PFAS - Comparison of MS/MS and MS-TOF techniques & two extraction methods on lean and fatty fish

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INTRODUCTION

Expanding monitoring activities as well as advances in available instrumentation have resulted in the detection of various xenobiotics in the human environment which have been escaping attention for decades. Perfluoroalkylated substances (PFAS) represent one group of emerging contaminants which are of high concern. They are generally persistent in the environment, they can be found over a broad concentration range and within the most parts of the food web in both aquatic and terrestrial organisms. Human food items, produced from natural ingredients (wild or farmed), is likely to be contaminated with PFAS as well, giving rise to human exposure. In terms of monitoring the food contamination, most European countries, as Czech Rep. and Norway, carry out national monitoring programs in order to access the daily intake of persistent organic pollutants. To date, only very few international studies focused on PFAS in food and the assessment of dietary intake has been published in Europe. As examples for highly consumed lean and fatty fish species, trout and salmon filet was analysed comparing two fast extraction methods and two detection techniques (low resolution MS/MS and high resolution TOF-MS).To compare the effect of matrix on the quantification results, solvent based and matrix based standards were applied.

COMPOUNDS

Analytes: 18 different PFAS substances:
- carboxylates (C_4 – C_{14})
- sulfonates (C_4, C_6, C_8, C_{10})
- perfluorooctane sulfonamid
- N-alkylsulfonamides (Me/EtFOSA)

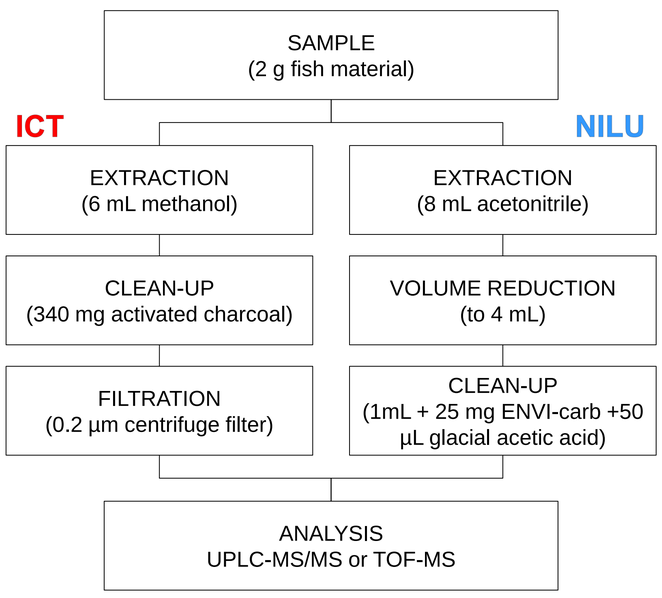
Internal standards: $^{13}C_4$-PFOA and $^{13}C_4$-PFOS
Recovery standard: brPFDcA
Solvent and matrix-matched standard calibration curves: 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50 pg/µL

MATERIAL

Lean fish –Trout

Fatty fish - Salmon

SAMPLE PREPARATION



ANALYSES

LC-system: Waters Acquity UPLC
Column: Waters HSS T3 (100 × 2.1mm, 1.8 µm)
Column oven temperature: 40ºC
Sample temperature: 10ºC
Injection volume: 5 µL

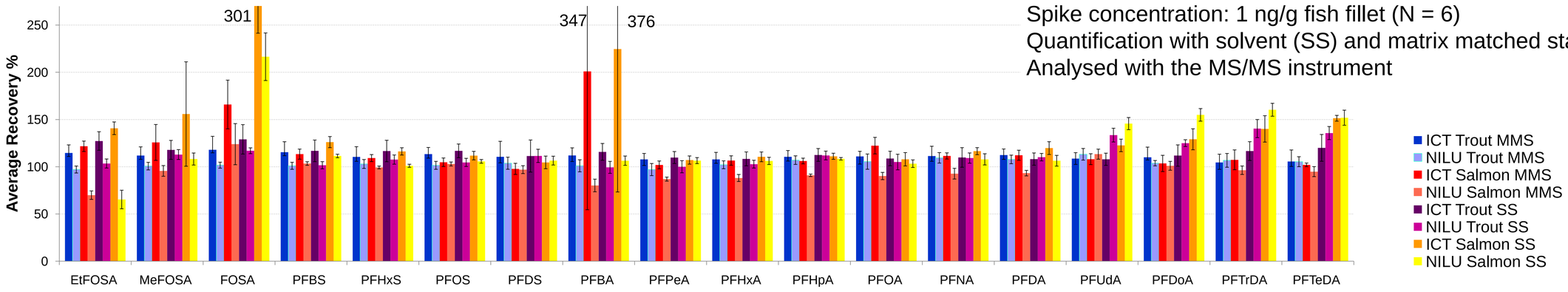
Mobile phase: A methanol and B 5mM NH_4OAc in water
Gradient: initial 0.3 mL/min 10% A; 0.5 min, 40% A; 7 min, 0.4 mL/min, 100% A; 2 min, 0.7 mL/min, 100% A; 2.5 min, 0.45 ml/min, 10% A.

Ionisation mode: ESI negative

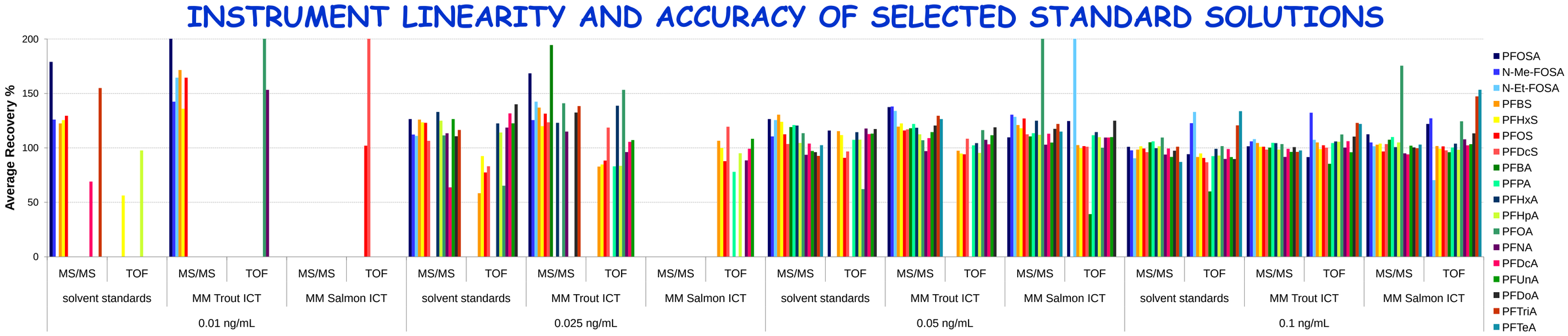
Low resolution MS-system: AB Sciex 5500 Q-TRAP tandem mass spectrometer with a Turbo V^{TM} ion source
High resolution MS-system: Waters LCT premiere XE high resolution time-of-flight mass spectrometer with a Z-spray ion source

ACCURACY AND REPEATABILITY OF THE SAMPLE PREPARATION METHODS

Spike concentration: 1 ng/g fish fillet (N = 6)
Quantification with solvent (SS) and matrix matched standards (MMS)
Analysed with the MS/MS instrument



INSTRUMENT LINEARITY AND ACCURACY OF SELECTED STANDARD SOLUTIONS



	Regression coefficient						Linear range (ng/mL)					
	Solvent standard		MMS Trout ICT		MMS Salmon ICT		Solvent standard		MMS Trout ICT		MMS Salmon ICT	
	MS/MS	TOF	MS/MS	TOF	MS/MS	TOF	MS/MS	TOF	MS/MS	TOF	MS/MS	TOF
PFOSA	0.9979	0.9990	0.9980	0.9977	0.9996	0.9990	0.01 - 50	0.05 - 50	0.01 - 50	0.1 - 50	0.05 - 50	0.05 - 50
N-Me-FOSA	0.9983	0.9993	0.9984	0.9968	0.9992	0.9989	0.01 - 50	0.1 - 50	0.01 - 50	0.1 - 50	0.05 - 50	0.1 - 50
N-Et-FOSA	0.9977	0.9849	0.9986	0.9911	0.9994	0.9991	0.025 - 50	0.1 - 50	0.01 - 50	0.1 - 50	0.05 - 50	0.01 - 50
PFBS	0.9974	0.9988	0.9996	0.9967	0.9995	0.9992	0.01 - 50	0.025 - 50	0.01 - 50	0.025 - 50	0.05 - 50	0.025 - 50
PFHxS	0.9991	0.9975	0.9996	0.9964	0.9997	0.9992	0.01 - 50	0.01 - 50	0.01 - 50	0.025 - 50	0.05 - 50	0.025 - 50
PFOS	0.9997	0.9986	0.9998	0.9973	0.9996	0.9981	0.01 - 50	0.025 - 50	0.01 - 50	0.025 - 50	0.05 - 50	0.01 - 50
PFDcS	0.9989	0.9973	0.9993	0.9970	0.9996	0.9994	0.025 - 50	0.025 - 50	0.025 - 50	0.025 - 50	0.05 - 50	0.01 - 50
PFBA	0.9991	0.9968	0.9995	0.9938	0.9994	0.9969	0.05 - 50	0.1 - 50	0.025 - 50	0.1 - 50	0.05 - 50	0.05 - 50
PFPA	0.9987	0.9998	0.9995	0.9992	0.9995	0.9989	0.05 - 50	0.05 - 50	0.05 - 50	0.05 - 50	0.05 - 50	0.05 - 50
PFHxA	0.9996	0.9990	0.9995	0.9991	0.9994	0.9993	0.025 - 50	0.025 - 50	0.025 - 50	0.025 - 50	0.05 - 50	0.05 - 50
PFHpA	0.9992	0.9997	0.9994	0.9990	0.9995	0.9997	0.025 - 50	0.025 - 50	0.05 - 50	0.025 - 50	0.05 - 50	0.025 - 50
PFOA	0.9996	0.9977	0.9996	0.9990	0.9998	0.9989	0.025 - 50	0.025 - 50	0.025 - 50	0.025 - 50	0.05 - 50	0.05 - 50
PFNA	0.9995	0.9993	0.9986	0.9999	0.9995	0.9998	0.025 - 50	0.025 - 50	0.025 - 50	0.025 - 50	0.05 - 50	0.025 - 50
PFDcA	0.9992	0.9984	0.9992	0.9987	0.9993	0.9989	0.01 - 50	0.025 - 50	0.05 - 50	0.025 - 50	0.05 - 50	0.025 - 50
PFUnA	0.9993	0.9994	0.9993	0.9988	0.9993	0.9995	0.025 - 50	0.025 - 50	0.05 - 50	0.025 - 50	0.05 - 50	0.025 - 50
PFDoA	0.9980	0.9981	0.9988	0.9978	0.9991	0.9981	0.025 - 50	0.025 - 50	0.025 - 50	0.05 - 50	0.05 - 50	0.05 - 50
PFTriA	0.9988	0.9988	0.9978	0.9983	0.9993	0.9974	0.01 - 50	0.1 - 50	0.05 - 50	0.1 - 50	0.05 - 50	0.1 - 50
PFTeA	0.9983	0.9983	0.9987	0.9977	0.9985	0.9971	0.05 - 50	0.1 - 50	0.05 - 50	0.1 - 50	0.05 - 50	0.1 - 50

LOQ = lowest calibration level

➢**At very low concentration levels the instrument accuracy is poor at both instruments, even if the levels are within the linear range of the instrument**

➢**Better selectivity for low chain PFCAs on the TOF instrument (only 1 transition available for detection)**

CONCLUSIONS

➢**Simple high throuput sample preparation methods are suitable for lean and fatty fish filets (10 – 20 samples per hours)**

➢ **Use of solvent standards overestimates longer chain PFCAs (from C_{11}-PFCA), therefore the application of matrix matched standards is recommended if only $^{13}C_4$-PFOA and $^{13}C_4$-PFOS are used as internal standards**

➢**In most cases LOQs are lower when using the MS/MS instrument**

➢**The MS/MS instrument shows slightly wider linear ranges and slightly better regression coefficients compared to the TOF-MS**

➢**Decreased linearity for PFSAs in TOF measurements but only little effect on the PFCAs**

➢**Fatty fish samples cause lower analyte signal in MS/MS – spray issue?**

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norway grants
National Training Fund
Framsenteret