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Application

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Application Note 135

The complementary roles of dynamic headspace and sorptive extraction in the analysis of fragranced consumer products using TD–GC–MS

Summary

This Application Note describes the analysis of three fragranced consumer products – fabric conditioner, washing detergent and washing powder – using three sampling approaches in conjunction with analysis by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). As well as comparing the analyte ranges covered by dynamic headspace sampling, headspace sorptive extraction and immersive sorptive extraction, the ability of Markes' re-collection technology to streamline method development and validation is discussed.

Introduction

The success of many personal care and household cleaning products has long depended on the precise mix of aroma-active compounds that they release. For example, manufacturers are continuously developing new formulations that offer different (or longer-lasting) fragrances, while consumers loyal to a well-established brand can notice even the slightest variation in fragrance quality. In addition, there has been increasing concern over the presence of potentially harmful compounds – such as allergens – in fragrance formulations. These factors have led to an ongoing need to monitor the volatile and semi-volatile organic compounds (VOCs and SVOCs) released by fragranced consumer products.

Sampling and analysing VOCs and SVOCs from a wide range of products and materials has long been carried out using gas chromatography (GC), enhanced by pre-concentration using thermal desorption (TD). TD provides a versatile and high-sensitivity alternative to traditional sample preparation methods for GC, such as solvent extraction or static headspace, and involves minimal manual sample handling while being applicable to the widest possible range of GC-compatible analytes. In the field of consumer products, TD has generally been associated with sampling vapours released from solid samples, but recent developments in sorptive extraction have improved the applicability of TD pre-concentration technology to aqueous samples.

This improvement in the versatility of TD is particularly valuable for analysis of fragranced products, where the samples requiring analysis may be powders, waxes, creams or liquids. This Application Note aims to highlight this versatility by demonstrating the use of dynamic headspace sampling, headspace sorptive extraction and immersive sorptive extraction for the analysis of VOCs and SVOCs in three fragranced cleaning products – two liquids and one powder.

Background to the sampling equipment

In this study, three sampling procedures were used, to establish how well they performed for each sample:

- Method A – Dynamic headspace sampling using the Micro-Chamber/Thermal Extractor™ (µ-CTE™) (Figure 1).
- Method B – Headspace sorptive extraction using HiSorb™ probes (Figure 2).
- Method C – Immersive sorptive extraction using HiSorb probes.

These three methods are outlined in Figure 3.

Figure 1: The six-chamber (left) and four-chamber (right) models of the µ-CTE™. Both models use gentle heating and a flow of inert gas to release VOCs and SVOCs from solid or liquid samples.

Figure 2: Regular-length and short-length HiSorb probes (left), available in stainless steel or inert-coated stainless steel. The probes are fitted with a section of PDMS (right) that adsorbs vapour-phase or solution-phase VOCs and SVOCs from the samples, facilitating minimal sample handling.

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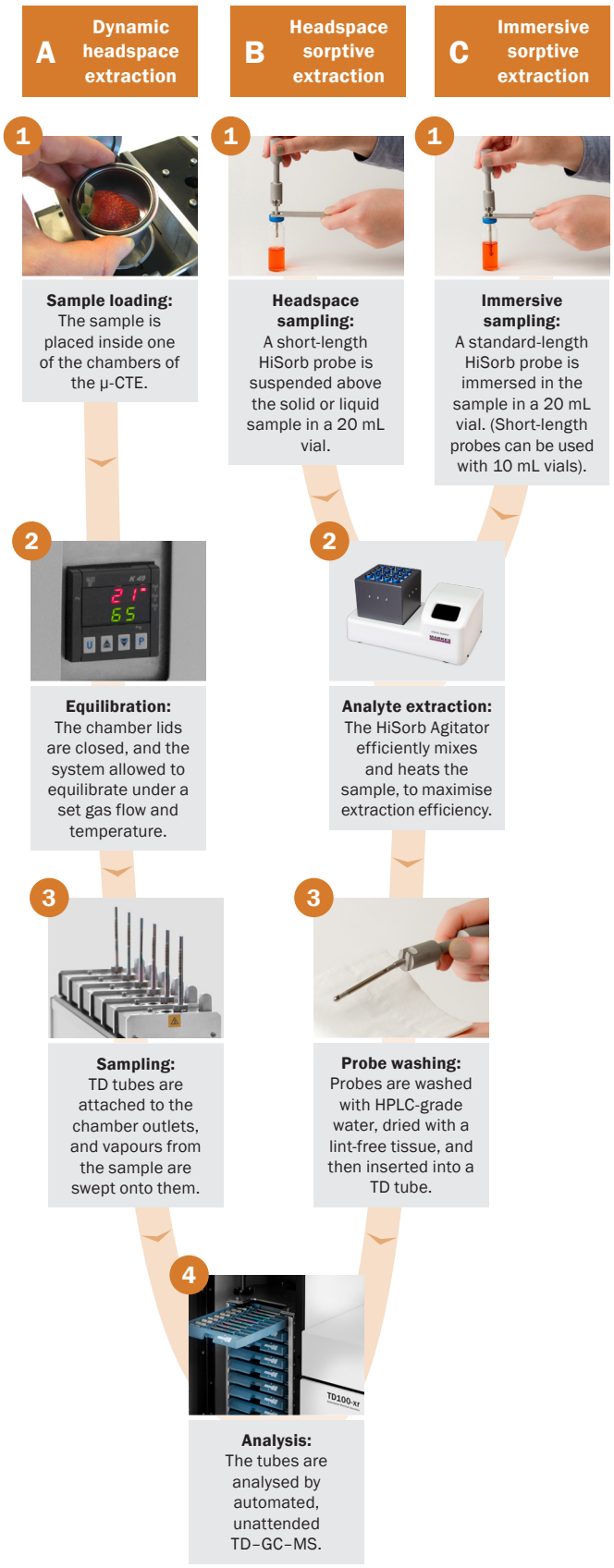


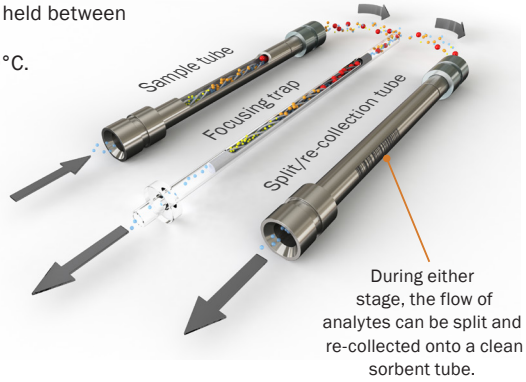
Figure 3: Workflow for the three sampling methods used in this study.

Background to thermal desorption

All three sampling approaches described above involve analysis by thermal desorption (TD). This is a versatile GC pre-concentration technology that is used to analyse VOCs and SVOCs in a wide range of sample types. By concentrating organic vapours from a sample into a very small volume of carrier gas (Figure 4), TD maximises sensitivity for trace-level target compounds, helps to minimise interferences, and routinely allows analyte detection at the ppb level or below. It also greatly improves sample throughput, by combining sample preparation, desorption/extraction, pre-concentration and GC injection. In this study we use the TD100-xr™ for fully automated analysis of up to 100 sample tubes.

A Tube desorption and inlet split:

Sample tube heated in a flow of carrier gas and analytes swept onto an electrically cooled focusing trap, typically held between ambient and –30°C.



B Trap desorption and outlet split:

Focusing trap rapidly heated (up to 100°C/s) in a reverse flow of carrier gas ('backflush' operation), to transfer the analytes to the GC column.

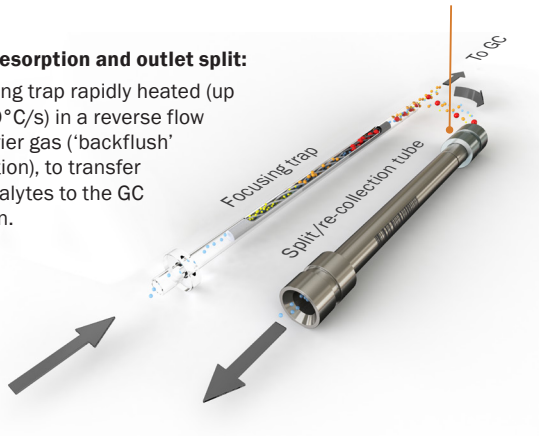


Figure 4: Schematic showing the operation of cryogen-free thermal desorption as used in Markes' instruments.

Experimental

Samples:
Three fragranced household products were analysed:

- Sample 1 – Liquid fabric conditioner
- Sample 2 – Liquid washing detergent
- Sample 3 – Washing powder. For the immersive sorptive extraction study, a solution was prepared by dissolving 1 g of powder in 18.5 mL water.

Dynamic headspace sampling (Method A):

Instrument:	Six-chamber Micro-Chamber/Thermal Extractor (Markes International)
Sample:	2 g (solid) or 1 mL (liquid) sample placed in disposable aluminium sample tray
Chamber temp.:	40°C
Chamber flow:	50 mL/min, nitrogen
Sampling time:	15 min
Sorbent tube:	Packed with Tenax® TA (Markes International part no. C1-AXXX-5003)

Headspace sorptive extraction (Method B):

Sample:	10 mL (liquid) or 2 g (solid) sample in 20 mL headspace vial, sealed with a HiSorb septum seal and cap
Sampler:	Short-length, inert HiSorb-P1 probe (Markes International part no. H1-AXABC-5)
TD tube:	Empty (Markes International part no. C0-AXXX-0000)
Sample incubation:	HiSorb Agitator (Markes International)
Sampling temp:	40°C
Agitation speed:	300 rpm
Sampling time:	90 min

Immersive sorptive extraction (Method C):

Sample:	18.5 mL sample in 20 mL headspace vial, sealed with a HiSorb septum seal and cap
Sampler:	Standard-length, inert HiSorb-P1 probe (Markes International part no. H1-AXAAC-5)

Other conditions as for Method B.

TD:

Instrument:	TD100-xr™ (Markes International)
Cold trap:	Tenax TA (Markes International part no. U-T9TNX-2S)
Desorption time:	10 min
Desorption temp.:	280°C
Trap low temp.:	25°C
Heating rate:	Max
Trap high temp.:	290°C
Trap hold time:	1.5 min
Outlet split:	100 mL/min
Split ratio:	51:1
Flow path temp.:	180°C

GC:

Column:	VF-624ms™, 60 m × 0.32 mm × 1.8 µm
Oven:	40°C (3 min), then 6°C/min to 230°C (15 min)
Inlet:	180°C
Carrier gas:	Helium, 2.0 mL/min
Septum purge:	3.0 mL/min
MS transfer line:	240°C

MS:

Ion source:	230°C
Quadrupole:	150°C
Mass range:	m/z 35–450

Data analysis:
TargetView™ GC–MS software (Markes International) was used to selectively remove unwanted background noise from the chromatograms, and so improve the identification of lower-level analytes during subsequent automated comparison against a 407-component fragrance-compound target library. TargetView also generated peak-area information that allowed the amounts of each analyte sampled with the different techniques to be compared.

Results and discussion

1. Overall fragrance profiles

The fragrance profiles of the fabric conditioner, washing detergent and washing powder (using each of the sampling techniques) are shown in Figures 5, 6 and 7 respectively, with major components being labelled. Corresponding lists of compounds identified by comparison against the fragrance-compound target library are shown in Tables A1–A3 (see Appendix).

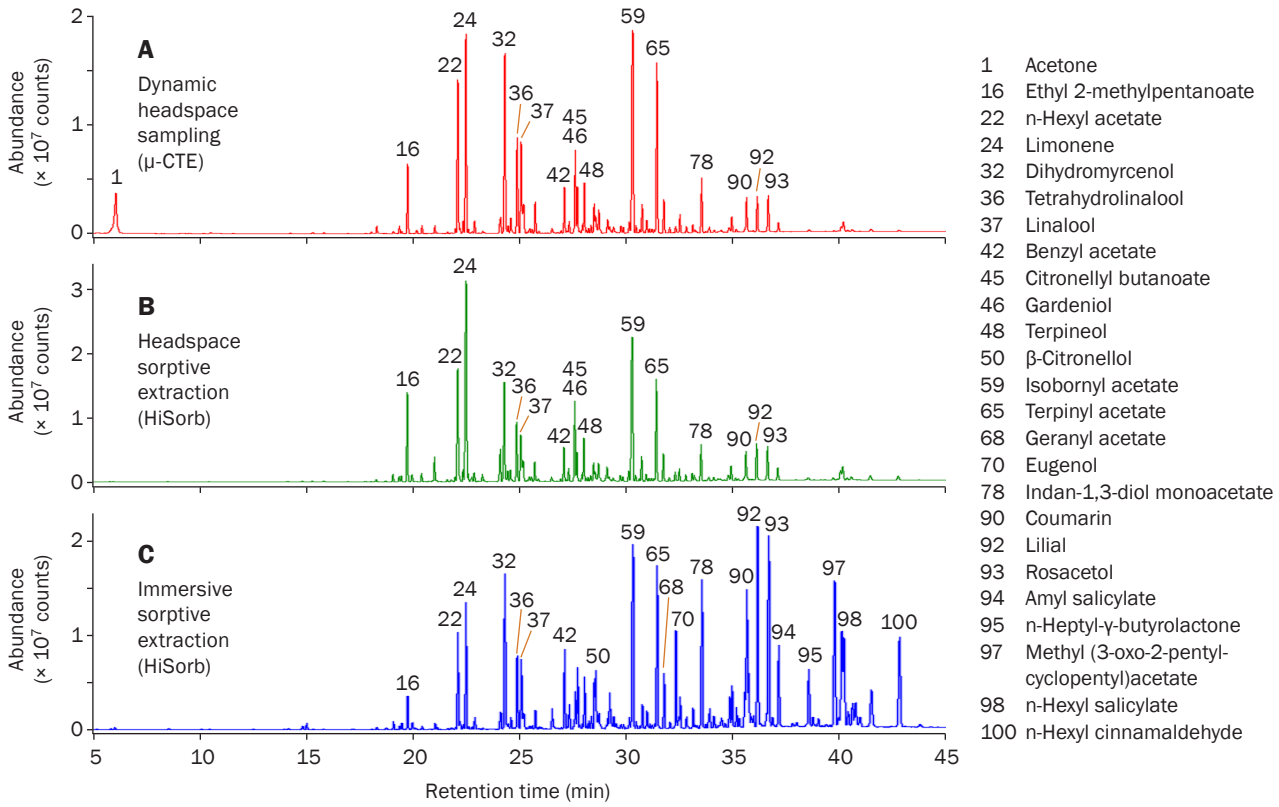


Figure 5: TD–GC–MS analysis of fabric conditioner using Methods A–C. Major peaks are labelled. A listing of compounds identified by comparison against the target library of fragrance compounds is provided in Table A1 (see Appendix).

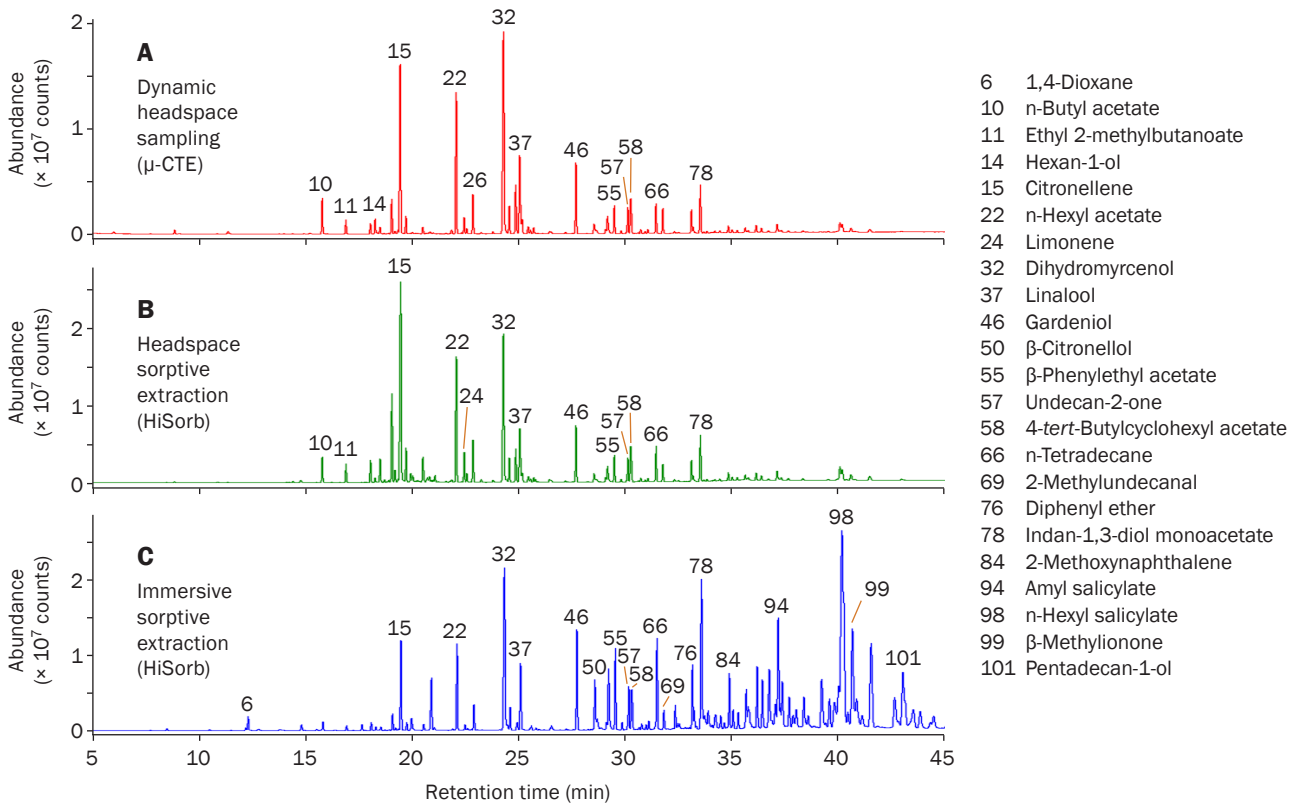


Figure 6: TD–GC–MS analysis of washing detergent using Methods A–C. Major peaks are labelled. A listing of compounds identified by comparison against the target library of fragrance compounds is provided in Table A2 (see Appendix).

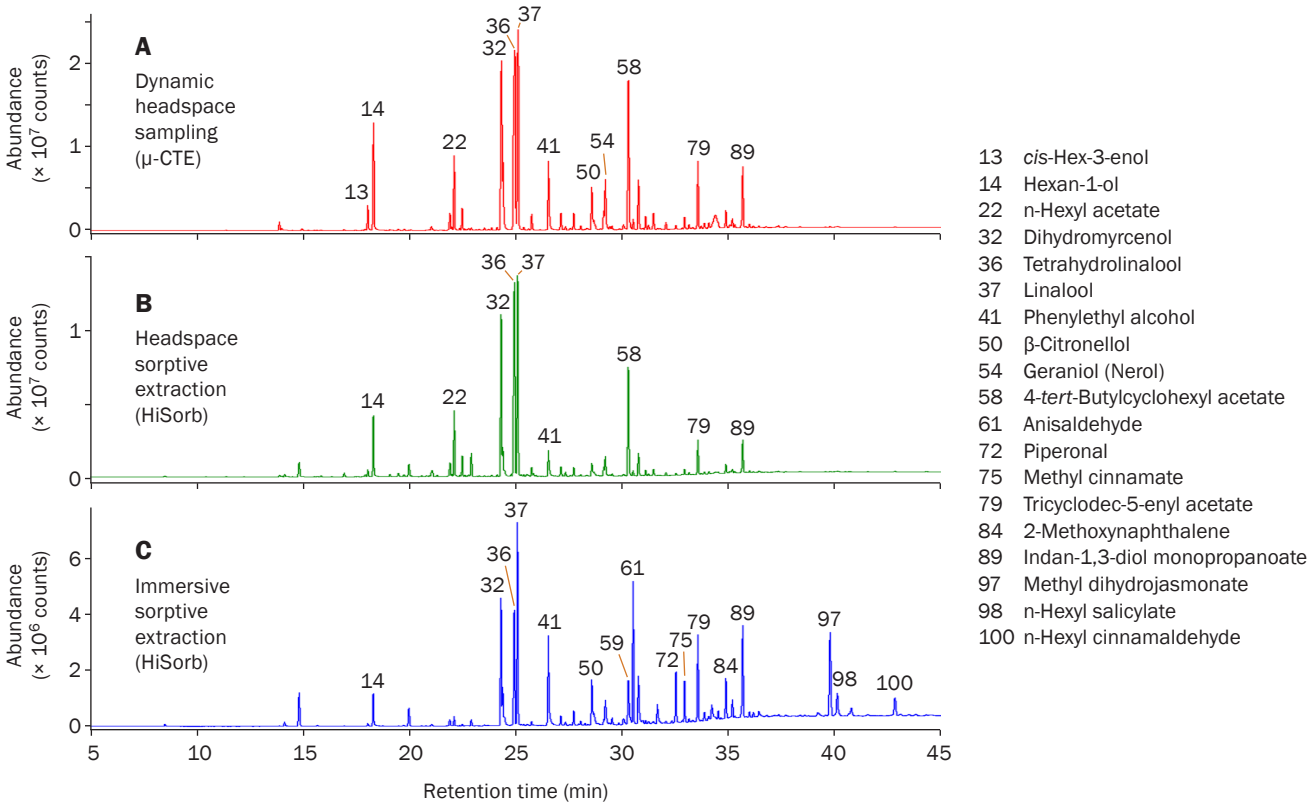


Figure 7: TD–GC–MS analysis of washing powder using Methods A–C. Major peaks are labelled. A listing of compounds identified by comparison against the target library of fragrance compounds is provided in Table A3 (see Appendix).

2. Comparison of headspace sampling techniques

For all samples studied, dynamic headspace sampling (using the μ-CTE) and headspace sorptive extraction (using HiSorb probes) gave very similar results, both in terms of the compounds identified and their relative proportions. As a result, it is clear that the two techniques are equally useful for the headspace profiling of fragranced consumer goods.

One exception to this rule is the tendency of certain highly polar, volatile compounds to have stronger responses with the dynamic headspace approach. This is exemplified by the case of the fabric conditioner (Figure 5), where the early-eluting acetone peak (#1) present in the μ-CTE run is not observed using HiSorb. This effect can be attributed to the low affinity of such compounds for the PDMS sampling phase used on the HiSorb probes, compared to the Tenax TA sorbent used for μ-CTE sampling. Such a tendency would be expected to correlate with a low octanol–water partition coefficient ($\log K_{o/w}$), and accordingly, the value for acetone is –0.24 (for comparison, decan-1-ol is 4.57 and hexadecanoic acid is 7.17).[1]

3. Comparison of immersive sorptive extraction with headspace sorptive extraction

For all three samples, although there remains a considerable degree of overlap in analyte range between immersive sorptive extraction and the two headspace approaches, it is clear that the immersive approach is better at sampling the less-volatile compounds. As a result, many of the later-eluting compounds identified using immersive sorptive extraction are not fragrance compounds – but they are nevertheless important constituents of the formulation that may have an effect on the overall product quality. Immersive sorptive extraction therefore provides a useful complement to the headspace techniques by allowing a more comprehensive understanding of the compounds present to be obtained.

4. Comparison of solid- and solution-phase washing powder

The compatibility of the sampling approaches with both solid and liquid samples allowed an additional comparison to be made, between the headspace profiles of washing powder in the solid and solution phases (Figure 8). The chromatograms show very few differences in the relative abundances of fragrance compounds sampled, indicating that either sampling approach can be used to obtain meaningful results, with the headspace sampling of the solid requiring less sample preparation.

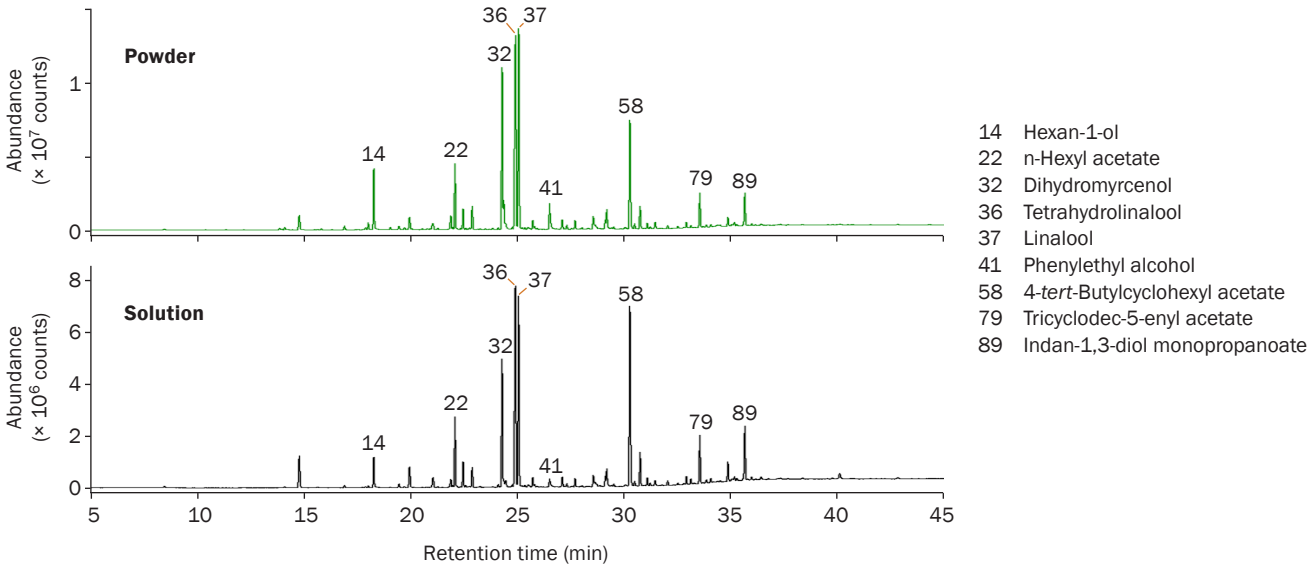


Figure 8: TD–GC–MS analysis of washing powder using Method B (headspace sorptive extraction with HiSorb), of (top) the solid sample, (bottom) an aqueous solution. Major peaks are labelled. A listing of compounds identified by comparison against the target library of fragrance compounds is provided in Table A3 (see Appendix).

5. Sample re-collection for repeat analysis

Markes' TD systems allow samples to be split and re-collected onto a clean sorbent tube at the tube desorption and/or trap desorption stages (see Figure 4). This is an important feature that enables analyses to be repeated, without the need for additional sample extraction. Repeat analysis under the same conditions allows the method to be validated, by demonstrating complete transfer of analytes and absence of analytical bias. The analysis can also be repeated using different method conditions (such as a lower split flow to improve detection of trace-level compounds), or with a different detector (to improve confidence in compound identity).

To illustrate the performance of the analytical system for re-collection, Figure 9 shows the results of a study into a different fabric conditioner, using immersive sorptive extraction and the same analytical conditions as described previously. The split portion was re-collected onto a clean TD tube packed with Tenax TA, and this was re-analysed under identical conditions. The two profiles show a high degree of similarity, indicating that sample re-collection is a powerful tool that allows automated re-analysis without having to repeat sample preparation.

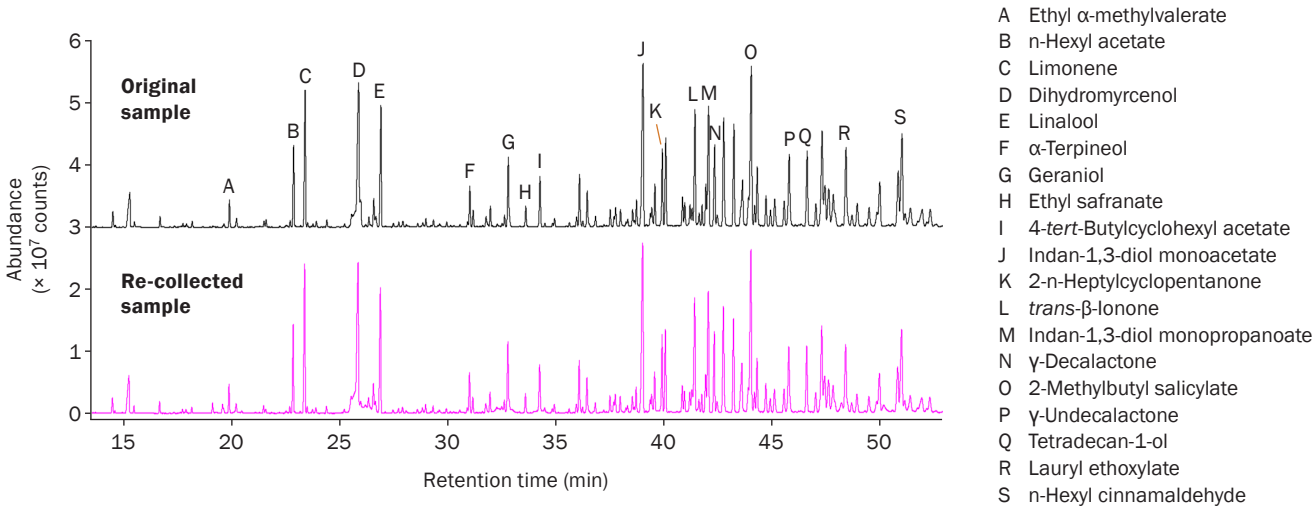


Figure 9: TD–GC–MS analysis of fabric conditioner using Method C (immersive sorptive extraction using HiSorb). (Top) Original sample. (Bottom) Repeat analysis of the same sample, following re-collection of the split portion onto a clean sorbent tube. Major peaks are labelled.

Conclusions

In this study, we have shown that either dynamic headspace sampling, headspace sorptive extraction or immersive sorptive extraction can be used in conjunction with TD–GC–MS analysis to provide valuable information on the volatile profiles of fragranced consumer products.

A key benefit of these approaches is versatility, with options available for sampling from solid or liquid samples. For example, the very similar results obtained for headspace sampling using the µ-CTE unit and HiSorb probes allows analysts to choose the most convenient method for their application.

Alternatively, immersive sorptive extraction using HiSorb probes, while sampling the vast majority of analytes found in the sample headspace, preferentially samples the less volatile compounds. This approach therefore provides complementary information to headspace sampling, delivering a more comprehensive understanding of the compounds present, and including those that would not typically contribute to the fragrance.

All three sampling techniques described here offer the benefit of ease of use, which becomes a major consideration when wishing to sample analytes directly from the liquid. The HiSorb probes used for immersive sorptive extraction in this study are robust and easy to handle, which is not the case for fragile SPME fibres. An additional consideration is that liquid can rise up into the SPME fibre casing as a result of capillary action, causing sample interference – a phenomenon that is entirely avoided with HiSorb probes.

The above factors, combined with the inherent advantages of TD–GC–MS, make these methods highly suitable for analysing fragranced consumer products for a range of purposes, including routine quality control, product comparison, troubleshooting customer complaints, and product development.

Trademarks

Reference

1. J. Sangster, Octanol-water partition coefficients of simple organic compounds, *Journal of Physical and Chemical Reference Data*, 1989, 18: 1111–1227, http://dx.doi.org/10.1063/1.555833.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

Appendix

No.	Compound	CAS No.	t_R (min)	Peak sum (TIC)		
				Method A	Method B	Method C
1	Acetone	67-64-1	5.84	4.53×10^6	3.13×10^5	9.45×10^5
3	2-Methylpropan-1-ol	78-83-1	10.18	4.02×10^5	5.20×10^4	4.43×10^4
4	Acetic acid	64-19-7	10.50	1.39×10^6	1.18×10^5	–
11	Ethyl 2-methylbutanoate	7452-79-1	16.93	1.13×10^5	2.91×10^5	7.96×10^4
13	*cis*-Hex-3-enol	928-97-2	18.05	1.85×10^6	3.33×10^5	2.75×10^5
14	Hexan-1-ol	220713-27-9	18.30	7.70×10^6	3.57×10^6	2.42×10^6
16	Ethyl 2-methylpentanoate	39255-32-8	19.75	7.01×10^7	1.69×10^8	3.58×10^7
17	Camphene	79-92-5	20.18	3.56×10^6	5.12×10^5	2.99×10^5
18	*p*-Menth-3-ene	500-00-5	21.14	3.18×10^5	2.71×10^6	8.52×10^5
19	Ethyl hexanoate	8068-81-3	21.63	1.45×10^6	3.41×10^6	7.56×10^5
22	n-Hexyl acetate	142-92-7	22.11	1.60×10^8	2.24×10^8	1.11×10^8
23	Octanal	124-13-0	22.36	8.66×10^6	1.22×10^7	2.84×10^6
24	Limonene	138-86-3	22.49	2.41×10^8	5.59×10^8	1.54×10^8
25	trans-β-Ocimene	3779-61-1	22.79	8.17×10^5	5.46×10^6	1.67×10^6
26	*p*-Methylanisole	104-93-8	22.89	5.01×10^6	7.22×10^6	3.15×10^6
27	Eucalyptol	470-82-6	22.91	6.01×10^6	4.91×10^6	1.09×10^7

Table A1: List of target analytes identified in the fabric conditioner (Figure 5) by a search against a 407-component library of fragrance compounds using TargetView. *(Continued on next page)*

No.	Compound	CAS No.	t_R (min)	Peak sum (TIC)		
				Method A	Method B	Method C
28	γ-Terpinene	99-85-4	23.28	1.95×10^6	9.56×10^6	1.08×10^6
30	1,4-Dipropylene glycol	110-98-5	24.10	–	–	2.04×10^6
31	Terpinolene	586-62-9	24.12	1.46×10^7	5.15×10^7	–
32	Dihydromyrcenol	25279-08-7	24.32	2.44×10^8	2.06×10^8	2.22×10^8
34	Ethyl heptanoate	106-30-9	24.47	5.91×10^6	1.37×10^7	–
35	Phenylethyl methyl ether	3558-60-9	24.60	1.35×10^7	1.65×10^7	1.13×10^7
36	Tetrahydrolinalool	78-69-3	24.93	1.04×10^7	1.12×10^7	–
38	Rose oxide	16409-43-1	25.11	2.87×10^6	6.03×10^6	2.98×10^6
39	2,4-Dimethylcyclohex-3-enyl-1-carboxaldehyde (Triplal)	68039-49-6	25.74	2.90×10^7	2.80×10^7	1.88×10^7
40	Thujone	471-15-8	25.92	1.47×10^6	5.55×10^5	1.58×10^6
41	Phenylethyl alcohol	60-12-8	26.53	7.02×10^6	8.42×10^6	2.79×10^7
42	Benzyl acetate	140-11-4	27.11	4.21×10^7	5.31×10^7	8.76×10^7
43	2-Isopropyl-5-methylcyclohexanone	3391-87-5	27.23	1.45×10^6	2.02×10^6	1.26×10^6
44	Camphor	76-22-2	27.34	1.15×10^7	2.26×10^7	2.88×10^7
47	Decanal	112-31-2	27.96	5.62×10^6	8.64×10^6	–
48	Terpineol	98-55-5	28.07	2.22×10^7	2.98×10^7	2.16×10^7
49	Methyl salicylate	119-36-8	28.25	3.58×10^6	5.31×10^6	7.83×10^6
50	β-Citronellol	106-22-9	28.57	1.68×10^7	1.30×10^7	6.81×10^7
51	Linalyl acetate	115-95-7	28.73	1.22×10^7	1.16×10^7	1.07×10^7
54	Geraniol (Nerol)	106-24-1	29.24	–	–	3.50×10^7
56	Benzylacetone	2550-26-7	29.84	–	–	1.21×10^5
59	Isobornyl acetate	125-12-2	30.33	1.84×10^8	2.36×10^8	1.91×10^8
60	Undecanal	112-44-7	30.48	3.31×10^6	4.72×10^6	4.20×10^6
63	2-Methyl-1-phenylpropan-2-yl acetate	151-05-3	30.98	1.16×10^7	1.01×10^7	1.73×10^7
65	Terpinyl acetate	80-26-2	31.46	1.97×10^8	1.98×10^8	2.17×10^8
68	Geranyl acetate	105-87-3	31.78	2.65×10^7	3.01×10^7	4.82×10^7
70	Eugenol	97-53-0	32.34	4.60×10^6	1.01×10^7	1.11×10^8
71	Methyl 2-aminobenzoate	134-20-3	32.47	5.47×10^5	1.08×10^6	1.27×10^7
73	*trans*-α-Damascone	57549-92-5	32.54	1.77×10^7	1.96×10^7	3.25×10^7
74	Dodecanal	112-54-9	32.84	6.28×10^6	9.53×10^6	1.25×10^7
76	Diphenyl ether	101-84-8	33.14	7.64×10^6	1.21×10^7	2.10×10^7
77	α-Guaiene	654-48-6	33.24	3.45×10^6	1.08×10^7	2.16×10^6
80	α-Ionone	127-41-3	33.93	4.74×10^6	4.76×10^6	1.91×10^7
81	Cinnamyl acetate	103-54-8	34.12	–	–	1.06×10^7
82	γ-Patchoulene	514-51-2	34.15	1.49×10^6	4.74×10^6	–
83	δ-Guaiene	3691-11-0	34.83	2.15×10^6	5.57×10^6	–
85	Butylated hydroxytoluene	53571-70-3	34.97	9.73×10^6	1.86×10^7	2.87×10^7
86	α-Isomethyl ionone	127-51-5	34.99	5.10×10^6	7.04×10^6	1.99×10^7
88	Ethyl vanillin	121-32-4	35.63	–	–	2.00×10^7
90	Coumarin	91-64-5	35.76	–	–	2.79×10^6
92	Lilial	80-54-6	36.17	3.05×10^7	5.43×10^7	9.45×10^5
94	Amyl salicylate	2050-08-0	37.16	1.08×10^7	2.40×10^7	4.43×10^4

Table A1: List of target analytes identified in the fabric conditioner (Figure 5) by a search against a 407-component library of fragrance compounds using TargetView. *(Continued from previous page)*

No.	Compound	CAS No.	t_R (min)	Peak sum (TIC)		
				Method A	Method B	Method C
2	Ethyl acetate	141-78-6	8.89	4.22×10^6	9.21×10^5	1.05×10^5
5	Butan-1-ol	220713-25-7	11.40	3.41×10^6	2.01×10^5	–
6	1,4-Dioxane	123-91-1	12.35	–	–	1.97×10^7
8	2,4-Dimethylheptane	2213-23-2	14.44	3.66×10^5	1.38×10^6	8.86×10^4
10	n-Butyl acetate	123-86-4	15.82	3.57×10^7	3.41×10^7	1.13×10^7
11	Ethyl 2-methylbutanoate	7452-79-1	16.93	1.46×10^7	2.60×10^7	6.95×10^6
14	Hexan-1-ol	220713-27-9	18.30	1.45×10^7	5.37×10^6	4.29×10^6
15	Citronellene	10281-56-8	19.48	2.14×10^8	4.29×10^8	–
19	Ethyl hexanoate	8068-81-3	21.62	6.83×10^5	1.20×10^6	–
20	Benzaldehyde	100-52-7	21.88	2.62×10^6	1.81×10^6	6.69×10^5
21	6-Methylhept-5-en-2-one	129085-68-3	21.91	1.87×10^6	1.86×10^6	1.19×10^6
22	n-Hexyl acetate	142-92-7	22.10	1.68×10^8	2.19×10^8	1.28×10^8
24	Limonene	138-86-3	22.48	1.58×10^7	4.03×10^7	7.02×10^6
26	*p*-Methylanisole	104-93-8	22.89	3.54×10^7	4.60×10^7	2.46×10^7
28	γ-Terpinene	99-85-4	23.28	1.33×10^6	3.44×10^6	4.69×10^5
32	Dihydromyrcenol	25279-08-7	24.32	3.15×10^8	2.96×10^8	3.59×10^8
33	Benzyl alcohol	100-51-6	24.40	6.56×10^6	6.00×10^6	1.39×10^7
35	Phenylethyl methyl ether	3558-60-9	24.60	2.63×10^7	3.18×10^7	2.99×10^7
36	Tetrahydrolinalool	78-69-3	24.93	4.35×10^6	3.63×10^6	8.35×10^6
37	Linalool	78-70-6	25.1	3.68×10^8	7.81×10^7	7.72×10^7
38	Rose oxide	16409-43-1	25.11	2.80×10^7	3.57×10^6	–
39	2,4-Dimethylcyclohex-3-enyl-1-carboxaldehyde (Triplal)	68039-49-6	25.74	4.13×10^7	4.33×10^6	–
41	Phenylethyl alcohol	60-12-8	26.54	2.37×10^6	3.64×10^6	7.66×10^6
42	Benzyl acetate	140-11-4	27.11	1.33×10^5	1.37×10^5	2.44×10^5
43	2-Isopropyl-5-methylcyclohexanone	3391-87-5	27.23	1.08×10^6	3.27×10^5	3.85×10^5
46	Gardeniol	93-92-5	27.75	2.76×10^7	3.56×10^7	1.12×10^8
49	Methyl salicylate	119-36-8	28.25	3.92×10^5	5.17×10^5	1.06×10^6
50	β-Citronellol	106-22-9	28.57	1.40×10^7	1.49×10^7	7.48×10^7
52	Tridecane	629-50-5	29.11	2.38×10^6	3.68×10^6	–
53	Citronellyl nitrile	51566-62-2	29.14	3.27×10^6	4.49×10^6	4.19×10^6
55	β-Phenylethyl acetate	103-45-7	29.52	2.75×10^7	3.59×10^7	1.13×10^8
56	Benzylacetone	2550-26-7	29.85	2.39×10^6	3.37×10^6	9.64×10^6
57	Undecan-2-one	112-12-9	30.16	2.49×10^7	3.15×10^7	5.86×10^7
58	4-*tert*-Butylcyclohexyl acetate	32210-23-4	30.28	3.93×10^6	5.37×10^6	7.33×10^6
63	2-Methyl-1-phenylpropan-2-yl acetate	151-05-3	30.98	1.69×10^6	2.01×10^6	5.77×10^6
64	Citronellol acetate	150-84-5	31.10	3.37×10^6	4.08×10^6	1.04×10^7
66	n-Tetradecane	629-59-4	31.48	2.95×10^7	4.94×10^7	1.42×10^8
69	2-Methylundecanal	110-41-8	31.80	2.46×10^7	2.35×10^7	2.82×10^7
70	Eugenol	97-53-0	32.34	1.58×10^6	2.53×10^6	3.12×10^7
71	Methyl 2-aminobenzoate	134-20-3	32.46	3.65×10^5	6.99×10^5	6.91×10^6
73	*trans*-α-Damascone	57549-92-5	32.54	–	–	6.05×10^6
76	Diphenyl ether	101-84-8	33.14	2.30×10^7	2.85×10^7	8.54×10^7
91	*trans*-2-Hydroxycinnamic acid	614-60-8	35.76	3.30×10^5	1.40×10^6	2.54×10^7
94	Amyl salicylate	2050-08-0	37.16	9.59×10^6	1.51×10^7	1.82×10^8
98	n-Hexyl salicylate	6259-76-3	40.11	1.44×10^7	2.86×10^7	4.49×10^8
99	β-Methylionone	127-43-5	40.64	–	–	1.67×10^8
101	Pentadecan-1-ol	629-76-5	42.63	–	–	1.03×10^8

Table A2: List of target analytes identified in the washing detergent (Figure 6) by a search against a 407-component library of fragrance compounds using TargetView.

No.	Compound	CAS No.	t_R (min)	Peak sum (TIC)			
				Method A	Method B (powder)	Method B (solution)	Method C
7	3-Methylbutan-1-ol	123-51-3	13.88	1.12×10^7	1.41×10^5	1.36×10^6	1.89×10^5
9	Hexanal	66-25-1	15.83	3.01×10^5	1.40×10^5	7.25×10^5	–
11	Ethyl 2-methylbutanoate	7452-79-1	16.92	1.17×10^6	8.42×10^5	2.58×10^6	1.14×10^5
12	Isoamyl acetate	29732-50-1	17.91	1.52×10^6	4.29×10^5	1.41×10^6	–
13	*cis*-Hex-3-enol	928-97-2	18.04	3.02×10^7	6.02×10^5	5.00×10^6	9.47×10^5
14	Hexan-1-ol	220713-27-9	18.31	1.66×10^8	1.21×10^7	4.27×10^7	1.20×10^7
20	Benzaldehyde	100-52-7	21.88	4.89×10^6	7.10×10^5	2.38×10^6	1.33×10^6
21	6-Methylhept-5-en-2-one	129085-68-3	21.91	1.88×10^7	2.66×10^6	7.87×10^6	1.64×10^6
22	n-Hexyl acetate	142-92-7	22.10	9.62×10^7	2.72×10^7	4.57×10^7	3.20×10^6
24	Limonene	138-86-3	22.48	2.70×10^7	9.79×10^6	1.39×10^7	–
27	Eucalyptol	470-82-6	22.90	2.33×10^6	8.60×10^6	1.79×10^7	2.26×10^6
28	γ-Terpinene	99-85-4	23.28	1.03×10^6	3.19×10^5	3.99×10^5	–
29	n-Undecane	1120-21-4	23.86	2.42×10^6	1.23×10^5	8.39×10^5	–
32	Dihydromyrcenol	25279-08-7	24.32	3.07×10^8	1.24×10^5	1.30×10^8	4.98×10^7
33	Benzyl alcohol	100-51-6	24.40	9.76×10^7	2.41×10^6	2.18×10^7	1.61×10^7
36	Tetrahydrolinalool	78-69-3	24.95	3.08×10^8	3.16×10^5	1.49×10^8	3.94×10^7
37	Linalool	78-70-6	25.10	3.68×10^8	1.20×10^6	1.58×10^8	7.72×10^7
39	2,4-Dimethylcyclohex-3-enyl-1-carboxaldehyde (Triplal)	68039-49-6	25.74	1.15×10^8	4.32×10^6	3.28×10^7	1.27×10^6
41	Phenylethyl alcohol	60-12-8	26.53	9.95×10^7	1.15×10^6	2.25×10^7	4.06×10^7
42	Benzyl acetate	140-11-4	27.11	1.03×10^7	2.89×10^5	3.62×10^6	2.87×10^6
44	Camphor	76-22-2	27.34	3.84×10^6	6.61×10^6	2.70×10^6	1.21×10^6
48	Terpineol	98-55-5	28.06	4.34×10^6	3.94×10^6	8.60×10^5	8.95×10^5
49	Methyl salicylate	119-36-8	28.25	8.81×10^5	6.32×10^5	2.21×10^5	6.89×10^5
50	β-Citronellol	106-22-9	28.57	6.15×10^7	1.88×10^6	1.16×10^7	2.05×10^7
53	Citronellyl nitrile	51566-62-3	29.14	2.14×10^7	–	5.51×10^6	1.64×10^6
54	Geraniol (Nerol)	106-24-1	29.20	1.12×10^7	2.48×10^6	1.60×10^6	4.17×10^6
55	β-Phenylethyl acetate	103-45-7	29.53	4.01×10^6	1.12×10^6	1.16×10^6	2.07×10^6
61	Anisaldehyde	123-11-5	30.52	1.18×10^7	1.04×10^6	3.43×10^6	5.16×10^7
62	Cinnamaldehyde	104-55-2	30.95	–	–	–	6.39×10^5
64	Citronellol acetate	150-84-5	31.10	1.41×10^7	1.83×10^6	3.15×10^6	–
65	Terpinyl acetate	80-26-2	31.45	6.38×10^6	–	1.17×10^6	3.04×10^5
66	n-Tetradecane	629-59-4	31.48	1.60×10^7	–	3.63×10^6	4.19×10^5
67	Cinnamyl alcohol	134-20-3	31.66	1.63×10^6	–	3.46×10^5	9.67×10^6
72	Piperonal	120-57-0	32.53	4.40×10^6	–	1.26×10^6	1.79×10^7
75	Methyl cinnamate	103-26-4	32.93	1.39×10^7	–	3.76×10^6	1.46×10^7
76	Diphenyl ether	101-84-8	33.14	4.90×10^6	–	1.35×10^6	8.71×10^5
79	Tricyclodec-5-enyl acetate	2500-83-6	33.56	2.37×10^7	1.63×10^7	1.31×10^7	2.01×10^6
84	2-Methoxynaphthalene	93-04-9	34.88	2.14×10^7	6.34×10^6	7.69×10^6	1.47×10^7
87	β-Ionone	14901-07-6	35.18	1.17×10^7	–	2.34×10^6	5.79×10^6
89	Indan-1,3-diol monopropanoate	–	35.67	2.12×10^7	2.46×10^7	2.52×10^7	3.96×10^7
92	Lilial	80-54-6	36.17	2.14×10^6	–	4.08×10^5	1.41×10^6
97	Methyl dihydrojasmonate	24851-98-7	39.78	–	–	–	4.87×10^7
98	n-Hexyl salicylate	6259-76-3	40.11	1.69×10^6	–	7.49×10^5	1.27×10^7
100	n-Hexyl cinnamaldehyde	101-86-0	42.83	–	–	–	1.21×10^7

Table A3: List of target analytes identified in the washing powder (Figures 7 and 8) by a search against a 407-component library of fragrance compounds using TargetView.