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PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT #5

Process and Non-Process Wastewater and Stormwater

Prepared by

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ACRONYMS AND ABBREVIATIONS

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

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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 fifth interim report.

First Interim Report

The samples assessed via the non-targeted program were divided into two categories:

- General Facility Discharge samples - samples of stormwater, treated non-Chemours process wastewater and/or non-contact cooling water discharging to the Cape Fear River. These samples were collected at five locations; and
- Chemours Process Wastewater samples - samples of process wastewater from Chemours manufacturing areas. These samples were collected at two locations.

Samples were analyzed by liquid chromatography (LC) coupled to high-resolution quadrupole time-of-flight (QToF) mass spectrometry (Chemours, 2020a). Unknown PFAS were assigned a tentative empirical formula (defined as the number of atoms present in a compound but not the arrangement of the atoms) from unidentified chromatographic peaks 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. 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 tentative empirical formulas of the five most abundant unknown PFAS in each sample category were:

- General Facility Discharge - $C_4H_5F_3O_2$, $C_4H_2F_4O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$; and

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- Chemours Process Wastewater - $C_8H_2F_{14}O_7S$, $C_8HF_{13}O_4$, $C_8H_5F_{13}O_6S$, $C_9H_2F_{14}O_6$ and $C_6HF_{11}O_4$.

None of the identified five potential PFAS in the General Facility Discharge samples were represented in the five potential PFAS in the Chemours Process Wastewater samples. These ten (10) unknown PFAS were advanced to the next step in the program - identifying molecular structures (defined as the arrangement of the atoms into a molecule).

Second Interim Report

Investigation into the five most abundant unknown PFAS in the General Facility Discharge samples revealed that four ($C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$) coeluted from the LC (Chemours, 2020b). 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 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.

Investigation into the five most abundant unknown PFAS in the Chemours Process Wastewater samples concluded:

- $C_8H_2F_{14}O_7S$ - the molecular 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 molecular 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 molecular 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 molecular structure was tentatively determined to be HOOC-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CF(CF_3)-COOH; and
- $C_6HF_{11}O_4$ - a molecular structure was not yet identified; background contamination in the samples had to date interfered with confirmation of a tentatively identified molecular structure.

[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.

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Third Interim Report

The five most abundant unknown "PFAS" in the General Facility Discharge samples were identified to be sodium or potassium adducts of acetate clusters, containing no fluorine, rather than PFAS (Chemours, 2021a). They were therefore eliminated from the list of unknown PFAS.

The third interim report (Chemours, 2021a) showed that (for the three remaining unidentified PFAS of the five most abundant unknown PFAS in the Chemours Process Wastewater samples):

- $C_8HF_{13}O_4$ was identified as EVE Acid, and was therefore no longer unknown;
- $C_8H_5F_{13}O_6S$'s identified molecular structure was found to not match an existing authentic standard, and therefore another molecular structure needs to be proposed; and
- $C_6HF_{11}O_4$ was tentatively identified as CF_3-O-CF_2-O-CF_2-CF_2-CF_2-COOH.

Fourth Interim Report

Because the first set of five most abundant unknown "PFAS" in the General Facility Discharge samples turned out to be non-PFAS, the second set of five most abundant unknown PFAS in the General Facility Discharge samples were carried forward to identification of their molecular structures (Chemours, 2021b). In order of relative abundance, this resulted in the following:

- $C_8HF_{15}O_8$ was no longer detected in the original samples and, therefore, could not be further investigated. A new sample from the same location (Location 42) was proposed for collection during a rain event to investigate the presence and temporal stability of this compound;
- $C_4H_2F_6O_2$ was identified as the sodium salt of a trifluoroacetate (TFA) and acetate adduct. The correct formula was identified as $C_4H_4F_3O_4Na$;
- $C_8HF_{13}O_4$ was identified as R-EVE;
- $C_4HF_9O_2S$ was identified as the sodium salt of sulfuric acid and acetate dimer adduct. The correct formula was identified as $C_4H_7SO_8Na_3$. This compound is not a PFAS; and
- $C_6H_3F_7O_2$ was identified as the sodium and potassium salt of an acetate dimer. The correct formula was identified as $C_6H_{10}O_6NaK$. This compound is not a PFAS.

There was one remaining unidentified PFAS (of the five most abundant unknown PFAS) in the Chemours Process Wastewater samples ($C_8H_5F_{13}O_6S$) for which the molecular structure identified was found to not match an existing authentic standard in Interim Report 3; a tentatively identified molecular structure for this unidentified PFAS continued to be in development.

Fifth Interim Report

This fifth interim report provides an update on:

- the identification of $C_8HF_{15}O_8$ (the one remaining unknown PFAS in the top 10 unidentified PFAS in the General Facility Discharge samples); and

- efforts to further identify the molecular structures of the four most abundant unknown PFAS in the Chemours Process Wastewater samples.

The remainder of this report consists of:

- Section 2: Investigation of the Second Set of Five Most Abundant Unknown PFAS in General Facility Discharge Samples
- Section 3: Investigation of the Five Most Abundant Unknown PFAS in Chemours Process Wastewater Samples; and
- Section 4: Summary and Next Steps.

2 INVESTIGATION OF THE SECOND SET OF FIVE MOST ABUNDANT UNKNOWN PFAS IN GENERAL FACILITY DISCHARGE SAMPLES

Of the second set of five most abundant unknown PFAS in the General Facility Discharge samples, there was one remaining unidentified PFAS ($C_8HF_{15}O_8$; mass-to-charge ratio 508.9357). This PFAS was observed in the General Facility Discharge sample from Location 42 (the location at which stormwater from rooftop gutters from the Chemours Monomers IXM area going to the Cooling Water Channel is collected) when the sample was analyzed in March 2020. However, as described in Interim Report #4, when the sample was re-analyzed in December 2021, the unknown PFAS was not detected (Chemours, 2021b).

A new sample was collected from Location 42 on March 17, 2022 during a rain event and analyzed. Initial analysis of the sample again showed that the peak (with a retention time of approximately 12.3 minutes) was not present. The sample was then concentrated 100-fold using solid-phase extraction (SPE) and re-analyzed. The peak corresponding to the unknown PFAS was then observed.

Further analysis of the sample by tandem mass spectrometry (MS/MS) (Figure 2) resulted in the proposal of the following molecular structure for $C_8HF_{15}O_8$:

- CF_3-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-COOH

The current status of the second set of five most abundant PFAS in the General Facility Discharge samples (as well as of the first set of five most abundant PFAS) is summarized in Table 1.

3 INVESTIGATION OF THE FIVE MOST ABUNDANT UNKNOWN PFAS IN CHEMOURS PROCESS WASTEWATER SAMPLES

Efforts to further identify the molecular structures of the four most abundant unknown PFAS in the Chemours Process Wastewater samples is summarized below:

- three unknown PFAS ($C_8H_2F_{14}O_7S$, $C_9H_2F_{14}O_6$ and $C_6HF_{11}O_4$) had tentatively identified molecular structures identified in previous Interim Reports. Synthesis of authentic standards for these compounds is the next step. Synthetic pathways are still being developed; and
- one unknown PFAS ($C_8H_5F_{13}O_6S$) had a previously tentatively identified molecular structure, which was found to be incorrect upon comparison to an existing authentic standard. A revised tentatively identified molecular structure is still being developed.

The current status of the five most abundant PFAS in the Chemours Process Wastewater samples is summarized in Table 1.

4 SUMMARY AND NEXT STEPS

A summary of results to date and the next steps for the potential unknown PFAS in General Facility Discharge and Chemours Process Wastewater samples is provided below and in Table 1.

In the General Facility Discharge samples, the 10 most abundant unknown “PFAS” have been identified:

- seven were identified as sodium or potassium adducts of acetate clusters. These are formed in the mass spectrometer source from sodium or potassium present in the sample matrix and acetate or sulfate present in the LC eluent buffer. The incorrect empirical formulas (containing fluorine) were generated by the computer algorithm used to determine empirical formulas and were mistakenly flagged as fluorinated compounds (Chemours, 2021a). These compounds are not PFAS and the proposed empirical formulas have been revised showing the absence of fluorine;
- one was identified as the sodium salt of a TFA acetate adduct. TFA is a known PFAS associated with the Facility;
- one was identified as R-EVE, which is a known PFAS associated with the Facility;
- one was identified as an unknown PFAS, and a molecular structure has been proposed.

In the Chemours Process Wastewater samples, the five most abundant unknown PFAS have been identified:

- one was identified as EVE Acid, which is a known PFAS associated with the Facility;
- three were identified as unknown PFAS, and molecular structures have been proposed;

- one was identified as an unknown PFAS, and a molecular structure has not yet been proposed.

Each sample category (General Facility Discharge and Chemours Process Wastewater) has at least one unknown compound that has been determined to be a PFAS and for which a molecular structure has been proposed. The next step will be to develop pathways for the synthesis of the authentic standards for the proposed molecular structures on paper for the most abundant unknown PFAS in each sample category ($C_8HF_{15}O_8$ for the General Facility Discharge samples and $C_8H_2F_{14}O_7S$ for the Chemours Process Wastewater samples).

Once that has been completed, the compounds will be synthesized. Note that the synthetic pathways are expected to be challenging, and this process may take considerable time to complete given the complex structure of these compounds. Comparison of the liquid chromatography retention time and tandem mass spectrometry fragmentation patterns of the authentic standard and the unknown PFAS will aid in identification of the unknown PFAS.

5 REFERENCES

Chemours, 2021a. PFAS Non-Targeted Analysis and Methods Interim Report #3. July 30, 2021.

Chemours, 2021b. PFAS Non-Targeted Analysis and Methods Interim Report #4. December 22, 2021.

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.

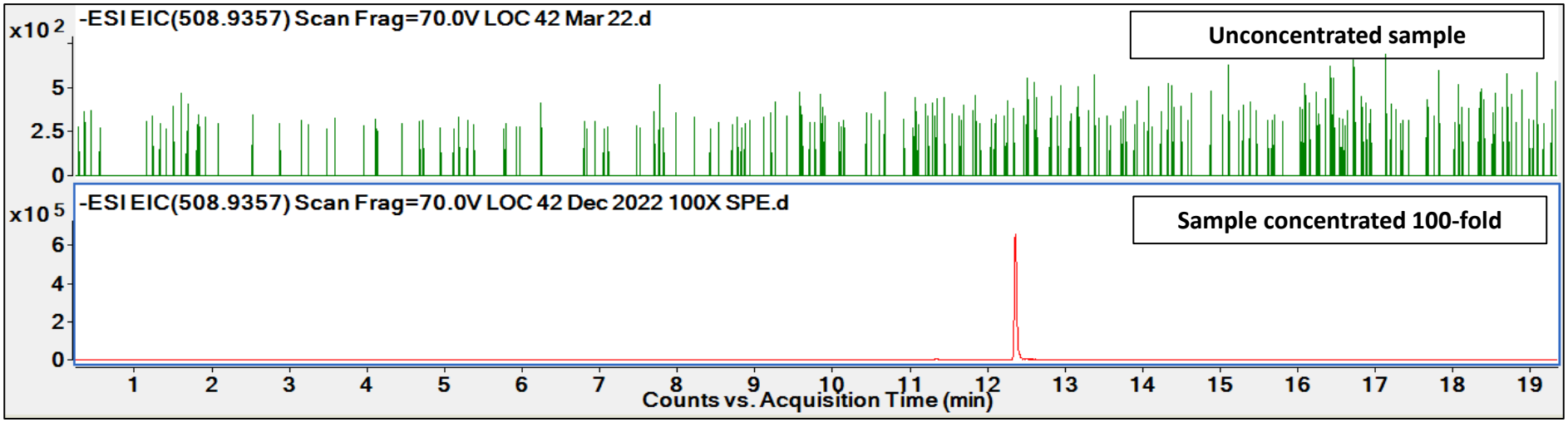
TABLE 1
STATUS OF UNKNOWN PFAS - INTERIM REPORT #5
Chemours Fayetteville Works, North Carolina

Sample Source	Mass (Da)	Mass to Charge Ratio (m/z)	Empirical Formula		Proposed Molecular Structure	Next Steps
			Tentative	Revised		
General Facility Discharge	142.0241	141.0168	$C_4H_5F_3O_2$*	$C_4H_7O_4Na$	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. Compounds are not PFAS.	None
	157.9983	156.9910	$C_4H_2F_4O_2$*	$C_4H_6O_4K$		
	224.0272	223.0199	$C_6H_6F_6O_2$*	$C_6H_{10}O_6Na_2$		
	306.0302	305.0230	$C_8H_7F_9O_2$*	$C_8H_{13}O_8Na_3$		
	388.0331	387.0258	$C_{10}H_8F_{12}O_2$*	$C_{10}H_{16}O_{10}Na_4$		
	509.9432	508.9357	$C_8HF_{15}O_8$	--	CF_3-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-COOH	Synthesis of an authentic standard is under consideration.
	195.9956	194.9884	$C_4H_2F_6O_2$*	$C_4H_4F_3O_4Na$	Structure identified as sodium salt of TFA and acetate adduct. Correct formula is $C_4H_4F_3O_4Na$	None
	407.9670	406.9596	$C_8HF_{13}O_4$	--	Identified as R-EVE	None
	283.9544	282.9471	$C_4HF_9O_2S$*	$C_4H_7SO_8Na_3$	Structure identified as sodium salt of sulfuric acid and acetate dimer adduct. Correct formula is $C_4H_7SO_8Na_3$. This compound is not a PFAS.	None
	240.0010	238.9937	$C_6H_3F_7O_2$*	$C_6H_{10}O_6NaK$	Structure identified as sodium and potassium salt of acetate dimer. Correct formula is $C_6H_{10}O_6NaK$. This compound is not a PFAS.	None
Chemours Process Wastewater	507.9302	506.9229	$C_8H_2F_{14}O_7S$	--	CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H	Synthesis of an authentic standard is under consideration.
	407.9670	406.9598	$C_8HF_{13}O_4$	--	Identified as EVE Acid	None
	475.9587	474.9515	$C_8H_5F_{13}O_6S$	--	No proposed molecular structure yet	Continue to develop a proposed molecular structure.
	471.9630	470.9556	$C_9H_2F_{14}O_6$	--	HOOC-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CF(CF_3)-COOH	Synthesis of an authentic standard is under consideration.
	345.9693	344.9620	$C_6HF_{11}O_4$	--	CF_3-O-CF_2-O-CF_2-CF_2-CF_2-COOH	Synthesis of an authentic standard is under consideration.

Notes:

* - tentative empirical formula has been revised following further investigation
-- - revised empirical formula not required
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
- further investigation not required

C - carbon
Da - dalton
F - fluorine
H - hydrogen
LC - liquid chromatograph
MS - mass spectrometer
O - oxygen
PFAS - per- and polyfluoroalkyl substances
S - sulfur



Notes:
EIC - extracted ion chromatogram
m/z - mass-to-charge ratio
SPE - solid-phase extraction

Extracted Ion Chromatograms (m/z 508.9357) of $C_8HF_{15}O_8$ in Stormwater Sample from Location 42
Collected March 17, 2022
Chemours Fayetteville Works, North Carolina

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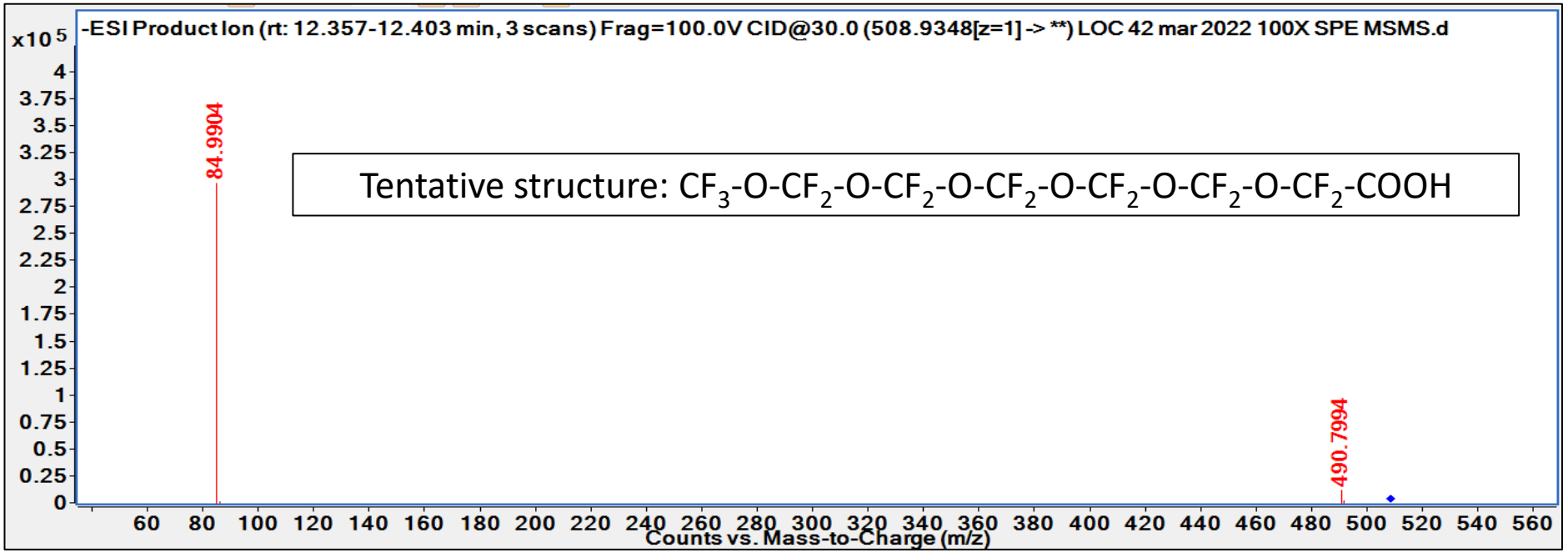
Figure **1**



Notes:
EIC - extracted ion chromatogram
m/z - mass-to-charge ratio
SPE - solid-phase extraction

Tandem Mass Spectrometry Fragmentation Pattern of $C_8HF_{15}O_8$
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Figure **2**