Initial Progress Report
Development of a Total Organic Fluorine (TOF) Method for the Analysis of Process Wastewater Streams and Air from Fayetteville Works (NC)
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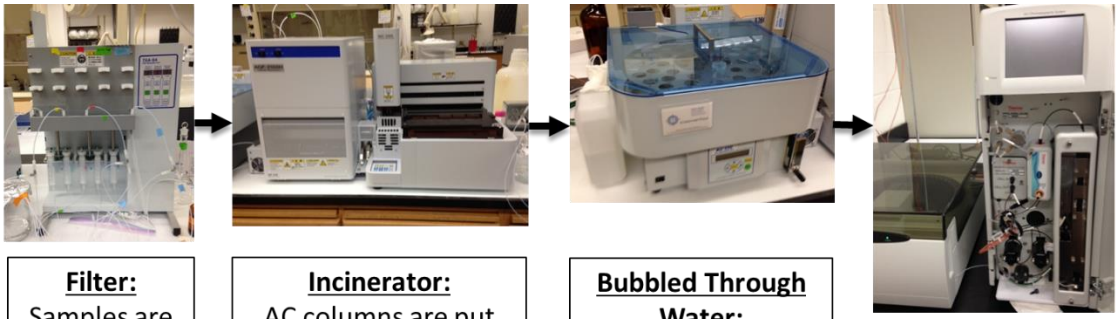
The contract with Chemours was officially signed on November 11, 2019. Despite this being only 2 weeks ago, we have already been conducting some preliminary work, including analytical method setup and fluorine background analysis, as well as establishing a per- and polyfluoroalkyl substance (PFAS) method on our liquid chromatograph (LC)-quadrupole-time-of-flight (QTOF) mass spectrometer for future LC-mass spectrometry (MS)/MS experiments. Below is a summary of the TOF method development work to-date.

1. Analytical method for TOF

Activated carbon (AC) - Combustion ion chromatography (CIC) for adsorbable organic fluorine (AOF) was set up in our lab, and the instruments have been tested (Figure 1).



Filter: Samples are passed through a small AC column. Organics are adsorbed.

Incinerator: AC columns are put into ceramic boats, which are auto-injected into a combustion furnace at 900~1000 °C. Organic matter burns off and results in gaseous CO_2, NO_x, SO_x, **HF**.

Bubbled Through Water: An argon/oxygen carrying gas is bubbled through the furnace and received in an aqueous solution.

Ion Chromatograph (IC): F^- is measured by ion chromatography (with conductivity detection)

Figure 1. Combustion ion chromatography (CIC) system for AOF method (Mitsubishi TOX analyzer and Dionex 1600 IC).

2. Quality assurance

2.1. Fluorine background of activated carbon

An important aspect of method optimization is selecting an AC with low fluorine background in order to allow lowest possible detection limits for our samples. We have tested three types of activated carbons for their fluorine background. These carbons, which are prepacked in quartz cartridges, are removed from the cartridges and placed into a ceramic boat for direct combustion, and then analyzed using ion chromatography (IC). The average fluorine background for each carbon is shown in Figure 2.

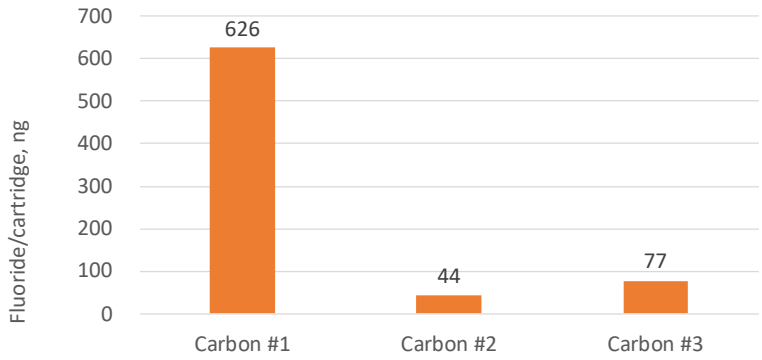


Figure 2. Fluorine background of three carbons (average value shown). 1: A1 Envirosciences; 2: Cosa-Xentaur; 3: Mitsubishi Chemical Analytech

Because Carbon 2 and 3 are currently out-of-stock in our lab (and they have been unavailable commercially for the last few months), Carbon 1 was used for the following initial experiments. However, Carbon 2 is now commercially available again, and we have now ordered more of these carbons, which should have a low fluorine background. We will re-test them as soon as they are received.

2.2. Fluorine background of the ceramic boat

In order to decrease the fluorine background of the whole system, the boat blank was tested. The ceramic boat was auto-injected into the combustion unit for a prebake, followed by the normal process (Figure 1). The prebake time was varied to minimize the fluorine background and ensure lack of carry-over from sample to sample. Results are shown in Table 1. According to the results, 10 minutes prebaking is selected for this method.

Table 1. Fluorine background of boats (4 replicates for each)

	Fluorine / ppb	**Fluorine** / ng	**Pre-baking time** / min
Boat Blank-10	ND	ND	10
Boat Blank-5	ND-6.9	ND-64	5

2.3. **Limit of Detection (LOD) and Limit of Quantification (LOQ) for Fluoride Ion by Ion Chromatography**

Sixteen Milli-Q water samples were used to calculate the limit of detection (LOD) and limit of quantitation (LOQ) of fluoride ion (F^-) by ion chromatography (IC), based on Equation 1 and Equation 2. According to the results, the LOD of IC is 0.5 µg/L, and the LOQ is 1.4 µg/L.

LOD=3*STDEV(Blank)+AVG(Blank) **Equation 1.**

LOQ=3*3*STDEV(Blank)+AVG(Blank) **Equation 2.**

Sodium fluoride (NaF) was used as the standard to establish the calibration curve for ion chromatography (Figure 3). The concentrations of the standard solution were set to 0, 1.0, 5.0, 10, 20, 50, and 100 µg/L, and the retention time of fluorine is 3.1 min (Figure 4).

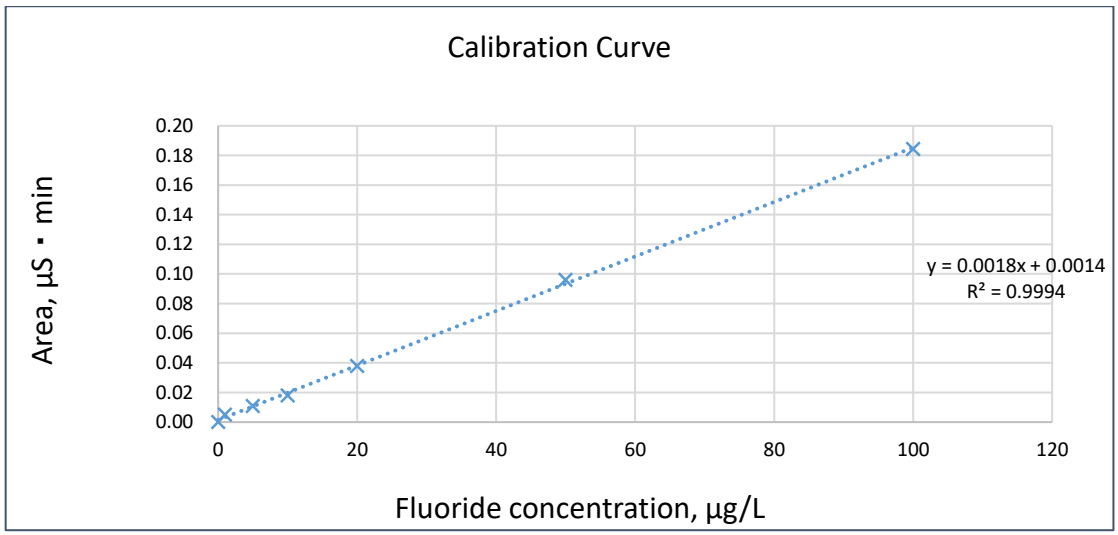


Figure 3. Calibration curve of fluoride by IC

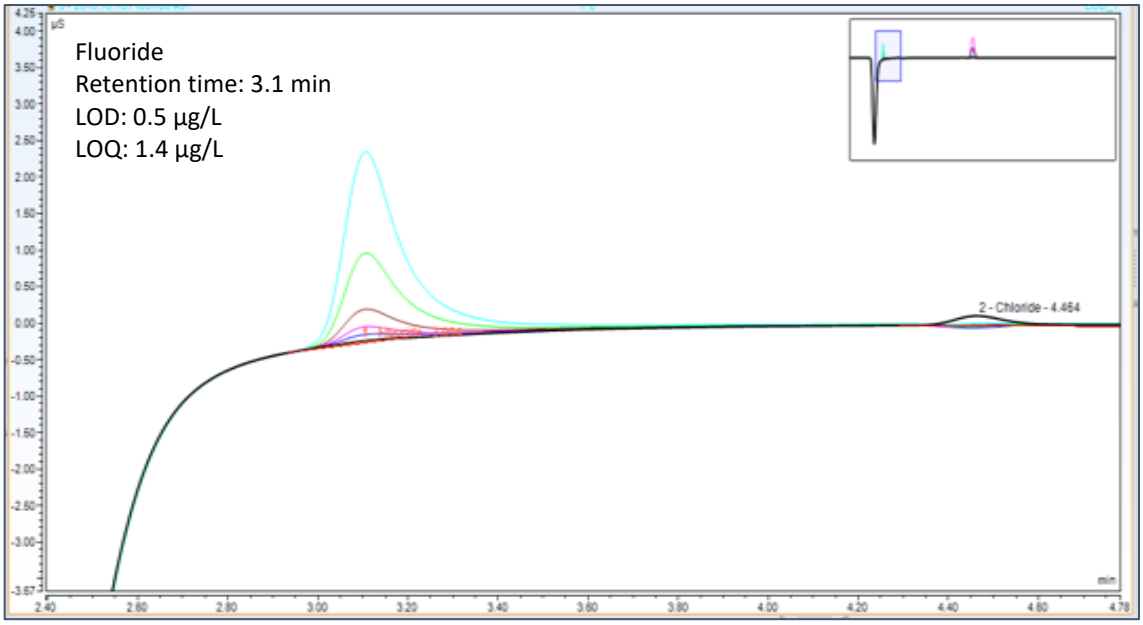


Figure 4. Elution of fluorine by IC (IonPac AS9-HC carbonate eluent column)

2.4. The fluorine background of the whole system

In order to estimate the fluorine background of the whole system, we used Milli-Q water as the sample and detected fluoride in the elution of each step to calculate the background (see Figure 5).

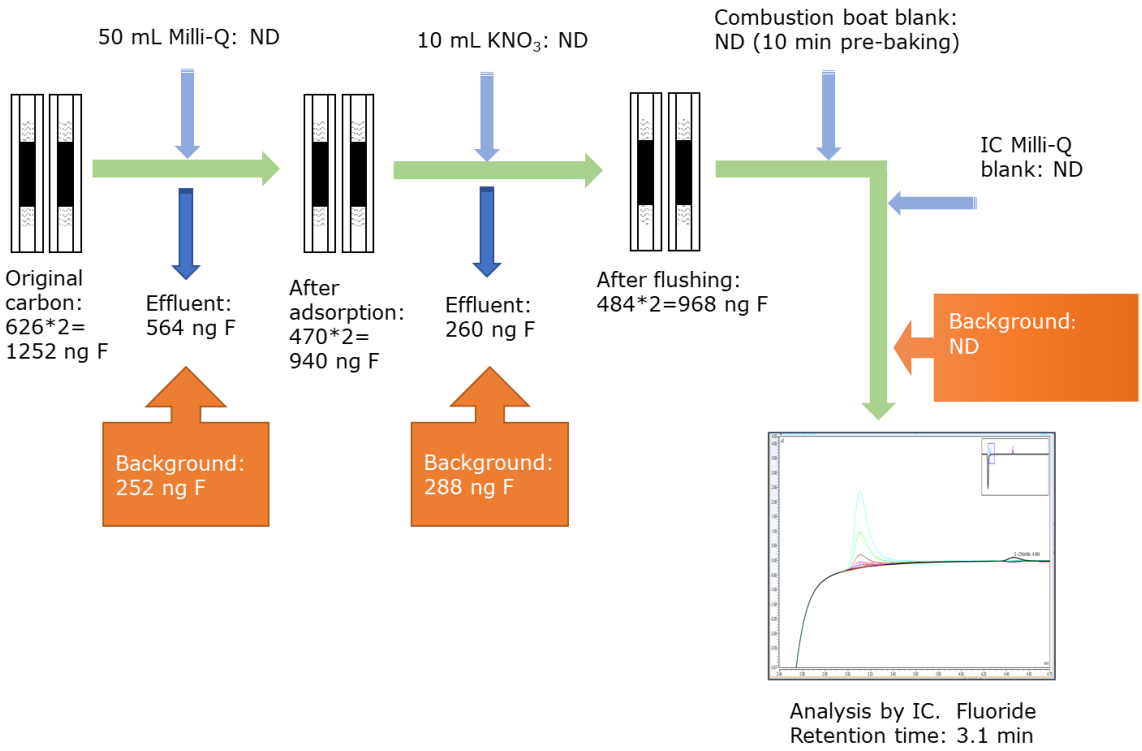


Figure 5. TOF background analysis of the whole CIC system