

# Fabric softeners caught in a whirl...

To determine fragrances used in household products and detergents, liquid-liquid extraction (LLE) combined with GC/MS is often used. Scientists in the Firmenich Research and Development department in Singapore have now turned to Stir Bar Sorptive Extraction (SBSE) in their search for an alternative extraction method – with promising results.

Fabric softeners are not too important for the washing process itself, but they offer many positive effects that are appreciated at the ironing board at the very latest. Additionally, fabric softeners endow textiles and clothes with a distinct fragrance, helping consumers to form lasting bonds with the product. What we perceive as a single scent or fragrance is typically a complex mixture of individual fragrance compounds. These interact to form the complete olfactory impression that distinguishes the consumer product. It is the task of the quality control department to ensure batch to batch uniformity of the olfactory impression or fingerprint. How efficiently this is achieved depends to a large extent on the extraction and sample preparation techniques used.

To isolate volatile fragrance compounds from soaps, detergents, or fabric softeners, the chemist traditionally reaches for the liquid/liquid extraction (LLE) technique. LLE is based on differences in analyte solubility in two immiscible solvents. These are typically a hydrophilic (aqueous) phase on the one side and a hydrophobic organic solvent on the other side of the phase divide. According to Khim Hui, scientist at Firmenich Asia Private Ltd. in Singapore, this is where the drawbacks of the LLE technique are seen: „The LLE technique is able to selectively pick out interesting analytes from complex

matrices, but overall, this sample preparation technique is very labor intensive and cumbersome.” Getting good phase separation is often difficult when the sample to be extracted contains surfactants. Furthermore, large quantities of costly solvent are required; solvents must be discharged in a responsible manner after use, which is both expensive and time consuming. And, last but not least, solvents can have a negative impact on the laboratory work environment.

The scientists Khim Hui and Diana Koh started searching for an attractive alternative to the LLE technique: “We looked for a technique that would minimize or even eliminate solvent use while extracting fragrance compounds with good recovery and delivering first rate validation data”, Diana Koh states. After a comprehensive search, the scientists decided to pursue Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister® [1]. Over the past decade since its introduc-



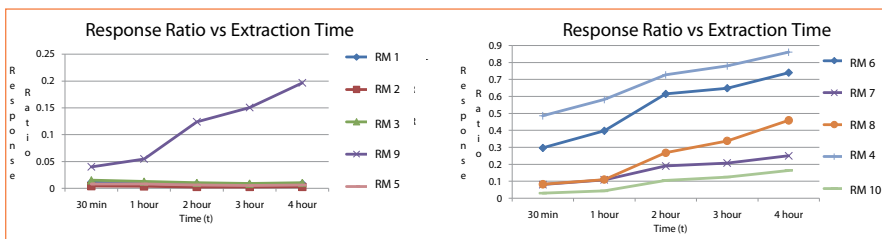
## Analysis conditions

TDU : Initial temperature: 50 °C; delay time: 0.50 min; initial time: 0.00 min; ramp at 80 °C/min; end temperature: 150 °C; hold: 1.00 min; Desorption mode: splitless

CIS 4 : Initial temperature: 10 °C; equilibration time: 0.50 min; initial time: 0.00 min; ramp at 12 °C/s; end temperature: 280 °C; hold: 10.00 min; CIS 4 liner – Tenax TA; Vent time: 0.00 min; Purge time: 0.00 min; Purge flow: 80 mL/min

Agilent GC/MS 6890/5973N  
GC oven: 50 °C (3.00 min); 3 °C/min; 260 °C 20 °C/min; 300 °C (5.00 min)  
Column: HP-5MS, 30m x 0.25mm x 0.25µm  
Constant flow rate: 1.2 mL/min, helium  
MSD: Mass range: 29.0 – 400.0, Quad: 150 °C, Source: 230 °C





Graph 1 and 2 (left to right): Response Ratio versus different extraction times



Graph 3 and 4 (left to right): Response Ratio versus different stirring speeds

tion, the Twister has proven its worth by efficiently extracting volatile- and semivolatile organic chemical compounds (VOCs and SVOCs) from a wide range of complex matrices. “SBSE not only requires little, if any, solvent”, says Khim Hui, “it is also surprisingly simple to perform”. SBSE is performed using a glass encased magnetic stir bar with a relatively large volume of sorbent phase coated on the outside. While the Twister stirs the sample, analytes are efficiently extracted into the sorbent phase, in this case PDMS, recovery rates are generally much higher than those obtained with SPME. A large number of samples can be extracted simultaneously and the subsequent Twister Desorption and analyte determination is fully automated making the overall process highly efficient. A GERSTEL Thermal Desorption Unit (TDU) mounted on a GERSTEL Cooled Injection System (CIS 4) PTV-type GC inlet and a GC 6890 /5973N MSD from Agilent Technologies were used.

As an aside, SBSE is based on the partition of analytes between PDMS and the sample. The Twister stirs the sample and non-polar or moderately polar compounds are extracted and concentrated. The partition coefficient of a compound between PDMS and water is very close to its  $K_{O/W}$  value (octanol/water partition coefficient).

$K_{O/W}$  is a physical chemical property used to describe hydrophilic or hydrophobic properties of a compound [2].  $K_{O/W}$  has been used, among other things, to describe whether an environmental pollutant such as a pesticide was likely to accumulate in fat tissue. A high  $\log K_{O/W}$  value is characteristic of a hydrophobic compound that would be extracted with high recovery using PDMS.

### Theory guides - experiment decides

To test the SBSE technique for their applications, the scientists analyzed fabric softener

samples spiked with the following flavor and fragrance compounds: 1,8-cineol (RM 1), Zestover (RM 2), camphor (RM 3), Verdox (RM 4), Decal (RM 5), Lilial (RM 6), amylcinnamaldehyde (RM 7), hexylsalicylate (RM 8), hexyl-cinnamaldehyde (RM 9) as well as Galaxolid 70 MIP (RM 10). An internal standard (IS) was added to the Twister stir bar prior to the extraction by letting it stir an IS solution, which was generated by adding 100  $\mu$ L IS stock solution (150 mg/L of 1,4-dibromobenzol in acetonitrile) to 20 mL deionized (DI) water and letting the Twister stir the IS solution for an hour. The kinetics of the extraction depend on the analyte migration rate to and into the PDMS phase of the Twister, which among other things, depend

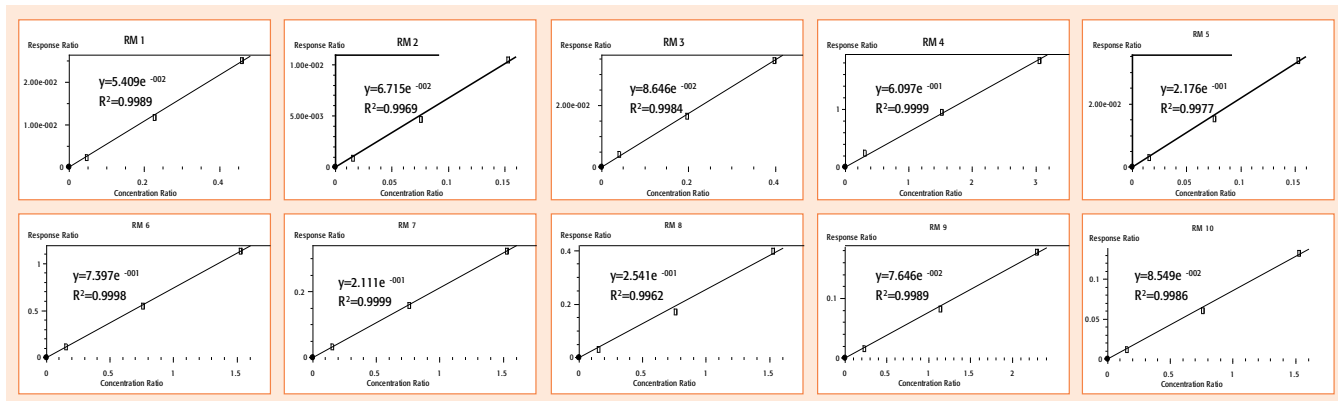
COMPOUNDS	Mean	STDEV	% RSD
Eucalyptol	0.012334	0.001270	10.3
Zestover	0.004390	0.000377	8.6
Camphor	0.016604	0.001255	7.6
Verdox	0.901589	0.059065	6.6
Decal	0.012918	0.001589	12.3
Lilial	0.549745	0.036067	6.6
Amylcinnamic Aldehyde	0.160250	0.0212906	8.1
Hexyl Salicylate	0.175772	0.021475	12.2
Hexylcinnamic Aldehyde	0.084914	0.009471	11.2
Galaxolid 70 MIP	0.059914	0.007433	12.4

Table 2: Calculated %RSD for Reproducibility (Mean of 50 measurements)

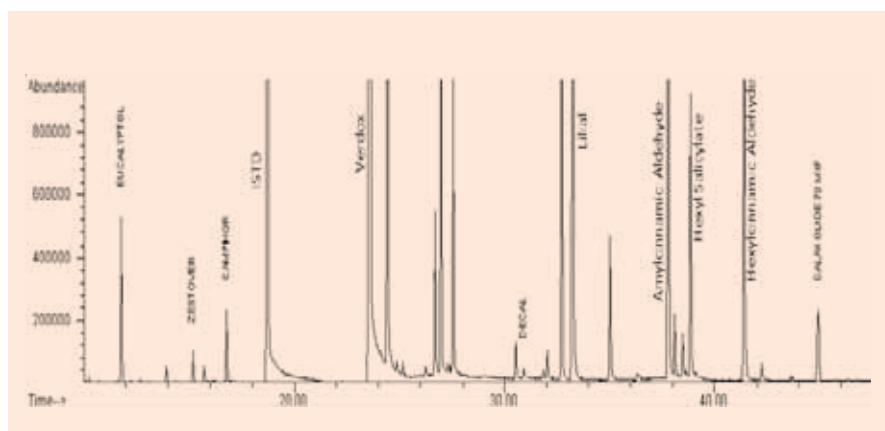
on diffusion rates, stirring conditions, and the sample volume. Diana Koh states: „The peak area depends on the extraction time“. In their study, the scientists determined the optimal extraction time to be one hour at room temperature while stirring the Twister at 800 rpm. To get reliable data, Diana Koh performed the analysis over five different days, achieving “good results with good reproducibility and RSDs of less than 16 percent across the board“. From the 50 determinations per compound performed over five days, Diana Koh determined the reproducibility to be less than 12.5 %. Three-point calibration curves

COMPOUNDS	Repeatability														
	Day 1			Day 2			Day 3			Day 4			Day 5		
	Mean	STDEV	RSD %	Mean	STDEV	RSD %	Mean	STDEV	RSD %	Mean	STDEV	RSD %	Mean	STDEV	RSD %
Eucalyptol	0.011391	0.000569	5.0	0.012481	0.001269	10.2	0.012263	0.000979	8.0	0.012726	0.001675	13.2	0.012806	0.001285	10.0
Zestover	0.004632	0.000450	9.7	0.004311	0.000264	6.1	0.004320	0.000135	3.1	0.004182	0.000423	10.1	0.004503	0.000408	9.1
Camphor	0.016166	0.000759	4.7	0.016907	0.001131	6.7	0.016440	0.000769	4.7	0.016788	0.002001	11.9	0.016717	0.001316	7.9
Verdox	0.915239	0.018752	2.0	0.972578	0.033094	3.4	0.866965	0.046048	5.3	0.861180	0.067641	7.9	0.891986	0.042382	4.8
Decal	0.014214	0.001540	10.8	0.013926	0.001113	8.0	0.012846	0.000584	4.5	0.011892	0.001824	15.3	0.011710	0.000817	7.0
Lilial	0.543458	0.019006	3.5	0.578859	0.027545	4.8	0.545785	0.035792	6.6	0.541996	0.053128	9.8	0.538627	0.025521	4.7
Amylcinnamic Aldehyde	0.157428	0.006136	3.9	0.171888	0.012369	7.2	0.155054	0.011036	7.1	0.156900	0.017694	11.3	0.159980	0.008911	5.6
Hexyl Salicylate	0.166794	0.015632	9.4	0.194849	0.020899	10.7	0.172095	0.019607	11.4	0.170137	0.026629	15.7	0.174985	0.013852	7.9
Hexylcinnamic Aldehyde	0.082476	0.006007	7.3	0.093632	0.009226	9.9	0.081535	0.008477	10.4	0.082533	0.012220	14.8	0.084395	0.005973	7.1
Galaxolid 70 MIP	0.058829	0.004466	7.6	0.067701	0.006918	10.2	0.058252	0.007216	12.4	0.056675	0.008331	14.7	0.058113	0.004954	8.5

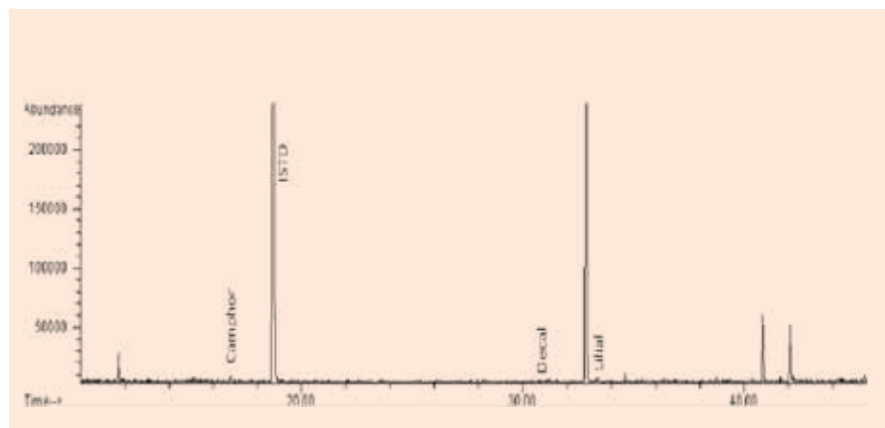
Table 1: % RSDs calculated based on 10 individual sample extractions for every listed result.



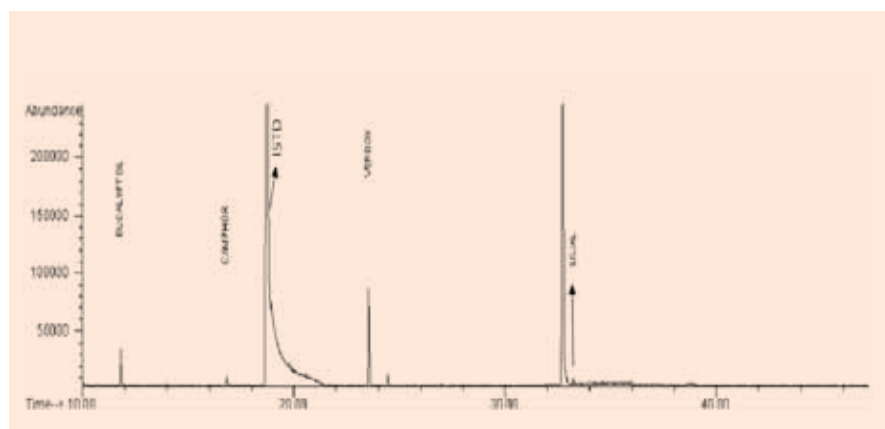
Graph 5: Twister calibration curve of each compound



Chromatogram 1: Monitored perfume raw materials in Liquid Softener using SBSE technique. Comparing LLE & SBSE method at same dosage (with Encapsulation Technology in softener application)



Chromatogram 2: Profile from Liquid-liquid Extraction. As observed, there is little/no signal detected for monitored compounds (10 RMs).



Chromatogram 3: Profile from Stir Bar Sorptive Extraction. Sensitivity is enhanced, thus allows detection of raw materials leakage in trace analysis.

### Method Comparison

Method	% Dosage found	% Leakage (Corrected)
LLE	0.53	0.1
SBSE	0.51	0.5

Table 3: Correlation of determination ( $R^2$ )

were established for each fragrance compound added resulting in good linearity with  $R^2$ -values higher than 0.996 for all compounds.

### Comparison of SBSE and LLE

But how did SBSE stack up to the LLE technique, which has been tested and validated extensively throughout the company and proven for real life samples over a long period of time? Khim Hui: „In order to compare the techniques, reference samples were prepared at different concentration levels: (0.30 %; 0.50 % and 0.75 %). It was shown that the analysis results obtained using SBSE were quite close to the results obtained with the traditional LLE technique. Further, the comparison showed that SBSE resulted in much higher sensitivity than LLE”. The final conclusion: “SBSE is a fast, sensitive, and highly reproducible alternative to standard sample preparation techniques such as LLE for the determination of fragrance compounds in fabric softener. In addition, SBSE can be performed using much smaller sample sizes while still allowing quantitative determination at lower concentration levels. Last, but not least, SBSE allows us to reduce use of organic solvents dramatically, this is a very positive result”, the scientist says.

### References

1. C. Franc, F. David, G. de Revel. J. Chromatogr. A 1216 (2009) 3318-3327
2. M.W. Maylan, P.H. Howard; J. Pharm. Sci. 1995,84, 83-92

### More information

Diana Koh Guat Fen, Khim Hui Ng, Firmenich Asia Private Limited, 10 Tuas West Road, Singapore 638377