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Design, Performance and Applicability of a Multi-Functional Thermodesorption System for Trace Analysis in Capillary GC

Andreas Hoffmann, Ralf Bremer
*Gerstel GmbH & Co.KG, Eberhard-Gerstel-Platz 1,
D-45473 Mülheim an der Ruhr, Germany*

KEYWORDS

Direct Thermal Desorption, Volatiles in Solids and Liquids,
Trace Analysis, Capillary GC-MS, Cooled Injection System
CIS

ABSTRACT

Thermodesorption is a well known technique for the analysis of volatile organic contaminants in air normally adsorbed on porous polymeres and has been previously discussed [1]. This operation principle can also be adapted for the direct thermal desorption of volatiles in solid samples.

In this paper the potential of a newly developed thermodesorption system for direct desorption and analysis of volatiles from liquid and solid samples is discussed and demonstrated.

It will be shown that the combination of thermal desorption with an intermediate cryofocusing step in the insert liner of a cooled injection system (CIS) is a reliable and fast method for the determination of volatiles within a wide boiling range.

INTRODUCTION

The determination of volatile trace compounds in gaseous, liquid and solid samples from industrial, environmental and biological origin is an everyday demand in capillary GC. In many cases these samples are not compatible with the gas chromatographic system to permit direct injection. Therefore time consuming preliminary sample preparation steps such as extraction and enrichment of the analytes are required prior to the analysis [2-6].

With the fully automated thermodesorption unit (TDS 2) described in this paper many of these samples can now be analysed directly, without any sample preparation. The compounds of interest are vaporised and subsequently trapped and cryofocused at subambient temperatures in the insert liner of a temperature programmable split/splitless injector (a cooled injection system, CIS), followed by direct transfer to the analytical column, whereas the matrix (or the adsorbent, respectively) remains in the thermodesorption unit.

With this technique it is possible to analyse samples over a wide boiling range, like volatiles in plastic food wraps, spices and pharmaceuticals, residual solvents in recycled polyethylene, fragrances in shampoos and laundry detergents, up to PAH's and PCB's in soils and Hydrocarbons in diesel filter paper.

EXPERIMENTAL

Instrumentation. The system consists of a thermodesorption system (TDS 2, Gerstel GmbH, Mülheim an der Ruhr, Germany, **Figure 1**), a temperature programmable cooled injection system (CIS 3, Gerstel GmbH, Mülheim an der Ruhr, Germany), a gas chromatograph (HP 5890 series II, Hewlett-Packard, Waldbronn, Germany) and a mass selective detector (HP 5972, Hewlett-Packard, Waldbronn, Germany).

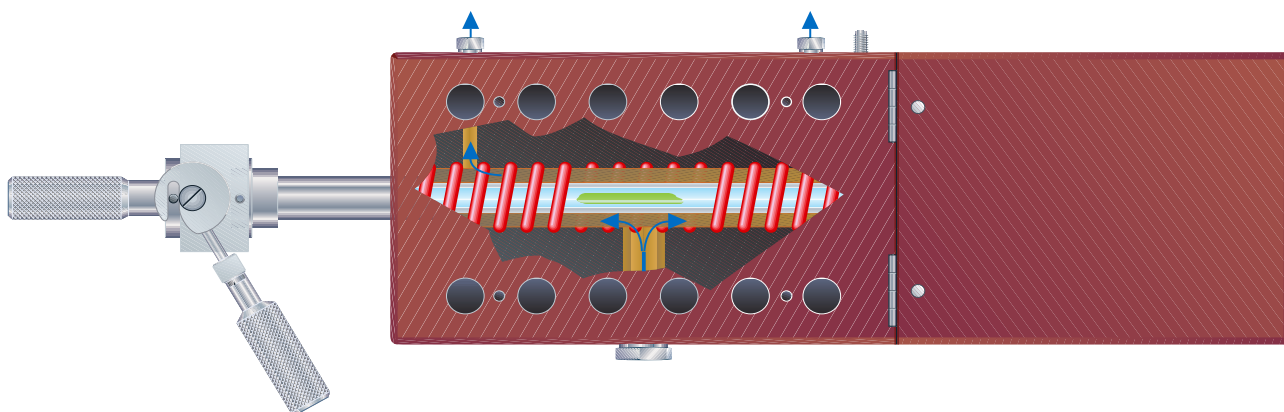


Figure 1. Thermodesorption system TDS 2 (topview).

Operation. A blank glass tube is filled with the sample and then inserted into the TDS 2 desorption chamber which is cooled down to subambient temperatures in order to prevent premature desorption. After purging the air out of the system, the tube is then heated to the desired temperature, while the carrier gas flowing through the tube transfers the volatiles in split- or splitless-mode (**Figure 2** and **3**) into the pre-cooled CIS, where they are cryofocused and concentrated.

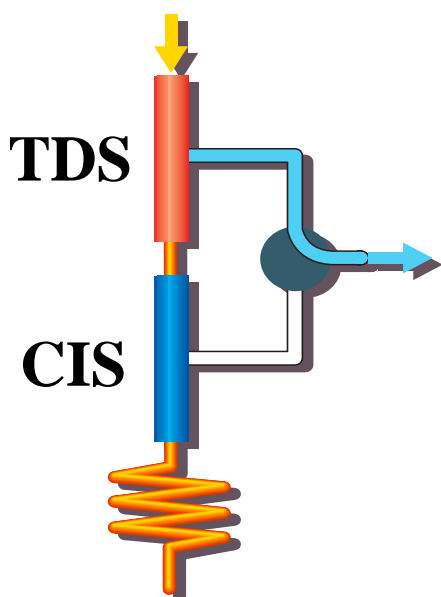


Figure 2. Desorption principle, TDS in split-mode.

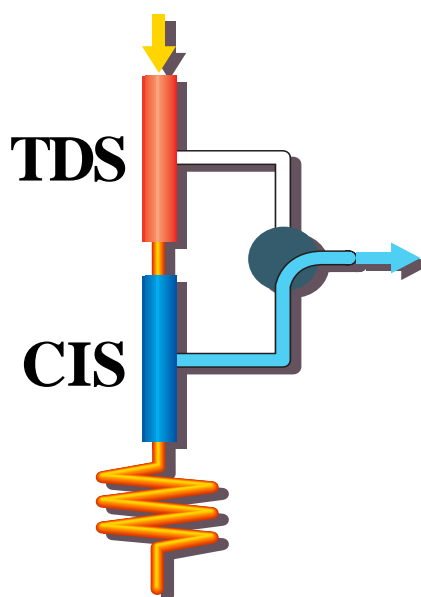


Figure 3. Desorption principle, TDS in splitless-mode.

After the desorption has finished the CIS is heated to the desired temperature to allow split or splitless transfer of the trapped compounds to the analytical column and further mass spectrometric detection. **Figure 4** describes the operation principle.

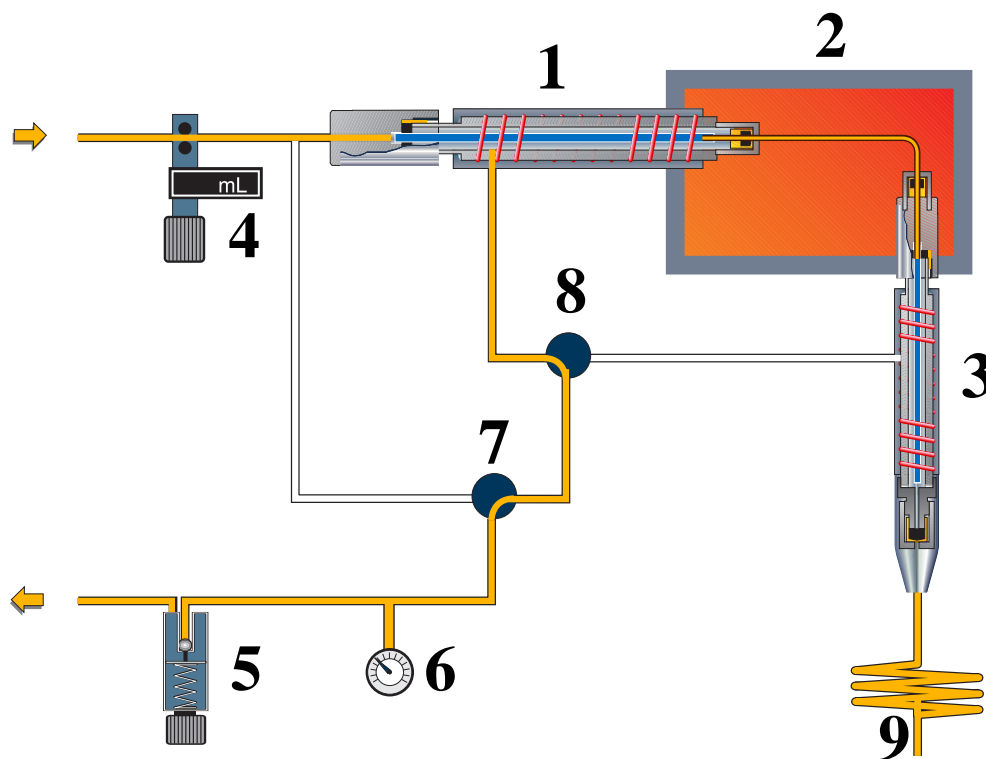


Figure 4. Schematic of the applied system which consists of a thermodesorption system (1), a temperaturized transfer capillary (2), a cooled injection system (3), standard backpressure Pneumatics with mass-flow controller (4), backpressure regulator (5), pressure gauge (6) and split/splitless valve (7), including an additional 3/2-way solenoid (8) to switch the splitflow between TDS and CIS. The analytical column (9) is directly connected to a mass selective detector.

RESULTS AND DISCUSSION

Example 1. Volatiles in plastic food wrap.

For the heating of food products in microwave ovens special packaging materials like plastic food wraps are recommended. It has to be ensured that nothing from the wrap can migrate into the food during the cooking process. For the analysis a few square centimeters of the wrap are placed into the desorption tube, which is then heated to the maximum allowed wrap temperature of 150°C. The result can be seen in **Figure 5**.

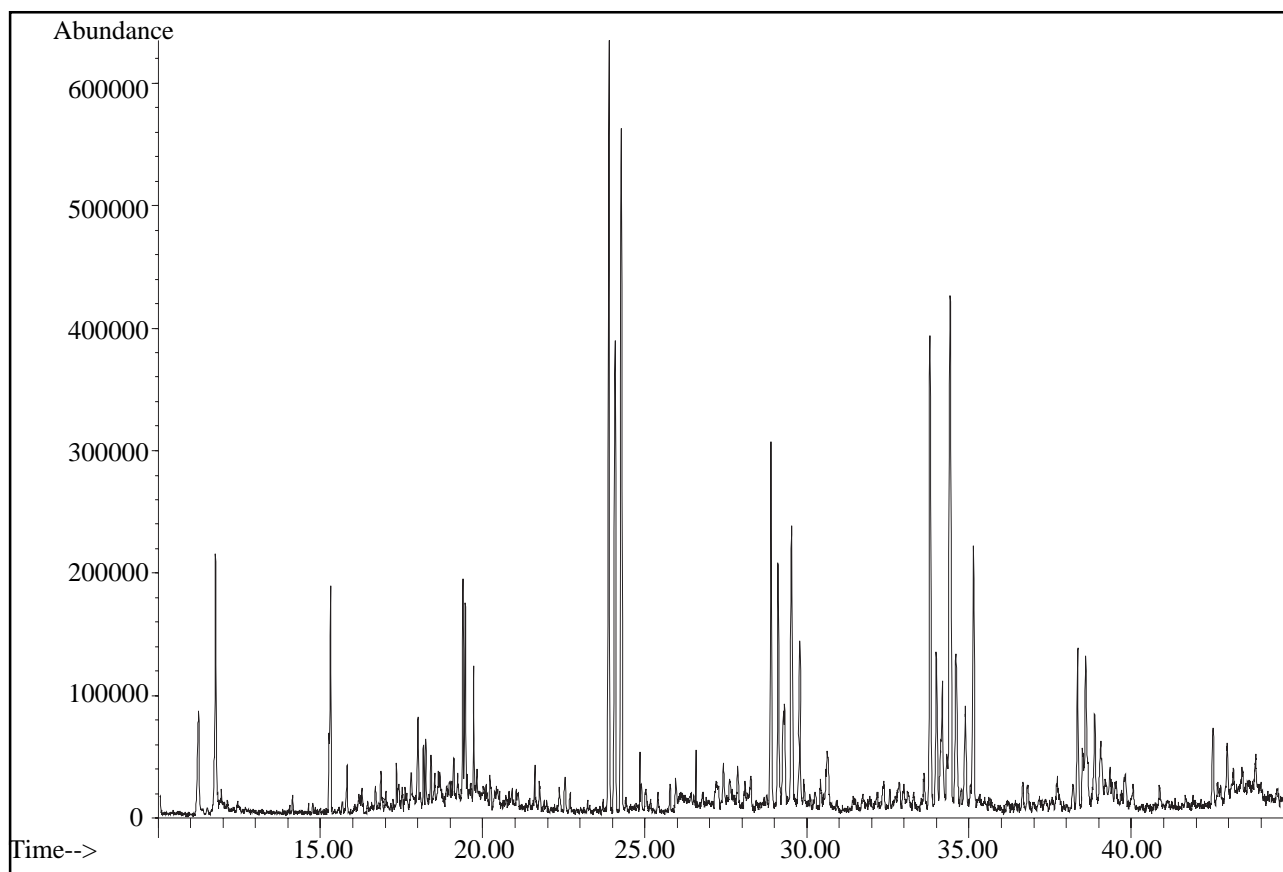


Figure 5. Analysis of volatiles in a microwave food wrap (splitless).

Analysis conditions.

Column: 25 m Ultra-2 (Hewlett-Packard), $d_i=0,2$ mm, $d_f = 0,33$ μ m
Pneumatics: He, $p_i=50$ kPa, split x:30
Temperatures: TDS: 50°C to 150°C with 20°C/min
CIS: -150°C to 300°C with 12°C/s
Oven: 40°C to 120°C with 10°C/min; to 280°C with 5°C/min
MSD: 280°C

Example 2. Volatiles in spices.

The direct thermal analysis of previously dried spices can easily be used as a technique for quality monitoring, where time consuming solvent extraction steps can be avoided. The two examples chosen demonstrate the feasibility of this method (**Figures 6 and 7**).

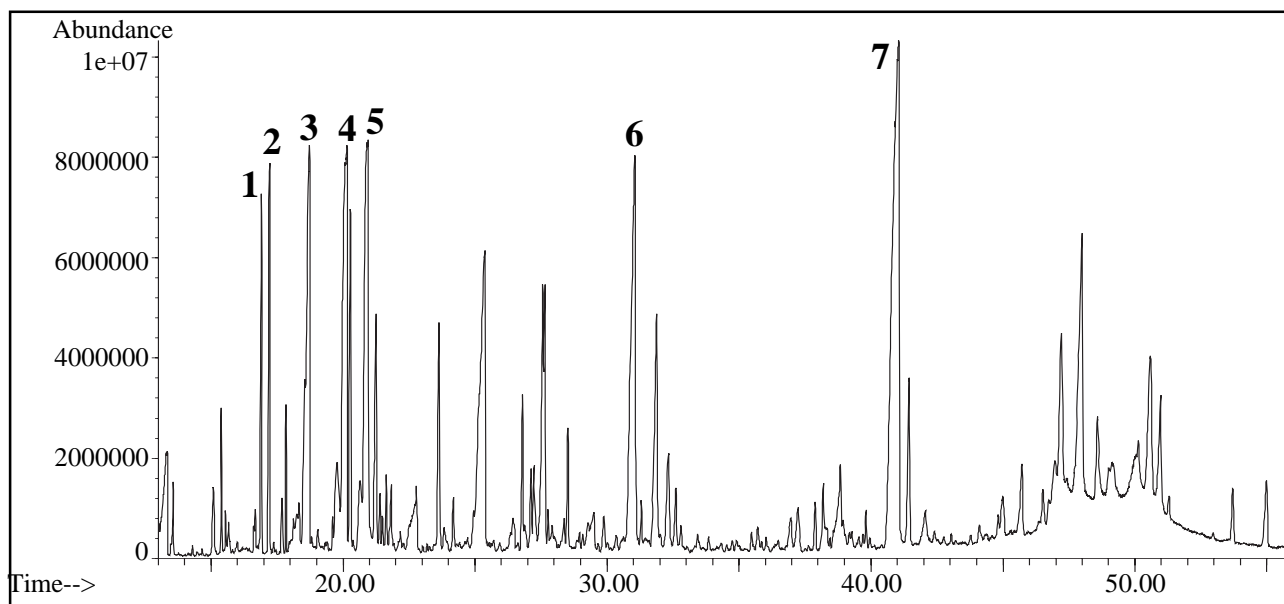


Figure 6. Thermal analysis of volatiles in sage (splitless).

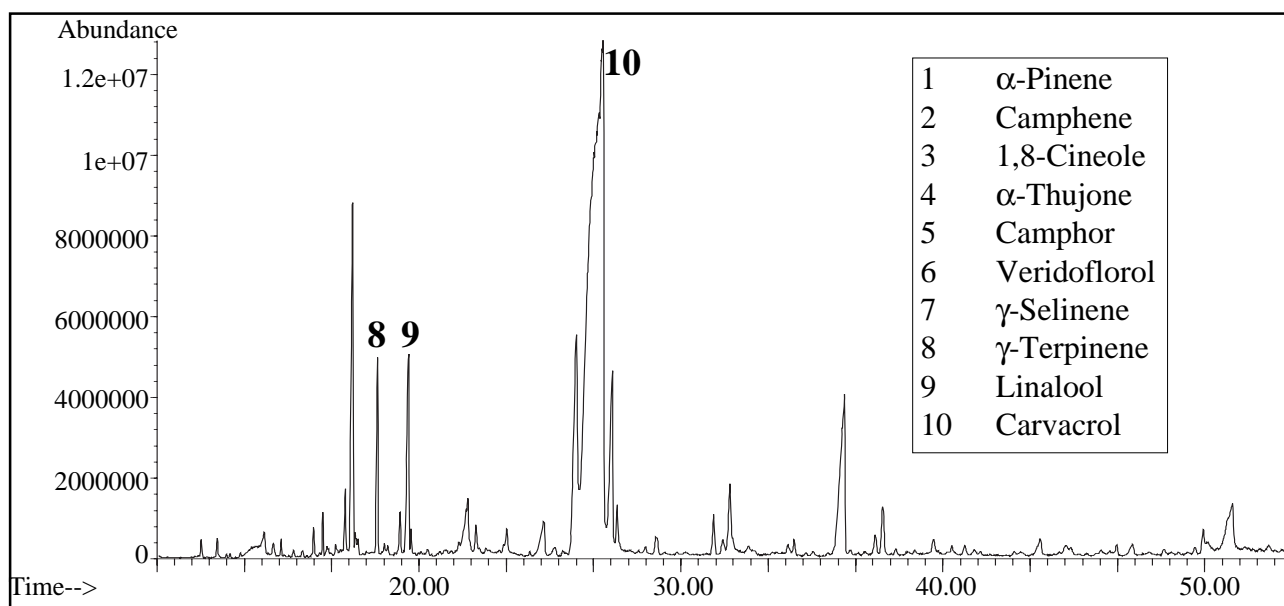


Figure 7. Thermal analysis of volatiles in oregano (splitless).

Analysis conditions.

Column: 25 m Ultra-2 (Hewlett-Packard), $d_i=0,2$ mm, $d_f = 0,33$ μ m
Pneumatics: He, $p_i=50$ kPa, split x:30
Temperatures: TDS: 50°C to 150°C with 20°C/min
CIS: -150°C to 300°C with 12°C/s
Oven: 40°C to 120°C with 10°C/min; to 280°C with 5°C/min
MSD: 280°C

Example 3. Volatiles in Pharmaceuticals.

The method of direct thermal desorption here can be utilized for the determination of residual compounds in pharmaceuticals, which were formed or used during manufacturing (**Figure 8**).

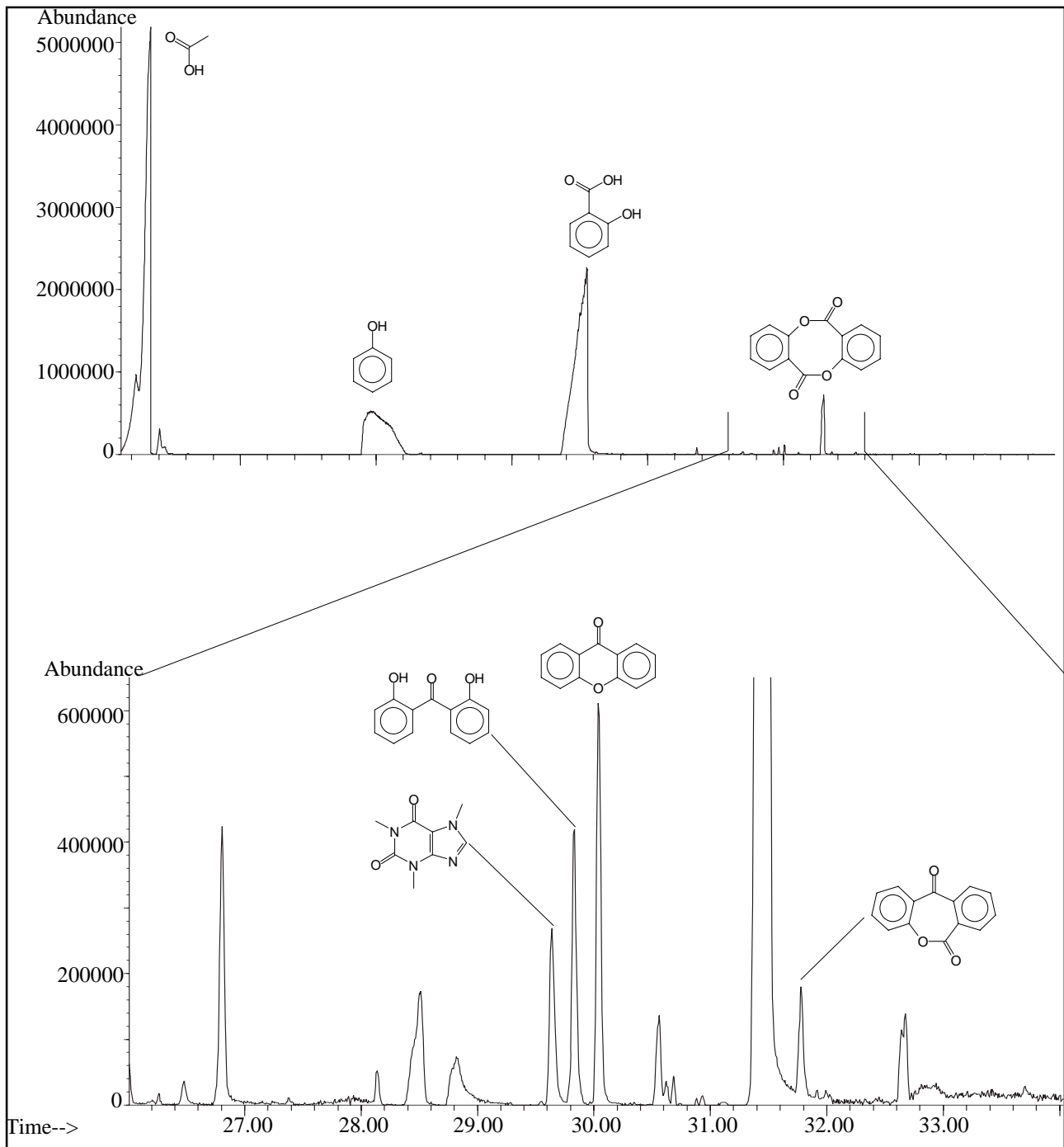


Figure 8. Analysis of volatiles in a pain-killer (split).

Analysis conditions.

Column: 60 m DB 5 (J & W), $d_i=0,25$ mm, $d_f = 0,25$ μ m
Pneumatics: He, $p_i=80$ kPa, split x:30
Temperatures: TDS: 50°C to 150°C with 20°C/min
CIS: -150°C to 300°C with 12°C/s
Oven: 60°C to 280°C with 10°C/min
MSD: 280°C

Example 4. Residual solvent in recycled polyethylene.

During the recycling process a solvent mixture has to be used to extract the polyethylene from solid impurities. After this clean-up procedure the solvent mixture has to be removed again. The success of this drying step can be monitored either through standard liquid injection after having dissolved the sample once again (this time in a single solvent, **Figure 9**), or through direct thermal desorption (**Figure 10**).

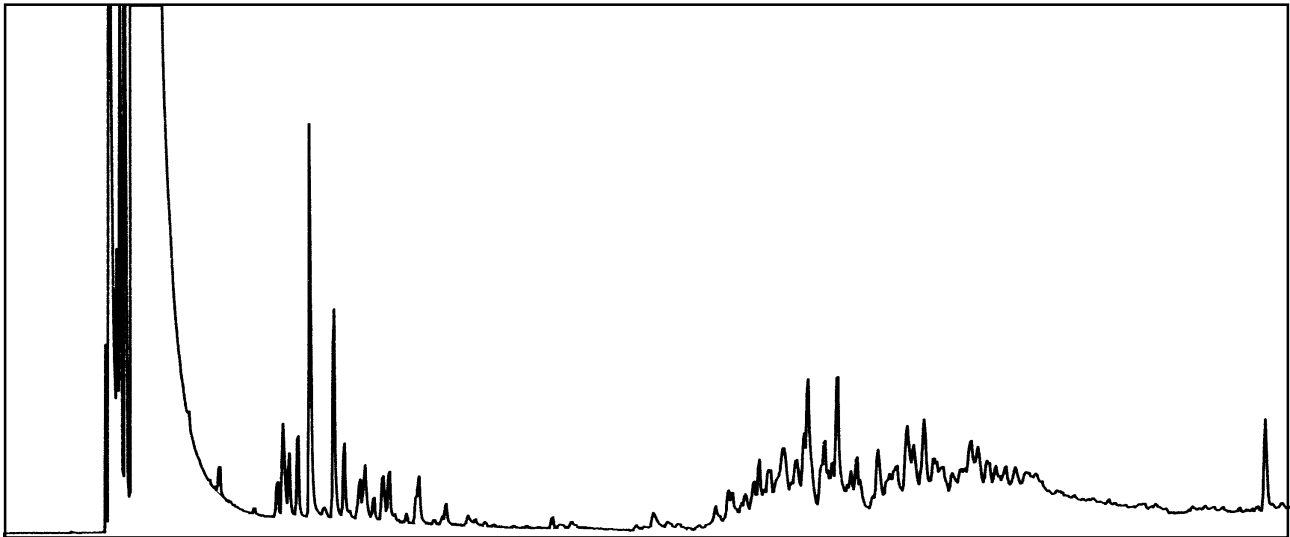


Figure 9. Residual solvent in recycled polyethylene, liquid injection (split).

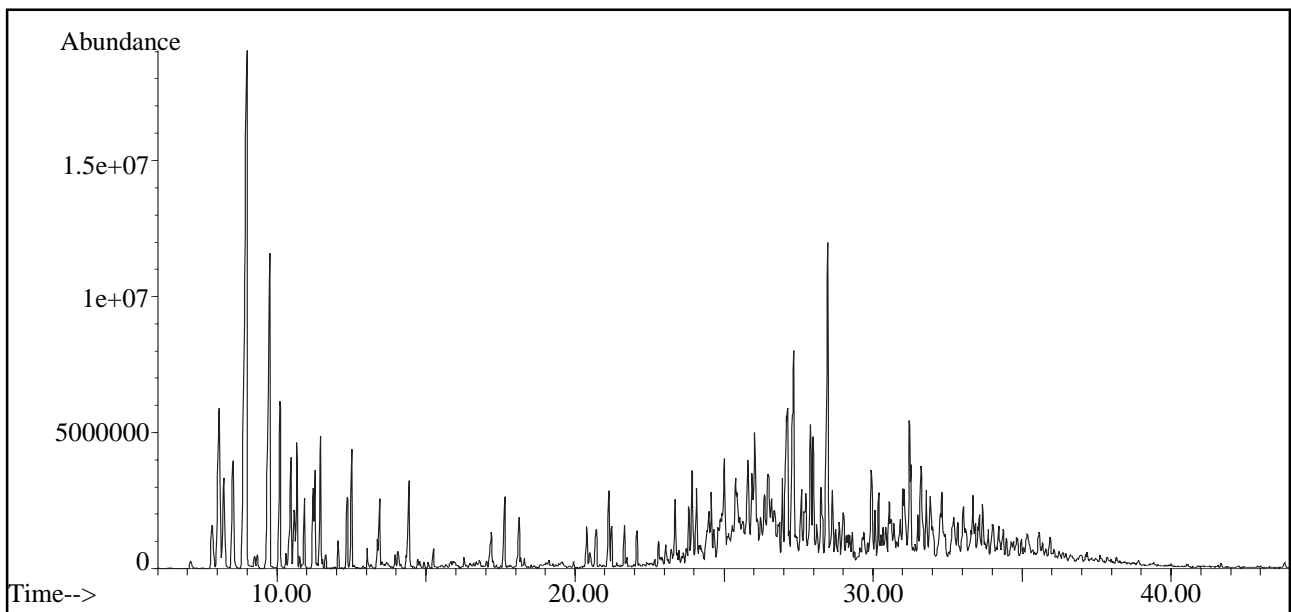


Figure 10. Residual solvent in recycled polyethylene, thermodesorption (split).

Analysis conditions.

Column: 50 m DB 5 (J & W), $d_i=0,25$ mm, $d_f = 0,25$ μ m
Pneumatics: He, $p_i=210$ kPa, split x:80
Temperatures: TDS: -50°C to 150°C with $60^\circ\text{C}/\text{min}$
CIS: -150°C to 300°C with $12^\circ\text{C}/\text{s}$
Oven: 60°C to 320°C with $5^\circ\text{C}/\text{min}$
MSD: 280°C

Example 5. Fragrances in shampoos and detergents.

The analysis of fragrances in shampoos and detergents usually needs a time consuming preliminary extraction step. Using direct thermal desorption it is possible to extract the flavour compounds (**Figure 11-13**) at low temperatures and cryofocus them in the cooled injection system, whereas the detergents remain in the the desorption tube.

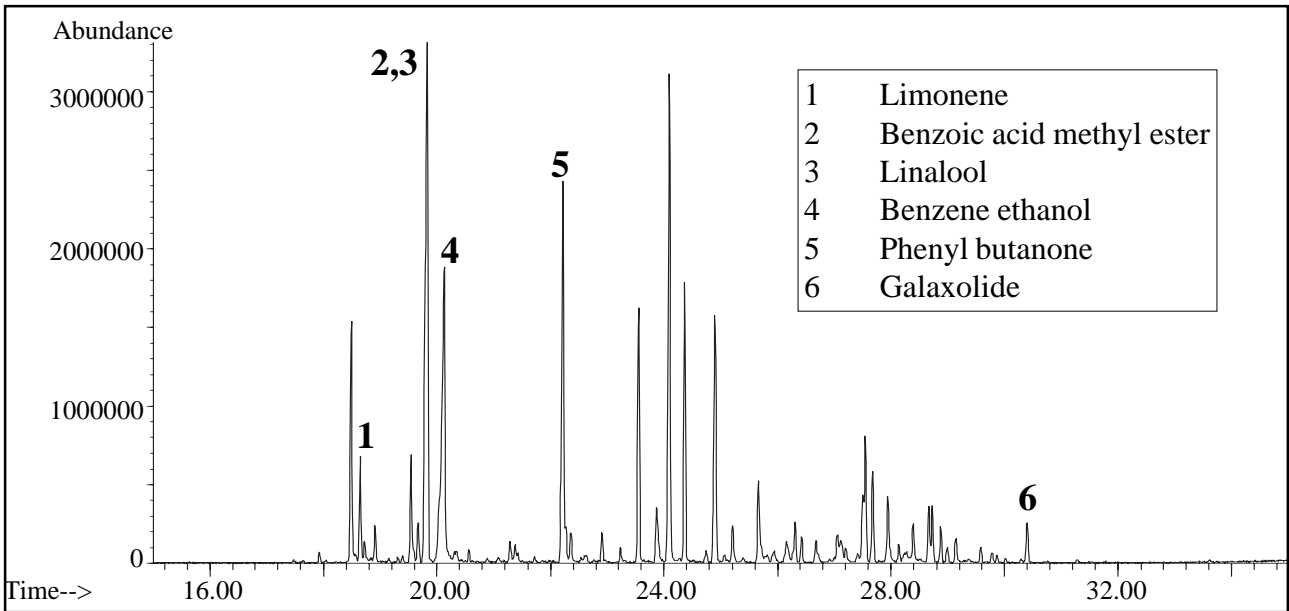


Figure 11. *Fragrances in powdered laundry detergent, brand A (split).*

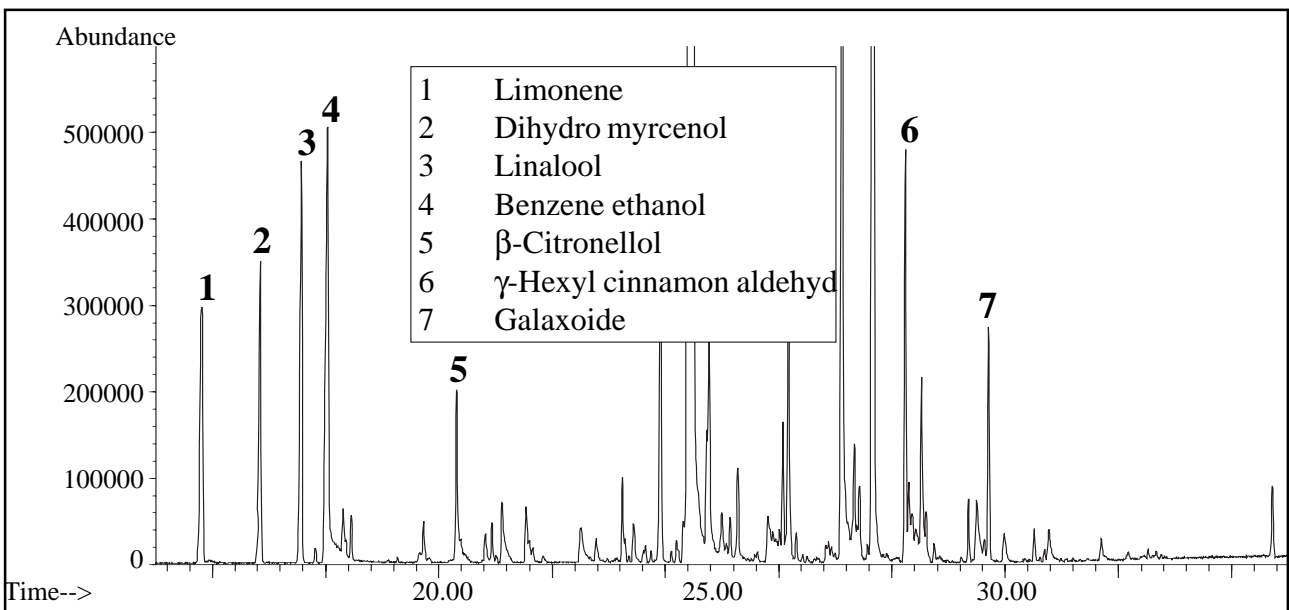


Figure 12. *Fragrances in powdered laundry detergent, brand B (split).*

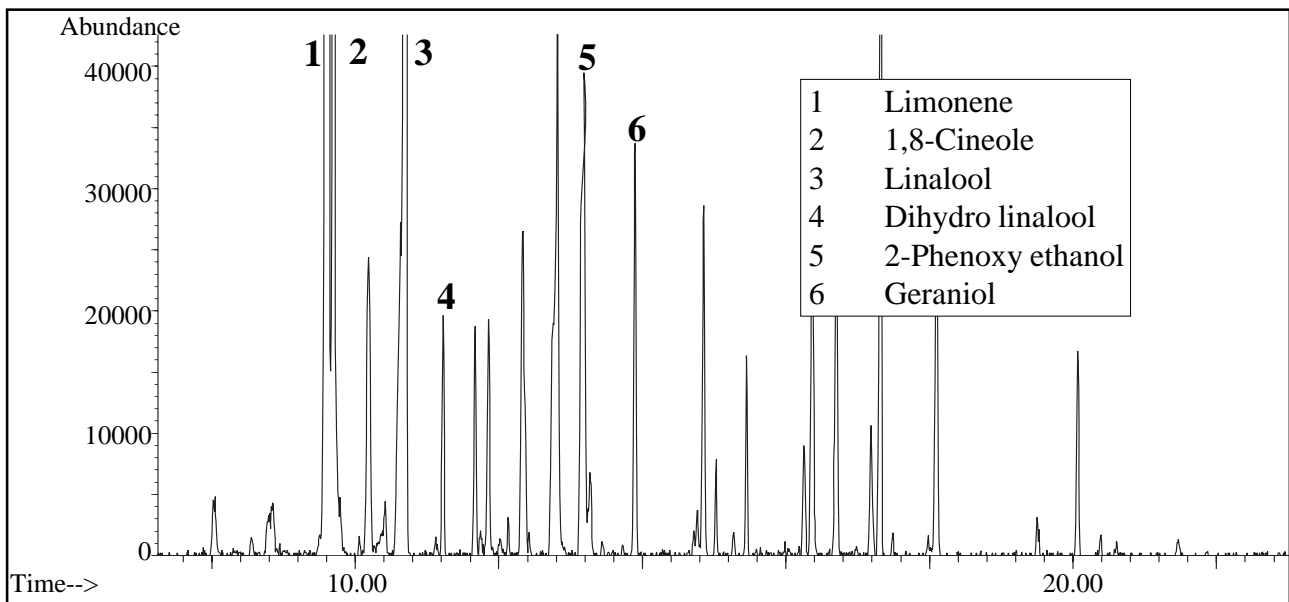


Figure 13. *Fragrances in shampoo (split).*

Analysis conditions, Example 5.

Column: 50 m DB 5 (J & W), $d_i=0,25$ mm, $d_f = 0,25$ μ m
 Pneumatics: He, $p_i=80$ kPa, split x:80
 Temperatures: TDS: -50°C to 80°C with $60^{\circ}\text{C}/\text{min}$
 CIS: -150°C to 300°C with $12^{\circ}\text{C}/\text{s}$
 Oven: 60°C to 300°C with $10^{\circ}\text{C}/\text{min}$
 MSD: 280°C

Analysis conditions, Example 6.

50 m DB 5 (J&W), $d_i=0,25$ mm, $d_f = 0,25$ μ m
 He, $p_i=210$ kPa, split x:80
 TDS: -50°C to 350°C with $60^{\circ}\text{C}/\text{min}$
 CIS: -150°C to 400°C with $12^{\circ}\text{C}/\text{s}$
 Oven: 60°C to 250°C with $10^{\circ}\text{C}/\text{min}$;
 320°C with $5^{\circ}\text{C}/\text{min}$
 MSD: 280°C

Example 6. *Analysis of diesel filter paper.*

Thermal desorption here offers a method for measuring diesel particulates trapped on a glass fibre filter (**Figure 14**) in order to optimise the combustion process in the engine.

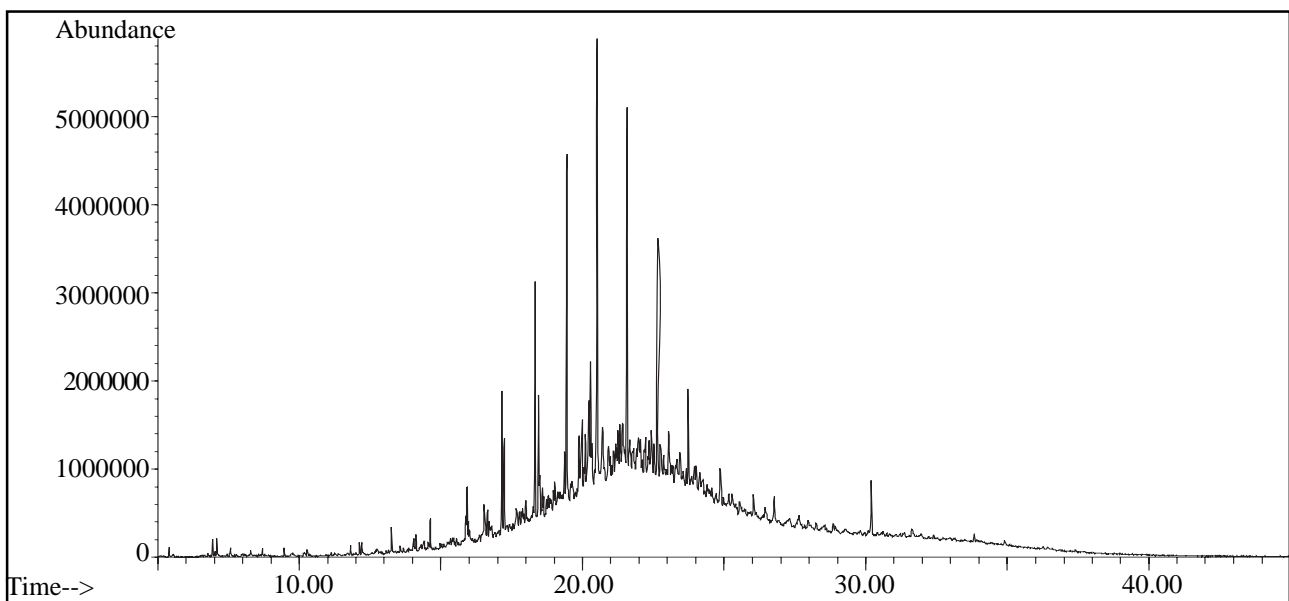


Figure 14. *Analysis of volatile organic compounds trapped on a glass fibre filter in a diesel engine (splitless).*

Example 7. Trace Analysis of PAH's and PCB's in contaminated soils.

Due to the hazards deriving from contaminated industrial sites, gaining an overview of the degree of contamination is a substantial need in modern environmental analysis. The complexity of the matrix soil requires difficult and time consuming sample preparation, so that a simpler and faster, but nevertheless accurate screening method would be of great interest. With the fully automated thermodesorption unit (TDS 2) described in this paper these samples can now be analyzed directly, without any other sample preparation than crushing to a particle size of <4mm. **Figures 15** and **16** demonstrate the usefulness of this technique for this purpose.

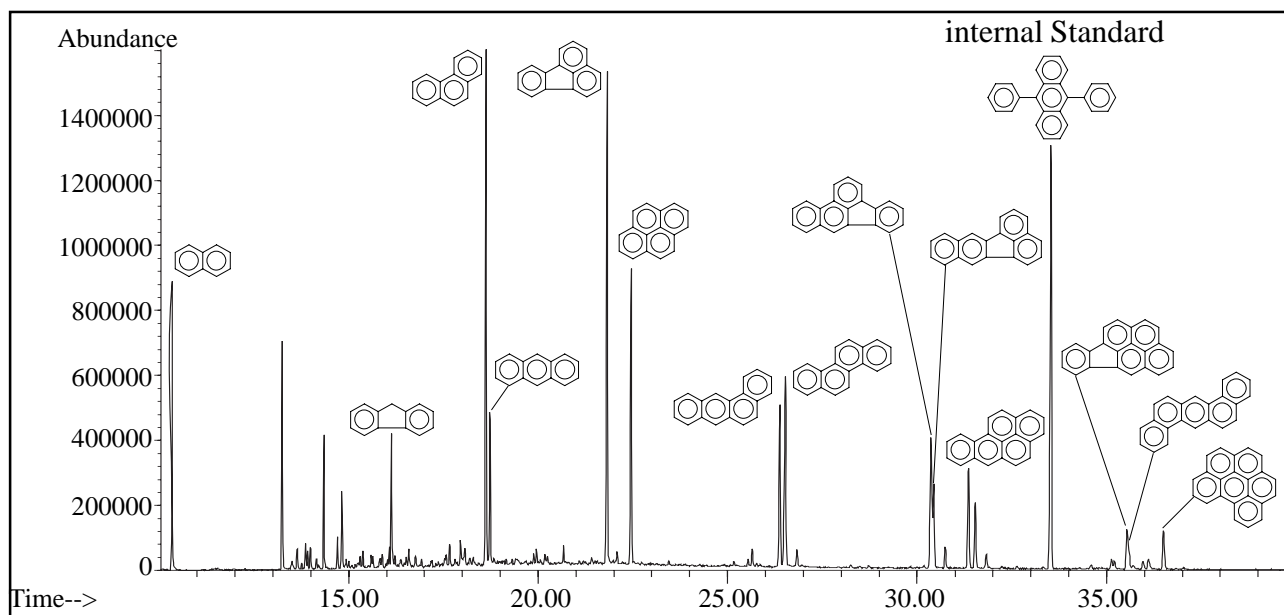


Figure 15. Direct thermal desorption of a contaminated soil, PAH-traces in extracted ion chromatogram mode.

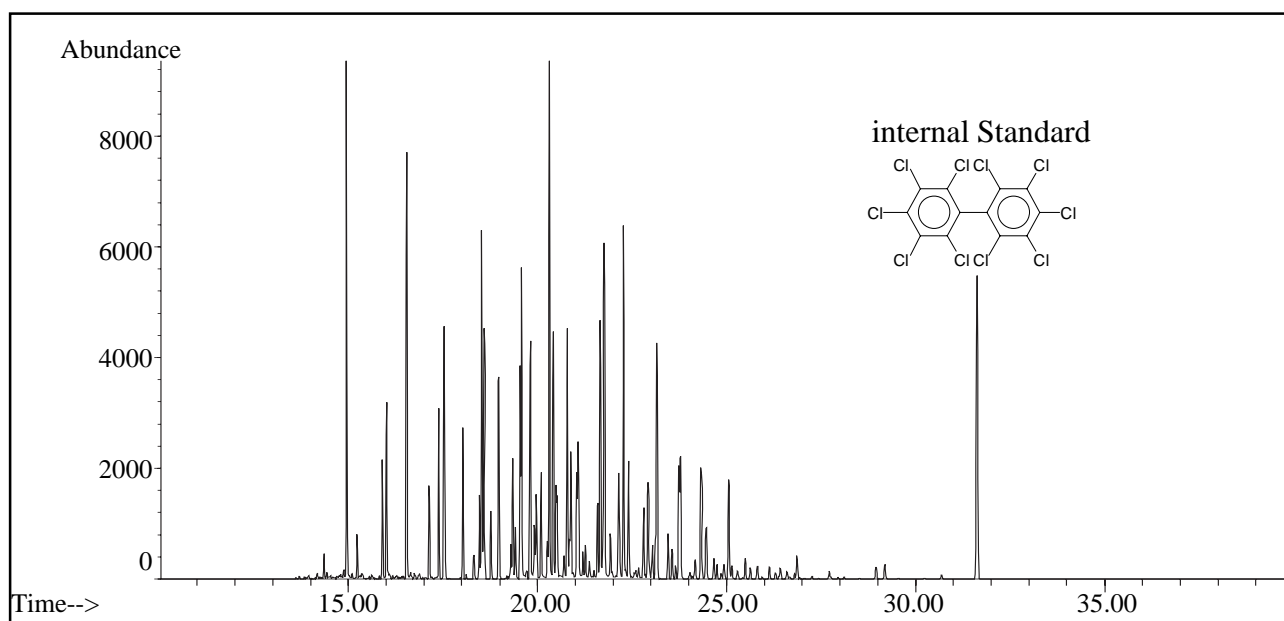


Figure 16. Direct thermal desorption of a contaminated soil, PCB-traces in selected ion mode.

CONCLUSIONS

The combination thermodesorption/cooled injection offers an analysis technique for a great variety of liquid and solid samples which normally are not directly compatible with a gas chromatographic system.

It has proven to be a time saving extraction method for volatiles over a wide boiling range, without any sample pretreatment.

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GERSTEL GmbH & Co. KG

Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany

+49 (0) 208 - 7 65 03-0
+49 (0) 208 - 7 65 03 33
gerstel@gerstel.com
www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.

701 Digital Drive, Suite J
Linthicum, MD 21090
USA

+1 (410) 247 5885
+1 (410) 247 5887
sales@gerstelus.com
www.gerstelus.com

GERSTEL AG

Wassergrabe 27
CH-6210 Sursee
Switzerland

+41 (41) 9 21 97 23
+41 (41) 9 21 97 25
swiss@ch.gerstel.com
www.gerstel.ch

GERSTEL K.K.

1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsu-dai Ekimae Bldg 4F
Japan

+81 3 5731 5321
+81 3 5731 5322
info@gerstel.co.jp
www.gerstel.co.jp

GERSTEL LLP

10 Science Park Road
#02-18 The Alpha
Singapore 117684

+65 6779 0933
+65 6779 0938
SEA@gerstel.com
www.gerstel.com

GERSTEL (Shanghai) Co. Ltd

Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District
Shanghai 201206

+86 21 50 93 30 57
china@gerstel.com
www.gerstel.cn

GERSTEL Brasil

Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil

+55 (11)5665-8931
+55 (11)5666-9084
gerstel-brasil@gerstel.com
www.gerstel.com.br

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