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응용 자료

Increasing Sensitivity for Tof-MS Detection of Polychlorinated Biphenyls (PCBs) Using Tof MRM

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This is an Application Brief and does not contain a detailed Experimental section.

Abstract

This application brief demonstrates the application of a novel data acquisition mode for Waters SYNAPT G2-S*i* which utilizes a targeted enhancement of selected product ions.

Benefits

Tof MRM affords increased sensitivity while maintaining the ability to acquire accurate mass full scan data in the same injection.

Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants which have been banned from production as a result of their observed accumulation in biota and the environment. Various levels of toxicity have also been associated with PCBs, in particular the 12 dioxin-like PCB congeners. Consequently, PCBs are monitored at sub-ppb levels in complex environmental matrices[1]. The use of product ions for 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 specific transitions of interest are monitored. 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 accurate mass measurement across a wide mass range, but historically have not met the same sensitivity levels achieved using tandem quadrupole MRMs. In this technology brief, we describe the application of a novel data acquisition mode for Waters SYNAPT G2-S*i* 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.

Results and Discussion

Tof MRM was achieved by first selecting a precursor ion in the quadrupole. Following CID in a T-Wave collision cell, the duty cycle of specified product ions were enhanced via timing of Tof pushes relative to the

specified product ion (Figure 1). For PCBs, the 35Cl and 37Cl isotopes of the product ion were monitored, while targeted enhancement of the average mass was utilized. A full spectral acquisition channel from *m/z* 100 to 800 was also acquired. Solvent standards of seven routinely monitored PCBs (28, 52, 101, 118, 138, 153, and 180) were prepared at concentrations ranging from 0.1 to 100 ng/mL and analyzed by PGC-QTof MS. Linearity of response across three orders of magnitude was excellent for all congeners, with correlation coefficient values >0.995. Analysis of the standard at 10 ng/mL were repeated six times giving %RSD values <10%).

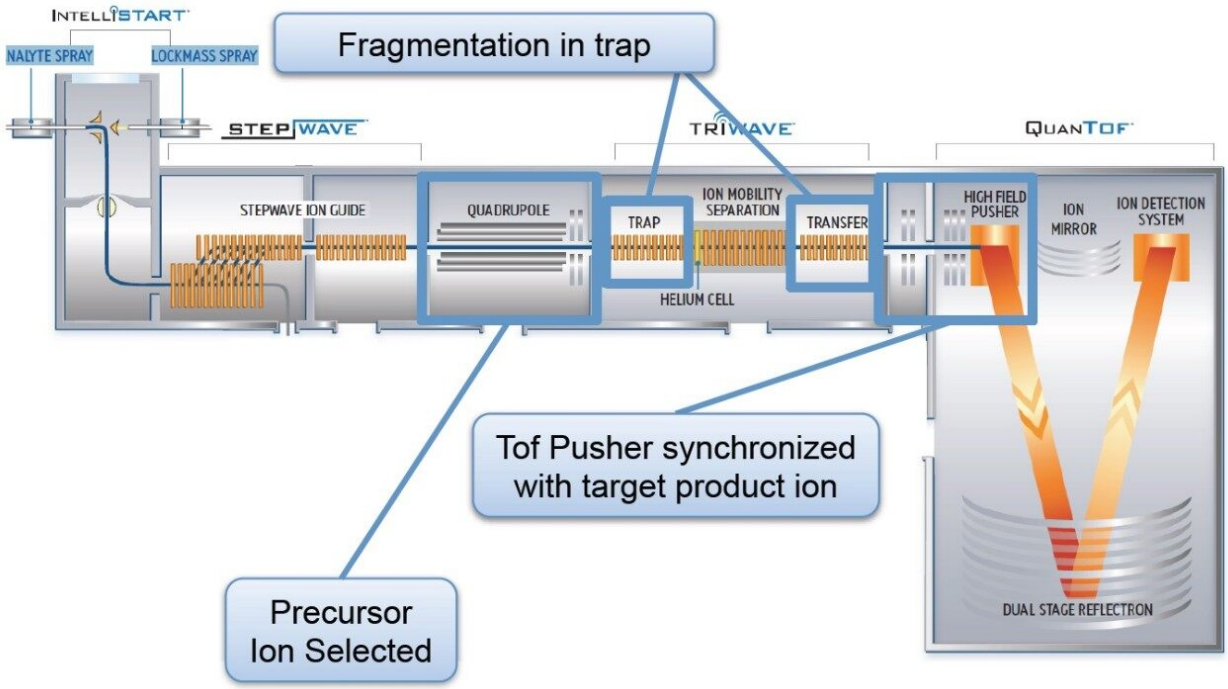

Figure 1. Instrument schematic of SYNAPT G2-Si. Tof MRM is achieved by the selection of a specified precursor ion in the quadrupole, followed by fragmentation induced in the trap, or transfer regions, and a pusher frequency synchronized with the specified product ion.

Increased sensitivity was evident for compounds monitored in this targeted experiment (Figure 2), as compared to a typical Tof MS full scan acquisition. Signal-to-noise (S/N) ratios were all above 7:1 for the 0.1 ng/mL standard injections.

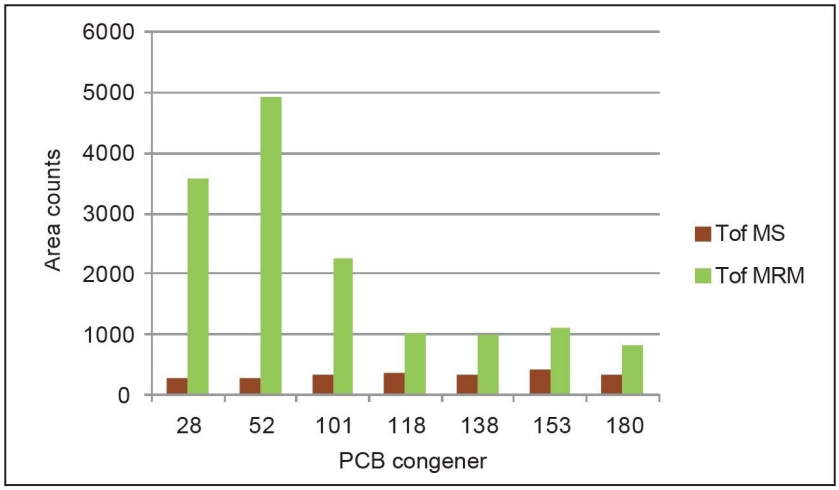

Figure 2. Comparison of peak area for PCB congeners using Tof MS (where peak was extracted ion chromatogram (EIC) from precursor mass) and Tof MRM (where peak was EIC from targeted product ion) acquisition modes. Sensitivity increases of at least 2x are a result of enhanced duty cycle for the specified product ions in Tof MRM mode.

In order to asses the method for the analysis of a complex biological matrix, whale blubber extracts were also analyzed using this method. PCB 118 was observed in all three extracts, as well as several other congeners. The use of Tof MRM in this analysis afforded the advantage of an improved S/N ratio in this complex matrix as compared to Tof MS acquisition (Figure 3). In addition to the targeted PCBs, the masses of selected polybrominated diphenyl eithers (PBDEs) were extracted from the full scan data, and positive identifications of congeners were made (Figure 4). Identifications were obtained using comparisons of accurate mass, isotope distribution patterns, and searching of online databases. Full spectral acquisition 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.

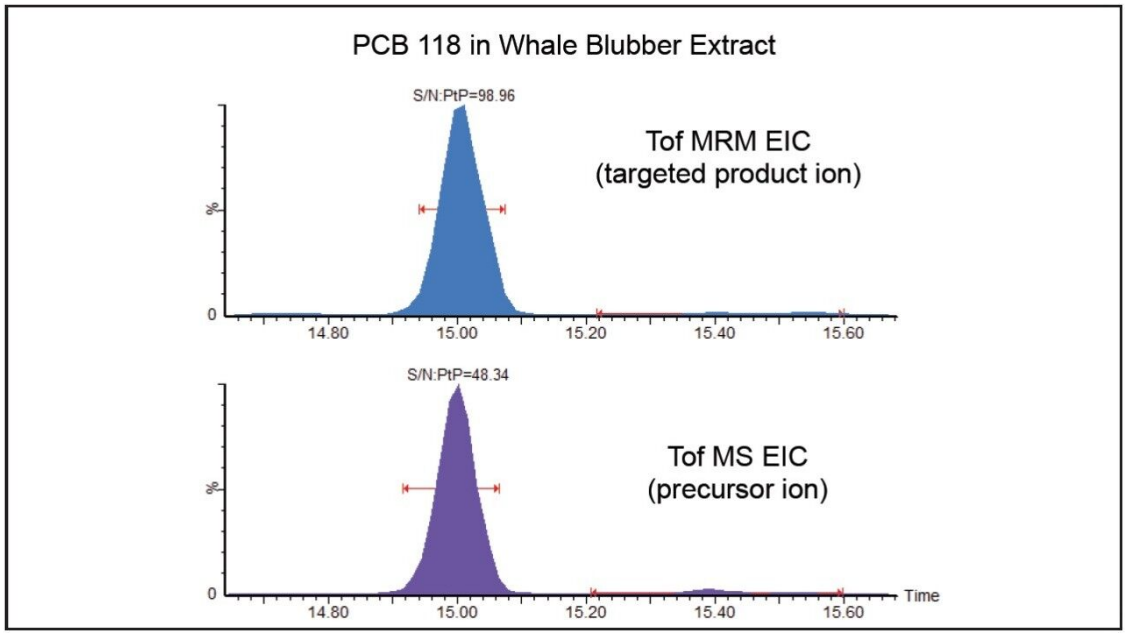

Figure 3. PCB 118 extracted ion chromatograms (EICs) for a Tof MRM (top) and Tof MS (bottom) analysis. The signal-to-noise ratio is almost doubled when using Tof MRM, which is the result of precursor ion selection in the quadrupole prior to CID and targeted enhancement of the production. This is advantageous in the analysis of complex matrices, such as the whale blubber shown here.

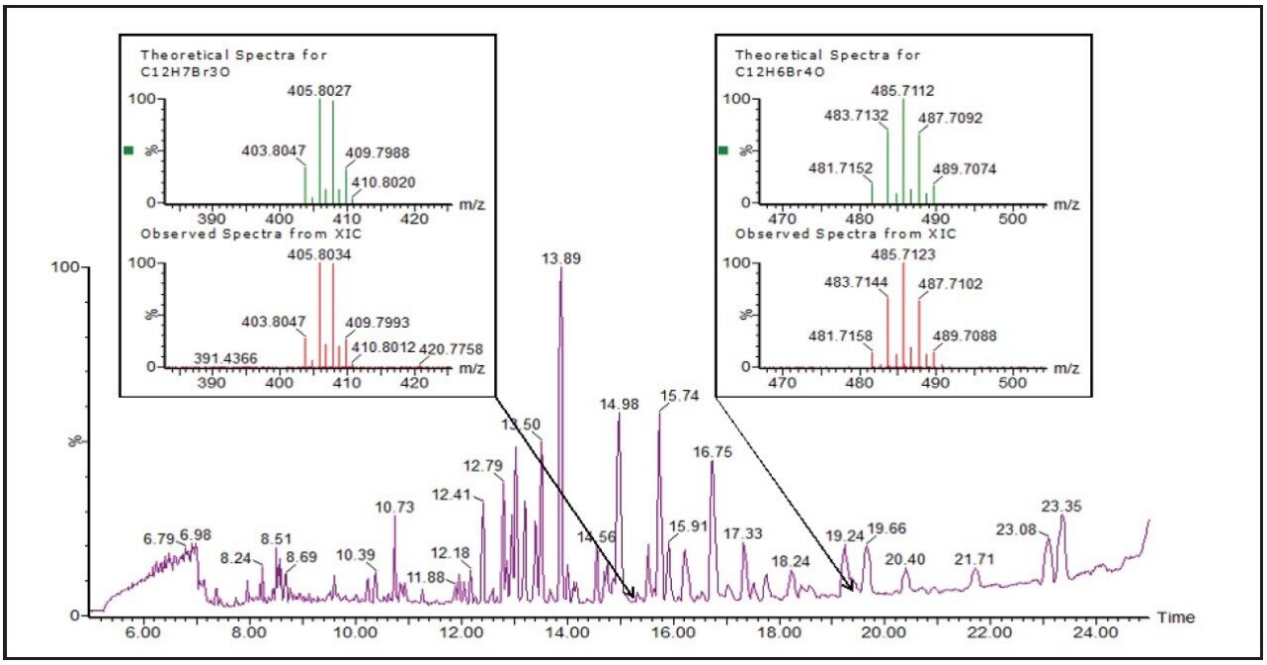

Figure 4. Full scan channel BPI from whale blubber extract. In addition to the targeted components in the Tof MRM method, the full spectral acquisition data can be searched for other contaminants such as PBDEs. Mass error for both identifications were <3ppm.

Conclusion

Tof MRM enhances the analytical capabilities of high resolution mass spectrometry, affording lower limits of detection while maintaining the ability to collect information rich accurate mass full scan data. These benefits have been applied here to the analysis of PCBs, which requires instrumental sensitivity and selectivity for detection in complex environmental matrices.

References

1. E Reiner, R Clement, A Okey, C Marvin. *Analytical and Bioanalytical Chemistry*, 386: 791–806; 2006.

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