WHITE PAPER

Robust and Sensitive PFAS Screening with Profiler^F

INTRODUCTION

PFAS, or per-and polyfluoroalkyl substances, are man-made fluorinated chemicals that are used in a variety of products, including fire-fighting foams, non-stick cookware, cleaning products, and more. These compounds persist in nature and can potentially have negative consequences on the environment and human health. While there are thousands of possible PFAS compounds, only a small portion of these are currently analyzed for. The most common technique for PFAS analysis is LC-MS/MS, which works well for targeted quantification of a small subset of PFAS, but does not paint a complete picture of the total PFAS contamination that may be present.

As an alternative to targeted analysis of specific PFAS compounds, non-targeted analysis for organic fluorine containing compounds can be performed to develop a better understanding of the true degree of PFAS

PROFILER^F SOLIDS CIC SYSTEM

Figure 1. Profiler^F Solids System.

contamination. One such method involves isolating adsorbable organic fluorine (AOF), followed by analysis using combustion ion chromatography (CIC).

The AOF method uses a sample preparation technique to separate organic fluorine containing compounds from inorganic fluoride. Tubes containing activated charcoal capture organic fluorine containing compounds, while inorganic fluoride is eluted out of the tube using a nitrate solution. The charcoal plug containing organic fluorine can then be analyzed by combustion ion chromatography to determine AOF.

Combustion Ion Chromatography is an effective and sensitive analytical technique for analyzing total fluorine in both solid and liquid sample matrices. Samples are combusted in a high temperature oven in order to break C-F bonds, leading to the production of free fluorine. The resulting free fluorine is passed through an adsorption module, where it is adsorbed into a liquid adsorber solution. This solution can then be injected into an ion chromatograph, where fluorine content can be determined with high sensitivity and specificity, based on its known elution time through an anion exchange column and subsequent detection with a conductivity detector.

A challenge facing existing technology is the ability to efficiently handle the corrosive HF generated post combustion. The Profiler^F Solids CIC system is engineered with combustion technology that is resistant to high loads of hydrogen fluoride, making it the ideal tool for screening samples of unknown fluoride concentration. A study was conducted on the Profiler^F Solids to examine accuracy, reproducibility, and ruggedness of AOF by combustion ion chromatography, using a variety of known standards as well as unknown water samples.

EXPERIMENTAL

Adsorbable Organic Fluorine (AOF) Sample Preparation

Water samples containing an unknown amount of PFAS were obtained as part of an Interlaboratory Study (ILS). Samples and recovery check standards were prepared using the AOF extraction method to separate out and discard any inorganic fluoride, leaving only the organic fluorine compounds bound to the charcoal bed. The sample preparation was performed as follows:

- 100 mL of sample was passed through two tubes in series, containing activated charcoal.
- 25 mL of 10 mM $NaNO_3$ was passed through the tubes to elute out any inorganic fluoride.
- The charcoal, containing organic fluorine compounds, was removed from the tubes to be analyzed by combustion ion chromatography.

Combustion Ion Chromatography (CIC) Analysis of AOF

The charcoal plugs from the tubes were placed into sample boats (Figure 2), which were loaded onto the solids autosampler of the Profiler^F combustion ion chromatography system. A method was optimized for combustion, adsorption, and ion chromatography.

Calibration Techniques

The Profiler^F analyzer provides the flexibility to calibrate the system using two different techniques, depending on method and user requirements. Calibration can be performed either directly through the IC or through the combustion oven, thereby providing a full CIC sytem calibration.

Direct IC Calibration

Direct calibration of the ion chromatograph using known fluoride standards in ultrapure water is the simplest way to achieve a calibration curve of instrument response vs. mass of fluoride.

The disadvantage of this approach is that it doesn't take the combustion process into account, which has potential to lead to biased, inaccurate quantitation.

Calibration through Combustion

For calibration through combustion, standards are loaded onto sample boats and taken through the entire combustion process, followed by IC analysis. This accounts for any biases that may be created through the combustion and adsorption process, since the samples will follow the same pathway as the standards.

CHARCOAL SAMPLES

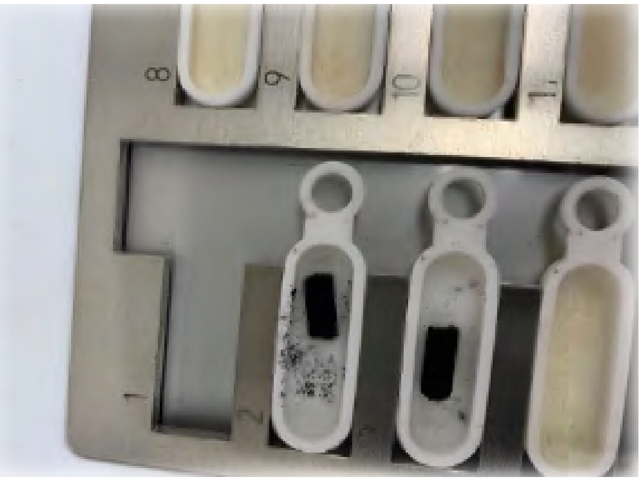


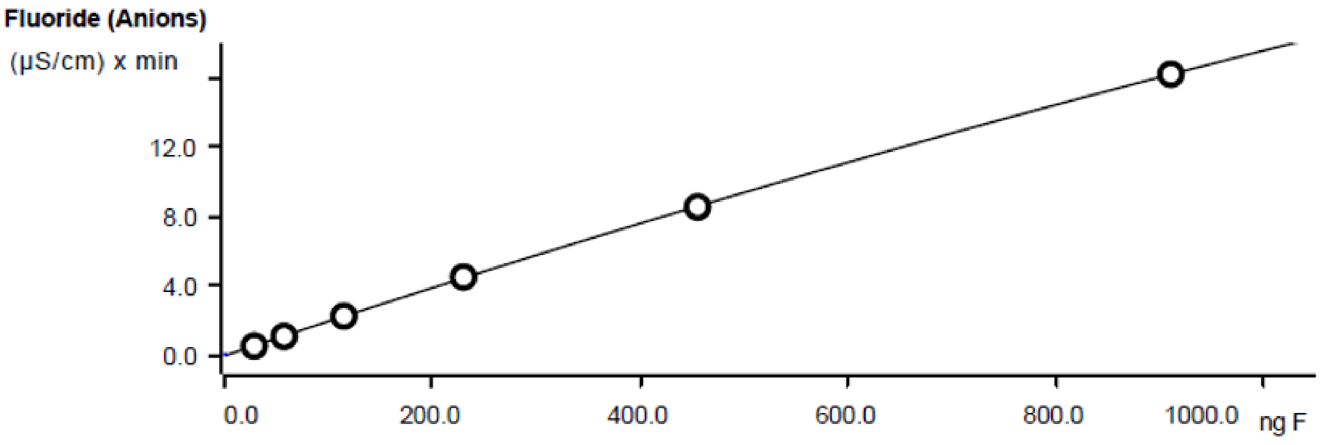
Figure 2. Charcoal plugs placed in sample boats on solids autosampler.

Check Standards

Due to the complexity of the combustion ion chromatography technique, it is important to monitor performance of check standards. When using the technique of direct IC calibration, it is necessary to include standards that are directly analyzed by IC, standards that are taken through the combustion process, and standards that are taken through the AOF extraction procedure, followed by combustion. Understanding the recoveries for each of these processes can help to identify method accuracy and if inaccuracies are present, whether they are due to ion chromatograph performance, combustion performance, or AOF extraction performance.

When performing calibration through combustion, it is only necessary to include a check standard that is also taken through the entire combustion process, as well as an AOF recovery check standard, to account for any losses that may occur during the AOF extraction procedure.

DIRECT IC CALIBRATION



Function: .... A = 0.0524388 + 2.11477E-5× Q - 2.72938E-12× Q^2
Relative standard deviation .... 0.837092 %
Correlation coefficient 0.999982

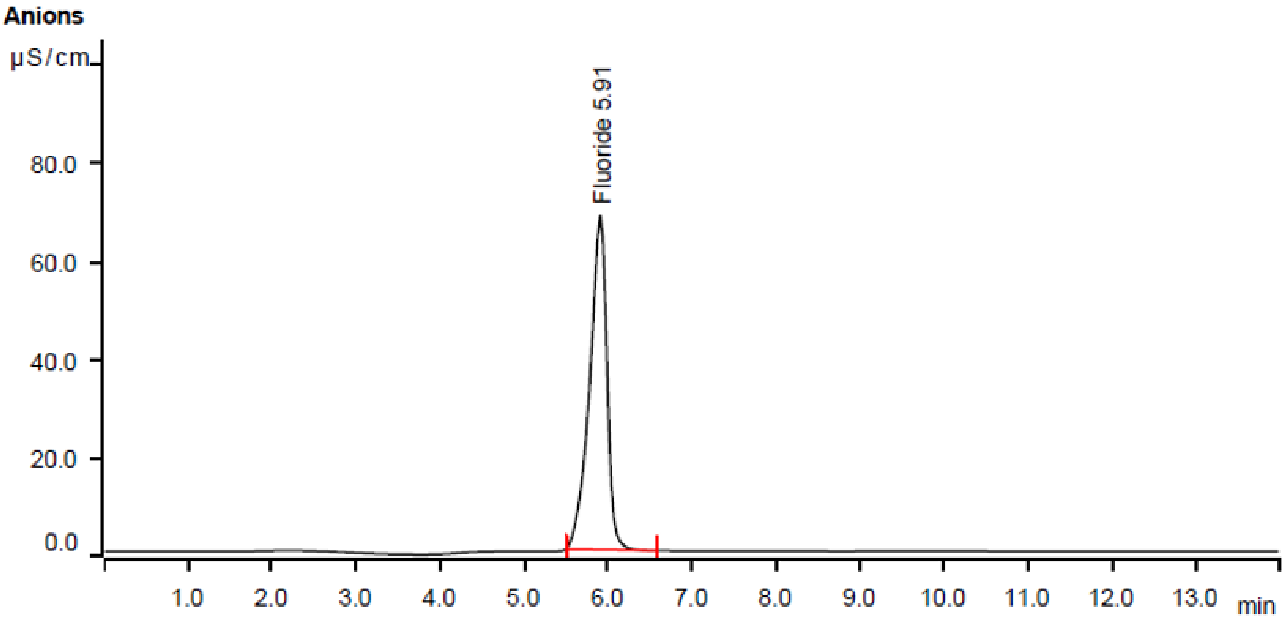


Figure 3.

RESULTS

Recovery Study

Known standards with concentrations ranging from 5-100 ppb were taken through the entire sample preparation process followed by CIC to determine method accuracy as % recovery. Due to the ubiquitous nature of fluoride, values were blank substracted to account for low levels of fluoride found in the blank.

Recoveries were between 80-120%, with the exception of the low 5 ppb standard, which had a slightly high recovery at 134%. This is likely due to trace contamination, which will have a larger impact on accuracy at lower concentrations.

Reproducibility and Ruggedness for Unknown Samples

Following the recovery study, three unknown water

KNOWN STANDARDS

Sample ID	Total peak area (µs/cm x min)	Total Mass F (ng) on-column	Concentration (µg/L, ppb)	% RSD	Recovery
Blank	3.20	157	10.98	5.9	-
5ppb FBA	4.99	221	6.68*	8.9	134%
10ppb FBA	6.36	316	11.16*	12.0	112%
50ppb FBA	20.05	1026	49.85*	6.4	100%
100ppb FBA	28.63	1523	84.65*	5.3	85%

Figure 4.

UNKNOWN WATER SAMPLES

Sample ID	Total peak area (µs/cm x min)	Total Mass F (ng) on-column	Concentration (µg/L, ppb)	% RSD
Blank	3.20	157	10.98	5.9
Standard	4.57	237	6.48*	0.9
Surface water	4.62	240	6.68*	4.1
Wastewater 1	9.82	510	15.65*	6.6
Wastewater 2	4.29	222	6.17*	7.6

Figure 5.

samples, a blank, and a low level standard were analyzed to determine adsorbable organic fluoride content. Four replicates of each sample were analyzed to determine reproducibility and ruggedness of the technique. %RSD for all samples was below 10%, indicating acceptable reproducibility for this technique.

Background Contamination

When using the AOF by CIC technique, there are several stages during which background fluoride contamination can adversely affect results and sensitivity, making it critical to minimize blank values. The use of suitable activated charcoal tubes, high purity water and reagents, and proper operation and maintenance of the combustion IC system are essential.

CONCLUSIONS

Non-targeted analysis of organic fluorine is a useful alternative to targeted analyses of PFAS, as it allows for a better understanding of the total impact of PFAS contamination, which is helpful for site remediation and clean-up. Using the adsorbable organic fluorine (AOF) sample preparation technique allows for isolation of fluorinated organic compounds from inorganic fluoride. Organic fluorine compounds collected onto activated charcoal can then be directly combusted using a Profiler^{F} Solids system, followed by adsorption into solution, and subsequent analysis and quantitation using anion exchange chromatography.

Several regulatory bodies are currently investigating the use of AOF-CIC as a screening tool for PFAS contamination.

AUTHOR

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