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Multidimensional Gaschromatographic Techniques in the advancement of Polychlorinated biphenyl (PCB) determination

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1. Introduction: Our present understanding of Polychlorinated biphenys (PCBs) as global environmental contaminants and their possible link to environmental health problems arise from studies conducted during the last few decades. When these complex group of chemicals had been first identified in environmental samples (Jensen, 1966)., the then available packed column gas chromatographic techniques were insufficient for the needed separation of individual chlorinated biphenyls (CBs) Introduction of high-resolution GC column techniques have greatly improved this picture presently. Even then no single GC column could offer the needed base-line separation of all the 209 PCB congeners. This has to be achieved using multidimensional gas chromatographic techniques using at least two high resolution columns of different polarity (Duinker, et al., 1988, Schulz, et al., 1989). In the meantime, to circumvent this problem, alternative techniques involving pre-GC separation of CBs into structure-dependent classes using several available column materials such as graphite etc. have been attempted (Creaser, et al., 1992). This is usually accompanied with high resolution mass spectrometry.

A joint study by Japanese, Dutch and German scientists have tested such pre-GC column materials for their proven separation efficiency (Kannan, et al., 1991). It was concluded that at ratios at which CBs occur normally in environmental samples coelution of CB congeners, especially in the determination of toxic non-*ortho* CBs was inevitable. Studies conducted in the USA using HRGC-HRMS demonstrated this point (Kuehl, et al., 1991, Schmidt and Hesselberg, 1992).

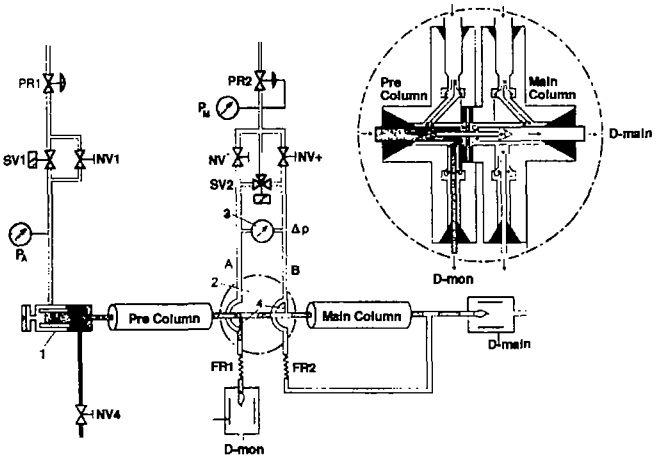
Most of the scientific reports on PCBs in recent times acknowledge this problem. The problem of coelution of compounds is more complex than one normally visualises because every new high resolution column that is being used brings with it, its own colelution pattern. This makes inter laboratory comparison of CB results even more complex. There is an urgent need for scientific consensus on using high resolution GC columns for CB determination. There is no need to point out that a column for which retention time indices of all the 209 PCB congeners have been established should be the choice. Till now, only SE-54 full fill this requirement. Unfortunately, this is not the choice of all the PCB researchers around the world.

Multidimensional gas chromatography (MDGC) technique with high resolution capillary columns such as SE-54 and OV-210 are still suited for accurate determination of CBs. We present here our preliminary results on a new MDGC-ECD system developed by Fisons.

2. Materials and Methods:

MDGC-ECD operating systems:

Siemens SiChromat system: All these years in our laboratory, we have used a MDGC-ECD system



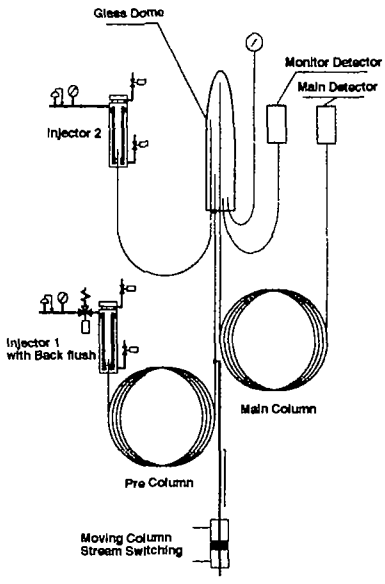
that was developed by Siemens (SiChromat II). The principle of operation of this system is as follows: The "live" switching system contains a special coupling unit ("live" T-piece) as part of the pneumatic bridge connection. The pressure P_M is applied to the flow resistors NV^+, NV^-, FR1 and FR2. The differential pressure Δp at the bridge diagonal can be adjusted in the positive direction using NV^+, in the negative direction using $NV^-$and 'switched over instantaneously using SV2.

The flow quantity and direction in the coupling tube can therefore be selected as required. The sample can be routed from the precolumn to the main column or to the monitor detector. The coupling unit is designed such that all gaps, especially that between the column and the coupling tube, are small and can thus be flushed easily. Back diffusion from the sample and peak deformation are therefore completely prevented. The coupling unit consists of a stainless steel body, a platinum-iridium capillary and a small adsorption-free metal gasket. Special flushing channels in the transverse path ensure perfect transfer of the sample through the fused silica capillary to the monitor detector.

Ample examples have been presented in our previous publications (Duinker et al. 1988; Schulz et al. 1989 and Kannan et al. 1991) on the performance of Siemen's SiChromat II.

Fisons M.C.S.S. System: Fison has come out with a system that advances further the use of MDGC. Their new development does not utilise any pneumatically forced switching of column effluents. The new "moving column stream switiching" (MCSS) cuts out parts of effluents from a pre column which *can be transferred completely or partially onto a second column.* This is done simply by moving the outlet of the precolumn very close towards the inlet of the second column, both installed in a dome shaped glass tip, located inside the GC-oven. Due to the fact that the analytes never get into contact with metal or any other absorptive material, excellent qualitative and quantitative results can be

achieved. Being free from diffusion, ECDs as well as MS systems can be used as detectors without limitation.



For the present investigation we have used this system with EC detectors. The GC was connected with a SE-54 (60m, 0.32 mm id., 0.25 μm) and a OV-210 (30 m, 0.32 mm id., 0.25 μm) column in series. Hydrogen was used as carrier gas. Both ECDs were kept at 300 °C.Temperatur programming conditions were first column from 70 to 160 °C at 25 °C min^{-1}, from 160 to 270 °C at 6 °C min^{-1} and then holding 270 °C for 10 min and the second column 20 min at 100 °C and then from 100 to 160 °C at 25 °C min^{-1}, from 160 to 240 °C at 4 °C min^{-1} and then holding the temperature for 2 min. On-column injection was used.

3. Results and Discussion:

Several environmental samples have been tested using the newly installed system. The figure in the next page shows chromatograms recored by monitor ECD as well as by main ECD. The sensitivity of the main ECD is far more higher than the monitor ECD. CB congeners are regularly determined at 0.1 to 0.5 pg (absolute) in the former whereas CBs give measureable peaks at 10 to 30 pg in the latter.

MDGC-ECD systems still offer one of the easy way to determine all the 209 CB congeners in environmental samples at differing ratios (see the difference in the ratio of CB-110 to CB-77 in the particle sample shown in the figure). The introduction of Fisons new MDGC system makes coupling of HRMS possible and that will be our future task. In the meantime, efforts are being made to resolve the extend of coeluting interferences in single column HRGC-HRMS in comparison to MDGC-ECD methods.

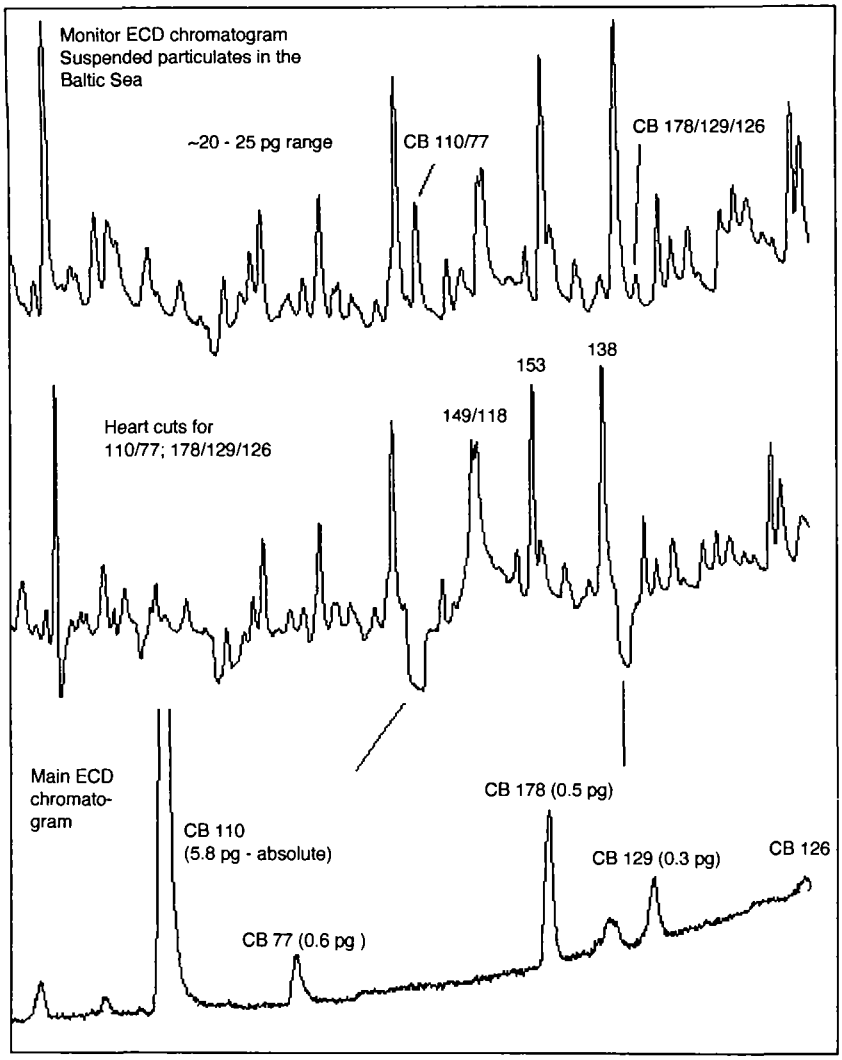
4. References:

1 C. S. Creaser, F. Krokos and J. R. Startin, (1992). Analytical methods for the determination of non-ortho substituted chlorobiphenyls: A review. *Chemosphere*, **25**, 1981-2008.

2 J. C. Duinker, D. E. Schulz and G. Petrick, (1988). Multidimensional gas chromatography with electron capture detection for the determination of toxic congeners in PCB mixtures. *Anal. Chem.*, **60**, 478-82.

3 S. Jensen, (1966). Report of a new chemical hazard. *New Sci.*, **32**, 612.

4 N. Kannan, G. Petrick, D. Schulz, J. Duinker, J. Boon, E. V. Arnhem and S. Jansen, (1991). A comparison between activated charcoals and multidimensional GC in the separation and determination of (non-*ortho* Cl substituted) toxic chlorobiphenyls. *Chemosphere*, **23**, 1055-1076.



5 D. W. Kuehl, B. C. Butterwoth, J. Libal and P. Marquis, (1991). An isotope dilution high resolution gas chromatographic-high resoltion mass spectrometric method for the determination of coplanar polychlorinated biphenyls:Application to fish and marine mammals. *Chemosphere*, **22**, 849-858.

6 L. J. Schmidt and R. J. Hesselberg, (1992). A mass spectroscopic method for analysis of AHH-inducing and other polychlorinated biphenyl congeners and selected pesticides in fish. *Arch. Environ. Contam. Toxicol.*, **23**, 37-44.

7 D. E. Schulz, G. Petrick and J. C. Duinker, (1989). Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.*, **23**, 852-859.