ANALYSIS OF DIOXINS, FURANS AND POLYCHLORINATED BIPHENYLS IN SEDIMENTS AND FISH USING NOVEL 7250 HIGH-RESOLUTION GC/Q-TOF

OVERVIEW
• The aim was to demonstrate how high-resolution GC/Q-TOF instruments can be used for flexible analysis of dioxin-like compounds
• Full spectra EI data was collected using the novel Agilent 7250 GC/Q-TOF and was queried using target, suspect and non-target analysis workflows
• We demonstrate excellent accuracy in dioxin and dioxin-like PCB analyses
• We illustrate how GC/Q-TOF instruments allow screening for known dioxin-like compounds and identification of unknown dioxin-like compounds

Introduction
• Dioxin-like compounds bind to the Ah receptor and produces toxic effects at very low levels\(^1\)
• Strong Ah ligands are all planar aromatic compounds and most are halogenated
• The total dioxin-like toxicity can be expressed as dioxin toxic equivalents (TEQs)\(^2\)
• Modern GC time-of-flight MS instruments are very sensitive and provide full EI spectra
• GC/Q-TOF instruments can be used for target analysis of dioxins and dioxin-like PCBs, and for suspect and non-target screening of dioxin-like compounds

Methods

Samples and clean-up
• Baltic Sea sediment and fish: in-house reference materials (RM s)
• Sediment was Soxhlet extracted with toluene
• Fish was column extracted with acetone:hexane and hexane:ether
• Bulk matrix was removed by H\(_2\)SO\(_4\) treatment
• Planar compounds were isolated through carbon column clean-up

GC-QTOF MS
• GC high-resolution EI-MS analysis was performed on an Agilent 7250 GC/Q-TOF
• Target compounds were detected by MassHunter (MH) Find-by-Fragments workflow
• MH Quantitative Analysis was used for quantification
• MH Qualitative Analysis was used for suspect screening of dioxin-like compounds
• MH Unknown Analysis was used for non-target screening of dioxin-like compounds
### Results – Target Analysis

**Table 1: Comparison of GC/Q-TOF and GC-magnetic sector high-resolution MS data (pg/g)**

<table>
<thead>
<tr>
<th>Congener</th>
<th>TEF*</th>
<th>QTOF HRMS</th>
<th>Sediment HRMS</th>
<th>RM Average</th>
<th>QTOF-HRMS</th>
<th>Salmon Sector-HRMS</th>
<th>RM Average</th>
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<td>PCB-77</td>
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<td>37</td>
<td>36</td>
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<td>53</td>
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<td>1.8</td>
<td>1.5</td>
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<td>2.3</td>
<td>2.6</td>
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<tr>
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<td>123478 -HxCDD</td>
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<td>15</td>
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* TEF: World Health Organization (WHO) Toxic Equivalency Factor.

- Good agreement of planar PCB and polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) concentrations from GC-QTOF-MS and GC-magnetic sector-MS (Table 1)
- The important tetra/penta-CDD/Fs, PCB-126, and TEQ are within ±25% of the reference values
- The deviation between QTOF-MS and Sector-MS data depends on the signal quality (S/N ratio) and is less than ±40% for all compounds with a S/N greater than 10
Results: Suspect screening

Suspects

- Chlorinated naphthalene (PCN)
- Chlorinated dibenzothiophene (PCDT)
- Chlorinated Thianthrene (PCTA)

- PCTAs were not detected
- PCDT were found in sediment at 10% of the PCDD/F levels
- PCNs were most abundant (Figure 1)
- PCN and PCDF levels were similar in sediment
- PCN levels were 100-fold higher than PCDD/F levels in salmon
- Metabolically stable PeCNs and HxCNs (wo. vicinal hydrogens) biomagnify in fish

Figure 1. PCN composition

Sediment: Non-target screening

- Polycyclic aromatic compounds (PACs), incl. PAHs, dominated the dioxin fraction
- Halogenated PAHs was also found (Figure 2)
- Halo-PAHs were dominated by lower halogenated congeners (Figure 3)

Figure 2. Tentative identification of chloropyrene

Figure 3. PAHs and halo-PAHs in sediment

References

1. [http://www.euro.who.int/__data/assets/pdf_file/0017/123065/AQG2ndEd_5_11PCDDPCDF.pdf?ua=1](http://www.euro.who.int/__data/assets/pdf_file/0017/123065/AQG2ndEd_5_11PCDDPCDF.pdf?ua=1)

2. [https://www.epa.gov/toxics-release-inventory-tri-program/dioxin-and-dioxin-compounds-toxic-equivalency-information](https://www.epa.gov/toxics-release-inventory-tri-program/dioxin-and-dioxin-compounds-toxic-equivalency-information)
**Sediment: Non-target screening**

- An abundant brominated unknown with formula C$_{13}$H$_7$NBr$_4$ was found in sediment (Figure 4)
- A Chemspider search returned on candidate: 1,3,6,8-Tetrabromo-9-methyl-carbazole
- C$_{13}$H$_7$NBr$_4$, unknown can be a metabolite of the natural product 1,3,6,8-Tetrabromocarbazole [1], which was also detected (Figure 5)
- The isotope clustering and fragmentation is supporting the proposed structure

**Figure 4.** EI spectrum of C$_{13}$H$_7$NBr$_4$

**Summary: Sediment contaminants**

- PAHs dominated the dioxin fraction (Figure 6)
- Halo-PAHs and brominated carbazoles and methyl carbazoles (BR-CZ/MCZ) were present at ca 100-fold lower levels
- PCNs, PCDFa and PCDDs were at comparable levels, whilst PCDTs were 10-fold lower
- Tetrahalogenated congeners dominated the bicyclic planar compound groups (Figure 7)

**Figure 6.** Concentrations in sediment

**Figure 7.** Congener distribution in sediment

**Conclusion**

The new GC-QTOF system generates PCDD/F and planar-PCB concentrations comparable to those of the Golden Standard: Magnetic sector HRMS

Full spectrum data is obtained in the same run, which can be used for suspect and non-target screening of other dioxin-like compounds