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Automated difficult matrix introduction (DMI) for identification of allergens and fragrances in shampoo with GC-MS-Olfactometry and a liner exchanger (LINEX)

Key Words:
Automated sample preparation
Difficult matrix introduction (DMI)
GC-MS-olfactrometry
Allergens, fragrances
Shampoo

Introduction

GC-MS analysis of shampoo is generally difficult because the compounds of interest are present at low levels in a complex water and oil containing emulsion. Using DMI* the matrix influence of shampoo can be almost eliminated. A small aliquot of the shampoo is put into a small glass vial which is automatically inserted into the injector. The injector is then heated to 120°C just high enough to transfer the compounds of interest from the sample onto the chromatographic column. Only the vaporized compounds are transported from the injector onto the GC-column where they are refocused at the low starting temperature of the GC program. Because the non-volatile matrix species remain in the vial and the injector liner, no column contamination occurs.

To automate the analysis a liner exchanger (LINEX) is used.

Results & specifications

• Detection limits of compounds which are thermo stable and also not very polar is approximately 0.1-0.02 ng/micro vial.
• Repeatability of DMI injections of shampoo is very well (see table 1).
• The molecule mass limits for this method (thus without cryo-trap and desorption of shampoo at temperature of 120°C) is between approximately $C_{11}H_{24}$ and $C_{22}H_{46}$.

Table 1: Repeatability of several compounds detected in shampoo (n=10).

Compound	RSD %
Linalool	7.3
Acetic acid, Phenyl methyl ester	5.3
1-propanol,2 (2-hydroxypropoxy)	12.6
n-Tetradecanol	16.2
ethanol, 2 (dodecyloxy)	10.6
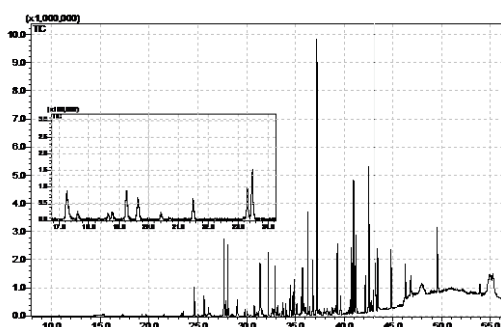
1. d-limonene (Rt 17.1 min)
2. tetrahydro linalool (Rt 24.6 min)
3. dihydromyrcenol (Rt 25.6 min)
4. linalool (Rt 27.7 min)
5. *tert*-butyl cyclohexyl acetate (Rt 28.1 min)
6. terpineols (Rt 29.8 min; 31.4 min)
7. benzyl acetate (Rt 32.2 min)
8. geraniol (Rt 32.6; 34.7 min)
9. citronellol (Rt 32.9 min)
10. nerol (Rt 33.7 min)
11. α-isomethyl ionone (Rt 34.8 min)
12. β-ionone (Rt 36.8 min)
13. 2-(4-*tert*-butylbenzyl)propionaldehyde (38.9 min)
14. n-hexyl salicylate (Rt 40.0 min)
15. piperonal (Rt 42.8 min)
16. cinnamal (Rt 43.0 min)

Fig 1: Typical chromatogram of shampoo with DMI-GC/MS

Discussion

Automated DMI-GC-MS-Olfactrometry is very a powerful technique for screening of shampoos as it is demonstrated at figure 1. Sample preparation is simple and not labour intensive and that reduces the cost of analysis but also it eliminates potential losses of the volatile target compounds during sample preparation. With the combination of olfactrometry and mass spectrometry the smelly compounds of the shampoo can be determined by the nose and identified at the same time.

It is also possible to quantify known (or identified) compounds because of the good repeatability of this method. Only when the viscosity of the shampoo is high it takes a long time (approximately 30 minutes) to get the whole amount of the compounds out of the shampoo.

Experimental:

Sample preparation:

Weight 1-8 mg shampoo into a micro-vial. Put the micro-vial into a DMI-liner.

Instrumentation:

Injector:	OPTIC 3 injector (ATAS GL International B.V., Veldhoven, the Netherlands).
GC/MS:	GC-MS-QP2010 (Shimadzu Deutschland GmBH, Germany).
Sniffing port:	PHASER (ATAS GL International)
Autosampler:	FOCUS (ATAS GL International)
	LINEX (ATAS GL International)

DMI-GC-MS conditions for shampoo:

GC-column:	Inertcap wax 0.32 mm x 60 m, film thickness 0.5 µm (GL Sciences)
GC program:	35°C (hold 8 min), 5°C/min to 230°C (hold 10 min)
Carrier gas:	Helium
PTV-injector:	35°C to 120°C rate 5°C/sec.
Column flow:	1,0 ml/min (without sniffing)
	5,0 ml/min (split MS/sniffing)
Split flow:	Start 1.5 min. 150 ml/min (flush liner)
	During heating: split less
	During analysis: 1:75
Liner:	DMI-liner with micro-vial.

* H. Jing, A. Amirav, Anal. Chem 1997,69, 1426-1434