



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

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KEYWORDS

Extraction methods, stability testing, quality control, market observation

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.

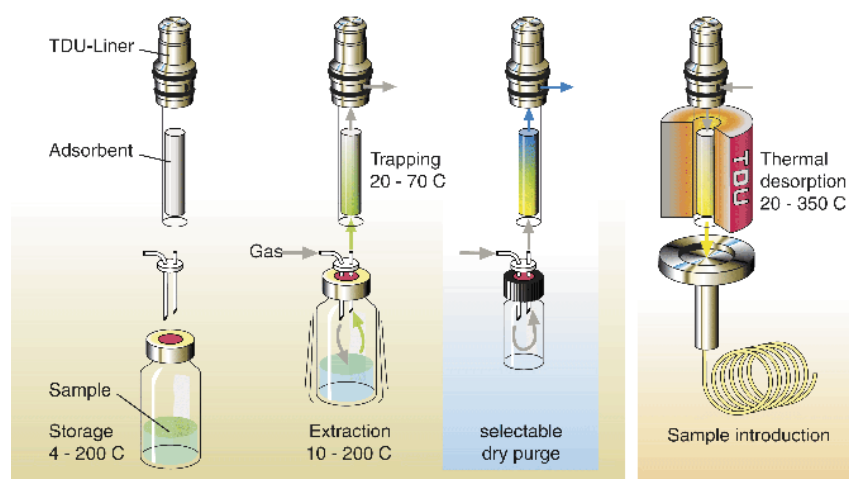


Figure 2. Schematic View of DHS Process.

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;
 250°C (5 min)
 PTV: Tenax TA liner,
 0.2 min solvent vent (30 mL/min)
 split 10:1
 20°C; 12°C/s; 280°C (5 min)
 Column: 30 m Stabilwax (Restek)
 $d_i = 0.25 \text{ mm}$ $d_f = 0.25 \mu\text{m}$
 Pneumatics: He, constant flow = 1 mL/min
 Oven: 40°C (1 min); 3°C/min;
 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 | β -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.

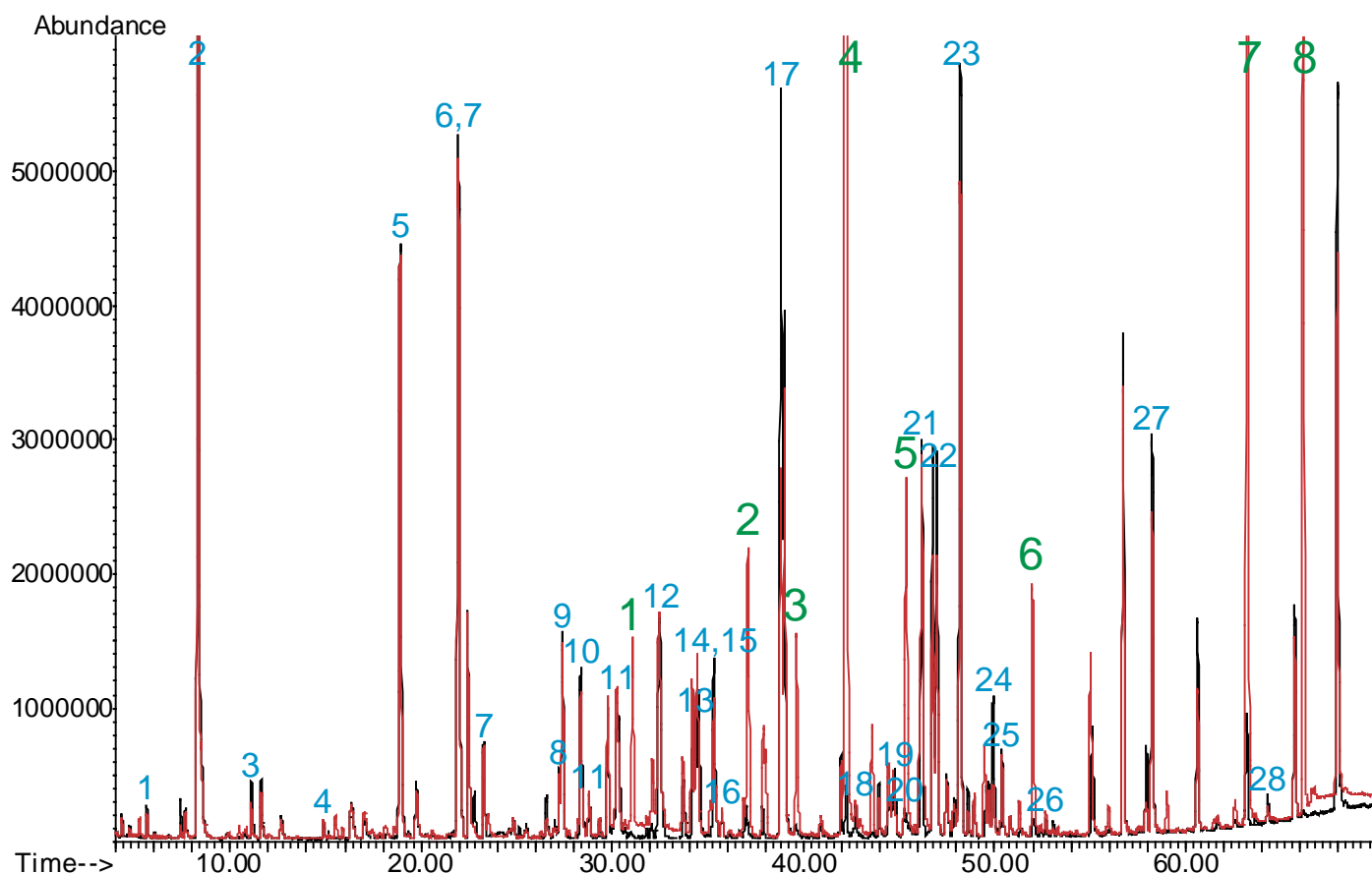


Figure 4. Overlay of fragrance standard trace (black) and shower gel trace (red). Blue annotations mark fragrance compounds (see tables), green annotations mark matrix compounds: 1. methyl laurate, 2. n-dodecanol, 3. caprylic acid, 4. 2-phenoxyethanol, 5. lauryl ethoxylate, 6. lauric acid, 7. methyl 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 | Dihydrojasmane | 95 | 105 | 43 | 49 | 19 |
| 13 | DMBC Butyrate | 101 | 110 | 56 | 87 | 24 |
| 14 | β -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 | Baccanol | 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 stable 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.

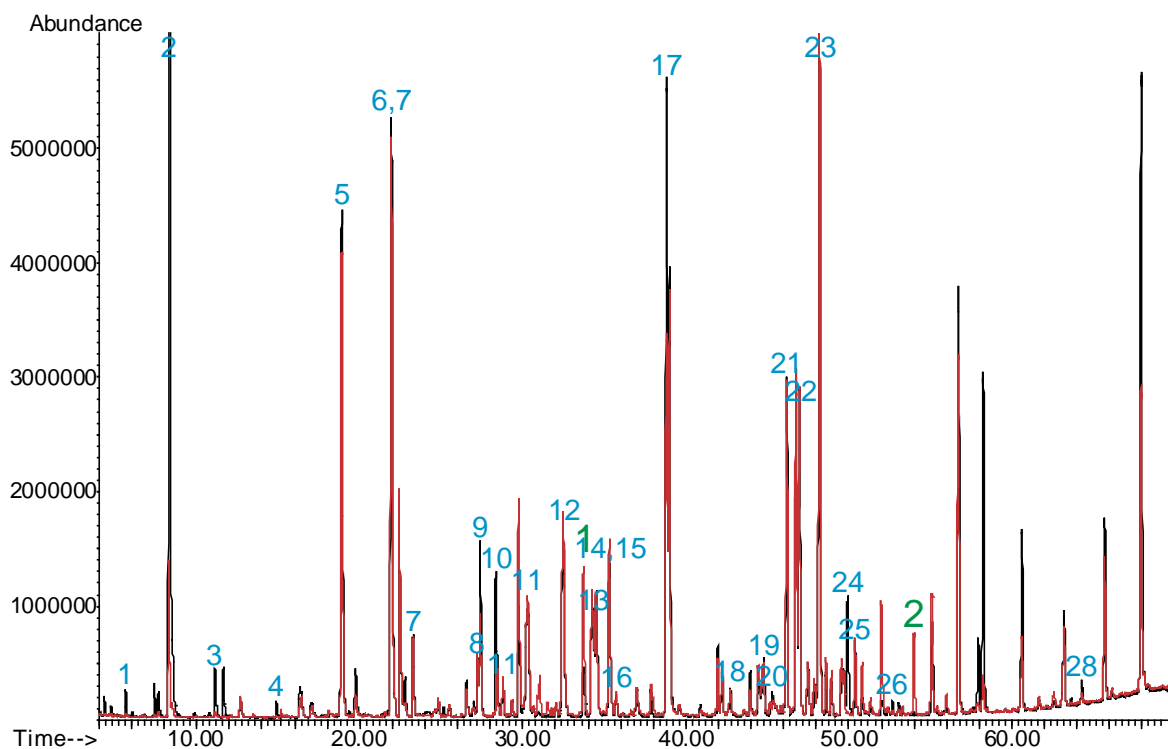


Figure 4. Overlay of fragrance standard trace (black) and bar soap trace (red). Blue annotations mark fragrance compounds (see tables), green annotations mark: 1. benzyl alcohol, 2. dimethyl brassylate.

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 stable (figure 5).

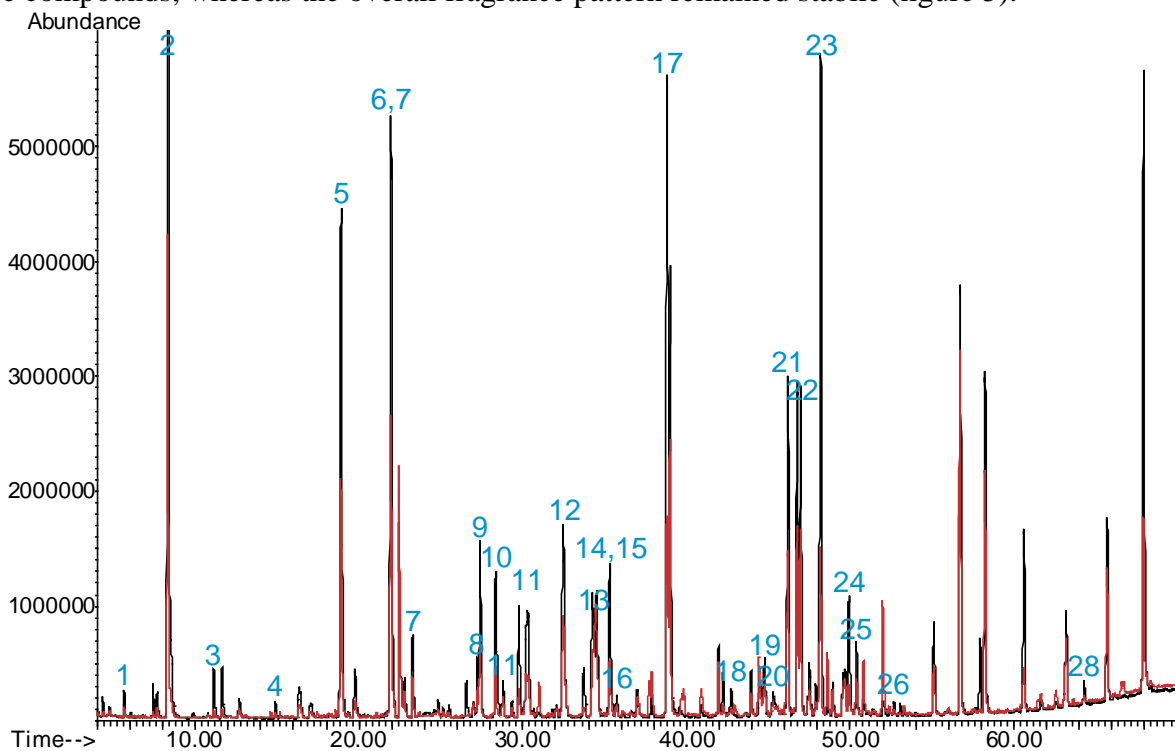


Figure 5. Overlay of fragrance standard trace (black) and candle wax trace (red). Blue annotations mark fragrance compounds (see tables).

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.

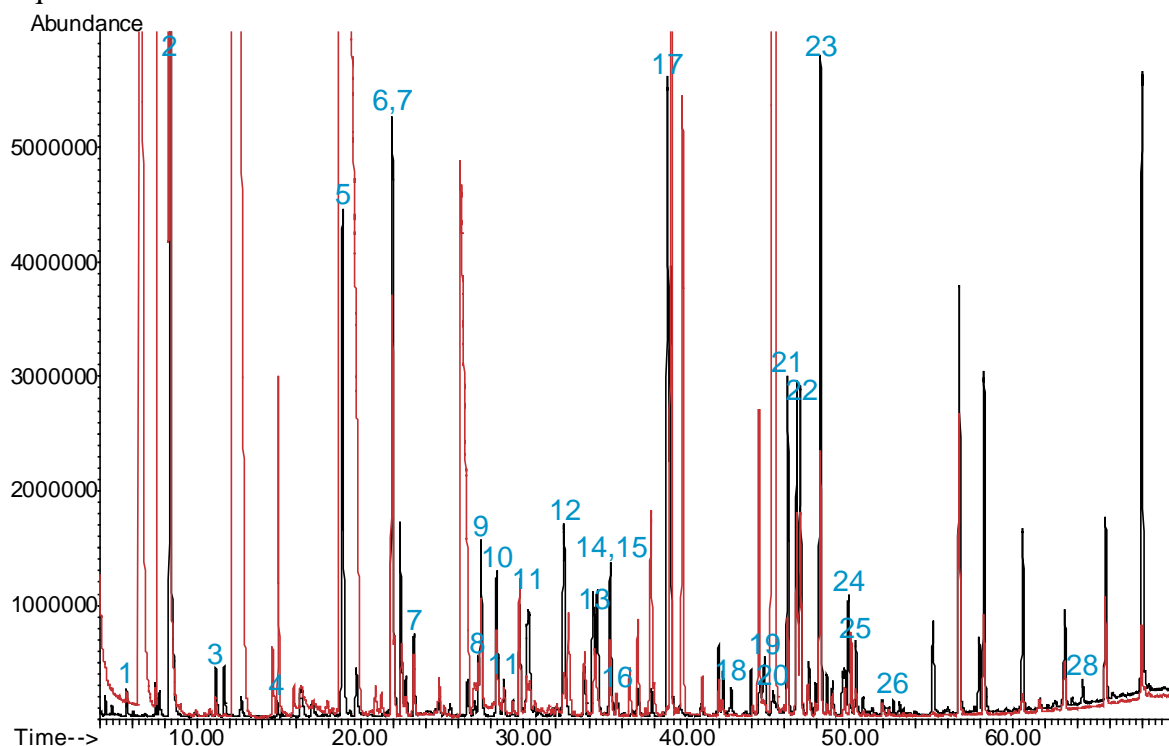


Figure 6. Overlay of fragrance standard trace (black) and antiperspirant trace (red). Blue annotations mark fragrance compounds (see tables).

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.

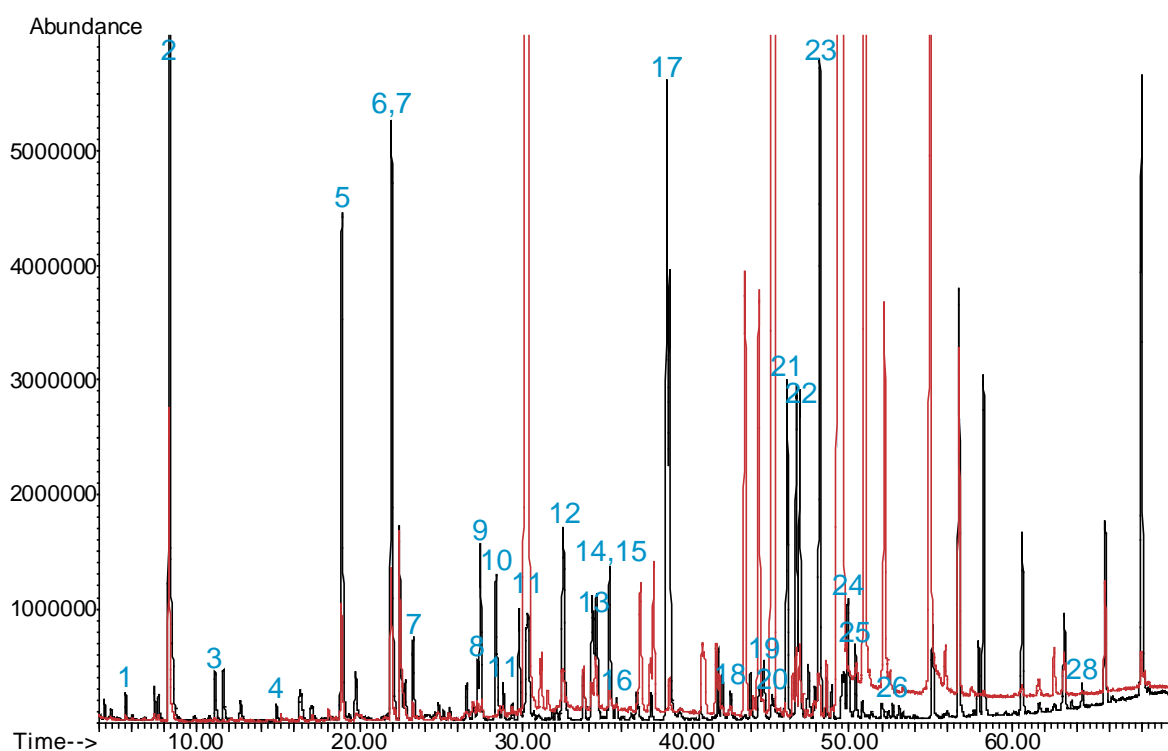


Figure 7. Overlay of fragrance standard trace (black) and haircoloration trace (red). Blue annotations mark fragrance compounds (see tables).

CONCLUSIONS

DHS is an excellent technique for the determination of fragrances in consumer products. DHS, using the fully evaporation 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.

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