Determination of PFAS Compounds in Food Packaging

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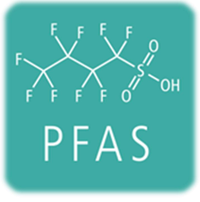
1. Introduction



Poly- and perfluoroalkyl substances (PFAS) – a.k.a. “forever chemicals” – are widely used in everyday applications, and there are approximately 5,000 known PFAS structures. In this poster we are presenting a targeted approach for detecting and quantifying 24 PFAS commonly found in paper and board matrices. Using accelerated solvent extraction to extract PFAS, identification and quantification was done using high-performance liquid chromatography coupled with triple quadrupole mass spectrometry.

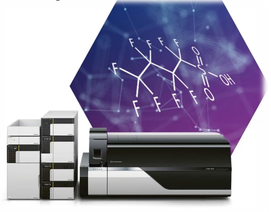
Apparent recovery values were in the 84–94 % range, with method detection limit values in the 0.1–0.5 ng/g range.

1.1 Forever Chemicals

Poly- and perfluoroalkyl substances – PFAS – are man-made chemicals which are widely used in a range of applications, from water-resistant clothing to food-packaging materials. Often called ”forever chemicals”, these compounds have a special chemical structure: multiple fluorine atoms attached to an alkyl chain. In addition to a fluorinated alkyl chain, compounds contain a terminal functional group, such as carboxylate, sulfonamide, phosphonate or alcohol.

The bond between carbon (C) and fluorine (F) is one of the strongest chemical bonds known. Additionally, the size of the fluorine atom is just right to pack closely around a carbon chain and shield it from interaction with other atoms. This is both good news and bad news. Because of their properties, PFAS repel water, fat and dirt. This makes them very useful for various applications, including non-stick cookware, stain-proof surfaces, firefighting foams, food packaging materials and various consumer products. But because PFAS are highly resistant towards chemical and physical strains, the bad news is that they are long-lasting, bio-accumulative and unfortunately toxic. This means that once they are released into the environment, they survive without degradation and potentially contaminate the food chain for decades. In recent years, PFAS have been increasingly detected in water, soil, air, as well as in wildlife and human beings.

This has raised public awareness of the chemicals, as well as caused growing concern about their presence. But so far only a few of the substances have been assessed for risk by the European Food Safety Authority (EFSA) or the Environmental Protection Agency (EPA).[1, 2]



Compound	Acronym	RT	Precursor Ion
1. Perfluoro-n-butanoic acid	PFBA	1,14	212.80
2. Perfluoro-n-pentanoic acid	PFPeA	3,22	262.80
3. Potassium perfluoro-1-butanesulfonate	L-PFBS	3,77	298.90
4. Sodium 1H.1H.2H.2H-perfluorohexane	4:2FTS	4,66	326.90
5. Perfluoro-n-hexanoic acid	PFHxA	4,75	312.90
6. Sodium perfluoro-1-pentanesulfonate	L-PFPeS	4,97	348.90
7. Perfluoro-n-hepatonic acid	PFHpA	5,62	363.00
8. Potassium perfluoro-1-hexanesulfonate	PFHxSK	5,71	398.90
9. Sodium 1H.1H.2H.2H-perfluorooctane sulfonate	6:2FTS	6,19	426.90
10. Perfluoro-n-octanoic acid	PFOA	6,23	413.00
11. Sodium perfluoro-1-heptanesulfonate	L-PFHpS	6,27	449.00
12. Perfluoro-n-nonanoic acid	PFNA	6,72	463.00
13. Potassium perfluorooctanesulfonate	PFOSK	6,74	498.90
14. Sodium 1H.1H.2H.2H.-perfluorodecane sulfonate	8:2FTS	7,12	526.90
15. Perfluoro-n-decanoic acid	PFDA	7,14	513.10
16. Sodium perfluoro-1-nonanesulfonate	L-PFNS	7,14	548.90
17. N-Methyl-Perfluorooctanesulfonamido acetic acid	N-MeFOSAA	7,31	570.00
18. N-Ethyl-Perfuorooctanesulfonamido acetic acid	N-EtFOSAA	7,49	584.00
19. Perfluoro-1-octanesulfonamide	FOSA	7,48	498.00
20. Perfluoro-n-undecanoic acid	PDUdA	7,5	562.80
21. Sodium perfluoro-1-decanesulfonate	L-PFDS	7,51	598.90
22. Perfluoro-n-dodecanoic acid	PFDoA	7,81	612.90
23. Perfluoro-n-tridecanoic acid	PFTrDA	8,08	662.90
24. Perfluoro-n-tetradecanoic acid	PFTeDA	8,32	713.00

Table 1: List of analytes, retention times (RT) and MRM transitions

2. Method

2.1 Analytical Conditions

We analyzed 24 PFAS substances most commonly found in paper food-contact materials. A mixture of these, with a concentration of 2,000 ng/mL, was purchased from Wellington Laboratories (Guelph, Ontario). For each substance, we identified the precursor ion and product ion, as well as the retention time (Table 1).

2.2 Preparation of Standard Solutions and Samples

Two series of calibration solutions were prepared by dilution with 50:50 % (v/v) methanol:water. For high-concentration calibration, we prepared a series of 9 calibration solutions at concentrations of 100, 50, 25, 20, 15, 10, 5, 2.5 and 1.25 pg/µL. For low-concentration calibration, 10 calibration solutions at concentrations of 20, 10, 5, 2.5, 1, 0.5, 0.25, 0.1, 0.05 and 0.01 pg/µL were prepared.

As a sample we used unprinted recycled paper (70 g/m²), which had previously been analyzed for the presence of PFAS. The paper was cut into small pieces, and 2 grams were used for experiments. The paper was spiked with a PFAS mixture with different concentrations of our standard solution – 100, 50, 20, 10, 5, 2.5, 1, 0.5 and 0.1 ng/g. After drying, the samples were extracted with methanol using accelerated solvent extraction (ASE). The collected extracts were placed in a nitrogen evaporator and evaporated to dryness under a gentle stream of nitrogen, and then reconstituted in methanol:water (50:50) % (v/v). Finally, the solutions were filtered using 0.22 µm regenerated cellulose filters and transferred into polypropylene vials for LC-MS/MS measurement.

We used an extraction method in combination with a chromatographic separation process and mass-selective detection. Specifically, the PFAS analysis was carried out by injecting 5 µL of the prepared solutions into a Shimadzu LCMS-8050 system with the parameters detailed in Table 2 and Table 3. The analytes were chromatographically separated using a Restek Raptor C18 column. To separate PFAS which could potentially leach out from the instrument upstream of the injector, we used a Restek Delay column installed between the mixer and autoinjector.

Shimadzu HPLC System	
Analytical Column	Restek Raptor C18 2.7µm 50 x 2.1 mm
Delay Column	Restek PFAS Delay Column 5 µm x 50 mm x 2.1 mm
Column Temperature	40°C
Injection	5 µl
Mobile Phase	A: 5 mM ammonium acetate, B: MeOH
Flow Rate	0.4 ml/min
RunTime	10 min

Table 2: Analytical conditions HPLC-System

Shimadzu LCMS-8050 System	
MS Instrument	LCMS-8050
Interface	ESI
Interface Temperature	300°C
Desolvation Line Temperature	100°C
Heat Block Temperature	200°C
Drying Gas Flow	10 l/min
Nebulizing Gas Flow	2 l/min
Interface Voltage	-0.5kV

Table 3: Analytical conditions LCMS-8050

3. Results

3.1 Calibration Curve Linearity

The calibration solutions were analyzed at five injections for each concentration. Both at high-range and low-range concentration solutions, the regression coefficient (R2) was above 0.99 for most analytes. However, the standard deviation between the five measurements at low-range concentrations was for some analytes – especially higher PFAS – somewhat higher.

3.2 Recovery

All the samples were measured five times, and linearity was determined from five measurements for each analyte. Recovery of the analyte was calculated using the calibration curves from previous experiments. Even after extraction the regression coefficient was above 0.99 for the majority of analytes, except for higher PFAS. It is evident that PFAS with 10 carbon-atom chains have lower linearity, which is decreasing with the length of the carbon chain. The average recovery between all the analytes is 88.8 %, which is within the required criteria (80–120 % of the true value) set by the EU Reference Laboratory for Halogenated POPs.[3]

4. Conclusion

We have developed a method to specifically identify and precisely quantify PFAS in food packaging material. The Shimadzu LCMS-8050 reliably measures PFAS concentration ranges down to 0.01 pg/µL. The combination of high sensitivity with outstanding speed parameters makes it well-suited for high-throughput multi-component analysis. This means that the LCMS-8050 can be beneficially used as an integral part of a simple and efficient method for the monitoring and quantification of PFAS in paper-based food-packaging materials.

References

[1] US EPA, “PFAS Laws and Regulations | US EPA,” 7/12/2021, https://www.epa.gov/newsreleases/epa-identifies-drinking-water-contaminants-potential-regulation.

[2]“Order on food contact materials and on provisions for penalties for breaches of related EU legislation,” European Commission.

[3] European Union Reference Laboratory for halogenated POPs in Feed and Food, “Guidance Document on Analytical Parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed,” Union Reference Laboratory for halogenated POPs in Feed and Food.