DETECTION OF PERSISTENT ORGANIC POLLUTANTS USING ATMOSHERIC PRESSURE GAS CHROMATOGRAPHY AND A NOVEL ACQUISITION MODE FOR QUADRUPOLE TIME-OF-FLIGHT MS

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Introduction

The detection of persistent organic pollutants (POPs) must meet low regulatory limits, typically on the order of sub ppb-levels in complex environmental matrices[1]. Additionally, the identification of product ions for confirmatory identification is important and can be achieved using multiple reaction monitoring (MRM) on tandem quadrupole MS (MS/MS) systems. For this well accepted technique, only the specific ions of interest are monitored, so while MRM provides excellent selectivity for those target compounds, unexpected yet highly abundant and significant components of the sample may go completely undetected. Conversely, time-of-flight (TOF) MS systems provide exact mass measurement across a wide mass range, but historically have not met the same sensitivity levels achieved using tandem quadrupole MRMs. The following work shows the application of a novel data acquisition mode for quadrupole TOF MS which utilizes a targeted enhancement of selected product ions. Full scan data was also collected in the same run time, providing comprehensive exact mass information for the samples.

This acquisition mode is demonstrated for the detection of polychlorinated dibenzo p-dioxins (PCDDs), polybrominated diphenyl ethers (PBDEs), and other POPs in a complex biological sample. Method LODs and LOQs were determined for selected PCDDs and polychlorinated biphenyls (PCBs) based on standard calibration curves. Overall, an increase in sensitivity was observed for the compounds acquired using targeted enhancement as compared to a typical TOF MS acquisition. Moreover, there was also a decrease in noise detected as a result of the specified product ion targeted enhancement. The advantage of a full scan channel with exact mass information was also exploited to identify PBDEs in the analysis of whale blubber extracts. Using this acquisition technique results in an enhancement of the analytical capabilities of high resolution mass spectrometry for the analysis of environmental contaminants.

Materials and methods

An Agilent 7890 GC was coupled to a Waters SYNAPT G2-Si MS using atmospheric pressure chemical ionization (Waters APGC source option) for this work. A Rtx 5MS 60m x 0.25mm 0.25µm column was used (Restek Corporation, Bellafonte PA USA) for separation of PCDDs and PCBs. For the PCDD analysis, an initial temperature of 120°C was held for 2 min., with a 35°C/min. ramp to 200°C with no hold, a 4°C/min. ramp to 280°C with no hold, a 20°C/min. ramp to 300°C with a 10 min. hold and final ramp of 30°C/min. to 320°C held for 1 min. The PCB analysis had the same temperature program with the exception of the final ramp and temperture of 20°C/min. to 300°C. Both analyses used a 1 µL pulsed splitless injection at 280°C with a splitless single taper gooseneck liner (Reste Corporation, Bellefont PA USA) The GC transfer line temperature was 360°C, and MS source conditions were source temperature of 150°C, sample cone 30V, cone gas flow 220L/hr, auxillary gas flow 200L/hr. Known precursors and product ions were delineated in the MS method. Simultaneous full scan data was acquired every 1 sec. from 100-800m/z. Calibration standards (5 points for PCBs and 6 points for PCDDs analyses) of aforementioned compounds were prepared across 3 orders of magnitude, and were assessed for linearity. For purposes of comparison, a MS full scan acquistion from m/z 100-5000 with no targeted enhancement was also acquired with the same GC conditions and standards. Compounds analyzed were PCDDs contained within the EPA 1613 calibration standards (CS) (Wellington

Laboratories, Guelph, Ontario, Canada) and the Dutch 7 PCBs (Accustandard, New Haven, CT, USA). Whale blubber extracts were prepared using the method described in Rotander et. al.[3]

Results and discussion

Targeted enhancement was achieved by specifying the precursor masses to be selected by the quadrupole. Upon CID in a stacked-ring ion guide device, specified product ions were signal enhanced through an increased pusher frequency. For both PCDDs and PCBs, the two product ions were respective ^{35}Cl and ^{37}Cl isotopes, and targeted enhancement of the average mass was found most suitable. Previous assessments comparing sensitivity using the targeted enhancement method applied here show increased sensitivity of MS signal by at least 2 times over normal full scan mode. Increased sensitivity was evident for PCBs and PCDDs monitored in this targeted experiment (Table 1), as compared to a typical MS TOF acquisition.

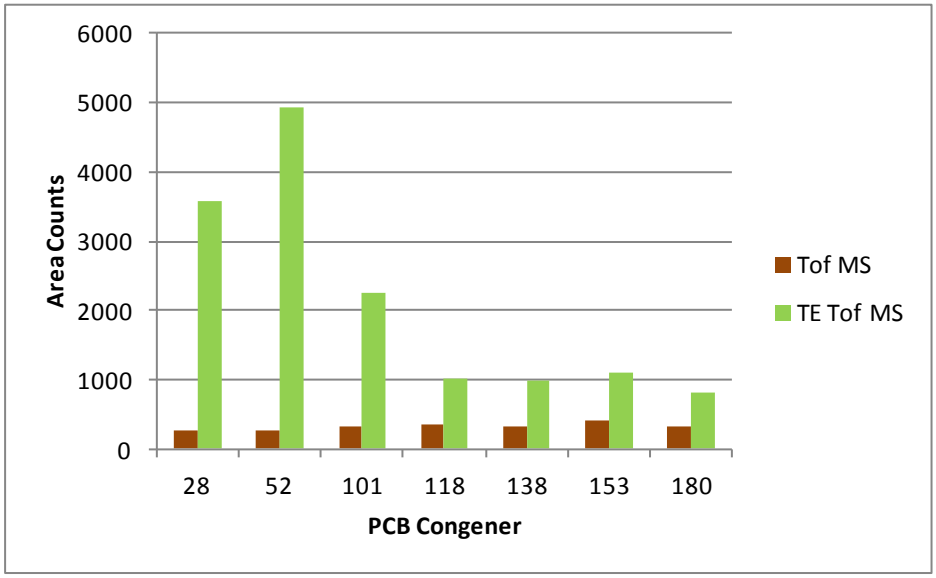

Table 1: Area counts for Dutch 7 PCBs as compared between targeted enhanced (TE in the legend) Tof MS and typical Tof MS acquisitions, in a 10 pg solvent standard.

The most toxic known PCDD congener (2,3,7,8-TCDD) was detected in the lowest calibration standard, at 0.05 pg. For the same congener, linearity was excellent with a coefficient of determination value of 0.999 (Table 2). For the PCBs analyzed in this experiment, all had peak-to-peak signal to noise ratios exceeding 10:1 for a 100 fg standard. Linearity was also acceptable with coefficient of determination values >0.99. Repeatability for PCBs was determined using 6 consecutive QC injections at 10 pg, and RSDs were all below 10%.

The masses of selected PBDEs were extracted from the full scan data, and positive identifications of several congeners in the blubber extracts (Figure 1). Identifications were obtained using comparisons of exact mass, isotope distribution patterns and searching of online databases. Mass errors for the congeners displayed in Figure 1 for the monoisotopic and most intense isotopic peaks were below 3ppm, which provides a high degree of confidence for compound identification. Full scan data affords the ability to mine the samples for a wide range of potentially unexpected contaminants, as well as facilitating historical data review. This feature will be useful for the identification of emerging contaminants and their occurance over time in samples. Based on this preliminary work, future analyses are intended in other complex biological matrices for PCDDs and PCBs.

Compound	Coefficient of Determination	Range (pg)
2,3,7,8-TCDD	0.999	0.05-10
1,2,3,7,8-PeCDD	0.992	0.25-50
1,2,3,4,7,8-HxCDD	0.99	0.25-50
1,2,3,6,7,8-HxCDD	0.999	0.25-50
1,2,3,7,8,9-HxCDD	0.996	0.25-50
1,2,3,4,6,7,8-HpCDD	0.996	0.25-50
OCDD	0.998	0.5-100
PCB 28	0.999	0.1-100
PCB 52	0.997	0.1-100
PCB 101	0.997	0.1-100
PCB 118	0.997	0.1-100
PCB 138	0.997	0.1-100
PCB 153	0.995	0.1-100
PCB 180	0.997	0.1-100

Table 2: Range and linearity for PCDDs and PCBs analyzed using targeted enhancement Tof MS method.

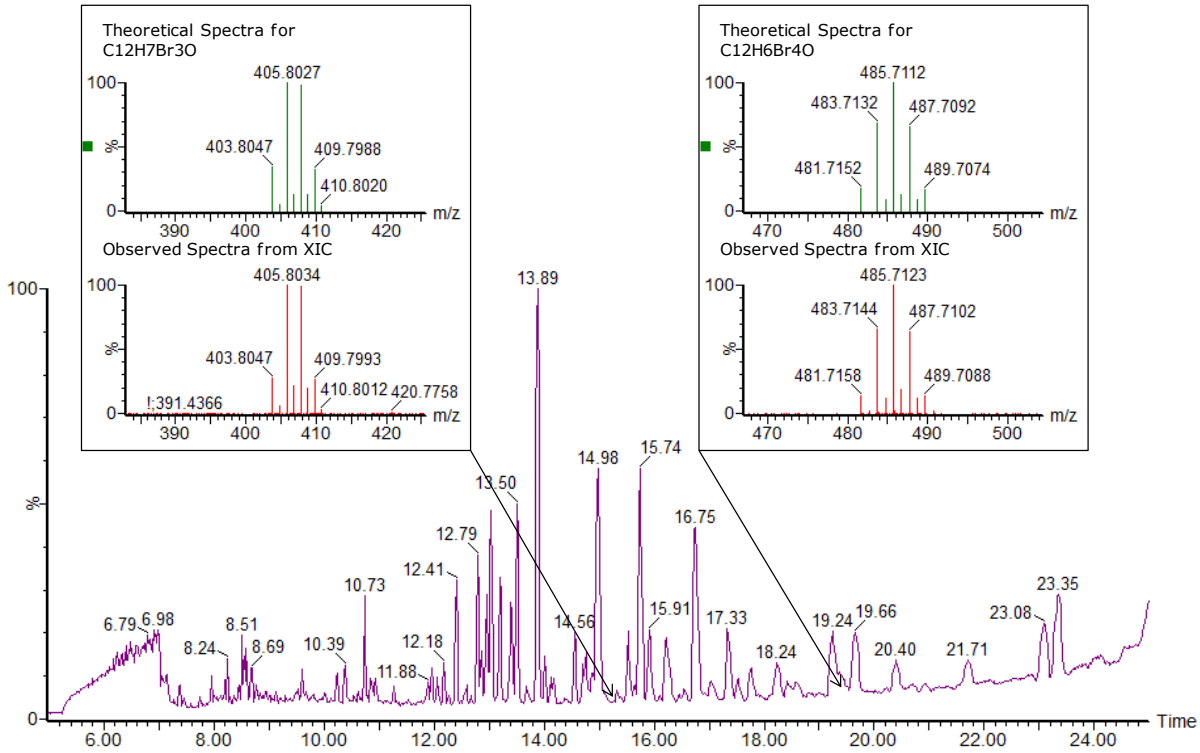

Figure 1: TIC of whale blubber extract, from full scan channel in targeted enhancementTof MS experiment. Spectra were obtained from extracted ion chromatograms (XICs) of masses for tri- and tetra-brominated PBDEs (each displayed in separate boxes with arrows indicating their relative retention times).

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References:

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2. Rotander A., van Bavel B., Rigét F., Auðunsson G., Polder A., Gabrielsen G., Víkingsson, Mikkelse B., Dam M. (2012); *Environ. Pollut.* 164: 118-124