

GC \times GC-(MR)TOFMS in Food and Feed Control: Going Beyond Dioxin Measurements

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Introduction: The measurement of dioxins and dioxin-like compounds in food and feed (ingredients) is an important task within the EU food safety policy. It has been heavily documented and described in detail in official EU Regulation documents for the last 20 years. Such measurements require the best available gas chromatography mass spectrometry (GC-MS) technology in terms of sensitivity and specificity. Both gold standard sector MS and triple quadrupole MS analyzers, performing in isotope dilution (ID) mode, are used as confirmatory tools for precise and accurate measurements under the EU legislation¹. The required sensitivity is achieved by performing in selected ion monitoring (SIM) or selected reaction monitoring (SRM), limiting the measurements to the specific target analytes for which EU maximum levels were established. Comprehensive two-dimensional GC coupled with time-of-flight MS (GC \times GC-TOFMS), acquiring all masses within a defined mass range, has been used for dioxin measurement in the past² but was suffering from limited sensitivity at the high fg level, despite the zone compression effect of the modulator³. A new generation of GC \times GC-TOFMS systems has been investigated in terms of target and non-target measurements of dioxins in food/feed samples.

Materials and Methods: All experiments were carried out inside an ISO 17025 certified dioxin laboratory. The GC \times GC-TOFMS instruments were the new medium resolution LECO Pegasus[®] BT4D. Food and feed samples were replicates of bentonite specimen processed under routine measurement in our lab. The egg sample originated from the State Veterinary and Food Institute (SVFI) in Košice, Slovakia. After reanalysis and confirmation of SVFI results it was provided to CART by the Bioassay Research Lab at the European Union Reference Laboratory (EU-RL) for Dioxins and PCBs in Feed and Food in Freiburg, Germany.

Results: The new generation of TOFMS allows to reach ultra-trace level (fg) detection at high acquisition frequency. Sensitivity and linearity of the GC \times GC-TOFMS instrument towards dioxins and related compounds provide new possibilities in food and feed sample screening. As a first approach, figures of merits were obtained on the 21 dioxins and dioxin-like compounds included in EU legislation. For TCDD, 10 fg on column could be detected with a S/N of 6. Pushing the detector voltage, we were able to reach 100 ag on column detection. For all 21 compounds the degree of linear correlation (goodness of fit, R²) was 0.97 to 0.99. We also considered several real food/feed samples to estimate a potential impact of matrix effects on performance. Three bentonite extracts were injected, and results showed that, despite the extensive sample preparation of the samples, an important background matrix noise was challenging full scan data acquisition at the high fg level for the TOF analyzer. Nevertheless, the capacity of the GC \times GC-TOFMS was tested to screen typical dioxin extracts for other emerging contaminants. An egg sample that displayed a non-typical behavior in the CALUX bioassay (60 pg BEQ/g fat) when compared to GC-ID-HRMS (0.6 pg TEQ/g fat) was investigated. The non-targeted screening using the TOFMS in full scan mode allowed for detection of various congeners of polybrominated dibenzofurans (PBDFs), some of which have been shown to exhibit considerable AhR-mediated dioxin-like activity^{4,5} and may therefore be responsible for the high response in the assay. PBDFs may contribute significantly in daily human background exposure to the total dioxin toxic equivalencies (TEQs)⁶. However, as brominated analogues of dioxin-like compounds are not (yet) included in the WHO Toxicity Equivalency Factor (TEF) scheme and thus in EU legislation, the egg sample would have to be declared “compliant” with EU legal limits, ignoring the general toxicity.

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