AUTOMATED DIFFICULT MATRIX INTRODUCTION FOR IDENTIFICATION OF ALLERGENS AND FRAGRANCES IN COSMETIC PRODUCTS WITH A LINER EXCHANGER AND A CAPPING-DECAPPING STATION

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Introduction

Difficult matrix introduction (DMI) is a powerful technique for fast screening of complex and difficult matrices as e.g. cosmetic products. DMI is based on selective exclusion of compounds using temperature. Only the (volatile) compounds of interest are vaporized. The matrix remains in the liner. With DMI screening it is possible to identify and (semi) quantify fragrances in complex samples such as hand crème and shampoo. To automate the analysis a Liner Exchanger (LINEX) and a capping decapping –station (CDC) were developed. Here the automated DMI analysis using the LINEX and the CDC-station is evaluated using an alkane mixture. Next, the DMI technique is applied for screening of shampoo.

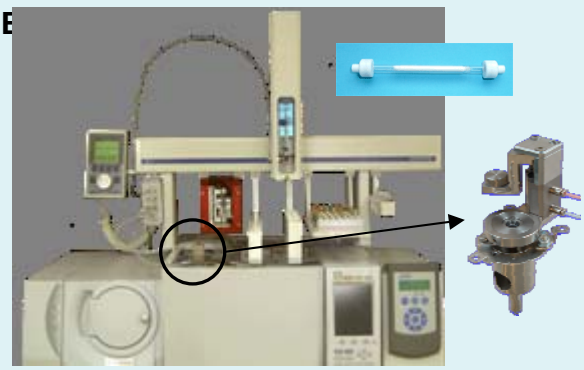

Figure 1: Shimadzu GCMS QP2010, ATAS GL Optic 3, LINEX and CDC station. Inserts: capped liner and LINEX-injector-head

Back flush

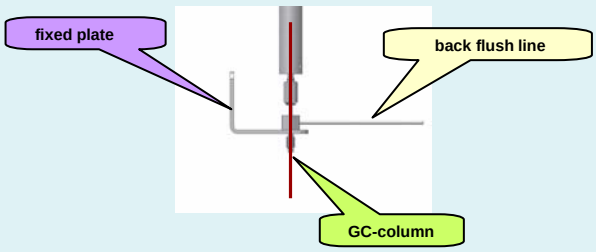

Figure 2: Schematic diagram of the tee-piece for back-flush.
When the LINEX-head is open, air can enter the system. This can adversely affect the vacuum (when an MS is used) and water or oxygen can destroy the GC column. To make sure that no air can enter the system during the head-open step, a special tool (T-piece) is designed to perform an effective injector back flush. The GC-column is put through the tee-piece and a high back-flush flow, typically 150 ml/min, is introduced coaxially to the column from the bottom of the injector.

Selective exclusion

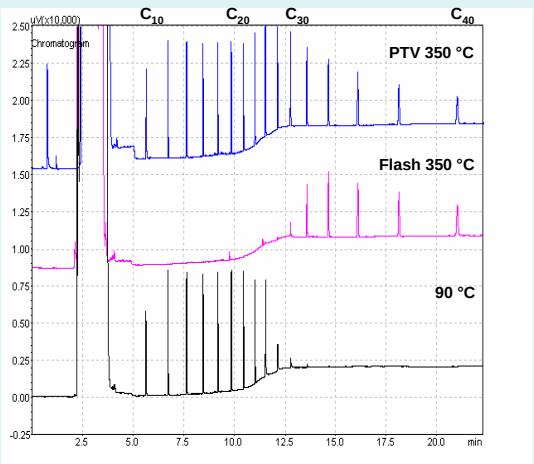

Figure 3: To demonstrate the selective exclusion, 10 µl of an alkane mixture is put into a micro vial. By using a PTV-injector temperature of 90 °C (black chromatogram), only C8 to C26 will be transferred to the GC-column. All other compounds will remain in the microcup of the liner and can be removed without contaminating the GC-system (pink chromatogram). As a reference, a 10 µl liquid injection of the alkane mixture is carried out using a PTV-injector temperature of 350 °C (black chromatogram).

Repeatability of automated DMI

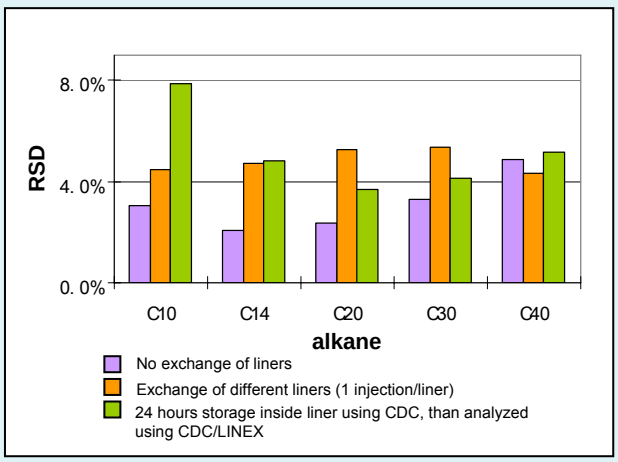

Figure 4: Comparison of the repeatability of normal liquid injections, injections on different liners using LINEX and injections after 24 hours storage of a standard solution inside the liner sealed with a septum cap. Conditions: inj.volume 10 µl; liner: DMI liner with cup; OPTIC Temp prog.: start 50 °C (10 sec.) to 350 °C (rate 10 °C/s); Flow: start 100 ml/min (before inj.) then split 1:40; column flow: 1 ml/min; column: TC5/MS, 0.25 mm x 30 m (0.25 µm film); GC-Oven prog.: 45 °C (2 min hold) to 325 °C (rate 30°C/min) hold for 11 min.

DMI of Shampoo

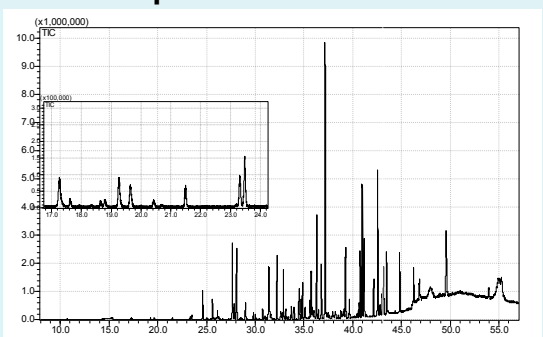

Figure 5: Typical GC-MS chromatogram of shampoo using DMI-GC/MS. GC-column: Inertcap Wax 0.32 mm x 60 m, film thickness 0.5 µm (GL Sciences). GC program: 35 °C (hold 8 min), 5 °C/min to 230 °C (hold 10 min). Optic program: 35 °C, 5 °C/sec to 120 °C, splitless. Identified peaks were: 1. d-limonene (Rt 17.1 min), 2. tetrahydrolinalool (Rt 24.6 min), 3. dihydromyrcenol (Rt 25.6 min), 4. linalool (Rt 27.7 min), 5. *tert*-butyl cyclohexylacetate (Rt 28.1 min), 6. terpineols (Rt 29.8 min; 31.4 min), 7. benzylacetate (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-isomethylionone (Rt 34.8 min), 12. β-ionone (Rt 36.8 min), 13. 2-(4-*tert*-butylbenzyl)propionaldehyde (38.9 min), 14. n-hexylsalicylate (Rt 40.0 min), 15. piperonal (Rt 42.8 min) and16. cinnamal (Rt 43.0 min).

Conclusions:

- DMI is a powerful technique for fast screening of cosmetic products. It requires only a minimum of sample preparation.
- The use of a LINEX and CDC-station allows fully automated operation of the PTV DMI system.
- The repeatability of DMI analysis using the LINEX and the CDC-station is similar to that of a liquid injection.
- The DMI method with the LINEX and CDC is applicable to many other difficult samples.

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