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# PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT #3

## Process and Non-Process Wastewater and Stormwater

*Prepared by*

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July 30, 2021

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## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| CFRW | Cape Fear River Watch |
| Chemours | The Chemours Company FC, LLC |
| Da | dalton |
| EIC | extracted ion chromatogram |
| Facility | Chemours Fayetteville Works, North Carolina |
| LC | liquid chromatography |
| MS | mass spectrometry |
| MS-MS | tandem mass spectrometry |
| m/z | mass-to-charge ratio |
| NCDEQ | NC Department of Environmental Quality |
| PFAS | per- and polyfluoroalkyl substances |
| QToF | quadrupole time-of-flight |

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# 1 INTRODUCTION

This interim report has been prepared by The Chemours Company FC, LLC (Chemours) to provide an update on the characterization of previously unidentified per- and polyfluoroalkyl substances (PFAS) in aqueous samples collected from process wastewater, non-process wastewater (i.e., non-contact cooling water) and stormwater at the Chemours Fayetteville Works, North Carolina site (the Facility). This work is being conducted pursuant to Paragraph 11 subpart (a) in the Consent Order executed 25 February 2019 between Chemours and the North Carolina Department of Environmental Quality (NCDEQ) with the Cape Fear River Watch (CFRW) as intervenor. The overall purpose of this program is to identify previously unknown PFAS that may be present in samples of collected water and to develop standards and methods to facilitate the quantitative analysis of these PFAS, as described in the PFAS Non-Targeted Analysis and Methods Development Plan, Version 2 (Chemours and Geosyntec, 2019). This is the third interim report.

In the first interim report (Chemours, 2020a), the five most abundant unknown PFAS in General Facility Discharge samples (samples of stormwater, treated non-Chemours process wastewater and/or non-contact cooling water discharging to the Cape Fear River) and in Chemours Process Wastewater samples (samples of process wastewater from Chemours manufacturing areas) were identified using liquid chromatography (LC) coupled to high-resolution quadrupole time-of-flight (QToF) mass spectrometry. The five most abundant unknown PFAS in the General Facility Discharge samples were identified as $C_4H_5F_3O_2$, $C_4H_2F_4O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$. The five most abundant unknown PFAS in the Chemours Process Wastewater samples were identified as $C_8H_2F_{14}O_7S$, $C_8HF_{13}O_4$, $C_8H_5F_{13}O_6S$, $C_9H_2F_{14}O_6$ and $C_6HF_{11}O_4$. None of the identified five potential PFAS compounds in the General Facility Discharge samples were represented in the five potential PFAS compounds in the Chemours Process Wastewater samples. These ten (10) unknown PFAS were advanced to the next step in the program - identifying molecular structures.

In the second interim report (Chemours, 2020b), investigation into the five most abundant unknown PFAS in the General Facility Discharge samples revealed that four of the compounds ($C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$) coeluted from the LC. These compounds have different molecular weights and were therefore expected to be chromatographically resolved. Examination of the empirical formulas showed that the four compounds are related by $C_2HF_3$, that is, the addition of $C_2HF_3$ (trifluoroethylene, which is a potential impurity in tetrafluoroethylene, a feedstock at the Facility) to each compound generates the empirical formula of the following compound. This suggested that these four compounds may represent a single compound, $C_4H_5F_3O_2$, which, upon elution from the LC, undergoes adduction[1] of $C_2HF_3$ in the ion source of

[1] Adduction is the process of the direct addition of two or more distinct molecules that result in a single reaction product referred to as an adduct which containing all atoms of the two initial reaction molecules.

the mass spectrometer. Furthermore, the single compound $C_4H_5F_3O_2$ itself could be generated from a reaction between $C_2HF_3$ and acetate ($CH_3COO^-$, present in the LC eluent) in the ion source of the mass spectrometer. The fifth unknown PFAS, $C_4H_2F_4O_2$, was not present in the samples at high enough concentrations to analyze by the QToF mass spectrometer.

In the second interim report (Chemours, 2020b), investigation into the five most abundant unknown PFAS in the Chemours Process Wastewater samples concluded:

- $C_8H_2F_{14}O_7S$: the structure was determined to be $CF_3$-CF(COOH)-O-$CF_2$-CF($CF_3$)-O-$CF_2$-$CF_2$-$SO_3H$
- $C_8HF_{13}O_4$: a structure was tentatively identified for this unknown PFAS, however, background interference in the samples had to date interfered with confirmation of the tentatively identified structure
- $C_8H_5F_{13}O_6S$: the structure was determined to be $HO_3S$-$CF_2$-$CF_2$-O-CF($CF_3$)-$CF_2$-O-CHF-$CF_2$-$OCH_3$
- $C_9H_2F_{14}O_6$: the structure was tentatively determined to be HOOC-$CF_2$-$CF_2$-O-CF($CF_3$)-$CF_2$-O-CF($CF_3$)-COOH
- $C_6HF_{11}O_4$ - a structure was not yet identified; background contamination in the samples had to date interfered with confirmation of a tentatively identified structure.

This third interim report provides an update on efforts completed to further identify the structures of the five most abundant unknown PFAS in the General Facility Discharge samples and the five most abundant unknown PFAS in the Chemours Process Wastewater samples.

The remainder of this report consists of:

- Section 2: Experimental Methods;
- Section 3: Results and Discussion; and
- Section 4: Summary and Next Steps.

# 2 EXPERIMENTAL METHODS

## 2.1 Investigation of the Four Related Unknown PFAS in General Facility Discharge Samples

To investigate the possibility that trifluoroethylene (an impurity in tetrafluoroethylene) combines with acetate (present in the LC eluent) in the ion source of the mass spectrometer to produce $C_4H_5F_3O_2$, with possible subsequent additions of trifluoroethylene to produce $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$, three experiments were conducted:

1) Trifluoroethylene was purged into demineralized water to create an aqueous solution of trifluoroethylene. This solution was then analyzed by LC-QToF using acetate buffer to look for the presence of the 141, 223, 305, 387 mass-to-charge ratio (m/z) ions corresponding to the m/z of $C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$.
2) A General Facility Discharge sample (from Location 20 [Outfall 002 to Cape Fear River]) was analyzed by LC-QToF using formate ($HCOO^-$) buffer instead of acetate ($CH_3COO^-$) buffer. Formate has a molecular weight of 45 daltons (Da) versus acetate which has a molecular weight of 59 Da.
3) A General Facility Discharge sample (from Location 20) was analyzed by LC-QToF using deuterated (isotopically labelled) acetate buffer ($CD_3COO^-$) as well as native acetate ($CH_3COO^-$) buffer to assess observed mass shifts. Deuterated acetate has a molecular weight of 62 Da versus native acetate which has a molecular weight of 59 Da.

### 2.2 Investigation of the Fifth Unknown PFAS in General Facility Discharge Samples

The fifth unknown PFAS in the General Facility Discharge samples was analyzed with deuterated acetate buffer as well as native (unlabelled) acetate buffer by LC-QToF to assess any observed mass shifts.

### 2.3 Investigation of the Five Most Abundant Unknown PFAS in Chemours Process Wastewater Samples

Three of the five most abundant unknown PFAS in the Chemours Process Wastewater samples were further investigated by extensively cleaning the analytical instrument to minimize background contamination and by comparison of the QToF fragmentation mass spectra to those of known compounds.

## 3 RESULTS AND DISCUSSION

### 3.1 Investigation of the 4 Related Unknown PFAS in General Facility Discharge Samples

An extracted ion chromatogram (EIC) was produced for the demineralized water through which trifluoroethylene had been purged, as well as for the demineralized water alone. The ions extracted were the 141, 223, 305, 387 m/z ions corresponding to the m/z of $C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$ (Figure 1). The results show that the EICs of the demineralized water alone and the demineralized water with trifluoroethylene purged through it are indistinguishable, which indicates that $C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$ are not present in either sample. This may mean that trifluoroethylene is not combining with acetate in the MS to produce $C_4H_5F_3O_2$, with possible subsequent additions of trifluoroethylene to produce $C_6H_6F_6O_2$,

$C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$; however, it may also mean that there was insufficient trifluoroethylene in the demineralized water following the purging step for the reactions, if possible, to occur.

A test was then conducted in which a General Facility Discharge sample, previously analyzed with acetate buffer as the LC eluent and showing the presence of the 141, 223, 305, 387 m/z ions, was analyzed with formate buffer as the LC eluent. This tested the theory that acetate (molecular weight 59 Da) reacts with trifluoroethylene (molecular weight 82 Da) to produce the 141 m/z ion, with subsequent sequential additions of trifluoroethylene to produce the 223, 305 and 387 m/z ions. The same reactions with formate should produce 127, 209, 291 and 373 m/z ions (that is, ions that are 14 Da lighter, because formate is 14 Da lighter than acetate). Mass spectral results, however, showed that the 127, 209, 291 and 373 m/z ions were not present (Figure 2). Instead, ions representing the adduction of formate (molecular weight 45 Da) with a repeating unit of 68 Da (113, 181, 249 and 317 m/z) were observed. The composition of the 68 Da repeating unit was not clear from this experiment. However, the results showed that the 141 m/z unknown was not composed of trifluoroethylene plus acetate, nor were the subsequent unknowns (223, 305, 387 m/z) formed by the addition of repeating units of trifluoroethylene (molecular weight 82 Da). The composition of the buffer (formate versus acetate) is integral to the composition of the 4 related unknowns, and trifluoroethylene is not.

A subsequent test was conducted in which the General Facility Discharge sample was analyzed with isotopically labelled acetate buffer. Mass spectral results showed that the 141, 223, 305, 387 m/z ions produced with the native acetate buffer shifted to 147, 232, 317 and 402 m/z, representing mass increases of 6, 9, 12 and 15 Da, respectively (Figure 3). Because the isotopically labelled acetate is 3 Da heavier than the native acetate, this showed that the initial 141 m/z unknown (which increased by 6 Da) contained 2 acetate moieties, the 223 m/z unknown (which increased by 9 Da) contained 3 acetate moieties, the 305 m/z unknown (which increased by 12 Da) contained 4 acetate moieties, and the 387 m/z unknown (which increased by 15 Da) contained 5 acetate moieties.

The composition of the 82 Da moiety that is the difference between the 141, 223, 305 and 387 m/z ions, as well as between acetate and the 141 m/z ion, has been shown to not be trifluoroethylene (molecular weight 82 Da). Additionally, it has been shown that the 141 m/z ion contains two acetate moieties (molecular weight 59 Da each, for a total of 118 Da). If 118 Da are subtracted from 141, the remaining mass is 23 Da, which is the atomic weight of a sodium ion; sodium ions are present in the water sample. The 82 Da moiety is, therefore, considered to be composed of sodium acetate.

The first four unknowns, corresponding to 141, 223, 305, 387 m/z ions, can now be explained as acetate clusters, and are not PFAS. An acetate molecule (molecular weight 59 Da) combined with sequential sodium acetate molecules (molecular weight 82 Da) produces the observed 141, 223, 305 and 387 m/z ions. When native acetate is replaced with deuterated acetate (molecular weight

62 Da) in the LC eluent, it combines with sequential deuterated sodium acetate molecules (molecular weight 85 Da) to produce the observed 147, 232, 317 and 402 m/z ions. When acetate is replaced with formate in the LC eluent, a formate molecule (molecular weight 45 Da) combined with sequential sodium formate molecules (molecular weight 68 Da) produces the observed 113, 181, 249 and 317 m/z ions. When the analysis is conducted with demineralized water through which trifluoroethylene had been purged (and native acetate buffer as the LC eluent), none of the 141, 223, 305, 387 m/z ions are observed because there is no sodium present (the sodium originates from the groundwater matrix of the sample, and there is no groundwater present in this experiment).

### 3.2 Investigation of the Fifth Unknown PFAS in General Facility Discharge Samples

The fifth unknown, with a m/z ratio of 157 and proposed in the second interim report to have an empirical formula of $C_4H_2F_4O_2$, was present in General Facility Discharge samples at concentrations too low with respect to background compounds to be able to propose a structure. In the second interim report, cleanup of the sample and concentration of the unknown was proposed. Given the results of the analysis of the other four unknown PFAS, however, the unknown was first analyzed with isotopically labelled acetate. Mass spectral results showed a shift of the 157 m/z peak by 6 Da to 163 Da, indicating that the 157 m/z peak contains two acetate moieties (Figure 4). If two acetate moieties (molecular weight 59 Da each, for a total of 118 Da) are subtracted from 157, the remaining mass is 39 Da, which is the atomic weight of a potassium ion, which are present in the water sample. The fifth unknown can now be explained as a potassium acetate cluster and is not a PFAS.

### 3.3 Explanation of the Initial Identification of Acetate Clusters as PFAS Unknowns

In this non-targeted analysis program, unknown PFAS were identified from unidentified chromatographic peaks from a QToF mass spectrometer with a signal-to-noise level greater than six and using the atomic mass defect of fluorine as the molecular feature. An atomic mass defect refers to the phenomenon that the mass of an atom is not exactly equal to the number of subatomic particles (protons and neutrons) or the atomic mass number (except for carbon-12 by definition) as a result of differences in mass lost (as energy) when the atomic nucleus is formed for each isotope. In this case, fluorine is well-known to have a negative mass defect, where the exact mass is slightly less than the mass number. When the QToF mass spectrometer is operated in the negative mode, one can select fluorine-containing features and empirical formulas using available software provided by the instrument vendor. (The exact procedures utilized adhered closely to what was outlined in McCord & Strynar (2019) which consists of using a software workflow of Agilent ProFinder, MassHunter, and Mass Profile.) However, the algorithm used to determine empirical formulas using the fluorine mass defect is not exact, especially when an unknown number of fluorines is present in the unknown compound; this is a known limitation of the mass

defect approach. Consequently, the algorithm may occasionally determine that an unknown compound contains fluorine when it does not, as is the case for the five most abundant unknown "PFAS" in the General Facility Discharge samples. In this case, both oxygen and sodium have negative mass defects and the five unknowns, four containing both oxygen and sodium and one containing oxygen, were mistakenly flagged as fluorinated.

### 3.4 Chemours Process Wastewater Samples

Progress in investigating the five most abundant potential PFAS compounds in the Chemours Process Wastewater samples is summarized below:

- $C_8HF_{13}O_4$ - a structure was tentatively identified for this unknown PFAS in interim report #2, however, background contamination interfered with confirmation of the tentatively identified structure. Following cleanup of the analytical instrument, a cleaner mass spectrum was obtained and confirmed to correspond to EVE Acid (Figure 5). EVE Acid (Chemical Abstracts Service Number 69087-46-3) has previously been identified as a Site-related PFAS and is found on the Table 3+ analyte list.
- $C_8H_5F_{13}O_6S$ - a tentative structure ($HO_3S$-$CF_2$-$CF_2$-O-$CF(CF_3)$-$CF_2$-O-CHF-$CF_2$-$OCH_3$) was identified for this unknown PFAS in interim report #2. An authentic standard was found to exist for this compound; however, the unknown PFAS did not match the retention time nor the MS-MS mass spectrum of the authentic standard. Consequently, the tentatively identified structure will be revised, followed by initiation of an authentic standard to confirm the structure.
- $C_6HF_{11}O_4$ - a tentative structure could not be identified for this unknown PFAS in interim report #2 due to background contamination. Following cleanup of the analytical instrument, a tentative structure ($CF_3$-O-$CF_2$-O-$CF_2$-$CF_2$-$CF_2$-COOH) was identified. Synthesis of an authentic standard to confirm this structure has been initiated.

These results are summarized in Table 1.

## 4 SUMMARY AND NEXT STEPS

A summary of the next steps for each of the 10 potential PFAS compounds discussed in this interim report is provided below and in Table 1.

The five most abundant unknown "PFAS" in the General Facility Discharge samples have been shown to be sodium or potassium adducts of acetate clusters, containing no fluorine, rather than PFAS. They can therefore be eliminated from the list of unknown PFAS. The next most abundant potential PFAS in the General Facility Discharge samples ($C_8HF_{15}O_8$) had an ion abundance of $3.3x10^7$ (Chemours, 2020a). This is two orders of magnitude smaller than the ion abundance of

the unknown PFAS in the Chemours Process Wastewater samples (the five most abundant unknown PFAS in the Chemours Process Wastewater samples had an ion abundance ranging from $3.8x10^9$ to $4.5x10^9$). Chemours will commence investigating the next five unknown PFAS in the General Facility Discharge samples; however, their low concentration reduces the possibility of identifying potential structures. Upcoming efforts for the non-targeted analysis program will be focused on the unknown PFAS in the Chemours Process Wastewater samples.

The identification of three of the five most abundant unknown PFAS in the Chemours Process Wastewater samples was advanced. One compound ($C_8HF_{13}O_4$) was identified as EVE Acid and is therefore no longer unknown. One compound's ($C_8H_5F_{13}O_6S$) tentatively identified structure was found to not match an existing authentic standard, and a new structure will be tentatively identified. One compound ($C_6HF_{11}O_4$) was tentatively identified as $CF_3$-O-$CF_2$-O-$CF_2$-$CF_2$-$CF_2$-COOH. Authentic standard synthesis has been initiated for this compound, as well as for the other two compounds ($C_8H_2F_{14}O_7S$ and $C_9H_2F_{14}O_6$), for which structures had been previously tentatively identified.

## 5 REFERENCES

Chemours, 2020a. PFAS Non-Targeted Analysis and Methods Interim Report. June 30, 2020.

Chemours, 2020b. PFAS Non-Targeted Analysis and Methods Interim Report #2. December 31, 2020.

Chemours and Geosyntec Consultants, 2019. PFAS Non-Targeted Analysis and Methods Development Plan. Version 2. December 5, 2019.

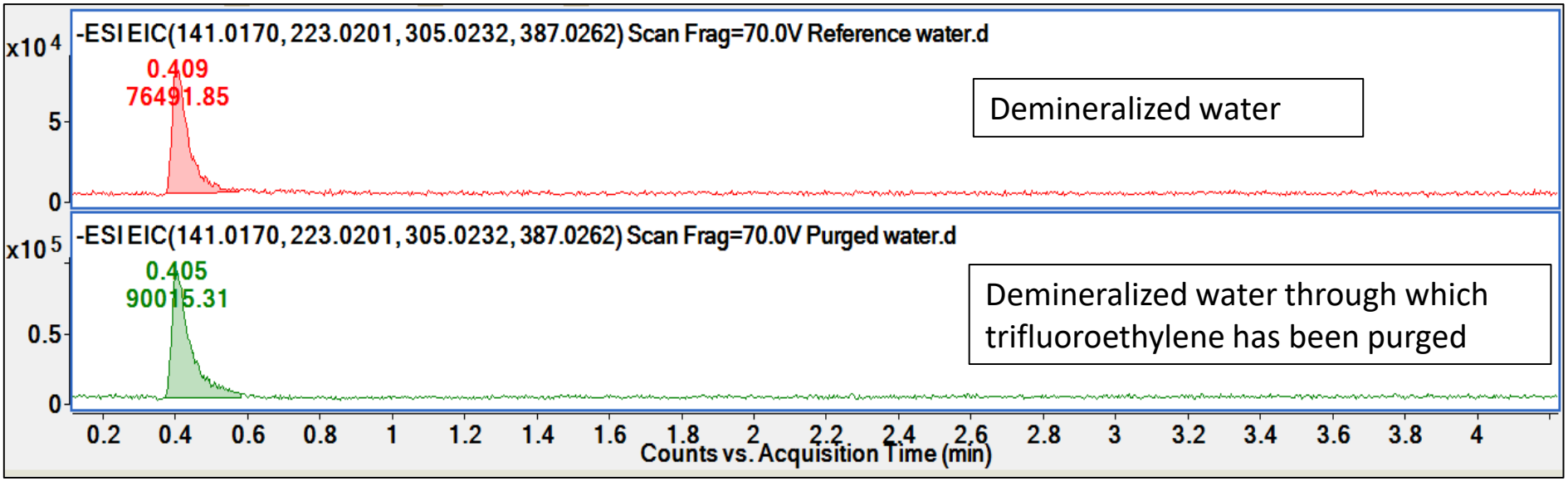
McCord, J. and Strynar, M., 2019. Identification of per-and polyfluoroalkyl substances in the Cape Fear river by high resolution mass spectrometry and nontargeted screening. Environmental science & technology, 53(9), pp. 4717-4727.

**TABLE 1**
**STATUS OF 10 UNKNOWN PFAS - INTERIM REPORT #3**
**Chemours Fayetteville Works, North Carolina**

| Sample Source | Suggested Empirical Formula | Mass (Da) | Mass to Charge Ratio (m/z) | Identified Structure | Next Steps |
|---|---|---|---|---|---|
| General Facility Discharge | $C_4H_5F_3O_2$ | 142.0241 | 141.0168 | Structures identified as sodium or potassium adducts of acetate clusters; these are formed in the MS source from sodium or potassium present in the sample matrix and acetate from the LC eluent buffer | Chemours will commence investigating the next five unknown PFAS in the General Facility Discharge samples; however, their low concentration reduces the possibility of identifying potential structures. |
| | $C_4H_2F_4O_2$ | 157.9983 | 156.9910 | | |
| | $C_6H_6F_6O_2$ | 224.0272 | 223.0199 | | |
| | $C_8H_7F_9O_2$ | 306.0302 | 305.0230 | | |
| | $C_{10}H_8F_{12}O_2$ | 388.0331 | 387.0258 | | |
| Chemours Process Wastewater | $C_8H_2F_{14}O_7S$ | 507.9302 | 506.9229 | Structure tentatively identified: $CF_3$-CF(COOH)-O-$CF_2$-CF($CF_3$)-O-$CF_2$-$CF_2$-$SO_3H$ | Continue synthesis of authentic standard |
| | $C_8HF_{13}O_4$ | 407.9670 | 406.9598 | Identified as EVE Acid (background interferences prevented identification previously) | None |
| | $C_8H_5F_{13}O_6S$ | 475.9587 | 474.9515 | Tentatively identified structure did not match authentic standard. | Revise tentatively identified structure and initiate synthesis of authentic standard |
| | $C_9H_2F_{14}O_6$ | 471.9630 | 470.9556 | Structure tentatively identified: HOOC-$CF_2$-$CF_2$-O-CF($CF_3$)-$CF_2$-O-CF($CF_3$)-COOH | Continue synthesis of authentic standard |
| | $C_6HF_{11}O_4$ | 345.9693 | 344.9620 | Structure tentatively identified: $CF_3$-O-$CF_2$-O-$CF_2$-$CF_2$-$CF_2$-COOH | Continue synthesis of authentic standard |

*Notes:*

adduct - a product of a direct addition of two or more distinct molecules resulting in a single reaction product containing all atoms of all components
C - carbon
Da - dalton
F - fluorine
H - hydrogen
LC - liquid chromatograph
MS - mass spectrometer
O - oxygen
PFAS - per- and polyfluoroalkyl substances
S - sulfur




*Notes:*

- the mass-to-charge ratios of four ions (141, 223, 305 and 387 mass-to-charge ratio), representing the four related unknowns in the General Facility Discharge samples, are combined in the extracted ion chromatograms

**Extracted Ion Chromatograms of Demineralized Water and Demineralized Water Through Which Trifluoroethylene Has Been Purged**

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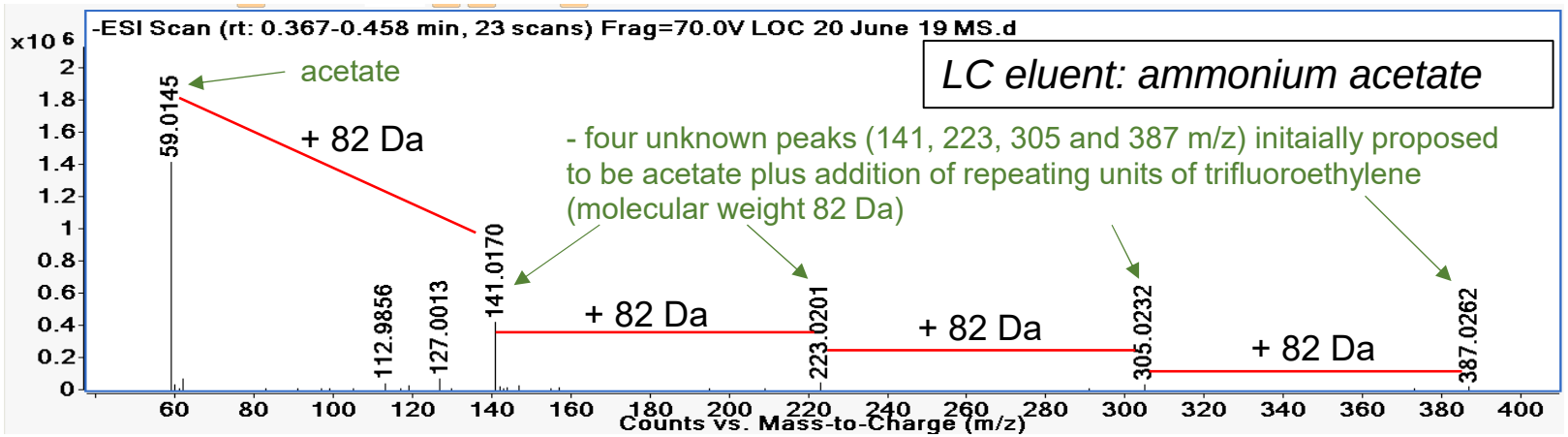
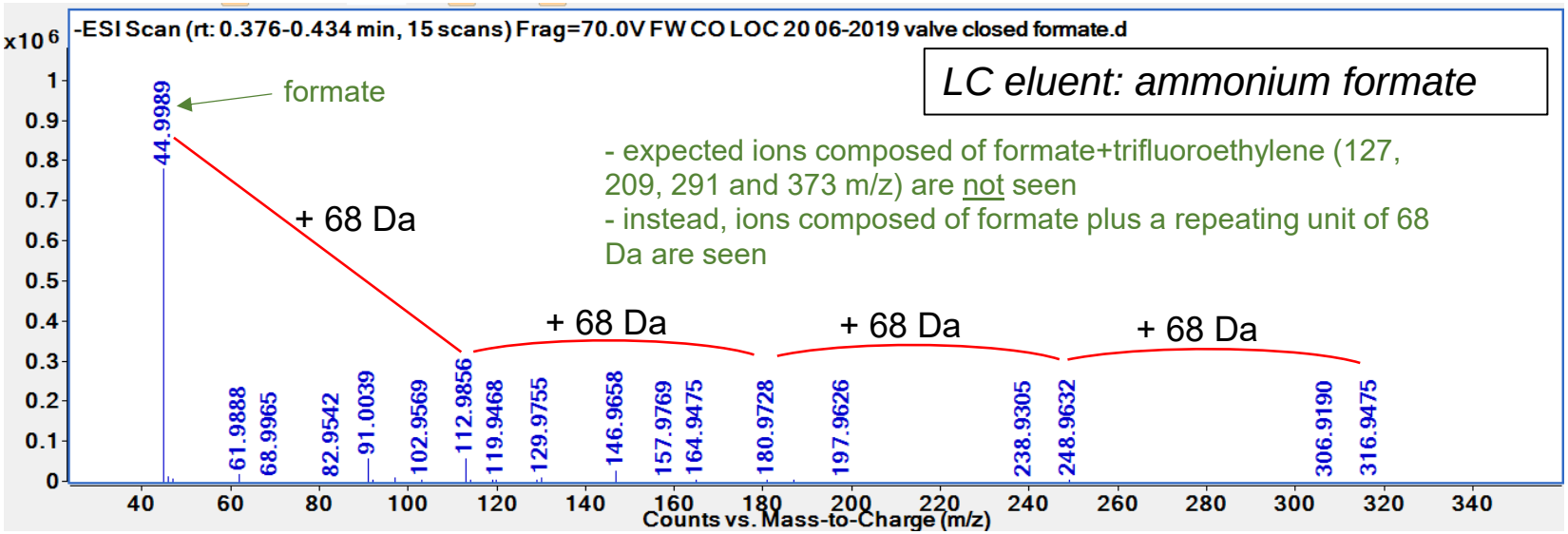
Figure 1




**Mass Spectra of Four Unknowns in a General Facility Discharge Sample Analyzed with Acetate and with Formate as the LC Eluent**

Chemours Fayetteville Works, North Carolina

*Notes:*
Da - dalton
LC - liquid chromatograph

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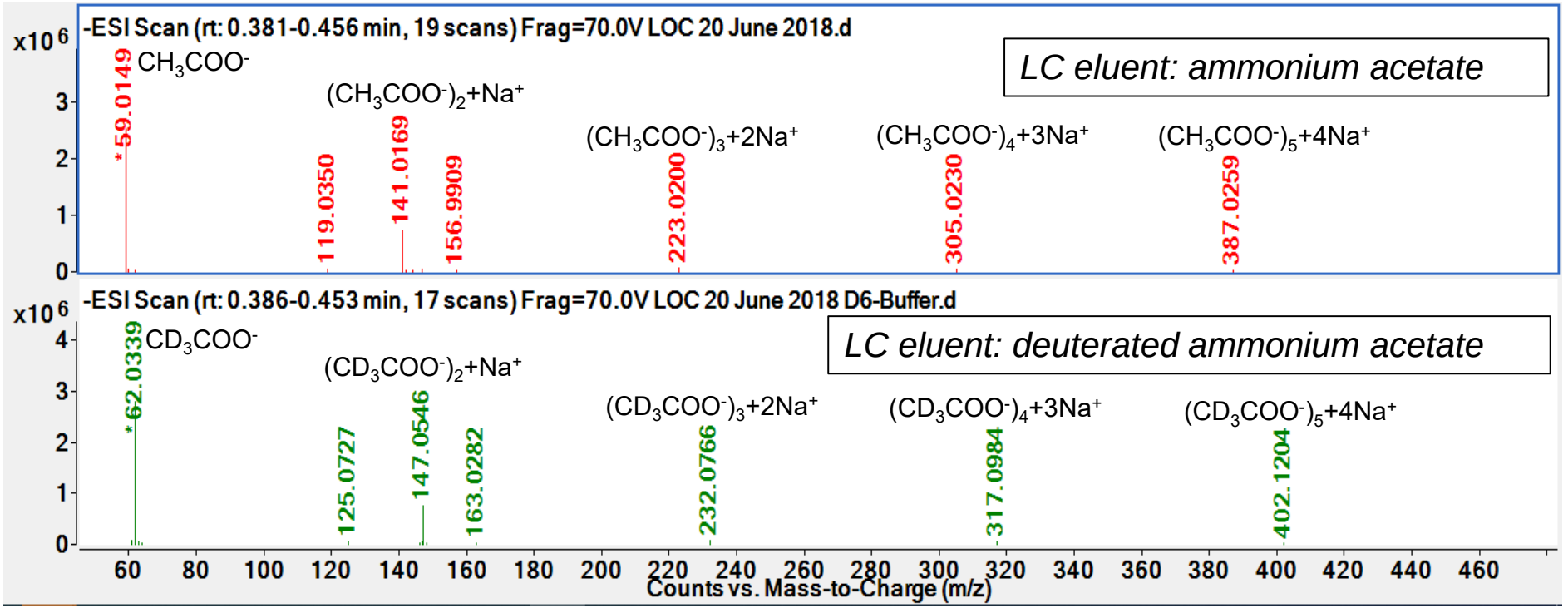
Figure **2**




*Notes:*

$CH_3COO^-$ - native acetate

$CD_3COO^-$ - deuterated acetate

Da - dalton

$Na^+$ - sodium ion

LC - liquid chromatograph

**Mass Spectra of Four Unknowns in a General Facility Discharge Sample Analyzed with Deuterated Acetate as the LC Eluent**

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Figure

**3**

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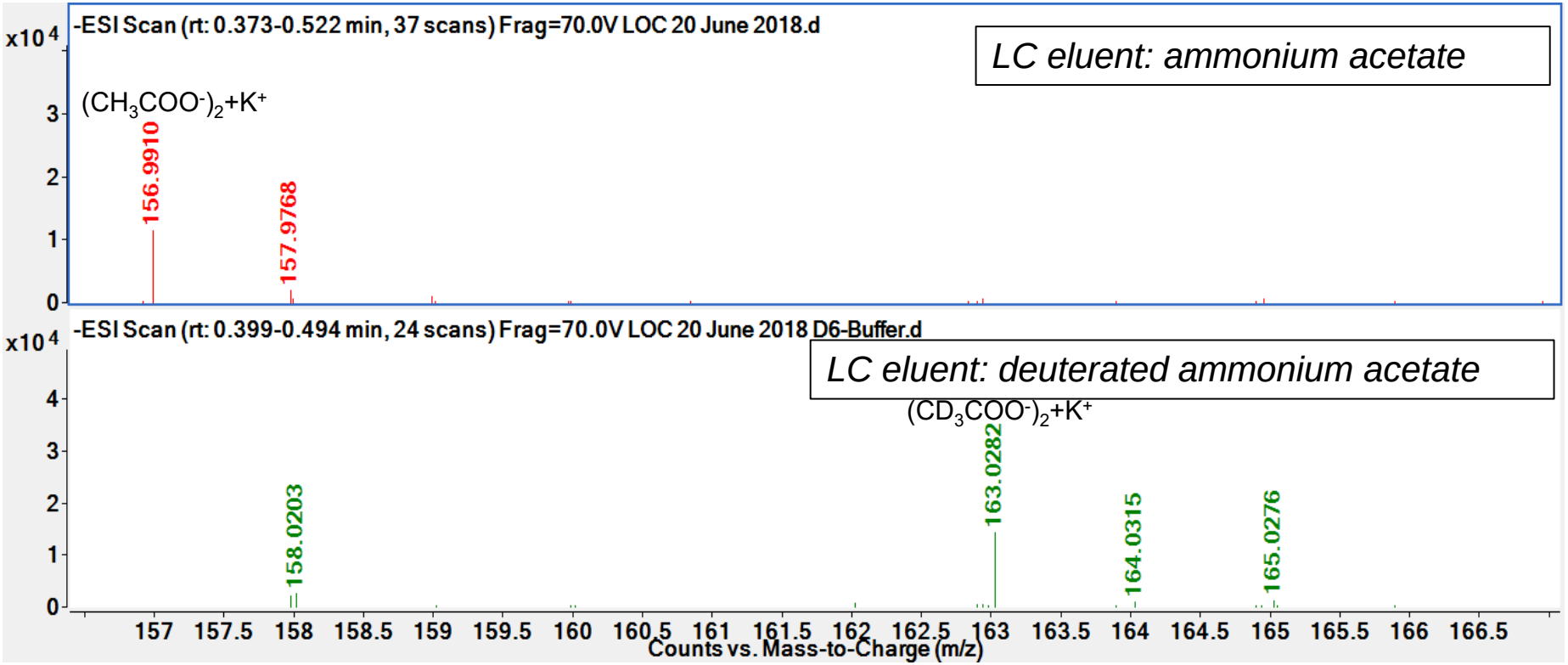


*Notes:*

$CH_3COO^-$ - native acetate

$CD_3COO^-$ - deuterated acetate

Da - dalton

$K^+$ - potassium ion

LC - liquid chromatograph

**Mass Spectra of the Fifth Unknown in a General Facility Discharge Sample Analyzed with Deuterated Acetate as the LC Eluent**

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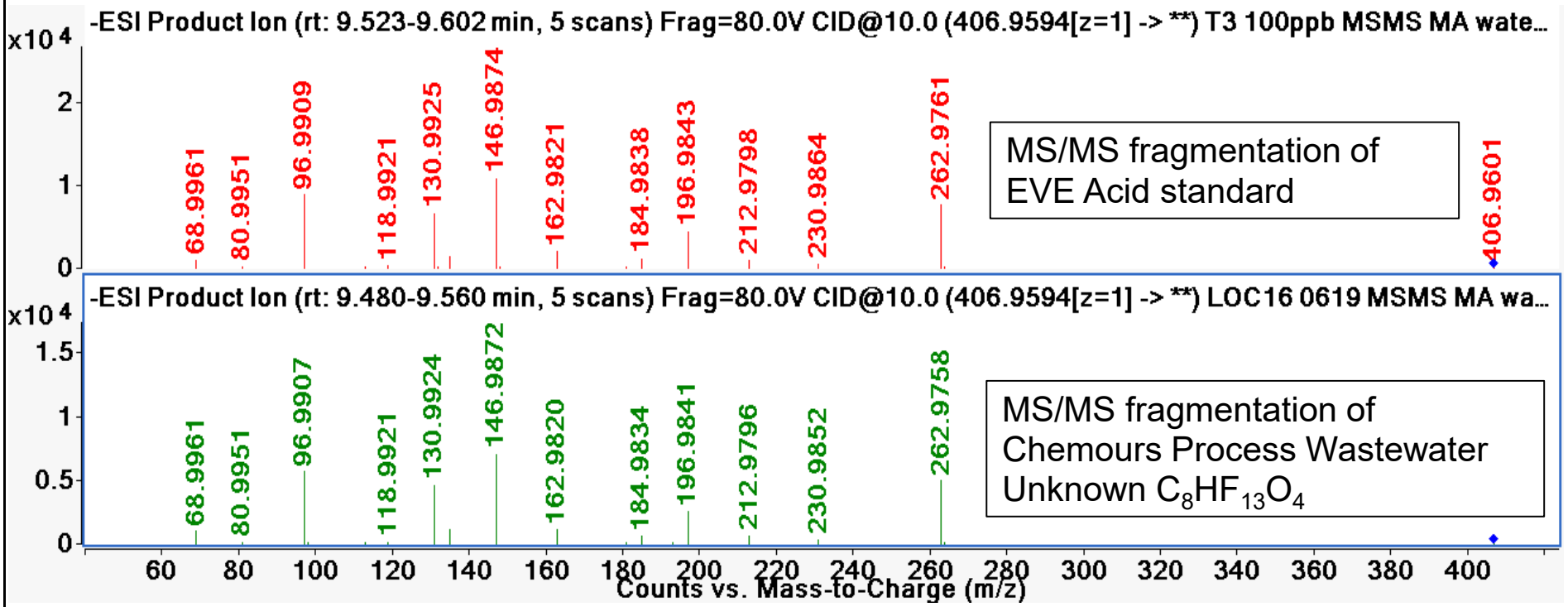
Figure

**4**




*Notes:*
MS/MS - tandem mass spectrometry
rt - retention time

**Mass Spectra of Eve Acid and of Chemours Process Wastewater Unknown $C_8HF_{13}O_4$**
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Figure **5**