



Overcoming the limitations of current analytical methods

Per- and polyfluoroalkyl substances (PFAS) are a group of human-made chemicals that include more than 4,000 individual compounds. PFAS possess unique chemical properties that make them desirable for a variety of industrial and commercial applications. However, those properties also make them recalcitrant in the natural environment. Researchers have not only found PFAS in food, water, soil, sediment, dust, and air, but also in the blood of more than 95% of the U.S. population¹.

PFAS compounds are ubiquitous in the environment, are linked to toxic effects at low concentrations, and are the focus of several high-profile court cases (such as the one documented in the 2019 film “Dark Waters”), leading to increased media and regulatory attention. Several states have published regulatory criteria for selected PFAS compounds that are typically in the parts per trillion range—orders of magnitude lower than criteria for many other environmental contaminants.

The complex chemical properties of PFAS, combined with the need to quantify concentrations at very low detection limits, present many challenges to PFAS chemical analysis. First, there are currently few standard methods. Industry demands for PFAS analysis, in the absence of federally standardized methods for analysis in most environmental media, have resulted in a patchwork of commercial laboratories all using their own modified methods. The lack of standardization can result in varied data from lab to lab with no guarantee of precision or accuracy².

Additionally, due to the widespread presence of PFAS in industrial processes and consumer products, laboratory

analysis requires particular care to [avoid cross-contamination of samples](#). Therefore, to evaluate a laboratory's ability to meet the needs of a PFAS project, the laboratory's analytical and quality control procedures must be thoroughly reviewed as part of the laboratory selection process. Further complicating matters for environmental practitioners, only a limited suite of PFAS compounds can be quantified in environmental samples due to the lack of reference standards—leading to only a partial picture of the total extent of contamination. To address this, practitioners must use advanced methods with limited commercial availability.

In this PFAS Technical Update, you'll find an explanation of the limitations in current standardized, modified, and advanced analytical methods, as well as guidance on how to overcome these shortcomings.

STANDARD METHODS

Commercial PFAS analysis generally uses liquid chromatography-tandem mass spectrometry (LC-MS/MS), an analytical technique appropriate for low-volatility analytes such as most PFAS. Two promulgated U.S. Environmental Protection Agency (EPA) methods for PFAS analysis currently exist—EPA 537.1 (which replaced the previous iteration, 537 rev 1.1) and EPA 533—and both are intended and approved only for analysis of drinking water³. There are several differences between the two methods, including the analyte list, sample preparation procedure, and quantitation method, so care should be taken to determine which method is more appropriate to meet the needs of a project.

MODIFIED METHODS

Responding to industry demands, commercial laboratories have developed their own proprietary methods for analyzing PFAS in matrices other than drinking water, often referring to these proprietary methods under the umbrella term “EPA 537 modified.” While EPA 537 allows for modifications to certain aspects of the method, such as LC column and MS conditions, many commercial laboratories have made modifications well outside the method scope. Changes to the analyte list, sample preparation procedure, quantitation method, and QC requirements have led to vocal disapproval from EPA administrators over use of the “EPA 537 modified” term⁴.

The shortage of standard methods leads to a lack of data comparability from lab to lab. This wide variety of methods includes laboratory quality control and sample preparation procedures (e.g., cleanup), as well as PFAS identification and quantitation calculations such as the ability to separate branched and linear chromatographic peaks. You must review a commercial laboratory’s standard operating procedures to ensure the lab is following best practices and providing quality, reliable data.

In an attempt to develop uniform quality control metrics for these modified methods, the U.S. Department of Defense (DoD) published PFAS-specific criteria in its current Quality Systems Manual (QSM) for Environmental Laboratories (Ver. 5.3, 2019). The QSM provides standardized procedures for measurement of PFAS in groundwater, surface water, soil, and sediments⁵. The DoD has also published a [database of laboratories](#) accredited to perform PFAS analysis compliant with its QSM, though you will still need to validate these labs’ data and ensure their compliance with QSM guidelines.

ADVANCED ANALYTICAL METHODS

As discussed, the currently available standard analytical methods can only quantify a limited number of PFAS compounds (fewer than 30). Quantitative analysis of the total PFAS mass present in an environmental media sample is challenging due to the large number of polyfluorinated compounds and the lack of available reference

Lack of quality control can cause several sources of error in PFAS data, including:

» The presence of certain constituents, such as organic carbon, can cause matrix interference. Matrix interference can result in the amplification or suppression of individual PFAS analytes’ “signals,” leading to either an overestimation or underestimation of concentrations. Matrix interferences are especially common with “dirtier” matrices such as wastewater, stormwater, landfill leachate, and sludge. Some labs use cleanup procedures such as ENVI-Carb™ cartridges to further prevent matrix interferences, but other labs do not. Matrix spike and matrix spike duplicates are commonly used quality control samples that can help the data user assess the impact of matrix interferences on sample data, but you’ll need to work with an experienced data validator who can interpret these results.

» The sample preparation procedure that includes an extraction process can lead to losses due to PFAS sorption onto sample containers or some analytes being preferentially extracted over others. Laboratories often spike samples with mass-labeled reference standards to assess losses during the extraction process; however, depending on the lab, they may not correct the final concentrations for those losses.

» Contamination from background sources of PFAS can be a significant issue, particularly if sample concentrations are low. Contamination can occur not only during the sampling process, but also during implementation of the sample preparation procedure and during sample analysis. Sampling and labware sometimes contain Teflon, which can contaminate samples. Even the tubing inside some analytical equipment can contain Teflon, so labs must take care to ensure they aren’t introducing any PFAS into the sample.

» Finally, several PFAS analytes exist as both linear and branched isomers in the environment, but mass-labeled branched reference standards don’t exist. Laboratories must take care to employ experienced analysts who can recognize branched isomers and ensure they are reporting the total mass of PFAS.

standards⁶. Some polyfluorinated compounds have been identified as precursors, meaning they can transform via biotic and abiotic (i.e., living and non-living) processes in the environment to produce perfluorinated compounds such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which are currently of regulatory interest⁷.

A 2013 paper by Houtz et al. reports that precursor PFAS compounds can make up 41% to 100% of the total concentration of PFAS in archived [aqueous film-forming foam \(AFFF\)](#) formulations⁸. To address this challenge, the following advanced analytical methods can estimate the total mass of PFAS in an environmental medium:

- Total oxidizable precursor (TOP) assay: This method exposes the sample to hydroxyl radicals generated by thermolysis of persulfate under basic pH conditions and perfluoroalkyl acid precursors are transformed to the perfluorinated carboxylic acids (PFCAs). By comparing PFCA concentrations before and after oxidation, the mass of total PFAS can be quantified⁹. TOP assay is currently commercially available¹⁰, but it is not a standardized method, so results can vary widely from lab to lab. Evaluation of TOP assay use in environmental matrices by a commercial laboratory found vast inconsistencies in the results of the TOP assay, suggesting that the lack of standardization can result in limited applicability¹¹.
- Adsorbable organic fluorine (AOF) analysis: This method involves sorption of PFAS onto a synthetic activated carbon followed by combustion and measurement of evolved fluoride by ion chromatography¹². AOF is still undergoing standardization and is offered by a limited number of commercial laboratories in Europe and Australia¹³.
- Particle-induced gamma emission (PIGE): This method involves PFAS separation from an aqueous sample via solid extraction cartridges followed by proton bombardment and measurement of the unique gamma ray signature emitted from any fluorine present¹⁴. It is more often used to quantify the total fluorine content in solid, unconventional matrices, such as textiles and paper. PIGE is not currently commercially available and

is only performed by a handful of university laboratories, mostly for research purposes.

- Quantitative time of flight mass spectrometry (QTOF-MS): This method can be used to determine both the chemical formula and structure of unknown PFAS in a sample¹⁵, or to estimate concentrations of “suspect” PFAS using semi-quantitation approaches¹⁶. QTOF-MS is not commercially available, and has limited applications for routine site assessment, but could be useful for forensic purposes at complex sites where contamination is known.

Each of these advanced methods provides unique analytical capability. Make sure to consult a PFAS expert to select a method that best fits your specific project needs.

RECENT DEVELOPMENTS

EPA published [Draft Method 8327](#) for analysis of 24 PFAS compounds in groundwater, surface water, and wastewater samples on June 12, 2019. This draft method eliminates the sample extraction step and instead utilizes direct aqueous injection of the sample matrix (e.g., 10-30 µL [microliters]) to the instrument, which negatively impacts the sensitivity of the analysis (raises reporting limits) and can lead to additional sample matrix interferences¹⁷. Also, the draft method uses an external standard quantitation method, instead of the powerful isotope dilution method. Consequently, this analytical approach is not suitable for low-level detection or rigorous reporting quality¹. More than a year later, EPA still has not formally promulgated this method.

EPA is also in the process of developing draft methods of analysis for complex environmental matrices and for additional PFAS target compounds. However, the process of multi-laboratory validation of standard methods can take years. Until a more robust set of standard methods for environmental matrices is available, data users must take care to choose qualified laboratories and data validators who can ensure data quality and defensibility.

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