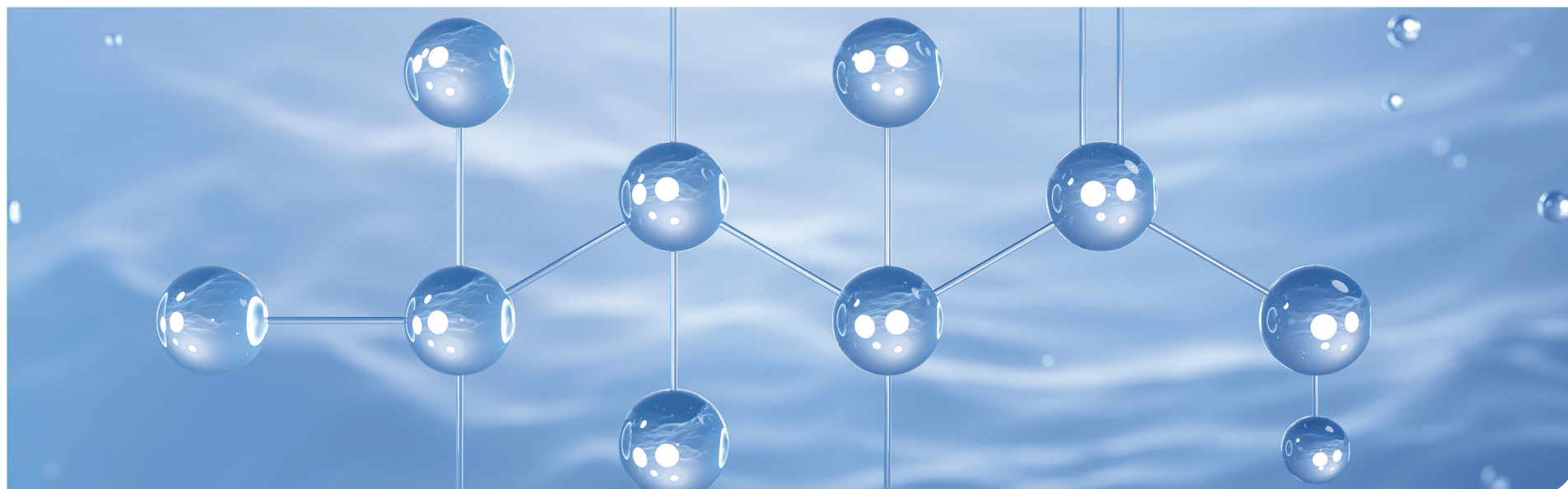


# TRACE LEVEL ANALYSIS FOR EXTRACTABLE ORGANIC FLUORINE (EOF) SCREENING IN WATER MATRICES, BY COMBUSTION ION-CHROMATOGRAPHY



## Introduction

**Extractable Organic Fluorines (EOF) are a group of compounds that contain fluorine atoms and are classified as persistent organic pollutants. EOF concentration values are the result of measuring a certain group of components which are also categorized as PFAS components. In most cases, PFAS (per- and polyfluoroalkyl substances) are human-made products that originally didn't occur in our environment. As a result, they are resistant to degradation and can accumulate in our environment. Due to this PFAS is also known as the forever chemicals. PFAS is used in a wide variety of industrial and commercial applications, including the production of non-stick cookware, firefighting foams, and textiles.**

PFAS compounds can be harmful to human health and the environment and may cause a variety of health problems. On an environmental scale, these compounds can interfere with the normal functioning of ecosystems. As such, the presence of PFAS in the environment can be a sign of environmental pollution which makes monitoring an important factor for the assessment of environmental quality.

Several examples of PFAS compounds include:

- Perfluorooctanoic acid (PFOA)
- Perfluorooctane sulfonate (PFOS)
- Perfluorononanoic acid (PFNA)
- Perfluorohexane sulfonate (PFHxS)

The origin of PFAS comes from several sources: industrial manufacturing processes and/ or emissions, agricultural runoff, municipal waste, or from consumer products. Currently, thousands of different PFAS components have been produced and identified, which makes the analyses for these components more and more complex.

PFAS can be found in a variety of environmental matrices, including soil, sediment, and water. PFAS can be analyzed as EOF (Extractable Organic Fluoride) or as AOF (Adsorbable Organic Fluoride). Depending on the sample preparation, results are either classified as EOF or AOF.

**AOF** is typically measured using a column adsorption method on which PFAS is adsorbed on activated carbon, by feeding liquid sample material through these columns. The PFAS-loaded carbon is then introduced into a combustion analyzer.

**EOF** is the result of a pre-concentration technique called SPE (Solid Phase Extraction) in which PFAS components are retained on a selective stationary phase and flushed off with a suitable solvent/ liquid or a combination of both. This flushed-off liquid is then introduced into a combustion analyzer.

In both cases, EOF or AOF is a total bulk analysis and gives the total sum of all Organic Fluorine containing compounds.

New standardized methods for screening purposes to measure total fluorine in water matrices have been introduced or are in the process of development. These methods all focus on pre-treating the samples using AOF:

- **DRAFT EPA Method 1621:** Screening method for the determination of Adsorbable Organic Fluorine (AOF) in aqueous Matrices by Combustion Ion Chromatography.
- **WK 68866** - New Test Method for Determination of Adsorbable Organic Fluorine in Waters and Waste Waters by Adsorption on Activated Carbon followed by Combustion Ion Chromatography
- **DIN 38409-59** German standard method for the examination of adsorbable organically bound fluorine, chlorine, bromine, and iodine (AOF, AOCl, AOBr, AOI) by means of combustion and subsequent ion chromatography in water, wastewater, and sludge.
- **DRAFT ISO 18127** Determination of adsorbable organically bound fluorine, chlorine, bromine, and iodine (AOF, AOCl, AOBr, AOI) Method using combustion and subsequent ion chromatographic measurement.

In this paper, we will discuss a possible alternative sample pretreatment technique using solid phase extraction (SPE) for measuring EOF instead of AOF.

## Sample preparation

Solid-phase extraction (SPE) is a sample preparation technique that is used to isolate and enrich analytes of interest from a complex sample matrix. It is based on the principle of chromatography, in which the analytes are selectively retained on

a solid phase while the matrix components are washed away.

When using SPE, it is important to select the correct sorbent phase and the proper wash/ flush procedures. The most used cartridges for PFAS currently are based on weak anionic exchange material (microporous polystyrene-divinylbenzene with amine functional groups), but other new stationary phases are to be in development.

In essence, SPE consists of the following procedural steps:

1. Preparation of the SPE columns (conditioning/washing)
2. Loading of sample material onto the SPE columns
3. Washing away undesired matrix and/or other components
4. Flushing of the desired measuring components
5. Preconcentration of flushed sample material by evaporation
6. Accurate addition of solvent applicable for combustion analysis
7. Injection in a combustion analyzer coupled with an ion chromatograph (C-IC)

Depending on the preparative SPE equipment, liquid handling for all these steps is carried out by using a vacuum and/or positive displacement pressure (accommodated by syringe drives/ pumps).

## Advantages of SPE (EOF) over Activated Carbon material (AOF)

### Matrix interference:

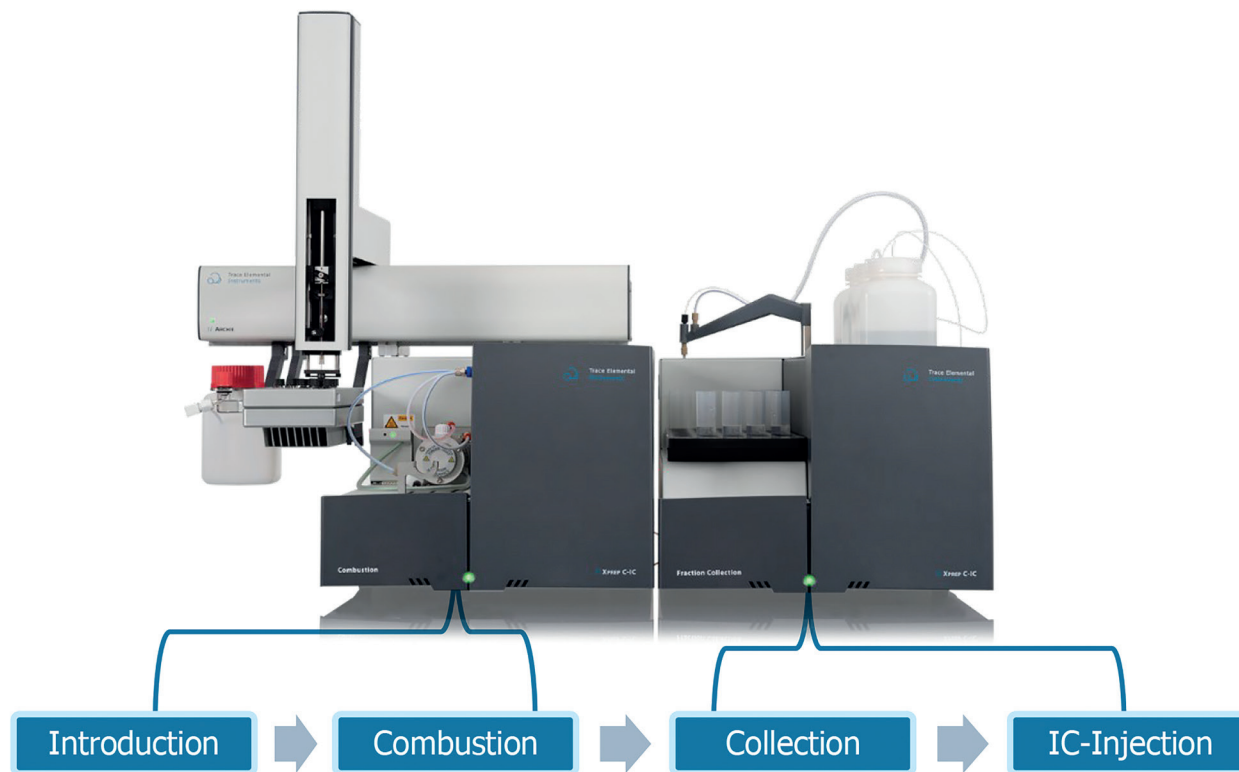
Real-world sample matrices often contain complex challenges, such as impurities, contaminants, or co-existing compounds, that can interfere with the accurate measurement of the target analyte. SPE allows for the selective removal of these interfering compounds, ensuring that only the analyte of interest is measured.

### Selectivity:

SPE can be used to selectively isolate and enrich analytes of interest from a complex sample matrix by using specific types of sorbents. This can improve the sensitivity and accuracy of subsequent analytical methods.

### Reproducibility:

SPE is a reproducible method for sample preparation. This is important for ensuring that the results of analytical methods are accurate and reliable.



C-IC Analytical Instrumentation setup: Xprep C-IC

Table 1: Overview of typical injection parameters for EOF analysis:

Combustion Conditions		
Injection Volume	250	µl
Injection Loops	3	
Injection Temperature	500	°C
Furnace Temperature	1000	°C
Argon Flow	100	mL/min
Oxygen Flow	300	mL/min
Collision Flow	100	mL/min
Pyrolysis Tube	Ceramic	
Absorption Solution	Ultra Pure Water	

**Blank levels:**

The blank levels of EOF analysis are much lower than those of activated carbon (AOF) analysis. This is because EOF analysis uses a more selective method for the removal of interfering compounds.

**Automation:**

Several SPE setups can be automated, which can save time and improve the efficiency of sample preparation. This is especially important for large sample batches.

**Sample introduction:**

Liquid sample introduction is always preferred over solid sample introduction in a combustion analyzer. This is because liquid samples are easier to handle and larger volumes can be introduced.

**Multi-purpose:**

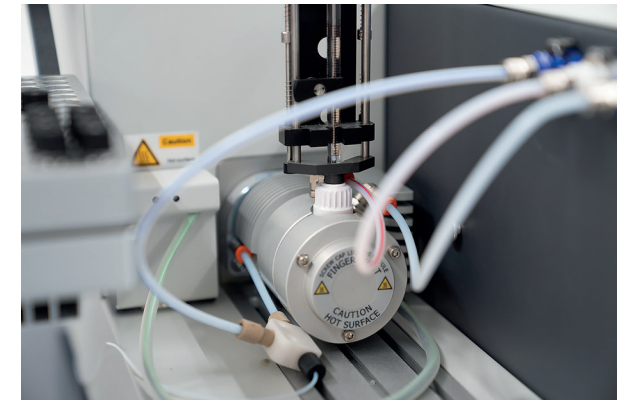
The prepared sample can directly be used for multiple analyses, for example, EOF and LC-MS/MS. So when the sample tests positive during the EOF analyses, the same sample can directly be transferred to an LC-MS/MS for analyses of the speciated PFAS components.

**Introduction** – For the introduction of the sample (prepared using SPE), the Liquids Autosampler is utilized. Equipped with a large volume syringe of 250 µl it is capable of continuously introducing

the sample into the pre-heated injection module. This module is directly connected to the Combustion Furnace and under an inert carrier gas, the sample material will evaporate. After evaporation, the gasses are guided to the furnace for complete combustion.

**Combustion** - The Combustion Unit has a dual-zone furnace that completely oxidizes every sample by pyrohydrolytic combustion in an oxygen-rich environment at a high temperature.

Standard AOX by MCD analysis focuses on chlorine, bromine, and iodine. However, the analysis of AOF or EOF by C-IC has a wider focus, including fluorine.



**Collection** – Following combustion, an absorber solution is automatically introduced into the output gas stream to ensure the thorough absorption of analytes in the Fraction Collection Unit. During this procedure, the conversion of H-X and X<sub>2</sub> to F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> takes place. These negatively charged ions undergo separation within the IC column.

**IC-Injection** – After completing the sample preparation, the absorbent containing the analytes is transferred from the Fraction Collection unit to an Ion Chromatograph automatically. The front of the Fraction Collection Unit features an integrated six-way valve and a 500 µL sample loop as the default setup. The internal syringe pump is responsible for loading and rinsing the Ion Chromatograph sample loop.

**Discussion**

The combustion ion chromatography (C-IC) market in the PFAS sector is a growing market with an expected growth of 8.5% year over year, fuelled by the rising need for precise and sensitive methods to measure PFAS. C-IC, a relatively recent technique for screening PFAS, offers advantages over other methods in terms of cost and analysis time. Utilizing sample pre-treatment methods like SPE achieves high sensitivity and can detect PFAS at low concentrations (PPT levels). Moreover, C-IC is notably swift, enabling quicker sample analysis compared to alternative methods, which is advantageous for high-volume laboratories. The surge in C-IC's market stems from stringent regulations demanding PFAS measurements due to their harmful effects. C-IC remains the sole technique capable of meeting these exacting criteria, thus driving its future demand. Growth factors encompass accurate PFAS measurement demand, regulatory mandates, technological C-IC advancements, and increased awareness of PFAS dangers.

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