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HIGH RESOLUTION ACCURATE MASS SCREENING FOR PERSISTENT ORGANIC POLLUTANTS IN FOOD SAMPLES USING GC-ORBITRAP MASS SPECTROMETRY

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Introduction

Persistent organic pollutants (POPs) are toxic organic chemicals harmful for humans and the environment[1]. These chemicals can be transported from the location of origin via wind and water and can affect people around the globe. The extreme toxicity of these compounds is related to the fact that these compounds persist in the environment for very long times and tend to accumulated in the trophic chains. Controlling the use and manufacturing of POPs is monitored through the Stockholm Convention at both national and global level[2].

POPs include a wide range of intentionally and unintentionally produced chemicals. Intentionally manufactured POPs include polychlorinated biphenyls (PCBs) and certain pesticides such DDT, whereas the unintentionally produced POPs consists mainly of dioxins and dioxin-like chemicals.

Current methodology for the detection, confirmation and quantification of POPs in food and environment follows strict regulations and guidelines. The regulatory levels set the allowable concentration at extremely low levels and typically these detection limits can be routinely achieved by using GC-MS/MS (triple quadrupole) and GC-high resolution magnetic sector mass spectrometry after a very thorough, costly, and time-consuming sample cleanup. 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.

New opportunities have recently emerged to be able to perform highly sensitive and selective full scan acquisitions of samples with the introduction of Orbitrap GC-MS. This technology offers resolving powers up to 120,000 (at m/z 200) with mass accuracy <1ppm in full scan often with sub-ppb detection limits and a large linear dynamic range of >6 orders. This means that untargeted acquisitions are possible, whilst still maintaining the ability to detect and quantify at very low levels and more importantly, with reduced sample clean-up procedures. This also allows the chance to mine full scan data to search for novel or unexpected compounds during the analysis, or in the future when new information becomes available. This work reports the first experiences with respect to the utilisation of this technology for POPs analysis.

Materials and methods

In the experiments described in this work a novel approach for screening food samples for the presence of POPs is presented. The analytical instrument used was a Thermo Scientific™ Orbitrap mass spectrometer coupled with a Thermo Scientific™ TRACE™ 1310 GC.

A total of 30 g of freeze-dried bonito (Sarda sarda) muscle meat was extracted in a Soxhlet for ~24h with toluene:cyclohexane (1:1). No internal standards were added. Next, the extract was rotary concentrated and transferred to n-hexane. The organic components, fats and other interfering substances were removed using a 140g silica gel column modified with sulphuric acid (44%) and the cleaned sample was subjected to GC-MS analysis.

Sample introduction was performed with a Thermo Scientific™ TriPlus™ RSH autosampler, and compound separation was achieved on a Thermo Scientific™ TraceGOLD TG-5SilMS 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. Peaks deconvolution and library search for compounds identification was automatically performed using the Thermo Scientific™ TraceFinder™ software.

Results and discussion

Using the GC-Orbitrap mass spectrometer operated at routine high resolving power of 60,000 (FWHM at m/z 200) one can detect and confidently identify halogenated POPs present in complex matrix samples and obtain comprehensive information related to relative intensities. Screening for chemical contaminants such as POPs using high resolution full scan acquisition offers the advantage of rapid detection, identification and reporting of unwanted chemicals in a sample. An example of the complexity of the bonito fish sample as compared to a solvent blank is given in Figure 1.

To assess the potential of an untargeted screening approach, full scan high resolution data was submitted to TraceFinder for automatic peak deconvolution, NIST library search and high resolution filtering for compound identification. Several contaminants were immediately detected and confirmed as shown for DDE (Figure 2).

The compounds that contributed the most to sample toxicity (based on peak intensity profile) were bifenthrin, DDE and PCBs, with hexachloro-PCBs as dominants POPs (Figure 3 & Figure 4). This is in accordance to recently published data which reports dominant levels of chlorinated pesticides (DDT) and PCBs in tuna fish[3].

In addition to automatic untargeted screening, a targeted screening for low level contaminants such as chlorinated dioxins and furans was performed using the exact mass information (mass window ±2 ppm) for each chlorination level. Example of positively detected dioxins and furans are shown in Figure 5 & Figure 6.

The approach described here recommends the GC-Orbitrap mass spectrometer for fast untargeted and targeted screening of POPs in complex samples that were subjected to little clean-up. These preliminary results show that this analytical system is a unique tool that can be successfully used for high resolution accurate mass screening of POPs. The routine high resolution offers excellent selectivity in difficult matrices and the mass accuracy obtained allows for unambiguous identification and elemental composition confirmation of chemical contaminants.

References

1. Carpenter (Editor) (2013) Effects of Persistent and Bioactive Organic Pollutants on Human Heath. John Wiley & Sons, Inc., Hoboken, New Jersey.
2. Stockholm Convention on Persistent Organic Pollutants Stockholm, 22 May 2001.
3. Munschy C. et al (2016) Persistent Organic Pollutants in albacore tuna (Thunnus alalunga) from Reunion Island (Southwest Indian Ocean) and South Africa in relation to biological and trophic characteristics. Environmental Research, 148:196-206 doi: 10.1016/j.envres.2016.03.042. Epub 2016 Apr 14.

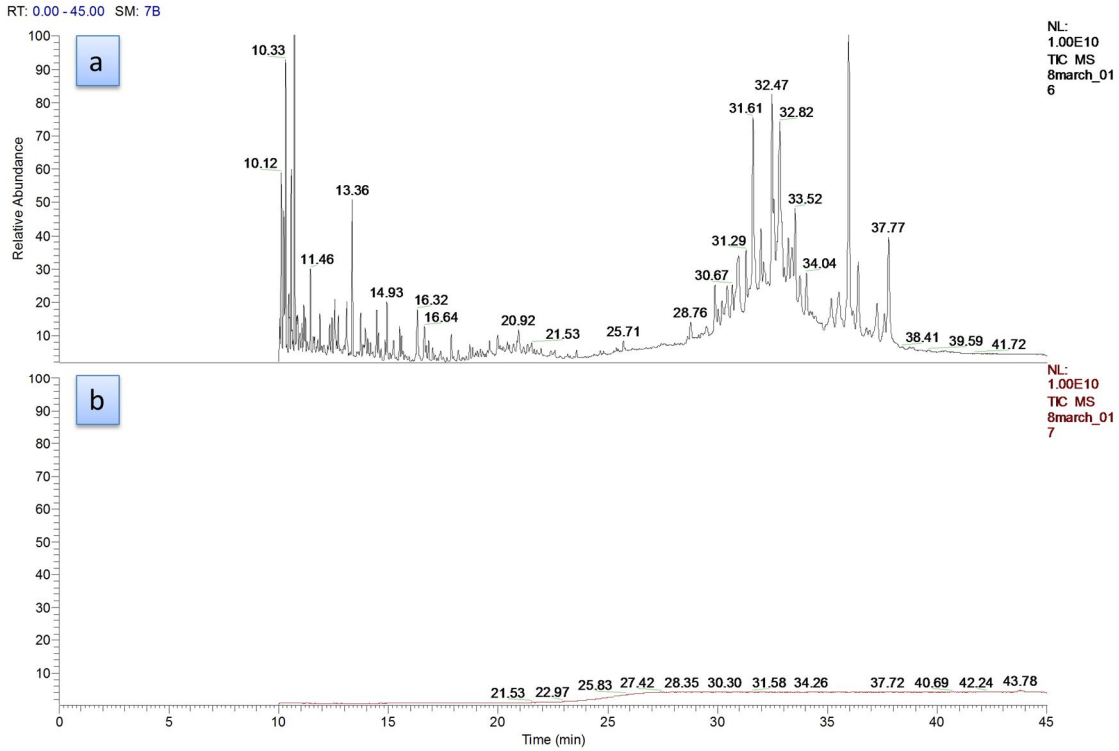

Figure 1. Full scan TIC of fish sample (a) and toluene solvent blank (b) showing the complexity of the matrix.

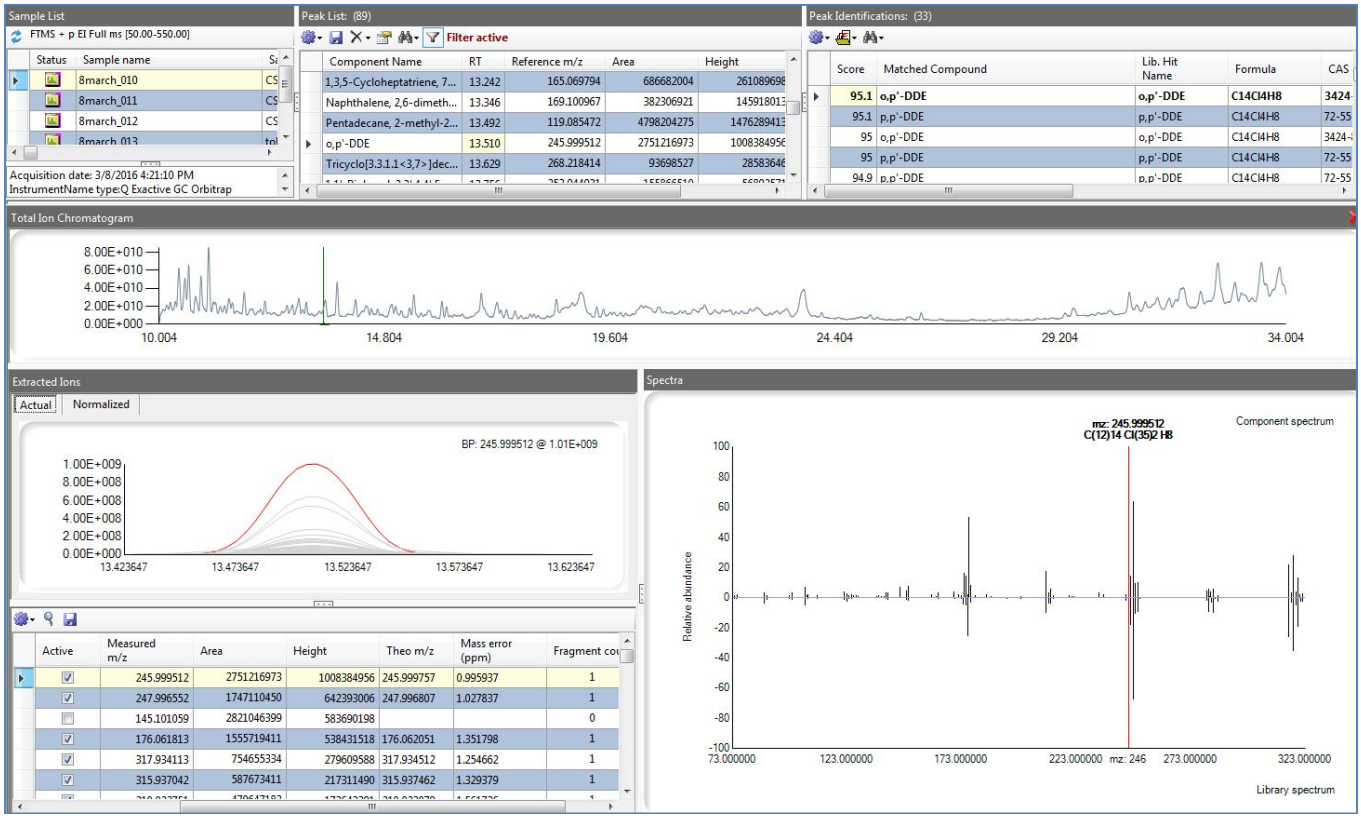

Figure 2. Untargeted screening for POPs in bonito sample. Example of TraceFinder deconvolution results browser showing o,p'-DDE detected and identified at RT=13.51 min.

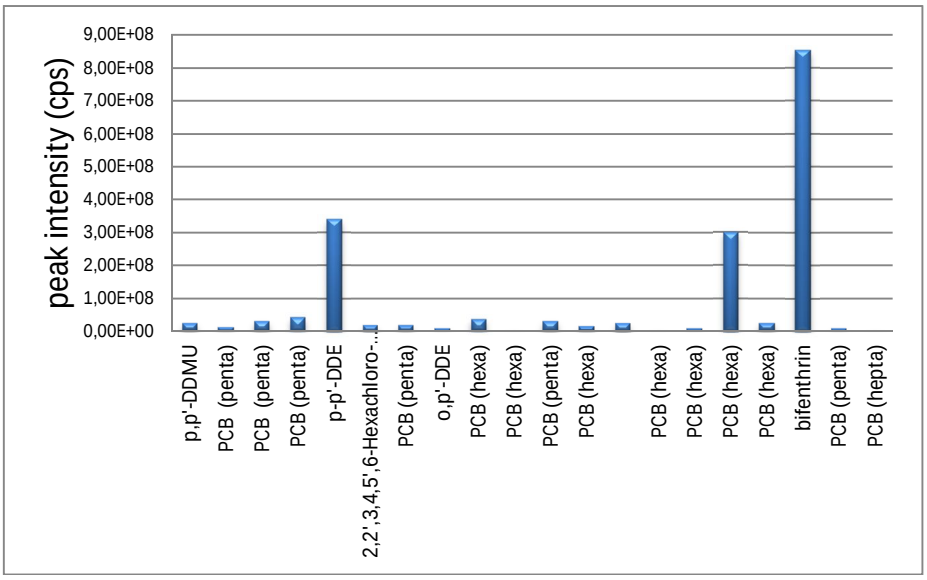

Figure 3. Main contaminants detected in the bonito fish sample.

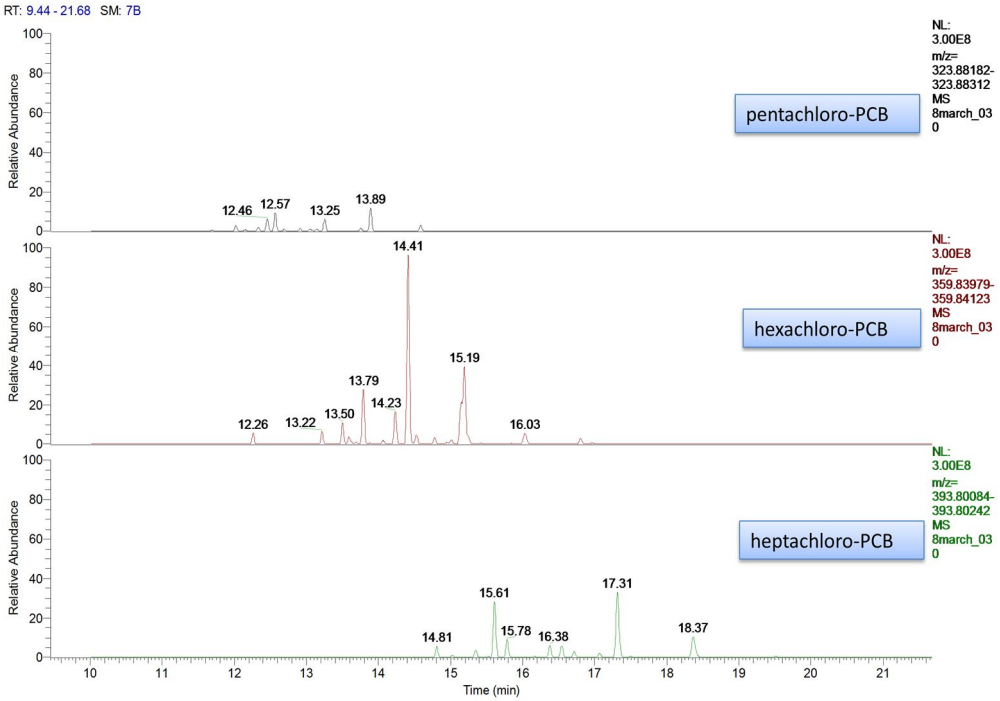

Figure 4. PCB profile of the bonito sample showing hexachloro-PCB as dominant POPs (normalised y-scale).

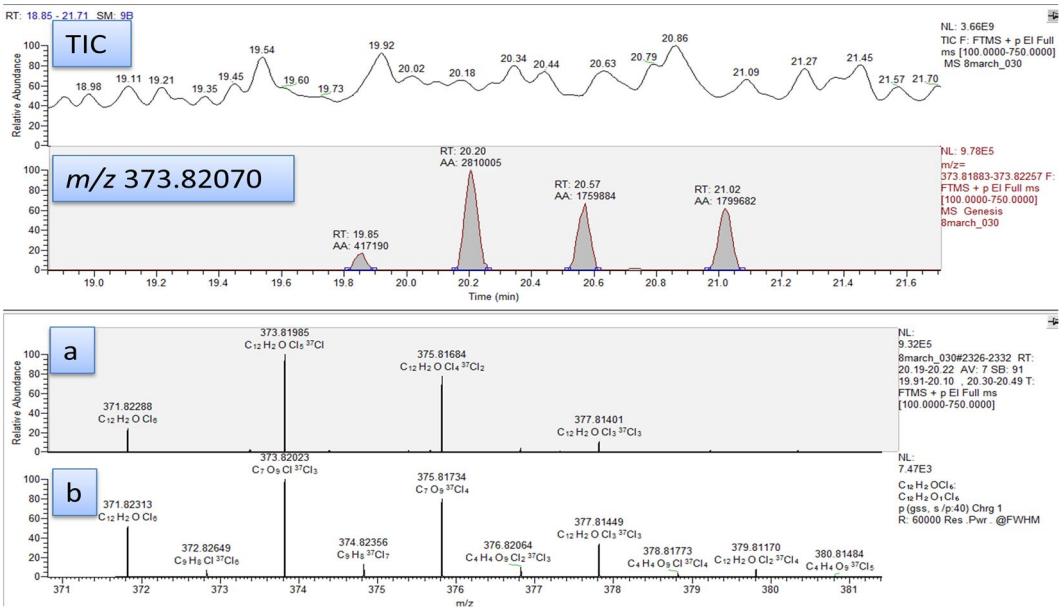

Figure 5. Targeted screening showing HxCDF congeners in the bonito fish sample. Measured (a) and theoretical isotopic cluster for $C_{12}H_2OCl_6$ are shown (b).

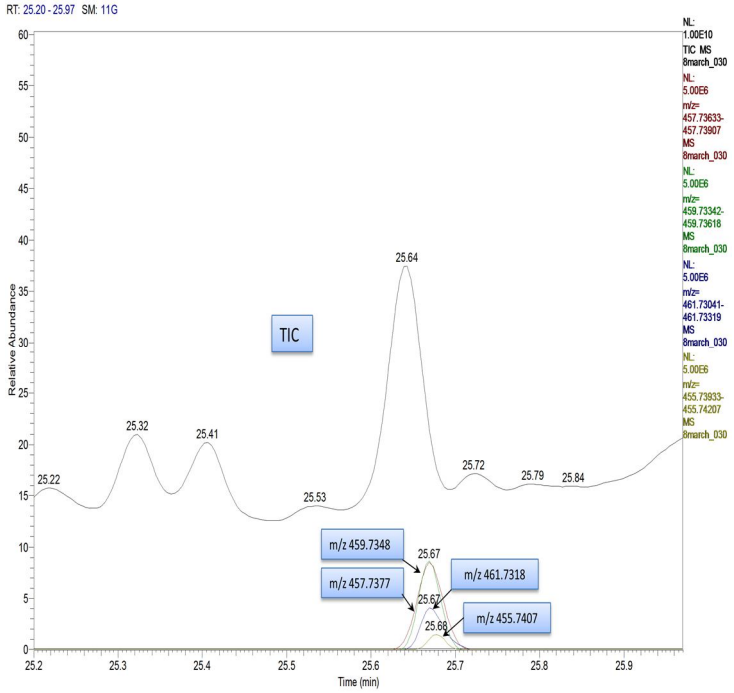

Figure 6. OCDD in bonito fish sample. Extracted ion chromatograms of the four most intense ions for OCDD and the total ion chromatogram (TIC) are shown.