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PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT #8

Process and Non-Process Wastewater and Stormwater

Prepared by

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ACRONYMS AND ABBREVIATIONS

Chemours	The Chemours Company FC, LLC
DA	diadduct
Facility	Chemours Fayetteville Works, North Carolina
LC	liquid chromatography
PFAS	per- and polyfluoroalkyl substances
PFO_6TeA	pentadecafluoro-2,4,6,8,12-hexaoxatetradecan-14-oic acid
RHDA	RSU/HFPO Diadduct
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 with the Cape Fear River Watch 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 8th 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) due to 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 analysis identified 21 potentially unknown PFAS present in General Facility Discharge samples and 250 potentially unknown PFAS present in Chemours Process Wastewater samples, with a total of 257 potential unique unknown PFAS (14 unknown PFAS were present in both types of samples). Two of the unknown PFAS were later identified as TFA and HFPO Trimer Acid, and not carried forward further in the non-targeted analysis program. Empirical formulas were determined for all unknown PFAS. This work represented the first part of the Initial Assessment step in the Development Plan. The second part of the Development Plan, the Enhanced Assessment

is to develop tentative molecular structures and subsequently, for the highest priority detected samples, develop authentic standards (i.e., synthesize samples of the compounds to facilitate traditional targeted analysis). To prioritize developing authentic standards for the most abundant unknown PFAS for each grouping of samples (General Facility Discharge and Chemours Process Wastewater), the 5 most abundant unknown PFAS from each group were advanced to the Enhanced Assessment step. As each group of 5 unknown PFAS from each group is resolved, the next group of 5 will be advanced to the Initial Assessment step. The status of the unknown PFAS in each group prior to this report is provided below; further details are provided in the references (Chemours, 2020a, 2020b, 2021a, 2021b, 2022a, 2022b, 2023).

General Facility Discharge Samples

The 5 most abundant unknown PFAS from the General Facility Discharge samples were 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 and are not PFAS. The next group of 5 unknown PFAS is currently under investigation.

The status of the 10 most abundant unknown PFAS in the General Facility Discharge samples prior to this report was:

- seven (GFD-1, -2, -3, -4, -5, -9 and -10) 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 (GFD-6) has a proposed molecular structure, and a commercial standard for the proposed molecular structure is available. The commercial standard has been purchased by Chemours and has undergone purification by Chemours so that accurate assessment of the $C_8HF_{15}O_8$ peak can be undertaken.
- one (GFD-7) was identified as the sodium salt of a TFA acetate adduct; and
- one (GFD-8) was identified as R-EVE, which is a known PFAS associated with the Facility.

Chemours Process Wastewater Samples

The status of the 5 most abundant unknown PFAS in the Chemours Process Wastewater samples prior to this report was:

- one (CPWW-1) was identified as potentially being present in one of the production processes at the Facility. Samples from the production process have been obtained from the Facility and have been purified to isolate the production PFAS at sufficient purity that it can be used as a standard;
- one (CPWW-2) was identified as EVE Acid, which is a known PFAS associated with the Facility;
- one (CPWW-3) was identified as an unknown PFAS, and a molecular structure has not yet been proposed; and
- two (CPWW-4 and -5) were identified as unknown PFAS, and molecular structures have been proposed.

The remainder of this 8th interim 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

The peak corresponding to $C_8HF_{15}O_8$ (GFD-6) in General Facility Discharge samples was assessed against the commercial standard (pentadecafluoro-2,4,6,8,12-hexaoxatetradecan-14-oic acid (PFO_6TeA)) corresponding to the structure proposed for $C_8HF_{15}O_8$ (CF_3-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-COOH). Results showed that:

- the retention times of the peaks on the liquid chromatograph were identical (Figure 1);
- the mass spectra of the peaks were identical (Figure 1); and
- the fragmentation patterns of the largest ion (with a mass-to-charge ratio of 508.93) in the mass spectra were identical (Figure 2).

The peak corresponding to $C_8HF_{15}O_8$ in General Facility Discharge samples was consequently concluded to be PFO_6TeA.

The current status of the second set of 5 most abundant PFAS in the General Facility Discharge samples (as well as of the first set of 5 most abundant PFAS) is summarized in Table 1.

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

The most abundant unknown PFAS in the Chemours Process Wastewater samples (CPWW-1; $C_8H_2F_{14}O_7S$) had the proposed structure of CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H which was identified as an intermediate product, RSU/HFPO Diadduct (RHDA), in one of the production processes at the Facility. RHDA was isolated from a production sample and the peak corresponding to CPWW-1 in Chemours Process Wastewater samples was then assessed against this RHDA standard.

Results showed that:

- the retention times of the peaks on the liquid chromatograph were identical (Figure 3);
- the mass spectra of the peaks were identical (Figure 3); and
- the fragmentation patterns of the largest ion (with a mass-to-charge ratio of 506.92) in the mass spectra were identical (Figure 2).

The peak corresponding to CPWW-1 in Chemours Process Wastewater samples was consequently concluded to be the RHDA salt.

The current status of the 5 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.

General Facility Discharge Samples

The current status of the 10 most abundant unknown PFAS in the General Facility Discharge samples is:

- seven (GFD-1, -2, -3, -4, -5, -9 and -10) 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 (GFD- 6) was identified as PFO_6TeA by comparison to a recently available commercial standard (this report);

- one (GFD-7) was identified as the sodium salt of a TFA acetate adduct. TFA is a known PFAS associated with the Facility; and
- one (GFD-8) was identified as R-EVE, which is a known PFAS associated with the Facility.

Of the 10 most abundant unknowns in the General Facility Discharge samples, 9 have been shown to not be PFAS or to be previously known PFAS. The tenth has been shown to be PFO_6TeA, for which an authentic standard is available. The next step for PFO_6TeA, according to the Workplan (Chemours and Geosyntec Consultants, 2019), is to develop a test method. PFO_6TeA will be analyzed using existing test methods to assess if it can be adequately separated and accurately quantified in the presence of other Table 3+ PFAS. If not, additional test methods will be developed. A method detection limit study will be conducted to establish a reporting limit and a matrix interference study will be conducted to assess the quantification of PFO_6TeA in environmental matrices related to the Facility.

Additionally, Chemours will begin work on identifying the molecular structures of the third set of five most abundant unknown PFAS (GFD-11 through -15) in the General Facility Discharge samples.

Chemours Process Wastewater Samples

The current status of the 5 most abundant unknown PFAS in the Chemours Process Wastewater samples is:

- one (CPWW-1) was identified as RHDA by comparison to a standard purified from production samples (this report);
- one (CPWW-2) was identified as EVE Acid, which is a known PFAS associated with the Facility;
- one (CPWW-3) was identified as a potential unknown PFAS, and a molecular structure has not yet been proposed; and
- two (CPWW-4 and -5) were identified as potential unknown PFAS, and molecular structures have been proposed.

The next step for the Chemours Process Wastewater samples to develop a synthetic pathway for RHDA so that an authentic standard can be produced. The production of an authentic RHDA standard will likely take several months, after which a test method can be developed (as described above for PFO_6TeA).

Additionally, Chemours will continue to develop a molecular structure for CPWW-3 (so that a synthetic pathway can be developed), and to develop synthetic pathways for CPWW-4 and -5 (so that authentic standards can be produced). Note that the synthetic pathways are challenging, and this process may take considerable time to complete given the complex structure of these

compounds. Chemours will also begin work on identifying the molecular structures of the second set of five most abundant unknown PFAS (CPWW-6 through -10) in the Chemours Process Wastewater samples.

5 REFERENCES

Chemours, 2023. PFAS Non-Targeted Analysis and Methods Interim Report #7. June 30, 2023.

Chemours, 2022a. PFAS Non-Targeted Analysis and Methods Interim Report #5. June 30, 2022.

Chemours, 2022b. PFAS Non-Targeted Analysis and Methods Interim Report #6. December 30, 2022.

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 #8
Chemours Fayetteville Works, North Carolina

Sample Source	Rank (by Ion Abundance in Sample Source)	Mass (Da)	Mass to Charge Ratio (m/z)	Empirical Formula		Proposed Molecular Structure	Next Step For Identification of Unknown
				Tentative	Revised		
General Facility Discharge	GFD-1	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
	GFD-2	157.9983	156.9910	$C_4H_2F_4O_2$*	$C_4H_6O_4K$		
	GFD-3	224.0272	223.0199	$C_6H_6F_6O_2$*	$C_6H_{10}O_6Na_2$		
	GFD-4	306.0302	305.0230	$C_8H_7F_9O_2$*	$C_8H_{13}O_8Na_3$		
	GFD-5	388.0331	387.0258	$C_{10}H_8F_{12}O_2$*	$C_{10}H_{16}O_{10}Na_4$		
	GFD-6	509.9432	508.9357	$C_8HF_{15}O_8$	--	Structure identified as pentadecafluoro-2,4,6,8,12-hexaoxatetradecan-14-oic acid by comparison to authentic standard.	None
	GFD-7	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
	GFD-8	407.9670	406.9596	$C_8HF_{13}O_4$	--	Identified as R-EVE	None
	GFD-9	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
	GFD-10	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	CPWW-1	507.9302	506.9229	$C_8H_2F_{14}O_7S$	--	Structure identified as a production intermediate, RSU/HFPO Diadduct, by comparison to authentic standard.	Develop a synthetic pathway for RSU/HFPO Diadduct so that standard solutions can be created.
	CPWW-2	407.9670	406.9598	$C_8HF_{13}O_4$	--	Identified as EVE Acid	None
	CPWW-3	475.9587	474.9515	$C_8H_5F_{13}O_6S$	--	No proposed molecular structure yet	Continue to develop a proposed molecular structure.
	CPWW-4	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.
	CPWW-5	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:

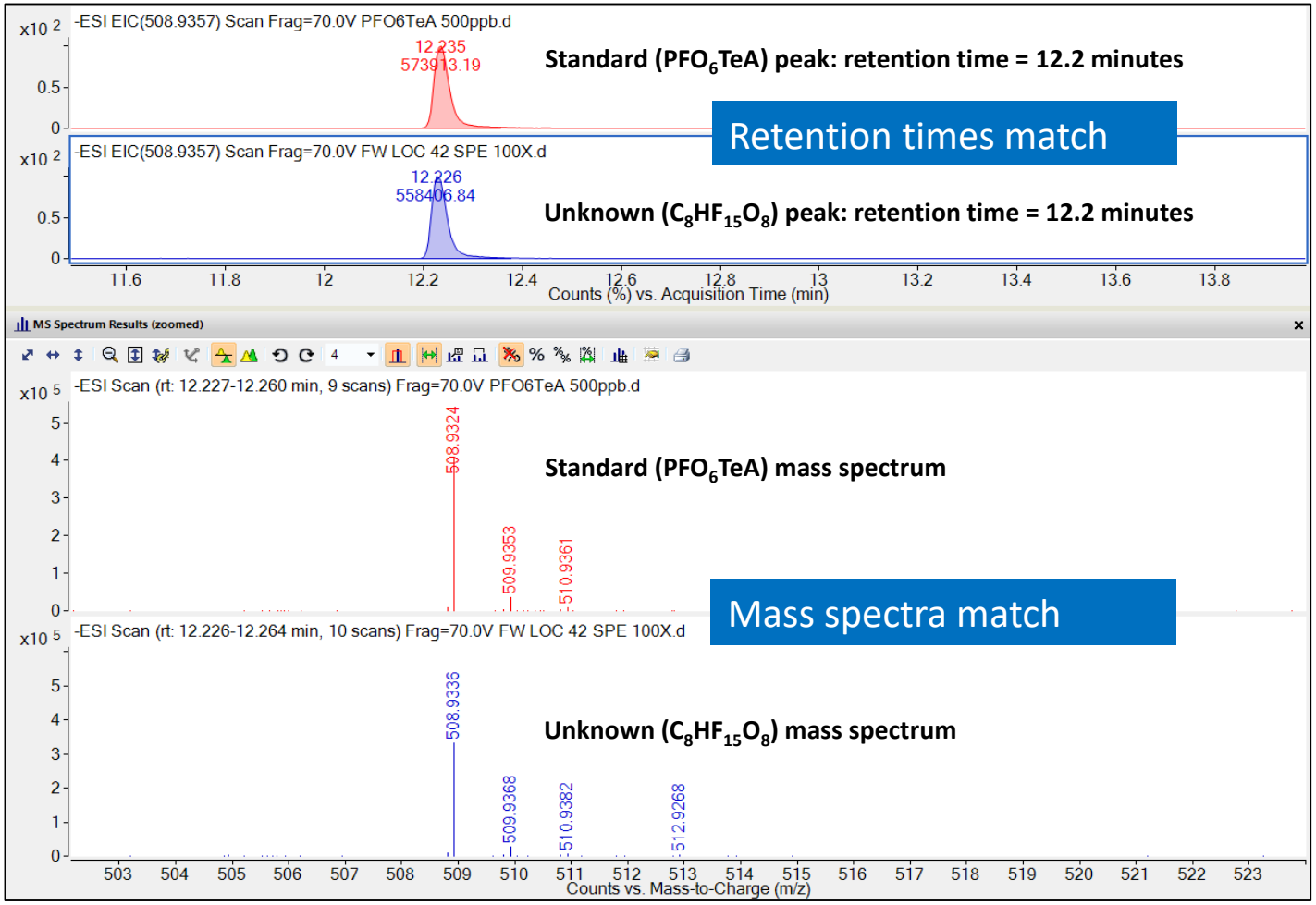
* - tentative empirical formula has been revised following further investigation

-- - 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 into identification of unknown 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

PFO_6TeA - pentadecafluoro-2,4,6,8,12-hexaoxatetradecan-14-oic acid

Retention Times and Mass Spectra for Unknown $C_8HF_{15}O_8$ (in Sample from Location 42) and PFO_6TeA Standard

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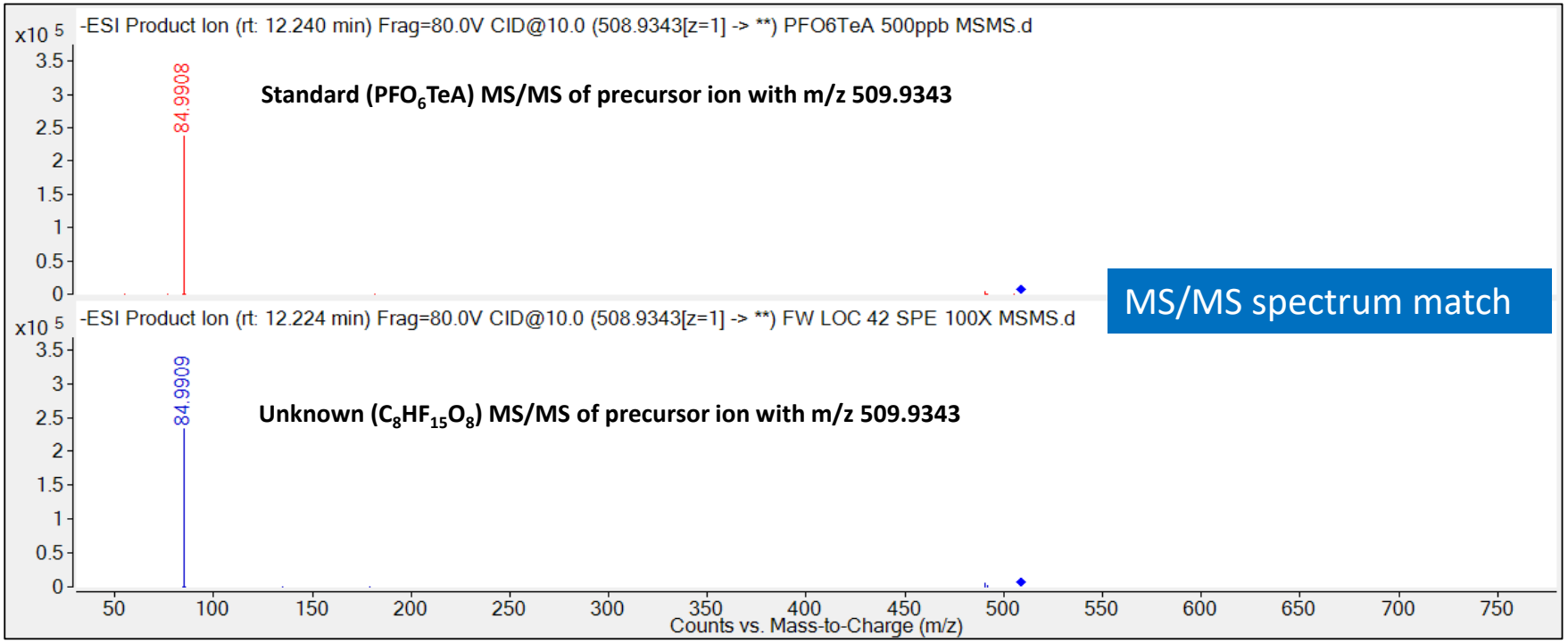
Figure

1



Notes:

EIC - extracted ion chromatogram for mass-to-charge ratio of 508.9343

m/z - mass to charge ratio

PFO_6TeA - pentadecafluoro-2,4,6,8,12-hexaoxatetradecan-14-oic acid

Tandem Mass Spectra for Unknown $C_8HF_{15}O_8$ (in Sample from Location 42) and PFO_6TeA Standard

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Figure **2**

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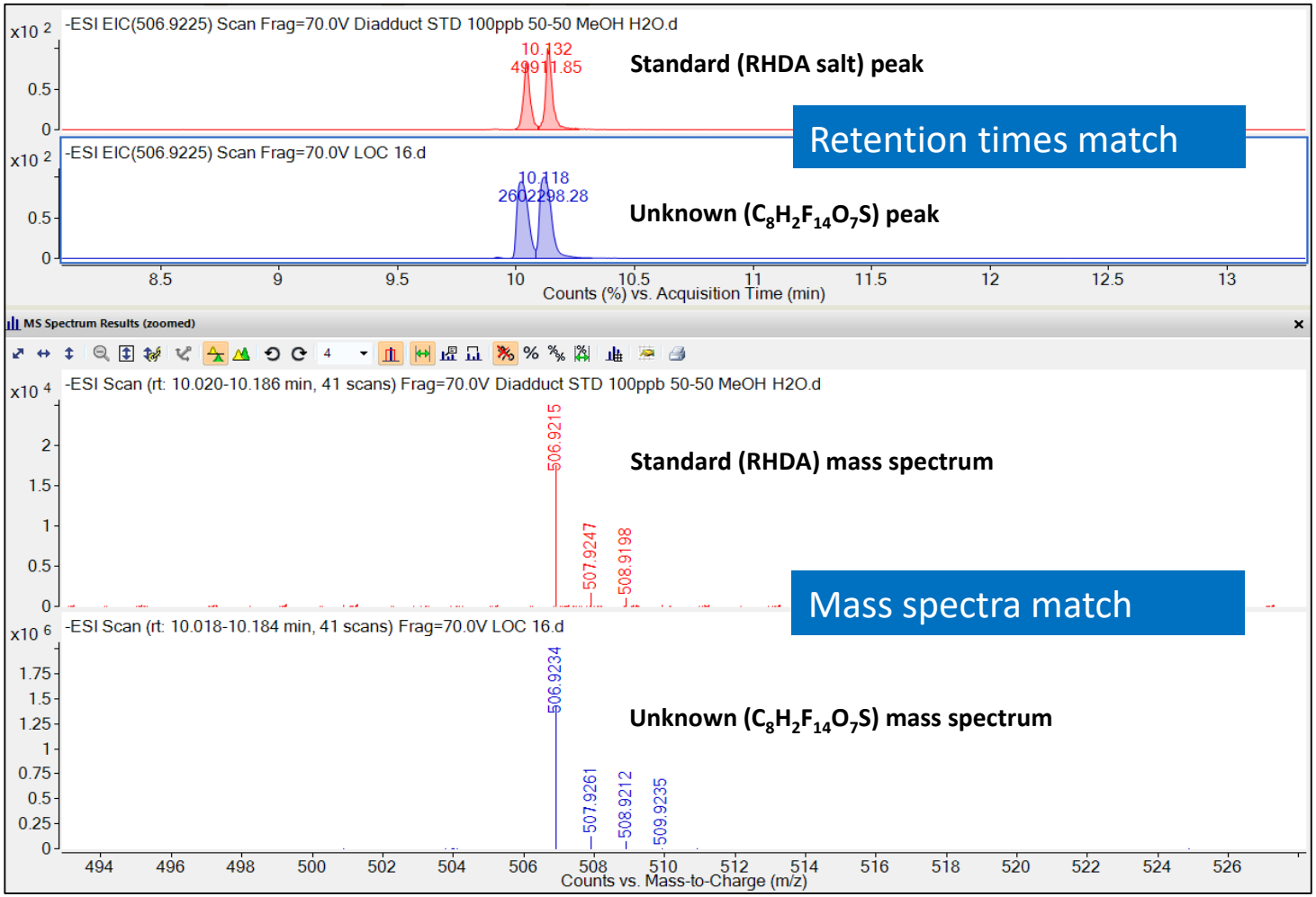

Notes:

EIC - extracted ion chromatogram
RHDA - RSU/HFPO Diadduct

Retention Times and Mass Spectra for Unknown $C_8H_2F_{14}O_7S$ (in Sample from Location 16) and RHDA Standard
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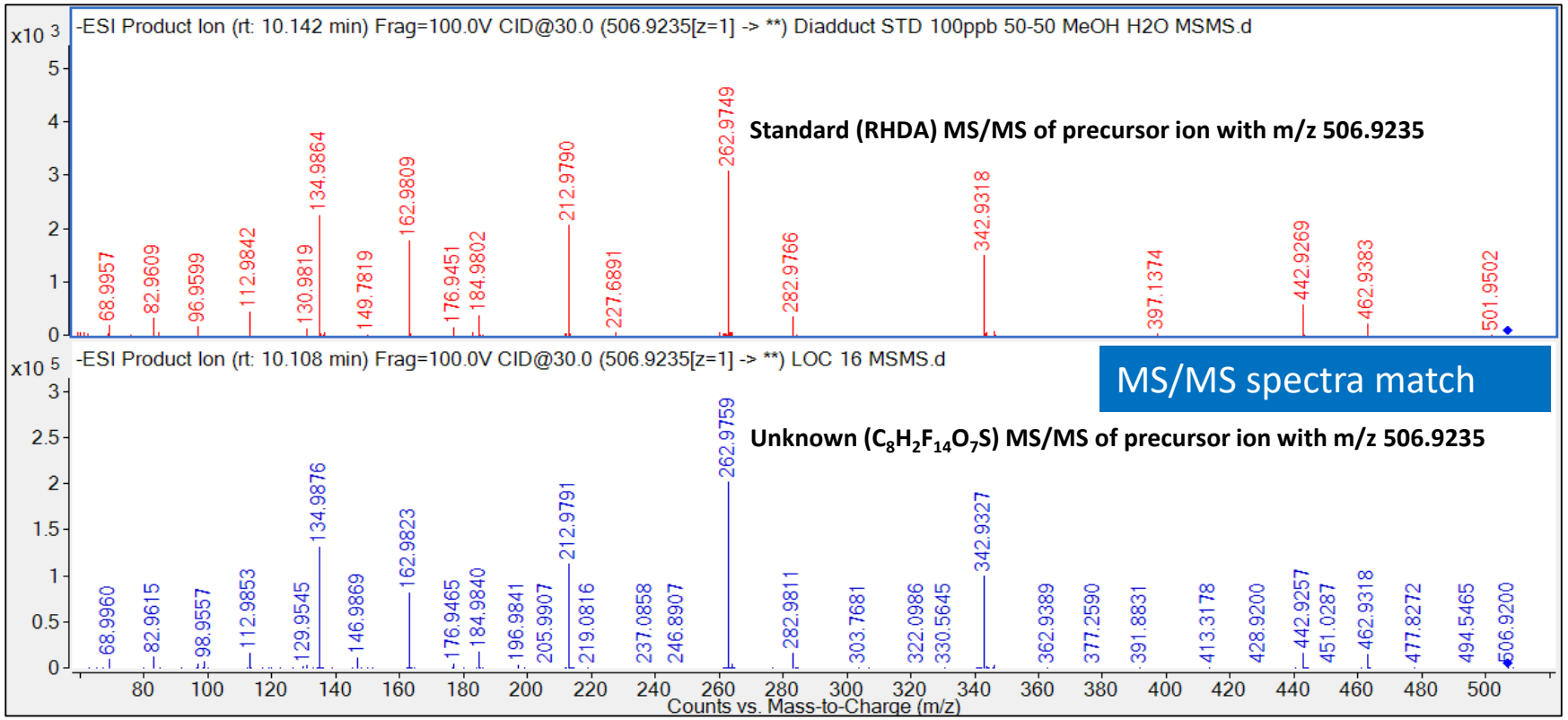
Figure

3



Notes:

EIC - extracted ion chromatogram for mass-to-charge ratio of 508.9343

m/z - mass to charge ratio

RHDA - RSU/HFPO Diadduct

Tandem Mass Spectra for Unknown $C_8H_2F_{14}O_7S$ (in Sample from Location 16) and RHDA Standard

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Figure

4