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Introduction

Thermal sample pre-treatment such as thermal desorption and head space analysis, are widely used in combination with gas chromatography for the preparation of solid samples. Because of their nature, it is difficult to automate the introduction of samples such as rock, wood or plastic to perform thermal desorption (TD - GC).

With one fairly advanced device, the samples are put into rather large so-called desorption tubes which are, next, heated in the desorption unit. A high gas flow causes the analytes to be transported to a PTV type injection device via a heated transfer line. The analytes are refocused in the PTV by cold trapping on a liner packed with a suitable sorbent. Subsequently, the PTV is rapidly heated in order to obtain a small injection band on the capillary column. It will be obvious that analyte losses can easily occur. A preferred approach is to use direct thermal desorption GC, or DTD - GC. With this technique, the head of the PTV injector is opened, the liner containing the sample is introduced and the head is closed. The liner is purged with carrier gas and, subsequently, heated and analysis is started. The advantage of this approach is the use of only one PTV, the absence of a heated transfer line and the use of gas at a flow rate suitable to create optimum GC column conditions. This poster presents some possibilities of DTD - GC - (MS) analysis of solid samples, enriched gaseous samples and samples with a difficult matrix.

Instrumentation

- OPTIC 2 programmable injector
- FOCUS XYZ sample preparation robot
- Agilent 6890 GC - 5973 MSD
- Varian Saturn 2000 GC/MS

SepLiner

The standard performed liner in the OPTIC injection interface has been re-designed to the patented SepLiner. As can be seen from is the SepLiner based on the standard fritted liner of the OPTIC injector, containing a glass frit and having the same dimensions. The top of the SepLiner is designed such that it can be tightened similar to an autosampler vial. The cap, which is a standard, commercial available, 11 mm cap to be used for sample vial capping, is made of a magnetic material to assist in its transportation by the FOCUS XYZ sample preparation robot. When the matrix of a sample is strongly contaminating the analytical system and/or damaging the liner making it difficult to perform a lot of analysis after each other there is a possibility to place a very cheap μ -vial onto the frit of the liner. After the liner is exchanged and de-capped, the μ -vial is disposed for a clean one and the liner is ready for reuse without laborious and time consuming cleaning of the liner or even throwing away just after one analysis.

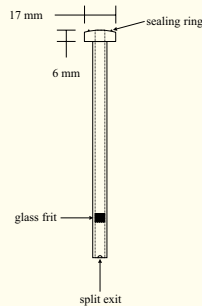


Figure 1: SepLiner for automated DTD - GC.

DTD Device

To be able to exchange the liners automatically the Focus XYZ sample preparation robot was equipped by a new developed injector head to open and close the OPTIC injection interface. To install this newly developed injector head, the original mounting brass of the injection interface is unscrewed. By this action all parts above the mounting brass are removed, including carrier tube, septum head and septum. On the free place the mounting brass of the new injector head is screwed. This injector head can be opened and closed by a pneumatic cylinder. When the head is opened the injector is free to place a liner. After placing a liner the head is automatically closed and a needle mounted inside the injector head penetrates the liner septum (re-)connecting the carrier gas.

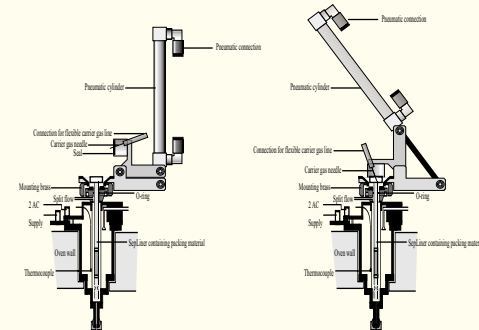


Figure 2: DTD automated liner exchanging injector head mounted onto the injector body. Left: open position. Right: closed position.

Analysis of Car Exhaust

SepLiners were packed with a 20-mm high bed of tenax TA 30-60 mesh and conditioned at 200 °C and a helium flow of 100 ml/min during 1 hour. The DTD liners were loaded manually in forward flow with car exhaust using a 60-ml syringe. After loading the liners were capped and placed in the DTD sample tray. Analysis was performed by automated DTD-GC-MS. Figure 3 shows a chromatogram of car exhaust with a cold engine catalyst. The peak shape of benzene and toluene are not very good due to insufficient column refocusing. For better peak shapes a thick film column or a cryo trap is recommended. After automatic placing the liner into the injection interface the liner was heated from 40 °C with 16°C·sec⁻¹ to a final temperature of 200°C. The split was set to 200 mL·min⁻¹. The GC oven program started at 40°C and ramped with 10 °C·min⁻¹ to the final temperature of 220 °C.

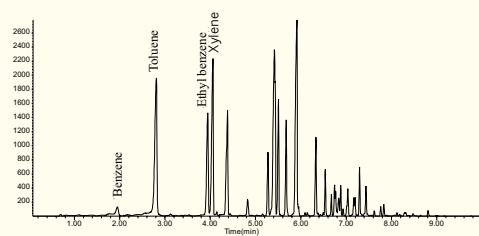


Figure 3: Full scan DTD - GC - MS chromatogram of 60 ml car exhaust. Column HP5-MS 25 m x 0.25 mm I.D., 0.25 μ m film thickness.

Nicotine in Tobacco

Another suitable application for DTD - GC - MS is the analysis of nicotine in tobacco. The origin tobacco-leaf was grind and 10 mg of it was put into a liner. After automated placing of the liner into the injection interface the liner was heated at 16°C·sec⁻¹ from 40°C to 300°C. The column oven was programmed from 40°C with a ramp of 30°C·min⁻¹ to 350°C which was held for 12.00 minutes. The split flow was set to 100 ml/min. An extracted ion chromatogram including the mass spectrum of the nicotine peak of the tobacco analysis is shown in Figure 4. When doing a second desorption of the same sample the chromatogram did not show any peak of either the nicotine or another analyte, indicating a quantitative desorption.

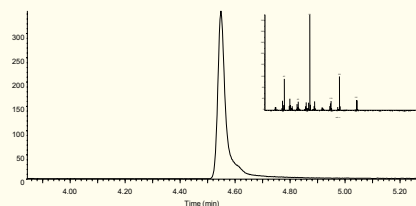


Figure 4: Extracted ion DTD - GC - MS chromatogram of 10 mg tobacco at $m/z=84$. Inset: Full mass spectrum of nicotine peak. Column HP5-MS 25 m x 0.25 mm I.D., 0.25 μ m film thickness.

Fatty Acid Profile in Vegetable Oils

The analysis of fatty acid profiles of natural lipids often involves intensive and laborious sample preparation procedures to hydrolyse the ester-bound fatty acids and remove non-volatile matrix components. Furthermore, derivatisation is essential to obtain the right chemical properties for GC analysis. The use of the DTD allowed a direct injection of a vegetable oil solution combined with a special transesterification reagent without prior sample preparation or purification. The transesterification reagent converts the triglycerides into their corresponding fatty acid methyl esters, which can subsequently be analysed with GC/MS. After analysis the SepLiner can be removed to avoid problems with eventual residues that remained in the liner. The following vegetable oils were studied: sunflower oil, hazelnut oil and olive oil. From these oils solutions were prepared into dichloromethane of subsequently 0.41 mg·mL⁻¹, 0.33 mg·mL⁻¹ and 0.28 mg·mL⁻¹. For the optimum FAME yields of the oils, the sample processor was programmed to transfer 1 μ L of a triglyceride solution into a GC sample vial. Subsequently, 9 μ L of a 0.1 M TMAH solution was added and the two solutions were mixed by multiple strokes of the syringe plunger. Then, 1 μ L was injected into a SepLiner at 40°C and dried for 5 sec under solvent venting conditions. After venting the temperature was increased to 350 °C by 16 °C·sec⁻¹ under splitless conditions. The GC oven was programmed from 60 °C (3 min initial time) to 120 °C at 30 °C·min⁻¹ followed by a rate of 8 °C·min⁻¹ to 320 °C (5 min final time). A C₂₅D₃₀ n-alkane internal standard was used to determine the relative FAME yields.

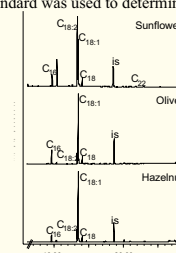


Figure 5: The THM - GC - MS (TIC) of three vegetable oils.

Chemical Analysis of Spores and Pollen

In paleontology microfossils are used for the reconstruction of past ecological communities and climates. Especially spores and pollen present in sediments and peat bogs play an important role in these reconstructions, since they provide information about the floral composition of the surroundings in ancient times. Paleontological information obtained in this fashion is solely based on the outer morphology of the spores and pollen. However, in system ecology there is a distinct need for additional, chemical information on these fossils spores and pollen. However, since pollen in sediments or peat bogs are often scarce and hard to isolate, the sample size (1-20 pollen per sample, ~20 μ m pollen size) hampers chemical analysis, especially when the compounds of interest are chemically bound. As with small sample sizes like these extraction procedures and chemolysis reactions are virtually impossible to perform, conventional pyrolysis methods are often applied. However, from a practical point of view handling samples like individual pollen is often difficult. The use of a DTD combined with the μ -vial inserts circumvented these problems. 10 pollen from an aqueous suspension of *Betula pendula* and *Pinus silvestris* were transferred to a μ -vial insert located in the SepLiner. Subsequently, 1 μ L of a 2 M MeOH tetramethylammonium hydroxide (TMAH) solution was injected into the cold liner. After drying under vacuum conditions, the SepLiner was transported automatically into the injection interface which was heated from 40 °C to 350 °C at a rate of 16 °C·sec⁻¹ after closing the injector head. The compounds released by the chemolysis reactions were transferred to the capillary column under splitless conditions. The GC oven was initially 3 minutes at 35 °C and then programmed by 20 °C·min⁻¹ to 120 °C, followed by programming to 260 °C by 8 °C·min⁻¹. Finally the GC oven stayed at 260 °C for 2 minutes. Since the sample could directly be introduced and automatically placed into the injection interface, this allowed the analysis of extremely low numbers of *Pinus* and *Betula* pollen, with detection limits for phenolic compounds like *p*-coumaric acid and ferulic acid of approx. 1 to 10-pollen. Furthermore, the use of the DTD-interface-FOCUS combination provided the opportunity to run large samples series, since unlike most conventional pyrolysis systems, the placement of the liner containing the insert and sample is automated.

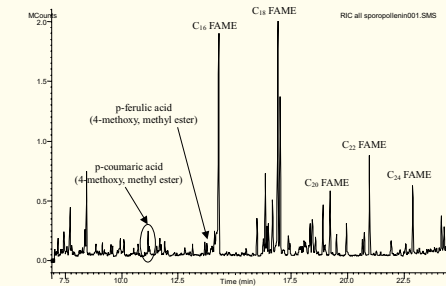


Figure 6: Full scan DTD - GC - MS chromatogram of methylated *Betula pendula* pollen.

Conclusion

The use of the newly developed liner exchanging system based on a XYZ sampling robot is a promising approach for the fully automated DTD - GC - MS analysis of solid and enriched samples. After insertion of a μ -vial is it also very powerful for the analysis of samples with a difficult matrix and samples that need derivatisation before analysis. The possibility of automated exchange of liners and the possibility of loading over 100 samples in the sampling tray of the XYZ robot make the system both robust as user-friendly. The automated liner exchange system can be considered as a breakthrough in sample preparation techniques for GC and will open a wider application range in PTV - GC. In future projects, the introduction possibilities of more difficult samples will be studied.