Development and validation of analytical methodology for the determination of per– and poly–fluoroalkyl substances (PFAS) in fish feed samples using modified QuEChERS and LC– HRMS.

Ourania Koloka, Vasiliki Boti, Dimitra Hela, Triantafyllos Albanis, Ioannis Konstantinou [a, b]

Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

e-mail: iokonst@uoi.gr

Per- and polyfluorinated alkyl substances (PFAS) contain a large number of compounds widely used in a variety of industrial and consumer products due to their properties such as resistance to high temperatures, thermal and chemical stability, water repellant properties etc. However, due to their high persistence, also called ‘’*forever chemicals*’’, they have been detected in various environmental matrices and biota tissues. PFAS have been also recently detected in fish feed samples, thus they that can be transferred and accumulated to fish and consequently to humans. It is therefore necessary to consider the quality control of the whole food production chain, including fish feed. To this purpose, a targeted method for the determination of PFAS in fish feed has been developed and fully validated in the current work using a modified “Original” QuEChERS extraction and liquid chromatography – high resolution linear ion trap-Orbitrap mass spectrometry (LC–HR-LTQ-Orbitrap-MS). Variations of sample amounts (2 and 5 g), sonication treatment times (15 and 30 min) and clean-up sorbent and protocols (Z–sep$^+$ (Method A), Z–sep$^+$ and PSA (Method B), EMR–Lipid (Method C) were tested to recover 18 PFAS from the fish-feed matrix. The optimum parameters were 2 g initial sample amount, 30 min sonication time and EMR–Lipid clean-up. The validation included the assessment of linearity, recovery, matrix effects, accuracy, intraday/interday precision, limits of detection and quantification, reporting limits and measurement uncertainty. Method validation was performed at two concentration levels (0.2 and 50 ng/g) showing good performance as follows: linearity (r^2 >0.99), recovery (51.1% – 101.2%), precision (RSD <20.7%), limit of detection (LOD: 0.01 – 0.15 ng/g) and quantification (LOQ: 0.03 – 0.50 ng/g), decision limit (CC_α: 0.01 – 0.09 ng/g), detection capability (CC_β : 0.03 – 0.16 ng/g), matrix effects (ME: -50 to -12.4%), and measurement uncertainty (MU: 24.56 – 57.66 ng/g) at the lowest concentration level of 0.2 ng/g. The validated method was applied to 30 fish feed samples of different origin revealing the presence of PFOA in one sample (concentration of 0.34 ng/g) and the PFOS in two samples (concentrations of 0.60 ng/g and 0.77 ng/g, respectively).

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