

POTENTIAL OF GAS CHROMATOGRAPHY COUPLED WITH ORBITRAB-BASED MASS SPECTROMETRY FOR THE ANALYSIS OF HALOGENATED PERSISTENT ORGANIC POLLUTANTS IN FOOD AND ENVIRONMENTAL SAMPLES

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Introduction

Persistent organic pollutants (POPs) comprise a variety of organic chemicals that persist in the environment and bioaccumulate in biological systems posing environmental risks to humans and ecosystems. Amongst POPs, halogenated compounds such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are of particular importance due to their extreme toxicity. Exposure to POPs can induce adverse health effects including certain cancers, birth defects, dysfunctional immune and reproductive systems¹.

Detection, confirmation and quantification of POPs in food and environment is very important and strict regulations and guidelines regarding the analytical methodologies used exist in most countries around the globe². Typically, the analytical methods of choice for routine POPs quantification and confirmation include GC-MS, GC-MS/MS and GC-high resolution magnetic sector mass spectrometry. These instrumentation are well characterised for routine analysis of POPs and offer excellent levels of sensitivity when operated in a targeted way using selected reaction monitoring (SRM), selected ion monitoring (SIM) or multiple ion detection (MID). However, when targeting only a specific class of POPs one can overlook possible metabolites of POPs and/or other emerging or unknown contaminants, compounds critical for risk assessment of human exposure to POPs. Screening for these compounds using low resolution instrumentation or high resolution with low scan speed and/or limited sensitivity can result in ambiguous results due to potential interferences that are not resolved. Hence, given the complexity of the matrices to be assessed, a comprehensive screening of samples for their POPs content requires analytical instrumentation that can deliver fast, full scan data acquisition, with high level of sensitivity and selectivity. A sensitive and selective full scan accurate mass acquisition will allow for a retrospective analysis of the data and could potentially lead to the discovery of new pollutants and help finding evidences of eventual synergies between the contaminants present in the samples even at background levels.

The objective of this study was a preliminary evaluation of the utility of Orbitrap based GC-MS technology for the analysis of halogenated organic pollutants in the environmental and food matrices.

Materials and methods

In this study, PCBs, PBDEs and chlorinated dioxins and furans were analyzed in standards and matrix samples using a novel Thermo ScientificTM Orbitrap mass spectrometer coupled with a Thermo ScientificTM TRACETM 1310 GC.

Samples extracts (soils, swage sludge, fly ash and fish) were obtained following a classical sample preparation procedure. Analytes were removed from the matrices by shoxlet extraction followed by a clean up step based on solid-liquid adsorption chromatography using sequential array of multilayer silica, basic alumina and activated carbon. The samples were spiked with ¹³C-labelled standards for dioxins, PCBs and PBDEs and concentrated using rotary concentration and gentle stream with N₂.

Sample introduction was performed with a Thermo ScientificTM TriPlusTM RSH autosampler, and compound separation was achieved on a Thermo ScientificTM TraceGOLD TG-5SiIMS 60 m x 0.25 mm I.D x 0.25 μM film capillary column. The mass spectrometer was tuned and calibrated using FC43 to achieve mass accuracy of < 0.5 ppm. The system was operated in electron ionization mode (EI) using full scan and 60,000 mass resolution (Full Width at Half Maxima, measured at *m/z* 200). Chromatographic data was acquired with a minimum of 12

points/peak to ensure consistent peak integration. Data was acquired and processed using the Thermo Scientific™ TraceFinder™ software. TraceFinder allows the analyst to build acquisition and processing methods for high throughput screening and quantitative analysis and incorporates library searching capabilities as well as easy data reviewing and data reporting.

Results and discussion:

In this study, the suitability of GC-orbitrap technology has been evaluated for the study of persistent organic pollutants including both chlorinated and brominated contaminants. Using the GC-Orbitrap mass spectrometer operated at routine high resolving power of 60,000 one can detect and identify halogenated POPs present in complex matrix samples and obtain comprehensive information related to relative intensities. Profiling a sample for its congeners composition can help elucidate the source of these compounds. It is known that the specific fingerprint of dioxins and furans occurring in a sample can be used in the search for sources of the contamination. An example of full scan accurate mass screening is given below for TCDFs congeners detected in several environmental samples (Figure 1 and Figure 2).

Figure 1. TCDF native, fly ash. Isotopic pattern fit and accurate mass measurements peak at RT = 28.33 min

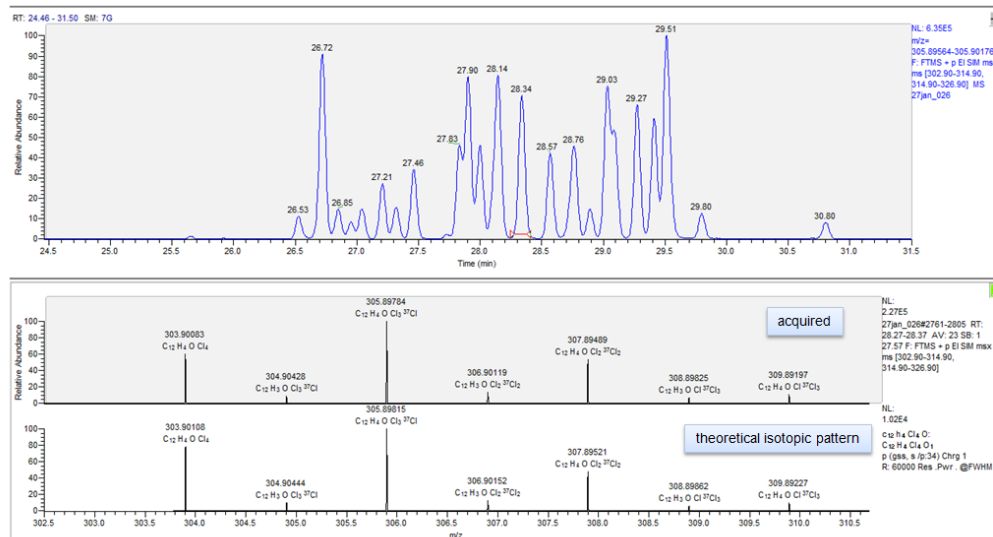
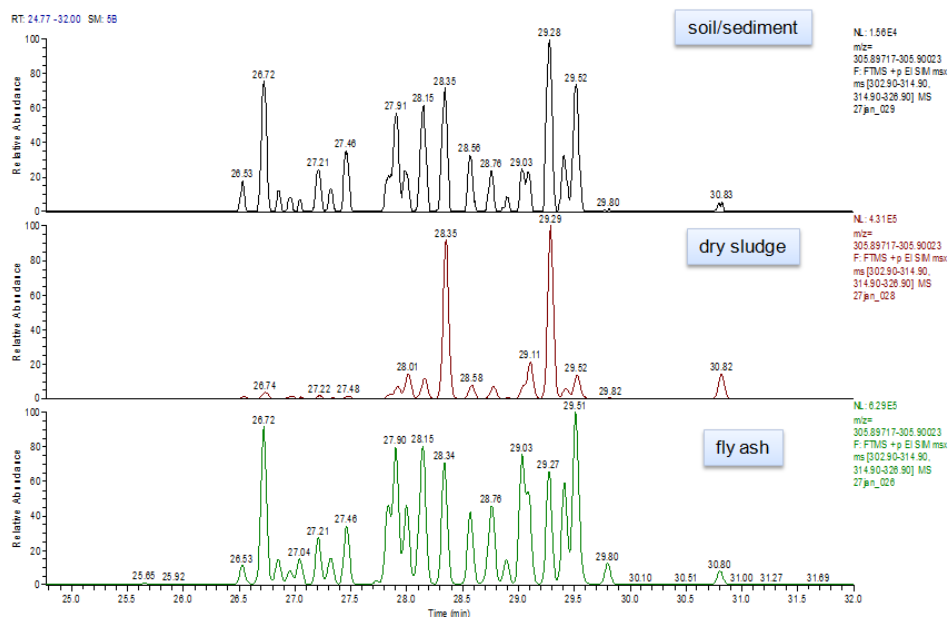


Figure 2. Native TCDF profile in environmental samples. Data acquired using 60,000 resolving power (FWHM at m/z 200) and electron ionization.



Samples containing challenging matrix components, such as fish, can be easily screened for their POPs content. In the examples below, a full profile of tetra- and pentachlorinated PCBs was obtained using high resolution full scan acquisition and by using this information one can rationalise the source of contamination (Figure 3 and Figure 4).

Figure 3. Extracted ion chromatogram of tetrachlorinated non-dioxin like PCBs profile in fish.

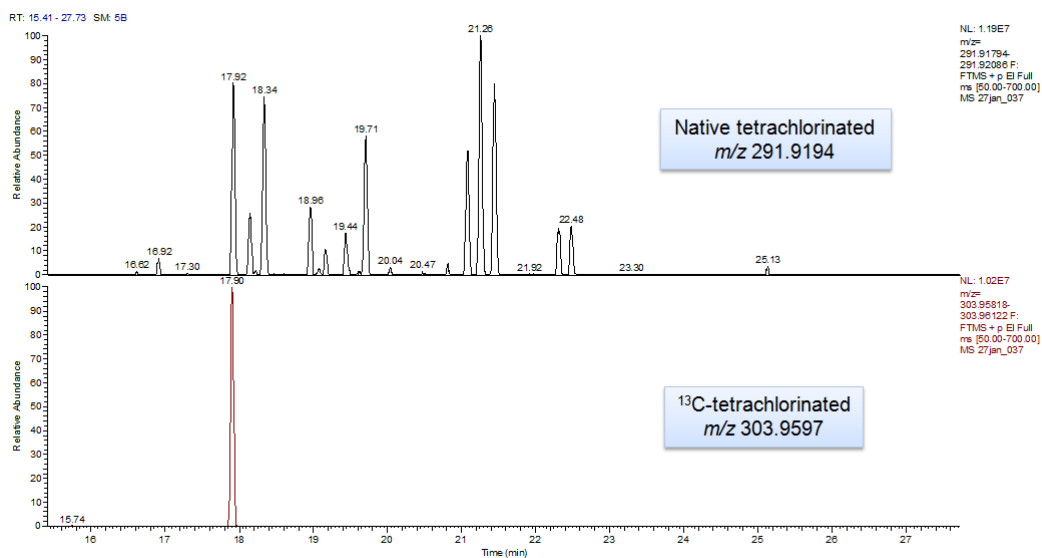
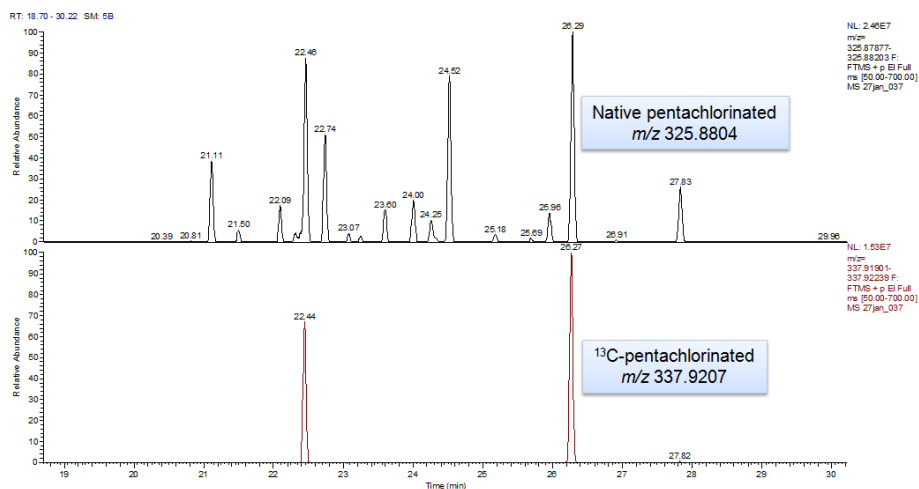
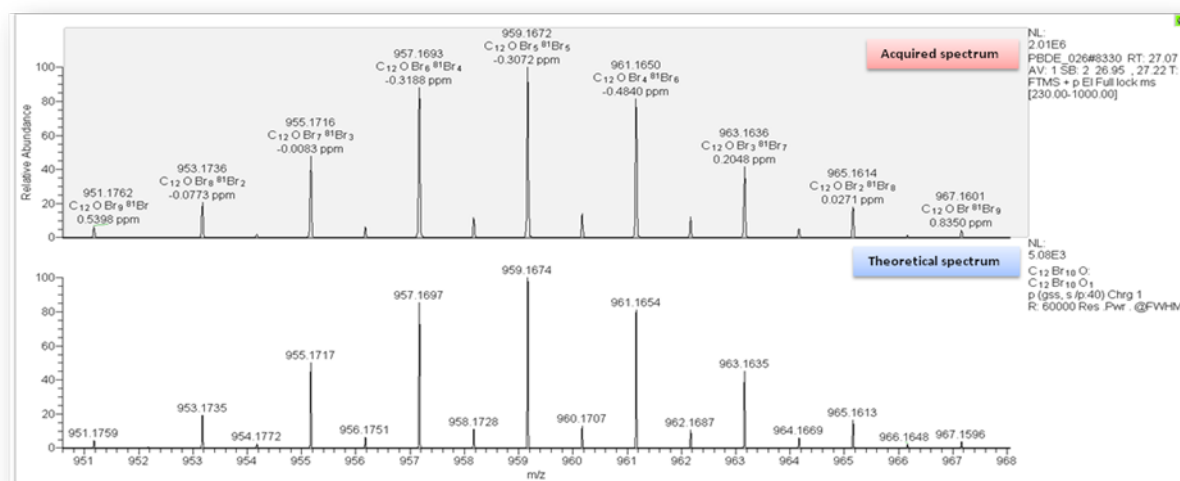


Figure 4. Extracted ion chromatogram of pentachlorinated non-dioxin like PCBs profile in fish.



Confirmation of detected compounds was based on both accurate mass and isotopic distribution information. An example of compound confirmation is shown below where the molecular ion cluster of deca-PBDE ($C_{12}Br_{10}O$) was compared with the theoretical isotopic distribution (Figure 5). In addition, the mass accuracy for each ion in the molecular ion cluster was <1 ppm with an overall mass error of <0.6 ppm RMS.

Figure 5. Mass accuracy (<0.6 ppm RMS) of high masses shown for deca-BDE molecular ion cluster ($C_{12}Br_{10}O$). Data acquired in full scan at 60k resolving power.



Taken together, the GC-Orbitrap mass spectrometer is a unique tool that can be successfully used for high resolution accurate mass screening of POPs in a wide range of sample types. The outstanding mass accuracy obtained allows for unambiguous identification and elemental composition confirmation of halogenated POPs whereas routine high resolving power allows for excellent selectivity in difficult matrices.

References:

1. Carpenter (Editor) (2013) Effects of Persistent and Bioactive Organic Pollutants on Human Health. John Wiley & Sons, Inc., Hoboken, New Jersey.
2. Commission Regulation (EU) No 589/2014 of 2 June 2014 laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EU) No 252/2012, OJ L 164, 3.6.2014, p. 18–40.
3. Stockholm Convention on Persistent Organic Pollutants Stockholm, 22 May 2001.