Valued GC-MS/MS confirmatory method for the EU official control of levels of PCDD/Fs and DL-PCBs in feed material of plant origin

L’Homme B., Scholl G., Eppe G., Facont J.-F.
CART, Organic and Biological Analytical Chemistry, Department of Chemistry, University of Liège, Belgium

Context

Introduction and strategy
Criteria for sampling and analysis for the official control of dioxins (PCDD and PCDF) and dioxin-like (DL) PCB in feeding stuffs and certain foodstuffs are described in Commission Regulation (EU) No 709/2014 and No 589/2014. They allow the use of GC–QQQ as confirmatory method in addition to GC-HRMS. We present a full validated method using the Agilent GC-QQQ 7000C instrument for the analysis of PCDD/Fs and DL-PCBs in vegetable oil (feed). We assessed individual analytical criteria specified in the above documents and checked that they meet the requirements. In this study we preferred observing performances of the QQQ (and their compliance with the Regulation), starting from basics, rather than simply comparing duplicated results on QQQ and HRMS. We therefore compiled results arising from different criteria and finally assessed the measurement uncertainty based on those.

Instrumentation & parameters
GC: Agilent 7890B GC equipped with a PTV injector and 7693A automated liquid sample (ALS).
Column: DB-5ms 60m x 250µm x 0.25µm
MS: Agilent 7000B series GC-QQQ with 7000C electron ionization (EI) source; ion source T=150°C; N2. nitrogen flow=1.5 mL/min; H2. quench flow=2.35 mL/min.
T = 120°C (5 min); 25°C/min until 250°C (5 min); 3°C/min until 285°C (15 min).
PTV injection mode: start at 40°C (3 min) and ramp at 720°C/min until 130°C; end flow=50 mL/min (P=5 psi) until 2.8 min; purge flow=50 mL/min at 5 min.

Validated GC-MS/MS confirmatory method for PCBs. The GC-HRMS method provides for GC-MS/MS. Unlike for GC-HRMS, signal-to-noise (S/N) ratio is not suitable (for tetra/penta dioxins and furans), 13C12-1,2,3,4,7,8,9-HpCDF (for PCBs) each compound is defined by a qualifier and a qualifier MMR transition whose collision energy (CE) has been optimized. Recovery experiments for accuracy and reproducibility tests are performed using fortified (with all congeners) sunflower oil.

Selectivity, linearity
Control of 3 criteria to be verified during analysis: 1) retention time (RT) of targets must be within ±5% window from the internal standard. 2) MMR transition ratio (quant/qual), determined experimentally from standard injections, must be within the ±15% tolerance window. 3) Separation valley between targets must be within a ±3σ window from the internal standard. 2) MRM

Results and validation

Table 1: results for injections of 6 series of fortified vegetable oil in 3 days (2 series injected per day)