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Flavor and Fragrance Analysis of Consumer Products - Dynamic Headspace Compared to Some Traditional Analysis Approaches

Andreas Hoffmann
Gerstel GmbH & Co. KG, Eberhard-Gerstel-Platz 1,
D-45473 Mülheim an der Ruhr, Germany

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Full evaporation dynamic headspace, fragrance, quality control, market observation

Abstract
The ability to perform accurate qualitative and quantitative analysis of perfumes 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 qualitative results and often rely on time consuming and cumbersome sample preparation techniques such as solvent extraction (liquid/liquid, Soxhlet, Likens-Nickerson).

In this work, the analysis of neat perfume oil is compared with that of consumer products containing the same oil, applying different traditional analytical techniques like static headspace, SPME, SDE, and comparing the results with those of a dynamic headspace approach.

It will be shown that the technique of dynamic headspace requires minimal sample preparation and significantly reduces overall analysis time while delivering improved data quality.

Introduction

The flavor of a consumer product is a key parameter for perception and acceptance by the consumer. Therefore the flavor industry is highly interested in having the analytical means to control product quality and to analyze such products in general. Several scenarios are possible:

During product development, when transferring the specific scent of a perfume to a range of personal care products, the question of how a fragrance formulation performs in different matrices such as shampoos, soap bars, deodorants etc., has to be answered. Does the recipe need to be changed and, if so, how? This consequently leads to quality control questions such as ageing and shelf life that have to be taken into account. To be successful, a product must be sensorically stable over time.

And last, but not least, companies in the flavor, fragrance and perfume industries need to monitor new trends by surveying and analyzing competitive products, whose composition is largely unknown, making it difficult to obtain accurate quantitative results, unless a suitable analysis technique is used.

The majority of odor compounds are volatiles, which are generally easy to extract from the sample using various established techniques. The challenge facing the analyst is to separate these from the sample matrix of a product without analyte discrimination such that the reconstituted flavor pattern matches the one experienced by the consumer.

The work presented here shows that the dynamic headspace technique, while requiring minimal sample preparation and significantly reduced overall analysis time, delivers improved data quality.

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 MultiPurpose Sampler (MPS) with SPME, Headspace, and DHS options (GERSTEL).

Figure 1. GC/MS system with GERSTEL MultiPurpose Sampler (MPS) used for automation of all sample introduction techniques.

Analysis conditions

Column: 30 m Rxi-5ms (Restek)
d_i = 0.25 mm d_f = 0.25 µm
Pneumatics: He, constant flow = 1 mL/min
Oven: 40°C; 5°C/min; 280°C (10 min)
MSD: Scan, 35 - 350 amu

Analysis conditions static headspace

MPS: 80°C incubation temperature (10 min)
90°C syringe temperature
1000 µL injection volume
PTV: Empty liner
split 10:1
250°C isothermal

Analysis conditions SPME

MPS: 80°C incubation temperature (10 min)
Fibre: DVB/CAR/PDMS
PTV: SPME liner
split 10:1
250°C isothermal

Analysis conditions DHS

Trap: Tenax TA
DHS: 25°C trap temperature
80°C incubation temperature
20 mL (1000 using FET) purge volume
10 mL/min (50 using FET) purge flow
1000 mL (0 using FET) dry purge volume
100 mL/min (0 using FET) dry purge flow
TDU: Solvent venting
30°C; 280°C/min; 280°C (5 min)
PTV: Glassbead liner,
0.2 min solvent vent (30 mL/min)
split 10:1 (50:1 using FET)
-120°C; 12°C/s; 250°C (5 min)

Samples. To compare the different analysis techniques, a fragrance of known composition (table 1) was incorporated into a shampoo (1 %), a dishwashing detergent (1 %), a fabric softener (1 %), a laundry detergent powder (1 %), and vanishing cream (0.5 %).

Table 1. Composition of the fragrance used for the measurements.

No.	Compound	No.	Compound
1	Ethyl-2-methyl butanoate	24	Calone
2	Manzanate	25	Damascone alpha
3	α-Pinene	26	Diphenyloxide
4	n-Octanal	27	Coumarin
5	Limonene	28	Allylcyclohexyl propionate
6	γ-Terpinene	29	Ethylvanillin
7	Dihydromyrcenol	30	Caryophyllene
8	Maltol	31	Clonal
9	Linalool	32	ß-Ionone
10	cis-Rose oxide	33	Frambinone
11	Fructone	34	Lilial
12	Benzylacetate	35	Isoeugenolacetate
13	Ethylmaltol	36	Cedrol
14	Methylheptincarbonate	37	Hedione
15	Decanal	38	Cedramber
16	Citronellylnitril	39	Hexylsalicylate
17	Nerol	40	Boisambrene forte
18	Hydroxycitronellal	41	Benzylbenzoate
19	Argumex I	42	Ambroxan
20	Heliotropin	43	Fixolide
21	Argumex II	44	Ethylenbrassylate
22	Eugenol	45	Benzylcinnamate
23	Vanillin		

Results and Discussion

The perfume oil test mix was diluted with methanol and injected in split mode. The resulting chromatogram is shown in figure 2.

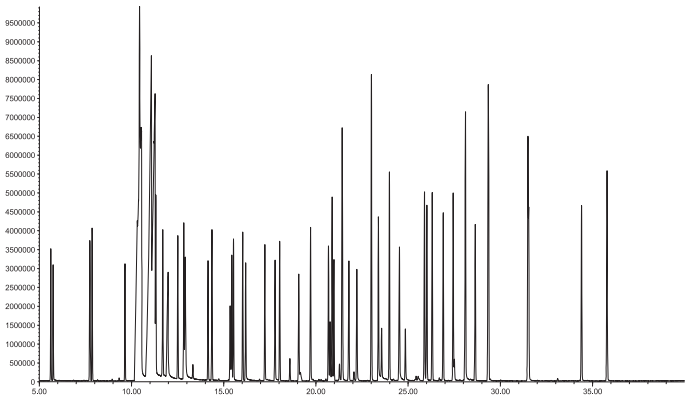

Figure 2. GC/MS system used for automation of all sample introduction techniques.

The determined peak areas of each analyte from the liquid injection are „normalized“, that is through applying an individual conversion factor they are brought to the same scale (e.g. 100 %). The obtained pattern serves as benchmark and as an easy-to-recognize „fingerprint“.

When analyzing an unknown sample containing the same analytes and applying the conversion factors to the determined peak areas, a comparison between the „fingerprints“ is easily possible. If e.g. the same pattern is obtained, the fragrance compound composition of the sample is identical to that of the test mix.

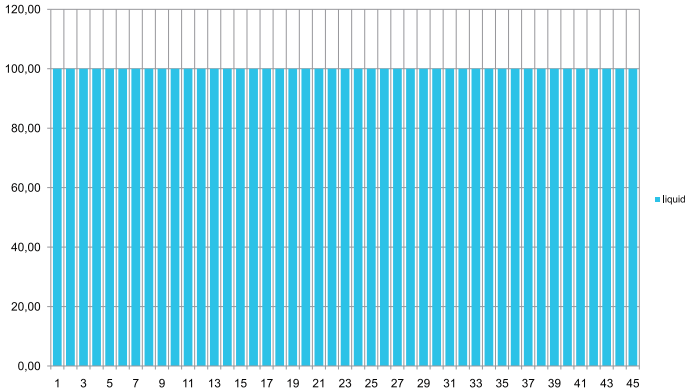

Figure 3. Fingerprint of the test mix liquid injection (= 100 % match).

Static headspace. Static headspace (SHS) is a well established technique which at first glance seems ideal for odor analysis since it is simple, solvent less, leaves non-volatile matrix behind and is fully automated. But the resulting chromatogram (figure 4) of a sample of headspace in equilibrium with a 2 g sample of spiked shampoo incubated at 80°C, shows relative recoveries of individual compounds that are far from the results obtained using liquid injection. The fingerprint in figure 5 confirms this.

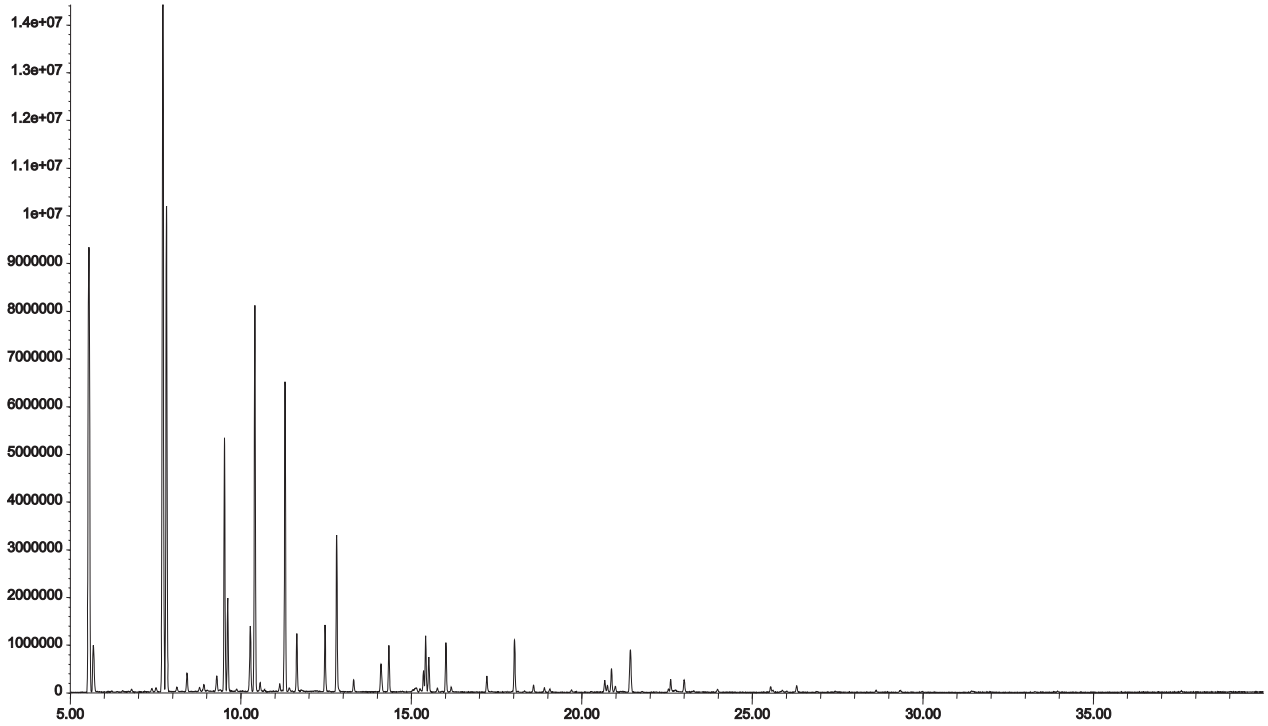

Figure 4. Static headspace chromatogram of 2 g of spiked shampoo.

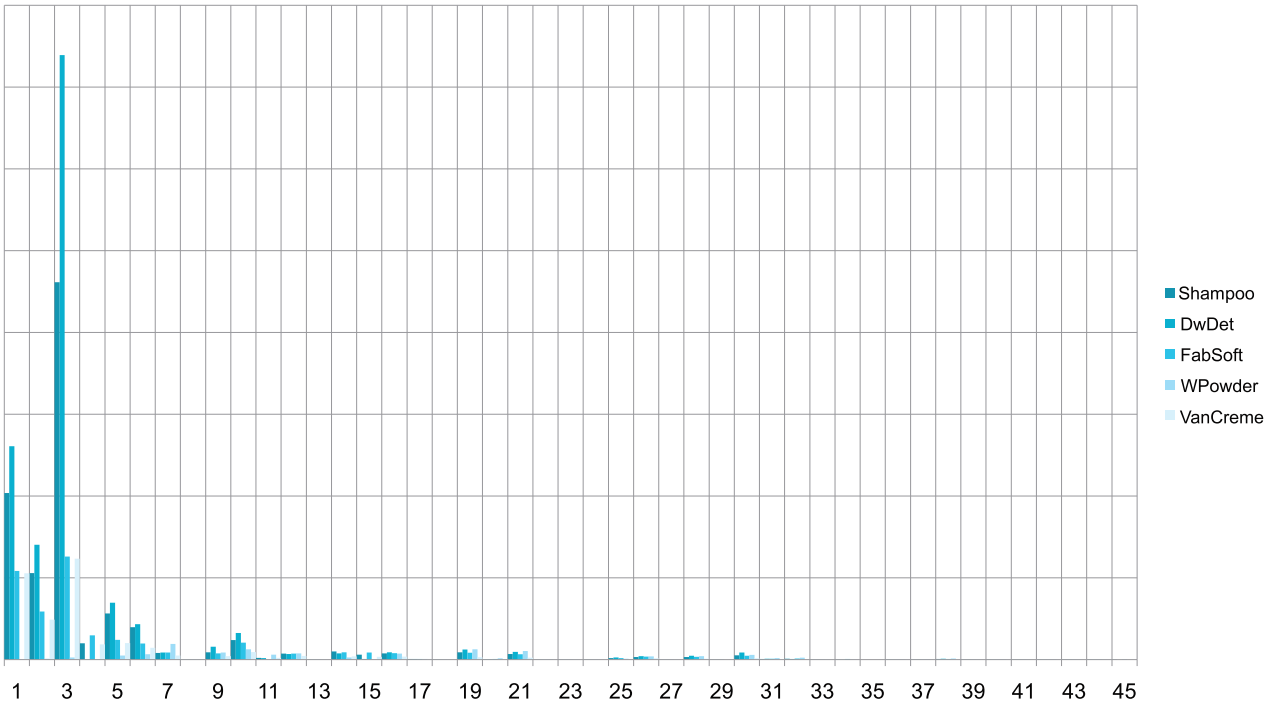

Figure 5. Fingerprints resulting from headspace analysis of the samples.

SHS is an equilibrium technique, based on partitioning of analytes between the gas phase and the condensed sample phase. The analyte concentration in the gas phase (headspace) above the sample depends on the partitioning coefficient of that analyte between the phases at the given temperature. The partitioning coefficient is highly dependent on the analyte boiling point. In general, highly volatile analytes partition more readily

into the gas phase resulting in much higher recovery relative to higher boiling compounds. There are however other important factors at play, such as polarity of the analyte, solubility in the sample phase or even surface adsorption in case of solid samples. This means that recovery for some analytes is affected not only by their volatility, but also by their polarity, by other physical chemical properties and by the matrix, as can be seen by comparing the recoveries of the first ten analytes (figure 6).

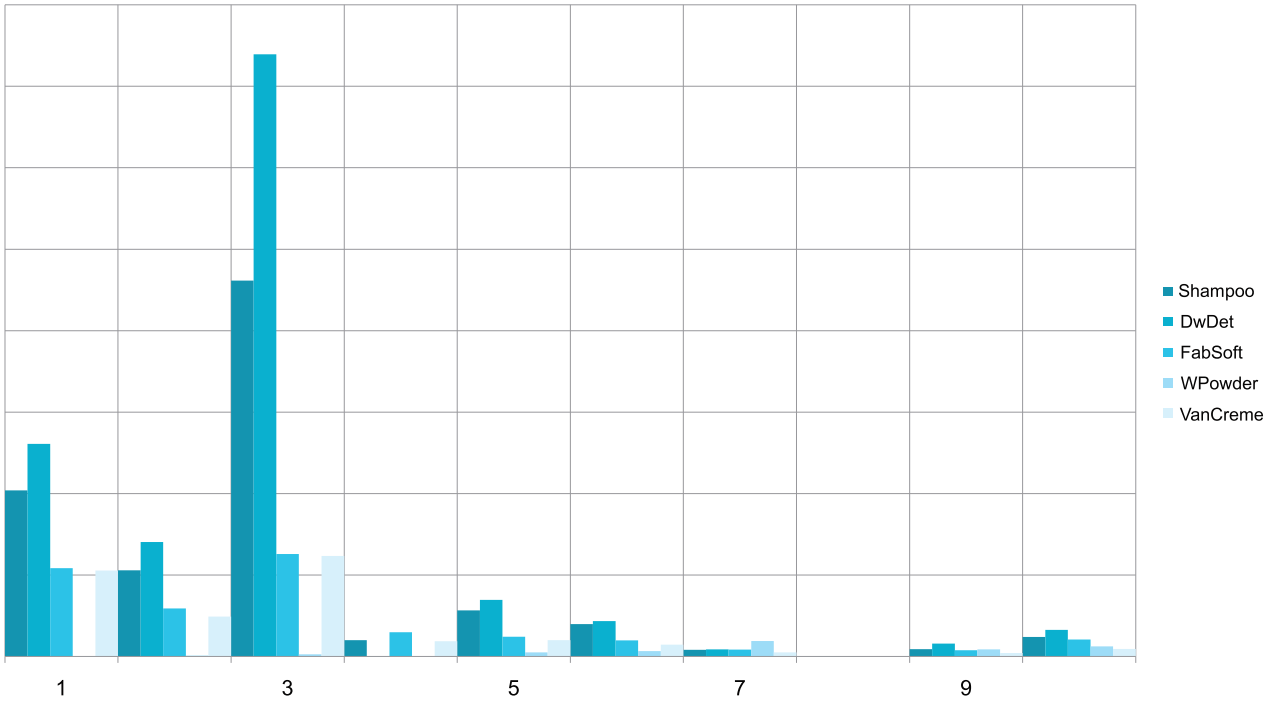

Figure 6. Fingerprints resulting from headspace analysis of the samples, first ten analytes.

Solid Phase Microextraction. The use of Solid Phase Microectraction (SPME) in combination with headspace (HS-SPME) significantly improves the quality of the results in terms of analyte recovery. The analytes from the headspace above 2 g sample of spiked shampoo are now concentrated on a fiber coated with a polymer film. Different fiber coatings are available with different polarities making it possible to fine-tune the selectivity of the extraction process. Figure 7 shows the corresponding chromatogram using a DVB/CAR/PDMS fiber, which covers a range of polarities.

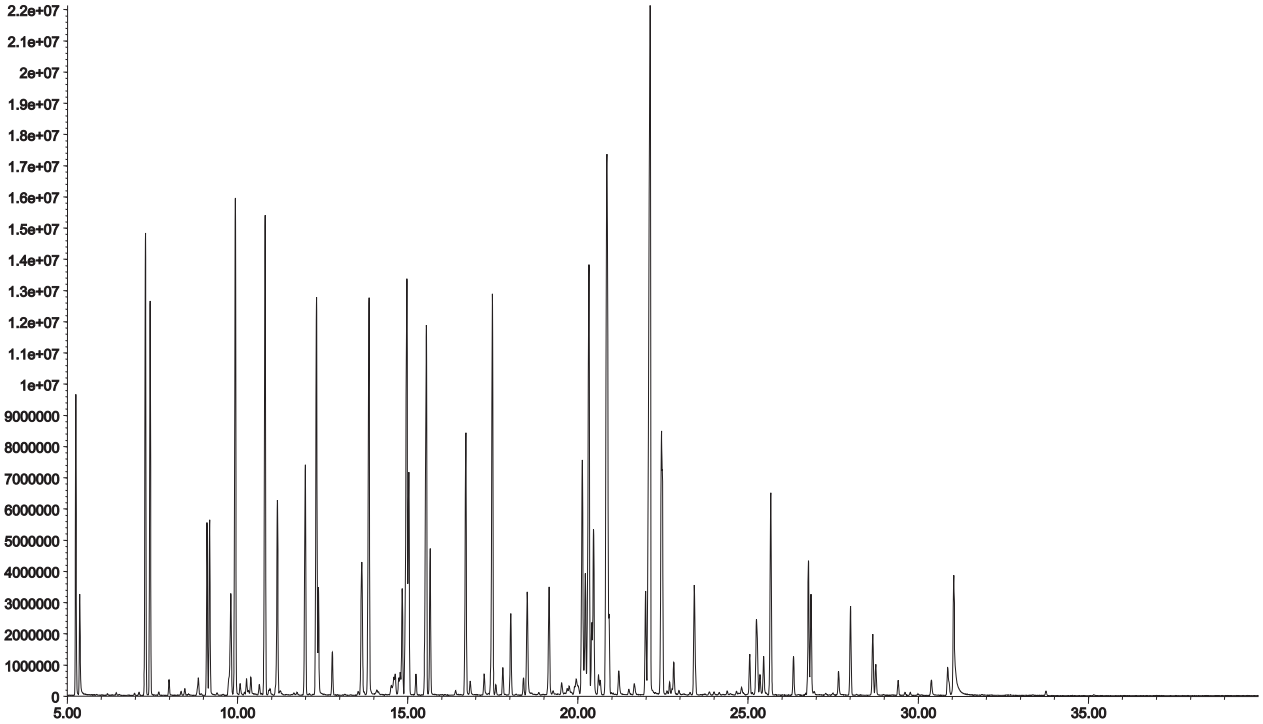

Figure 7. Chromatogram resulting from HS-SPME of a 2 g sample of spiked shampoo using a DVB/CAR/PDMS fiber.

The equilibrium between sample and headspace is now „combined“ with a second equilibrium inside the confined space of the sealed vial, namely that between the headspace and fiber coating. The fiber coating extracts analytes from the headspace forcing the sample/headspace equilibrium to re-establish itself by moving more and more analytes into the vapor phase. This results in much more complete analyte extraction, better recovery and improved fingerprints (figure 8).

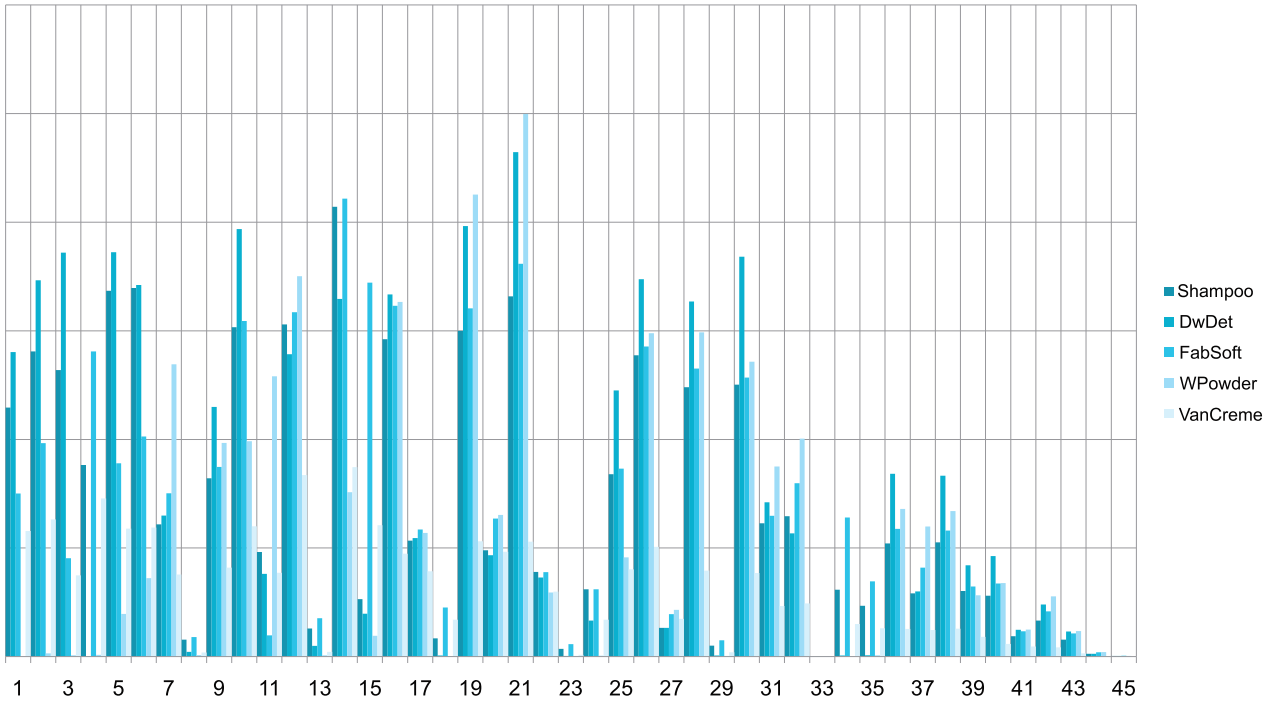

Figure 8. Fingerprints resulting from HS-SPME analysis of the samples.

Some of the compounds still show very poor or no recovery at all. Most of these are solids at the temperatures used here and are thus present at extremely low concentration in the gas phase.

The scope of this work was to investigate, whether a further improvement in recoveries could be reached by applying a dynamic process in which the headspace is continually replaced.

Dynamic headspace. Dynamic headspace using the GERSTEL DHS enables dynamic purging of the headspace above a sample combined with trapping of purged analytes 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, where they are focused in the Cooled Injection System (CIS 4) inlet in order to improve peak shape and increase overall analysis sensitivity. In figure 9 a schematic of the trapping and desorption process is shown.

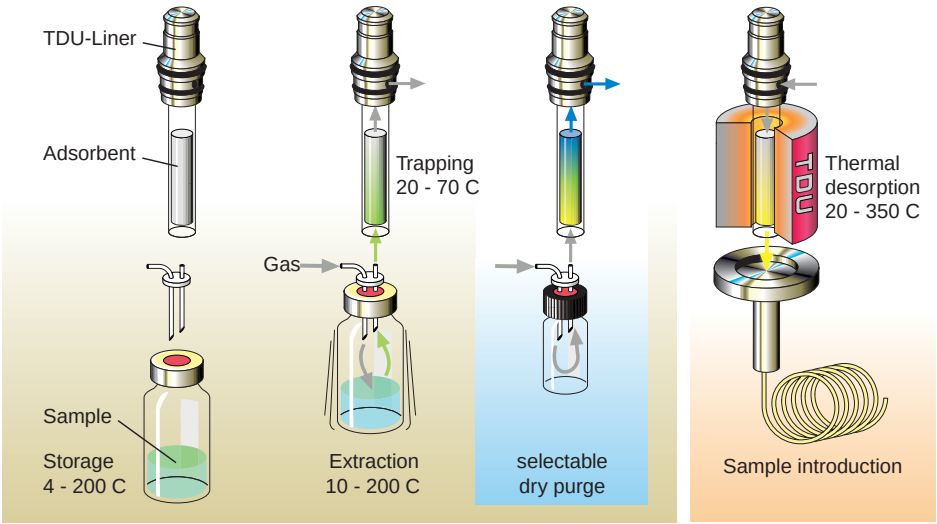

Figure 9. Schematic view of the DHS Process.

In figure 10, a chromatogram resulting from a large volume headspace analysis of a 2 g spiked shampoo sample is shown. In this case, only 10 mL of headspace vapor could be transferred to the trap due to the high analyte concentration and we found only a slight improvement over static headspace and even a decline compared with results obtained using HS-SPME as can be seen in the fingerprints shown in figure 11.

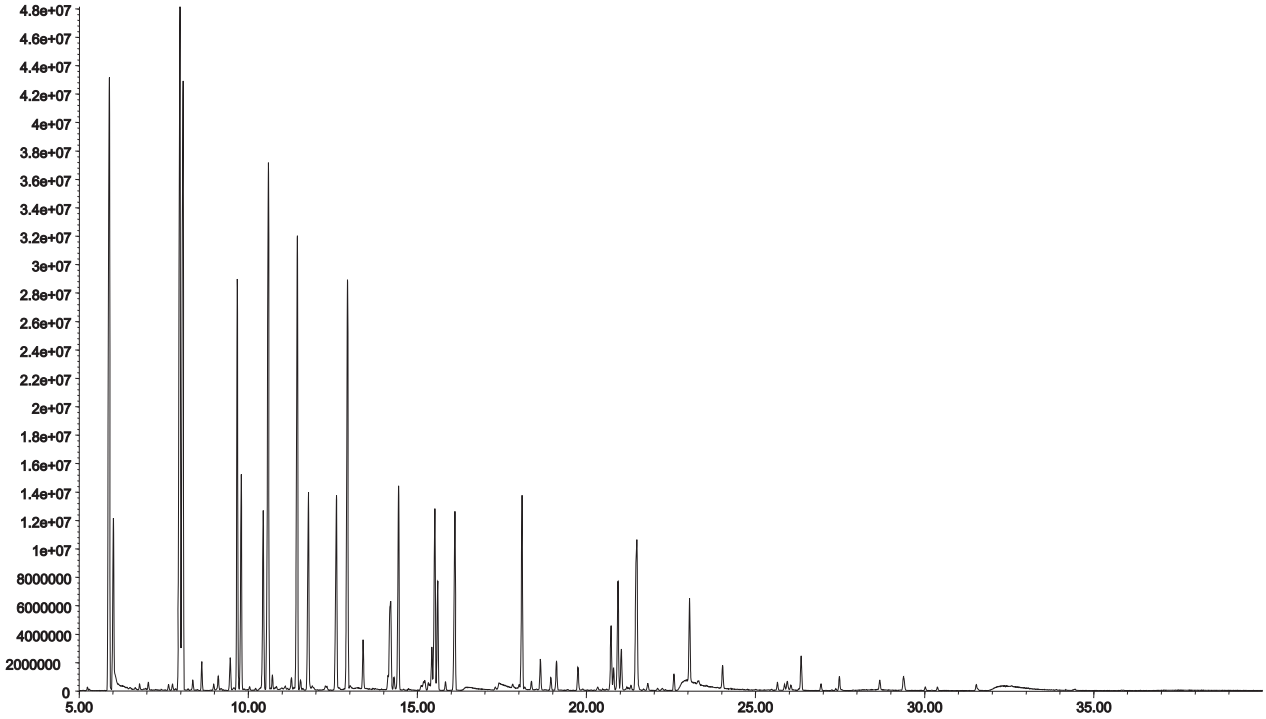

Figure 10. DHS chromatogram of 2 g of spiked shampoo.

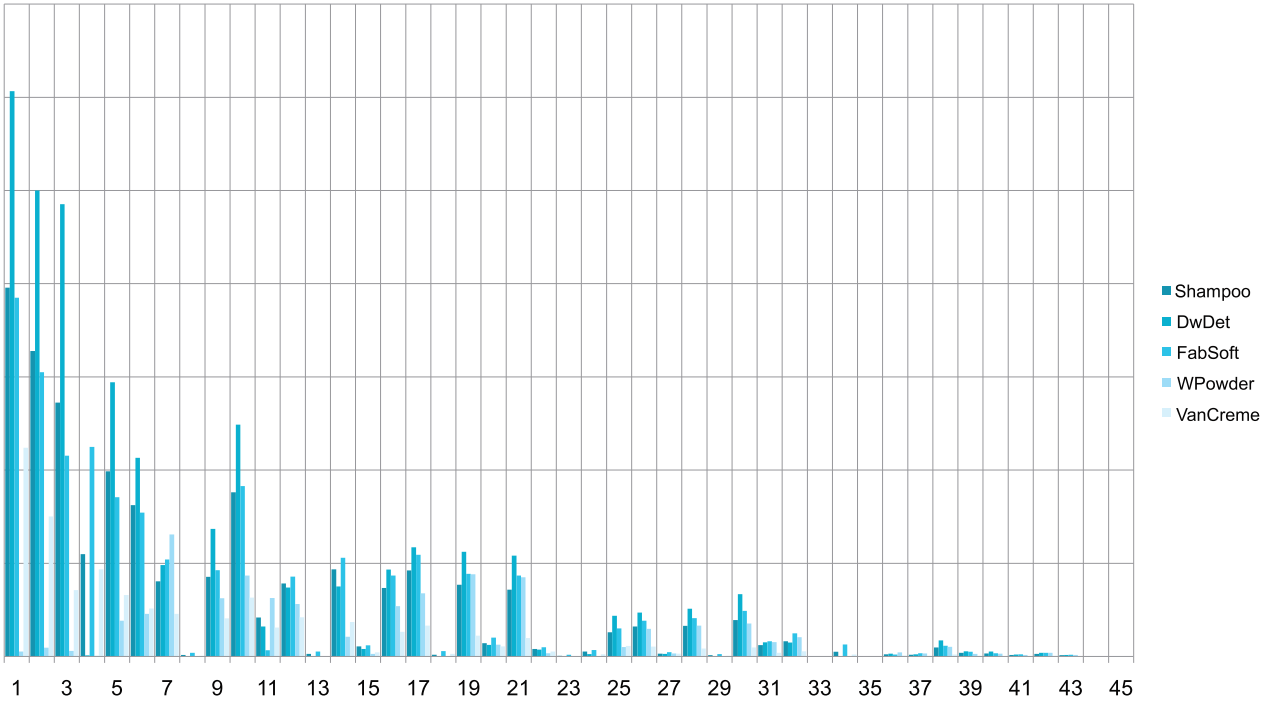

Figure 11. Fingerprints resulting from dynamic headspace analysis of the samples.

Consequently, the amount of sample placed in the headspace vial was drastically reduced by diluting the samples with methanol and only injecting a few microliters into the empty headspace vials. This technique of introducing a small volume of sample and allowing the analytes to evaporate completely inside the headspace vial, without having to rely on establishing an equilibrium between two phases, is called “FET” or full evaporation technique

[1, 2]. The chromatogram shown in figure 12 resulted from FET-DHS analysis of a 20 µL spiked shampoo sample, diluted 1:9 with methanol.

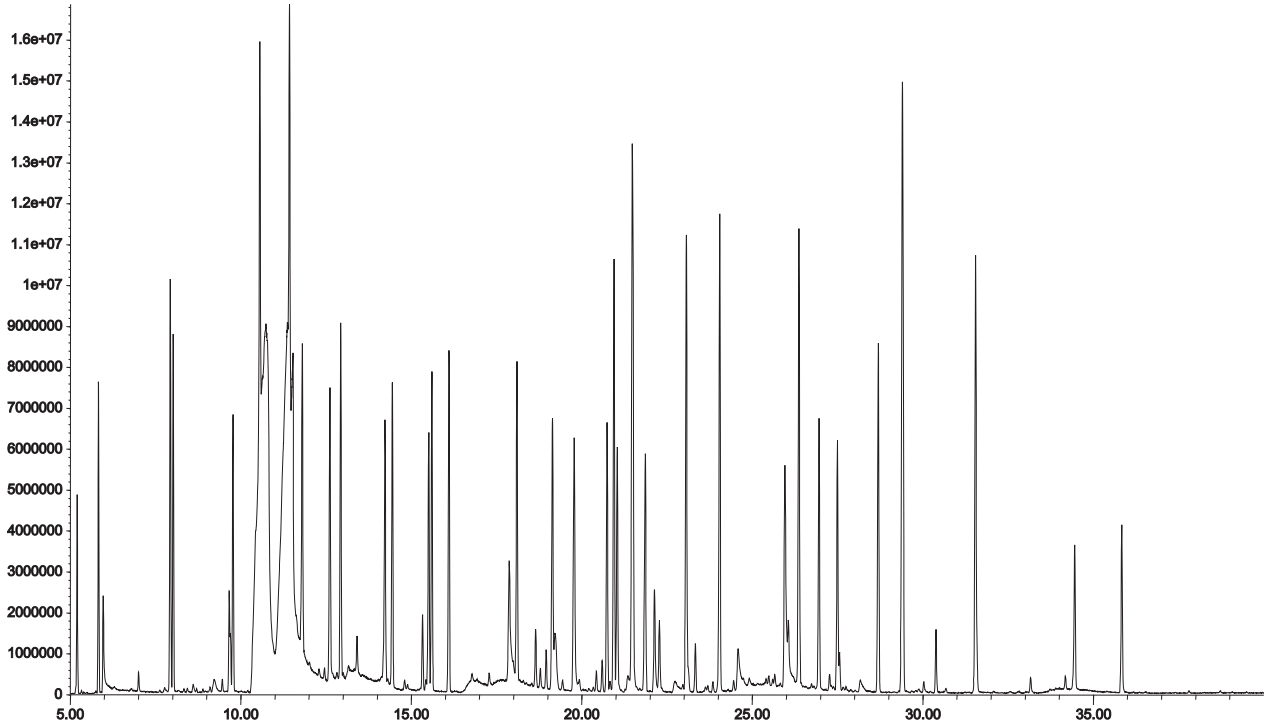

Figure 12. Chromatogram resulting from FET-DHS analysis of a 20 µL sample of spiked shampoo (1:9 in methanol).

The graphics in figure 13 confirm, that there is now very good correlation between the results obtained from liquid injection of the test mix and the FET-DHS results from the different samples. Since the evaporation and transfer to the analytical GC system is exhaustive, real recoveries (in percent) can now be calculated using the liquid injection results as external calibration.

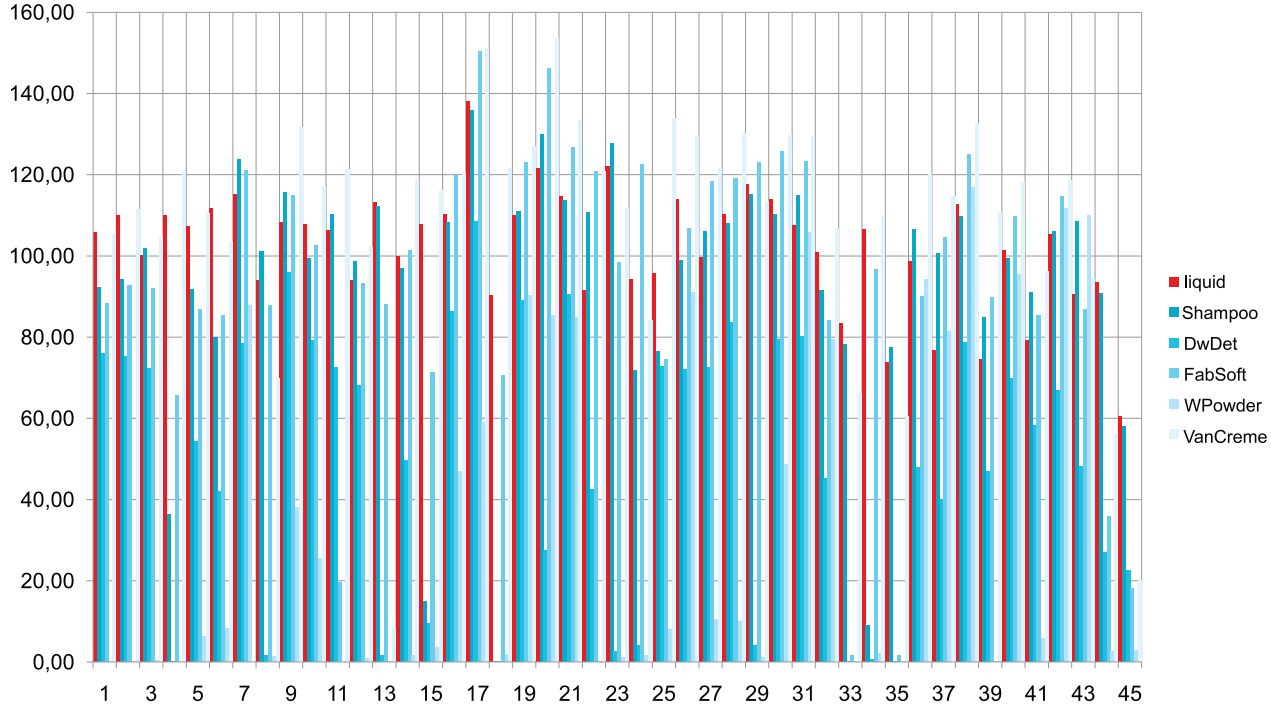

Figure 13. Recoveries of all samples compared to test-mix using full evaporation technique (FET-DHS).

An important condition that must be met in order to perform quantitative analysis and calculation of recoveries is a complete evaporation of the sample. To test this, the shampoo sample was analyzed as previously before (blue trace) and the same vial was then been run a second time (red trace). The results shown in figure 14 prove that the sample was almost completely evaporated in the first run. The compounds missing in figure 14 (4 aldehydes) reacted with the shampoo matrix resulting in poor recoveries.

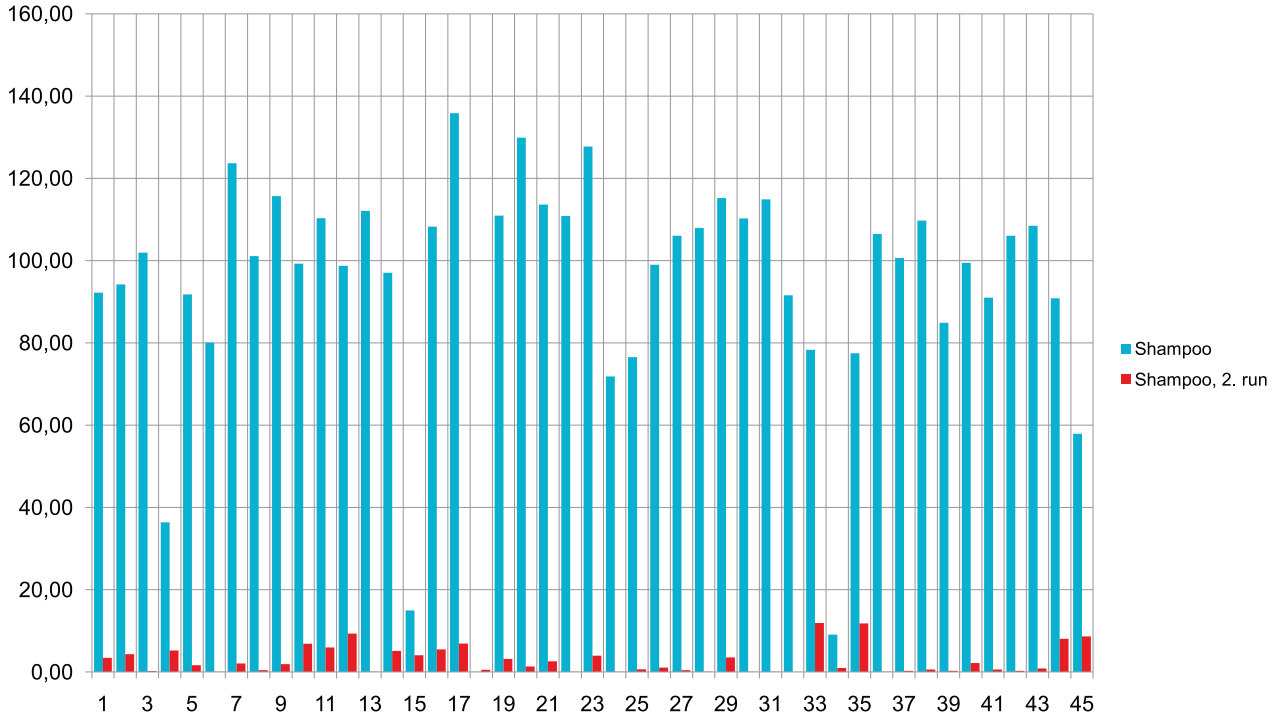

Figure 14. Fingerprints from FET-DHS analysis of 20 µL sample of spiked shampoo (1:9 in methanol, blue bars) and a second run using the same vial (red bars).

Apart from SPME, the sample preparation method most commonly used when determining fragrance compounds in consumer products is simultaneous distillation/extraction or SDE. This technique is the industry standard when comprehensive results are requested. SDE provides good results for a wide range of compounds, but still some polar and semi-volatile compounds can be lost during sample preparation. The main disadvantage of SDE is that it is labor and time intensitive and requries large amounts of solvent. A study was performed comparing extraction recoveries achieved using SDE with hexane, SDE with frigene, and FET-DHS. A range of compounds were extracted from a spiked shower gel using the listed techniques, the results are shown in figure 15. In general the results obtained using the FET-DHS technique were closer to the original composition of the fragrance than those obtained by SDE extraction.

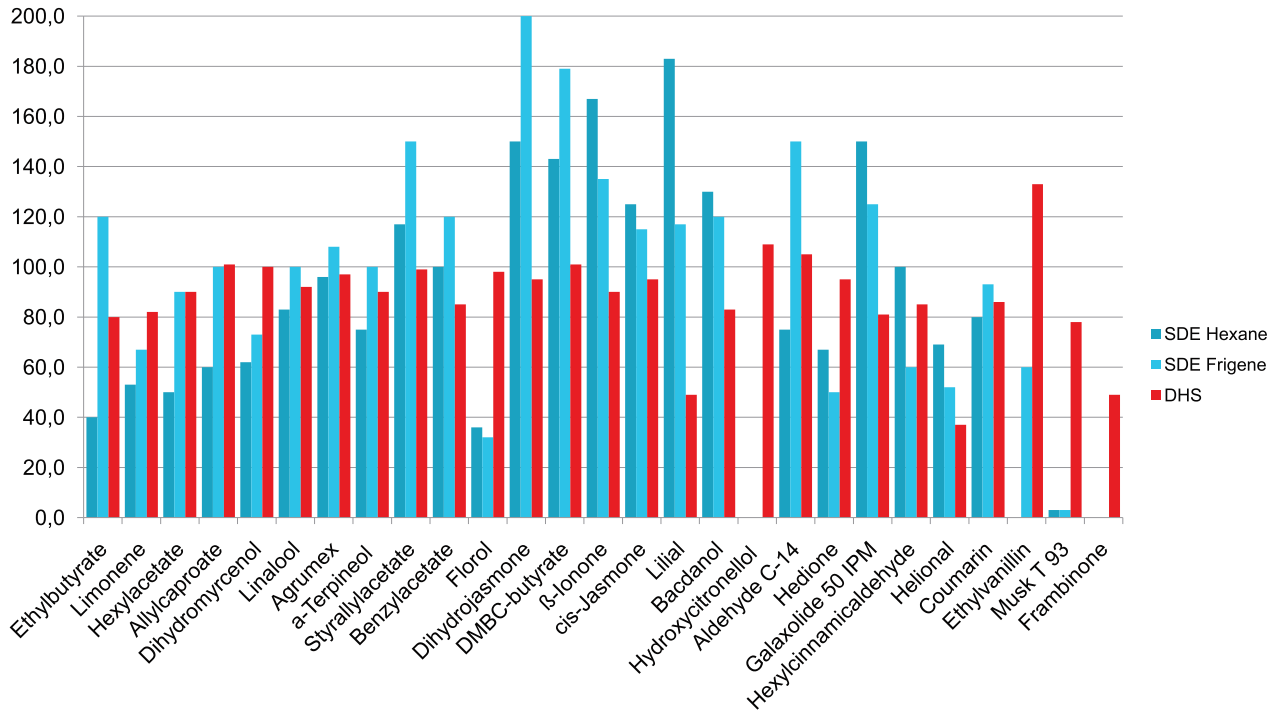

Figure 15. Comparison of recoveries of fragrance compounds using different extraction techniques.

Conclusions

DHS is an excellent, fully automated technique for the determination of fragrances in consumer products. The Full Evaporization Technique (FET) in combination with DHS enables quantitative extraction of fragrance compounds across a wide volatility range, 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, which could not be determined with commonly used extraction techniques, were successfully determined using FET-DHS.

References

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[2] M. Markelov, O.A. Bershevits, Analytica Chimica Acta, 432 (2001) 213-227

G L O B A L A N A L Y T I C A L S O L U T I O N S

GERSTEL GmbH & Co. KG
Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany
☎ +49 (0) 208 - 7 65 03-0
🖷 +49 (0) 208 - 7 65 03 33
@ gerstel@gerstel.com
🌐 www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.
701 Digital Drive, Suite J
Linthicum, MD 21090
USA
☎ +1 (410) 247 5885
🖷 +1 (410) 247 5887
@ sales@gerstelus.com
🌐 www.gerstelus.com

GERSTEL AG
Wassergrabe 27
CH-6210 Sursee
Switzerland
☎ +41 (41) 9 21 97 23
🖷 +41 (41) 9 21 97 25
@ swiss@ch.gerstel.com
🌐 www.gerstel.ch

GERSTEL K.K.
1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan
☎ +81 3 5731 5321
🖷 +81 3 5731 5322
@ info@gerstel.co.jp
🌐 www.gerstel.co.jp

GERSTEL LLP
Level 25, North Tower
One Raffles Quay
Singapore 048583
☎ +65 6622 5486
🖷 +65 6622 5999
@ SEA@gerstel.com
🌐 www.gerstel.com

GERSTEL Brasil
Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
☎ +55 (11)5665-8931
🖷 +55 (11)5666-9084
@ gerstel-brasil@gerstel.com
🌐 www.gerstel.com.br

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