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Trace Analysis of PAH´s and PCB´s in Soil through On-Line Direct Thermal Desorption

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ABSTRACT

Thermodesorption is a well known technique for the analysis of volatile organic contaminants in air and normally employs adsorption on porous polymeres. This operation principle can also be adapted for the direct thermal desorption of volatiles within a wide boiling range directly from soil samples.

In this paper the potential of a newly developed thermodesorption system for direct desorption and analysis of volatiles from soil 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 even with such high boiling points associated with PAHs and PCBs.

INTRODUCTION

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, clean-up and enrichment procedures, which can even nowadays not be automated and so have to be done manually. High quality results, concerning accuracy and precision, are obtained through the classical, especially the standardized methods, but often require a day of work. In many cases it is sufficient to know the magnitude of the contaminant´s concentration, so that a simpler and faster, but nevertheless accurate screening method would be of great interest.

Currently used methods are the following [1]: Soxhlet-extraction, which requires a minimum of 3, usually 12 hours [2]; supercritical fluid extraction (SFE), which needs 1.5 hours [3] and ultrasonic extraction (30 minutes, [4]), which is not always reliable.

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. The compounds of interest are vaporized 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 remains in the thermodesorption unit. This technique was tested as a screening method for the direct determination of PAH´s, PCB´s and mineral oil hydrocarbons in soils.

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).
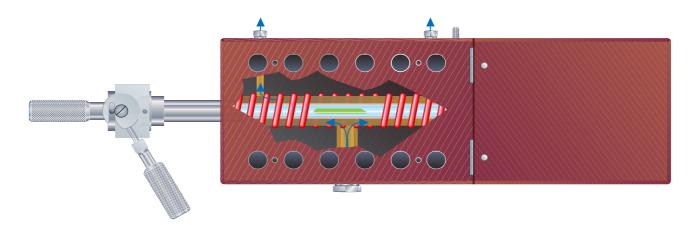

Figure 1. *Thermodesorption system TDS 2 (topview).*

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 350°C, while the carrier gas flowing through the tube transferres the volatiles in split- or splitless-mode (**Figure 2** and **3**) into the pre-cooled CIS, where they are cryofocused and concentrated.
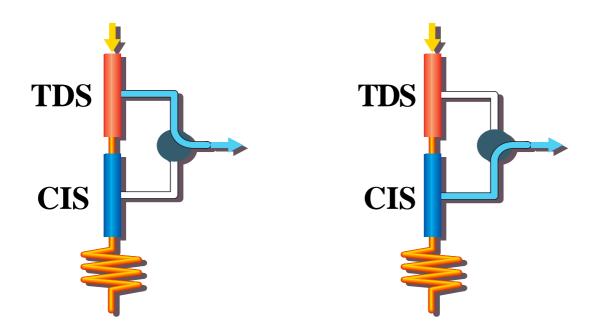

Figure 2. *Desorption principle, TDS in split-mode.*

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

After the desorption has finished the CIS is heated to the 400°C 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.
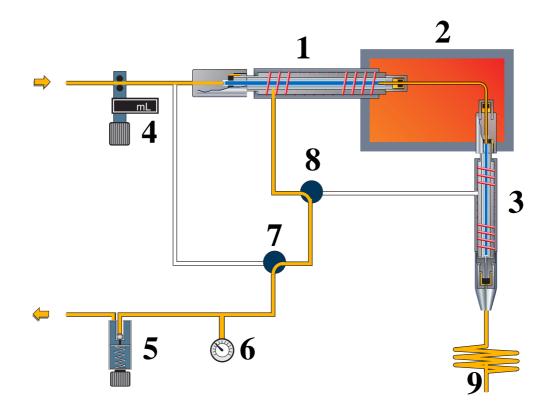

Figure 4. *Schematic of the applied system which consists of a thermodesorption system (1), a temperature controlled transfer capillary (2), a cooled injection system (3), standard backpressure Pneumatics with mass-flow controller (4), backpressure regulator (5), pressure gauge (6) and split/ splitless 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.*

In order to avoid a drying step, the soil samples are analysed with their original humidity. Previous approaches could only handle predried samples [5,6], because water would also be thermally desorbed and clog the cryotrap. A preliminary drying step at 100°C failed due to water of hydration set free during the subsequent thermal desorption.

For that reason the TDS unit was operated in split mode. Therefore clogging of the CIS could be avoided, whereas the amount of sample transferred into the CIS was sufficient to guarantee the desired sensitivity.

Materials. The properties of the tested samples are listed in **Table I**.

Sample No.	1	2	3	4	5
Description	Paddy field loam, gravelly, gray-brown. Organic matter invisible.	Loam, sandy, gravelly, stony. Aggradation?	Gravelly sand with plant remains, clayish, uncohesive soil. Single grain structure.	Loam, slightly sandy, residuum of weathered rocks (Devon?). Organic matter invisible. Cohesive soil.	Arable soil, para-brown earth
Clay content in comparison	medium clay content	medium clay content	low clay content	high clay content	
Dry residue	87.4 %	88.1 %	96.1 %	85.4 %	99.3 %
Hydrocarbons, total	1120 mg/kg	400 mg/kg	1140 mg/kg	31 mg/kg	< 10 mg/kg
PCB, total					
- extraction	5.56 mg/kg	6.37 mg/kg	38.3 mg/kg	< 0.05 mg/kg	-
- thermal desorption	2.81 mg/kg	1.33 mg/kg	16.6 mg/kg	< 0.05 mg/kg	-
- recovery rate	50 %	21 %	43 %	-	-
PAH, total					
- extraction	239 mg/kg	137 mg/kg	9.74 mg/kg	189 mg/kg	1.33 mg/kg
- thermal desorption	227 mg/kg	69 mg/kg	9.85 mg/kg	32 mg/kg	1.5 mg/kg
- recovery rate	95 %	50 %	102 %	17 %	113 %

Table I. *Properties of soil samples.*

All soil samples were designated to be decontaminated by pyrolysis. One sample is cohesive due to a comparably high clay content; two samples are of medium clay content, while the fourth is an uncohesive soil with single grain structure. As a reference, a para-brown earth (arable soil) with a very low PAH and hydrocarbon content was analyzed.

Sample preparation. No other sample preparation than crushing the material with a jaw crusher to a maximum grain size of 4 mm was necessary.

Reference methods. PAH´s, PCB´s and Hydrocarbons were determined according to the established standard methods and used for comparison with the thermodesorption results.

    (a) PAH-method [9, modified] : 10 g of sample are mixed with calcinated sodium sulfate and soxhlet extracted with toluene for 15 hours. The reconcentrated extract was cleaned through column chromatography on silica gel, spiked with 9,10-Diphenylanthracene as internal standard and analyzed via GC/MS. The determination limit is established at 0.01 mg/kg dry sample.
    (b) PCB-method according to Klärschlamm-Verordnung [10], but sample preparation as described under (a).
    (c) Mineral oil hydrocarbons according to [2], No. 58 (IR-spectroscopic, after extraction with 1,1,2-Trichlortrifluoroethane.

Analysis conditions.

Column:	50 m DB 5 (J&W)		$d_i = 0,25$ mm		$d_f = 0,25$ μm

Pneumatics:	Carriergas	He	$p_i = 210$ kPa	split x:100

Temperatures:	TDS	-50°C; ↗ 350°C;	60°C/min
	CIS	-150°C; ↗ 400°C;	12°C/s
	Oven	60°C; ↗ 250°C;	10°C/min;
		↗ 320°C;	5°C/min
	MSD	300°C	

RESULTS AND DISCUSSION

Determination of recovery rates of PAH´s with an artificial sample. For performance testing an empty TDS glass tube was filled with purified quartz sand and then spiked with a standard solution of 16 EPA PAH´s [7] . The quartz sand was used to avoid adsorption effects and hindering of the gas flows due to sintering of the sample, an often observed effect with real life samples.

The recoveries were determined through calibration and comparison with the liquid injection of the same standard solution. **Figure 5** and **Table II** reveal that even high boilers like Dibenzo[a,h]anthracene (b.p. 535°C, [8]) are desorbed quantitatively. The standard deviation is not much higher than with liquid injection.
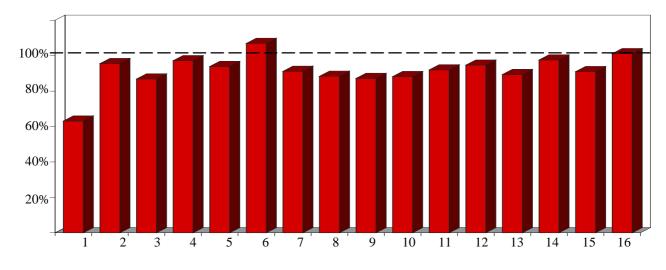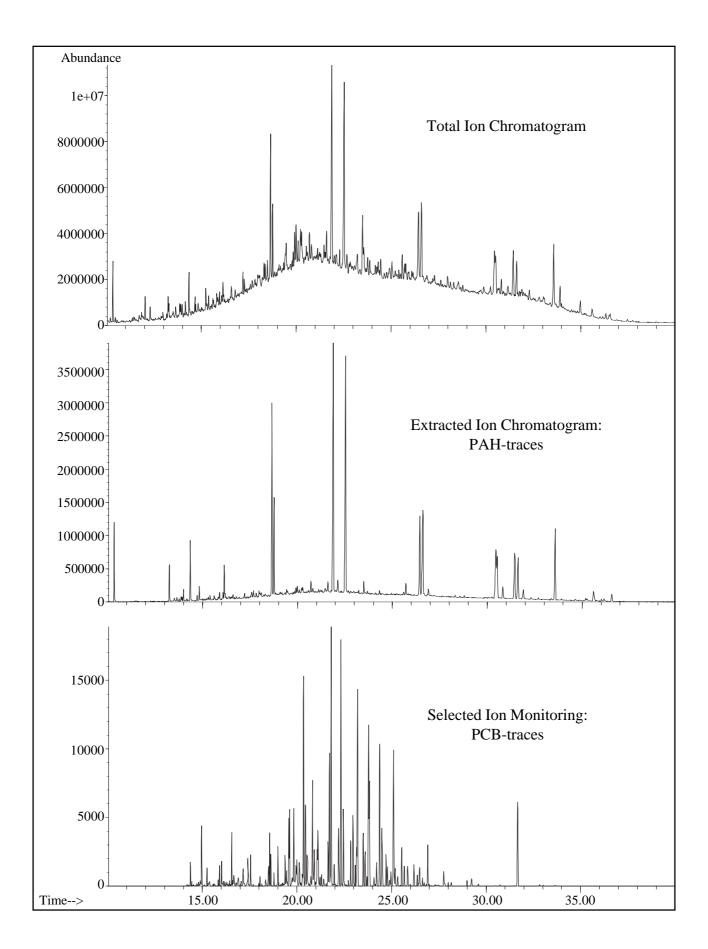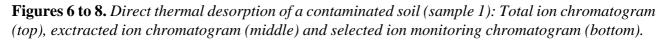
Figure 5. *Recoveries of PAH´s (mean) compared to liquid injection (see also Table II).*

Compound	run 1	run 2	run 3	run 4	mean
1. Naphtalene	45.2	51.4	22.4	133.4	63.1
2. Acenaphtene	98.9	92.9	84.9	105.5	95.6
3. Acenaphtylene	81.0	89.7	70.9	105.8	86.9
4. Fluorene	99.2	94.8	91.8	102.9	97.2
5. Anthracene	90.8	92.9	94.0	97.9	93.9
6. Phenantrene	119.9	106.1	99.8	102.0	107.0
7. Fluoranthene	89.1	91.5	97.9	86.2	91.2
8. Pyrene	86.2	87.6	94.2	85.6	88.4
9. Benzo[a]anthracene	84.0	90.3	88.2	86.2	87.2
10. Chrysene	86.6	90.3	89.7	86.2	88.2
11. Benzo[b]fluoranthene	91.4	93.1	92.6	90.9	92.0
12. Benzo[k]fluoranthene	93.9	94.9	95.2	94.7	94.7
13. Benzo[a]pyrene	91.7	87.7	88.4	89.7	89.4
14. Indeno[1,2,3-c,d]pyrene	100.2	90.8	91.0	108.4	97.6
15. Benzo[ghi]perylene	96.4	85.6	84.3	97.8	91.0
16. Dibenz[a,h]anthracene	101.3	96.3	93.3	113.6	101.1

Table II. *Recoveries (in %) of PAH´s compared to liquid injection.*

Determination of PAH´s and PCB´s in real soil samples. The method used in this application provides all qualitative and quantitative information about the volatile compounds in the sample. The total ion chromatogram (**Figure 6**) clearly reveals that a mass spectrometer is absolutely essential for that purpose, because only in extracted ion chromatogram- (**Figure 7**) or selected ion chromatogram-mode (**Figure 8**) respectively, the necessary selectivity can be achieved.

Figures 6 to 8. *Direct thermal desorption of a contaminated soil (sample 1): Total ion chromatogram (top), exctracted ion chromatogram (middle) and selected ion monitoring chromatogram (bottom).*

Recovery and detection limits. The recovery decreases with increasing boiling temperature possibly due to adsorption effects to values of about 20% (above 500°C, **Figures 9 to 12**) . It can be estimated that the results for the lower boiling compounds, especially Naphtalene, are closer to the real amount in the sample because losses due to evaporation during sample pretreatment, are here minimized.

Samples 1, 3 and 5 show excellent total recoveries, whereas the samples 2 and 4 decrease in recovery (**Table I**). A correlation with the clay content or organic matter could not be found. Detection limits are comparable to the established methods, even the low PAH amounts found in a sample from uncontaminated arable land could be confirmed (**Table I**, sample 5).
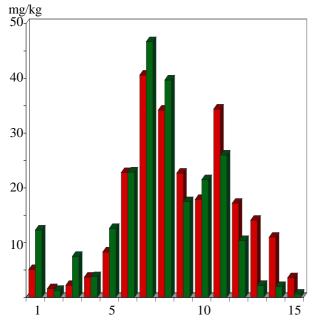

Figure 9. *Comparison between extraction (light grey) and thermodesorption (dark grey), sample 1.*
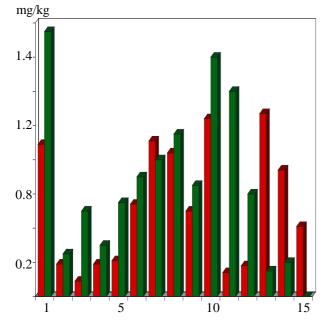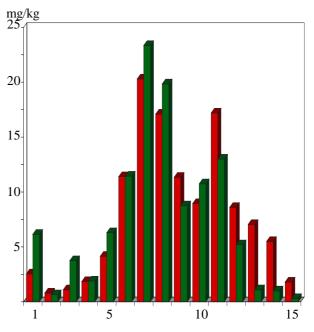

Figure 10. *Comparison between extraction (light grey) and thermodesorption (dark grey), sample 2.*

Figure 11. *Comparison between extraction (light grey) and thermodesorption (dark grey), sample 3.*
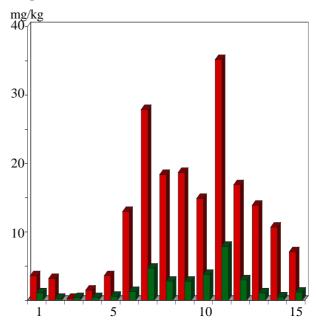

Figure 12. *Comparison between extraction (light grey) and thermodesorption (dark grey), sample 4.*

CONCLUSION

The combination thermodesorption/cooled injection/GC/MS offers for the first time a technique for semi-quantitative trace analysis of volatile contaminants in soils. In contrast to other screening methods also medium and high boiling compounds even in coherent, clay and humus containing soils can be analyzed.

Thermodesorption has proven to be a time saving extraction method. This extraction step can now be reduced to 30 minutes.

Low sample amount (approx. 500 mg) and the necessity to crunch the sample have to be regarded as slight disadvantages.

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