SHIMADZU
Excellence in Science

FREQUENTLY ASKED QUESTIONS

Per- and Polyfluorinated Alkyl Substances (PFAS)

1 What are PFAS (previously referred to as PFCs)?

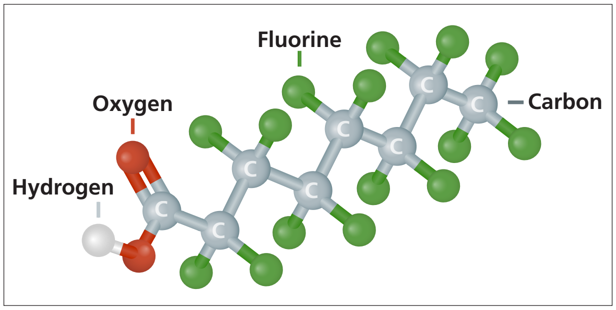
Per- and polyfluorinated alkyl substances (PFAS) are a group of man-made chemicals that are highly stable and resistant to degradation. These chemicals are manufactured and used in many consumer and industrial products (e.g., food packaging materials, firefighting foams and textiles) due to their heat-resistant and oil- and water-repellent properties. As these PFAS compounds are persistent, toxic and potentially harmful to humans and ecosystems, the leaching and presence of PFAS in our environment have raised serious concerns globally.

2 How widespread is PFAS occurrence?

Around the world, communities are discovering that PFAS are commonly found in the environment. In fact, according to the Agency for Toxic Substances and Disease Registry, most people in the United States have been exposed to PFAS and have them in their blood. Similar scenarios are expected in other countries too. Consequently, PFAS are currently of great public health and environmental concern.

3 How do people get exposed to PFAS?

Because their properties have been perceived as commercially attractive, PFAS have been used in a wide range of consumer products. So, unfortunately there are many ways people can be exposed to these chemicals, including ingesting contaminated food or water, or breathing in contaminated air. Exposure can also occur while working directly with PFAS compounds (like firefighting foams) or working in facilities that manufacture PFAS or materials that contain them.



PFOA (Perfluorooctanoic acid)

4 What are the human health risks associated with PFAS exposure?

Scientific studies have linked exposure to PFAS to various adverse health effects, including increased risk of cancer and infertility, abnormal development in children, and disruption of hormonal and immune systems. PFAS are very persistent, with very strong carbon-fluorine chemical bonds that are extremely difficult to break. As a result, they can accumulate and remain in the human body—and also in the environment—for long periods of time. For that reason, PFAS compounds are sometimes referred to as "forever chemicals."

5 Have any guidelines been set for limiting PFAS occurrence in the environment?

In the U.S., there are multiple ongoing efforts at the state and federal levels to establish proper regulations for controlling the presence of PFAS in the environment and manage their risk. In October 2021, the U.S. EPA announced its PFAS Strategic Roadmap that aims to safeguard communities from PFAS contamination through a whole-agency approach. The most relevant actions are as follows:

Safe Drinking Water Act

- Reassess occurrence through UCMR 5 (2022–2026)
- Determine revised Health Advisory (draft published June 2022)
- Update National Primary Drinking Water Regulations (expected 2022–2023)
- Publication of new analytical methods (expected 2022–2024)

Clean Water Act, Resource Conservation and Recovery Act and others

- Use of NPDES program, applicable to publicly owned treatment works, industrial facilities, and stormwater discharges, to restrict discharges, require monitoring, and establish and use best practices for managing PFAS, and inform the Effluent Limitation Guidelines program (2022)
- Publicize information to help federal, state and tribal agencies with the development of relevant regulation for ambient water, fish tissue and biosolids (2022–2024)
- Designate specific PFAS as CERCLA hazardous substances and incorporate them into new rulemaking for enhancing remediation (2021–2023)

Clean Air Act

- Identify sources and establish monitoring approaches for stack emissions and ambient air (from 2022)
- Develop information for cost-effective mitigation approaches (from 2022)
- Collect knowledge to inform potential regulatory and nonregulatory mitigation options (from 2022)

6 How are PFAS levels measured and analyzed?

With concerns rising quickly about the risks attributed to PFAS exposure, it is important to ensure proper monitoring of these chemicals in the environment. However, because PFAS are a complex group of chemicals, robust and accurate workflows are essential to identify and quantify them. That's why scientists turned to liquid chromatography coupled with mass spectrometry technology. Liquid chromatography coupled with triple-quadrupole mass spectrometry (LC-MS/MS) has become widely used for the quantification of PFAS in environmental matrices because of its high sensitivity and specificity.

To incorporate the growing list of PFAS compounds and to enhance the specificity and sensitivity of the LC-MS/MS analysis, multiple reaction monitoring (MRM), where two specific mass fragments from the same compound are monitored, is commonly utilized. Shimadzu's ultra-fast mass spectrometry (UFMS) systems, which operate without any compromise in sensitivity, prove to be ideal for the fast and sensitive analysis of many PFAS compounds in a single run. Given the social importance of PFAS monitoring, standardized analytical methods for LC-MS/MS are already available, and more are being developed and validated to ensure that all results are consistent and reliable, particularly if the data were to be used for enforcing regulations.

The use of LC with quadrupole time-of-flight (QTOF) instruments for the analysis of PFAS is becoming more prevalent, although methods are not yet standardized. The use of LC-QTOF enables the detection of PFAS suspected to be in the samples and the discovery of unknown compounds.

7 What methods have been established for measuring PFAS in the environment?

Organizations like the U.S. Environmental Protection Agency (EPA) and ASTM International, among others, have established standardized LC-MS/MS methods for measuring PFAS.

EPA methods 533 and 537.1 both analyze compounds in drinking water but differ in sample preparation and quantitation techniques. Method 533 analyzes 25 compounds and 537.1 lists 18 compounds, with 14 of those compounds in common. Although EPA 537.1 already included some of the emerging PFAS compounds, such as GenX and ADONA, EPA 533 includes a larger number of short-chain PFAS that were introduced in the market after the EPA's 2010/2015 PFOA Stewardship Program that led to the phaseout of PFOA, PFOS and long-chain PFAS from products and emissions.

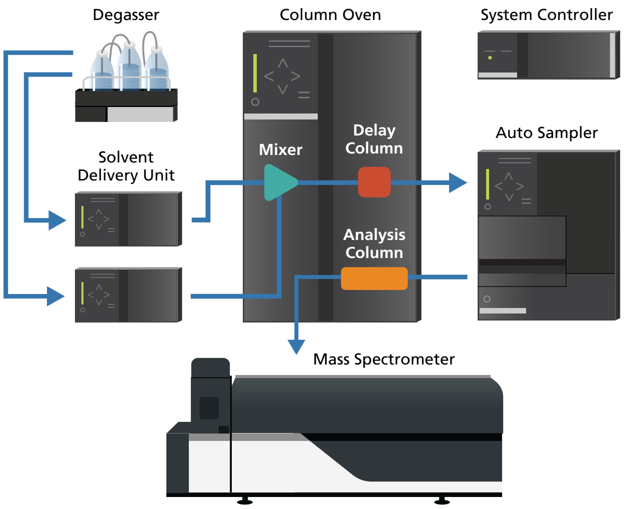
EPA also released method 8327 for surface water, groundwater, and wastewater matrices. A major difference between method 8327 and those for drinking water (EPA 533 and 537.1) is that, in EPA 8327, sample preconcentration is not required, hence, analysis time is much shorter, and sample volume required is smaller. Recently, EPA issued draft method 1633 for analysis of PFAS in aqueous, solid, biosolid and tissue samples. With the publication of this draft method, EPA completes a suite of methods suitable for the quantification of PFAS throughout the full water treatment cycle, although new methods are being prepared for addressing emerging needs. ASTM International published methods D7968-19 and D8421-22, which are used to analyze selected PFAS in multiple types of samples: water, sludge, wastewater, effluent and soils. All these methods use LC-MS/MS for quantifying PFAS and are additional tools to understand the fate of PFAS in the environment. EPA and ASTM continue to develop and publish new standardized methods to better understand the occurrence of PFAS in the environment.

To help support these advancements in PFAS research and testing, Shimadzu collaborates with these organizations and has vetted some of their standardized methods using Shimadzu LC-MS/MS instruments.

8 What should be done to prepare your LC-MS/MS for analysis?

Several components of LC-MS/MS instruments (e.g., degassers, solvent lines) and consumables (e.g., caps, syringe filters) may contain materials derived from PFAS and contribute to sample contamination. Historically, to prevent background contamination from these components during PFAS analysis, the liquid chromatograph was reconfigured to eliminate as many PFAS-based components as possible. As a result, maintaining, operating and troubleshooting the LC became more cumbersome.

However, Shimadzu has confirmed that a standard LC configuration, even with fluoropolymer-containing tubing and degasser in-line, can be successfully used for trace analysis of PFAS. There is one essential modification required—installing a delay column.



The delay column is installed after the mixer and before the injection port. The solvents used for the analysis (or mobile phases) continuously flow through this column. Any PFAS leaching from the instrument or already present in the mobile phases is retained on the delay column during system equilibration and the early portion of the analysis, when strength of solvents in gradient is not enough to elute the contaminants. From the delay column, the clean mobile phases flow through the analytical column, placed after the injection port, as in any regular LC analysis. When the gradient reaches sufficient strength, the accumulated PFAS contamination is eluted from the delay column and then moves through the analytical column until reaching the detector. The delay column ensures a retention time separation between the contaminant and the PFAS of interest present in the samples, as the latest only flows through the analytical column.

9 How should the integrity of PFAS standards and samples be preserved?

Stability of the PFAS standards solutions and samples during the time required for analysis is essential for ensuring the quality of the analytical results.

Stock solutions should be prepared and stored in PFAS-free high-density polyethylene (HDPE) or polypropylene (PP) containers with Teflon-free caps. Lined or unlined HDPE or PP caps should be used instead. Do not store samples in containers made of Teflon, glass or low-density polyethylene (LDPE) materials. PFAS can adsorb to glass, especially when the chemicals are stored for long periods of time.

When preparing standards of a variety of PFAS compounds, a mixture of 50% methanol in water is the optimal solution for dissolving PFAS and maintaining them in solution. Thorough testing has demonstrated that solvent mixtures with lower concentrations of methanol (10% and 30%) show larger losses of PFAS due to the insolubility of some PFAS in the solvent used. The results from testing 70% and 90% methanol in water are similar to that of 50% methanol in water. However, the higher methanol content evaporates faster and causes an increase in the PFAS concentration in the standard.

When PFAS calibration standards and samples are analyzed in the LC-MS/MS, the PFAS concentration in the vial may change after the vial cap is pierced, as the organic solvent (e.g., methanol in water) evaporates through the puncture. If calibration standards are to be used multiple times, it is recommended to use an amber glass vial with sealed replaceable caps. Sealing the vials immediately after injection may reduce the loss of PFAS.

10 Are there additional recommendations for PFAS analysis?

Some currently published methods (EPA 533, EPA 537.1) require a step of sample preconcentration by solid phase extraction (SPE). Materials used in the manufacturing of supplies for preparing the samples by SPE may also contain PFAS. To prevent preconcentrating the background PFAS during this step of the analysis, all new SPE cartridges, solvents and vials for collecting samples must be tested for PFAS prior to the first use and whenever a new lot is started.

Fluoropolymer-containing tubing for loading samples into the SPE cartridges should be replaced with an alternate material and, if possible, completely eliminated. If automatic sample extractors are employed for this step of the analysis, checking with the manufacturer is strongly recommended to identify all components made of polytetrafluoro-ethylene (PTFE) or other fluoropolymers and replace them when feasible.

Once samples are preconcentrated and ready for injection in the LC-MS/MS, or samples are prepared according to methods that allow for large volume injection, they may sit in the autosampler tray for extended periods of time. In these situations, some PFAS compounds may settle, precipitate or adsorb on the vials. It is important to remember to mix the extract/sample before (re)injection. Vortexing the solution before injection ensures a homogenous solution and optimum results.

To learn more, visit **www.OneLabOneEarth.com/pfas**.

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