Total Organofluorine (TOF) Assay Provides Estimates of Maximum Total PFAS Levels

Background and Value of TOF

Testing for Total Organofluorines (TOF) has recently generated substantial interest as a simple way to account for the total mass of Per- and Polyfluoroalkyl Substances (PFAS) in environmental or commercial product samples. PFAS represents a group of thousands of man-made organofluorine compounds (e.g. PFOS & PFOA) which have been shown to be globally distributed, environmentally persistent, and bioaccumulative. Due to their unique water and oil resistant properties and thermal stability, PFAS have been used in a wide range of commercial applications including food packaging, cleaners, floor polishes, photographic film, cosmetics, insecticides, Teflon® production, and in surface treatments of paper, clothing, carpets, and other products. Large-scale environmental releases have been associated with their use in firefighting foams (AFFFs, aqueous film-forming foams), where fluorinated surfactants are key ingredients that provide low surface tension, enabling film formation on top of fuels, to starve fires of oxygen.

Conventional PFAS analysis by LC/MS/MS typically quantifies a relatively small set of key analytes (~30 compounds) and therefore may greatly underestimate the total extent of PFAS presence in the environment. Leading international PFAS environmental management programs (such as Australia's National Environmental Monitoring Program) stress the importance of incorporating qualitative tests into environmental assessments to consider the likely total mass and distribution of all PFAS present, using techniques such as the Total Oxidisable Precursor (TOP) and TOF assays, to provide multiple lines of evidence for informed risk assessments. The US EPA also recognizes both TOP and TOF assays as important "emerging techniques" for non-targeted "Total PFAS" analysis. ALS offers both the TOP assay (refer to Enviromails #2 and #7 – see links below), and now also the TOF assay, to provide comprehensive options for PFAS accounting of environmental and commercial product samples.

TOF Versus TOP Assays for PFAS

The TOP assay is particularly useful to predict the formation potential for PFAS parameters with specific regulatory importance. However, a key limitation of the TOP test is that it relies on the analytical scope provided by conventional LC/MS/MS analysis and therefore fails to account for oxidation products with carbon chain lengths <C4 and >C14, and other non-targeted PFAS. The oxidation process also forms perfluoroalkyl carboxylic acid products from fluorotelomer "precursors" with chain lengths shorter than the parent fluorotelomer; the fluorinated portions of the carbon chains lost during this process are therefore also excluded.

While TOF analysis is not subject to these limitations, it provides no information about chain length and is not selective for PFAS, rather providing an estimate of the total fluorine content from organic (carbon-based) substances in a sample. TOF analysis can therefore be used to verify the degree to which the TOP assay accounts for potential precursors. The TOF analysis is a less sensitive measurement technique than LC/MS/MS for discrete PFAS parameters, with a higher limit of reporting (LOR). It may therefore not be suitable for low-level environmental screening, but is more appropriate as a screening and diagnostic tool for higher impact zones and circumstances where information on carbon chain length is not required.

Ultimately, a combination of TOP, TOF, and standard LC/MS/MS analysis for discrete PFAS parameters can provide the most well-rounded information about the current and potential future PFAS content of a sample or site.

Figure 1 illustrates relative proportions of TOF vs TOP vs PFAS discrete analytes in three commercial AFFF products. 3M Light Water™ is a PFOS-based product that was phased out in 2002. The other two AFFF products shown represent more recently produced short-chain fluorotelomer surfactants.

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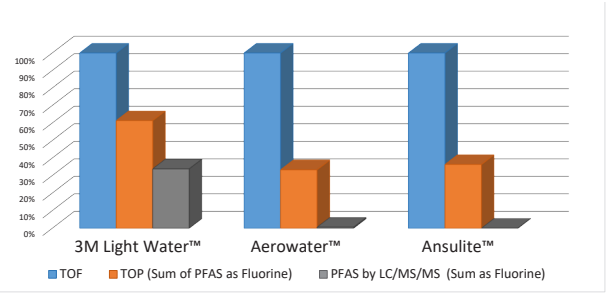
Figure 1. TOF vs TOP vs PFAS for 3 AFFF Products



TOF Analytical Method

Organic forms of fluorine are isolated from soil, product, or water samples, and are then combusted at high temperature (900-1000°C) in the presence of oxygen and excess water, mineralizing the organofluorine compounds to hydrogen fluoride (HF) via oxidative hydropyrolysis. The hydrogen and fluorine dissociate in an aqueous trapping solution forming hydrogen (H+) and fluoride (F-) ions.

A portion of this solution is injected into an Ion Chromatograph (IC), which separates and quantifies the fluoride ions. Test results are provided in weight of fluorine per mL (µg/mL for liquid samples) or per gram (µg/g for solid or product samples). Fluorine quantified by this method more specifically represents extractable organic fluorine (EOF), i.e. organic substances containing fluorine that can be isolated from the sample based on physical or chemical properties.

In contrast, discrete PFAS analytical results by LC/MS/MS are reported as mass of PFAS per volume or weight of sample. On average, perfluorinated alkyl substances consist of approximately 65% fluorine by mass (e.g. PFOS is 64.6% fluorine by mass, PFOA is 68.8%, and PFBA is 62.1%, with the remainder composed primarily of carbon and oxygen). Therefore one must multiply TOF concentrations by ~ 1.5 to estimate the Maximum Total PFAS content of a sample.

Figure 2. TOF Combustion-IC Analyzer Schematic

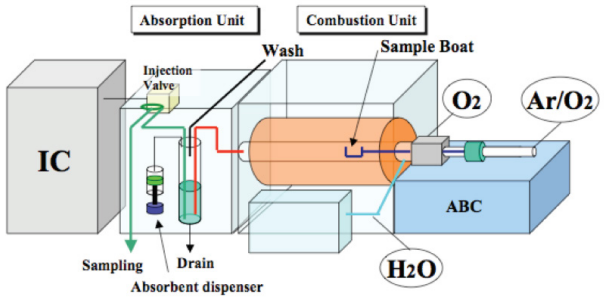


Image courtesy of Thermo Fisher Scientific

Sampling and Analysis Details

The same protocols for sampling PFAS apply to sampling for TOF, including sample container requirements and holding times. Refer to Table 1 below for details. Non-detectable TOF test results for AFFF products using a low-level test method (with 1 mg/kg LOR) may be sufficient for substantiation or verification of "PFAS-free" product claims, subject to specific product or regulatory requirements.

Table 1. TOF Sampling and Analysis Details

Testing Details	Waters & Landfill Leachates	Soils, Sediments, Biosolids	AFFF Products
Limits of Reporting	0.02 mg/L	1 mg/kg or 0.1 mg/kg low-level	50 mg/kg or 1 mg/kg low-level
Sampling Containers	60 mL HDPE	120 mL HDPE	60 mL HDPE
Storage Temp.*	≤6°C	≤6°C	≤6°C
Holding Time	28 days	28 days	28 days
Methodology	Combustion – Ion Chromatography		
Accreditation	ISO 17025:2017		

* ≤10°C during transport to lab

Please contact your ALS Account Manager or ALSWTInfo@alsglobal.com for more information about PFAS Testing.

Other ALS Canada PFAS EnviroMails:

EnviroMail Canada #1 - Perfluoroalkyl Substances (PFAS)

EnviroMail Canada #2 - Total Oxidisable Precursor Assay (TOP)

EnviroMail Canada #7 - TOP Assay Challenges and Developments