

BREAKING BOUNDARIES: THE RACE AGAINST FOREVER CHEMICALS WITH XPREP C-IC'S RAPID AOF ANALYSIS REVOLUTION



Per- and polyfluoroalkyl substances (PFAS) have a complex history, marked by their widespread use, benefits, and subsequent concerns leading to bans and regulations. In the 1940's the first developments of PFAS components were made in various industrial and commercial applications due to their unique properties, including resistance to heat, water, and oil. Later in the 1960's the use of PFAS gained popularity in the production of non-stick cookware, water-resistant fabrics, and firefighting foam. With the success of PFAS also the effects became more visible which raised concerns over time. Several studies in the early 1990's revealed the potential health and environmental impacts of exposure to PFAS. Research linked PFAS exposure to various health issues, including cancer, reproductive problems, and immune system disorders. The presence of PFAS compounds worldwide poses an increasingly significant threat to the environment and human health. These compounds, often termed "forever chemicals" due to their enduring nature, pose a formidable threat as they persist in the environment indefinitely, resisting natural breakdown processes.

Despite the establishment of regulatory measures targeting specific PFAS compounds over the course of numerous years, it has not yet been possible to ban PFAS as a group. Adding to the problem, manufacturers continue to create new PFAS formulations to get around existing regulations. This ongoing cycle increases the number of various PFAS compounds, making environmental damage and health risks worse worldwide. Currently, specific PFAS compound concentrations are regulated using LC-MS/MS measuring techniques to identify and quantify. These techniques are known for their high sensitivity and



Xprep C-IC with Tuscan Autosampler, and Xprep-A6 Sample Preparation System

selectivity but involve significant investment and running costs. They may not, however, identify all PFAS components due to their diverse chemical structures and properties.

As an alternative, the Total Organic Fluorine (TOF) can be measured by collecting the Adsorbable Organic Fluorine (AOF) and combining this with Combustion Ion-Chromatography (C-IC) measuring techniques. By doing this, the measurement of AOF by C-IC can be used as a powerful screening tool prior to in-depth component specific LC-MS/MS analysis.

Therefore, multiple standardization bodies have started to develop measuring methodologies. New methods have been published and the first regulations have started. The German Institute for Standardization (DIN) was the first to publish an official method for screening adsorbable organic fluorine (AOF). DIN 38409-59 was released in 2022. Recently, in 2024, the United States Environmental Protection Agency (EPA) also introduced EPA 1621, the method for measuring AOF. Currently, many other standardization bodies such as ASTM and ISO are working on developing methods based on the AOF principle. As these methods are being placed into practice, governments are beginning to set limits on the maximum allowable amount of AOF in water. France is among the first countries worldwide to establish governmental regulations specifying the maximum AOF concentration across all water sources. It is anticipated that more countries will soon follow.

Principle of adsorbable organic fluorine (AOF) measurements:

The principle of measuring AOF consists of three main steps, known as: Sample Pretreatment, Sample introduction & Combustion, and finally Sample Measurement by an Ion Chromatograph.

Sample Pretreatment:

A known amount of pH-neutralized water sample is collected and is set up to pass through two activated carbon columns arranged in series. These columns effectively capture all organic materials, including PFAS compounds. Once the sample has been passed through the columns, any potentially adsorbed inorganic fluoride is removed by eluting a nitrate over the activated carbon. Depending on the method being followed, an additional wash step is added to wash the carbon with a known quantity of ultra-pure water with the purpose of rinsing off any remaining sodium nitrate from the activated carbon. This additional wash step is done to minimize the degradation of quartz parts in the combustion system that can be caused by the sodium cations in the next step of the analysis method.

To streamline this process, Trace Elemental Instruments has redesigned its Xprep-A6 sample preparation system, making it even more user-friendly and efficient. With fit for purpose parts

and consumables with no contribution to blank levels and guaranteed high recoveries for PFAS components. The new Xprep-A6 AOF model includes several default features:

- A 6-channel system for simultaneous sample preparation.
- Automated and adaptable washing with wash solution.
- Automated and adaptable washing with ultra-pure water.
- An intuitive display for controlling the Xprep-A6 AOF.

Introduction and Combustion:

Once the sample pretreatment is complete, the columns filled with the activated carbon containing the adsorbed AOF are emptied in a boat introduction device and introduced into a high-temperature combustion furnace. During the introduction, the samples are combusted to release all fluoride through pyrohydrolytic combustion. This involves controlled combustion under high humidity conditions in an oxygen-rich environment at temperatures of at least 950°C. The high humidity prevents hydrogen fluoride from interacting with the combustion tube surfaces. The combustion gases are then cooled to ambient temperature and directed into an absorption tube filled with an absorption solution. At this stage, the absorption tube contains the component of interest in the form of hydrogen fluoride.

Sample Measurement:

After the sample is collected in the absorption tube, the sample is ready to be transferred to an IC for quantification. For transferring the sample there are two options:

- **Online:** The Xprep Fraction Collector system is linked to an IC as a fully integrated configuration. By means of the internal syringe driver with a valve and loop system. A known volume will be loaded directly onto the IC.
- **Offline:** The IC is not connected to the Xprep Fraction Collector and the sample can be placed onto a separate sample handling system of an IC situated at a different location in the laboratory.

Instrumentation:

The Xprep C-IC, integrated with the Tuscan autosampler for columns from Trace Elemental Instruments, addresses the requirements of high-throughput AOF users by significantly reducing the analysis time for a single activated carbon glass column to less than 14 minutes, all while maintaining analytical integrity.

Implementing automated mechanisms for glass column handling and sample introduction will streamline the analytical process. By automating the transfer of collected AOF into the combustion device, the need for manual intervention is eliminated and reduces the overall analysis time. This not only enhances efficiency but also minimizes the potential for human error.

To clarify the mechanisms behind these expedited AOF measurements, the Xprep C-IC system is designed into two primary components: the combustion unit and the fraction collection unit, each with unique attributes to facilitate rapid analyses.

Table 1: Example AOF results of multiple standards and real wastewater samples measured by C-IC

Name	Measurement 1		Measurement 2	
	Dilution factor	Concentration (µg/l)	Dilution factor	Concentration (µg/l)
Check standard 1 µg/L	-	1.10	-	1.11
Check standard 10 µg/L	-	10.01	-	9.92
Wastewater 1	4	547	10	560
Wastewater 2	-	2.55	2	2.22
Wastewater 3	-	5.65	2	5.75
Wastewater 4	2	57.6	4	58.0

The Tuscan autosampler is strictly engineered for compatibility with the AOF/AOX column method. Upon sample preparation in the Xprep-A6 AOF, the glass columns are transferred to the Tuscan autosampler. Where for up to 42 positions the glass columns are shielded within a controlled atmosphere to prevent contamination.



Detail Xprep C-IC with Tuscan Autosampler

During combustion, the activated carbon and its supporting filters are efficiently transferred from the glass column into a specialized boat, designed to optimize combustion dynamics and ensure thorough oxidation.

The glass columns filled with activated carbon supplied by Trace Elemental Instruments are characterized by their low fluorine

content and minimal ash residue post-combustion. To avert blockages or damage to analytical IC columns, a dedicated filter is positioned at the rear of the furnace tube to capture any residual ash particles in the collected sample stream.

The Fraction Collection Unit is predicated on the utilization of fresh absorption tubes for each analysis. This offers multiple distinct advantages, including the elimination of time-consuming rinsing procedures in between analyses and the facilitation of sample storage for potential reanalysis.

In cases where the Xprep C-IC interfaces with an IC, combusted samples are seamlessly injected into the IC for analysis, enabling concurrent sample processing and data acquisition. Furthermore, the integrated sampler within the fraction collection unit can be directly employed for IC operations, streamlining the injection of aqueous samples/standards into the IC in fully automated configurations.

Incorporating a rinsing system with automated capabilities combined with the fraction sample collection mechanism that enables the rerunning or storage of samples enhances flexibility and efficiency. This not only optimizes analysis time but also maximizes the utility of collected samples for alternative analytical measurements, contributing to overall laboratory productivity.

Collectively, these features culminate in the achievement of a significantly faster sample-to-sample time with the Xprep C-IC system. By embracing automation, streamlining processes, and optimizing sample handling, laboratories can meet the growing demand for AOF measurements while maintaining sensitivity and instrument robustness. Critical to this endeavor is the requirement for the IC to possess an analysis time that is similar to or less than the sample combustion time. This may be realized through the implementation of various strategies, including eluent gradient, flow gradient adjustment, and utilization of faster analytical columns.

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