Analysis of PFAS from Food Samples Using EluCLEAN® PFAS SPE Cartridges

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Content

Key Features

- No detectable PFAS background contamination from special SPE cartridges
- Better for clean-up and enrichment for food and feed samples
- Excellent recovery rates and low standard deviations for 50+ PFAS analytes
- EluCLEAN® PFAS – Universal SPE column is a special combination phase that improves the recovery rates of PFAS analytes through numerous interactions. It can be used in a wide variety of matrices.
- EluCLEAN® PFAS – Universal HP version with an improved matrix reduction e.g. for highly pigmented/coloured matrices

LCTech Products

SPE cartridges

Part No.: 20841, 20842, 20843 (Universal) // 20851, 20852, 20853 (Universal HP)

EluCLEAN® PFAS – Universal and Universal HP

Sorbent: special combination phase

Other Relevant LCTech Application Notes and Product Information

https://www.lctech.de/application-notes

https://www.lctech.de/en/products/pfas-workflow

Figure 1. EluCLEAN® PFAS – SPE cartridges for food and feed

Introduction

Per- and polyfluorinated alkyl substances (PFAS) have been in use for over six decades. They are released into the environment during their production, application, and disposal stages. PFAS have negative impacts in human health. Apart from typical PFAS hotspots (where PFAS were manufactured or firefighting foams were used), the use of contaminated biosolids has been one of the major contributors for spreading PFAS in agriculture land.

EU Regulation 2022/2388 sets maximum levels for certain PFAS substances in food such as eggs, fish, mussels, crustaceans, meat and game meat (this regulation is in effect since first of January 2023)[1]. The maximum permitted limit values for PFOS, PFOA, PFNA and PFHxS in animal foods are in the range of 0.3 to 1 µg/kg. This regulation also recommends monitoring of more than 20 other PFAS. These maximum levels have in the meanwhile been included in the Annex to Regulation (EU) 2023/915 [2].

The analytical focus on these compounds has grown significantly in recent years. All methods require solid phase extraction (SPE) prior to liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis. All methods apply SPE cartridges containing a weak anion exchanger, mixed-mode polymeric sorbent, whereas the US EPA 1633 [3] and the DoD/QSM 5.1/5.3 additionally use a dispersive clean-up step depending on the type of matrices.

Nonetheless, analyzing these PFAS compounds can be challenging depending upon different types of food matrices. Furthermore, achieving the LOQs within the framework of the methods also becomes difficult. Solid phase extraction (SPE) is often used to purify and isolate target analytes from impurities. However, this process also becomes difficult especially in matrices with a high number of impurities or certain types of impurities. This challenge can be taken by using special combination of SPE cartridges which were developed to overcome issues with using SPE cartridges with merely WAX.

In this application note two different types of columns; EluCLEAN® PFAS – Universal and EluCLEAN® PFAS – Universal HP SPE cartridges, have been used (which can be used for a variety of food matrices) and also comply to both US EPA and EU regulations.

Figure 2: Workflow for sample preparation of food samples

Experimental

Sample Preparation

1-5 g of different food matrix was spiked with 50+ Native PFAS and 24 isotope dilution standard as mentioned in table below.

Table 1. 50+ Native PFAS and 24 isotope dilution standard spiked concentrations

Compounds	ng
Labelled compounds	**0.42– 3.33**
11Cl-PF3OUdS, 9Cl-PF3ONS, ADONA, HFPO-DA, NFDHA, PFEESA, PFMB, PFMPA, PFPeA	**2**
PFBA, 4:2FTS, 6:2FTS, 8:2FTS	**4**
N-MeFOSE, N-EtFOSE	**10**
5:3 FTCA, 7:3 FTCA	**20**
FBSA-I, PFECHS, FHXSA-I, P37DMOA, FOUEA, 6:2 diPAP, 8:2 diPAP	**1.67**
PFHxDA, PFODA	**0.835**
L-PFUdS, L-PFTrDS	**3.35**
6:2 PAP, 8:2 PAP, PFDPA	**16.75**
All other PFAS*	**1**

*All PFAS are visible in Fig 5. below

Sample Extraction

For extraction, 10 mL 0.3% NH_4OH in MeOH was added to the falcon tubes with food matrices. The sample was then vertically vortexed for 5 minutes at 800 rpm and then centrifuged at 2700 rpm for 10 minutes. The extracts is then transferred to another falcon tubes. The process was repeated 2 times with different volume of 0.3% NH_4OH in MeOH; 1x with 15 mL and another time with 5 mL. The total of 30 mL volume of extracts was collected. The extraction method was similar to US EPA 1633 method (also to comply with the regulation method). However, other extraction procedure like pressuriuzed fluid extraction (as mentioned in Fig. 2) can also be implemented based on their performance.

Evaporation of extract

The collected extract is then evaporated using vacuum centrifuge automated evaporation device called D-EVA to around 5-7 mL end volume. Then the extract is again diluted with reagent water to 50 mL final volume and acidified with 50% formic acid to pH 4-6.

Solid phase extraction

For the enrichment and/or purification of PFAS compounds solid phase extraction process was done with newly developed SPE cartridges. SPE method was similar to US EPA 1633 method except final elution volume was increased to 10 mL. Then, 50 µL of concentrated acetic acid and 10 µL NIS (MPFAC-HIF-IS) solution

were added to each sample eluate and vortexed. (In case eluate looks turbid or with particles: the eluates can be filtered through a syringe filter (25 mm filter, 0.2 µm nylon membrane) into another clean 15 mL polypropylene centrifuge tube).

Evaporation/Concentration of Eluate

All Eluates were evaporated to around 1 mL using D-EVA Rotational Vacuum Concentrator (temperature: 45°C, vacuum: 20 mbar) and transferred into a 1.5 mL polypropylene vial and analyzed LC-MS/MS analysis.

Instrumentation

Table 3. MS Parameters

Parameter	Value
MS	TSQ Quantis (Thermo)
Polarity	Negative
Spray voltage	2500 V
Sheath Gas	50 Arb
Aux Gas	10
CID Gas	2 mTorr
Ion transfer tube temp	325 °C
Vaporizer Temp	300 °C
Q1 resolution	0.7 FWHM
Q3 resolution	1.2 FWHM
Cycle time	0.5 sec
Chromatographic peak width	6 sec

Table 4. LC Parameters

Parameter	Value	
LC	Thermo Scientific Vanquish Flex UHPLC system	
Analytical column	Accucore RP-MS, 2.1*100 mM, 2.6 µm	
Delay column	Agilent ZOBRAX Eclipse plus C18, 4.6*50 mm; 3.5 µm	
Column temperature	45 °C	
Injection volume	5 µL	
Mobile Phase	A) 20 mM ammonium acetate H2O with 2 % MeOH and 0.1 % acetic acid B) 20 mM ammonium acetate MeOH with 2 % H2O and 0.1 % acetic acid	
Gradient Flow rate	0.5 mL/min	
Gradient	Time (min) 0 1 6 13 14 17 20 22 25	% 0 30 45 80 95 95 95 0 0

Results

Blind value of columns

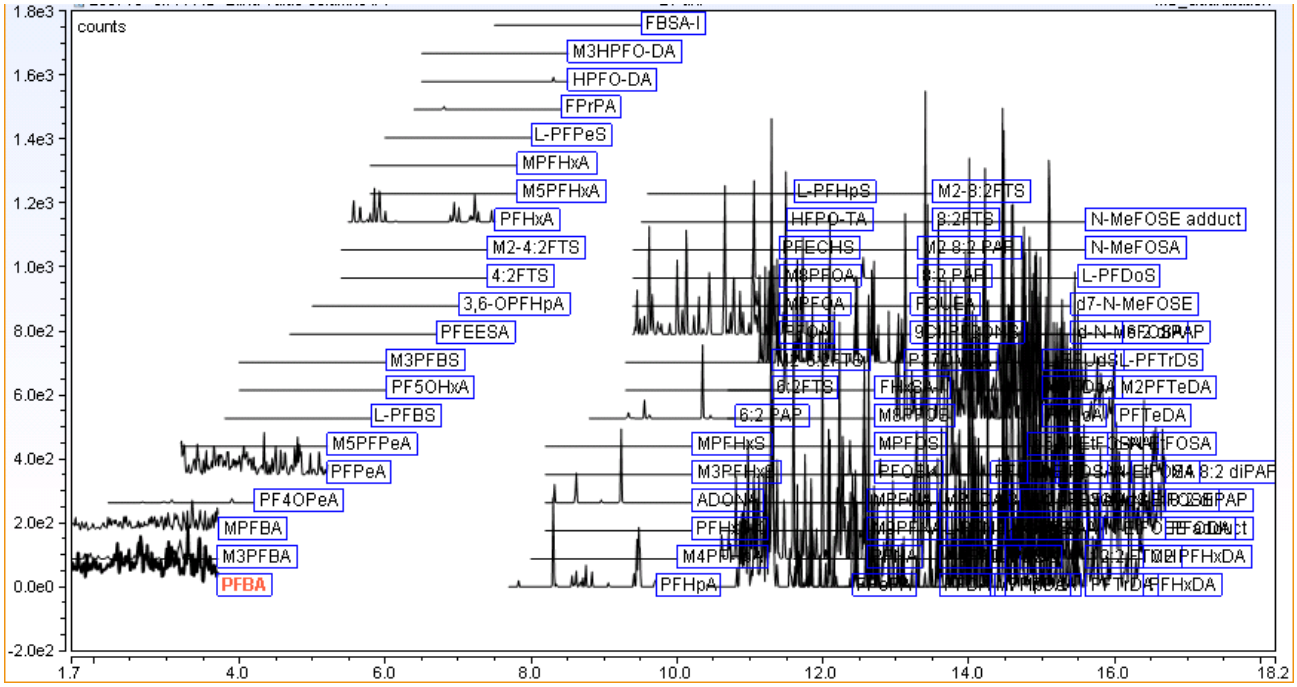

Figure 3. Chromatogram demonstrating EluCLEAN® PFAS –Universal cartridges show no PFAS background contamination when screened for 55 PFAS analytes

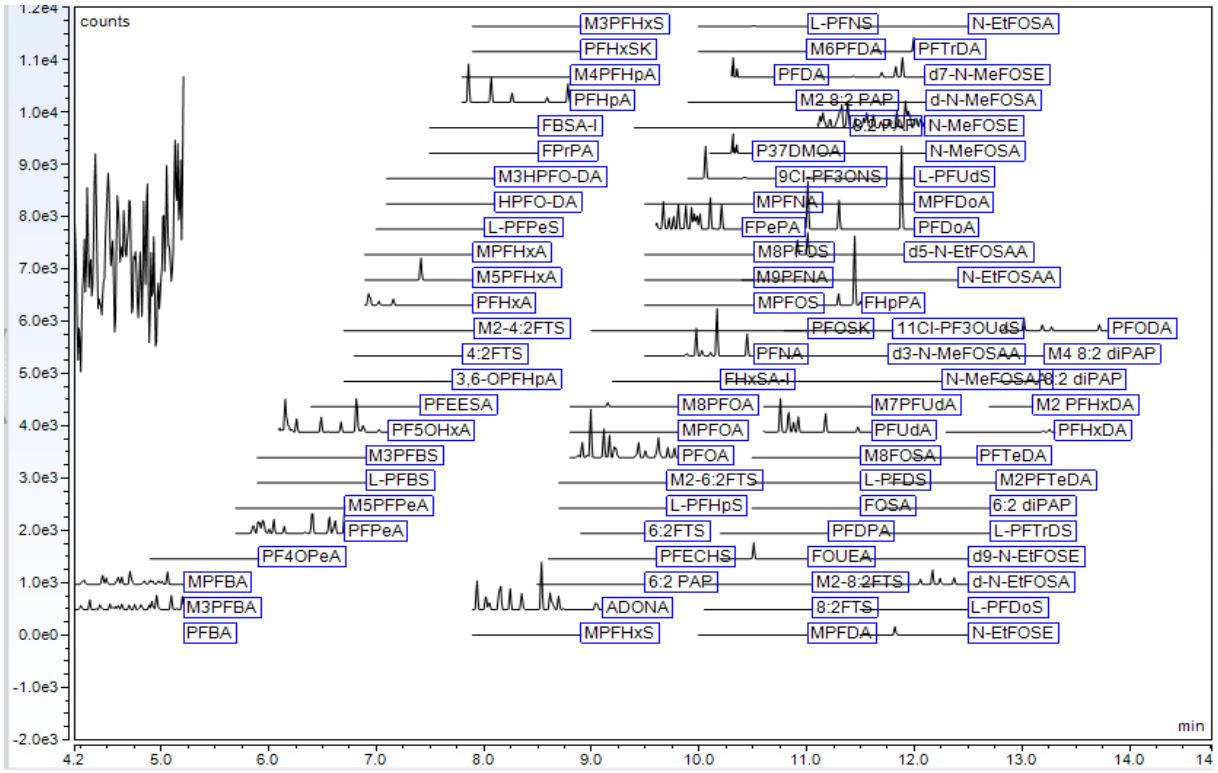

Figure 4. Chromatogram demonstrating EluCLEAN® PFAS – Universal HP cartridges show no PFAS background contamination when screened for 55 PFAS analytes

Recovery Rates and RSD % of PFAS analytes

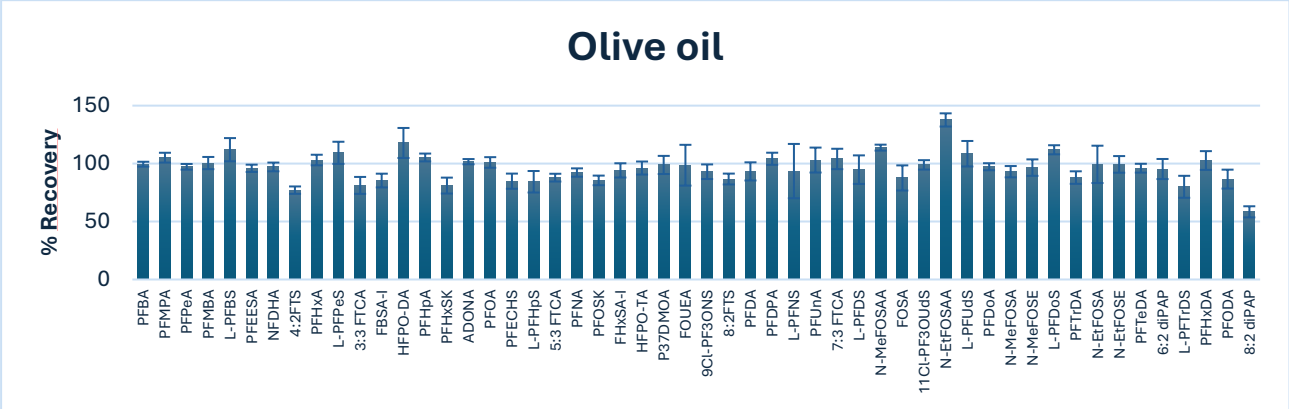

Figure 5: Recovery rates in % of 53 PFAS analytes in Olive oil using EluCLEAN ® PFAS - Universal HP cartridges, n = 4, spiked conc. 3 - 60 ng

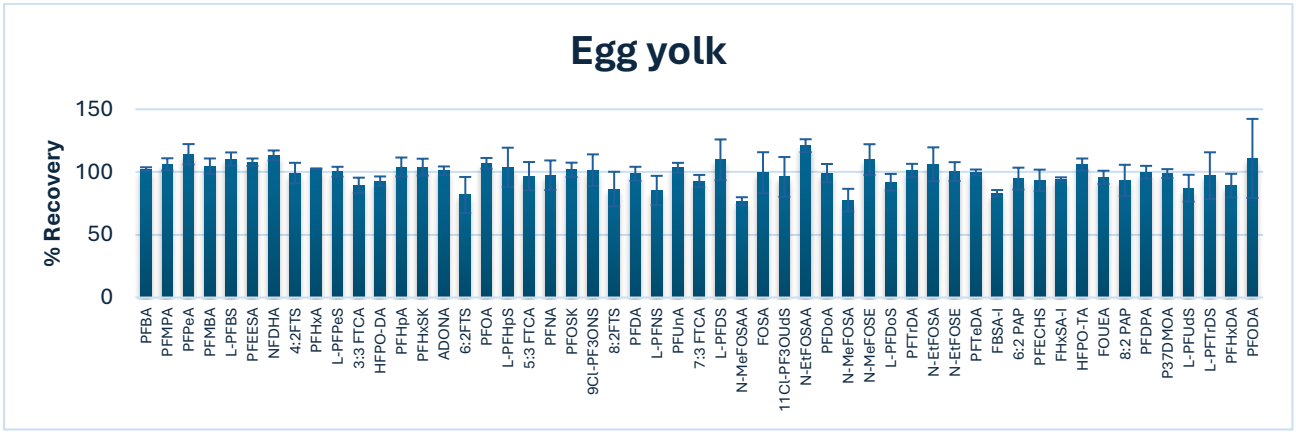

Figure 6: Recovery rates in % of 53 PFAS analytes in egg yolk using EluCLEAN® PFAS – Universal cartridges, n = 4, spiked conc. 3 - 60 ng

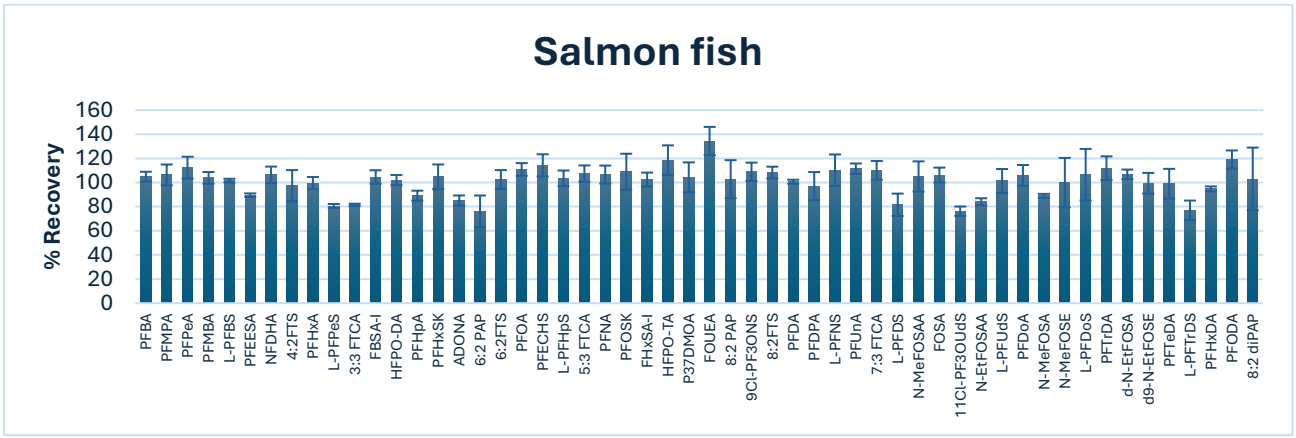

Figure 7: Recovery rates in % of 53 PFAS analytes in Salmon fish using EluCLEAN® PFAS – Universal HP cartridges, n = 4, spike conc. 2 – 40 ng

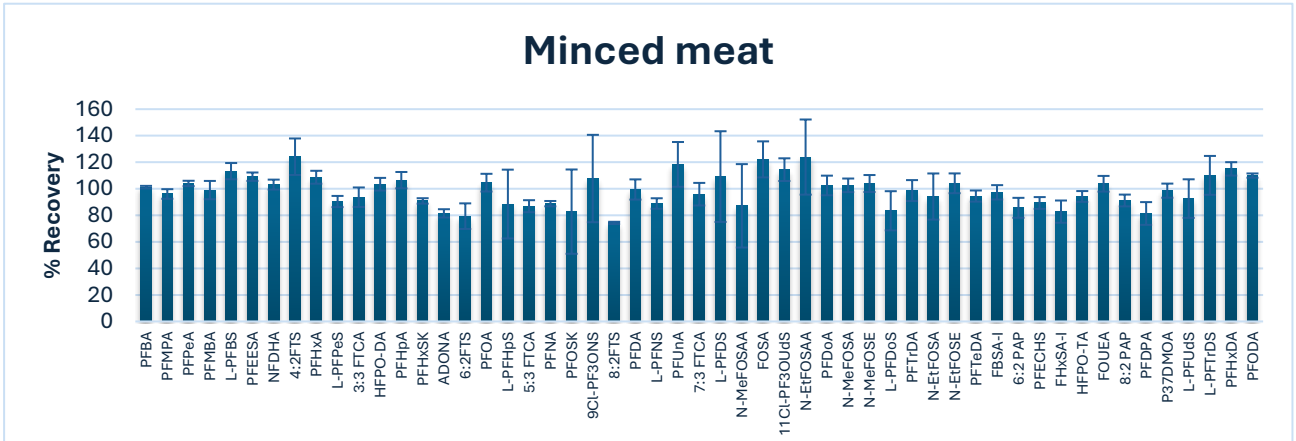

Figure 8: Recovery rates in % of 53 PFAS analytes in minced meat using EluCLEAN® PFAS – Universal HP cartridges, n = 4, spiked conc. 2 – 40 ng

Conclusion

- EluCLEAN® PFAS – Universal, EluCLEAN® PFAS – Universal HP cartridges and FREESTYLE XANA PFAS TableTop have no detectable PFAS background contamination.
- The cartridge EluCLEAN® PFAS – Universal and EluCLEAN® PFAS – Universal HP are suitable for US EPA 1633 according to their performance. Recoveries of samples are very well in between the acceptable criteria of 70 - 130 % with RSD below 20%. Therefore, the desired accuracy is given.
- The presented EluCLEAN® PFAS - Universal and EluCLEAN® PFAS - Universal HP SPE cartridges show a superior performance for enrichment and clean-up of PFAS in various difficult food matrices.
- These special cartridges fit the analytical criteria of EU Regulation and US EPA in regards of precision and accuracy.

References

[1] Commission Regulation (EU) 2022/2388, amending Regulation (EC) No 1881/2006 as regards maximum levels of perfluoroalkyl substances in certain foodstuffs, L 316/38, 8.12.2022

[2] European Union. (2023). Regulation (EU) 2023/915 of the European Parliament and of the Council of 5 June 2023 amending Regulation (EC) No 1881/2006 as regards maximum levels for certain contaminants in food. Official Journal of the European Union, L 153/10. https://eur-lex.europa.eu/eli/reg/2023/915/oj

[3] **Environmental Protection Agency (EPA). (2024).** *Method 1633A: Determination of per- and polyfluoroalkyl substances in water, soil, and biosolids by liquid chromatography-tandem mass spectrometry (LC-MS/MS).* U.S. Environmental Protection Agency. https://www.epa.gov/system/files/documents/2024-12/method-1633a-december-5-2024-508-compliant.pdf

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