Dual Microbore Column GC/HRMS Analysis of Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Dioxin-Like Polychlorinated Biphenyls (DLPCBs).

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Introduction

The use of microbore Gas Chromatograph (GC) columns to reduce analysis times by 50-80% with Fast GC (column head pressures of >60psi and temperature ramp rates of >75EC/min.), has been demonstrated previously for a variety of organic analytes[1]. Furthermore, the capability for dual columns with dual autosamplers and simultaneous injection allows for the development of more efficient, less expensive analytical testing methods. This paper describes the simultaneous injection of separate Dioxin/Furan/Co-planar PCB and Mono-ortho PCB fractions on microbore GC columns to significantly reduce analysis times.

Up to three separate analytical methods can be used to analyze for Polychlorinated Dibenzo-p-dioxins (PCDDs) Polychlorinated Dibenzofurans (PCDFs)[2], Co-planar Polychlorinated Biphenyls (PCBs) and ortho-substituted PCBs[3]. The Ontario Ministry of Environment (MOE) has developed an analytical method (DFPCB3418) for the determination of PCDDs, PCDFs and all 12 DLPCBs as identified by the World Health Organization (WHO). With MOE method 3418, PCDD/Fs and co-planar PCBs are analyzed from one sample fraction and the remaining mono-ortho DLPCB congeners are analyzed from a second fraction. Due to the presence of polychlorinated diphenyl ethers (PCDEs) in the mono-ortho sample fraction and their known interference with PCDFs using mass spectrometry, this fraction is analyzed separately to avoid these interferences and false positive results for the PCDFs. Using the method reported here, PCDDs, PCDFs and DLPCBs can be analyzed from the same injection event.

Method

Extracts were prepared using a 3 stage cleanup (silica/alumina and carbon) as described in detail elsewhere[4,5]. All analyses were performed using an HP 6890+ GC coupled to a Micromass Autospec-Ultima-NT HRMS @ 10,000+ RP, running MassLynx (V3.5) software.

Two columns were installed in parallel into the HRMS ion source, a 20M Restek Rtx5, 0.1Φmm i.d., 0.1Φm film thickness and a 40M Restek Rtx5, 0.18mm, 0.18Φm.

Both HP 7683 Autosamplers were set up with nanolitre adapter belts necessary to accommodate 5ΦL syringes and allow for .5ΦL injection volumes. The .5ΦL injection volume was required to avoid overloading the injector and columns. Although a .2ΦL injection volume would be preferable on the 20M column, there are software limitations which precludes individual control of front and back autosampler/injection parameters and therefore a .5ΦL injection volume was used on the 20M column.

A double taper, 2mm injection liner was used on the 40M column and a single gooseneck, 2mm liner was used in the injection port for the 20M column.

The GC conditions were as follows:

40M (front injector - 280EC)	20M (back injector - 280EC)
Rtx5, 0.18mm, 0.18Φm	Rtx5, 0.1mm, 0.1Φm
380kPa, (constant pressure)	610 kPa, (constant pressure)

Start temp:	130EC	hold	1 min.
52EC/min.	200EC		0 min.
2.9EC/min.	235EC		10.2 min.
6.9EC/min.	300EC		3.5 min.

The sample fraction containing PCDD/Fs and co-planar DLPCBs was injected on the Rtx5 40M column while the fraction containing the mono-ortho DLPCBs was injected simultaneously onto the 20M Rtx5 column. A six function SIR experiment was set up to monitor PCDD/Fs and DLPCBs. Ions monitored for detection of native analytes had a dwell time of 50ms. Detection of corresponding $^{13}C_{12}$-labeled analyte ions had dwell times of 25ms. Delay times were set at 10ms. The HRMS experiment was also designed to survey for potential interference from PCDEs in the PCDF traces and for co-elution from PCBs of higher degree of chlorination.

Results and Discussion

GC parameters were optimized to maintain critical congener pair separations required for PCDD/F analysis, separation of 2,3,7,8-TCDD from 1237/1238-TCDD and PCB123 and PCB 118 for DLPCB analysis. The chromatographic resolution specifications for 2,3,7,8-TCDD were easily met on the 40M column. There were no interferences or artifacts seen in the Dioxin/Furan ion channels.

The data in Figure 1 is from a spiked blank soil sample, fortified with 17 native PCDD/Fs, 12 WHO DLPCBs and corresponding $^{13}C_{12}$- labeled surrogates. This figure shows the 8 mono-ortho DLPCBs from the 20M column, the 4 co-planar congeners from the 40M column and retention times for the 1st and last eluting tetra chlorinated PCDF congeners. Separation of PCB123 and 118 is shown in the top chromatogram.

Separation of some PCDDs and PCB ion channels require almost 40,000 resolution. MOE Method 3418 uses ^{37}Cl-TCDD as a cleanup standard and artifacts of its isotope cluster is seen in some PCB 126 ion channels (bottom trace Figure 1). This artifact does not co-elute with PCB 126 and thus does not affect quantification of PCB126.

The sample preparation scheme (Method 3418) was originally developed to force PCDEs into the mono-ortho DLPCB fraction, away from the PCDD/Fs. To prevent the interference of PCDEs with PCDFs, it is necessary to elute the mono-ortho DLPCB fraction, including all interfering PCDEs, from the 20m column prior to the elution of corresponding PCDFs from the 40m column. Figure 1 shows that with simultaneous injection on parallel columns, all of the congeners in the mono-ortho DLPCB

fraction (with the exception of PCB 189) elute from the 20M column before the PCDD/Fs elute from the 40M column. Furthermore, many of the higher chlorinated PCBs that are known to co-elute with the co-planar PCBs on 5%phenyl columns (e.g. PCB 110 with PCB 77), elute from the 20M column in the mono-ortho fraction well before the co-planar congeners on the 40M column.

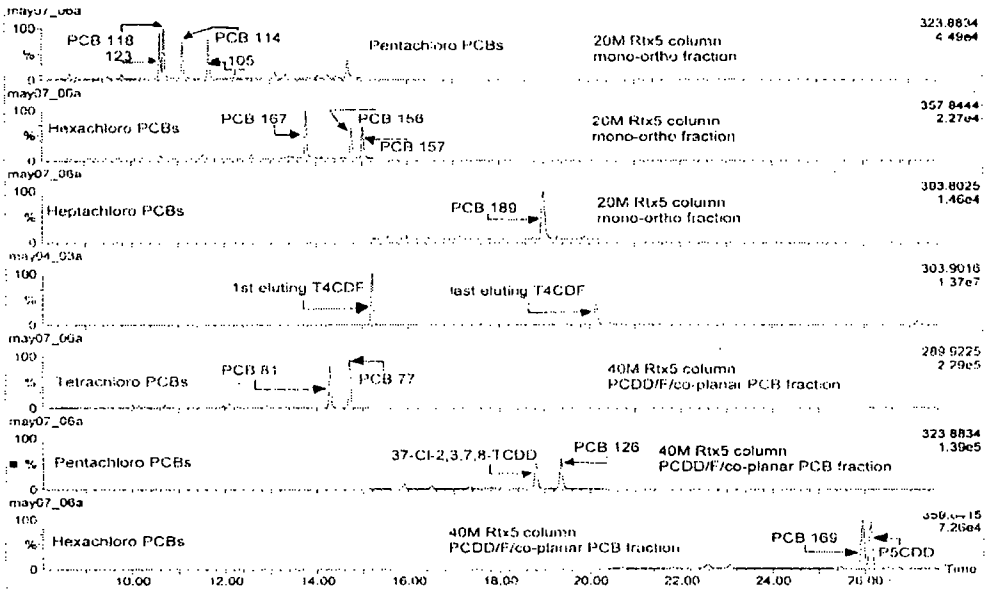
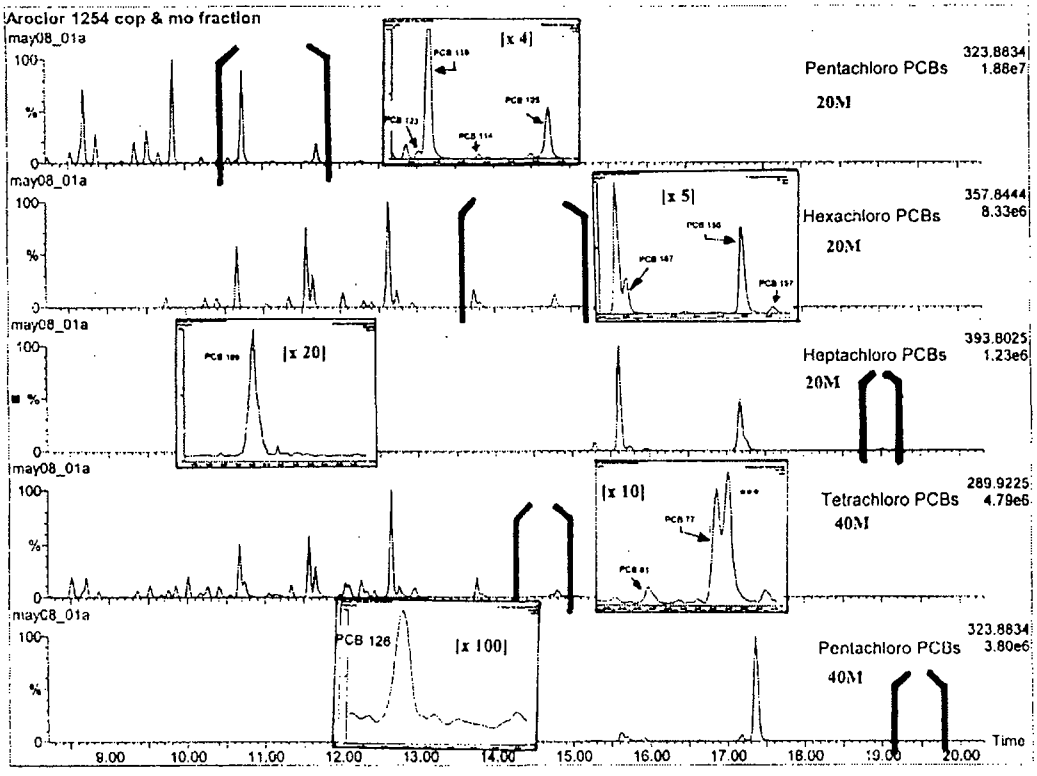


Figure 1 – Simultaneous injection of mono-ortho and PCDD/F/coplanar PCB fractions from a Spiked Matrix Sample

The peak eluting after PCB169 is the contribution from native 1,2,3,7,8-P_5CDD. This specific trace was included to show that PCB 169 and 1,2,3,7,8- P_5CDD are separated chromatographically on the 40M column. This also occurs on 60M columns in standard Dioxin methods (e.g. 1613).

Figure 2 shows results of simultaneous injection of both fractions generated using Method 3418 for a sample of pure Aroclor 1254. Aroclor 1254 contains PCB congeners with 5-8 chlorines and is expected to result in the greatest amount of interference for the DLPCBs. Traces are shown along with a magnified portion relative to the time of elution for the DLPCB congeners. PCB 169 was not detected. Relative contributions of tetra-through-hepta-chloro DLPCBs correlate well with values reported elsewhere for Aroclor 1254[6].



Conclusions

This method reduces the time of analysis for the determination of all PCDDs, PCDFs and DLPCBs to under 40min. with time savings of approximately 60% over standard methods which require two separate injections with run times of about 50 minutes each. The PCDEs, mono-ortho DLPCBs and interfering PCB congeners resident in the mono-ortho fraction elute on the 20M column well before the Dioxin, Furan and coplanar DLPCB congeners of interest, free from interferences on the 40M column. Additionally, group totals can also be determined on the 40M microbore columns which actually have more theoretical plates than the corresponding 60M column[1].

Figure 2 - Simultaneous injection of mono-ortho and PCDD/F/coplanar PCB fractions from Aroclor 1254 (boxes contain magnified chromatograms for time indicated with hash marks).

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