The Chemours Company
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PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT #4

Process and Non-Process Wastewater and Stormwater

Prepared by

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December 22, 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
TFA	trifluoroacetate

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1 INTRODUCTION

This fourth 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 fourth interim report.

First 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.

Second Interim Report

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 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.

Third Interim Report

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

The third interim report (Chemours, 2021) showed that, of 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 structure was found to not match an existing authentic standard, and therefore another 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.

This fourth interim report provides an update on the initial assessment of the second five most abundant unknown PFAS in the General Facility Discharge samples (of the original top five) and on efforts to further identify the structures of the four most abundant unknown PFAS in the Chemours Process Wastewater samples.

[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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The remainder of this report consists of:

- Section 2: Investigation of the Next 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 Next Five Most Abundant Unknown PFAS in General Facility Discharge Samples

Results of the work conducted on the next five most abundant PFAS in the General Facility Discharge samples during July-December 2021 are described below and summarized in Table 1.

$C_8HF_{15}O_8$ (mass to charge ratio 508.9357)

The compound with the initially suggested empirical formula of $C_8HF_{15}O_8$ was seen in the General Facility Discharge sample from Location 42 when the sample was analyzed in March 2020. However, when the sample was re-analyzed in December 2021, the compound was not detected (Figure 1).

The blank run just prior to the March 2020 analysis of the sample from Location 42 did not contain $C_8HF_{15}O_8$; therefore, the presence of $C_8HF_{15}O_8$ in the sample was not a result of carryover from a previous analysis.

The mass spectrum of $C_8HF_{15}O_8$ from March 2020 shows the presence of both the deprotonated compound ($C_8F_{15}O_8^-$) and the bicarbonate adduct ($C_8HF_{15}O_8 \bullet HCO_3^-$), confirming that the $C_8HF_{15}O_8$ itself is not the result of fragmentation of another compound in the ion source of the mass spectrometer (Figure 2). This bicarbonate anion adduct is usually seen in the analysis of per- and polyfluoroalkyl carboxylic acids and per- and polyfluoroalkyl ether carboxylic acids. The bicarbonate likely originates from dissolved carbon dioxide.

The sample from Location 42 consisted of four sample bottles. All four sample bottles were analyzed, with the same result that the compound was not detected; the possibility that the compound was present in one sample bottle but not another was therefore discounted (Figure 3).

$C_8HF_{15}O_8$ had not been detected initially (in March 2020) in any other General Facility Discharge locations; however, it had been detected initially in the sample from Location 16 (a Chemours Process Wastewater location). When the sample from Location 16 was re-analyzed in December 2021, $C_8HF_{15}O_8$ was also not detected (Figure 4).

"$C_4H_2F_6O_2$" (mass-to-charge ratio 194.9884)

The compound with the initially suggested empirical formula of $C_4H_2F_6O_2$ was shown to fragment to acetate and trifluoroacetate (TFA) and was therefore concluded to be a cluster consisting of an acetate ion, a sodium ion and a TFA ion, which formed in the ion source of the mass spectrometer. The correct empirical formula of this compound, therefore, is $C_4H_4F_3O_4Na$ and not $C_4H_2F_6O_2$. This was further supported by the presence of ion masses corresponding to TFA, a potassium/acetate/TFA cluster, a sodium/TFA dimer cluster and a potassium/TFA dimer cluster (Figure 5).

As was shown clearly in Interim Report #3, organic anions (such as acetate and TFA) along with sodium and potassium ions can combine in the ion source of the mass spectrometer to generate ion clusters that correspond to the mass-to-charge ratio of unknown compounds that can be misinterpreted to contain fluorine because the algorithm used to determine empirical formulas during the non-targeted analysis is not exact. This is a known limitation of the negative mass defect approach used in the algorithm. Fluorine, oxygen and sodium all have negative mass defects, and the unknown compound, containing both oxygen and sodium, was mistakenly flagged as fluorinated.

$C_8HF_{13}O_4$ (mass-to-charge ratio 406.9596)

The compound with the initially suggested empirical formula of $C_8HF_{13}O_4$ was shown to be R-EVE via standard confirmation (accurate mass and MS/MS fragmentation pattern; Figure 6). R-EVE (Chemical Abstracts Service Number 2416366-22-6) has previously been identified as a Site-related PFAS and is found on the Table 3+ analyte list.

"$C_4HF_9O_2S$" (mass-to-charge ratio 282.9471)

The compound with the initially suggested empirical formula of $C_4HF_9O_2S$ was shown to fragment to acetate and sulfate and was therefore concluded to be a cluster of two acetate ions, three sodium ion and a sulfate ion (SO_4^{2-}), which formed in the ion source of the mass spectrometer. The correct empirical formula of this compound, therefore, is $C_4H_7SO_8Na_3$ and not $C_4HF_9O_2S$. This was further supported by the presence of ion masses corresponding to bisulfate (HSO_4^-), a cluster of two sodium ions, an acetate ion and a sulfate ion and a cluster of four sodium ions, three acetate ions and a sulfate ion (Figure 7).

Sodium ions, sulfate and acetate combined in the ion source of the mass spectrometer to generate salts of the adduct corresponding to the mass-to-charge ratio of this compound. The compound is not fluorinated and, therefore, is not a PFAS.

"$C_6H_3F_7O_2$" (mass-to-charge ratio 238.9937)

The compound with the initially suggested empirical formula of $C_6H_3F_7O_2$ was shown to fragment to acetate and was therefore concluded to be a cluster of a sodium ion, a potassium ion, and three

acetate ions. The correct empirical formula of this compound, therefore, is $C_6H_{10}O_6NaK$ and not $C_6H_3F_7O_2$. This was further supported by the presence of an ion mass corresponding to a cluster containing two acetate ions and a sodium ion (Figure 8).

Sodium ions, potassium ions and acetate combined in the ion source of the mass spectrometer to generate a cluster ion corresponding to the mass-to-charge ratio of this compound. The compound is not fluorinated and, therefore, is not a PFAS.

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

Of the five most abundant PFAS in samples from Chemours Process Wastewater:

- three compounds had previously tentatively identified structures. Synthesis of authentic standards for these compounds is the next step. Synthetic pathways are under consideration.
- one compound had a previously tentatively identified structure, which was found to be incorrect upon comparison to an existing authentic standard. A revised tentatively identified structure is being developed.
- one compound had previously been identified as EVE Acid, and no further work is required for this compound.

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

4 SUMMARY AND NEXT STEPS

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

Of the next five most abundant unknown “PFAS” in the General Facility Discharge samples, one compound ($C_8HF_{15}O_8$) was not detected in the samples where it had been previously detected. Further investigation into this compound will be conducted by collecting a new sample from Location 42 (during a rain event, as had been done previously). The new sample will be analyzed for the presence of $C_8HF_{15}O_8$, and, if found, the sample will be analyzed several times over a period of months to see if the compound remains stable. The remaining four compounds were successfully identified (one as R-EVE, one as an adduct of TFA, and two as adducts of acetate that do not contain fluorine and are not PFAS).

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Of the five most abundant unknown PFAS in the Chemours Process Wastewater samples, synthesis of authentic standards for three of compounds is the next step. Synthetic pathways, which are expected to be challenging, are under consideration. A tentatively identified structure for the fourth unidentified compound, $C_8H_5F_{13}O_6S$, is being developed. The fifth compound had previously been identified as EVE Acid and does not require additional work.

5 REFERENCES

Chemours, 2021. PFAS Non-Targeted Analysis and Methods Interim Report #3. July 30, 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 #4
Chemours Fayetteville Works, North Carolina

Sample Source	Mass (Da)	Mass to Charge Ratio (m/z)	Empirical Formula		Identified Structure	Next Steps
			Initially Suggested	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. 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.
	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	$C_8HF_{15}O_8$	--	Compound no longer detected in original samples.	Collect new sample from Location 42 during a rain event to investigate presence and temporal stability of this compound
	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	$C_8H_2F_{14}O_7S$	--	Structure tentatively identified: CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H	Synthesis of an authentic standard for this compound is under consideration.
	407.9670	406.9598	$C_8HF_{13}O_4$	--	Identified as EVE Acid in Interim Report #3 (July 2021)	None
	475.9587	474.9515	$C_8H_5F_{13}O_6S$	--	No tentatively identified structure yet	Continue to develop a tentatively identified structure
	471.9630	470.9556	$C_9H_2F_{14}O_6$	--	Structure tentatively identified: HOOC-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CF(CF_3)-COOH	Synthesis of an authentic standard for this compound is under consideration.
	345.9693	344.9620	$C_6HF_{11}O_4$	--	Structure tentatively identified: CF_3-O-CF_2-O-CF_2-CF_2-CF_2-COOH	Synthesis of an authentic standard for this compound is under consideration.

Notes:

* - empirical formula initially suggested has been revised following further investigation

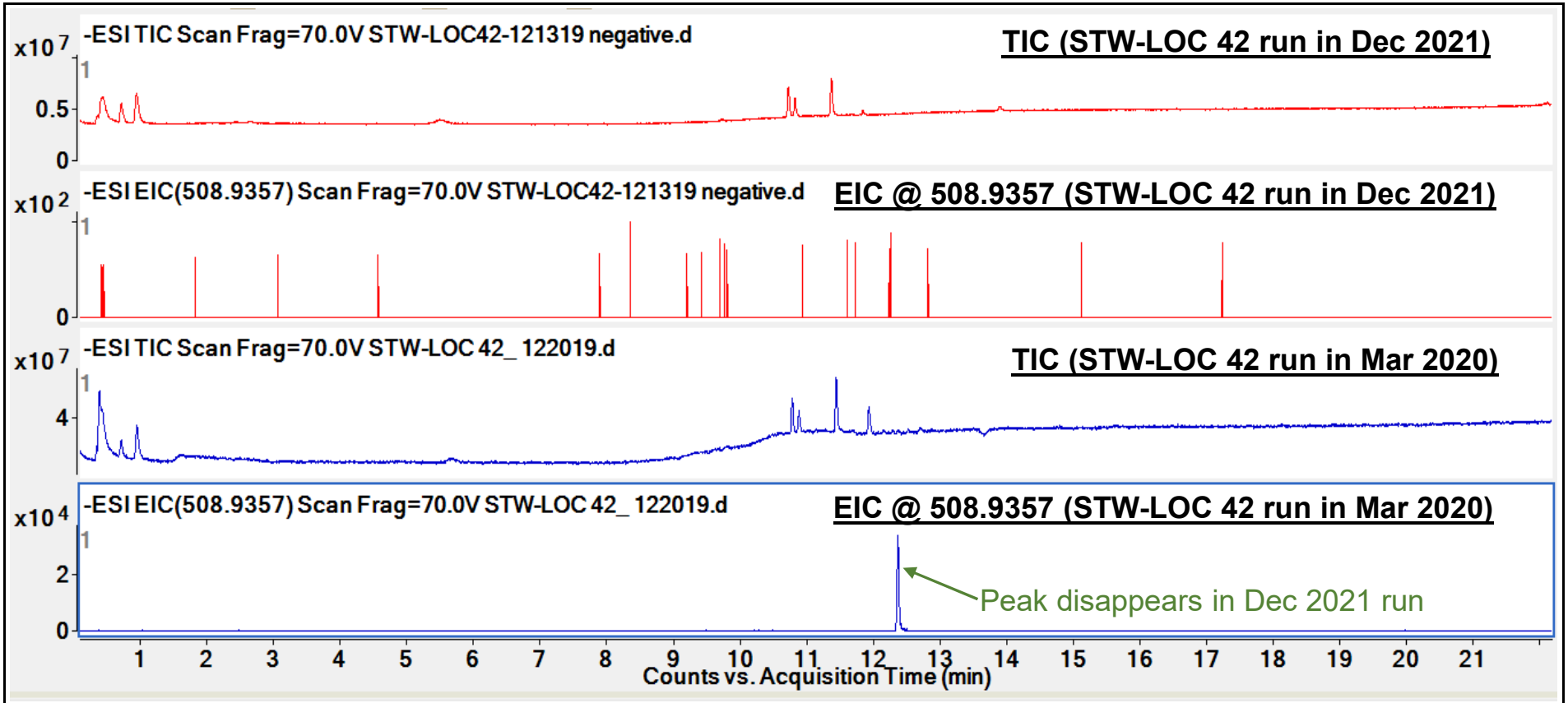
-- - revised empirical formula not required

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 as determined during January-June 2021 work

- further investigation not required as determined during July-December 2021 work

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 for mass-to-charge ratio of 508.9357
TIC - total ion chromatogram
m/z - mass-to-charge ratio

Total Ion Chromatograms and Extracted Ion Chromatograms (m/z 508.9357) of $C_8HF_{15}O_8$ in December 2021 and March 2020 Analyses of Sample from Location 42
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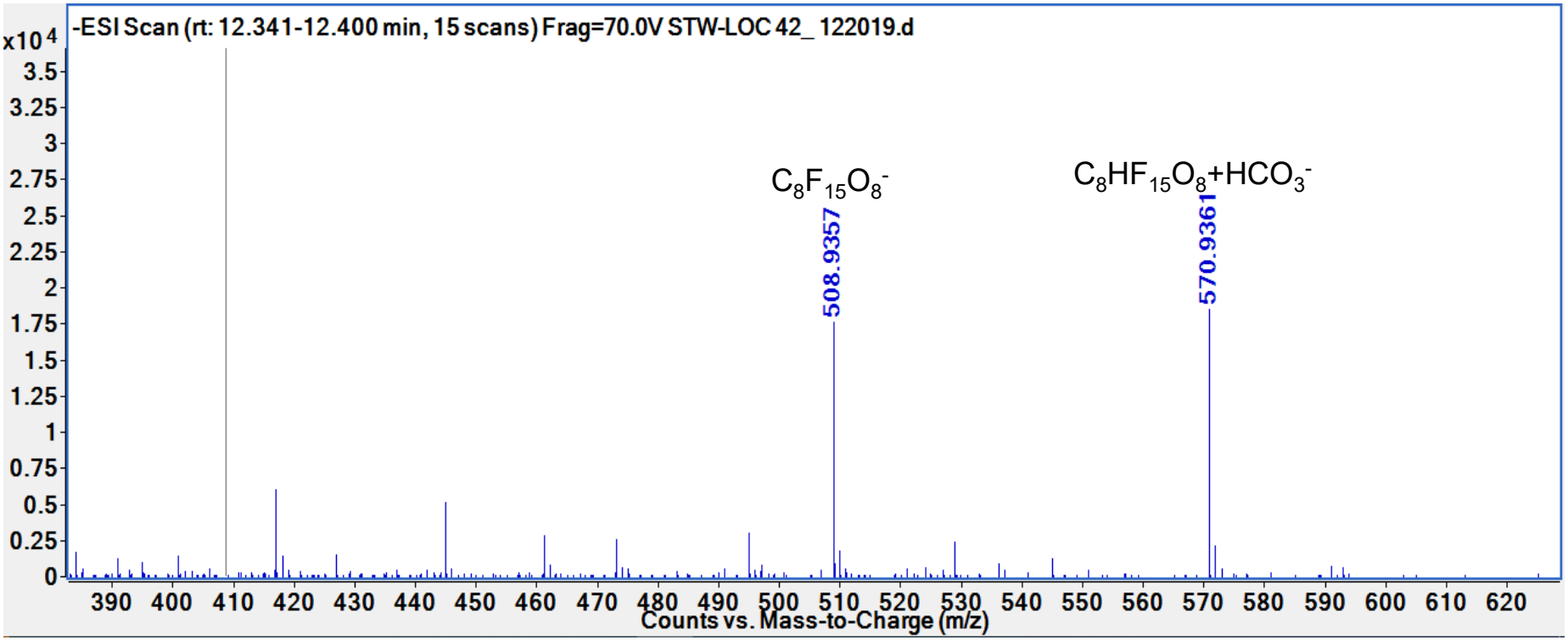
Figure 1



Notes:
EIC - extracted ion chromatogram
HCO_3^- - bicarbonate

Detection of Deprotonated $C_8HF_{15}O_8$ and Bicarbonate Adduct of $C_8HF_{15}O_8$
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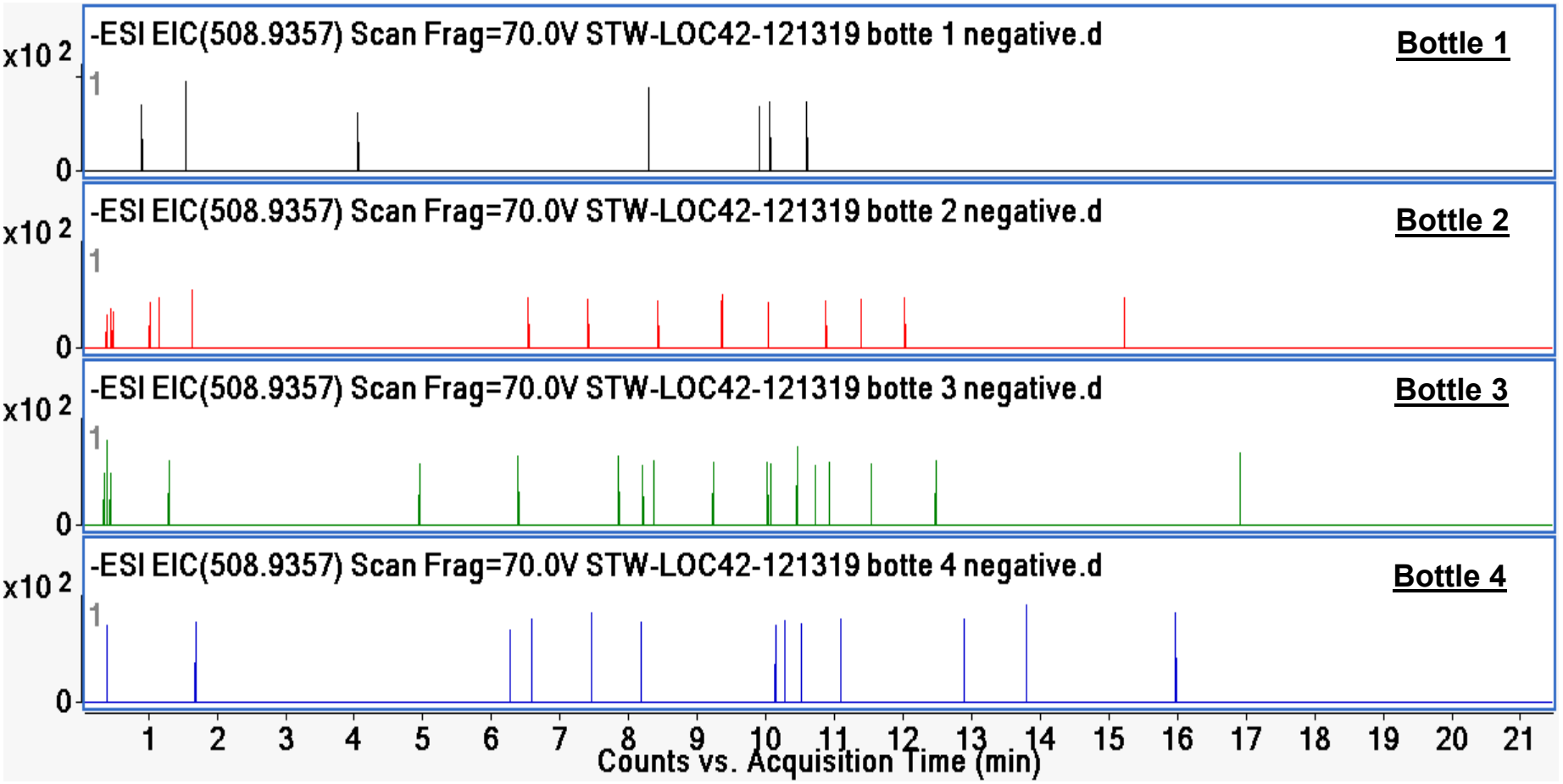
Figure **2**



Notes:
EIC - extracted ion chromatogram for mass-to-charge ratio of 508.9357

Extracted Ion Chromatograms (m/z 508.9357) of Four Sample Bottles from Location 42 Analyzed in December 2021

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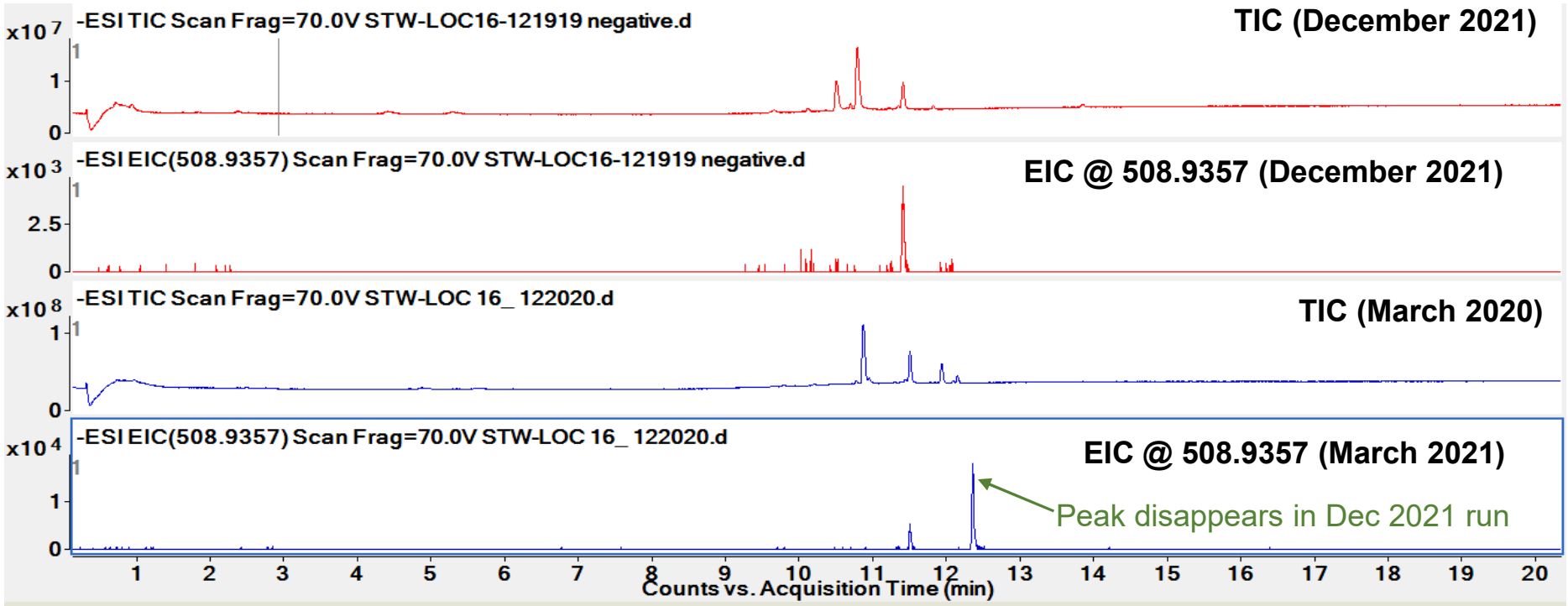
Figure **3**



Notes:
EIC - extracted ion chromatogram for mass-to-charge ratio of 508.9357
TIC - total ion chromatogram

Total Ion Chromatograms and Extracted Ion Chromatograms (m/z 508.9357) of $C_8HF_{15}O_8$ in December 2021 and March 2020 Analyses of Sample from Location 16
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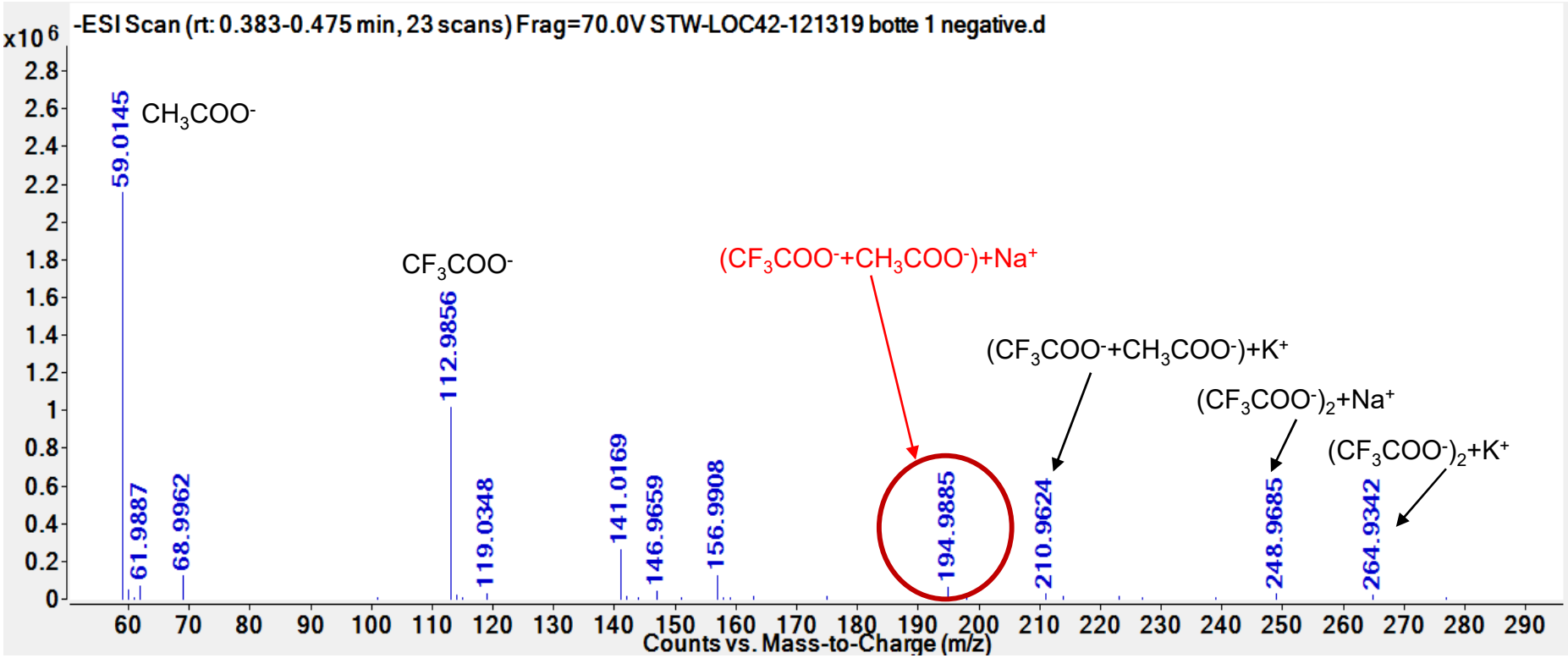
Figure 4



Notes:

CH_3COO^- - acetate

CF_3COO^- - trifluoroacetate

K^+ - potassium ion

Na^+ - sodium ion

Extracted Ion Chromatogram for "$C_4H_2F_6O_2$"

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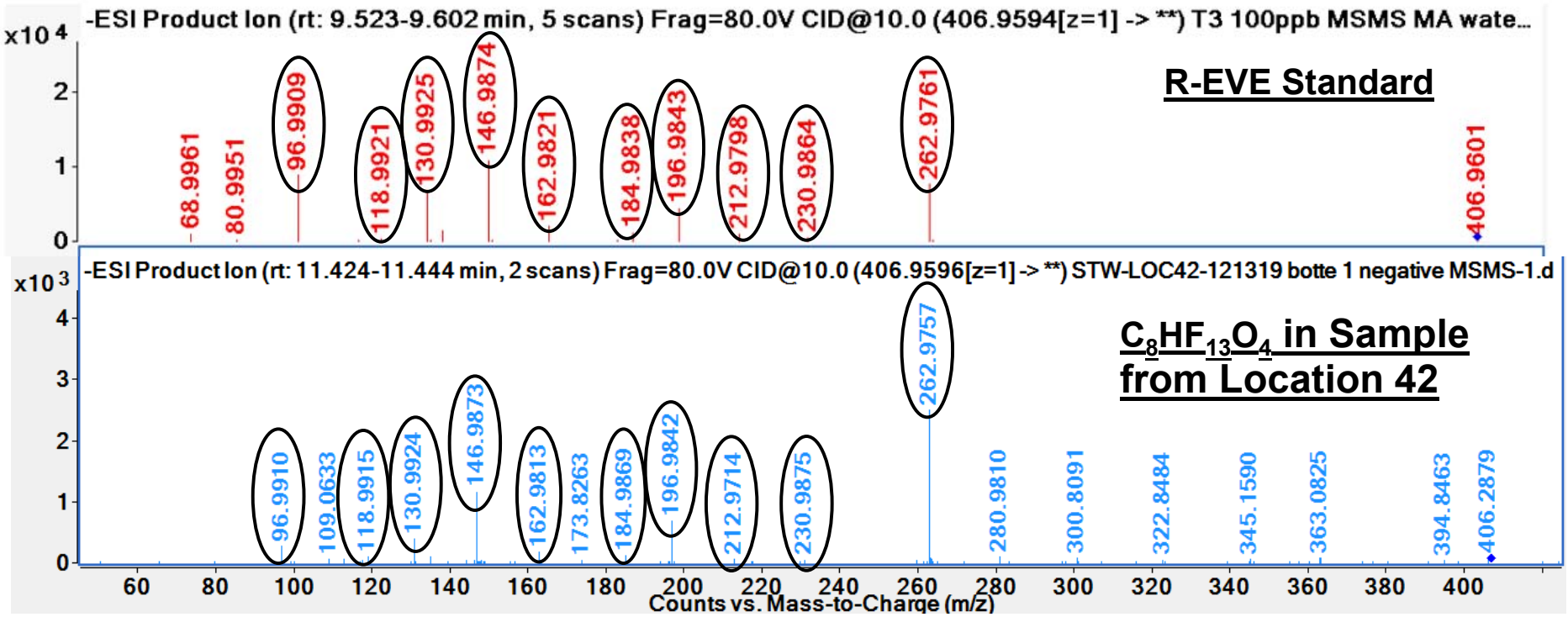
Figure

5



MS/MS Fragmentation of R-EVE Standard and of $C_8HF_{13}O_4$ in Sample from Location 42

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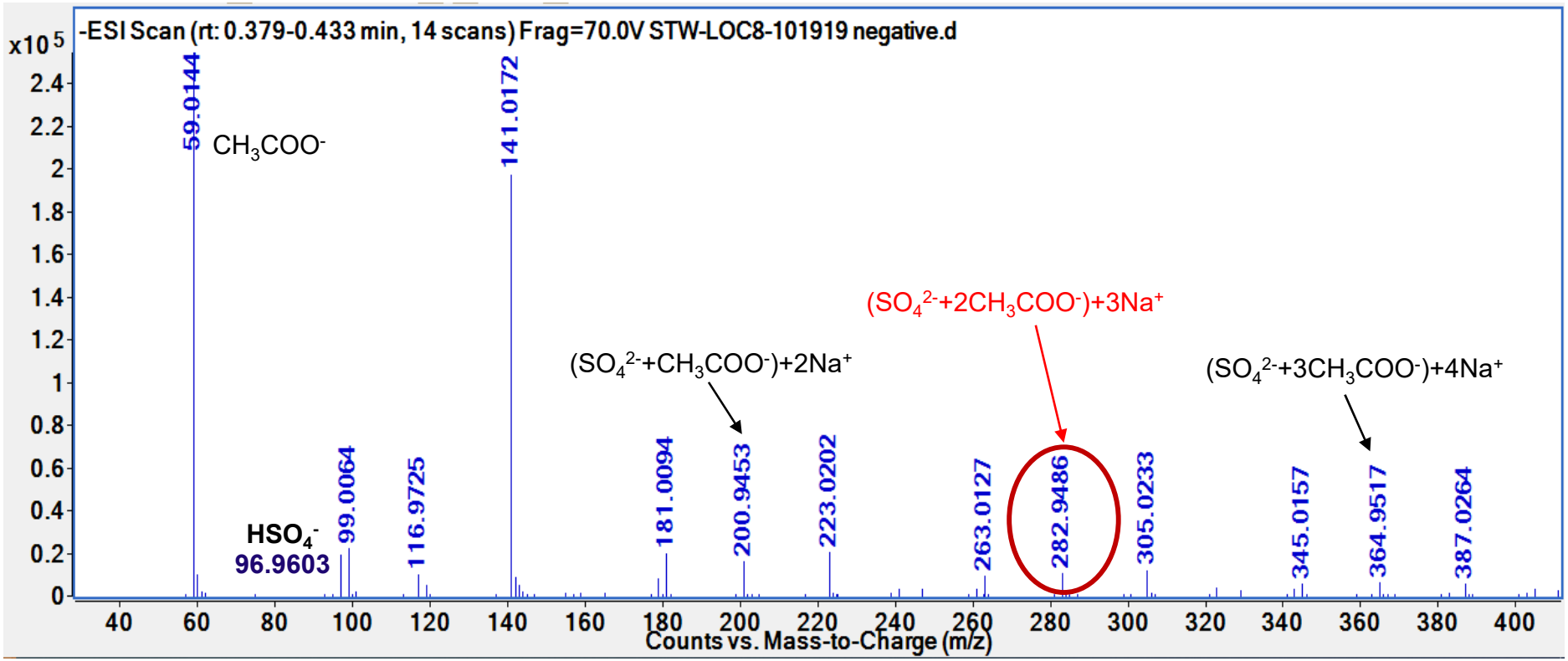
Figure 6



Notes:

CH_3COO^- - acetate

HSO_4^- - bisulfate

Na^+ - sodium ion

SO_4^{2-} - sulfate

Extracted Ion Chromatogram for "$C_4HF_9O_2S$"

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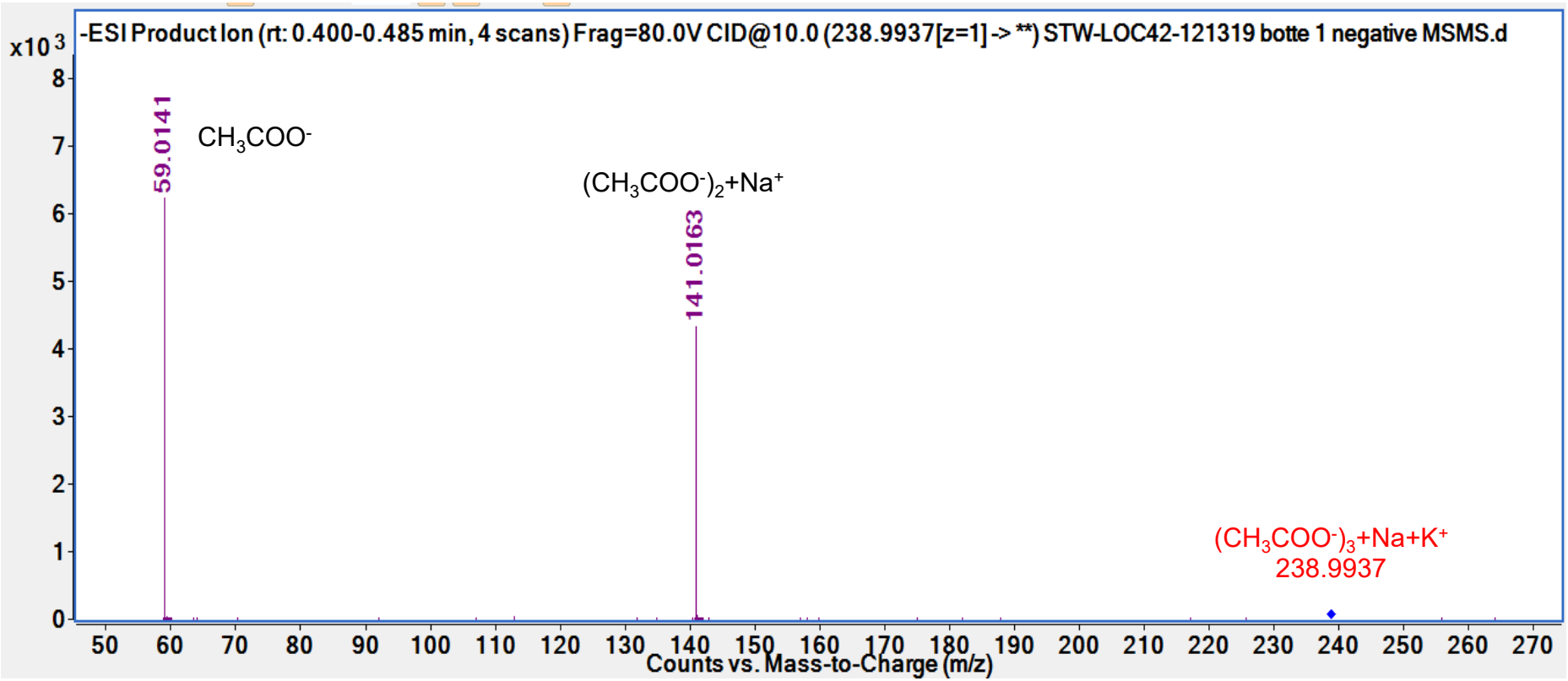
Figure

7



Notes:

CH_3COO^- - acetate

K^+ - potassium ion

Na^+ - sodium ion

Extracted Ion Chromatogram for "$C_6H_3F_7O_2$"

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Figure

8