# Adsorbable Organic Fluoride (AOF) Analysis by CIC Conforming to USEPA Draft 1621 Method

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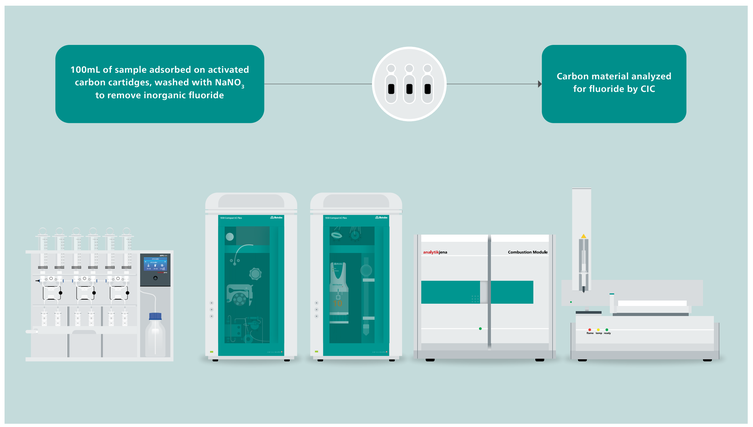
## INTRODUCTION

PFAS, or per- and polyfluoroalkyl substances, have become ubiquitous in the environment. These manmade chemicals are used in industry to manufacture a wide range of consumer products. Often referred to as "forever chemicals", they persist in the environment and long-term exposure has been linked to negative health effects. To date, thousands of different PFAS-related compounds have been identified, making subsequent instrumental analysis difficult. Traditional targeted quantification using LC-MS/MS is limited with regards to the number of compounds that can be analyzed. Non-targeted approaches are gaining traction as a complimentary screening method. Adsorbable Organic Fluorine (AOF) determined using combustion ion chromatography (CIC) is a non-targeted approach that looks at overall fluorine. This screening method is being formalized by the US EPA in Method 1621, currently in draft form.

## INSTRUMENTATION




- 930 Compact Flex IC
- 920 Absorber Module
- 941 Eluent Production Module
- MMS 5000 Autosampler with Solids Sample Kit
- Analytik Jena Combustion Module
- Metrohm MagIC Net Software for full system control
- Analytik Jena – APU SIM sample prep unit

## ANALYSIS

US EPA Draft Method 1621 provides guidance for the non-targeted analysis of AOF in water samples by CIC. As per the method, 100 mL of water sample is passed through granular activated carbon (GAC), where organofluorine compounds are retained. Inorganic fluoride is removed using a sodium nitrate rinse. Following this, carbon plugs are transferred to a ceramic boat that is loaded onto a CIC autosampler. Boats are introduced to an oven, where samples undergo pyrohydrolytic combustion, followed by subsequent absorption in ultrapure water that is injected into an ion chromatograph for fluorine analysis. Following the requirements of EPA Draft 1621, an MDL study was performed, along with a calibration and precision/recovery study.

## EXPERIMENTAL CONDITIONS

### ION CHROMATOGRAPHY

IC – Metrohm 930 Compact Flex
Column – Metrosep A Supp 7 – 250/4.0
Eluent – 3.2 mM $Na_2CO_3$ + 1 mM $NaHCO_3$
Column Flow – 0.7 mL/min
MSM Regenerant – 0.5 M Sulfuric Acid
MSM Rinse – Application of STREAM technology

### COMBUSTION

Oven temperature – 1050 °C
Oxygen Flow – 300 mL/min
Pyrolysis gas flow – 200 mL/min
Absorption solution – Ultrapure water
Final absorption volume – 7.0 mL

### SAMPLE PREPARATION

Analytik Jena APU SIM (6 channels of sample preparation)
Vertically Aligned two Carbon Cartridges
Sample Volume – 100 mL
Sample Flow rate for adsorption – 3 mL/minute
Post adsorption wash solution – 0.01 M $NaNO_3$

## CALIBRATION CURVE

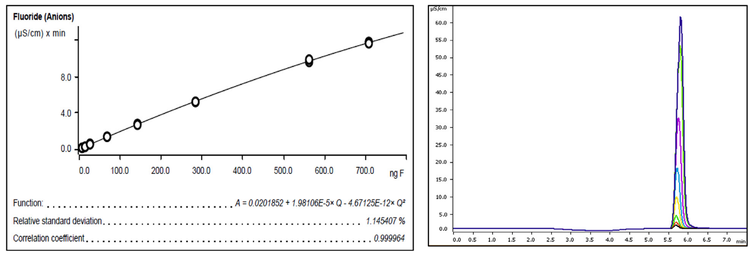



Fig. 1 – Calibration Curve (0.5ppb to 50 ppb AOF equivalent) – Calibrated with PFBS

## MDL – DATA

| | Sample | Average (ppb) | Std Dev (ppb) | RSD (%) | MDL (ppb) |
|---|---|---|---|---|---|
| $MDL_B$ | Reagent blank | 0.83 | 0.17 | 20.5 | 1.36 |
| $MDL_S$ | 5ppb F Spike | 4.50 | 0.095 | 2.1 | 0.30 |

## PRECISION AND RECOVERY

Experiments were performed to demonstrate precision and recovery of a known PFAS compound using the complete AOF sample preparation procedure followed by combustion IC quantification. The following table describes the recovery and precision results for ultrapure water spiked at 5 and 25 ppb of perfluorohexanesulfonic acid, or PFHxS. Replicates of surface water and spiked surface water were also analyzed to evaluate precision and recovery of a realistic sample matrix. Results fell within the proposed draft 1621 method requirements for spiked reagent water (RSD: < 20%, recovery: 70-130%) and matrix spikes (recovery: 50-150%, RPD: < 20%)

| Sample | Replicates | Conc. (ppb) | RSD (%) | Recovery (%) |
|---|---|---|---|---|
| 5 ppb UPW | n = 9 | 4.48 | 4.3 | 90 |
| 25 ppb UPW | n = 6 | 21.03 | 1.8 | 83 |
| Surface Water | n = 6 | 1.82 | 5.2 | - |
| Surface Water Spike (10 ppb) | n = 6 | 10.11 | 4.2 | 83 |

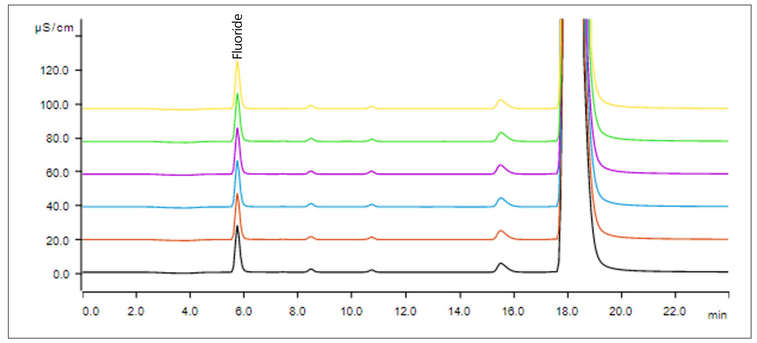



Fig. 2 – Replicates of Precision and Recovery Study at 25 ppb AOF equivalent

## CONCLUSION

With increased concern over the environmental and health risks of PFAS compounds, accurate monitoring of these compounds is essential. The Metrohm CIC with Analytik Jena oven was demonstrated to reliably test non-targeted adsorbable organic fluorine (AOF) as per EPA Draft 1621. This can be done with sensitivity down to an MDL blank around 1 ppb, while demonstrating repeatability and accuracy to meet the requirements of EPA Draft 1621.

EPA Draft Method 1621 is a simple but powerful screening method that can be used to better understand the total fluorine impact on the environment. This method functions as a complimentary tool to targeted LC-MS/MS analysis

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