

METHOD FOR THE SIMULTANEOUS ANALYSIS OF PCDD/FS AND DLPCBS USING DUAL MICROBORE COLUMN GC/HRMS IN SINTER ASH SAMPLES, ALLOWING THE DETERMINATION OF 'TOTALS' GROUP CONCENTRATIONS

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Introduction

The capability for analysis using dual microbore GC columns with dual autosamplers and simultaneous injection of sample extracts has been demonstrated for Polychlorinated Dibenzo-p-dioxins/Furans (PCDD/Fs) and Dioxin-Like Polychlorinated Biphenyls (DLPCBs)¹, giving a reduction in analysis time and costs. This paper describes the implementation of a method using dual microbore GC columns, with a single autosampler and staggered injections to further increase separations, necessary for the analysis of sinter ash samples containing large concentrations of non-2,3,7,8-chlorinated PCDD/Fs.

Method

A number of sinter ash extracts were extracted and cleaned up using methods based upon legislative USEPA methods^{2,3,4}. All analysis was performed using an Agilent 6890+ GC coupled directly to a Micromass Autospec Ultima-NT HRMS, in positive EI mode, an electron energy of 30eV and resolution greater than 10,000RP. All acquisition was performed using Masslynx version 4.0 software. Injections were made using a CTC GC-PAL autosampler, controlled using CTC cyclecomposer interfaced directly into Masslynx.

The GC oven was fitted with split/splitless injectors, containing 2 mm ID quartz injection liners. The GC columns were installed, interfaced directly into the ion source. Front injector: - J&W DB5-ms, 20 m, 0.180 mm ID, 0.180 mm film. Back injector: - Restek RTX5, 40 m, 0.180 mm ID, 0.180 mm film.

The autosampler control was set up such that injections of the DLPCB fractions were made to the front injector (20m column) and 2.4 minutes later the PCDD/F fractions were injected to the back injector. Both injections were of 1ml volumes.

The GC conditions were as follows: -

Front injector 280 °C, splitless, purge time 5min, Helium flow 0.8ml/min constant flow.

Back injector 280 °C, splitless, purge time 5min, Helium flow 0.6ml/min constant flow.

Oven temperatures

Time(min)	Rate(°C/min)	Temperature(°C)
5	0	140
0	11.0	220
0	1.4	260
4.0	6.3	310

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A six-function voltage selected ion recording acquisition system was used for analysis, monitoring the dioxin-like PCBs, PCDD/Fs and QC check channels for lockmass check and Chlorinated diphenyl ethers. The total cycle times were such that a minimum of eight data points across each GC peak were acquired.

Results and Discussion

The complex nature of sinter ash extract chromatograms meant that GC conditions had to be optimised firstly to meet the separations required for legislative methods² for selected congener pairs (2,3,7,8-TCDD from close eluting non-2,3,7,8-TCDDs), (PCBs 123 and 118). After this the conditions then needed to be further optimised to ensure adequate separations of all 2,3,7,8 chlorinated PCDD/Fs from close eluting non-2,3,7,8 chlorinated PCDD/Fs, most specifically the hexa-chlorinated congeners. Using fast GC ramps reduced the separations in this group to a point that quantification could not be achieved rapidly and reliably.

It was found that using a GC ramp, based upon one translated from a standard 60 m 0.250 mm ID, 0.25 mm film method used for routine PCDD/F analysis (translation performed using Hewlett Packard GC method translation software version 2.0) provided suitable separations for these congeners, whilst maintaining good separations for the lower chlorinated DLPCBs and PCDD/Fs.

Figure 1 shows the separations obtained for the HxCDD/Fs, plus the separation of PCB169 from 1,2,3,7,8-PeCDD.

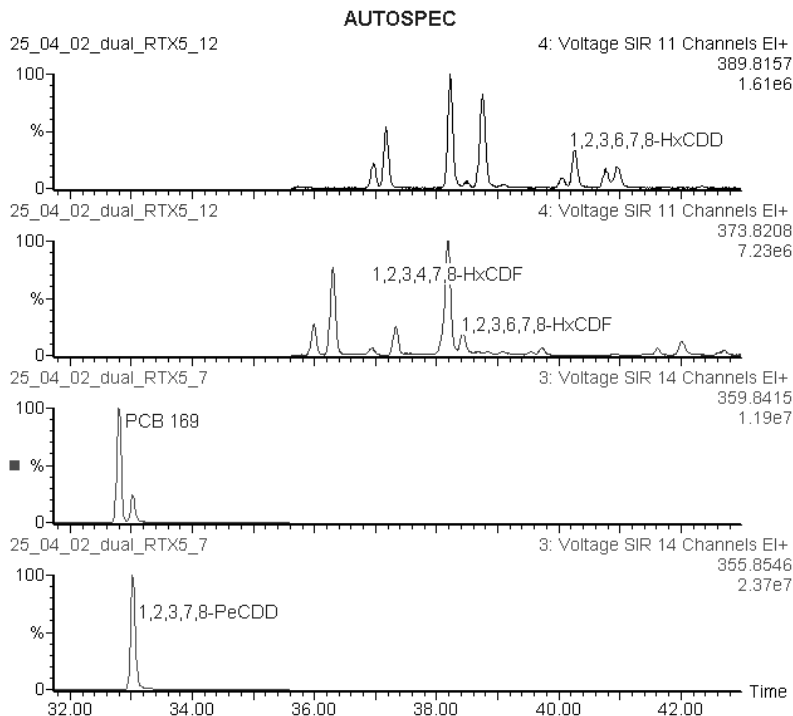


Figure 1. separation of critical congener pairs, including the HxCDD/F groups for a sinter ash sample.

Delaying the injection of the injection of the PCDD/F and non-ortho PCB fraction onto the 40m column by 2.4 minutes allowed the determination of totals concentrations for all levels of chlorination of PCBs injected (tetra-hepta), giving separation of the last eluting hepta PCB from the 20 m column and the first eluting tetra-furan from the 40 m column. This also increased the separation of the CDPEs that were forced into the mono-ortho PCB fraction during clean-up from the PCDD/F channels where they were likely to cause interference.

Figure 2 shows the separation of the hepta-chloro PCB totals group on the 20 m column from the first eluting tetra-furan on the 40m column.

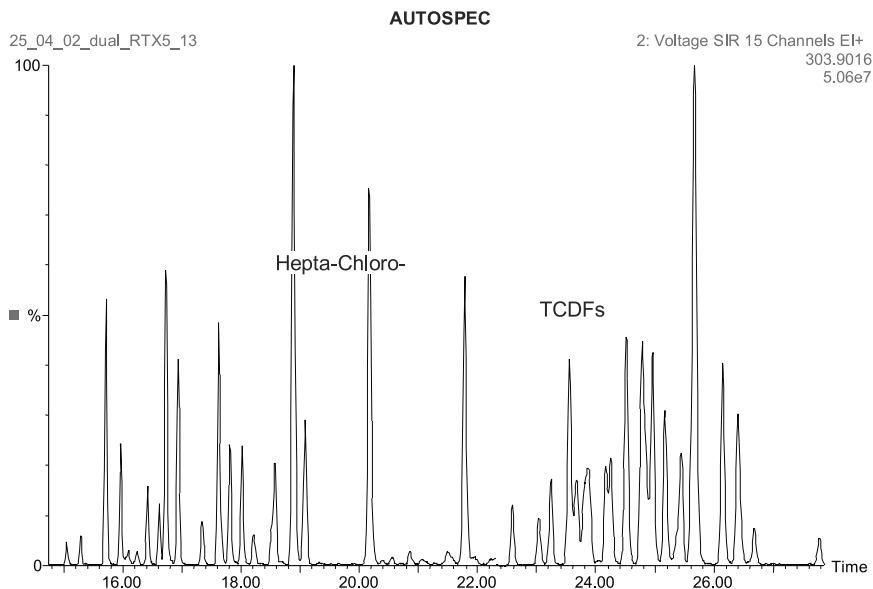


Figure 2. PCB and PCDD/F totals calculation ability.

The sample analysis was performed by the acquisition of a five-point calibration curve, injecting Wellington WHO-PCB CS2 to CS6 standards on the 20 m column and mixed WHO-PCB CS2-CS6 with EPA1613 CS1-CS5 on the 40 m column.

The linearity of the calibration curves was found to be very good, with rrf %RSD values easily meeting the required QC limits. Figure 3 displays an example calibration curve acquired for 2,3,7,8-TCDD co-injected with WHO-PCBs, with a rrf %RSD of 1.0 %. The calculated WHO-TEQ limit of detection, based upon the signal to noise values for the lowest standard and a sample mass of 10 g was 0.0082 pg/g WHO-TEQ.

Conclusions

Applying this method reduces the analysis time and hence increases the throughput in the environmental laboratory. It also enables the reporting of totals groups for the tetra to hepta chlorinated

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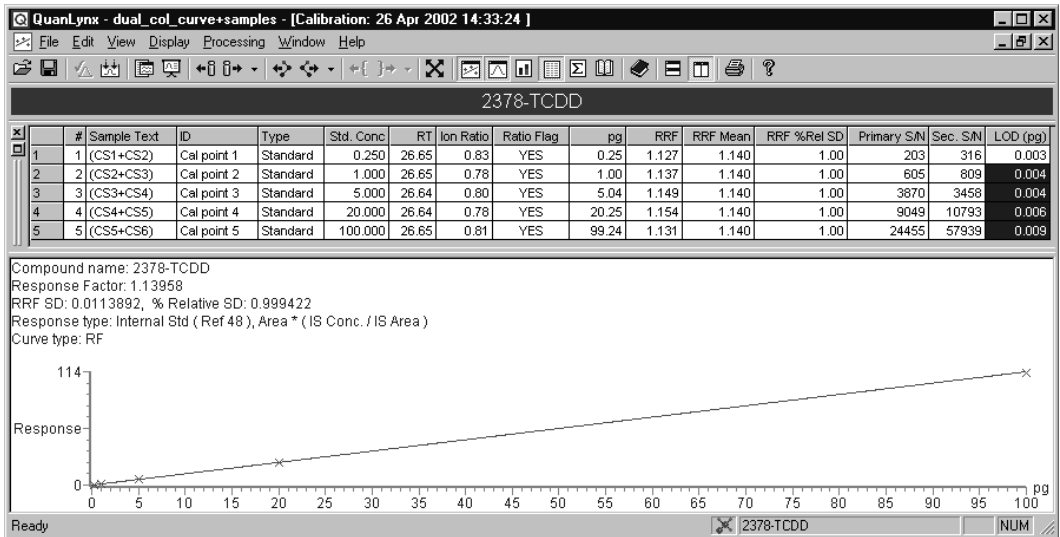


Figure 3. example calibration curve for 2,3,7,8-TCDD, acquired immediately prior to sample analysis.

PCBs plus tetra to hepta chlorinated PCDD/Fs.

As described previously¹ the chlorinated diphenyl ethers injected from the mono-ortho fractions are separated from the analyte channels of interest, with the separation increased by the use of staggered injections.

References

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4. USEPA Office of water, method 1668 revision A. "Chlorinated Biphenyl Congeners in water, soil, sediment and tissue by HRGC-HRMS", December 1999