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Applicability of a New Versatile Temperature Programmed Thermodesorption System in Single and Multi Column Capillary GC/MS

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ABSTRACT

The on-line technique by which organic contaminants in gaseous samples are analyzed by adsorption on porous polymers and subsequent thermal desorption prior to GC analysis, is gaining popularity.

This paper is dealing with the introduction, design and the applicability of a new simple versatile temperature programmed thermodesorption system which is compatible with existing commercial GC equipment. Its applicability is illustrated in combination with a cooled programmed temperature injection system, a dual column switching double oven system, provided with a cryotrap at the inlet of the second column. A mass selective detector is coupled on-line for identification.

INTRODUCTION

In trace analysis of volatiles in samples from industrial, environmental and biological sources the samples are often too complex, too dilute or not compatible with the chromatographic system, to permit analysis by direct injection. Preliminary fractionation, isolation and enrichment of the analytes is required prior to chromatographic analysis in many cases.

A combination of adsorption and subsequent thermal desorption, where the components which are trapped on a preferably selective adsorbent, are thermally desorbed after achievement of the required enrichment, and subsequently transferred onto the column. In this way also the volatile constituents of solid and liquid samples can be extracted (thermally, dynamic headspace or gas phase stripping) and transferred onto the column, either directly or via an adsorption/desorption device e.g. a PTV injector provided with a packed liner.

Major features of such an on-line adsorption/thermodesorption device (TDS), are the decreased detection limits, the traps can be reused many times and the samples can be taken at any desired location. Furthermore the flexibility, the suitability for on-line selective pre-separation and a significantly improved reproducibility are additional advantages of such systems.

In this paper we report on the applicability of a new versatile temperature programmed thermodesorption device as is described in the experimental part.

EXPERIMENTAL

Instrumentation. The system consists of a thermodesorption system (TDS-1, Gerstel GmbH, Mülheim an der Ruhr, Germany), a temperature programmable cold injection system (CIS-3, Gerstel GmbH, Mülheim an der Ruhr, Germany), a multi column switching system (MCS A, Gerstel GmbH, Mülheim an der Ruhr, Germany), Pre- and Main Column, 2 Ovens (HP 5890 series II, Hewlett-Packard, Avondale, USA), with a cryotrap system (CTS-1, Gerstel GmbH, Mülheim an der Ruhr, Germany) in between and a mass selective detector (HP 5971, Hewlett-Packard, Avondale, USA) as illustrated in **Figure 1**.

Analysis conditions.

Columns:

TDS adsorption tube	5 cm Carbotrap (Supelco)
	$d_i = 4.0 \text{ mm}$ 20/40 mesh
Pre-column in GC 1	25 m OV-17 (home made)
	$d_i = 0.32 \text{ mm}$ $d_r = 1.0 \mu\text{m}$
main column in GC 2	25 m Ultra-1 (Hewlett-Packard)
	$d_i = 0.2 \text{ mm}$ $d_r = 0.33 \mu\text{m}$

Temperatures:

TDS	50°C;	↗ 280°C;	40°C/min.
CIS	-150°C;	↗ 280°C;	12°C/s.
Oven-1	40°C;	↘ 250°C;	10°C/min.
Oven-2	40°C;	↗ 200°C;	5°C/min.
CTS	250°C;	-150°C;	12°C/s;
		250°C;	12°C/s.

Detectors:

Monitor-Detector	FID
Main Detector	MSD Scan 10-350 amu

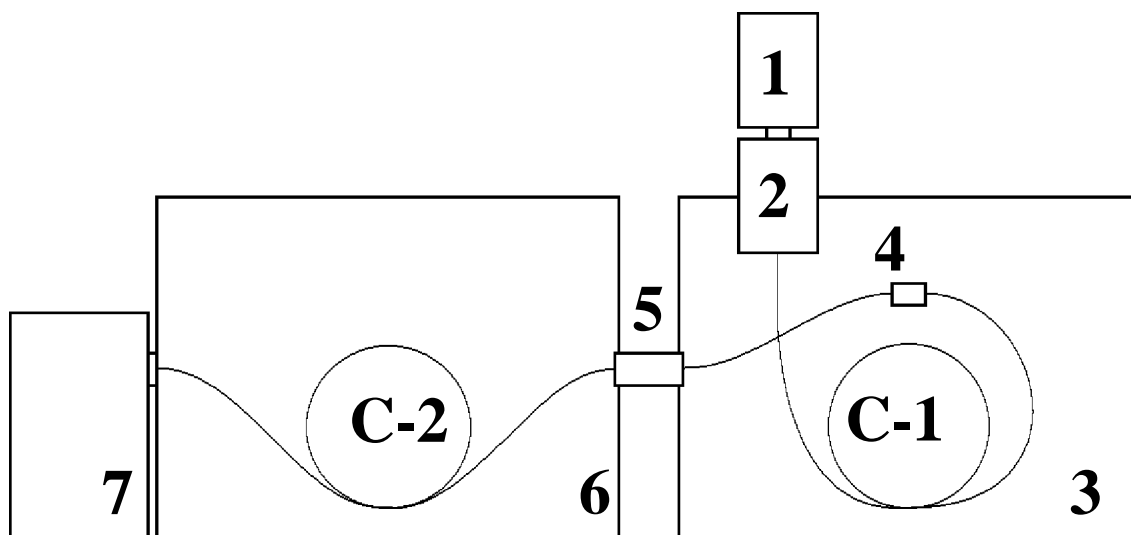


Figure 1. Schematic diagram of the applied system consisting of a thermodesorption system (1), a temperature programmable cold injection system with septumless sampling head (2), a GC (3) configured with monitor-FID, column switching device (4) and dual column switching module, connected via a heated transferline with included cryotrap (5) to a second GC (6) with a mass selective detector (7).

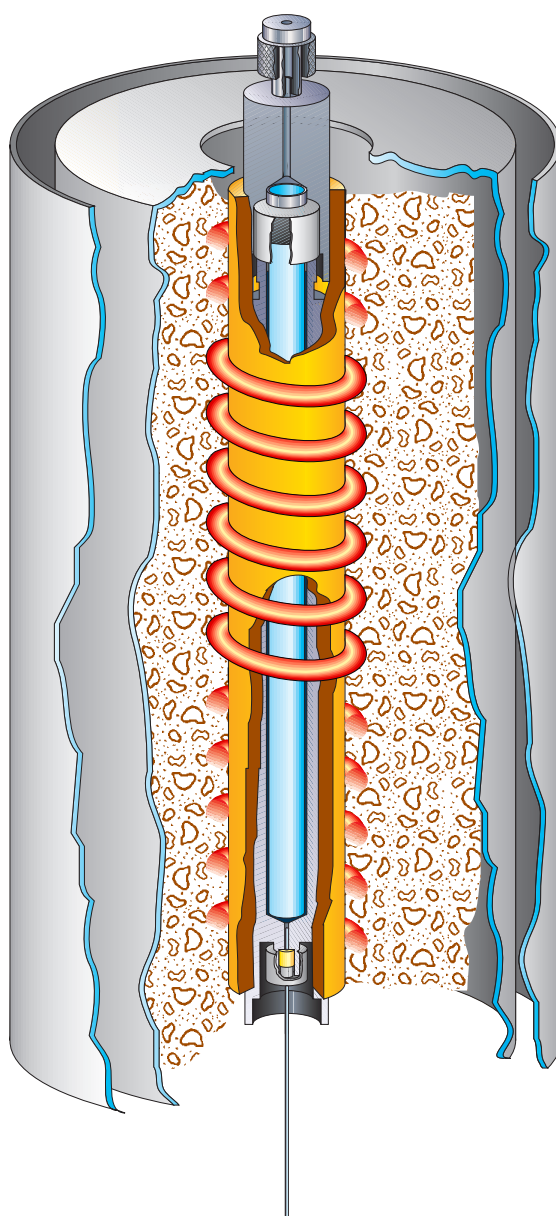


Figure 2. *Schematic design of the programmed temperature thermodesorption system (TDS-1).*

RESULTS AND DISCUSSION

Some of the features of the new adsorption/thermodesorption device, which have been mentioned in the introduction, are illustrated in the following on some examples with an extremely powerful separation/identification combination as described in the experimental part. This system allows focussing of the desorbed components prior to the first column by the cooled liner of the temperature programmed injector, which is partly filled with an adsorbent. In case the adsorbent in the TDS-unit and the injector liner are identical, all the components which are trapped in the TDS-unit will be refocussed in the cold CIS-liner. With a selective material in the liner on-line fractionation of the desorbed fraction can be achieved.

Example 1. In this example the chromatographic profiles are compared of the liquid and a static headspace sample of an industrial solvent mixture, with a TDS/CIS-3/single column/FID combination. The mixture consists of a Shell-Sol and a mixture of 1,1,1-trichloroethane and perchloroethylene. The profiles of the liquid samples with and without the TDS-unit appeared identical. For obvious reasons the volatile part of the sample is highly enriched in the headspace sample as can be seen from the different relative peak areas in both runs.

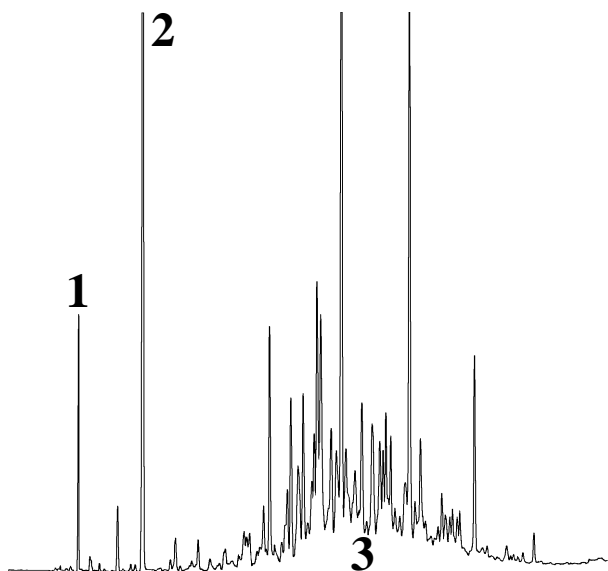


Figure 3a. Single column (#1) chromatogram of a liquid sample of a degreasing solvent mixture, 1 μ l, split ratio x:30, experimental conditions: see instrumental.

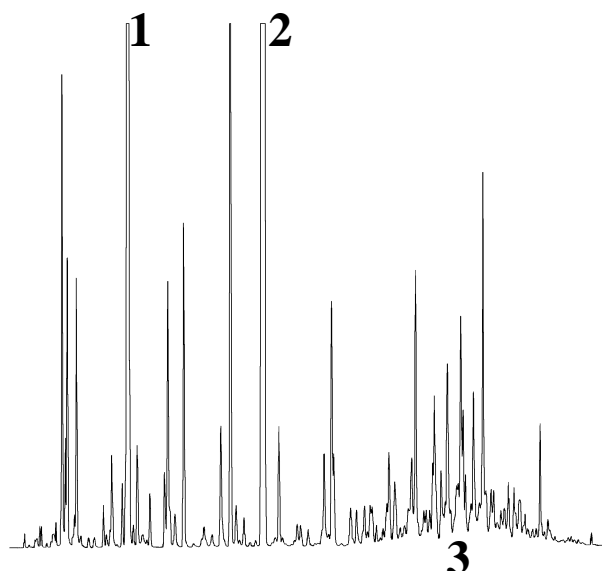


Figure 3b. Single column (#1) chromatogram of a vapour sample of the same degreasing solvent mixture, 20 ml, split ratio x:30, experimental conditions: see instrumental.

Compounds:

1. 1,1,1-Trichloroethane
2. Perchloroethylene
3. "Shell-Sol"

Example 2. These chromatograms illustrate the effect of different operating conditions of a car engine on the composition of car exhaust gases. A combination of TDS-1/CIS-3/single column/FID is used for this purpose.

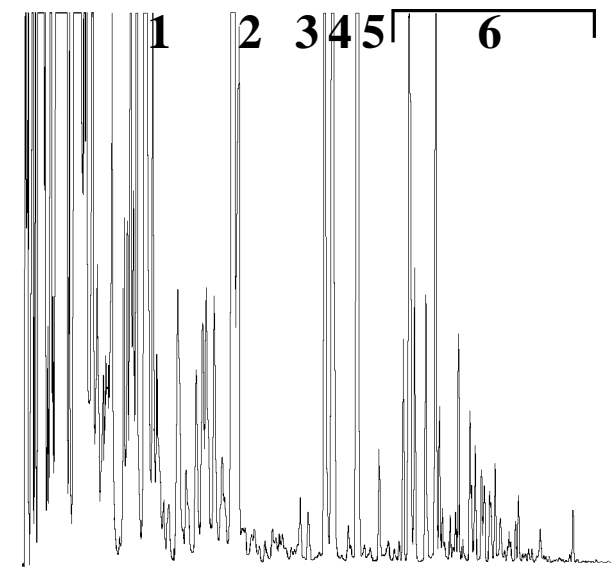


Figure 4a. Single column (#1) chromatogram of car exhaust gases, cold engine without catalyst, 25 ml, split ratio x:30, experimental conditions: see instrumental.

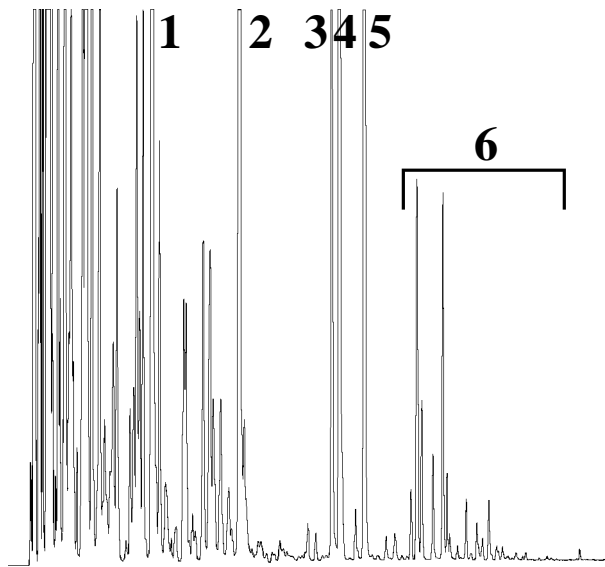


Figure 4b. Single column (#1) chromatogram of car exhaust gases, cold engine with controlled catalyst, 25 ml, split ratio x:30, experimental conditions: see instrumental.

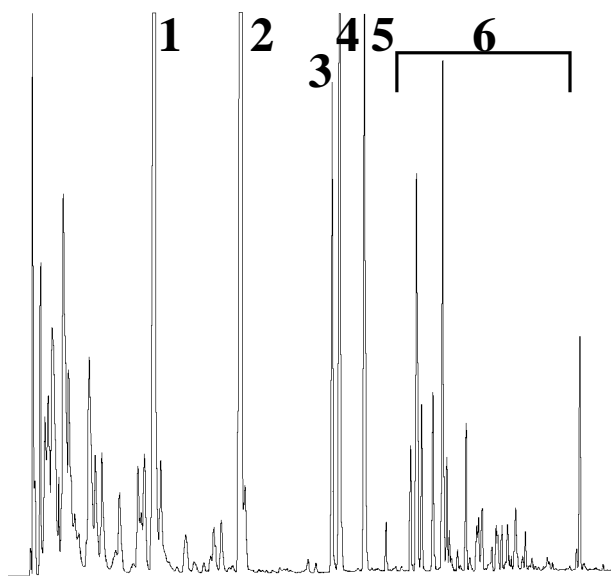


Figure 4c. Single column (#1) chromatogram of car exhaust gases, hot engine with uncontrolled catalyst, 25 ml, split ratio x:30, experimental conditions: see instrumental.

Compounds:

1. Benzene
2. Toluene
3. Ethylbenzene
4. m,p-Xylene
5. o-Xylene
6. Trimethylbenzenes

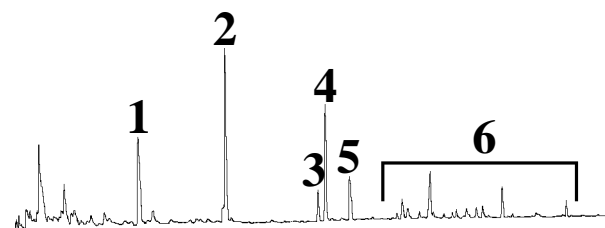


Figure 4d. Single column (#1) chromatogram of car exhaust gases, hot engine with controlled catalyst, 25 ml, split ratio x:30, experimental conditions: see instrumental.

Comparing **Figure 4a** and **4b** obviously the effect of the catalyst for the cold engine is relatively small, although the amount of higher (C_9 and C_{10}) aromatics is already greatly reduced. The effect of the catalyst for a warm car engine, given in **Figure 4c** and **4d**, however, is dramatic. For the uncontrolled catalyst the concentration of lower hydrocarbons is greatly reduced, but the concentrations of C_7 and C_8 - aromatics, is still far from satisfying. The reduction of the concentrations of pollutants in exhaust gases of a warm car engine equipped with a controlled 3-way catalyst is impressive. Further systematic investigations and quantitation of these results, for the estimation of environmental pollution is an interesting application area for TDS sample enrichment and combination with sophisticated sample introduction, separation and identification systems.

Example 3. In this example a TIC chromatographic profile of milled coffee aroma are analyzed with a combination TDS-1/CIS-3/single column/MSD. Unexpected was the presence of furans, which are highly toxic and dimethyldisulfide. Consulted experts have confirmed these results.

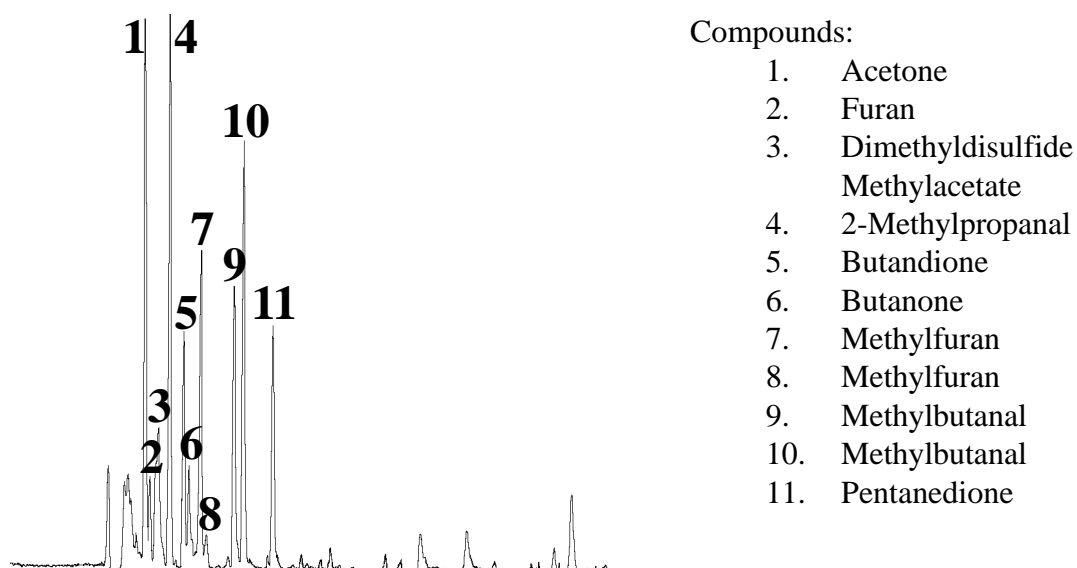


Figure 5. Single column (# 1) chromatogram of milled coffee aroma, 250 ml, split ratio x:30, experimental conditions: see instrumental.

Example 4. In this example some heartcut fractions of cigarette smoke, which is trapped on a TDS-1 adsorption tube packed with Carbotrap and analyzed with a combination TDS-1/CIS-3/dual column-double oven and MSD provided with a cryo trap (CTS-1). The sample is trapped by sucking 25 ml of the air around the hot end of a cigarette through the adsorption tube.

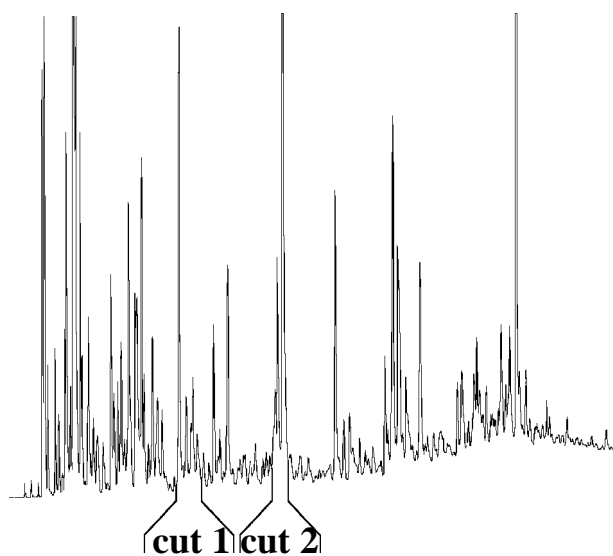


Figure 6a. Precolumn chromatogram of cigarette smoke, 25 ml, split ratio $x:30$, marked components transferred to main column, experimental conditions: see instrumental.

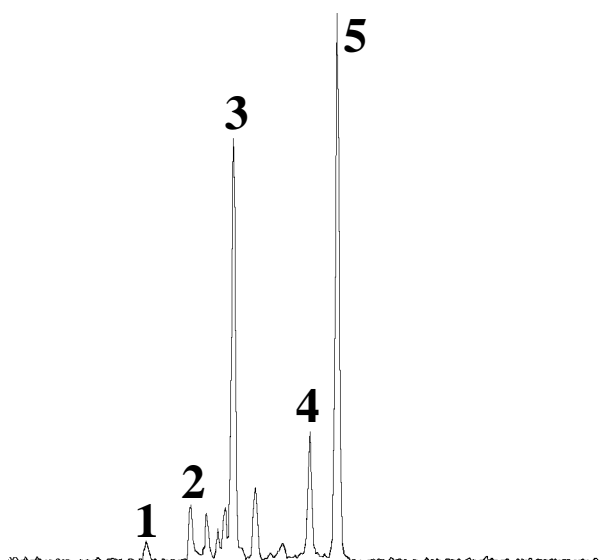


Figure 6b. Main column chromatogram (TIC) of heart cut fraction 1, experimental conditions: see instrumental.

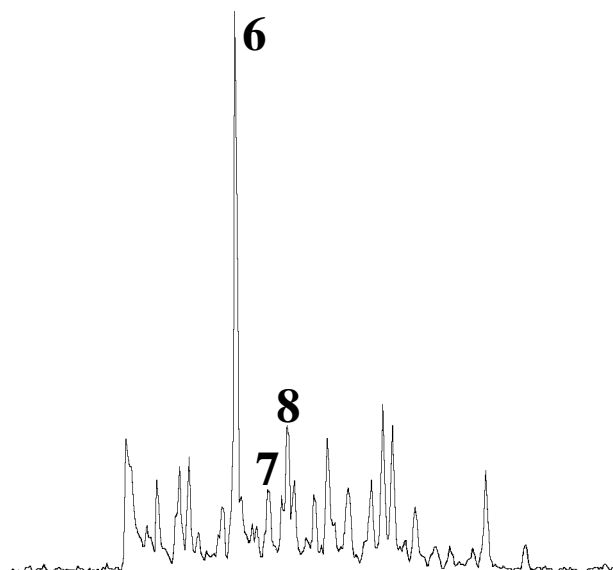


Figure 6c. Main column chromatogram (TIC) of heart cut fraction 2, experimental conditions: see instrumental.

Compounds:

1. 2-Methylpropanitrile
2. Butenal
3. Benzene
4. Heptene
5. Heptane
6. 2,5-Dimethylfuran
7. Phenol
8. 1-Methylpyrrol

The monitor chromatogram (**Figure 6a**) shows a similar pattern as the car exhaust gases given in **Figure 4**. The two indicated fractions are selectively transferred to the second column. It was provided with a cryo trap at the inlet. TIC chromatograms of these fractions are presented in **Figure 6b** and **6c**. Highly toxic substances like 2-methyl-propanitrile, benzene, furans, phenol, etc., appear to be present in these fractions. This must be considered as a frightening experience for all passive smokers.

CONCLUSIONS

The new simple versatile programmed temperature desorption system is a powerful tool for enrichment of organic traces of volatiles in solid, liquid and gaseous samples.

Its combination with sophisticated PTV injection systems and multi column switching, online coupled with mass selective detection allows reproducible analysis of complex sample matrices of traces of volatile components for a wide range of applications.



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