Method validation of PFAS compounds in fish tissue based on guidelines of EURL-POPS

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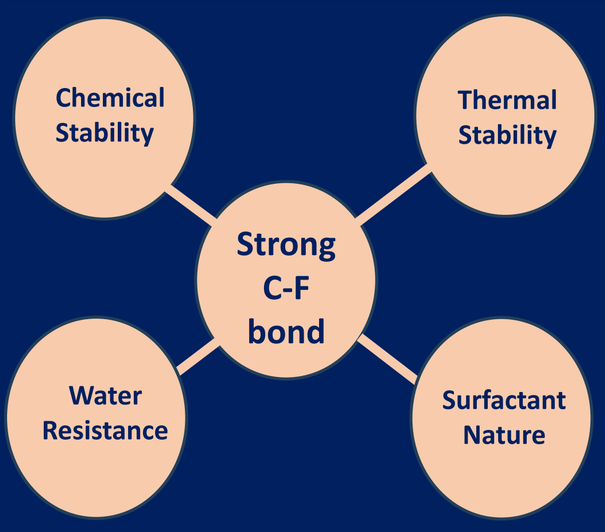
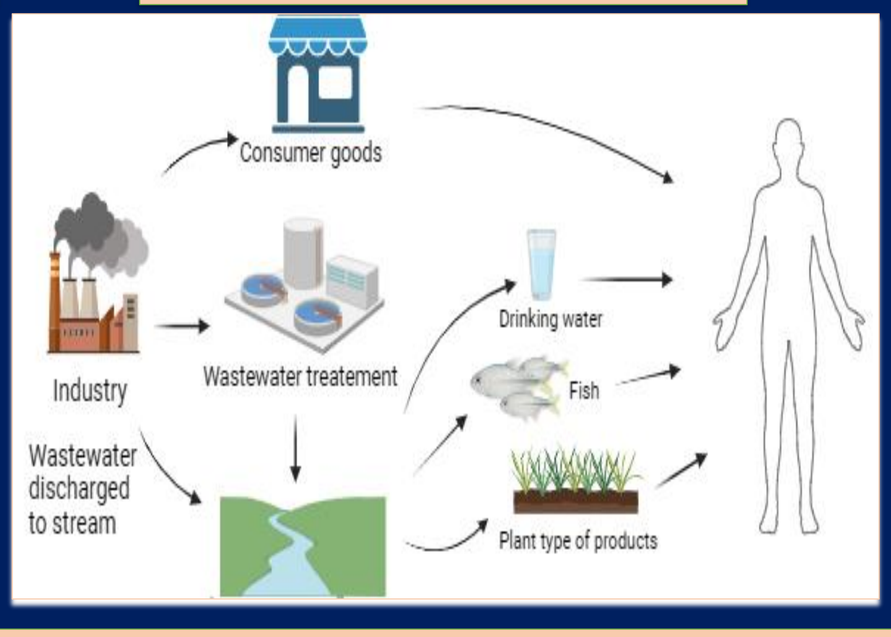
ABSTRACT

Per- and polyfluoric alkylated substances (PFAS) are chemical compounds used by the industry from the decade of 1940s. Although they are widely used for so many years, the last decade became known that they have harmful effects for the environment and all the living species. Due to the existence of the strong chemical bond C-F, this kind of compounds cannot be destroyed by a chemical or biological reaction. This is the main reason why PFAS are connected with devastating consequences for the health, such as the existence of cancer, hormone malfunctions and problems in the reproductive system. The most significant way that PFAS can exist in every human being is from food. Unfortunately, the industry wastes end up to the sea and all creatures living there interact with harmful compounds. The result is that fish, which consist the main source of a lot of nutrients and traditional dish for many civilisations, end up with a big amount of PFAS. The increased interest in PFAS and the need to determine this kind of substances in an important part of a healthy diet lead to the need of methods for the determination of PFAS in food and feed. Recently, European Union Reference Laboratory for Halogenated Persistent Organic Pollutants (EURL-POPs) issued a dedicated guideline with the requirements of performance characteristics for analytical methods of PFAS in food and feed. The aim of this study is to present the fitness of purpose of a LC-MS/MS method for the determination of PFAS in fish tissue. Trueness, precision, Limit of Detection and Limit of Quantification were estimated based on the requirements of EURL-POPs guidelines for regulated (PFOS, PFOA, PFNA, PFHxS) and non-regulated (PFBS, PFDA, PFUdA) PFAS.

Physical & Chemical Properties



PFAS Cycle



Experimental Part & Instrumentation

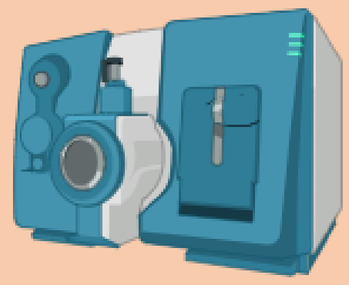
LC-MS/MS: AB Sciex QTRAP 6500+ Exion LC

Column: Zorbax Eclipse Plus C18

Delay Column: Rapid Resolution HT 2.1×100 mm. 1.8 µm

Negative ionization (-)

QuECheERS method: use of ACN as extraction solvent and $MgSO_4$, NaCl, PSA and C18 as cleaning salts



Performance Characteristics according to EURL- POPs

Maximum Residue Level (µg/kg) of PFAS in fish tissue	
PFOS	7.0
PFOA	1.0
PFNA	2.5
PFHxS	0.2
PFBS. PFDA. PFUdA	1.0

Linearity	Trueness	Precision	LOD & LOQ
Deviation of back-calculated concentration from true concentration ≤ 20 %	80-120% for compliance testing and 65-135% for monitoring purposes	≤20% for compliance testing and ≤25% for monitoring purposes	LOQ: ≤ 0.10 µg/kg
Spiking curve of concentrations 0.1, 0.25, 0.5, 1, 2 and 4 X MRL	Spike in 3 levels of concentration (0.5, 1 and 2 X MRL) and calculation of %Recovery	Calculation of %RSD from results generated under repeatability and intermediate precision conditions	Spike in the lowest level of concentration and calculation of SD of different measurements

Validation Results

Analyte	IS	Linearity (Σ%RE)	Trueness (%Recovery) [Level MRL]	Repeatability (%RSD) [Level MRL]	Intermediate precision (%RSD) [Level MRL]	LOD (µg/kg)	LOQ (µg/kg)
PFOS	M8PFOS	3.44	88.3	1.9	9.6	0.022	0.073
PFOA	M8PFOA	4.47	82.1	1.1	18.2	0.027	0.089
PFNA	M4:2FTS	8.33	107.2	2.9	3.9	0.021	0.069
PFHxS	M3PFHxS	17.4	118.4	0.4	7.2	0.022	0.073
PFBS	M3PFBS	4.40	92.7	24.3	24.9	0.029	0.096
PFDA	M4:2FTS	15.7	105.1	13.5	13.3	0.016	0.053
PFUdA	M4PFHpA	9.98	78.8	1.0	6.2	0.020	0.065

Conclusions & Perspectives

- ✓ The deviation of back-calculated concentration from true concentration is ≤ 20 % for all the regulated substances
- ✓ The calculated recovery is in the range of 80-120% for the regulated substances and 65-135% for the non-regulated substances% for the regulated substances and 65-135% for the non-regulated substances
- ✓ Precision is calculated from results generated under repeatability and intermediate precision conditions and it is less than 20% for the regulated substances less than 25% for the non-regulated substances
- ✓ The calculated LOQs are less than 0.10 µg/kg
- ✓ A perspective is to include in the method more compounds which belong to PFAS

References

1. *EURL-POPs. Guidance Document on Analytical Parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed. version 1.2 (2022)*
2. *Commission Regulation (EU) 2023/915 of 25 April 2023 on maximum levels for certain contaminants in food and repealing Regulation (EC)*

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