

Simplified and rapid determination of PCBs, PBDEs and PAHs in fishfeed using GC×GC–TOFMS and GC-MS/MS

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Abstract In this study, a new rapid and flexible method for the simultaneous determination of 18 key representatives of polychlorinated biphenyls (PCBs), 7 polybrominated diphenyl ethers (PBDEs), and 16 polycyclic aromatic hydrocarbons (PAHs) in fishfeed by gas chromatography coupled to mass spectrometry (GC–MS) was developed and validated. A substantial simplification of sample processing prior to quantification step was achieved: after addition of water to homogenized sample, transfer of hydrophobic analytes into ethyl acetate was supported by added inorganic salts. Bulk fat, contained in crude organic extract obtained by partition, was subsequently removed on a silica minicolumn. This approach enabled to process six samples in less than 1 h; moreover, the volume of an extraction solvent and consumption of other chemicals can be significantly reduced compared to, e.g., traditional Soxhlet extraction followed by gel permeation chromatography. The recoveries of target analytes were between 70% and 120% even at the lowest spiking level (1 µg/kg), repeatabilities (relative standard deviations, RSDs) ranged from 1 to 20%.



Following the development of an integrated sample preparation procedure, a comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometry (GC×GC–TOFMS) for the simultaneous determination of all mentioned groups of contaminants in fishfeed extracts was optimized to obtain the best chromatographic resolution and low quantification limits (LOQs) of all target analytes in a complex mixture. Two injection techniques, pulsed splitless and large volume programmable temperature vaporization (LV-PTV), and several capillary column combinations (BPX5, BPX50 and Rxi-17Sil-ms in the 1st dimension and BPX5, BPX50, Rt-LC35 and HT8 in the 2nd dimension) were tested within the experiments. Only BPX5×BPX50 set-up was able to separate all critical groups of PAHs as well as all PCBs and PBDEs. Application of LV-PTV injection decreased LOQs of some analytes even more than 10-times. The LOQs achieved using LV-PTV–GC×GC–TOFMS were as follows: PCBs 0.01–0.25 µg/kg, PBDEs 0.05–5 µg/kg, PAHs 0.05–0.5 µg/kg.

Finally, GC coupled to triple quadrupole mass spectrometry (GC–MS/MS) for the identification and quantification of PCBs, BFRs and PAHs in fishfeed was employed. LOQs obtained using this instrumental technique were as follows: PCBs 0.01–0.025 µg/kg, BFRs 0.025–0.1 µg/kg and PAHs 0.01–0.05 µg/kg, which means decrease of LOQs especially in

case of higher PBDEs, compared to single quadrupole MS. Moreover, further improvement might be possibly achieved by LV-PTV injection technique.

Keywords fishfeed;POPs;PAHs;PCBS;PBDEs;GC-MS/MS;GCxGC-TOFMS

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