

Total Organofluorine Analysis & PFAS Investigations

What is TOFA?

The PFAS National Environmental Management Plan (NEMP) January 2018 defines TOFA as the Total Organic Fluorine Assay and states **"Total fluoride in organic and inorganic forms"** are included in the analysis and the NEMP goes on to say **"Can be used in conjunction with a US EPA method (viz 537 or 821) to understand the total presence of organic fluorine in a sample and compare this to the organic fluorine equivalent detected by the US EPA method"**. Eurofins has invested in automated combustion ion chromatography instrumentation to allow this analysis to be conducted for AFFF concentrates, water and solid samples such as soil, biosolids, granulated and powdered activated carbon as well as wipes or filter samples.

Total Organofluorine - Combustion Ion Chromatography (TOF-CIC)

Samples are contained in ceramic boats and are introduced into the furnace where pyrohydrolysis occurs at 900–1000 °C in a humid, O₂-rich environment. The samples are oxidised under these conditions, breaking the strong carbon-fluorine bond, and the vapours are sparged through an absorption solution using Ar. The HF evolved from combustion of organic fluorine dissociates to form H⁺ and F⁻ ions in the absorption solution, which also contains an internal standard to calibrate the analytical results. The samples are then transferred to the ion chromatograph for analysis where fluoride is measured. The method, LTM-INO-4370, is derived from NATA-accredited (ASTM D7359-08 compliant) in-house method LTM-INO-4150 (Part A) for fluoride analysis in solids.



Direct combustion of materials results in a LOR of 0.05 mg F/kg that is well below the NEMP's landfill acceptance criteria and also meets the Interim soil criteria for ecological direct exposure for public open spaces. Note that the criteria expressed for PFOS/PFHxS and PFOA must take into consideration that TOF, as determined by the TOF-CIC method, is only approximately 60% of these values given the relative molecular weights of the molecules and their total fluorine content.

Adsorbable Organofluorine (AOF)

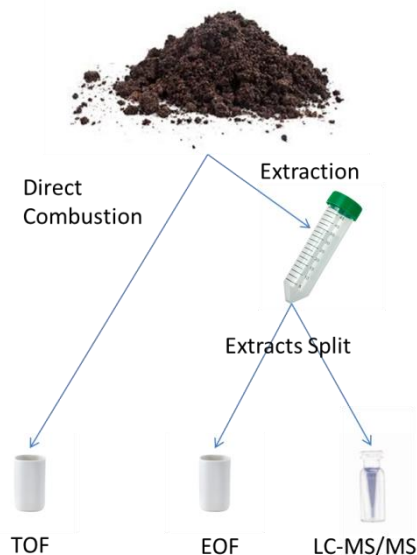
For the trace level determination of adsorbable organic fluorine (AOF) in water, the sample must first be passed through a mixed-mode weak anion exchange solid-phase extraction (SPE) cartridge thereby adsorbing the PFAS compounds. AOF is then determined by eluting the contents of the SPE cartridge with NaOH in methanol, evaporating and reconstituting the extract, and finally determining the fluoride

content of the extract by CIC. The LOR is dependent on the volume passed through the SPE, so the presence of suspended solids does impose limits on the procedure, but for clean waters the LOR is 0.001 mg F/L. Where significant levels of suspended solids are encountered the LOR may be limited to 0.01 mg F/L and the suspended solids may be determined separately by direct combustion.

Extractable Organofluorine (EOF)

For solid samples, where LORs lower than the direct combustion method of 0.05 mg F/kg are required, extraction can be performed using the same solvent systems used for conventional targeted LC-MS/MS methods. The resulting concentrate is then combusted giving an extractable organofluorine result. A LOR of 0.02 mg F/kg is achievable.

Case Study



Total Organic Fluorine (TOF)	410 mg F/kg
Extractable Organic Fluorine (EOF)	390 mg F/kg
LC-MS/MS ΣPFAS (n=28)	120 mg/kg

The TOF and EOF results are within experimental measurement uncertainty but demonstrate a large difference between the conventional targeted LC-MS/MS analysis, meaning that there are considerable amounts of unknown PFAS in the above example. These unknown PFAS are most likely precursor compounds which could be identified using LC-QToF-MS or a TOP assay.

Eurofins | mgt Expertise

If you would like to discuss details for your upcoming projects then please contact your local Analytical Service Manager or one of our Business Development team listed below.

Technical support can be provided by contacting Dr Edward Nagul or Dr. Bob Symons.

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