partially transformed to benzyl alcohol and the aldehydes (20, 24) had reacted with amines from the matrix. Musk T 93 (Ethylen brassylate) seems to have been partially converted to dimethyl brassylate.

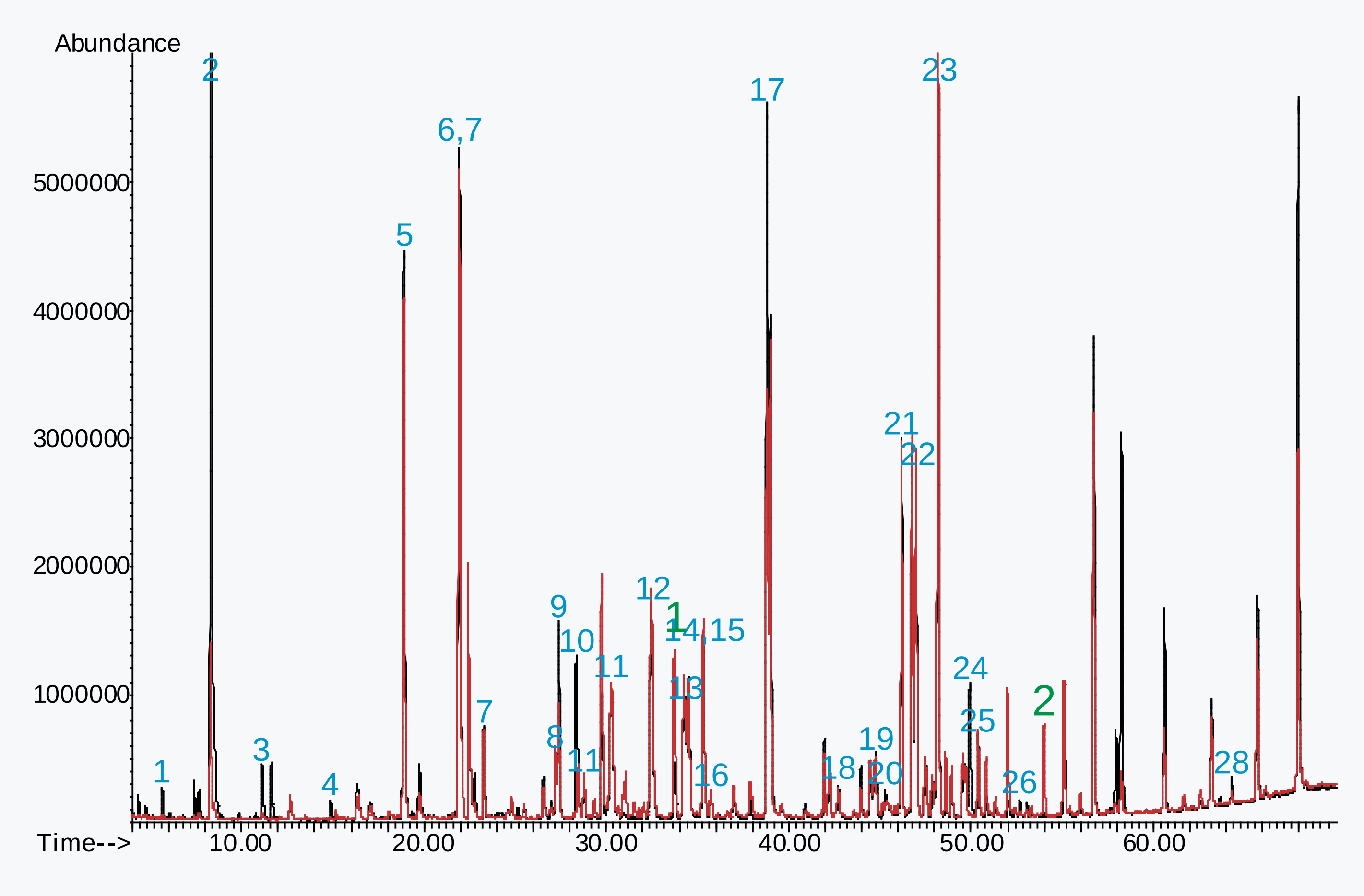

Figure 4: Overlay of fragrance standard trace (black) and bar soap trace (red). Blue annotations mark fragrance compounds (see tables), green annotations mark: 1. benzyl alcohol, 2. dimethyl brassylate.

In the candle wax sample the high processing temperature of 125 °C caused losses over the entire range of fragrance compounds, whereas the overall fragrance pattern remained stabile (figure 5).

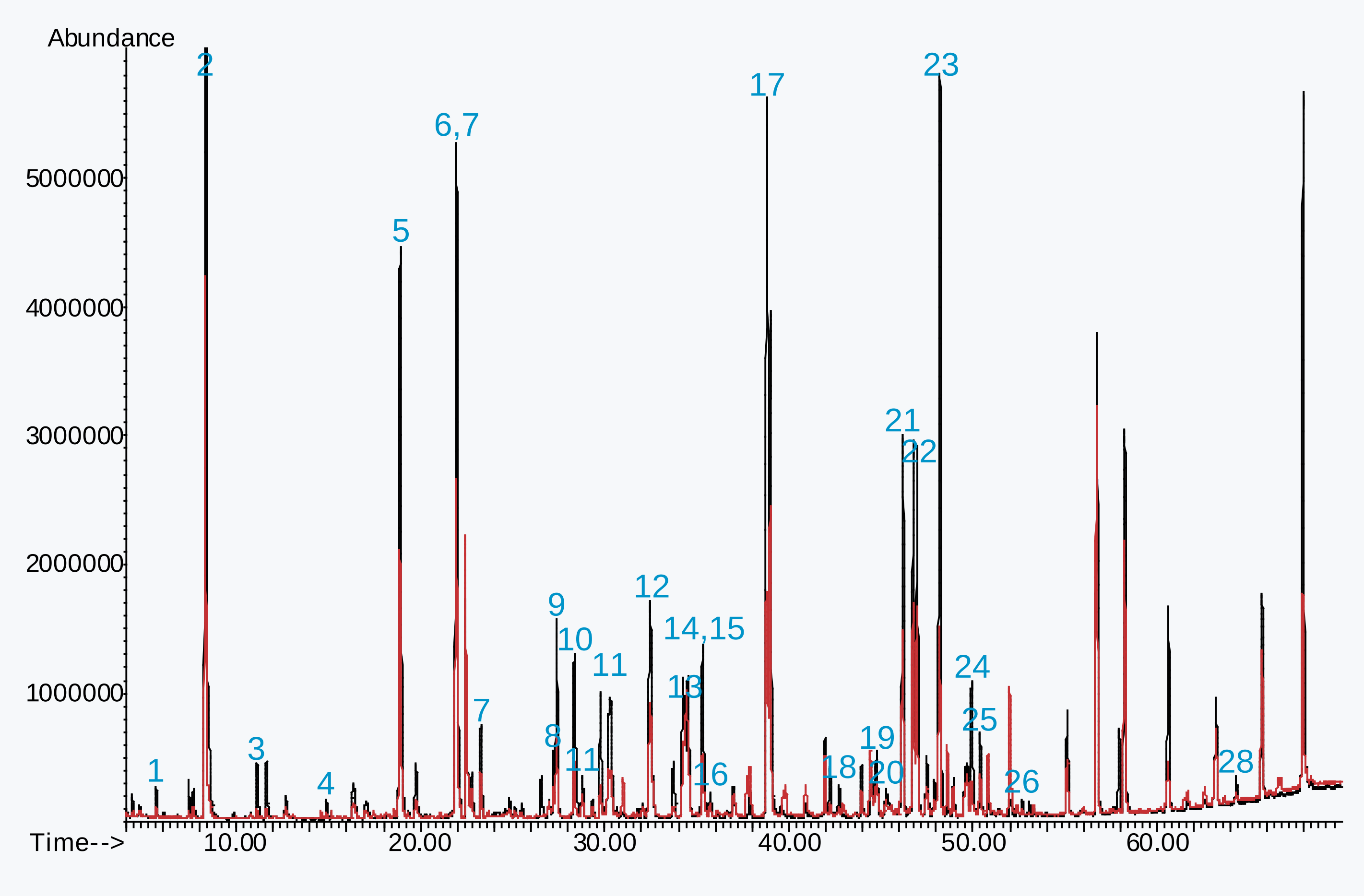

Figure 5: Overlay of fragrance standard trace (black) and candle wax trace (red). Blue annotations mark fragrance compounds (see tables).

For some applications, such as the antiperspirant spray, using the classical technique of SDE is not even an option since, due to the products composition (mainly propellant), the amount of sample coming from a commercial product is quite low.

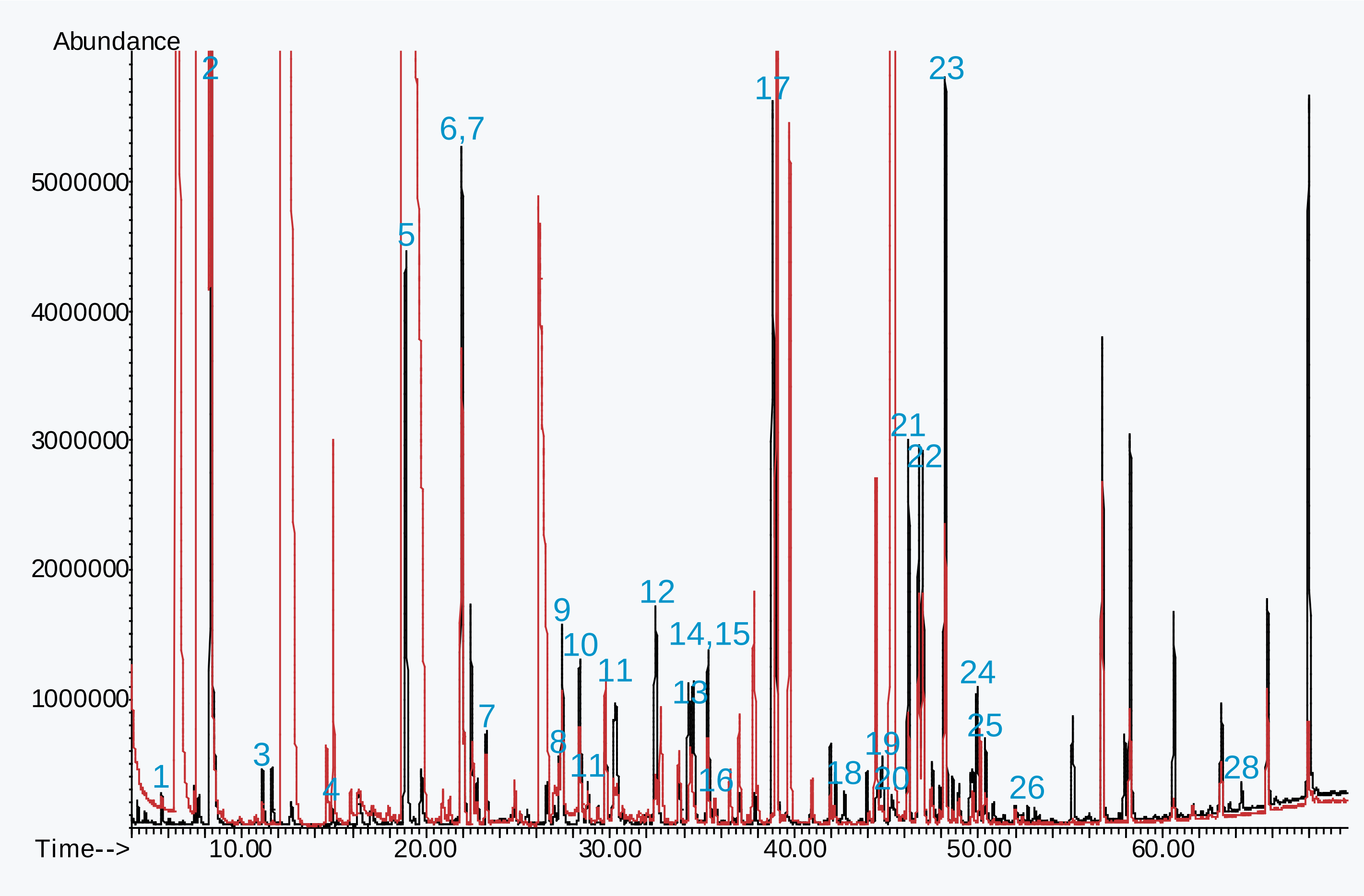

Figure 6: Overlay of fragrance standard trace (black) and antitranspirant trace (red). Blue annotations mark fragrance compounds (see tables).

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Regarding stability testing of fragrances in hair dye products DHS is a powerful tool for evaluating both performance & stability. As can be seen in figure 7 the DHS analysis clearly shows that some of the compounds present in the original fragrance (Lilial, Hedione, Hexyl cinnamic aldehyde etc…) vanished almost completely in the aggressive environment in the hair dyes.

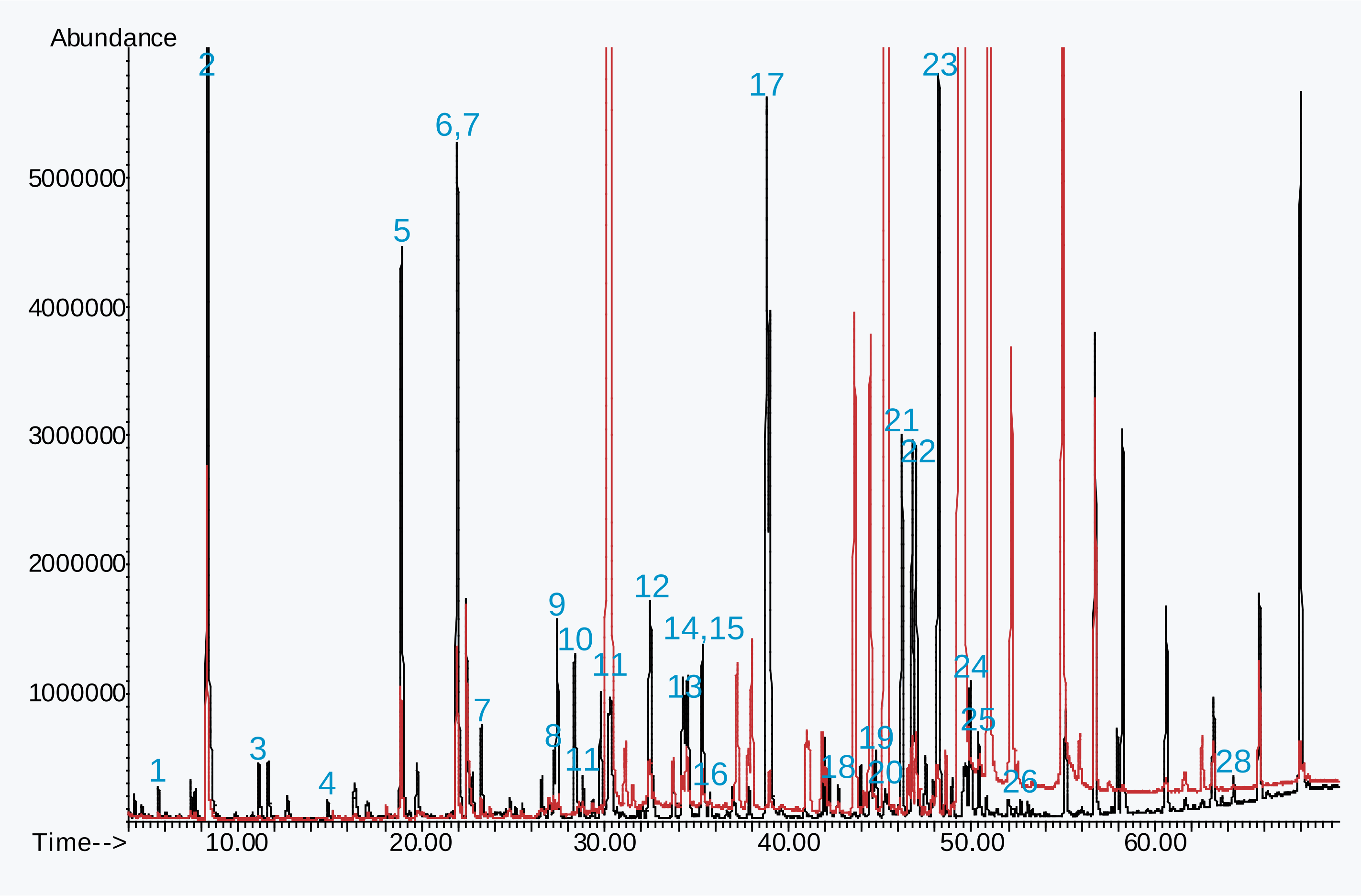

Figure 7: Overlay of fragrance standard trace (black) and haircoloration trace (red). Blue annotations mark fragrance compounds (see tables).

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Conclusions

DHS is an excellent technique for the determination of fragrances in consumer products. DHS, using the fully evaporization technique FET, enables quantitative extraction of fragrance compounds across a wide range of volatility, leading to results that are closer to the actual fragrance composition than those obtained with other commonly used analysis techniques. In addition, less volatile compounds that could not be determined when common extraction techniques were used, were determined using DHS.

References

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