BIOMONITORING OF GC AND LC AMENABLE ENVIRONMENTAL CONTAMINANTS USING A SINGLE HRMS PLATFORM

Mullin L.[1,2], Ladak A.[1], Cleland G.[1], Ericson Jogsten I.[2]

[1] *Waters Corporation, 34 Maple Street, Milford MA 01757*

[2] *Man-Technology-Environment Research Centre, Örebro University, 701 82 Örebro, Sweden*

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INTRODUCTION

Monitoring of environmental contaminants in biological samples is typically performed by targeted analysis using a tandem quadrupole system on separate GC and LC platforms in order to cover the expansive range of compounds classes and concentrations. Use of multiple systems can add complexity to the analysis and increase turnaround times for samples to be reported. The work that will be presented will show the analysis of common environmental contaminants in a biomonitoring context on a single high resolution mass spectrometric (HRMS) platform. The compounds of interest include:

- GC amenable compounds: PCDD/Fs, PCBs and PBDEs
- LC amenable compounds: Perfluoroalkyl substances (PFASs)

MATERIALS AND METHODS

The analyses were performed on a QTof MS instrument with universal ionization source architecture. The system was operated in LC electrospray (ESI) mode (Table 1a and b) and GC atmospheric pressure chemical ionization mode (APGC) (Table 2a and b). The ionization for APGC is summarized in Figure 1. The Qtof MS system was operated in a full spectral acquisition MS^E mode from 50-1200 Da (Table 3), as well as a target enhanced mode for certain analytes which were detected at low levels in samples. Samples (mink liver, whale blubber, and fish extract) were prepared according to previously described methods[1-3].

Table 1: LC parameters (a) and gradient (b) for PFASs analysis.

a.

Parameter	Value
Column	BEH C18 1.7µm 2.1x50mm
Column temperature (°C)	55
MP A	98:2 Water:MeOH 2mM ammonium acetate
MP B	MeOH 2mM ammonium acetate

b.

Time (min.)	Flow Rate (ml/min.)	%A	%B
Initial	0.65	90	10
0.50	0.65	90	10
5.10	0.65	0	100
6.60	0.65	0	100
6.70	0.65	90	10
8.50	0.65	90	10

Table 1: GC parameters (a) and gradient (b) for PCDD/Fs, PCB and PBDEs analysis.

a.

Parameter	Value
Column	Rxi 5Sil 60m x 0.25 mm 0.25µm (Restek)
Carrier gas	Nitrogen
Injection mode	Splitless
Liner	Gooseneck Splitless, Deactivated (Restek)
Column pneumatics	Constant flow
Column flow (mL/min)	1.2
Injector temperature (°C)	280

b.

Temperature (°C)	Temperature Ramp(°C/min)	Hold time (min)
100		4
240	5	15

Table 3: QTof conditions.

Parameter	Value
Acquisition mode	MS^E
Ionization mode	**$APCI^+$/ESI^-**
Scan Rate (s)	0.2
Source temperature (°C)	**150/120**
Interface temperature (°C)	**310**
Corona current (µA)	**5**
Capillary voltage (kV)	**1.5**
Cone voltage (V)	**30/15**
Cone gas (L/hr)	**200/50**
Auxiliary gas (L/hr)	**250**
Desolvation gas (L/hr)	**1000**
Low Collision Energy (eV)	6
High Collision Energy (eV)	**20-70/30-75**
Lock Mass	**281.0512/554.2620**

Key: GC, LC

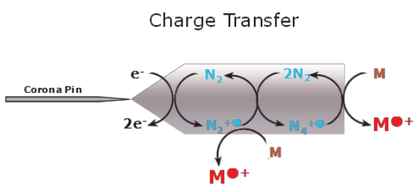

Figure 1: Ionization mechanism for APGC analysis.

RESULTS AND DISCUSSION

Solvent standard injections were used to generate expected retention times and product ions. This information was put in a library and used in the analysis of samples. Figure 2 shows this data approach in a binary compare view for both LC and GC analyses.

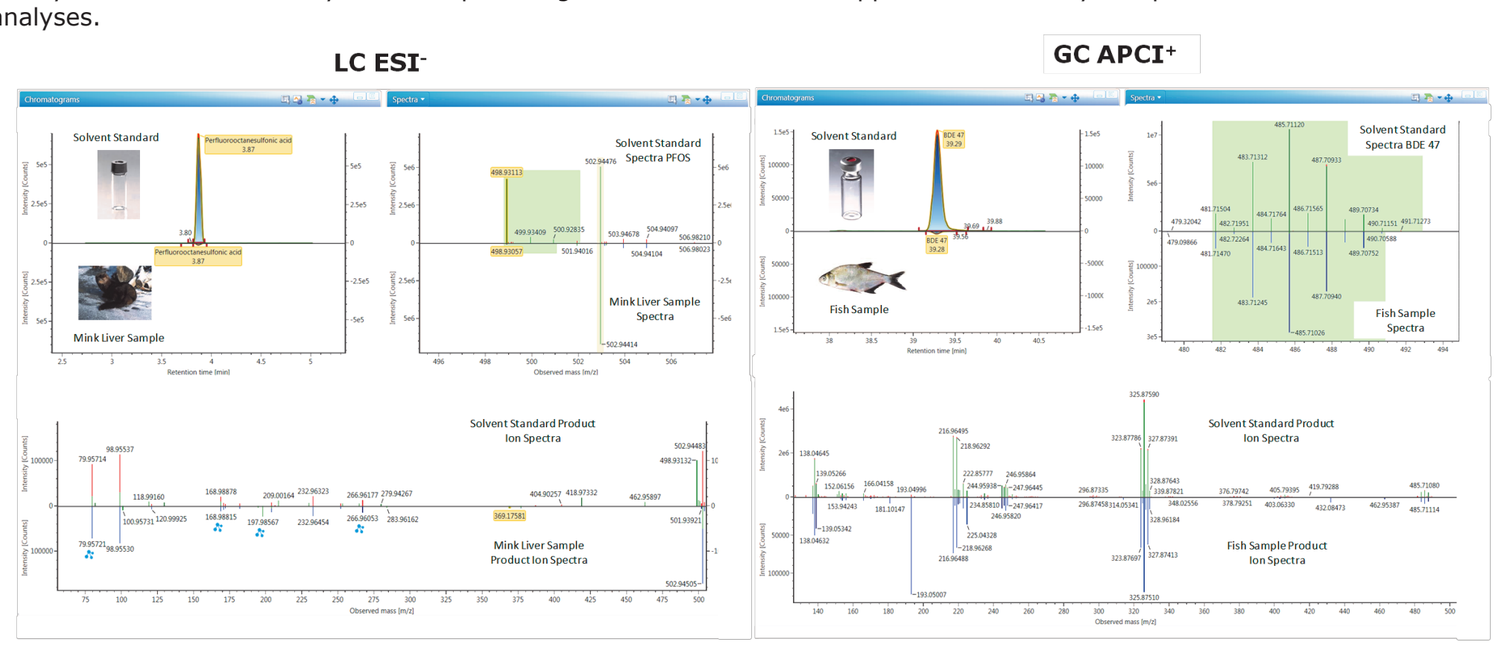

Figure 2: Despite large variations in response and injected make-up (solvent vs. matrix), spectral and chromatographic data integrity is conserved with regards to observed product ions, isotopic patterns and mass accuracy.

Detected concentrations covered in bioanalytical studies vary in range by orders of magnitude[4] and this is reflected in Figure 3. Despite these variations in concentration as they are measured on the instrument, mass accuracy is well retained and a criteria of +/- 3 ppm is used for all identifications, in addition to characteristic product ions expected to be present.

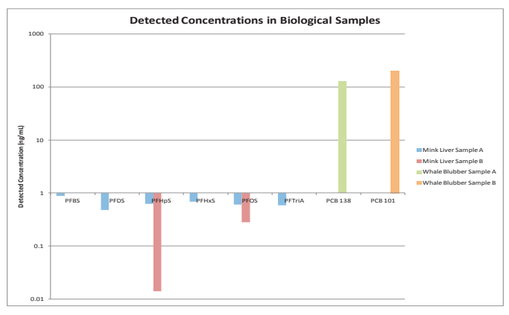

Figure 3: Concentrations of various contaminants as they are detected on the MS system against a solvent calibration

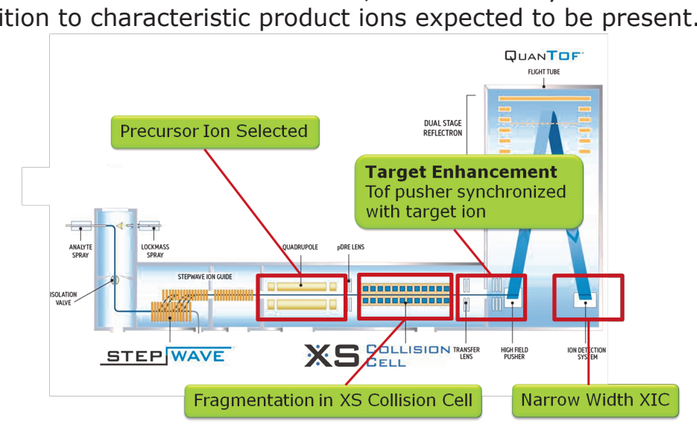

Figure 4: Schematic of target enhanced operation on the QTof MS system used in this study.

Though legislative and relevant levels of sensitivity were met while operating under full spectral acquisition, the implementation of an target enhanced operation mode (Figure 4) was used to increase sensitivity of the analysis. Figure 5 shows the resulting S/N when implemented on 2,3,7,8-TCDD. When used in a complex matrix, signal is increased as well as a reduction in noise.

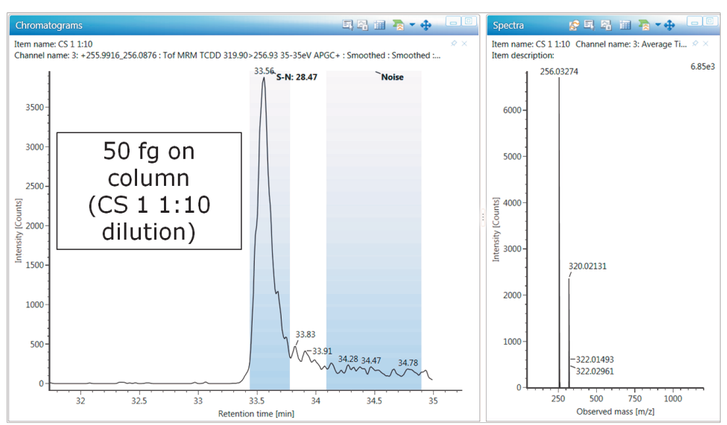

Figure 5: 2,3,7,8 TCDD as acquired via target enhancement.

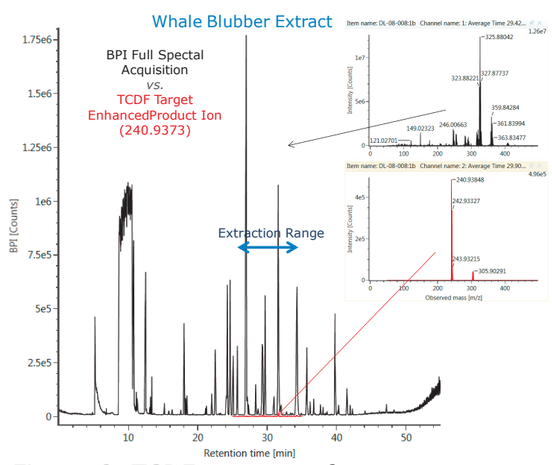

Figure 6: TCDF spectrum for same range extracted from BPI (top) and target enhanced acquisition.

CONCLUSIONS

- **Comprehensive analysis of contaminants in achieved using QTof MS with atmospheric source LC and GC interface**
- **Target enhancement (Tof MRM) increases sensitivity of signal for low-level (ng/g) as well as reducing background spectra for complex sample analyses**
- **Further sample analysis is planned, with a focus on improvement of sample preparation strategy**

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