

THEMAL DESORPTION GAS CHROMATOGRAPHY: A QUICK SCREENING
TECHNIQUE FOR POLYCHLORINATED BIPHENYLS

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ABSTRACT

Polychlorinated biphenyls (PCBs) can be purged from a range of sample matrices onto selective Carbotrap adsorbents and analysed. The adsorbent may be solvent desorbed or else as in this study thermally desorbed. The study illustrates that high temperature thermal stripping and combined thermal desorption gas chromatography (TD-GC) offers a cheap quick effective method with good reproducibility. Two thermal desorption systems were evaluated.

INTRODUCTION

PCBs are semi-volatile/involatile materials which are ubiquitous in today's environment. The requirement to screen soil, foliage, water, and air samples for elevated levels above background, due to industrial impact or accidents (1) is of key importance. The report of highly retentive adsorbents which are selective for C5-C12 species and have been demonstrated on Aroclors 1260 led us to evaluate two thermal desorption systems (2).

The first unit, a Spantech TD-4 two stage thermal desorber was evaluated whilst interfaced to an HP-5890 coupled to a VG-70S high resolution double focusing mass spectrometer. The system utilised a liquid CO₂ cooled packed cold trap. The trap can be ballistically heated, and the sample carried through a heated glass lined transfer line terminating in a syringe needle which is inserted into a standard Grob-type split/splitless injector.

The second unit, a Supelco Thermal Desorber consists of two parts. A thermal stripping unit was used for sample preparation (by steam distillation), and a single-stage thermal desorption unit (TDU). This latter system was interfaced to a Perkin Elmer PE8700 gas chromatograph and evaluated on a range of PCBs, including Aroclors 1016, 1232, 1242, 1254 and 1260 in water, soil, foliage and air filters. The sample was transferred to the gas chromatograph via a fused silica transfer line to the analytical column. The system uses no cryofocusing but relies on the zone focusing conferred by the highly retentive adsorbents. This new methodology was compared with traditional solvent based extraction and injection methodology and the recoveries and reproducibility of the method evaluated at the ppb level for PCBs.

EXPERIMENTAL

Spantech TD-4 Unit (available from Spantech, South Godstone, Surrey U.K)

Primary Desorption Temp: 350°C; Secondary Cold trap (Tenax); Low Temp: -25°C, High Temp: 350°C; Transfer line; 250°C.

HP-5890A and VG-70S GC-MS System

Split Injector; 300°C with a split ratio of 50:1; DB 1 column 0.25mm ID, 0.25µ film thickness, 30m length, initial temperature 130°C held for 1 min then 30°C/min to 175°C and finally 3°C/min to 250°C and held for 30 min.

Mass Spectrometric Conditions:

(a) PCBs

VG-70S mass spectrometer in negative ion CI mode with methane as the energy transfer gas, selective ion monitoring mode for the following ions:
154, 188, 222, 256, 290, 324, 354, 358, 392, 426, 460, 494 at low resolution $M/\Delta M = 1000$ (10% valley definition) 1mA emission current, electron energy 100eV.

(b) Paraffins: Chlorobenzenes

EI +ve scanning mode, electron energy 70eV, trap current 500uA, scanning from 550amu to 50amu at 1 s/decade, $M/\Delta M = 1000$ (10% valley definition)

Supelco Thermal Stripper Unit

Spurge gas: Nitrogen 100ml/ min, preheat time set to 5 minutes with a spurge time of 60 minutes and a dry period of 50 minutes. Oven temp. 110°C, block temp. 110°C and tube heaters 80°C. Adsorbent: Carbotrap 150 tubes from Supelchem U.K. Ltd.

Supelco Thermal Desorption System

Primary desorb temp. 350°C for 4 min, desorb flow, 7 ml/min with a split ratio of 1:1 of the sample to the column. The valve and transfer line temperatures were set to 250°C.

Perkin Elmer 8700 Gas Chromatograph

SPB-5 60m x 0.32mm ID x 1µ film thickness capillary column, 150°C for 2 min then ramped at 8°C/min to 290°C and held for 20 min. ECD temperature was set at 300°C with a nitrogen make up flow of 60 ml/min.

Standards:

Internal Standard Spike: Chloronaphthalene (13ng/µl) and decachlorobiphenyl (1.3ng/µl) in toluene. Typically 10ul of this spike mix was applied to the samples.

Calibration Standard: Chloronaphthalene (13ng/µl), Aroclor 1242(3.3ng/µl), Aroclor 1254 (3.3ng/µl), Aroclor 1260 (3.3ng/µl) and decachlorobiphenyl (1.3 ng/µl). Typically 10µl of this was used to calibrate the system.

RESULTS AND DISCUSSION

Spantech TD-4 Thermal Desorber.

When biphenyl, Aroclors 1242, 1254, 1260 and ¹³C monochlorobiphenyl, dichlorobiphenyl and tetrachlorobiphenyls at 1µg/µl were thermally desorbed from a sample tube, only biphenyl could be detected. With these failures it was decided to evaluate the highest non polar and semi polar species which could be transferred using a standard TD-4 unit. A solution of n-paraffins C7-C22 and ¹³C chlorobenzenes were injected onto a Tenax tube each at 1µg/µl level and the mass spectra recorded in positive EI scanning mode. This revealed that transmission up to only C16 and hexachlorobenzene was possible. Unfortunately memory effects became evident at these concentrations, due to the use of an O ring in the heated manifold and valve switching unit and could only be overcome with a re-design of the equipment.

Supelco Thermal Stripper and Thermal Desorption System

The thermal desorption system was initially evaluated by sparging Aroclor 1242, 1254 and 1260 spiked into 20ml of distilled water onto "Carbotrap 150" tubes and comparing this against

standards injected through a standard splitless injector port. The results showed that quantitative results were obtained. This sparging of the calibration standard was then adopted as the method of calibration for all further experiments with the incorporation of an internal standard. Table 1 shows the results for 5 replicate samples and the internal standard recoveries possible on decachlorobiphenyl.

ACTUAL LEVELS SPIKED (ng)	OBSERVED LEVELS CALCULATED (ng)	ISTD RECOVERY (%)	ERROR (%)
20	17	95	14
200	238	97	20
99	116	98	17
99	114	104	14
99*	169	52	70

TABLE 1

* Probably not sparged correct time

The system was then evaluated on real environmental samples known to be contaminated with PCBs. Foliage samples were prepared (3) and 100mg and 50mg of each sample sparged. The effect of the sparge time was also investigated. The most reproducible results were obtained with 50mg of sample and sparge times of 60 min. Table 2 shows the results and illustrates the good reproducibility of the experiments although internal standard recoveries seemed, unusually, to decrease with a longer sparge time.

PCBS IN FOLIAGE

AMOUNT OF SAMPLE	OBSERVED LEVEL ng/g	DEVIATION FROM AVERAGE	TRADITIONAL METHOD	PURGE TIME (min)	RECOVERIES OF ISTD %
100mg	316	54%	870	30	100
	680	2%		30	52
	1080	56%		60	110
Average	692	37%	870		87%
50mg	1501	9%	870	60	26
	1243	9%			44
	1248	9%			53
	1618	17%			45
	1255	9%			59
Average	1373	11%	870		45%

TABLE 2

The chromatograms were easy to interpret with only the early portions (<15 min) having interference peaks. The sample was analysed by traditional methods (4) and found to have a concentration lower than that determined by TD-GC this was attributed either to inhomogeneities of the sample becoming more evident at such small sample sizes, or else to the

problems we encountered with the Perkin Elmer Peak detection software. The same problem was observed when contaminated soil was analysed, although the chromatograms were much cleaner and the recoveries of the internal standard were almost quantitative (Table 3). Air filters have been used to collect airborne PCBs at some installations. These air filters were divided into eighths and the segments put into sparge vessels made upto 20ml with distilled water and the sparged PCBs trapped and analysed on the GC. The results of these experiments are shown in Table 4.

PCBs IN SOIL

AMOUNT OF SAMPLE ng	OBSERVED LEVEL ng/g	DEVIATION FROM AVERAGE	RECOVERIES OF ISTD %	TRADITIONAL METHOD
50 - 60	654	17%	79	470
	1002	26%	75	
	714	10%	111	
	838	6%	117	
	753	5%	110	
Average	792	13%	98%	

TABLE 3

PCBs IN AIR SAMPLES

LOCATION	OBSERVED LEVELS ng/m ³	RECOVERY OF ISTD %
Roof Air	5.66	61%
	3.15	
	2.07	

TABLE 4

CONCLUSION

The Spantech TD-4 unit cannot be used for the analysis of PCBs and has a maximum transmission of C16, hexachlorobenzene and biphenyl. Potential memory effects are apparent at higher concentrations of sample. The Supelco thermal desorber and stripper unit are easy to use quantitative tools easily applied to the screening of samples for elevated PCB levels.

REFERENCES

1. PCBs, PCDDs and PCDFs: Prevention and Control of Accidental and Environmental Exposures, WHO, 1987, EH23.
2. Supelco Reporter. 8 (4), 9-12, 1989
3. Eduljee, G.H., Badsha, K.S. and Mundy, K.J. Chemosphere, 16, 1583, 1987
4. Webb, R.G. and McCall, A.C., J. Chromatog. Sci., 11, 386, 1973.