INCREASING SENSITIVITY OF BDE-209 USING TIMED-CRYOGENIC ZONE COMPRESSION (t-CZC)

Mehlmann H[1]*, Krumwiede D[1], D'Silva K[1]
[1]POPs Center of Excellence, Thermo Fisher Scientific, Hanna-Kunath Strasse 11, 28199 Bremen, Germany

Introduction:
Many POPs are toxic at trace concentrations. Consequently method sensitivity is paramount when only limited sample amount is available. Highly optimized mass spectral detection and chromatography is required to ensure toxic POPs are sufficiently resolved from other nontoxic isomers or isobars. The conditions to obtain the required chromatographic separation are frequently compromised; and lead to peak broadening and reduced peak height for some compounds. This situation is apparent with multi-analyte methods including PBDEs. Careful chromatographic separation of early eluting analytes often compromises the chromatography and sensitivity of late eluting analytes such as BDE-209.

An additional challenge analyzing BDE-209 is that it is thermally labile. Therefore most PBDE methods are optimized to use low eluting temperature in regards of the BDE-209[1]. This can reduce thermal degradation[1], but increases peak broadening and compromises ultimate sensitivity.

GCxGC experiments which are typically used to increase the separation power of complex mixtures show as a side effect sharp narrow peaks with increased S/N. By using long modulation times, this effect can be used to increase sensitivity for the analysis of POPs[2,3].

In contrast to permanent modulation used in GCxGC; timed Cryogenic Zone Compression (t-CZC) allows the selection of analytes, based on their retention time, see Figure 1. These analytes can be completely trapped and focused towards the end of the analytical column followed by release or re-injection onto the column shortly before the mass spectrometer. The resulting chromatographic peak shape observed at the MS is now defined by the dimensions of the second column and the reinjection conditions as shown by Krumwiede et al[4].

Figure 1 **Cryogenic signal enhancement in GCxGC versus t-CZC[4].**

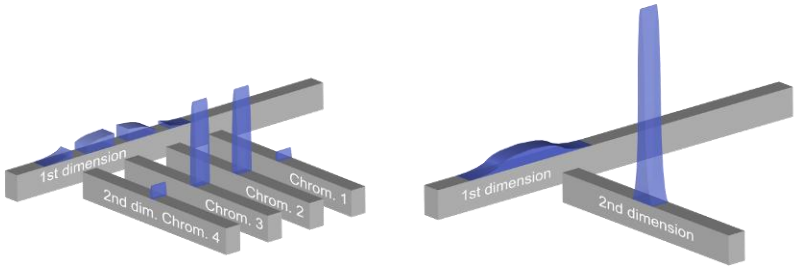
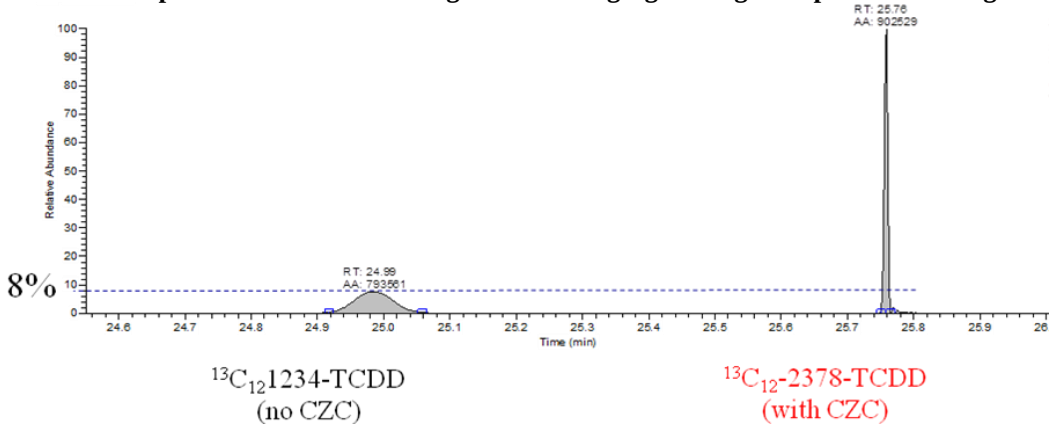


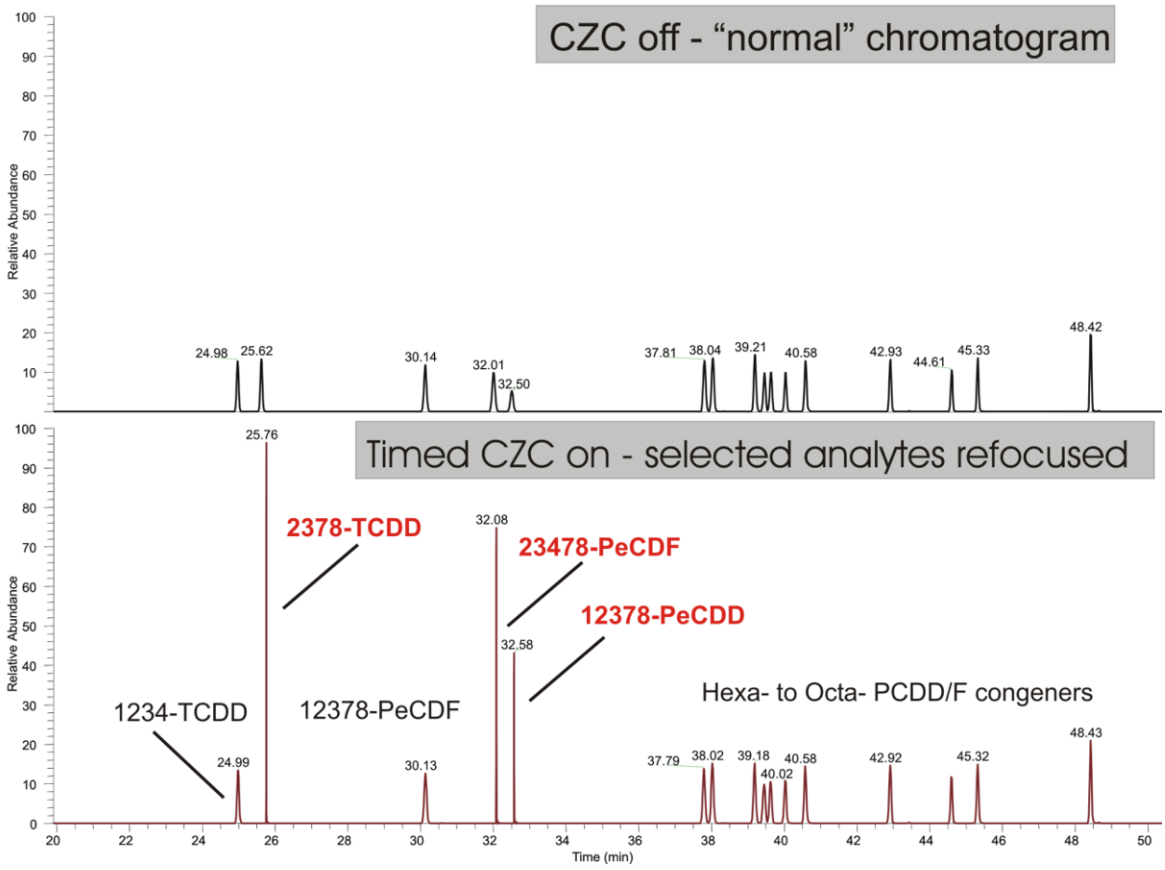
Figure 2 **Comparison of two dioxin congeners showing signal height amplification using t-CZC[4].**



This technique combines the required separation power of a long column and the benefit of a short column in terms of the peak shape. Figure 2 shows the effect of t-CZC on one of two $^{13}C_{12}$ TCDD congeners in a single measurement. Typically the peak height for both congeners is similar. However, the t-CZC focused peak is circa tenfold higher intensity.

In a single measurement, the peak height for selected analytes can be increased by using this technique[4]. The 'focused' analytes stay well separated but have a gain in peak height up to a factor of 10 compared to the unfocused peak. Surrounding 'unfocussed' analytes are unaffected by the measurement.

Figure 3 **Above shows a normal chromatogram of dioxins/furans, below shows the same chromatogram repeated to include selected analytes focused using t-CZC[4].**

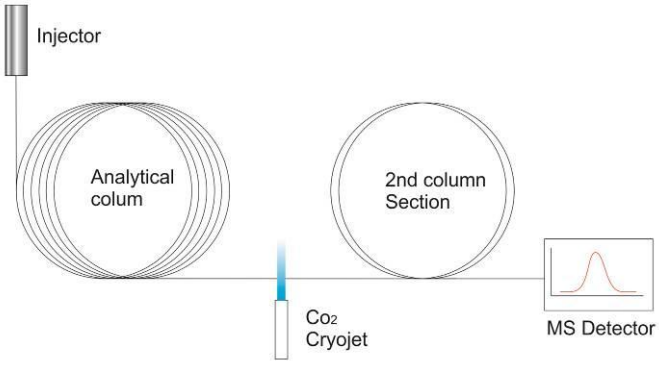


Here, for the first time we present newly developed modular hardware to perform t-CZC applied to BDE-209 as a tool to increase signal height and reduce method limits of detection.

Materials and methods:
All experiments were performed with a Thermo Scientific™ DFS™ high resolution mass spectrometer coupled to a Thermo Scientific Trace™ 1310 GC in combination with a Thermo Scientific TriPlus RSH™ auto sampler.

A newly designed experimental t-CZC module was fitted into the Trace 1310 GC. The t-CZC module housed a cryogenic gas modulator connected to liquid off-take CO_2. Timing events for the module were all software controlled using Thermo Scientific Xcalibur™. The cryo jet was located at the end of the analytical column at a distance between 4m and 0.5m to the mass spectrometer.

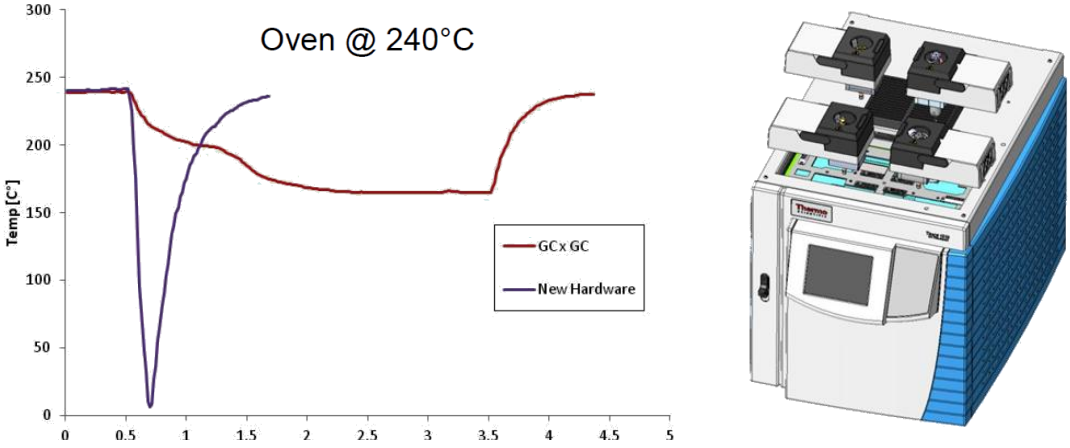
Figure 4 **Location of the t-CZC cryogenic jet on the analytical column**



Results and discussion:

Rapid cooling and subsequent rapid heating of the column within the t-CZC device is critical to achieve efficient 'focusing' and reinjection of the analytes onto the column. Slow cooling makes precise timing more difficult with t-CZC, especially for high boiling components like BDE-209. Previously trialed cryogenic jets exhibited slow cooling and subsequent warming. Therefore, a brand new hardware was developed to improve the cool down speed and the achievable minimum temperature, Figure 5. Using this hardware, t-CZC could also be applied to BDE-209 in an existing PBDE method with an eluting temperature of 300°C. 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 other cryogenic modulators. This and the faster cool down speed made the determination of the timing for the cryo jet easier, and more precise trapping of the peak could be performed.

Figure 5 **The newly developed module showed significantly improved cooling characteristics and installed easily into the spare module bays on top of the Trace 1310 GC**



A significant fourfold increase in signal height for BDE-209 was achieved, Figure 6. This meant that low concentrations, previously at the limit of detection were now analyzable by implementing t-CZC, Figure 7.

Initial evaluations calculated that t-CZC lead to a decrease in overall method LOD by a factor of two to three for BDE-209. Further work is underway to optimize t-CZC as a tool for improving analytical performance for troublesome analytes.

Figure 6 **Overlaid chromatograms of BDE-209, analysed using standard chromatography (blue) and also with t-CZC cryo-focusing (red).**

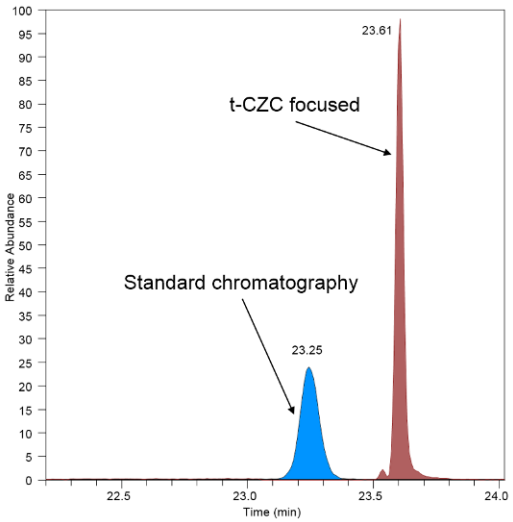
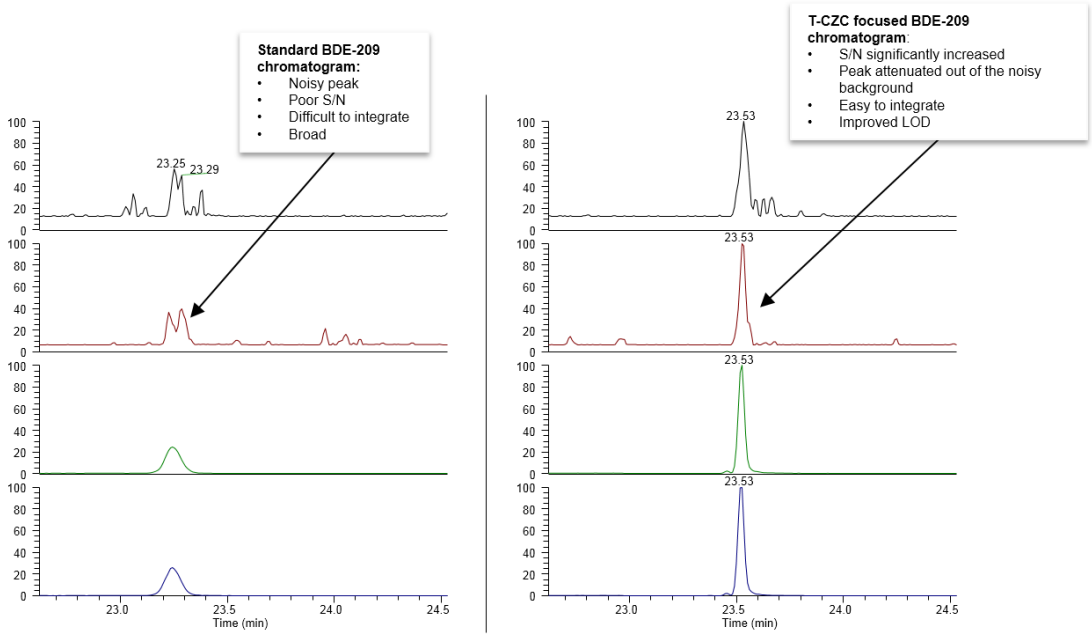


Figure 7 **Low level BDE-209 calibration standard at the limit of detection using standard GCMS, is now easily analyzable using t-CZC**



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References:

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