Characterization of the Profile of Dioxin-like Compounds and Other Polyhalogentaed Aromatics in Foods, Food Materials, and Feedstuffs Using Gas-Chromatography Ultra-High Resolution Time of Flight Mass Spectrometry

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Introduction

The qualitative and quantitative analysis of dioxins and dioxin-like compounds poses one of the most complex and challenging analytical problems. This POP subset including dioxins and select PCBs is characterized by their extreme toxicity and high level of regulation. The analysis requires sensitivity in the sub-pg range and requires a high performance MS system capable of high resolving power at or exceeding the values mandated by regulatory bodies (e.g. US EPA Method 1613). Historically this has been achieved using magnetic sector instruments. The down fall of magnetic sectors is their narrow mass window or using only selected ion monitoring. There have been attempts to analyze these compounds using Fourier Transform MS systems [1] with no demonstrated ability to quantify the analytes. New developments in time of flight mass spectrometry have generated instruments with the capability to provide in excess of 25,000 resolving power (FWHM). This specific configuration of a TOFMS uses Folded Flight Path (FFP™) technology [2] to provide high acquisition speeds, high-integrity relative isotope measurements, and strong mass accuracy. The utility of FTMS and TOFMS systems is that they provide the ability to analyze not only the analytes of interest but to provide information on other compounds which might also be present in the samples under analysis. Here the analysis of foods, food materials (used in or related to food processing) and feedstuffs is undertaken using a TOFMS with the novel FFP™ technology. The analysis includes fish and other seafood, meat, liver products, freshwater fish and water animals, eggs, and fish oils among other food stuff. The findings are compared to the recently published findings where possible. In addition to the targeted efforts on dioxin-like compounds, the characterization of the profile of polyhalogenated aromatics in these food materials is also provided.

Materials and methods

Food samples were obtained from locally available sources whenever possible and samples processed in a fashion similar to that described previously [3]. A portion of the extracts was injected into the gas chromatograph's split/splitless inlet with helium carrier gas under splitless conditions. A separation column used consisted of a 60 m x 0.18 mm x 0.10 µm Rxi-5 Sil MS film column (Restek). A variety of temperature programs were used, such as a 80°C (1 min) to 160°C at 30°C/min to 270°C at 3°C/min heating rate program. The ion source was operated using EI conditions optimized for response for the analytes of interest and their molecular ions. All analyses were performed using the LECO Pegasus® GC-HRT data equipped with an Agilent 7890 gas chromatograph. Spectra were acquired in the instrument's high resolution operating mode, yielding a nominal mass resolving power of 25,000 (FWHM), as well as the ultra high resolution mode 50,000 (FWHM). Resultant spectra were searched against NIST databases and formulae determined from accurate mass measurements and relative isotopic abundances. The quantitative capabilities of the analysis using the high performance TOFMS are described including LOD for select analytes.

Results and discussion:

The analysis of polyhalogenated compounds in food and related materials using the high performance time-of-flight MS have indicated the capability of the system to provide the requisite resolving power and mass accuracy selectively to detect these classes of compounds in representative matrices. This is typified by the extracted ion chromatograms from PCBs spiked into fish oil which are shown in Figure 1 as a TIC (A), extraction at 1 mass unit window (B) and extraction using a 1 mmu window (C). In a similar fashion, dioxin congeners have been analyzed in mussel tissue and the total and extracted ion chromatograms are shown in Figure 2 below. The

preliminary findings indicate that the performance capabilities of the high performance TOFMS provides the required resolving power (10,000 at 10% peak height) as demonstrated (Figure 2) in the analysis of polybrominated dioxins and their derivatives in the extracted ion chromatogram from mussel extract (B) and the resultant spectrum from the molecular ion region for a brominated dioxin derivative (C). The capability of having the response for targeted compounds without compromising the ability to acquire data and achieve identification on other compounds present in the sample provides a unique tool for environmental, safety and forensic analyses. This is particularly true as new compounds are constantly added to the "to be monitored" lists around the world.

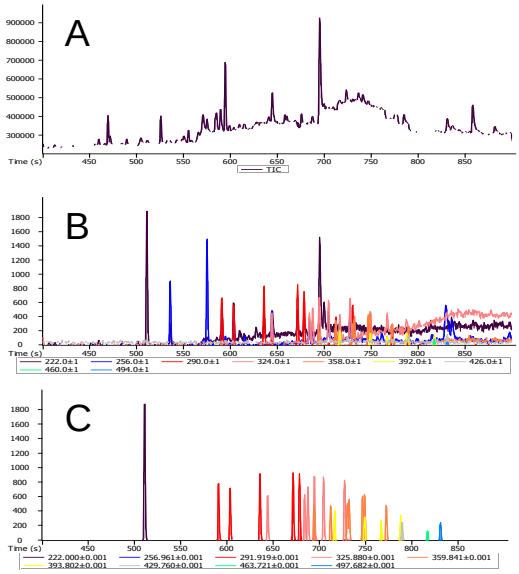

Figure 1 – PCBs in Fish Oil

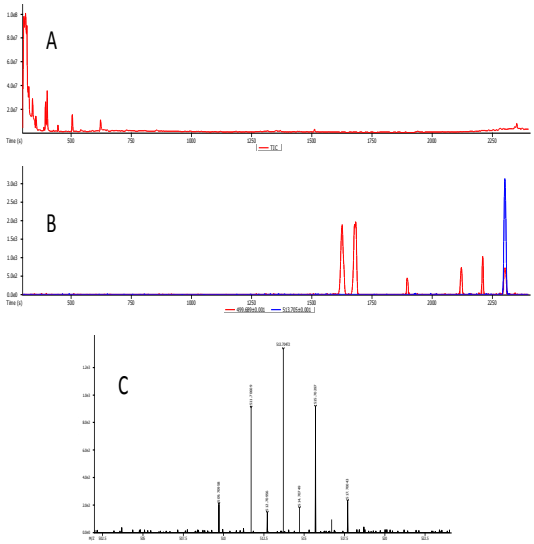

Figure 2 – Analysis of polybrominated dioxins and derivatives in a mussel extract (XIC and spectrum from molecular ion region)

References:

1. Vince Y. Taguchi, Robert J. Nieckarz, Ray E. Clement, Stefan Krolik, Robert Williams, J Am Soc Mass Spectrom (2010), 21(11), 1918.
2. J.S. Patrick, "Ultra Performance Mass Spectrometry Without Comprise: High Resolving Power Multireflecting Time-of-flight Technology with High Speed Data Acquisition", PittCon 2011, March 2011.
3. European Food Safety Authority, EFSA Journal 2010; 8(3):1385