



Poster Note PN-21

Trace Analysis of TCDD and PBDE Persistent Organic Pollutants Using an Atmospheric Pressure Chemical Ionization GC Coupled to a High-resolution QTOF - MS

Introduction

Polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polybrominated diphenyl ethers (PBDE) belong to the class of persistent organic pollutants (POPs). They are one of the major concerns in present environmental discussion. Due to their environmental persistence, their accumulation in the food chain it is of general interest to analyze them with good sensitivity and confidence.

GC-APCI coupled to a high resolution QTOF-MS offers a suitable and sensitive analytical approach for the analysis of these POPs. Here we report a method for Decabromodiphenylether (decaBDE) and 2,3,7,8-Tetrachlorodibenzodioxin (2,3,7,8- T_4 CDD or TCDD) as they are key substances for their compound classes. PBDEs are among the EU priority substances and decaBDE is most difficult to analyze, because it is less volatile and additionally thermolabile. TCDD is a priority pollutant world-wide and is the most toxic substance of the PCDD/PCDF family.

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| Keywords | Instrumentation and Software |
|----------------|------------------------------|
| GC-APCI | impact II |
| QTOF-MS | 456-GC |
| Accurate mass | GC-APCI II |
| Quantification | DataAnalysis 4.3 |
| POPs | |
| Dioxin | |
| PBDE | |

Methods

- 450-GC with PAL Combi-xt Autoinjector coupled to a GC-APCI II source to an impact II QTOF mass spectrometer (all Bruker Daltonics).
- decaBDE: 15 m Rxi-5Sil MS capillary column (0.25 mm ID, 0.10 μm film thickness; Restek), operated at 0.9 ml/min constant helium flow and a GC oven temperature program at 50°C – to 330°C (50°C/min) – hold for 7 min, 1 μl splitless injection.
- TCDD: 40 m Rxi-5Sil MS capillary column (0.18 mm ID, 0.18 μm film thickness; Restek), operated at 0.8 ml/min constant helium flow and a GC oven temperature program at 140°C – to 200°C (50°C/min) – 235°C (2.9°C/min) – 267°C (3°C/min) – 310°C (7°C/min) – hold for 10 min, 1 μl splitless injection.
- MS Data were acquired from 50 - 1000 m/z with 4 Hz in positive mode. Quantitation was done in fullscan mode and a 1/x weighting applied.
- EIC traces were smoothed (1 cycle Gauss, 0.77 smoothing width).

Results TCDD:

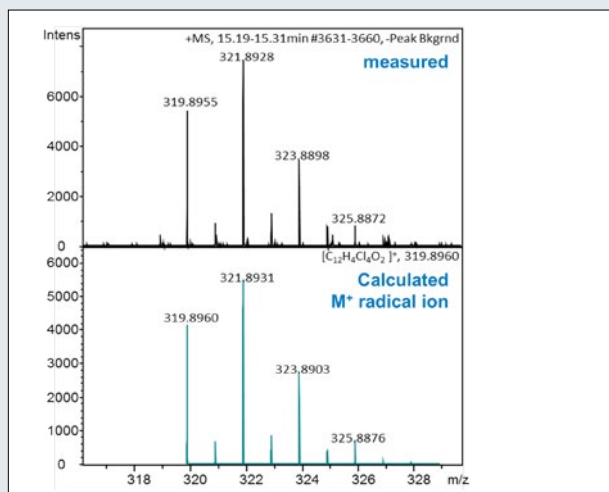


Figure 1: Comparison of measured & calculated mass spectra of TCDD. Average mass accuracy of the molecular ion isotopic pattern is 0.6 mDa.

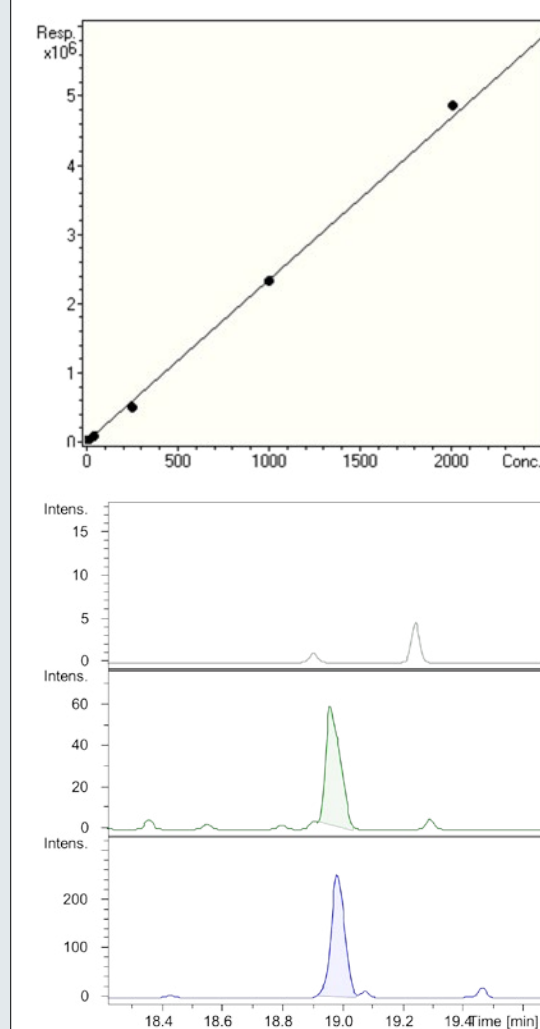
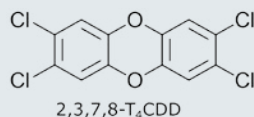


Figure 2, top: Quantitation of TCDD in a linear working range of 0.1 – 2000 $\mu\text{g}/\mu\text{L}$. The R² value was 0.99925.

Bottom: Smoothed EIC traces of TCDD; from top to bottom: blank, 0.1 pg on column, 0.5 pg on column. A clear peak can still be seen for 0.1 pg (S/N = 13) while there is no signal in the blank.

Results decaBDE:

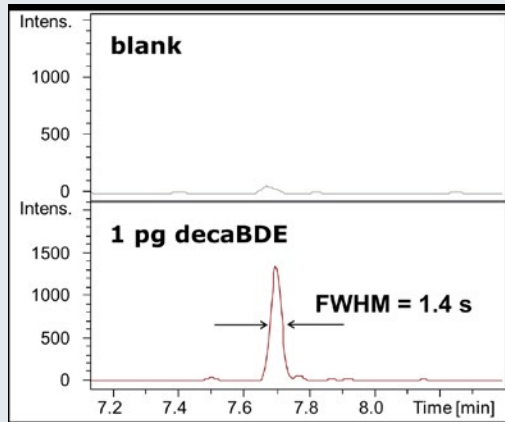


Figure 3: EIC traces of **decaBDE** at 960.1754 ± 0.003 Da: above: blank run, below: 1 pg on column (S/N = 18).

Replicate measurements @ 5 pg/ μ l (n=5) show good reproducibility of 3.8% area RSD and good peak shapes with peak widths between 1-2 s.

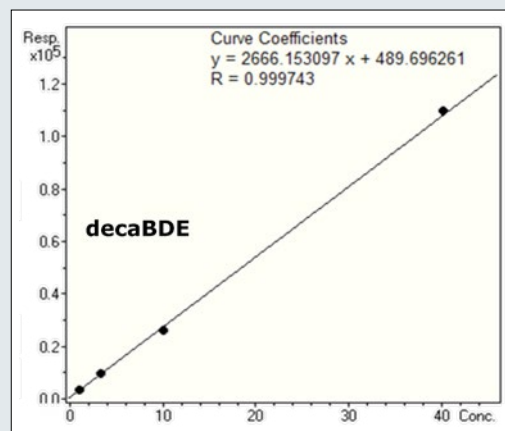
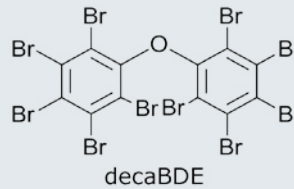


Figure 4: Quantitation of decaBDE was tested in a linear working range of **1 pg/ μ L – 40 pg/ μ L**, the R^2 value was **0.99974**.

Conclusion:

- GC-APCI is a complementary analytical technique to LC/MS which extends the scope of analytes that are detectable with QTOF-MS.
- DecaBDE is well analyzed with GC-APCI without any thermal degradation, LOD of decaBDE is below < 1pg on column.
- TCDD dioxin elutes very reproducibly with a sharp peak at 19 min, LOD of TCDD is 0.1 pg on column (with S/N = 13).
- Accurate mass analysis, i.e. working on ion chromatogram traces with small extraction windows, enables the analysis of small concentrations of POPs without any interferences. The isotope pattern allows the verification of a positive finding and is therefore an additional quality criterion.

View of GC-MS System

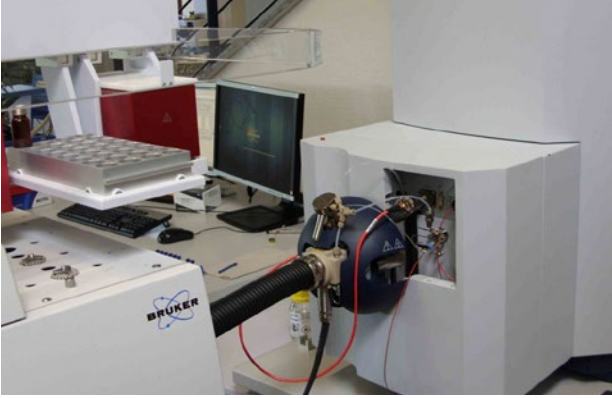


Figure 5: GC-APCI II coupled to a QTOF mass spectrometer (450-GC with PAL Combi-xt Autoinjector and impact II)

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