

Determination of PFAS in Environmental Wastewater Samples by Combustion Ion Chromatography: Collaboration Results from the EPA Draft Method 1621

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Abstract

Purpose: To demonstrate EPA Method 1621 using a combustion IC system.

Methods: Wastewater samples were adsorbed onto granular activated carbon (GAC). The resultant carbon samples were pyro-hydrolytically combusted and fluoride determined by ion chromatography with suppressed conductivity (IC).

Results: Wastewater samples with varying total suspended solids were analyzed for adsorbable organic fluorine (AOF) using combustion IC (CIC) with <1 ng/mL to 12 ng/mL fluoride. Recovery results of added PFAS were 80 to 120%, meeting the EPA 1621 requirements.

Introduction

Per- and polyfluoroalkyl substances (PFAS) is the collective name for over 9000 synthetic fluorinated compounds.^{1,2} PFAS compounds are persistent and bioaccumulate; they can have varying toxicity effects, potentially impacting reproductive health and causing epigenetic effects.³ The EPA has defined PFAS analysis methods, including its recent method, EPA Method 1633, that are targeted to a small subset of PFAS compounds in aqueous, solid, biosolid, and tissue samples.⁴ These methods all use LC-MS/MS approaches that are targeted to the level of tens of PFAS compounds; however, comprehensive analysis of the total PFAS content in samples is challenging. In addition to the large number of PFAS compounds, pure standards are not always available and can be costly. A screening method is needed to assess the extent of PFAS contamination in various matrices, including wastewater. Combustion ion chromatography (CIC) has been previously implemented for the analysis of adsorbable organic fluorine (AOF). The organofluorine compounds, including PFAS, are converted to HF, and the subsequent fluoride is analyzed by ion chromatography (IC). Here, we show our lab's results for the EPA draft Method 1621 multi-laboratory studies.

Materials and methods

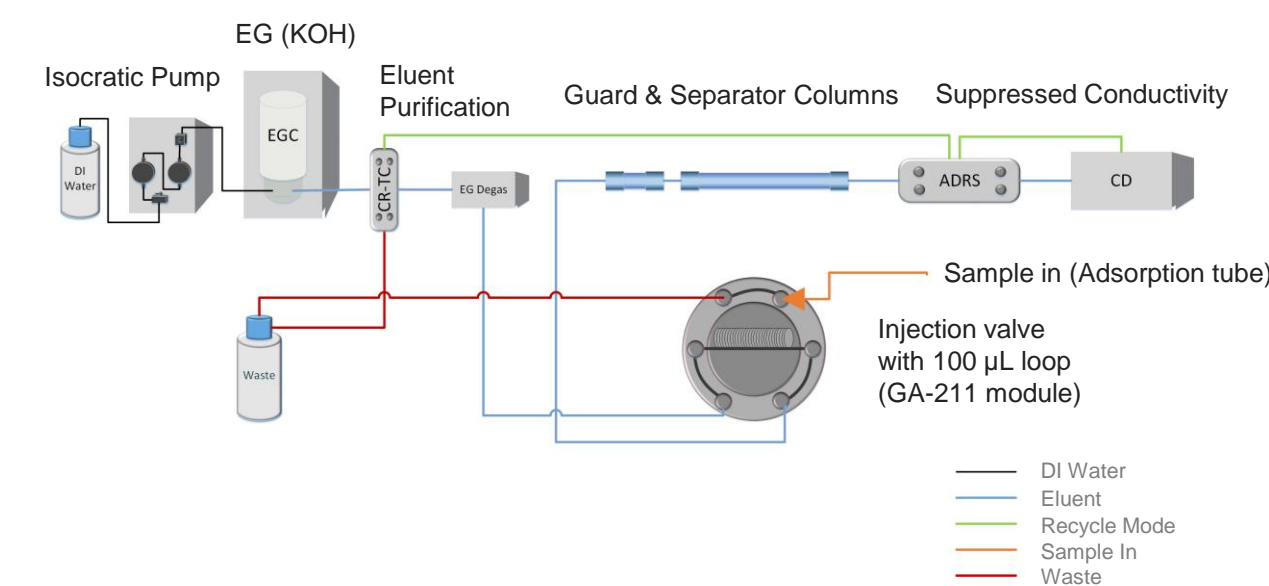
Sample Preparation

Wastewater samples were provided by General Dynamics Information Technology, Inc. for this multi-lab study. All standards and samples were processed according to section 11.3 in EPA Method 1621.⁵ The empty boats, calibration standards, and calibration verification standards (CV) are the exceptions. They skip the adsorption process and enter the workflow at the combustion stage.

Instrumentation

Any Thermo Scientific™ Dionex™ RFIC systems with a conductivity detector (CD) combined with any combustion-absorption system and offline adsorption system can be used.

Figure 1. Flow diagram of combustion ion chromatography system.



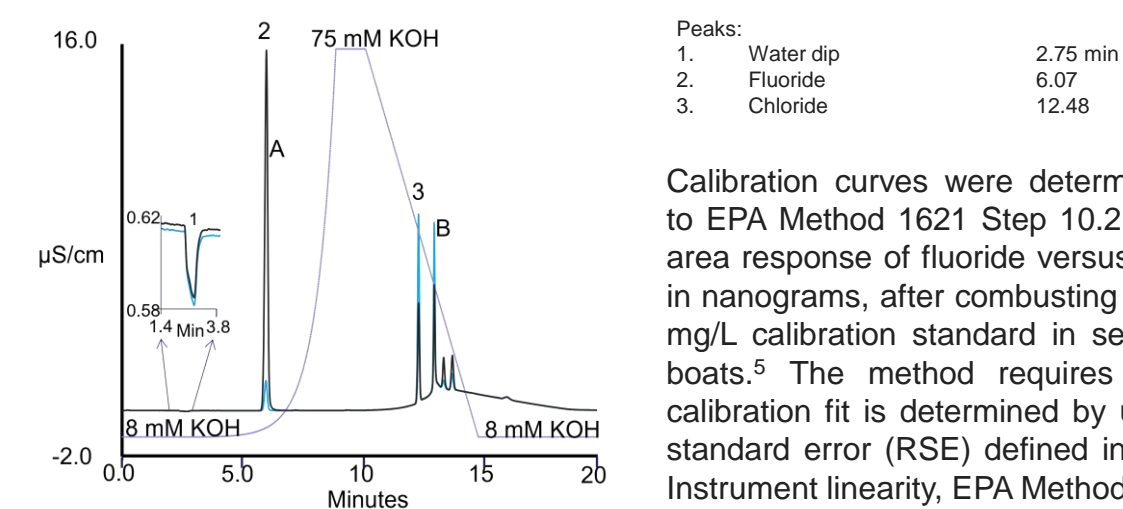
Results

Method qualification

The method was qualified by establishing the separation of fluoride from the water dip and chloride, calibration response curve of fluoride using relative standard error (RSE), determining the method detection limit of water blanks and 5 ng/mL equivalent fluoride (PFHxS), and initial demonstration of capability by analyzing 15 ng/mL equivalent fluoride (PFHxS) initial precision and accuracy standards.

The fluoride and chloride retention times were determined by combusting 0.1 mL of 12.5 µg/mL fluoride and 50 µg/mL chloride, n=3. Figure 2 shows the fluoride and chloride retention times.

Figure 2. Determining fluoride retention window. Using RFIC ion chromatography, fluoride elutes well past the water dip. A 0.1 mL aliquot of 12.5 µg/mL fluoride and 50 µg/mL chloride standards were combusted in triplicate for 10 min at 950 °C to 1000 °C, resulting in 1250 ng fluoride and 5000 ng of chloride.



Calibration curves were determined according to EPA Method 1621 Step 10.2.2, by the peak area response of fluoride versus concentration, in nanograms, after combusting 200 µL of each mg/L calibration standard in separate ceramic boats.⁵ The method requires that the best calibration fit is determined by using a relative standard error (RSE) defined in section 10.3.3 Instrument linearity, EPA Method 1621.⁵

To determine the RSE, we evaluated linear and quadratic fits by allowing offset from zero and calculating the curve fit without weighting and with weighting (1/A, 1/A²) by area. The calibration curve with the lowest RSE was selected. In our experiments, we used a linear fit with 1/A² area weighting, providing the lowest RSE (0.774) and compliance with the RSE limit of 20% set by the EPA.

MDLs of method blanks (MDL_(b)) and MDL standards (MDL_(s)) were determined over three days, n=7. Table 1 shows the results for the MDL_(b) of 1.23 ng/mL and MDL_(s) of 2.50 ng/mL fluoride. To meet the initial demonstration of capability (IDC) requirements, 4 replicate samples of 15 ng/mL equivalent fluoride (PFHxS) were prepared and analyzed. The initial determination of accuracy (IDA) is shown in Table 2 as recovery, and the initial determination of precision (IDP) results are shown as RSD.

Table 1. Determining MDL for method blanks and standard over three days.

	Method blank Fluoride (ng/mL)	5 ng/mL fluoride (PFHxS) MDL standard Fluoride (ng/mL)
Average	0.69	4.76
Standard Deviation	0.17	0.80
MDL	MDL _(b) = 1.23	MDL _(s) = 2.50

Table 2. Summary of IDC requirements.

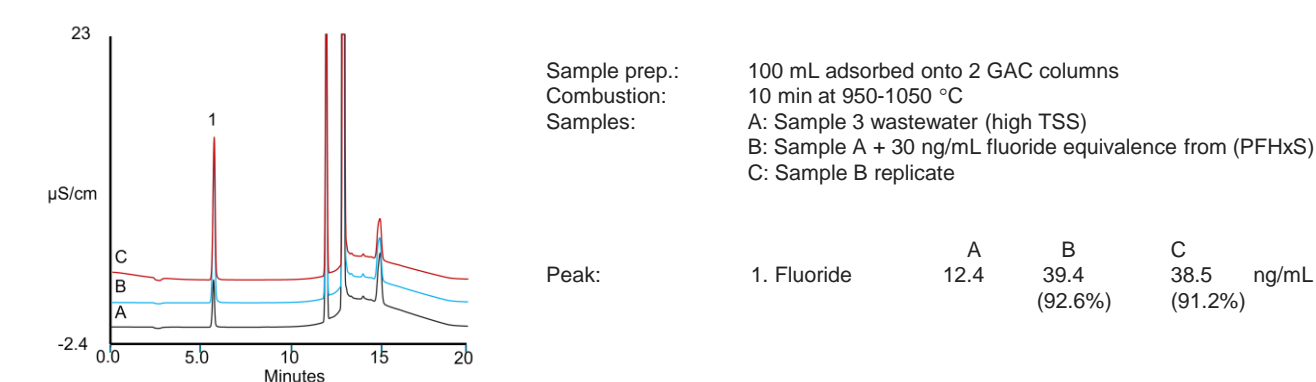
IDC requirement (Section from EPA Method 1621) ⁵	Specification	Experimental value
IDA (9.2.1)	Recovery 80% to 120%	Recovery = 98.5%
IDP (9.2.1)	RSD < 20	RSD = 4.6

Samples

The method was applied to wastewater samples. Total suspended solids (TSS) exceeding 100 mg/L were reported in samples 2, 3, and 6, requiring additional quartz wool to filter and collect the particulates. All wastewater samples were processed through adsorption and analyzed by CIC. With each sample sequence, two method blanks and one 15 ng/mL equivalent fluoride (PFHxS) ongoing precision and recovery standard were processed similarly to the samples. To monitor the CIC system, two empty boats/cups and a low and medium concentration CV standard were used as brackets for the sample analysis. These standards were analyzed directly by CIC without adsorption.

To determine recoveries of added PFHxS standard, aliquots of the 50 mg/L PFHxS standard (29.26 mg/L equivalent fluoride) were added to sample replicates and processed the same as the standards. The wastewater samples had 0.53 ng/mL to 12.22 mg/L total fluoride. Recoveries of added PFHxS standard ranged from 80 to 117%. Figure 3 shows the chromatograms comparing high-TSS Sample 3 with replicates of Sample 3 with added 30 ng/mL equivalent fluoride (PFHxS).

Figure 3. Comparison of CIC chromatogram of high-TSS Sample 3 with replicate recovery samples containing 30 ng/mL added fluoride (PFHxS). The chromatograms represent the top GAC for each sample.

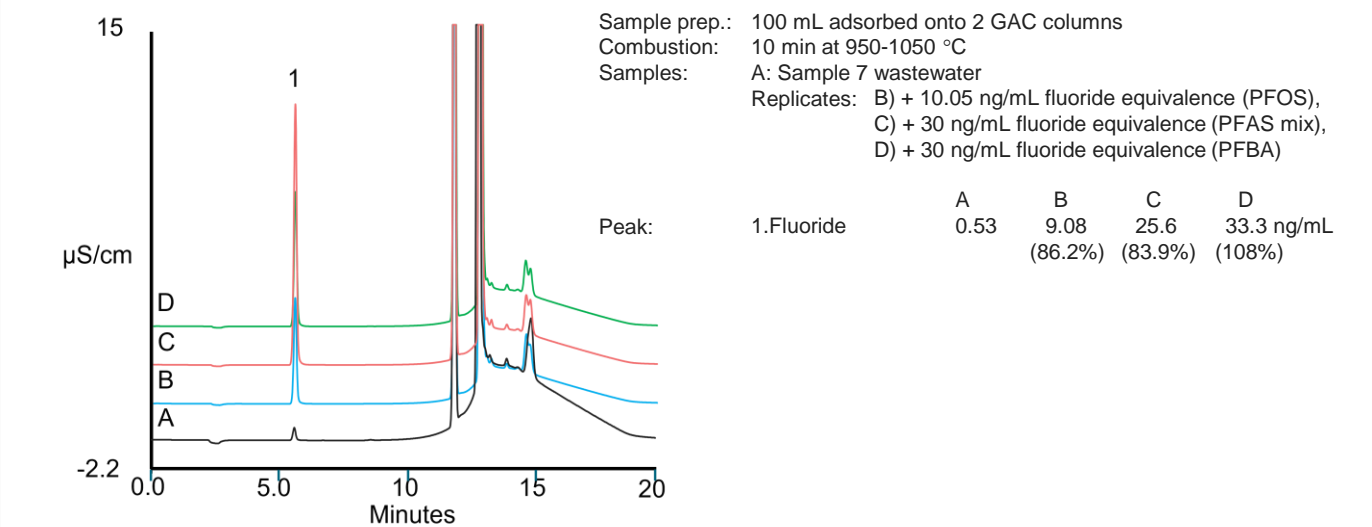


To determine recoveries of select PFAS compounds, aliquots of PFOS, PFAS mixture, and PFBA were added to replicates of Sample 7 wastewater and processed the same as previous samples. The results are summarized in Table 3. Figure 4 shows the CIC chromatograms comparing Sample 7 and Sample 7 with added PFAS.

Table 3. Recovery results of added PFBA, PFOS, PFOA, and a mixed PFAS standard. Recoveries of added PFAS standards were 76 to 114%.

Sample	Total Fluoride		
	Added (ng/mL)	Measured (ng/mL)	Recovered (%)
Sample 7	--	0.53	--
	10.0	10.86	103
	30.3	33.31	108
Sample 7 with PFBA	10.0	10.19	96.8
	30.3	29.16	94.6
	30.3	35.2	114
Sample 7 with PFOS	10.0	9.08	86.2
	30.3	29.16	94.6
	30.3	35.2	114
Sample 7 with PFAS mix	9.99	11.05	105
	9.99	8.98	85.4
	30.0	25.8	83.9
	30.0	24.91	81.6

Figure 4. Comparison of CIC chromatograms of Sample 7 with added PFAS compounds: PFOS, PFAS mix, and PFBA. The chromatograms represent the top GAC for each sample.



Conclusions

- CIC is an excellent tool to measure AOF and screen for PFAS in wastewater.
- RFIC provides accurate results, as fluoride is well-separated from the water dip, ensuring optimized automated peak integration.
- The method is sensitive, with MBs of 1 ng/mL and MDLs of 2.5 ng/mL, and accurate, with recoveries of 80–120%.

Together, these data highlight the power of CIC in eliminating the sample matrix and measuring only the adsorbable organically bound fluorine content in samples, successfully achieving the goals outlined in EPA draft Method 1621.

More information can be found in U.S. EPA Method 1621, Thermo Fisher Scientific application note AN002748.^{5,6} See the QR code below!

References

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- Thermo Fisher Scientific Application Note AN002748

Acknowledgements

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