EnviroMail™

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ALS Now NATA Accredited for Total Organic Fluorine (TOF)

Introduction

ALS is pleased to announce that the recently established capability in its Brisbane Laboratory for the analysis of Total Organic Fluorine in soils, sediments, waters (including landfill leachates) and Aqueous Film Forming Foam (AFFF) products, is **now NATA Accredited**. This makes ALS the first laboratory in Australia to do so.

Method Information

ALS METHOD CODE

EP040

LIMIT OF REPORTING (LOR)

Water (including landfill leachate)	0.02 mg/L
Soil & Sediment	1 mg/kg
AFFF Products	50 mg/kg

SAMPLING CONTAINERS

Water/AFFF Product	60mL HDPE plastic bottle (Unpreserved), grey label
Soil/Sediment	200mL HDPE plastic specimen jar (Unpreserved), grey label

Note – for soils/sediments, the same specimen jar can be used for both PFAS and TOF analysis. A separate 60mL bottle is required for waters if also testing for PFAS.

HOLDING TIME

28 days

NATA ACCREDITATION

Accredited

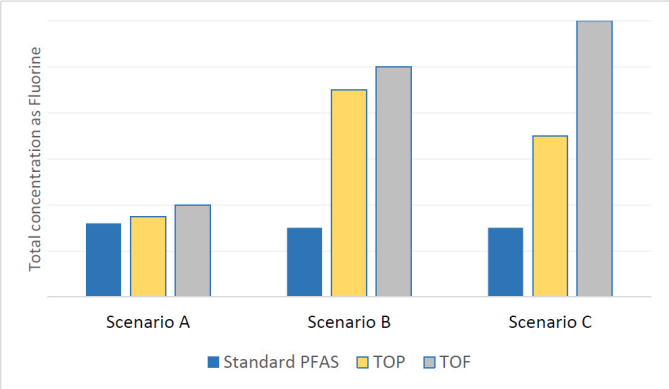
Background

Interest in TOF analysis is primarily associated with accounting for the total mass of Per- and Polyfluoroalkyl Substances (PFAS) in a sample. 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, such as protection of paper, clothing and carpets. Large-scale releases have been associated with their use in fire-fighting foams (i.e AFFF), where the fluorinated surfactants are key ingredients that provide low surface tension, enabling film formation on top of fuels, starving the fire of oxygen.

Conventional PFAS analysis by LCMSMS typically quantifies a relatively small set of key analytes (~30 compounds) and therefore may greatly underestimate the extent of PFAS in the environment. The PFAS National Environmental Management Plan (NEMP) states that it is "important that environmental assessments qualitatively consider the likely total mass and distribution of all PFAS present" using techniques such as the Total Oxidisable Precursor (TOP) and TOF assays, as a multiple lines of evidence approach to inform risk assessments. ALS currently holds NATA accreditation for the TOP assay (refer to Enviromails™ 110 & 117), and the addition of TOF rounds out ALS' analytical capabilities for comprehensive PFAS accounting.

A key limitation of the Total Oxidisable Precursor (TOP) assay is that it relies on the analytical scope provided by conventional LCMSMS analysis and therefore fails to account for oxidation products with carbon chain lengths <C4 and >C14. 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 chain lost during this process are therefore also unaccounted for.

While TOF analysis is not subject to these limitations, it provides no information of chain length and is not selective for PFAS, rather providing an estimate of the total fluorine from organic forms in a sample. TOF analysis can therefore be used to verify the degree to which the TOP assay accounts for potential precursors. Note, TOF analysis is not as sensitive a technique as conventional LCMSMS and so has higher limits of reporting (LOR). It may therefore not be suitable for low level screening, but more appropriate as a screening tool for higher impact zones and circumstances where information on the approximate carbon chain length is not required. Ultimately, a combination of TOP, TOF and standard LCMSMS analysis may be appropriate to provide a well-rounded understanding of the PFAS content of a sample. Scenarios are provided below which demonstrate how the combination of tests may be useful.



Scenario A: Standard PFAS ≈ TOP ≈ TOF (relative equivalence). No evidence of precursors present.

Scenario B: Standard PFAS < TOP ≈ TOF. Evidence of precursors, largely accounted for by TOP.

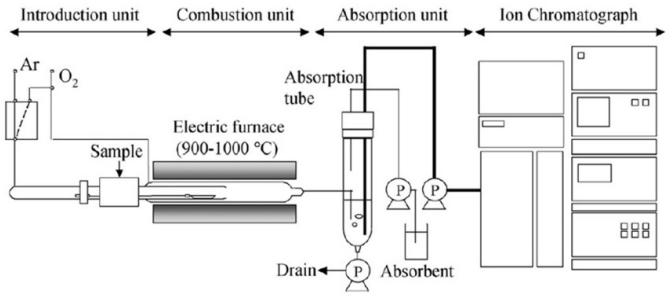
Scenario C: Standard PFAS < TOP < TOF. Evidence of precursors but not fully accounted for by TOP.

QLD Waste Disposal (ERA 60)

Refer to Enviromail #126.

Analytical Approach

Organic forms of fluorine isolated from soil and water samples are combusted at high temperature (900-1000°C) in the presence of oxygen and excess water, mineralising 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 the solution is injected into the Ion Chromatograph which isolates and measures the fluoride ions present. Results are provided in weight of fluorine per volume (for liquid samples) or per weight (for solid samples).



Schematic illustration of combustion ion chromatograph for fluorine (CIC-F).

Note, the fluorine quantified by this method more specifically represents extractable organic fluorine (EOF), i.e. those organic forms able to be isolated from the sample.

Sampling and Holding Time

The same protocols for sampling PFAS apply to sampling for TOF (e.g. refer to the NEMP for guidance), including sampling container requirements, i.e. 200mL HDPE plastic specimen jars for soils and 60mL HDPE plastic bottles for waters (and product samples). If analysing for both standard PFAS and TOF, a single HDPE specimen jar is sufficient for soils, however for waters, a separate 60mL HDPE bottle should be supplied for TOF analysis. A conservative holding time of 28 days has been applied for both soils and waters.

References

ALS Enviromail™ #110. Identifying Hidden PFAS Chemicals in Environmental Samples & Fire-Fighting Foams, 2016.

ALS Enviromail™ #117. PFAS Testing in Brisbane and TOP Assay Challenges and Developments, 2017.

ALS Enviromail™ #126. Total Organic Fluorine (TOF) for Compliance with QLD Waste Disposal Guideline ERA 60 Now NATA Accredited.

HEPA (2018). *PFAS National Environmental Management Plan 2018*. Heads of EPA Australia and New Zealand.