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Analysis of PFAS from food samples

Hans Rainer, Wollseifen[1], Lukas Emmerich[2]

[1] MACHEREY-NAGEL GmbH & Co. KG, Dueren, Germany, hwollseifen@mn-net.com

[2] MACHEREY-NAGEL GmbH & Co. KG, Dueren, Germany

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group of man-made chemicals which are used in a veriety of industries around the world (e.g. textiles, household products, fire-fighting, automotive, food processing, construction, electronics). The exposure to PFAS may lead to adverse health effects. To protect human health, the exposure of the levels of PFAS along the food chain must be investigated intensively. Therefore, there is need for more sensitive analytical methods for PFAS in food of animal and plant-based origin. This work compares the analysis of PFAS from food according to FDA Method C-010.02 and the Guidance of the network of the European Union References Laboratory (EURL) on Analytical Parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed [1, 2].

This work presents the dispersive solid-phase extraction (dSPE) method module.

Sample pretreatment

Extraction

1. Weigh 5 g of sample and 5 mL of LC/MS grade water into an empty 50 mL centrifuge tube (REF 730223)
2. Add 0.1 mL of internal standard solution (0.1 µg/mL each compound in methanol) and 0.1 mL of native standard solution (0.1 µg/mL each compound in methanol) for determining recovery rate
3. Shake the mixture for 1 min
4. Add 9.8 mL acetonitrile and 150 µL formic acid
5. Shake the mixture for 1 min
6. Add CHROMABOND® QuEChERS Mix XII (REF 730648)
7. Shake the mixture for 1 min
8. Centrifuge the mixture for 5 min at 4500 rpm at 5 °C

Cleanup

1. Transfer 6 mL supernatant to a 15 mL centrifuge tube, which is prefilled with CHROMABOND® QuEChERS Mix L (REF 730008)
2. Shake for 1 minute
3. Centrifuge again for 5 min at 4500 rpm at 5 °C
4. Supernatant is ready to be analyzed by LC-MS/MS

Analysis by HPLC-MS / MS

Chromatographic conditions

DELAY Column	EC 50/2 NUCLEODUR® PFAS Delay (REF 760673.20)
Column	EC 100/2 NUCLEODUR® PFAS, 3 µm (REF 760666.20)
Eluent A	5 mM ammonium acetate in water
Eluent B	5 mM ammonium acetate in methanol
Gradient	hold 40 % B for 1 min, in 8 min from 40 % B to 95 % B, hold 95 % B for 3 min, in 0.1 min to 40 % B, hold 40 % B for 2.9 min
Flow rate	0.3 mL/min
Temperature	40 °C
Injection volume	1 µL

MS conditions

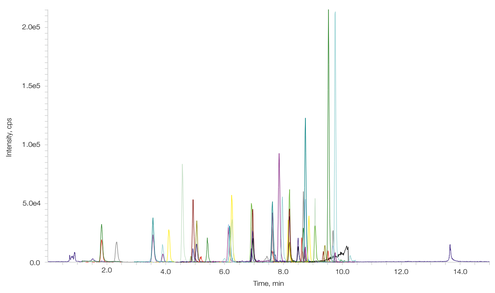
Acquisition mode	SRM	Ionspray Voltage	-4500 V
Interface	ESI	Temperature	400 °C
Polarity	negative	Ion Source Gas 1	50
Curtain Gas	30	Ion Source Gas 2	60
Collision Gas	medium	Detection Window	60 sec

MRM transitions

Analyte	Abbreviation	CAS number	Q1 mass [Da]	Q3 mass [Da]	Retention time [min]
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	229.00	85.00	1.96
Perfluoro-*n*-butanoic acid	PFBA	375-22-4	212.90	168.80	2.01
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5	241.00	177.00	3.33
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	279.00	85.00	3.64
Perfluoro-*n*-pentanoic	PFPeA	2706-90-3	262.88	219.00	3.90
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	315.00	135.00	4.14
Perfluoro-*n*-butanesulfonic acid	PFBS	375-73-5	298.93	98.90	4.20
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	295.00	201.00	4.48
1H, 1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	326.94	306.90	5.27
Perfluoro-*n*-hexanoic acid	PFHxA	307-24-4	312.91	268.80	5.40
Perfluoropentansulfonic acid	PFPeS	2706-91-4	348.85	80.00	5.54
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	284.99	168.70	5.77
2H, 2H, 3H, 3H-Perfluorooctanoic acid	5:3FTCA	914637-49-3	341.00	237.00	6.33
Perfluoro-*n*-heptanoic acid	PFHpA	375-85-9	362.93	318.80	6.45
Perfluoro-*n*-hexanesulfonic acid	PFHxS	355-46-4	398.94	79.80	6.49
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	376.90	250.70	6.58
1H, 1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	426.93	406.90	7.24
Perfluoro-*n*-heptanesulfonic acid	PFHpS	375-92-8	448.93	79.80	7.26
Perfluoro-*n*-octanoic acid	PFOA	335-67-1	412.91	369.00	7.26
Perfluoro-*n*-octanesulfonic acid	PFOS	1763-23-1	498.84	79.90	7.89
Perfluoro-*n*-nonanoic acid	PFNA	375-95-1	462.89	418.90	7.92
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4	441.00	317.00	8.00
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	73606-19-6	530.75	350.70	8.25
Perfluorononanesulfonic acid	PFNS	68259-12-1	548.81	79.90	8.45
Perfluoro-*n*-decanoic acid	PFDA	335-76-2	512.84	468.90	8.49
1H, 1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	526.00	506.80	8.50
N-methyl perfluorooctanesulfonamidacetic acid	*N*-MeFOSAA	2355-31-9	569.80	418.90	8.78
Perfluorooctanesulfonamide	FOSA	754-91-6	497.87	77.80	8.84
Perfluoro-*n*-decanesulfonic	PFDS	335-77-3	598.79	79.90	8.90
Perfluoro-*n*-undecanoic acid	PFUnDA	2058-94-8	562.80	518.90	8.95
N-ethyl perfluorooctanesulfonamidoacetic acid	*N*-EtFOSAA	2991-50-6	583.81	418.80	9.02
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	630.74	451.00	9.15
Perfluoro-*n*-dodecanoic acid	PFDoDA	307-55-1	612.79	568.90	9.33
N-methyl perfluorooctanesulfonamide	*N*-MeFOSA	31506-32-8	512.00	169.00	9.55
Perfluoro-*n*-tridecanoic acid	PFTrDA	72629-94-8	662.77	618.90	9.66
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	698.72	80.00	9.70
N-ethyl perfluorooctanesulfonamide	*N*-EtFOSA	4151-50-2	526.00	169.00	9.80
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	616.00	59.00	9.82
Perfluoro-*n*-tetradecanoic acid	PFTeDA	376-06-7	712.77	668.80	9.94
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1961-99-2	630.00	59.00	10.04

Chromatogram

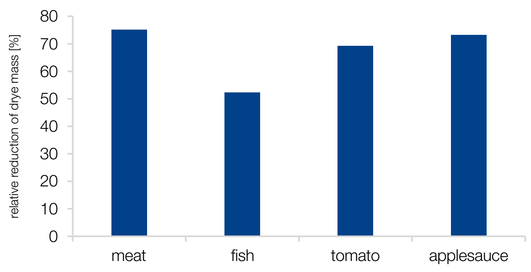
Figure 1:



Chromatogram of a sample eluate of meat (= 1 ng/mLfor each compound).

Matrix reduction

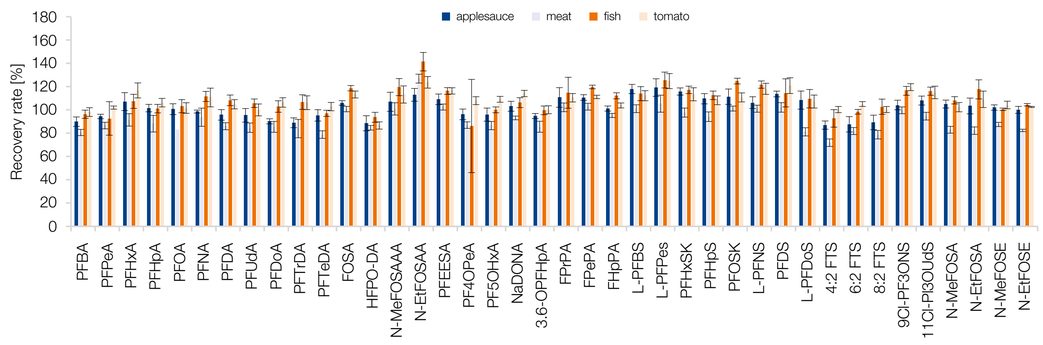
Figure 2:



Relative reduction of dry mass related to dry mass of raw extract.

Recovery rates

Figure 3:



Recovery rates for the presented dSPE method using CHROMABOND® QuEChERS Mix XII for extraction step.

Conclusion

This application note presents the reliable and successful determination of 40 PFAS from several matrices of animal and plant-based origin according to regulative recommendations of FDA Method C-010.02. By using CHROMABOND® QuEChERS Mix L, it was possible to achieve high recovery rates for PFAS from six food matrices with good reproducibility.

The used QuEChERS clean-up mix shows effective matrix reduction presented in figure 2. The high amount of Primary Secondary Amine removes organic and fatty acids, sugars and pigments and leads to very clean dSPE extracts. The effective matrix depletion additionally offers the possibility of concentration and the analysis of larger sample amounts. This could significantly increase the sensitivity of the methodology.

References

[1] FDA Method C-010.02 - Determination of 16 Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Food using Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)

[2] Guidance Document on Analytical Parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed, 2022, ANEX Version 1.0