No.000134

Dioxin Food Crises and New POPs: Challenges in Analyses

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Keywords: Food; Screening; SectorHRMS; HRTOFMS; GCxGC

When more than a million of broiler chickens suddenly and unexpectedly died in the eastern and midwestern parts of the United States in late 1957, the first dioxin crisis record was set. The 1999 Belgian dioxin chicken gate affair ultimately demonstrated the economic damage such a contamination episode could yield to and pushed the European Union (EU) to set an efficient and pro-active monitoring program to ensure proper quality of the European food and feed web and try to maintain most of the population below tolerable weekly intake. The current European Commission (EC) strategy relies on the implementation of maximum (and action) residue levels (MRLs) for selected polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) (both families actually called 'dioxins'), and dioxin-like polychlorinated biphenyls (DL-PCBs).

To ensure the adequate production of comprehensive and reliable data on the presence of PCDD/Fs dioxins and DL-PCBs in food and feed, a screening-confirmatory approach was thus early adopted for the official control of the PCDD/F dioxins and DL-PCBs. In practice, screening is most of the time performed using chemical activated luciferase gene expression (CALUX) bioassays, response-binding assays (RBAs) based on the aryl hydrocarbon receptor (AhR), although the sole confirmatory method is gas chromatography coupled to ^{13}C-labeled isotope dilution sector high resolution mass spectrometry (GC-IDHRMS) [1]. More than 10 years after the implementation of the screening-confirmatory approach, the analytical situation has drastically evolved because of advances in automation and hyphenation of parallel sample preparation techniques that allowed both cost and result delivery time to be significantly reduced (down to 350 EUR and 24h, respectively) for the confirmatory GC-IDHRMS method.

Nevertheless, RBAs could and should now be used with non-restrictive sample preparation techniques that would allow most toxicants present in the sample to interact with the AhR to give a general persistent organic pollutant (POP) toxicity information rather than an estimation limited to dioxin regulation compliance. This would be much more biologically relevant and would allow to enlarge current food safety practices to other known and unknown POPs. Sample showing high response for the biological screening should be further analyzed in the hope of identifying new compounds. The extension of the list of target compounds to more 'exotic' (un)suspected persistent molecules present in our food requires both chromatographic resolution and instrumental limits of detection (iLODs) to be improved.

Using comprehensive two-dimensional GC (GCxGC) [2] or cryogenic zone compression (CZC) [3] GC coupled to HR time-of-flight MS (HRTOFMS) operating in full scan (FS) mode [4] could nicely complement the classical GC-sector IDHRMS performing in selected ion monitoring (SIM) used for target analyses. This would open the possibility to screen for other compounds (organochlorine pesticides, halogenated flame retardants, GC-amenable perfluorinated compounds,) than the one under current regulation without compromising sensitivity. Recent advances in coupling between GCxGC and HRTOFMS nicely put this approach one step further as it allows to produce elemental composition data for unknown compounds present in complex mixtures. Furthermore, when considering halogenated compounds, such a system can be granted by a tremendous improvement in sensitivity (back to low fg iLODs) by favoring resonance electron capture (REC) when operating in negative chemical ionization (NCI) rather than electron impact (EI). Major recent analytical advances in the GC-MS of emerging GC-amenable POPs in the context of prioritization of new targets for food control will be highlighted.

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Novel aspects:
Comprehensive emerging POP analyses