C10G-E109

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Excellence in Science

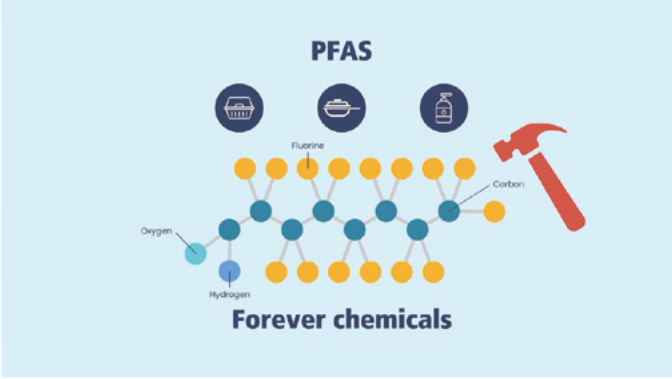
Analytical Solutions for

PFAS Testing

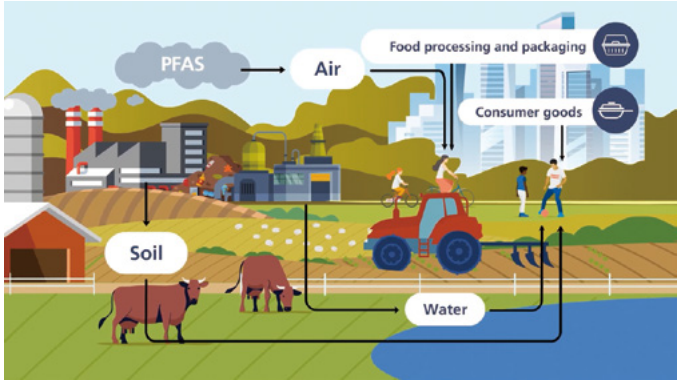
Routine to Discovery Analysis in Environmental Samples and Consumer Products

Tackling PFAS contamination with cutting-edge robust analytical solutions

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of over 4000 organic fluorinated compounds, which have been widely used in industry since the 1950s. Their properties make these substances heat-resistant, oil-and-water-repellent, and chemically and thermally stable.
For these reasons, PFAS have multiple uses and commonly function as surface treatment agents, water repellents, coatings, and fire extinguishers. Those very properties make them resistant to degradation and this has led to their persistence in the environment and bioaccumulation through food chains and other routes of exposure.



PFAS enter our environment during manufacturing and waste management of products that contain PFAS. Building up in our water, soil, and air, they contaminate plants, animals, and drinking water. The food we consume is further contaminated through materials used to process, package, and store it.
In addition, PFAS accumulates in our bodies through contact with other consumer goods. Today, PFAS are present in many products we consume, the air we breathe, the food we eat, and the water we drink. As a result, they accumulate inside our bodies posing significant health risks.



PFAS are now so ubiquitous that they have been labeled by the media as 'forever chemicals'. Scientists and engineers around the world are developing alternative materials and implementing treatment technologies that can mitigate the presence of PFAS in industrial processes, consumer products, food, and the environment. Concerns about their toxicity to humans through diet and drinking water has led to increasingly stringent regulations and directives from both the US Environmental Protection Agency (EPA) and the European Union regarding permitted levels in food and drinking water. Recent advancements in analytical instruments and methodologies have significantly enhanced the accuracy, speed, and automation of PFAS detection, contributing to a deeper understanding of their occurrence, behavior, and impact across various sample types. These technological innovations are also paving the way for more efficient PFAS testing, ensuring compliance with current regulations and supporting future regulatory developments.

In recent years, advances in analytical instrumentation have driven the evolution of PFAS analysis. While triple quad liquid chromatography-mass spectrometry (LC-MS/MS) has long been the primary tool, an increasing number of applications now use other techniques, such as LC-MS, gas chromatography-mass spectrometry (GC-MS) and combustion ion chromatography (CIC), to expand the scope of PFAS analysis. At the same time, methods have become more standardized, with validated AOAC methods being developed and supported by instrument manufacturers such as Shimadzu. This improves the reliability and comparability of data across laboratories.
In this eBook, we explore our range of chromatography and mass spectrometry (MS) solutions for detecting very low levels of PFAS in matrices such as drinking water, wastewater, ambient air, foodstuffs, and consumer products. Plus, learn through a series of case studies how our LC-MS/MS systems and other analytical instruments (GCMS, CIC, QTOF…) meet and often exceed performance criteria included in EPA and AOAC methods for PFAS analysis – generating accurate results with fast turnaround times that enhance lab productivity.

Optimized PFAS Analysis in Drinking Water

Accurate and fast analysis of PFAS in drinking water is crucial for protecting public health. On the following pages, we'll explore the suitability and full method demonstrations of our triple quadrupole LCMS-RX series for PFAS analysis in drinking water according to EPA 537.1. In addition, using one triple quadrupole mass spectrometer with automatic method switching, we'll demonstrate the analysis of PFAS (EPA 533) and cyanotoxins, including microcystins and nodularin (EPA 544), as well as cylindrospermopsin and anatoxin-a (EPA 545).
Another application highlights the recently released LCMS-8065XE ultra-high-sensitivity mass spectrometer, which enables analysis using direct injection. This simplifies sample preparation while achieving accurate quantification results with good recovery and reproducibility.

Enhanced Method for PFAS Analysis in Wastewater, Soils and Tissue by LC-MS/MS

EPA Method 1633 quantifies multiple PFAS in wastewater, soil, tissue, and biosolids using LC-MS/MS. LCMS-8065XE can analyze a wide range of PFAS with high sensitivity. The application news demonstrates high throughput and robust instrument performance, maintaining accurate quantification in complex chicken tissue.
ISO 21675 is a standard method that includes short-chain PFAS with 4 carbon atoms and long-chain PFAS with 16 and 18 carbon atoms for aqueous samples. In the example presented here, a wastewater sample is applied to the method and accurate measurements are achieved even in low-concentration spiking recovery tests.
ASTM D8421 allows for the rapid and cost-effective analysis of PFAS in wastewater. The application showcases how our triple quadrupole LCMS instrument analyzed 44 PFAS compounds and 24 labeled isotopes in non-potable water samples, exceeding the method performance criteria. This resource also highlights how optimized chromatographic conditions can achieve excellent peak shape, even for those compounds that elute early.

Exploring Adsorbable Organic Fluorine (AOF) Through CIC Analysis

Adsorbable Organic Fluorine (AOF) compounds serve as a broad proxy for PFAS and other organic compounds containing fluorine. Analyzing these compounds using combustion ion chromatography (CIC) reveals the total PFAS content in a sample, including those not detected by more selective chromatography methods.
The US EPA's Method 1621 describes a screening method for determining AOF in water. In this method, the sample passes through a column of granular activated carbon, adsorbing the compounds on to the column for subsequent combustion and analysis. Our application note details how the HIC-ESP Ion Chromatograph was used to analyze AOF in water, demonstrating excellent recovery and precision. It also explains how AOF detection in river water is possible down to parts per billion.

High-Throughput Analysis of PFAS in Ambient Air

PFAS are exhausted from production facilities and remain in the environment. As a result, those PFAS could be present in drinking water, soil, and crops. To evaluate PFAS contaminants in ambient air, our gas chromatograph mass spectrometer, GCMS-QP2020 NX, coupled with the TD-30R thermal desorption system, which doesn't require a solvent extraction, was used. This application note finds that the system acquired successful data on fluorotelomer alcohols (FTOHs) and other neutral PFAS.

Non-Targeted Analysis in Water Using LC-QTOF

PFAS represent over 4000 different chemicals, many of which are not routinely monitored in current targeted methods. In our application note, discover how a non-targeted analysis method for suspect and unknown PFAS in water samples was developed using our QTOF, based on high-resolution accurate mass-data-independent acquisition. The method was verified using 14 PFAS standards before using it for the analysis of water samples, from which 16 PFAS were discovered and further characterized.

High-Performance Analysis of PFAS in Food Matrices

PFAS screening in foods is becoming increasingly important as concerns grow around bioaccumulation in the food chain and the risks PFAS pose to human health. This application news shows how our triple quadrupole LCMS instrument successfully analyzed 30 PFAS compounds in fish fillets within 15 minutes. In the case of milk samples, our system shows accurate results. Automation and streamlined workflows (with as few sample preparation steps as possible) are essential to support the efficient testing of food products.

Another application note shows how an automated workflow using our LCMS system, paired with the Nexera UHPLC system equipped for online solid phase extraction, provides a highly sensitive method for detecting 27 PFAS in egg matrices.

Detection of PFAS in Fast Food Packaging and Consumer Products

PFAS have been detected in food contact materials (FCM), such as paper wrappers and beverage cups. Our application news explores how a triple quadrupole LCMS instrument was used to quantify 15 target PFAS compounds in FCM. The results revealed 12 of those compounds in seven fast food packaging samples at concentrations far below the limits set in 2020 by the Danish Government. Plus, our system was used for PFAS detection in plastic products and nonstick aluminum foil. Those data achieved affordable recoveries on 25 PFAS compounds.

Energy-dispersive X-ray fluorescence (EDXRF) spectrometry can detect the element fluorine in fluorine resin coatings. This measurement method does not require complicated sample preparation; analysis can be started simply by placing the sample in the instrument. Checking for the presence of fluorine in products by EDXRF is a simple technique for investigating the possibility that PFAS exist in a sample.

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Analysis of PFAS in Drinking Water in Accordance with EPA Method 537.1

Application

In April 2024, the U.S. Environmental Protection Agency (EPA) announced the final maximum contaminant levels (final MCLs) for certain PFAS in drinking water. This article describes the results from using the LC/MS/MS Method Package for PFAS in Drinking Water to simultaneously analyze 18 PFAS target compounds in drinking water in accordance with EPA Method 537.1, which was published by the EPA in 2018.

benefits

- Based on EPA Method 537.1, 18 PFAS in drinking water can be accurately analyzed at concentrations equivalent to EPA's final MCLs.
- PFAS analysis can start immediately by using the LC/MS/MS Method Package for PFAS in Drinking Water, minimizing the effort required to set up a workflow.

■ Measurement Results

MRM chromatograms for the lowest calibration curve concentrations (0.05 µg/L in solution) of the 18 target PFAS are shown in Fig. 1. Good chromatograms were confirmed for each component. Also, all compounds showed good linearity with correlation coefficients (R) >0.997, and the area %RSD at the lowest calibration curve concentration (0.05 µg/L) was less than 11 %, confirming good repeatability. Furthermore, the accuracy of concentrations at each calibration point was within ±30 % at all calibration point concentrations.

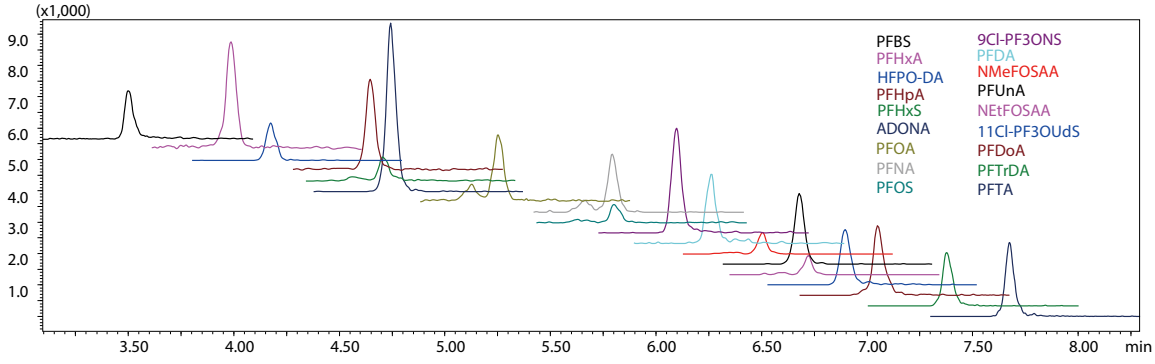

Fig. 1 MRM chromatograms at lowest calibration curve concentration (0.05 µg/L)

Based on spike-and-recovery test results using ultrapure water, good recovery rates and repeatability results were obtained when spiking the ultrapure water with the equivalent of 1/4 the final MCLs (1 ng/L in sample water) (Fig. 2). Similarly, good recovery rates and repeatability results were obtained when spiking drinking water samples with the final MCLs (4 ng/L in sample water). These results confirm that PFAS compounds can be simultaneously analyzed with good accuracy in accordance with EPA Method 537.1.

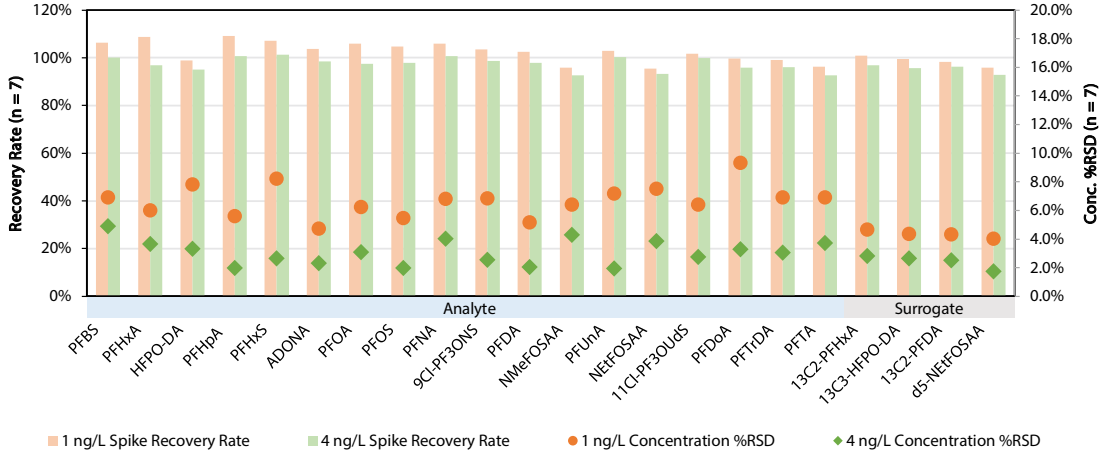

Fig. 2 Spike-and-recovery test results using ultrapure water

Extended Evaluation of Method Performance for PFAS & Cyanotoxins Analysis in Water

Application

Beyond PFAS, other drinking water contaminants such as cyanotoxins also pose serious health risks. While dedicated instruments for PFAS and cyanotoxin analysis are ideal to avoid cross-contamination, a single system capable of multi-method testing offers a practical and cost-effective alternative, especially during high-demand or emergency situations.

benefits

- Using automatic method switching, a single Shimadzu LCMS-8060RX triple quadrupole mass spectrometer can effectively measure both PFAS and cyanotoxins in water following EPA Methods 533, 545, and 544.
- The system sustains high performance over extended operation time and multiple method changes with only a five-minute rinse.
- High performance with lower cost enables labs to respond swiftly to harmful algal blooms without impacting routine workflows.

■ Measurement Results

The system enables automated switching between EPA Methods 533, 544, and 545. For EPA Method 533 (PFAS analysis), the delay column is included in the flow path to reduce background interference. For cyanotoxin analyses (EPA Methods 544 and 545), the delay column is bypassed to prevent cross-contamination, ensuring accurate and reliable results. This flexible configuration enhances both workflow efficiency and analytical versatility on a single LC-MS platform.

Continuing calibration checks were performed after triplicate calibration injections for each method, starting with Method 533, followed by Methods 545 and 544. This sequence was repeated three times to assess rinse effectiveness and system consistency. Fig. 1 presents the results, showing accuracy across the lower limit of quantitation (LLOQ), mid-concentration, and higher limit of quantitation (HLOQ). The y-axis represents average accuracy, with error bars showing %RSD values. All analytes across the three methods maintained accuracies between 80 to 120 %, with %RSD below 15 %, confirming system reliability and stability. These findings highlight the effectiveness of the rinsing procedure in preventing carryover and maintaining system performance across different analytical methods.

This streamlined approach enables precise and reliable measurements while maintaining high accuracy and sensitivity throughout extended analytical runs, despite multiple injections and frequent method transitions.

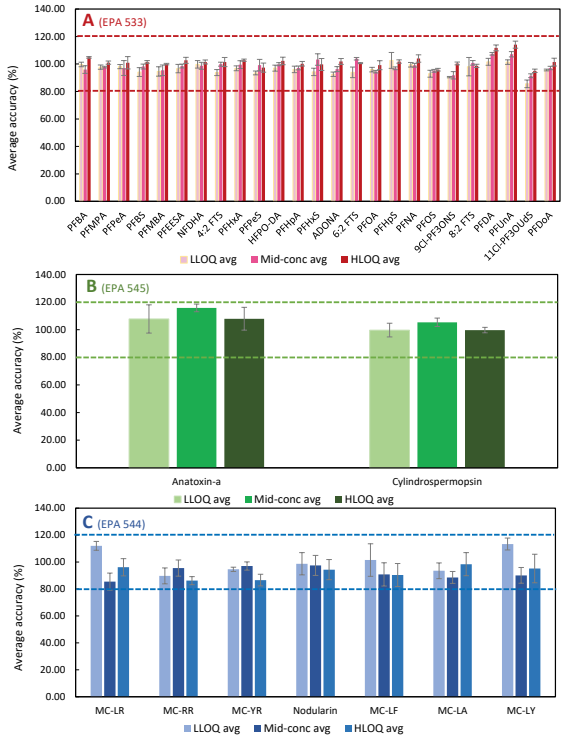

Fig. 1 Results of continuing calibration checks for the three EPA methods. A: EPA Method 533. B: EPA Method 545. C: EPA Method 544.

Liquid Chromatograph Mass Spectrometer LCMS-TQ RX Series

Shimadzu's RX Series expands the capability and productivity of a triple quadrupole mass spectrometer with performance that can be relied upon. The RX Series has been designed to generate a highly focused ion beam from the ion source to detector, bringing together advanced ion guide and collision cell technologies. The result is higher data quality that makes an impact on any LC-MS/MS assay.

Product

LC/MS/MS Method Package for PFAS in Drinking Water

This method package includes ready-to-use analytical conditions for EPA Methods 533 and 537.1, examples of analytical procedures for the methods, and various other information, such as precautions for sample preparation and analysis. Using this product, 52 PFAS compounds in drinking water can be analyzed.

Product

An Ultra-High Sensitivity Analysis of 29 PFAS in Drinking Water by Direct Injection

Application

With the tightening of regulations, more sensitive, accurate and rapid methods are required for PFAS analysis. In addition, due to the increasing number of analytes, there is an increasing demand for high-throughput analysis using direct injection, which does not require a pretreatment procedure such as solid-phase extraction. This application introduces the ultra-high-sensitivity analysis of 29 PFAS in drinking water by direct injection using the LCMS-8065XE and addresses the demands of testing laboratories for PFAS quantification.

benefits

- The LCMS-8065XE enables highly sensitive and accurate analysis of 29 PFAS down to less than 1 ng/L.
- 29 PFAS can be analyzed in one cycle in 18 minutes without sample preconcentration.
- Good recovery of target PFAS is achieved in drinking water, enabling highly accurate quantification analysis.

■ Measurement Results

The LCMS-8065XE is equipped with a new ESI probe (StreamFocus) and a new collision cell (UFsweeper IV), providing more sensitive and accurate results in PFAS analysis.

A series of PFAS mixed standard samples were prepared so that the target compounds were in the range of 1 to 100 ng/L to create a calibration curve. As an example, Fig. 1 shows the calibration curves for PFOA and PFOS, as well as the MRM chromatogram at 1 ng/L, the lowest point of the calibration range. The calibration curves showed good linearity for both PFOA and PFOS, with the accuracy of each calibration point being within the range of 80 to 120 %. Furthermore, the accuracy of each calibration point for the other target compounds was within the range of 70 to 130 %.

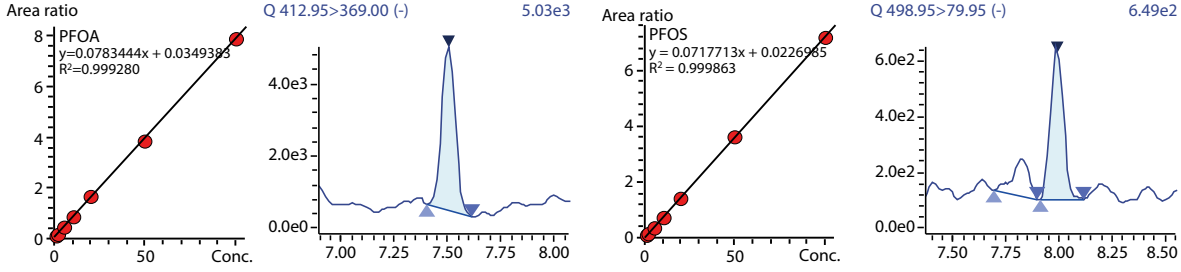

Fig. 1 Calibration curves and MRM chromatograms of PFOA (left) and PFOS (right)

The drinking water samples were diluted with MeOH (50/50, v/v) before analysis. The samples were fortified with a PFAS standard at a concentration of 4 ng/L of each compound. PFBA and PFHxA were quantified in the drinking water samples and recovery was calculated by subtracting the concentration detected in the drinking water. Fortified samples were analyzed 7 times. Each sample showed excellent recovery in the range of 80 to 120 % for all tested compounds with reproducibility within 20 % (Fig. 2).

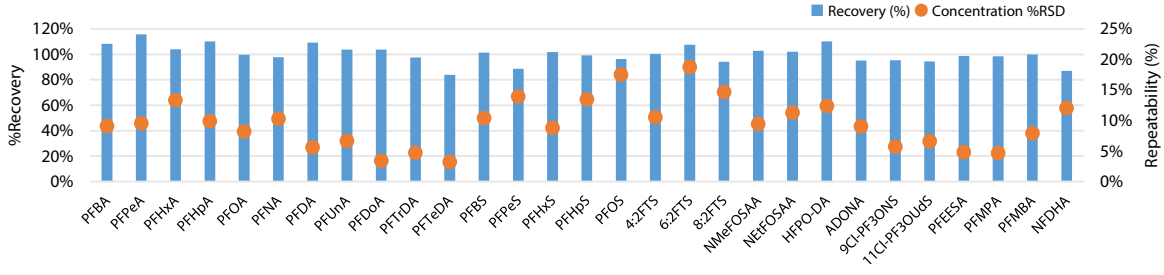

Fig. 2 Recovery and reproducibility of drinking water spiked with 4 ng/L (n=7)

Analysis of PFAS in Non-Potable Waters by ASTM D8421-22

Application

ASTM International published ASTM D8421 for the analysis of 44 per- and polyfluorinated alkyl substances and 24 labeled isotopes in non-potable water samples. This method extracts the substances in a 1+1 ratio of sample and methanol, filters and then measures the targeted compounds using external standard calibration liquid chromatography-tandem mass spectrometry (LC-MS/MS). PFAS with short to long chains are specified as the target compounds for measurement, and it is necessary to devise analysis conditions to realize simultaneous analysis of compounds with different carbon chain lengths.

benefits

- Shimadzu LC-MS/MS easily exceeds method performance criteria of ASTM D8421 for 44 PFAS and 24 surrogates.
- Optimized chromatography and MS conditions enabled excellent peak shape for improved precision and accuracy.
- ASTM D8421 is a simple extraction procedure validated by ASTM for the analysis of PFAS in wastewater samples.

■ Measurement Results

For this application news, a study was made to improve peak shape, particularly of early-eluting compounds, such as PFPrA and PFBA. This included evaluation of injection technique, columns, and flow rate. Co-injection of a 25 µL sample with 25 µL 0.1 % acetic acid in reagent water significantly improved the peak shapes of PFPrA, PFBA, and PFMPA. A large diameter column with a long column length and large particle size, combined with a high flow rate, allowed greater axial diffusion, improving peak shape (Fig. 1). Calibration curves for each analyte were found by Shimadzu LabSolutions Insight data processing software to have a %RSD of less than 30 %, as required by ASTM D8421. Calibration curves along with a midpoint standard chromatogram of PFOA, PFOS, PFPrA, and NEtFOSE are shown in Fig. 2.

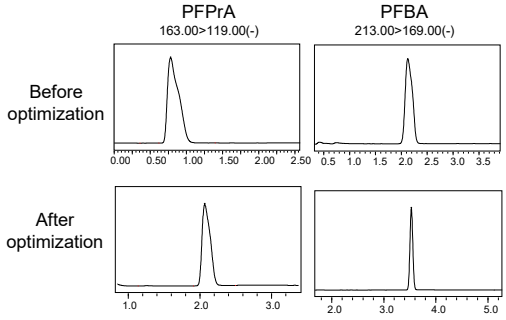

Fig. 1 Chromatograms of final column and flow rate with co-injection method

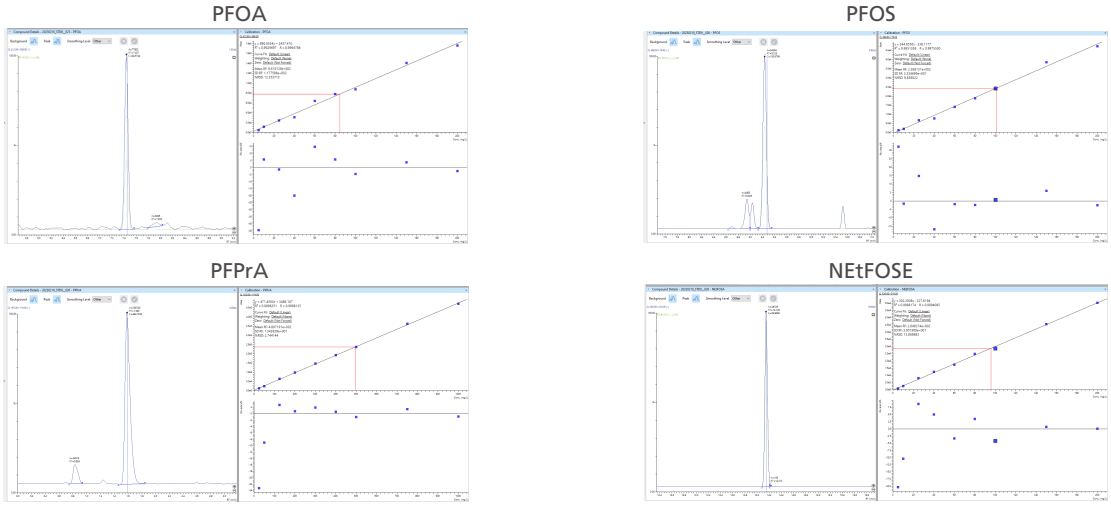

Fig. 2 Calibration curve and midpoint chromatogram for PFOA, PFOS, PFPrA, and NEtFOSE

Recovery and repeatability were evaluated in reagent water and wastewater, each spiked four times at the concentration indicated. Recovery was calculated after subtracting the native PFAS found in the unspiked sample matrices. These data are well within the 70 to 130 % recovery and ≤ 30 %RSD limits of the method.

This application news demonstrates the analysis of 44 PFAS and 24 surrogate compounds in non-potable water by ASTM D8421. Chromatographic conditions were optimized to achieve excellent peak shape, even for the earliest eluting compounds, such as PFPrA and PFBA. As shown, result easily exceed method performance criteria of the ASTM method, providing testing laboratories with highly accurate and reliable, repeatable results for PFAS in wastewater samples.

Analysis of PFAS in Wastewater Based on ISO 21675

Application

ISO 21675 is an international standard for determining PFAS in water samples. It was drafted by the National Institute of Advanced Industrial Science and Technology (AIST) and then developed by the International Organization for Standardization (ISO). The U.S. Environmental Protection Agency (EPA) Method 1633 targets PFAS with 4 to 14 carbons in water samples, while ISO 21675 includes additional long-chain PFAS with 16 and 18 carbons, which are not covered by EPA Method 1633.

benefits

- Based on ISO 21675, 30 PFAS can be analyzed in various water samples, including short-chain PFAS with 4 carbon atoms and long-chain PFAS with 16 and 18 carbon atoms.
- Accurate measurements are possible even in low-concentration spike recovery tests using ultrapure water and wastewater.

■ Measurement Results

Sample pretreatment was performed according to ISO 21675. An internal standard was added to a 100 mL water sample, and solid-phase extraction was performed with a mixed-mode reversed-phase/anion-exchange column. After washing and drying the solid-phase column, neutral PFAS were eluted first (first elution), followed by the elution of ionic PFAS (second elution). The eluate was dried down and reconstituted to 1 mL, and then the 100-fold concentrated sample was analyzed by LC-MS/MS.

A matrix blank test was conducted using ultrapure water and industrial wastewater, and spike recovery tests were performed by spiking each water sample with either a "Low" concentration (1 ng/L in wastewater, 0.1 ng/mL in solution) or a "High" concentration (10 ng/L in wastewater, 1 ng/mL in solution). The results of the spike recovery tests using ultrapure water and industrial wastewater are shown in Tables 1 and 2.

For ultrapure water, satisfactory recoveries were obtained, from 80 to 119 % for the "Low" concentration samples and from 93 to 116 % for the "High" concentration samples. In contrast, for wastewater samples spiked at the "Low" concentration level, recoveries varied widely from 59 to 170 %. In cases where compounds were present in the matrix blank at concentrations exceeding the spike level, recovery rates were insufficient, indicating potential interference from the blank matrix. However, the "High" concentration wastewater samples generally showed acceptable recoveries, ranging from 81 to 116 %.

Table 1 Spike recovery test using ultrapure water

Compound	Concentration (ng/L in ultrapure water)			Recovery Rate* (%)	
	Blank	Low	High	Low	High
PFBS	0.03	0.97	10.01	97	100
PFHxS	-	1.09	9.58	109	96
PFHpS	-	0.96	9.83	96	98
PFOS	-	0.99	9.60	99	96
PFDS	-	0.94	9.44	94	94
FOSA	0.01	0.96	10.57	96	106
NMeFOSA	-	0.93	10.07	93	101
NEtFOSA	-	1.00	10.37	100	104
NMeFOSAA	-	0.88	10.17	88	102
NEtFOSAA	-	0.94	10.48	94	105
6:2FTSA	-	0.91	11.23	91	112
8:2FTSA	-	0.80	11.63	80	116
9Cl-PF3ONS	-	0.90	9.50	90	95
PFBA	0.18	1.06	9.90	106	99
PFPeA	0.17	1.12	10.66	112	107
PFHxA	0.15	1.17	9.86	117	99
PFHpA	0.17	1.02	9.37	102	94
PFOA	0.19	1.11	9.78	111	98
PFNA	0.17	1.19	9.90	119	99
PFDA	0.14	1.05	9.82	105	98
PFUnA	0.09	0.90	9.29	90	93
PFDoA	0.09	1.05	10.13	105	101
PFTrDA	0.07	1.02	10.42	102	104
PFTeDA	0.04	0.97	10.17	97	102
PFHxDA	0.03	1.00	10.22	100	102
PFOcDA	-	0.89	9.85	89	99
8:2 FTUCA	-	0.99	9.95	99	100
8:2 diPAP	-	0.93	9.96	93	100
HFPO-DA	-	0.99	10.30	99	103
DONA	-	0.95	9.29	95	93

*As prescribed by ISO 21675, percentage recoveries were calculated without considering the procedure blank results.

Table 2 Spike recovery test using industrial wastewater

Compound	Concentration (ng/L in wastewater)			Recovery Rate* (%)	
	Blank	Low	High	Low	High
PFBS	0.78	1.68	10.36	90	96
PFHxS	0.38	1.32	9.95	95	96
PFHpS	-	1.00	9.84	100	98
PFOS	1.65	2.49	11.58	85	99
PFDS	-	0.80	8.49	80	85
FOSA	0.12	1.12	11.15	100	110
NMeFOSA	-	0.96	10.30	96	103
NEtFOSA	-	0.92	10.97	92	110
NMeFOSAA	0.03	0.91	10.65	88	106
NEtFOSAA	0.18	1.06	10.23	88	100
6:2FTSA	3.70	4.30	15.02	59	113
8:2FTSA	-	0.84	11.19	84	112
9Cl-PF3ONS	-	0.92	9.29	92	93
PFBA	16.02	17.29	24.17	127	81
PFPeA	7.97	9.43	19.06	147	111
PFHxA	12.77	13.39	23.08	62	103
PFHpA	6.49	7.19	16.46	69	100
PFOA	9.99	11.50	20.15	151	102
PFNA	9.17	10.86	20.74	170	116
PFDA	5.86	6.63	15.75	77	99
PFUnA	3.38	4.20	12.56	82	92
PFDoA	1.68	2.69	12.08	101	104
PFTrDA	0.50	1.33	8.96	83	85
PFTeDA	0.29	1.23	10.59	93	103
PFHxDA	0.09	0.96	10.23	100	101
PFOcDA	0.02	0.84	9.96	82	99
8:2 FTUCA	0.03	0.96	10.04	93	100
8:2 diPAP	-	0.83	9.81	95	98
HFPO-DA	0.75	1.64	11.44	90	107
DONA	-	0.87	9.82	87	98

*High concentrations of PFAS were detected in the blank wastewater. Recovery was calculated using the difference between the blank concentrations and the spiked sample concentrations.

Robustness Evaluation of PFAS Analysis in Soil Using LCMS-8060RX

Application

Research has shown that PFAS accumulate in the bodies of humans from drinking water and in livestock, agricultural, and marine products from water and soil, and that they may have an adverse effect on health. This has created a need for highly accurate and reliable methods for measuring PFAS in not only water but also in soil and other samples with relatively complex matrixes.

benefits

- The LCMS RX series, which improved stability and robustness with CoreSpray technology, showed excellent peak area repeatability when measuring PFAS at low concentrations 500 consecutive times in a soil matrix.
- Quality control samples measured for every 20 soil sample also showed good recovery rates for all PFAS remaining between 80 and 120 %.

■ Measurement Results

Once the soil matrix was ready, the standard was added to create a soil sample with a target compound concentration of 0.1 µg/L in solution. The soil matrix content of the resulting soil sample was at least 90 %. This soil sample was then analyzed 500 times in succession. Fig. 1 shows the normalized peak areas of five major compounds (HFPO-DA, PFOA, PFHxS, PFNA, and PFOS) in the spiked soil sample. MRM chromatograms from the first and 500th analysis of these five compounds are shown in Fig. 2. Good peak shapes were obtained at the start and end of the 500 analyses and peak area repeatability was good for PFAS in the soil matrix sample. Quality control samples were also analyzed (n=3) every 20 analyses. Recovery from the quality control samples was within 80 to 120 % for all target compounds for the duration of the 500 consecutive analyses.

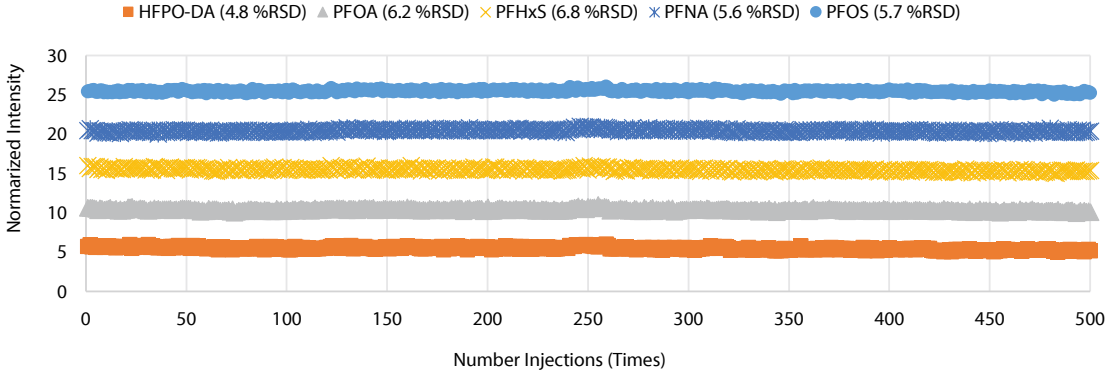

Fig. 1 Peak area repeatability (n=500) for the soil sample spiked to 0.1 µg/L (concentration in solution)

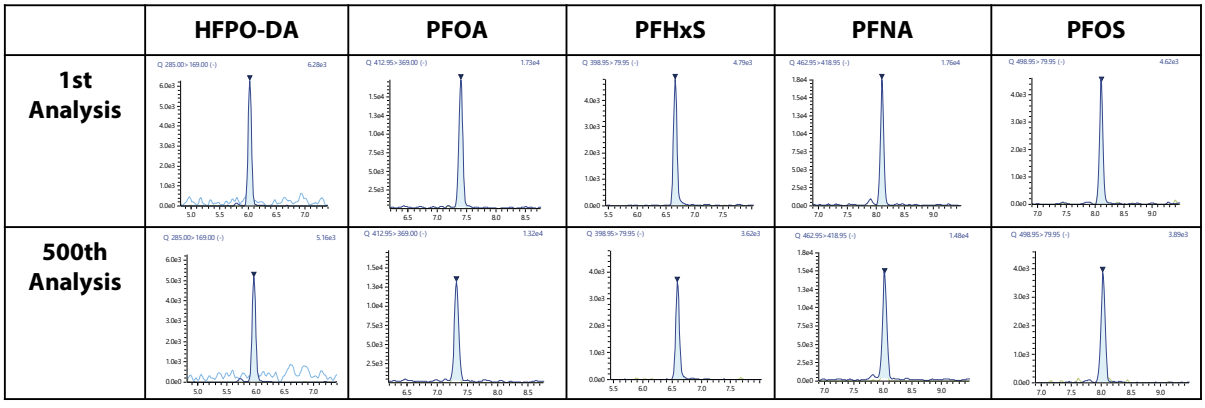

Fig. 2 MRM chromatograms of the first and 500th analysis of the soil sample spiked to 0.1 µg/L (concentration in solution)

The LCMS-8060RX performed 500 consecutive measurements of 30 PFAS added to a soil matrix sample. The results showed good peak area repeatability, good peak shapes, and good recovery. The LCMS-8060RX, which is now equipped with CoreSpray technology for improved stability and robustness, provides reliable analysis even with samples containing numerous impurities, such as soil matrix samples.

PFAS Analysis in Tissue According to EPA Method 1633A

Application

The U.S. Environmental Protection Agency (EPA) has developed standardized analytical methods, including EPA Method 1633A, to monitor PFAS contamination in a wide range of environmental and biological matrices. This study evaluates the performance of the LCMS-8065XE for PFAS analysis in accordance with EPA Method 1633A. By assessing calibration stability over the course of one week, we demonstrate the system's suitability for routine PFAS monitoring.

benefits

- LCMS-8065XE achieved up to 80 times lower limit of quantifications (LLOQ) than what's specified in EPA Method 1633A.
- The measurement time was 10 min while meeting the chromatographic requirements included in EPA Method 1633A.
- This method showed excellent robustness across seven days of over 900 continuous injections of the matrix sample.

■ Measurement Results

Cholic acids, such as taurodeoxycholic acid (TDCA), taurochenodeoxycholic acid (TCDCA), and tauroursodeoxycholic acid (TUDCA), can interfere with PFOS during the ionization process because their precursor and product ions are similar. These bile acids are present in tissue and wastewater samples. Therefore, one of the requirements of the LC method for EPA Method 1633A is to achieve separation of at least 1 min between PFOS and these cholic acids. In this study, acetonitrile was used as mobile phase B to meet this requirement. Fig. 1 shows the chromatographic separation of forty PFAS listed in EPA Method 1633A. With acetonitrile, the cholic acids eluted much earlier than both branched and linear PFOS. The retention time difference was 1.5 min, which exceeded the required one-minute separation.

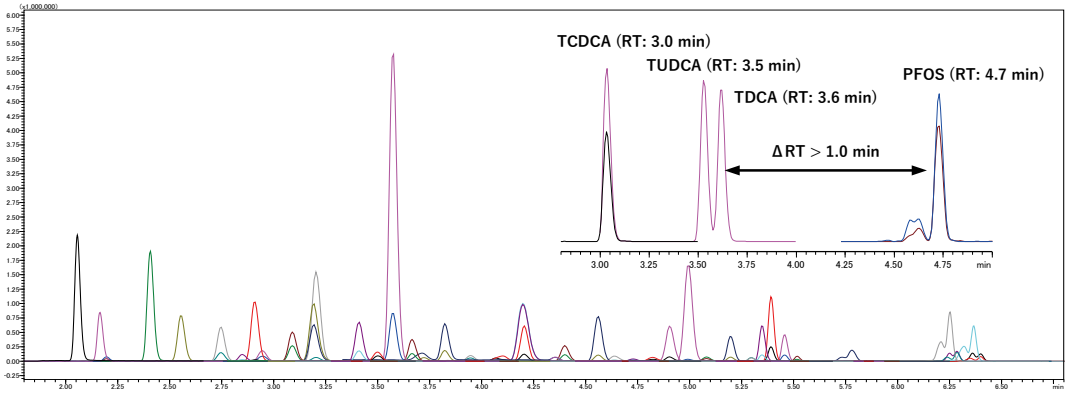

Fig. 1 MS chromatograms of 40 PFAS and 3 cholic acids

The LCMS-8065XE was able to detect concentrations up to 80 times lower than the LLOQ required in EPA Method 1633A, using a neat standard solution. Excellent linearity was achieved with the developed method, as indicated by RSE values below 20 % and high R^2 values (Fig. 2). This method demonstrates high throughput and robust instrument performance, maintaining accurate quantification in complex chicken tissue matrices without the need for maintenance or cleaning.

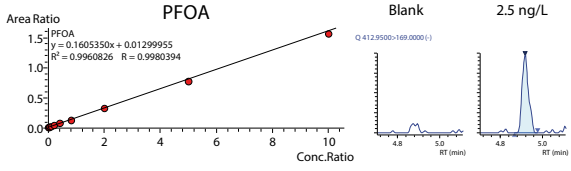

Fig. 2 Calibration curves and MS chromatograms of blank and LLOQ for PFOA

Liquid Chromatograph Mass Spectrometer LCMS-8065XE

The LCMS-8065XE is a triple-quadrupole mass spectrometer with EVOLVED, EFFICIENT, and EXACT capabilities. These exceptional capabilities ensure high reliability and enhanced productivity, empowering the laboratory for the future.

Product

Analysis of AOF (Adsorbable Organic Fluorine) According to EPA Method 1621

Application

The US Environmental Protection Agency (EPA) has published Method 1621, a screening method for the determination of AOF in aqueous matrices using a combustion Ion chromatograph (CIC). This method detects organic fluorine compounds that are dissolved in water. An advantage of this technique is that it provides information on the total amount of PFAS that may not be targeted by other selective chromatography methods.

benefits

- The combination of the combustion unit and IC can perform AOF analysis according to EPA Method 1621.
- AOF analysis is a simplified and useful technique for screening PFAS.
- The CIC system enables automation of the entire process from sample combustion to ion chromatography analysis.

■ Measurement Results

The sample preparation and analysis process is summarized below.

1. The sample is passed through the TXA-04 absorption unit. (Nittoseiko Analytech Co., Ltd.)
2. GAC column is rinsed to remove inorganic fluorine.
3. GAC is transferred to the ceramic boat and combusted.
4. Combustion products are captured in the absorption solution.
5. Absorption solution is analyzed by ion chromatography.

In this analysis, sodium fluoride solution was used as the standard solution, and 200 µL of the standard solution was combusted and absorbed in 11.3 mL of ultrapure water. A six point calibration curve was prepared from the analysis results of standard solutions with fluoride ion concentrations between 1.8 µg/L and 442.5 µg/L. The resulting calibration curve is shown in Table 1. The calibration curve was prepared using a quadratic equation, and measured concentrations of each calibration point were within 80 to 120 % according to EPA 1621. Table 1 shows the accuracy (%) of each calibration point concentration and the calculated concentrations.
Four aliquots of ultrapure water were spiked with 25 µg/L PFHxS as a fluoride ion. Fig. 1 shows the chromatogram of the PFHxS standard solution. The result of Average Recovery (%) and repeatability (%RSD) in four consecutive analysis of PFHxS standard solutions were 95.5 and 2.42, respectively, both of which were within the criteria of EPA 1621.
The MDL was determined to be in accordance with the procedures specified in EPA 1621 was 1.27 µg/L.

Table 1 IPR calculation results

Normal concentration (µg/L)	Area	Measured concentrations (µg/L)	Accuracy (%)
1.8	198	2.04	113.2
8.8	663	8.79	99.9
17.7	1,265	17.5	99.1
88.5	6,154	88.3	99.8
177.0	12,332	177.2	100.1
442.5	31,031	442.5	100

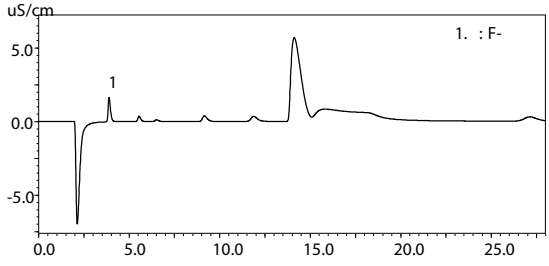

Fig. 1 Chromatogram of 25 µg/L PFHxS standard solution

Combustion Ion Chromatograph

A combustion ion chromatograph is a device that can quantify halogens contained in samples. The Shimadzu HIC-ESP ion chromatograph was equipped with the Nittoseiko Analytech Co., Ltd. AQF-5000H combustion unit. AQF-5000H combusts the sample, collects the resulting halogen gases in an absorbing solution, and automatically introduces the halogen-containing solution into HIC-ESP.

Analysis of Neutral PFAS in Ambient Air Using Thermal Desorption GC-MS

Application

As one of the pollution routes of PFAS, the atmospheric dispersion of PFAS exhaust gas emitted from factories using PFAS is a concern. Therefore, monitoring studies have been conducted to determine the risk of long-term exposure of PFAS to the respiratory system and the spread of PFAS pollution from atmospheric dispersion of PFAS. While most analysis methods for PFAS target non-volatile (ionic) PFAS and use a liquid chromatograph-mass spectrometer (LC-MS/MS), volatile or semivolatile neutral PFAS are not easily measured by LC-MS/MS. A gas chromatograph-mass spectrometer (GC-MS) is suitable for those compounds.

benefits

- A thermal desorption GC-MS system can accurately measure quantities of volatile and semivolatile per- and polyfluoroalkyl substances (PFAS) in ambient air.
- The TD-30R thermal desorption system can perform high-throughput analysis as it does not require solvent extraction.

■ Measurement Results

In this example, the TD-30R thermal desorption system coupled to a GC-MS system measured the quantities of nine volatile and semivolatile neutral PFAS in ambient air.

The calibration curve (0.05 to 12.5 ng) and SIM chromatogram (0.2 ng) for 6:2 FTOH are shown in Fig. 1. The results confirm that the analysis method can detect all compounds from a minimum amount of 0.05 ng. The correlation coefficient R was greater than 0.998, which is in the range of 0.05 to 12.5 ng for all calibration curves, showing good linearity. All the area and concentration %RSD (n=3) results at 0.2 ng were below 6, so again showing good repeatability.

Standard solutions were prepared containing 10 ng of four FTOHs and 1 ng of three FTACs and two FOSAs and then added to the Tenax TA/Carboxen 1000 sample tubes. 20 L of ambient air was also collected at 100 mL/min. The spike-and-recovery test and repeatability results are shown in Table 1. The recovery rates were between 77 and 106 % and all concentration %RSD (n=3) were below 8, showing generally good performance.

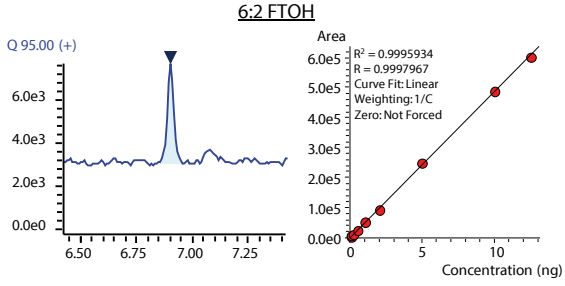

Fig. 1 SIM chromatogram (0.2 ng) and calibration curve

Table 1 Spike-and-recovery test results with ambient air

	Spike Concentration (ng)	Mean Recovery (%, n = 3)	Conc. %RSD (n=3)
4:2 FTOH	10	77	3.0
6:2 FTOH	10	97	4.8
8:2 FTOH	10	98	1.0
10:2 FTOH	10	98	5.0
6:2 FTAcr	1	93	4.8
8:2 FTAcr	1	99	7.9
10:2 FTAcr	1	99	7.2
N-MeFOSA	1	99	4.3
N-EtFOSA	1	106	3.5

Gas Chromatograph Mass Spectrometer
GCMS-QP2020 NX

The Shimadzu single quadrupole GCMS-QP2020 NX gas chromatograph-mass spectrometer (GC-MS) not only boasts the best performance in its class, but also the highest efficiency. This high-end single-quad GCMS excels in both ease-of-use and robustness. The role of high-performance analytical instruments is expanding in areas as diverse as environmental pollution monitoring, forensics and material science. Whatever your field, the efficient and reliable GCMS-QP2020 NX is tailored to meet the needs of your laboratory.

Product

Thermal Desorption System
TD-30R

The TD-30 was developed as the optimal solution for gas and materials analysis. Its outstanding processing ability and excellent expandability provide strong support for all types of analysis, from work in research departments to quality control.

GCMS-QP2020 NX and TD-30R

Product

Analysis of 28 PFAS Using the Compact Single Quadrupole LCMS-2050

Application

The growing concern of per- and polyfluoroalkyl substances (PFAS) in the environment has driven the need for quick, inexpensive measurement of PFAS for evaluating PFAS removal by novel treatment technologies, monitoring of remediation projects, or for detecting emerging contaminants. Most PFAS applications require the sensitivity and specificity of the triple quadrupole mass spectrometer; however, this system requires significantly higher maintenance costs and a much larger laboratory footprint. The compact, affordable LCMS-2050 single quadrupole mass spectrometer can be easily integrated into existing laboratories for measurement of PFAS in diverse samples where adherence to regulated methods (e.g., EPA 533, 537.1, and 1633) is not required, or for samples where expected concentrations are larger than sub ppb levels.

benefits

- Can quantitatively acquire LCMS data of individual PFAS compounds with a straightforward workflow.
- Sensitive analysis of PFAS targets detected down to 0.5 ng/mL.
- Fast and accurate separation with a compact, single quadrupole detector — the Shimadzu LCMS-2050.
- Simultaneous analysis in SIM and scan modes allows monitoring of suspected degradation or transformation products.

■ Measurement Results

The compact, single quadrupole LCMS-2050 was used to separate and quantify 28 commonly studied PFAS in neat standards. Fig. 1 shows the SIM chromatogram at the maximum concentration of the calibration curve, and Fig. 2 shows the SIM chromatograms at the LOQ for PFOA and PFOS. The limits of quantitation (LOQ) were in the low ng/mL concentration range with %accuracy between 80 to 120 % and %RSD area < 12 %. This result showcased the ability of the LCMS-2050 for PFAS quantitation with a user-friendly software interface for optimization and data analysis.
The inclusion of the scan event did not hinder the separation and quantitation of the PFAS, which demonstrates the additional benefit of scanning for degradation products and obtaining additional mass information.
The Shimadzu LCMS-2050 compact single quadrupole mass spectrometer was successfully employed for the accurate separation and quantitation of 28 commonly studied PFAS. These results demonstrate the accessible, effective, and cost-effective Shimadzu LCMS-2050 for measuring PFAS for applications such as determining PFAS removal by current and novel treatment technologies.

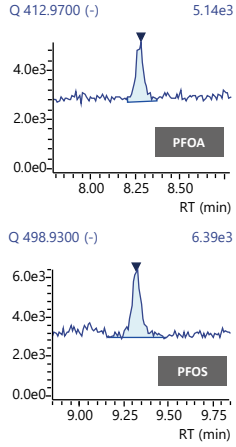

Fig. 2 SIM chromatograms at LOQ 0.5 ng/mL for PFOA and PFOS

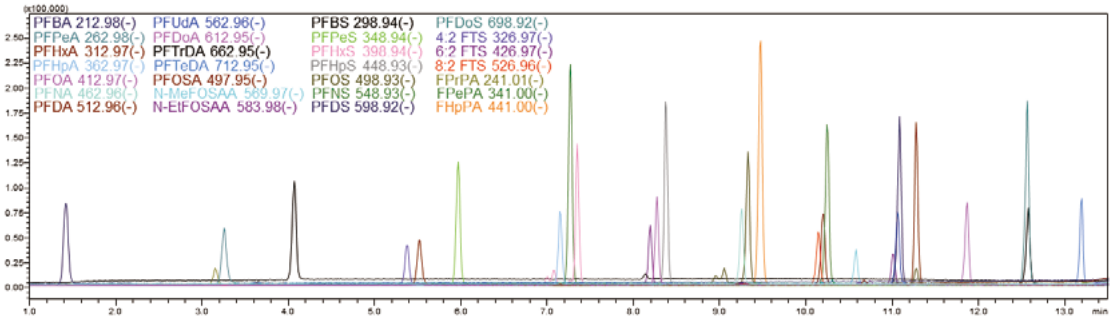

Fig. 1 Representative chromatogram of the 28 PFAS analytes at the highest calibration standard (20 to 200 ng/mL) by SIM acquisition

Liquid Chromatograph Mass Spectrometer
LCMS-2050

The LCMS-2050 single quadrupole mass spectrometer combines the user-friendliness of an LC detector with the excellent performance of MS to provide a complete package of easy-to-use high-level performance and compactness. To make it accessible to all users, the system is enhanced with technology and functions to ensure that even technicians unfamiliar with mass spectrometers can easily and efficiently perform analysis. While delivering operational convenience on par with an LC detector, the LCMS-2050 provides the high speed, high sensitivity, and wide mass range that are the hallmarks of Shimadzu mass spectrometers.

Product

Untargeted Screening of PFAS by HRAM-DIA Method Using LC-QTOF

Application

Because of how PFAS are defined, they include an extremely wide range of compounds. Therefore, the number of compounds covered by various official analytical methods will presumably increase in the future. It is becoming increasingly important to verify the presence of latent and unknown PFAS compounds. That will require screening methods that are highly effective at identifying PFAS.

benefits

- A sensitive untargeted screening method was established based on HRAM-DIA data acquisition using the LCMS-9030. The method was successfully verified with 14 PFAS standards at 1 ng/mL in water.
- Data analysis was performed using LabSolutions Insight Explore – Analyze. PFAS-like species could be extracted by specific elemental settings which function as mass defect filtering for PFAS. This procedure was used for an unknown sample, and 16 PFAS-like species were discovered and characterized.

■ Measurement Results

The XIC chromatograms of a 1 ng/mL sample are displayed in Fig. 1 (a) and the spectrum of the first XIC peak (PFPA) is shown in Fig. 1 (b). The lowest detectable concentrations by HRAM are 0.01 ng/mL for 11 PFAS, 0.02 ng/mL for PFDA, 0.05 ng/mL for PFPA and 0.1 ng/mL for PFTrA and PFTeA. The mass accuracy is better than (+/-) 3.3ppm, with most compounds less than (+/-) 2 ppm. Linear calibration curves were established from the lowest concentrations to 5 ng/mL for all the PFAS with R^2 between 0.94 and 0.99. PFOA, PFOS and their isotope labelled standards (M-PFOA, M-PFOS) could also be detected at the 0.01 ng/mL level. These results indicate that a highly-sensitive screening and quantitation method could be established based on HRAM using the LCMS-9030.

The data processing using Analyze was adopted for untargeted screening of PFAS in unknown samples. The 16 PFAS-like precursor peaks extracted from DIA data via Analyze are displayed in Fig. 2 (a). Taking the peak at 1.824 min (*m/z* 212.9787) as an example, the deconvoluted MS/MS spectrum and library search are shown in Fig. 2 (b) and (c). The results confirm the presence of PFBA in the sample. The deconvoluted MS/MS spectrum was sent to the Assign program, which links to a database search (ChemSpider). Heptafluorobutyric acid (CAS No.: 375-22-4) was found as a matched structure and the precursor as well as a fragment were annotated (Fig. 2 (d)). It is actually the same as perfluorobutanoic acid (PFBA).

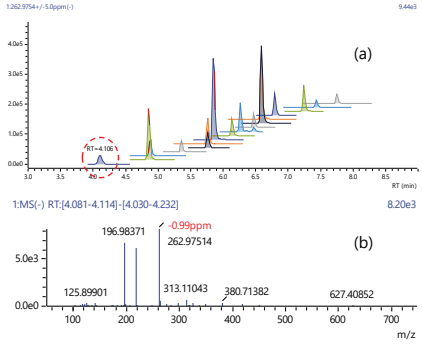

Fig. 1 (a) XICs of 14 PFAS and 2 ISTD (1 ng/mL each),
(b) MS spectrum of the 1st peak (PFPA).

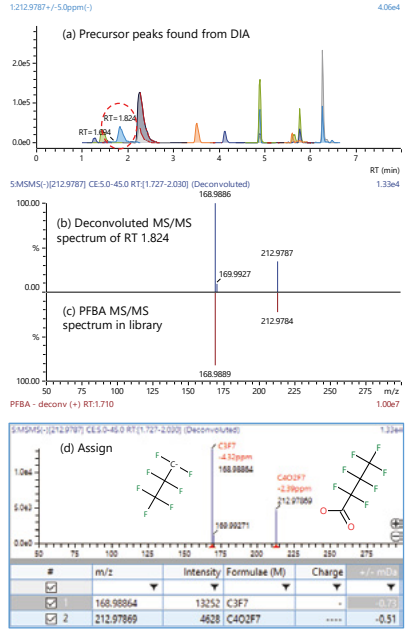

Fig. 2 (a) Detection of unknown PFAS-like compounds from DIA,
(b) deconvoluted spectrum of peak at RT 1.824,
(c) matches to library spectrum of PFBA,
(d) Assign to Heptafluorobutyric acid structure and fragment (same as PFBA).

Liquid Chromatograph Mass Spectrometer LCMS-9050

The LCMS-9050 is a QTOF mass spectrometer designed for the most reliable and easy acquisition of accurate masses in real laboratory settings. Incorporating proprietary innovation for fast polarity switching, it has the unique capability for high-confidence identification of challenging compounds and high-throughput screening of multiple unknowns. All sorts of applications are possible with the abundance of optional accessories and front-end configurations that leverage the instrument's power.

Product

Analysis of PFAS Using a Triple Quadrupole Mass Spectrometer –Fish Fillet–

Application

There are concerns about health risks associated with human consumption of fish that have ingested seawater, river water, or feed contaminated with PFAS. Therefore, quantitative assessment of PFAS levels in fish is important.
Thirty principal PFAS targeted by AOAC INTERNATIONAL were analyzed using a newly created method, which was investigated from the pretreatment procedure and then validated by a recovery test.

benefits

- The optimized pretreatment procedure and LC-MS/MS analytical conditions enable accurate quantification of thirty major PFAS targeted by AOAC SMPR from 0.1 µg/kg.
- The method allows the initiation of PFAS analysis in food.

■ Measurement Results

Recovery tests were conducted at 0.1, 1, and 5 µg/kg, and the recovery rates and repeatability were evaluated. The results are shown in Fig. 2. The procedure was performed from pretreatment in triplicate, and the area values were corrected using internal standards, with quantification carried out using a matrix calibration curve. According to the requirements of AOAC SMPR, PFOS, PFOA, PFNA, and PFHxS are specified to have a limit of quantification (LOQ) of 0.1 µg/kg or less, recovery rate within 80 to 120 %, and repeatability of 10 % or less. For other compounds, an LOQ of 1.0 µg/kg or less, recovery rate within 65 to 135 %, and repeatability of 25 % or less.
For all compounds, recovery rates within 81.6 to 114.1 % and repeatability below 17.1 % were achieved at spiked concentrations of 0.1, 1, and 5 µg/kg.

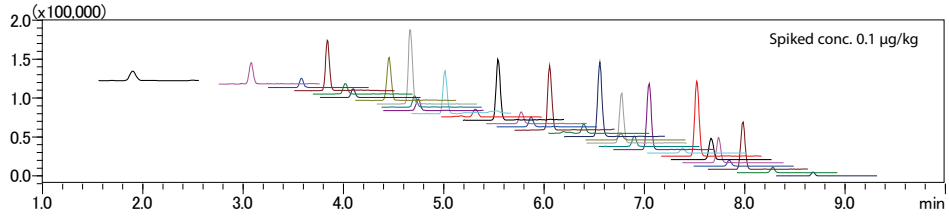

Fig. 1 MRM chromatograms of spiked PFAS in tuna fillet samples

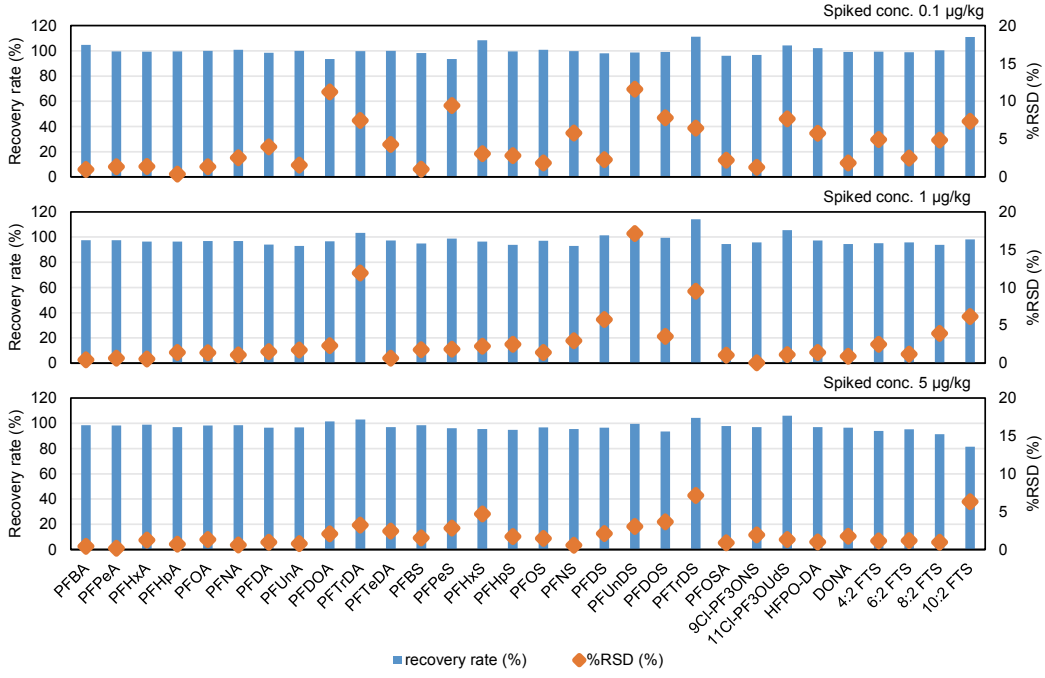

Fig. 2 Recovery rate and repeatability of QC samples (n=3)

Analysis of PFAS Using a Triple Quadrupole Mass Spectrometer –Milk–

Application

Recent studies have revealed that PFAS can transfer into dairy products when dairy cows ingest feed or water contaminated with PFAS. There are concerns about the potential health risks caused by human ingestion of PFAS-contaminated dairy products. Therefore, quantitative assessment of PFAS levels in dairy products is important. To monitor PFAS concentrations in dairy products, a highly accurate and sensitive quantification method is essential.
Thirty PFAS targeted by AOAC INTERNATIONAL were analyzed and evaluated by a spike recovery test.

benefits

- The optimized pretreatment procedure and LC-MS/MS analytical conditions enable accurate quantification of thirty major PFAS targeted by AOAC SMPR from 0.01 µg/kg in milk.
- The method allows the initiation of PFAS analysis in food.

■ Measurement Results

Recovery tests were conducted at 0.01, 0.1, and 1 µg/kg, and the recovery rates and repeatability were evaluated. The results are shown in Fig. 2. The procedure was performed from pretreatment in triplicate, and quantification was carried out using a matrix-matched calibration curve. According to the requirements of AOAC SMPR, PFOS, PFOA, PFNA, and PFHxS are specified to have a limit of quantification (LOQ) of 0.01 µg/kg or less, a recovery rate within 65 to 135 %, and repeatability of 25 % or less. The LOQs for other PFAS are 1.0 µg/kg for PFBA and PFPeA, and 0.1 µg/kg for the others.
In this validation, recovery rates for all compounds at a spiked concentration of 0.01 µg/kg were 92.0 to 119.6 % with reproducibility of 15.7 % or less, 96.6 to 107.8 % with reproducibility of 8.1 % or less at an added concentration of 0.1 µg/kg, and 93.9 to 101.7% with reproducibility of 4.4 % or less at an added concentration of 1 µg/kg.

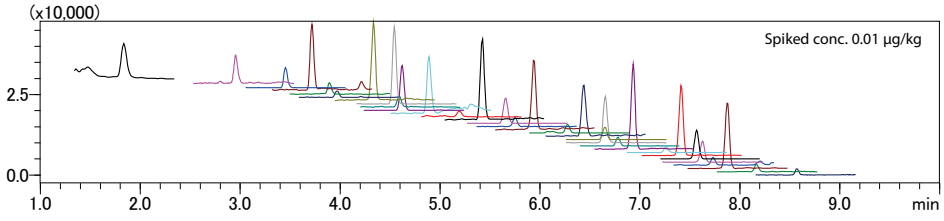

Fig. 1 MRM chromatograms of spiked PFAS in milk samples

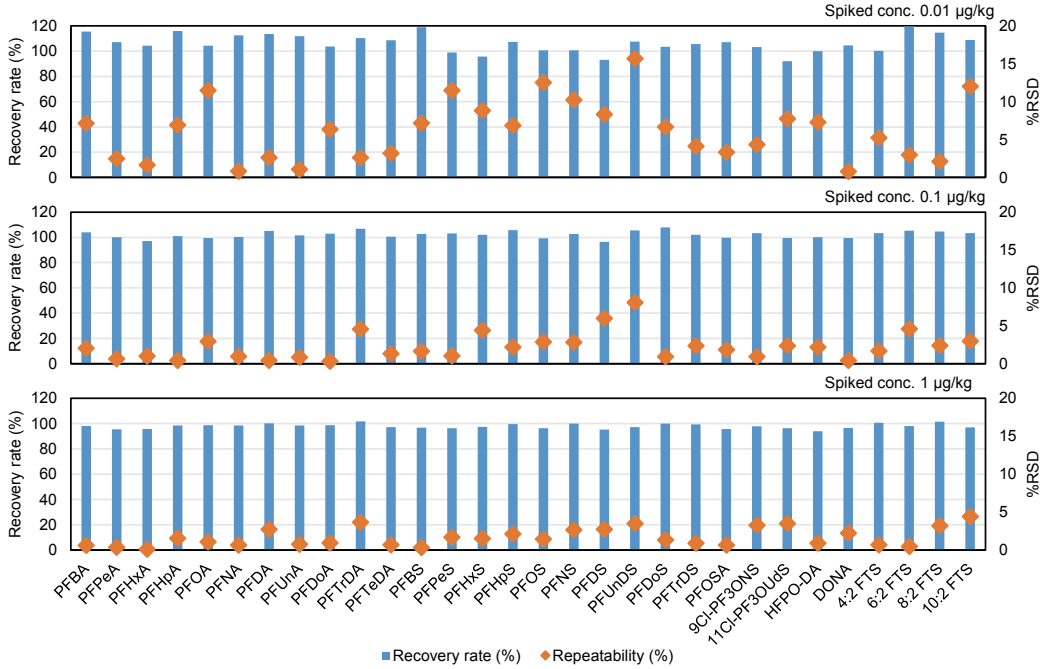

Fig. 2 Recovery rate and repeatability of QC samples (n=3)

Automated Analysis of PFAS in Food Matrices

Application

Due to their anthropogenic origin, PFAS cannot be degraded. As a result, they accumulate and can now be detected ubiquitously in the environment. Due to this, PFAS have found their way into the food chain and accordingly into our food. Increasing concerns about human exposure to PFAS through diet have led studies on the status of food contamination in various countries.
Here we describe the determination of various PFAS in egg matrix in a relevant concentration range. The analysis is based on a simple QuEChERS extraction coupled to an on-line SPE approach. This omits additional sample preparation steps like dSPE.

benefits

- Single-vendor solution for UHPLC and MS system
- Quantification of 27 PFAS in the ng/mL range using an on-line SPE approach
- Increased sensitivity due to the stacked injection combined with on-line SPE

■ Measurement Results

Samples were extracted on the basis of the QuEChERS AOAC method. 50µL of sample was injected directly on a SPE-trap column using the stacked injection function offered by the Nexera SIL-40 autosampler. This results in 5x10 µL injections, where each injection is followed by an aqueous sample loading phase that removes the organic solvent from the sample extraction. This leads to improved trapping capability. With this approach higher volumes of the pure QuEChERS extract can be injected.
Depending on availability of an appropriate ISTD, either an internal or external standard method was used for quantification. Five eggs from different origins were purchased locally and analyzed together with the calibration samples. In addition, these eggs were spiked with PFAS before extraction at concentrations of 0.01 ng/mL and 0.1 ng/ml. Good recoveries and reproducibility were obtained for all compounds by simple pretreatment.

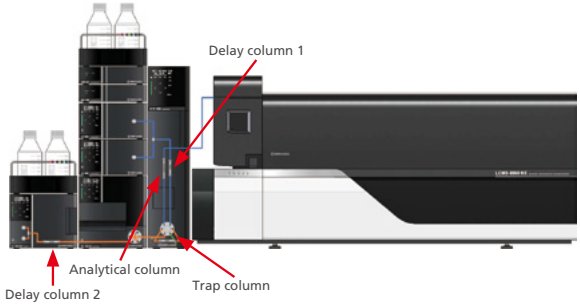

Fig. 1 MRM chromatograms of spiked PFAS in milk samples

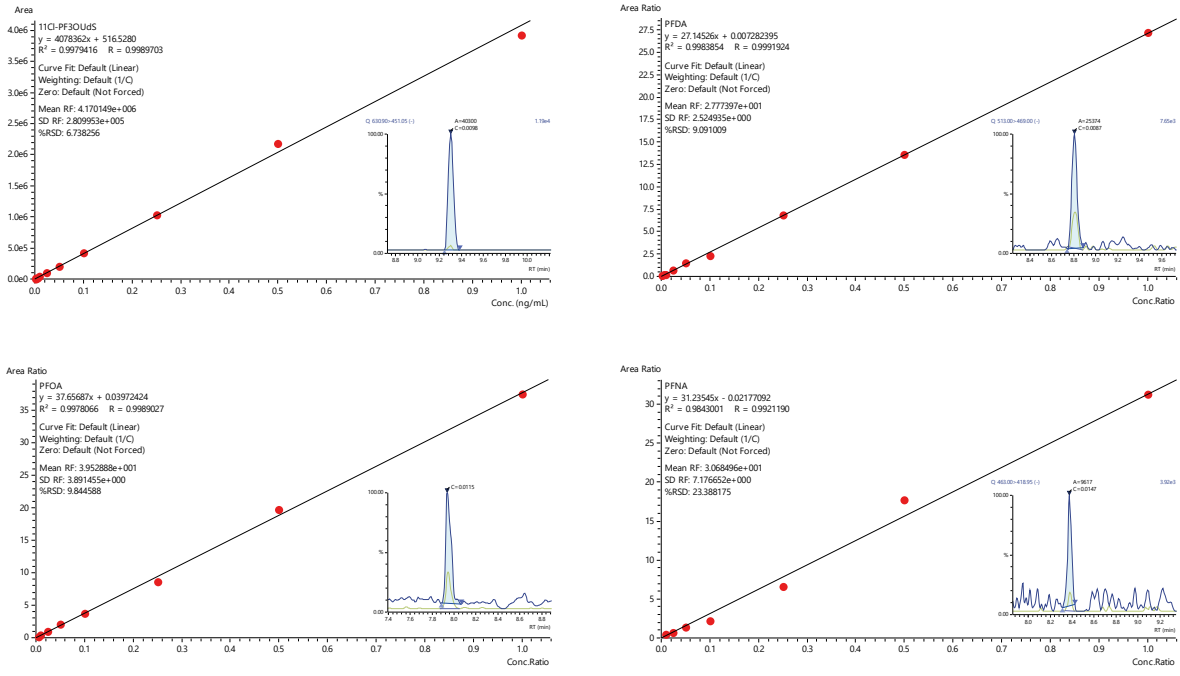

Fig. 2 Calibration curves and typical chromatograms at the 0.01 ng/mL level

Food Contact Materials: Targeted PFAS Analysis to Support Regulations

Application

Due to the unique properties of PFAS, they are widely used in food packaging, textiles, household items, and many other products. However, those same properties make them likely to accumulate in humans, animals, and the environment. Due to the increasing concerns about PFAS exposure to consumers and the environment, extensive investigative studies and research are being conducted on a wide variety of consumer products and food packaging materials.

benefits

- A direct LC-MS/MS method was established for quantitative determination of 15 targeted PFAS compounds in food contact materials (FCM) using the LCMS-8050.
- The results show that 12 out of 15 targeted PFAS were present in seven fast food packaging samples. The concentrations of the PFAS were far below the limit set by the Danish Ministry of Environmental and Food Guideline in 2015.

■ Measurement Results

Seven food contact material (FCM) samples, including paper wrappers, paperboard clamshells and beverage cups, were cut into 10 cm x 10 cm (100 cm^2) pieces and weighed. Each sample was further cut into smaller pieces for extraction and immersed in 20 mL of MeOH in a polypropylene (PP) centrifuge tube. Approximately 4 mL of the extract was cleaned using Supelclean ENVI-Carb SPE (6 mL/500 mg). The collected extract was evaporated to dryness with N_2 on a TurboVap LV evaporator (Biotag). The dried sample was reconstituted with 0.8 mL of 5 mM ammonium acetate solution and transferred into a 1.5 mL glass vial for LC-MS analysis (Fig. 1).

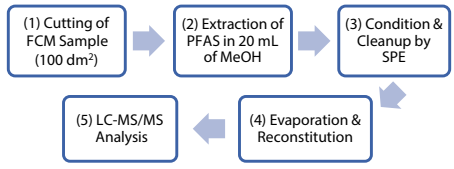

Fig. 1 Flowchart of sample pretreatment for PFAS in food contact materials (FCM)

Seven fast food packaging samples (Table 1) were analyzed using the validated LC-MS/MS method with external calibration. Each sample was analyzed in triplicate using LC-MS/MS to ensure repeatability of results (RSD<10 %). The average results of the seven fast food packaging samples are shown in Table 2, while PFAS profiles of P1, P3 and P6 are shown in Fig. 2. Multiple PFAS were found in every sample. PFOA, a PFAS banned under the POPs regulation in 2020, was detected in every sample, ranging from 0.19 ng/dm^2 to 1.69 ng/dm^2. In contrast, PFOS was not detected in any of the samples. The PFAS with the highest amount detected was PF-3,7-DMOA (up to 53.03 ng/dm^2). It is worth noting that the total amount of the 15 PFAS measured ranged from 6.07 ng/dm^2 (P3) to 95.9 ng/dm^2 (P1), levels are far below the limit set by the Danish Ministry of Environment and Food in 2015 for total organic fluorine (0.35 ug/dm^2) in food contact materials (FCM). Laurel A. Schaider et al. reported various fluorinated compounds, including known PFAS, in 20 FCM samples by LC-HRMS, with 70 % having a total fluorine level greater than 200 nmol/cm^2.

Table 1 Fast food packaging samples for PFAS screening by LC-MS/MS

S. No.	FCM Type	Description	Weight (mg /100 cm^2)
P1	paper	wrapping paper	302.4
P2	paper	pouch	551.3
P3	paper	wrapping paper	306.5
P4	paperboard	clamshell	2686.9
P5	paperboard	clamshell	2831.0
P6	paperboard	clamshell	2765.6
P7	paperboard	beverage cup	2406.2

Table 2 Types and amounts of PFAS in seven fast food packaging samples

PFAS	PFAS Content (ng/dm^2)						
(Abbr.)	P1	P2	P3	P4	P5	P6	P7
PFBA	19.89	2.59	2.59	4.43	6.32	7.02	3.93
PFPeA	10.93	1.46	1.47	1.87	2.48	3.20	2.1
PFBS	-	-	-	-	-	0.32	-
PFHxA	30.47	1.68	1.15	2.91	3.66	5.33	2.42
PFHpA	2.58	0.44	0.21	0.62	0.46	0.59	0.53
PFOA	1.69	0.23	0.17	0.73	0.19	0.33	0.24
PFHxS	-	-	-	-	-	-	-
PFNA	0.32	0.11	0.09	0.44	0.17	0.41	0.17
PF-3,7-DMOA	28.98	0.36	0.2	2.14	1.41	53.03	0.56
PFDA	0.92	0.36	0.2	2.1	0.59	1.73	0.51
PFOS	-	-	-	-	-	-	-
PFUnA	0.12	-	-	-	-	0.07	-
PFDS	-	-	-	-	-	-	-
PFTrA	-	-	-	0.92	1.23	0.91	-
PFTeA	-	-	-	1.73	1.96	2.24	-
Total	**95.9**	**7.23**	**6.07**	**17.88**	**18.47**	**75.17**	**10.45**

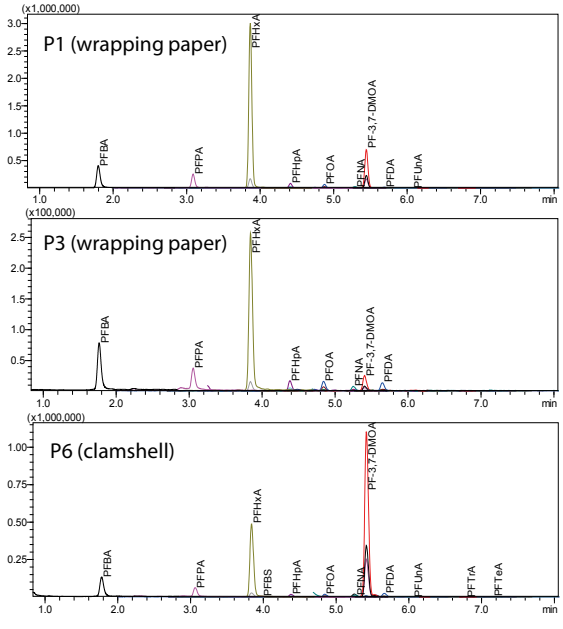

Fig. 2 PFAS detected in P1, P3 and P6 samples

Quantitation of Extractable PFAS in Consumer Products Using the LCMS-8060NX

Application

In response to growing concerns regarding consumer exposure to PFAS, many states have initiated bans on the use of PFAS in various consumer products and food packaging materials. These bans have led to a need for analytical testing to determine the amount of PFAS in consumer products; however, the lack of standardized methods presents challenges in ensuring reliability and reproducibility between labs.

benefits

- A newly developed and cost-effective full workflow for the analysis of extractable PFAS in consumer products without the need of labor-intensive solid phase extraction.
- Meets of exceeds the proposed reporting limits of the new ASTM method for 46 PFAS and 25 surrogates using the highly sensitive LCMS-8060NX.
- Reduce pressure failures with the new Nexcol PFAS Delay column (backpressure tolerance of 15,000 psi) while minimizing PFAS background levels.

■ Measurement Results

Samples (0.5 grams +/- 0.01 g) were weighed into a 50 mL polypropylene centrifuge tube and spiked with 40 µL of surrogate spiking solutions (SSS). The mixture was briefly mixed and allowed to equilibrate at room temperature for 15 minutes. A 50:50 (vol:vol) methanol:water solution was added to the sample and vortexed for approximately 1 minute. The sample's pH was then adjusted to approximately 9-10 using 20 µL of ammonium hydroxide, and briefly vortexed again. The centrifuge tubes were then tumbled on a rotator for 2 hours. After tumbling, the entire sample was filtered through a 0.2 µm polypropylene syringe filter (preconditioned with two 10 mL aliquots of methanol), into a 15 mL polypropylene centrifuge tube, to remove particulates while retaining solids behind. Post filtration, the sample's pH was adjusted to approximately 3-4 using 5 µL acetic acid per 1 mL recovered filtered sample volume. The samples were then briefly vortexed and centrifuged at 8 ˚C for 15 minutes at 3000 rpm. Following centrifugation, the sample was aliquoted into a silanized glass LC vial with a polyethylene/silicone septa, verified to be free of PFAS analytes contained within this method. The sample preparation is outlined in Fig. 1.

Fig. 1 Sample preparation procedure for consumer products

Recovery and repeatability were evaluated for the surrogates in PFAS-free Ottawa sand, a plastic product, and nonstick aluminum foil. Each matrix was spiked with surrogate spiking solution at the concentration specified in Table 1, based on a 0.5 g sample. Three replicates of each matrix were extracted and analyzed with the method. Excellent surrogate recoveries were obtained on the plastic and non-stick foil samples, with recovery values within 70 to 130 %. Triplicate extractions resulted in %RSD less than 15 %.

This method provides a foundation for ongoing efforts to develop a new standardized method with ASTM for PFAS analysis in consumer products.

Table 1 Blank sand matrix, plastic product, and non-stick foil surrogate spiking recovery (n=3)

Compound	Spike Conc. ng/kg	Sand Matrix Recovery (%)	Sand %RSD	Plastic Product Recovery (%)	Plastic Product %RSD	Non-stick Foil Recovery (%)	Non-stick Foil %RSD
13C4-PFBA_Surr	8000	104.6	9.7	102.6	2.4	100.5	1.4
13C5-PFPeA_Surr	8000	99.8	6.3	103.4	0.5	101.5	0.6
13C5-PFHxA_Surr	1600	95.7	5.6	98.2	1.4	99.3	0.4
13C4-PFHpA_Surr	1600	96.2	2.1	100.4	2.9	105.3	2.5
13C8-PFOA_Surr	1600	96.4	1.9	96.7	0.8	102.9	3.3
13C9-PFNA_Surr	1600	95.9	2.1	98.1	3.6	95.3	7.1
13C6-PFDA_Surr	1600	95.9	1.6	102.1	2.4	101.4	4.3
13C7-PFUnA_Surr	1600	95.0	4.6	96.7	1.0	103.7	0.5
13C2-PFDoA_Surr	1600	97.0	3.8	119.2	1.6	118.4	2.9
13C2-PFTreA_Surr	1600	92.0	8.6	116.4	0.9	104.1	4.7
13C8-PFOSA_Surr	1600	96.0	7.0	90.8	3.1	93.2	2.0
D3-NMeFOSAA_Surr	1600	97.7	2.5	105.3	1.7	112.0	12.5
D5-NEtFOSAA_Surr	1600	102.2	4.1	98.5	4.1	88.2	12.7
D3-NMeFOSA_Surr	1600	91.2	13.2	97.3	2.5	93.5	4.1
D5-NEtFOSA_Surr	1600	93.4	5.4	88.1	3.5	90.8	3.5
D5-NEtFOSA_Surr	1600	91.5	0.8	99.0	1.5	93.9	1.7
D9-NEtFOSE_Surr	1600	85.1	5.0	91.0	0.5	90.1	3.3
13C3-HFPO-DA_Surr	1600	95.1	3.6	104.5	1.0	103.1	2.9
13C2-4:2FTS_Surr	1600	97.1	6.7	102.7	8.2	104.4	8.2
13C2-6:2FTS_Surr	1600	96.0	14.8	93.4	2.5	102.7	0.2
13C2-8:2FTS_Surr	1600	94.7	12.9	102.5	15.4	101.9	9.6
13C8-PFOS_Surr	1600	99.0	10.3	102.6	1.5	102.4	4.4
13C3-PFBS_Surr	1600	103.0	3.1	100.1	3.4	98.4	1.0
13C3-PFHxS_Surr	1600	95.3	2.1	97.7	8.4	102.1	4.5
M4-6:2-diPAP_Surr	8000	128.7	3.2	117.8	3.2	102.2	6.4

Simple Check for Existence of PFAS in Textile and Kitchen Supplies by EDXRF

Application

In response to limits on the use of PFAS, analysis of PFAS in products is required. EDXRF can detect the element fluorine (F) in water-repellent-treated cloth and water- and oil-repellent-treated cooking products without complicated sample preparation. Development of fluorine-free alternatives to these water- and oil-repellent materials is now underway. Analysis by EDXRF is useful as a simple and quick test method for confirming the possibility that PFAS were used in products.

benefits

- EDXRF can detect the element fluorine (F) in fluorine resin coatings.
- Measurement does not require complicated sample preparation, and can be started simply by placing the sample in the instrument.
- Checking for the presence of fluorine in products by EDXRF is a simple technique for investigating the possibility that PFAS were used.

■ Measurement Results

Four synthetic fabrics treated for water repellency—samples A and B (polyester) and samples C and D (nylon)—were prepared for analysis. As shown in Fig. 1, each sample was cut to a size sufficient to cover the 10 mm analysis diameter and used directly without additional processing. The results of qualitative and quantitative analyses are presented in Fig. 2 and Table 1, respectively. Fluorine peaks were clearly detected in samples A and B, whereas no fluorine was detected in samples C and D, suggesting that their concentrations were below the lower limit of detection (LOD: 486 ppm, 3 σ of sample D was used as the LOD). These findings indicate that fluorine can be reliably detected at approximately the 1 % level within one minute of analysis.

Fig. 1 Water-repellent cloth (Sample B)

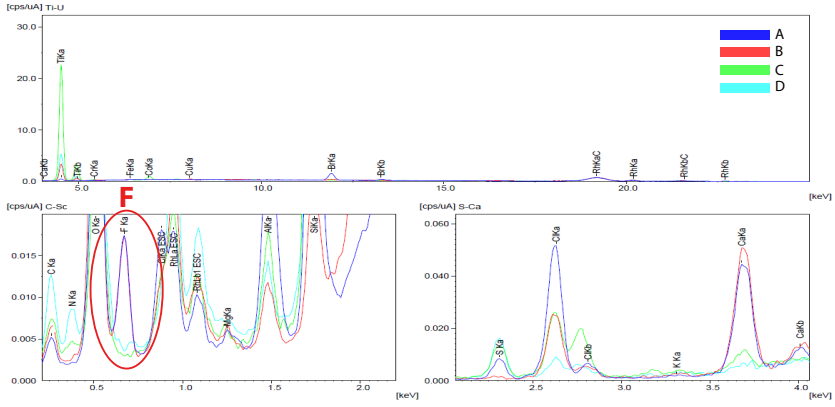

Fig. 2 Results of qualitative analysis of water-repellent cloths

Table 1 Results of quantitative analysis of water-repellent cloths [%]

Sample	F	Ti	S	Cl	Si	P	Al	Cu	Mg	Fe	Ca	K	Co	Cr	Br	$C_{10}H_8O_4$*1	$C_8H_{11}NO$*2
A	2.05	0.013	0.070	0.252	0.048	-	0.042	0.002	0.006	0.003	0.033	0.001	0.002	0.001	0.050	97.43	-
B	1.53	0.11	0.008	0.099	0.009	0.009	0.008	0.003	0.006	0.003	0.031	0.001	-	-	0.005	98.18	-
C	-	0.75	0.063	0.087	0.043	0.005	0.010	0.002	0.005	0.002	0.004	0.002	0.017	0.004	-	-	99.01
D	-	0.17	0.054	0.018	0.012	0.006	0.004	0.003	0.003	0.002	0.001	0.001	-	-	-	-	99.73

– : Not detected.
*1: Quantitative calculation of the balance (residual amount), assuming samples A and B are polyester ($C_{10}H_8O_4$).
*2: Quantitative calculation of the balance (residual amount), assuming samples C and D are nylon ($C_8H_{11}NO$).

Energy Dispersive X-ray Fluorescence Spectrometer EDX-8100

The EDX-8100 energy dispersive X-ray fluorescence spectrometer offers a high level of accuracy and speed in analyzing elements contained in various samples. It supports ultra-light element analysis of 6C to 92U, and can be used in conjunction with the helium substitution option to analyze liquid samples containing light elements (F to Al) as is.

Product

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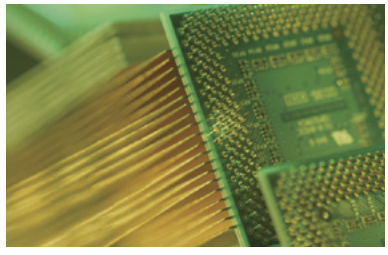

PBT Chemicals under TSCA – Analysis of PIP (3:1)

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