INCREASE OF SENSITIVITY BY USING TIMED-CRYOGENIC ZONE COMPRESSION (t-CZC) APPLIED TO BDE-209 ON GC/HRMS

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Introduction

Sensitivity for POPs analysis is of great concern, especially when only limited Sample amount is available. Therefore a sensitive mass spectral detection and optimized chromatography is needed. The conditions to obtain the required chromatographic separation power consequently lead to peak broadening and reduced peak height.
An additional challenge analyzing BDE-209 is its thermo labiality. Therefore PBDE Methods are optimized to a low eluting temperature in regards of the BDE-209. With a new developed Hardware, timed Cryogenic Zone Compression can also be applied to BDE-209 and used as a helpful tool to increase the LOD.

GCxGC experiments which are typically used to increase the separation power of complex mixtures show as a side effect sharp narrow peaks with increased SN. By using long modulation times, this effect can be used to increase sensitivity for the analysis of POPs[1,2].

In contrast to permanent modulation like used in GCxGC, the timed Cryogenic Zone Compression allows the selection of analytes which can be completely trapped and refocused at the end of the analytical column followed by re injection to a short column section towards the MS. The resulting chromatography peak shape observed at the MS is now defined by the dimensions of the second column and the reinjection conditions.

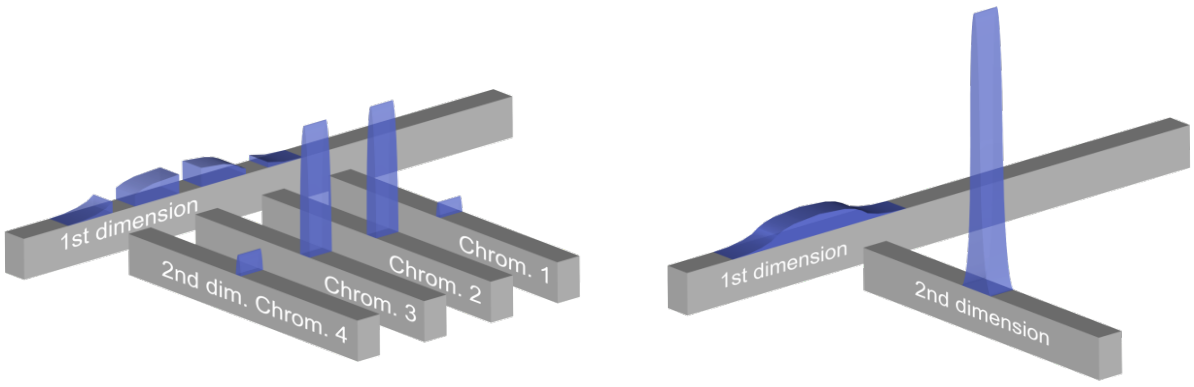

Figure 1. Cryogenic signal enhancement in GCxGC versus CZC.

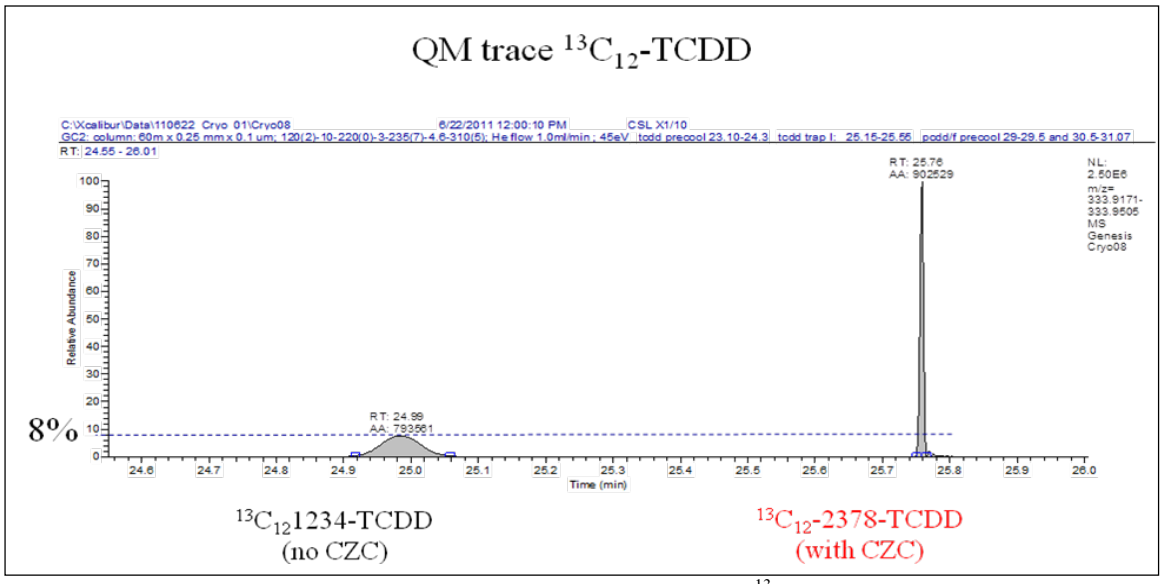

Figure 2. Comparison of non-cryofocused versus cryofocused peak of $^{13}C_{12}$ TCDD internal Standards with same instrument response.

Materials and methods

All experiments were carried out on Thermo Scientific DFS™ high resolution mass spectrometer coupled to a Thermo Scientific GCxGC Trace Ultra™ or modified Trace 1310 GCs in combination with ether a Thermo Scientific TriPlus™ or RSH™ Auto sampler.

A GCxGC cryogenic modulator in timed mode was used for Dioxin analysis while a new Hardware was developed based on a Thermo Scientific Trace 1310 GC and applied to PBDE measurements. The cryo Jet was located at the end of the analytical column in a distance between 4m and 0.5m to the Mass Spectrometer.

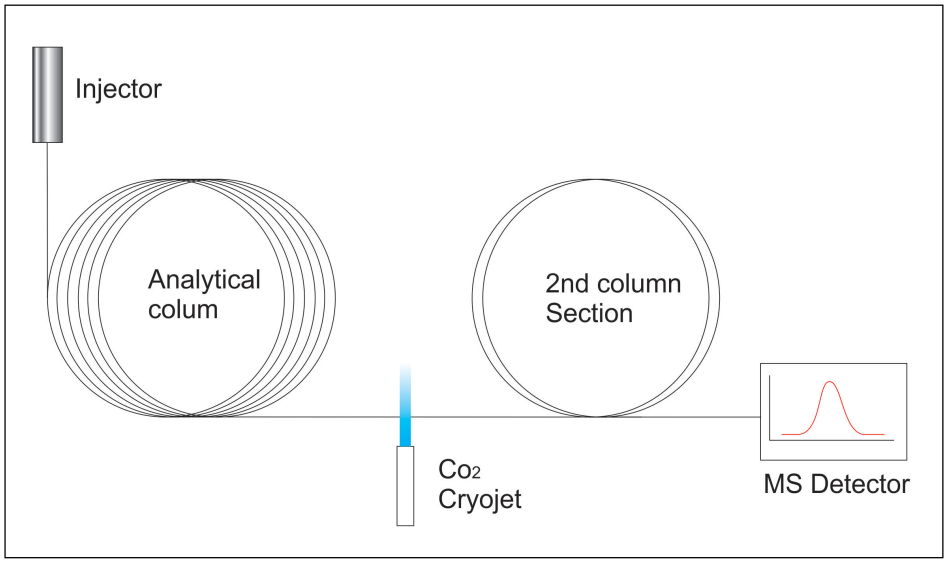

Figure 3. Schematic of the timed cryogenic zone compression.

Results and discussion

In a single measurement, the peak height for selected analytes can be increased by using this technique. The analytes stay well separated but show a comparable small peak width with a resulting gain in peak height up to a factor of 10 compared to the unfocused peak. All other congeners where the cryo focusing is not applied stay like in a normal measurement. Timed Cryogenic Zone compression was proved to increase sensitivity for Dioxin and Furans congeners using a modified GCxGC cryo modulator[3].

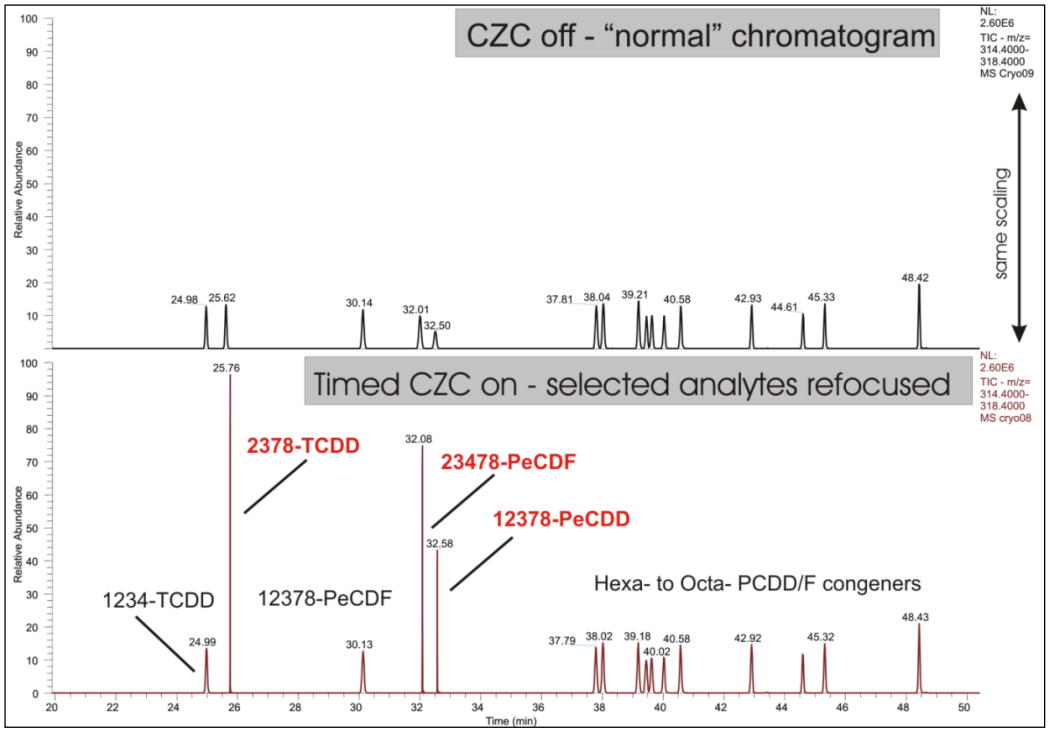

Figure 4. Upper mass trace - standard dioxin/furan chromatogram; lower mass trace: CZC chromatogram with 3 CZC cryo-focused target analytes; same scaling for both traces

For 2,3,7,8-TCDD a LOD in the sub femto gram range was achieved using this technique.

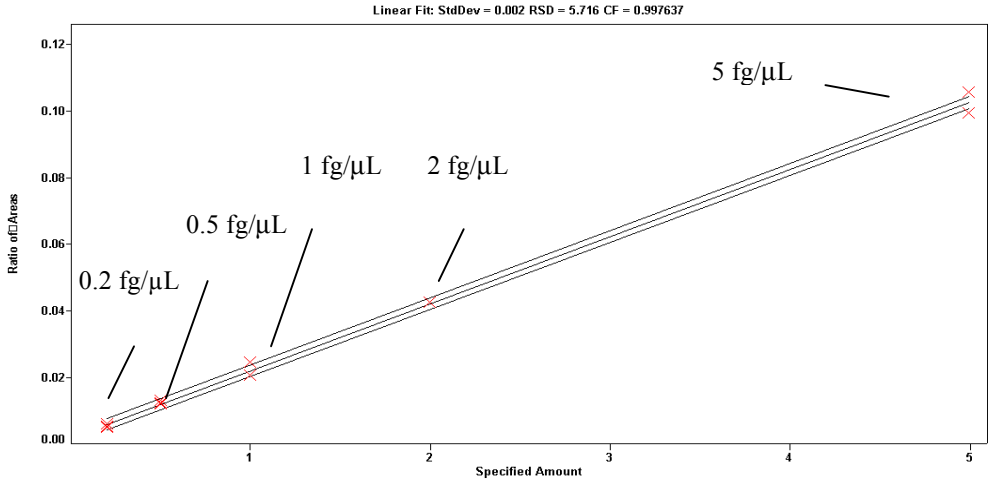

Figure 5. Triplicate five point calibration curve of TCDD (4uL injected) using t-CZC.

Temperature profiling of the GCxGC Modulator showed a relatively slow cool down to a limited temperature when used in timed mode. The cause of this behavior is due to the hardware, designed for using it in modulation rather than timed mode. A slow cool down makes a precise timing more difficult especially for high boiling components like BDE-209. Therefore a new Hardware was developed to improve the cool down speed and the achievable minimum temperature. Using this Hardware, timed controlled cryogenic zone compression could also be applied to BDE-209 into an existing PBDE method with an eluting temperature of 300°C for BDE-209. It was also possible to decrease the length of the column section between modulator and MS to approximately 50 cm compared to 4 m using the GCxGC modulator. This and the faster cool down speed made the determination of the timing for the cryo jet a lot easier and a precise trapping of the peak could be performed.

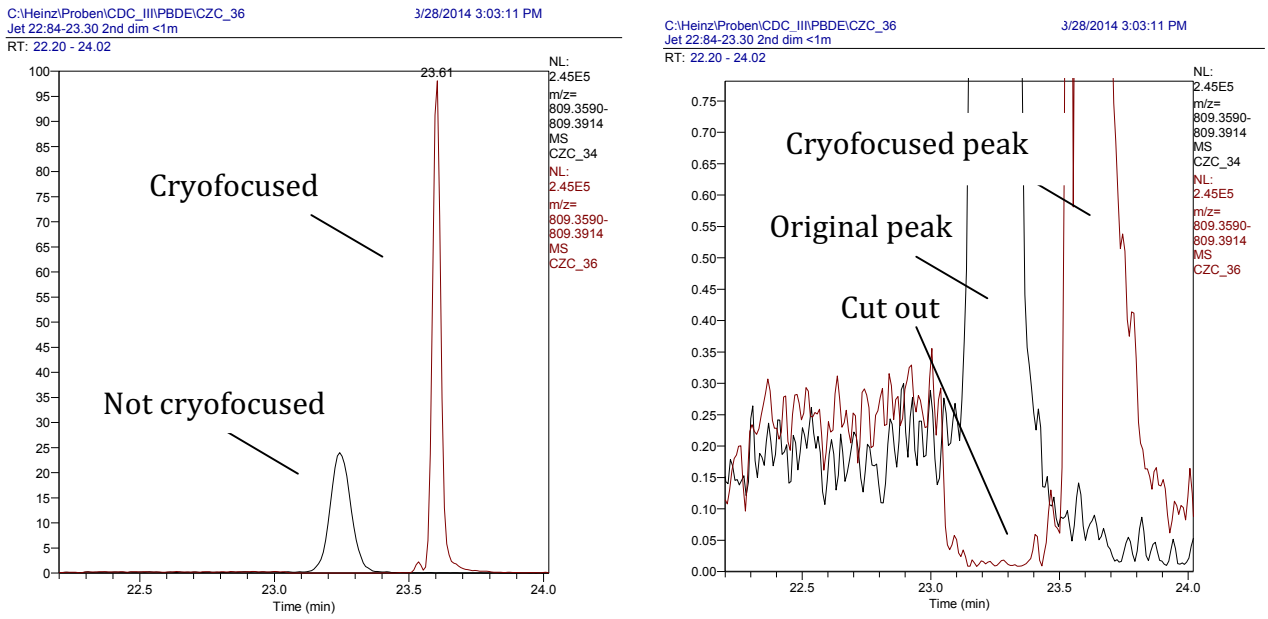

Figure 5a. Overlay of non non-cryofocused and cryofocused peak of BDE-209
Figure 5b. Zoom in the baseline shows a precise cut out at the original peak location.

Acknowledgements
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References:
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2. Focant, J-F., Pirard, C., Eppe, G., De Pauw. (2005), *Journal of Chromatography A*, 1067, 265–275
3. Krumwiede D, Mehlmann H, D'Silva K. (2012); *Chromatography Today* February / March 2012