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Novel Algorithms and Visualizations for Discovering Polymers and Chemical Series in Industrial and Environmental Applications

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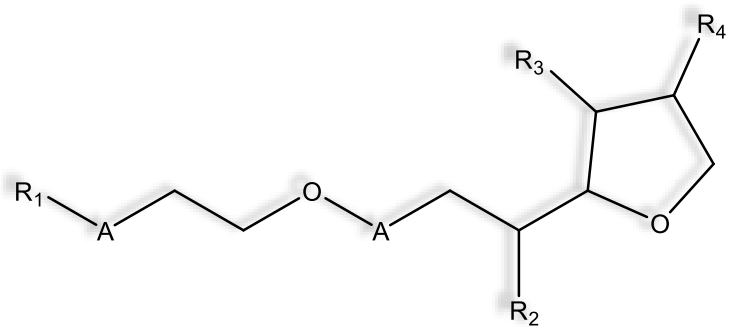
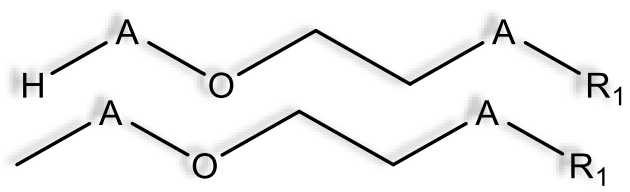
Introduction

Polymers and chemicals that form series are essential in every day products including plastics, emulsifiers, lubricants, and detergents. The physicochemical properties and health impacts of a product are determined by the properties of molecules in each mixture, such as number of repeating units, chemical moieties and degree of unsaturation. Thus, it is essential to be able to characterize these mixtures at the molecular level. The repeating nature of chemical moieties means that mass spectra and chromatographic data of polymers and chemical series have obvious patterns, which when discerned can be used to comprehensively characterize a sample. After the success of the LipidMatch and FluoroMatch workflows for non-targeted analysis which take advantage of these unique spectral patterns, we present a new workflow for polysorbates and related species.

Libraries

Class based libraries with fragmentation rules were generated for over 150,000+ species across 16 different types of polysorbate, polysorbide, and PEG classes, including with and without fatty acids.

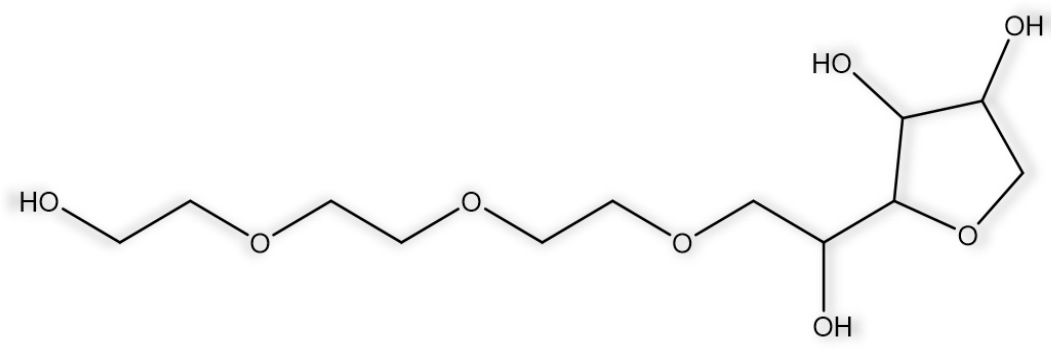




Libraries are also generated for data that just contain MS/MS fragments corresponding to PEG fragments, forming over 64,450 PEG species. Below is an example of the naming conventions and identifications in PolySorbate 80.

Simulated PEGs: **64,450** species

Structures and Naming Conventions:



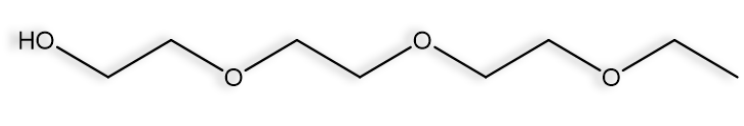
Polysorbate 80:

580+ unique structures

217 with at least one NH_3

74 with ketones

332 as NH_4^+ adducts…



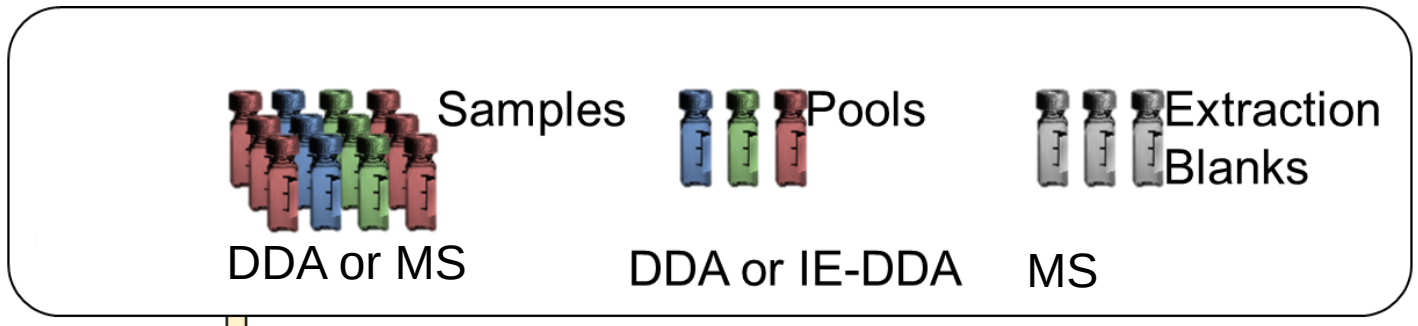
PEG(n=3_NH4+_CH2=6_DBE=4_(4-OH))

PEG(n=4_NH4+_CH2=0_DBE=0_)

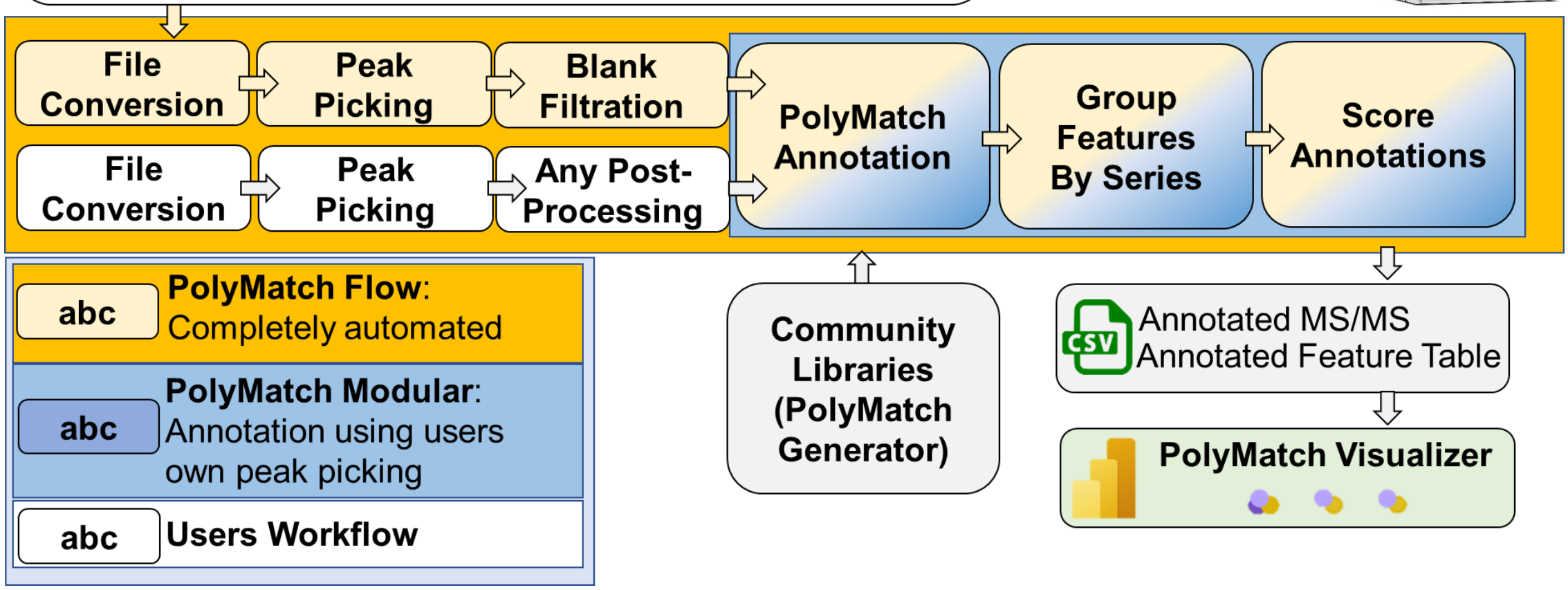
Example	Definition	Built-in Range
n=3	Number of PEG units	3 - 44
NH4+	Adduct	NH4+, Na+, H+
CH2=6	Number of carbons (non-PEG)	0 - 19
DBE=4	Double bond equivalents	0 - 6
(4-OH)	Functional groups	OH (0-4), NH3 (0-2), =O (0-2)

PolyMatch Flow and PolyMatch Modular (acquisition and data-processing workflow)

The PolyMatch software data analysis workflow starts by importing data collected using MS, and MS/MS data dependent (DDA), iterative exclusion MS/MS, or targeted MS/MS modes from individual, pooled and blank samples. PolyMatch algorithms cover file -conversion, blank filtering, feature annotation, and visualization via PolyVI (visualization software). One can also generate your own libraries using PolyMatch Generator from your own series of compounds. The PolyMatch Software also directly imports data processed initially using Agilent's Mass Profiler software or other peak picking software.

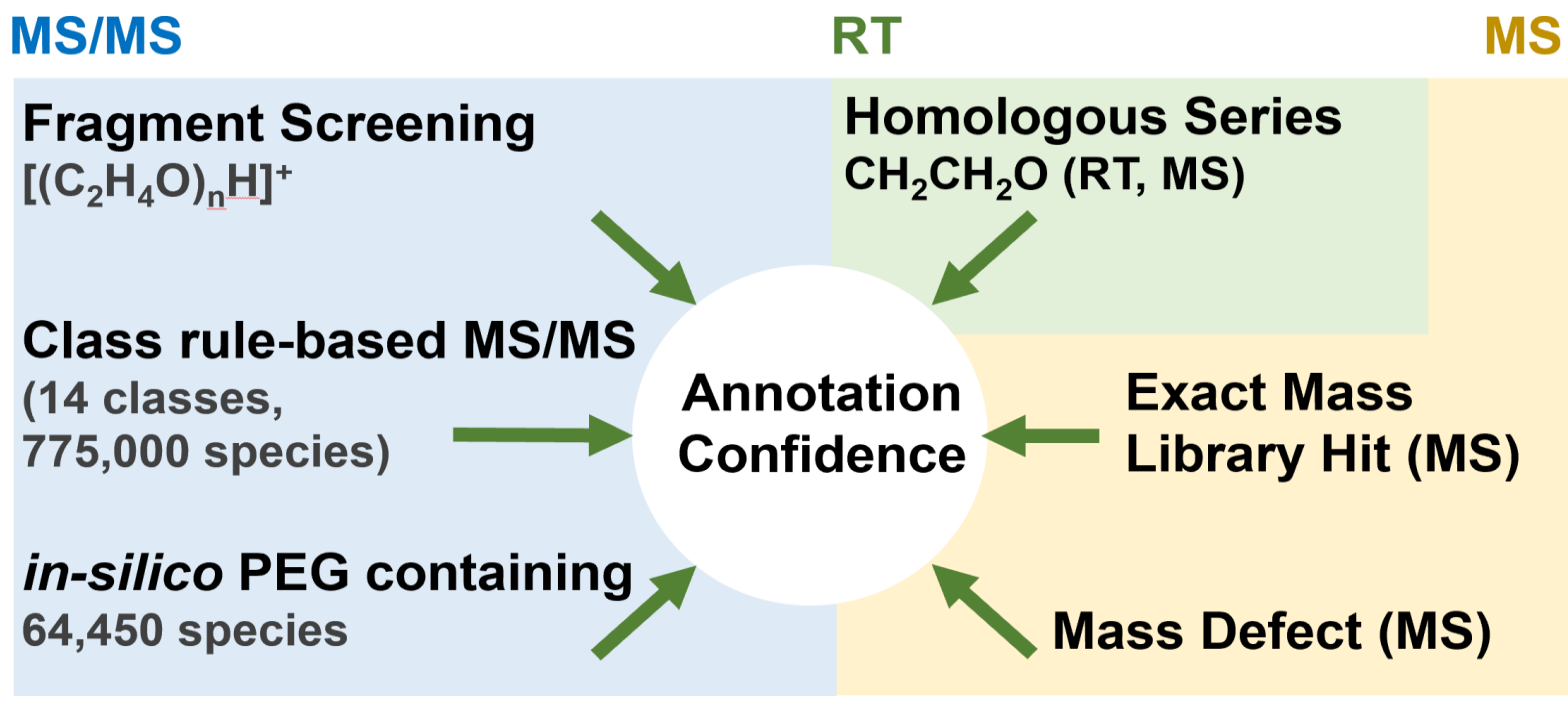


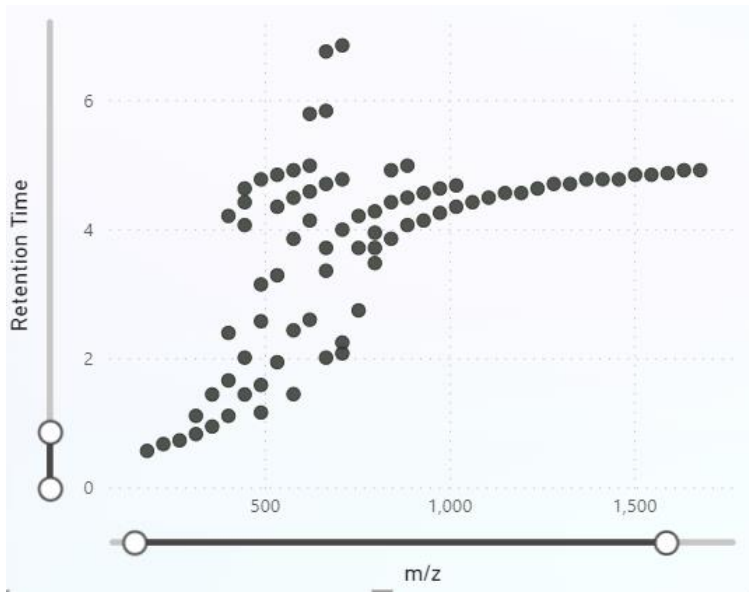
Data was acquired on an Agilent 6546 LC/Q-TOF for this study



Annotation Evidence Compiled by PolyMatch

PolyMatch integrates a wide range of evidence to classify polymers: mass defect, retention time, and exact mass can be used alongside homologous series to compile groups of chemicals that likely belong to the same class. MS/MS evidence can give structural information pertaining to class or species level assignments. Evidence used for annotation is shown bottom left and a homologous series retention time vs *m/z* is shown for Polysorbate-PEG bottom right.



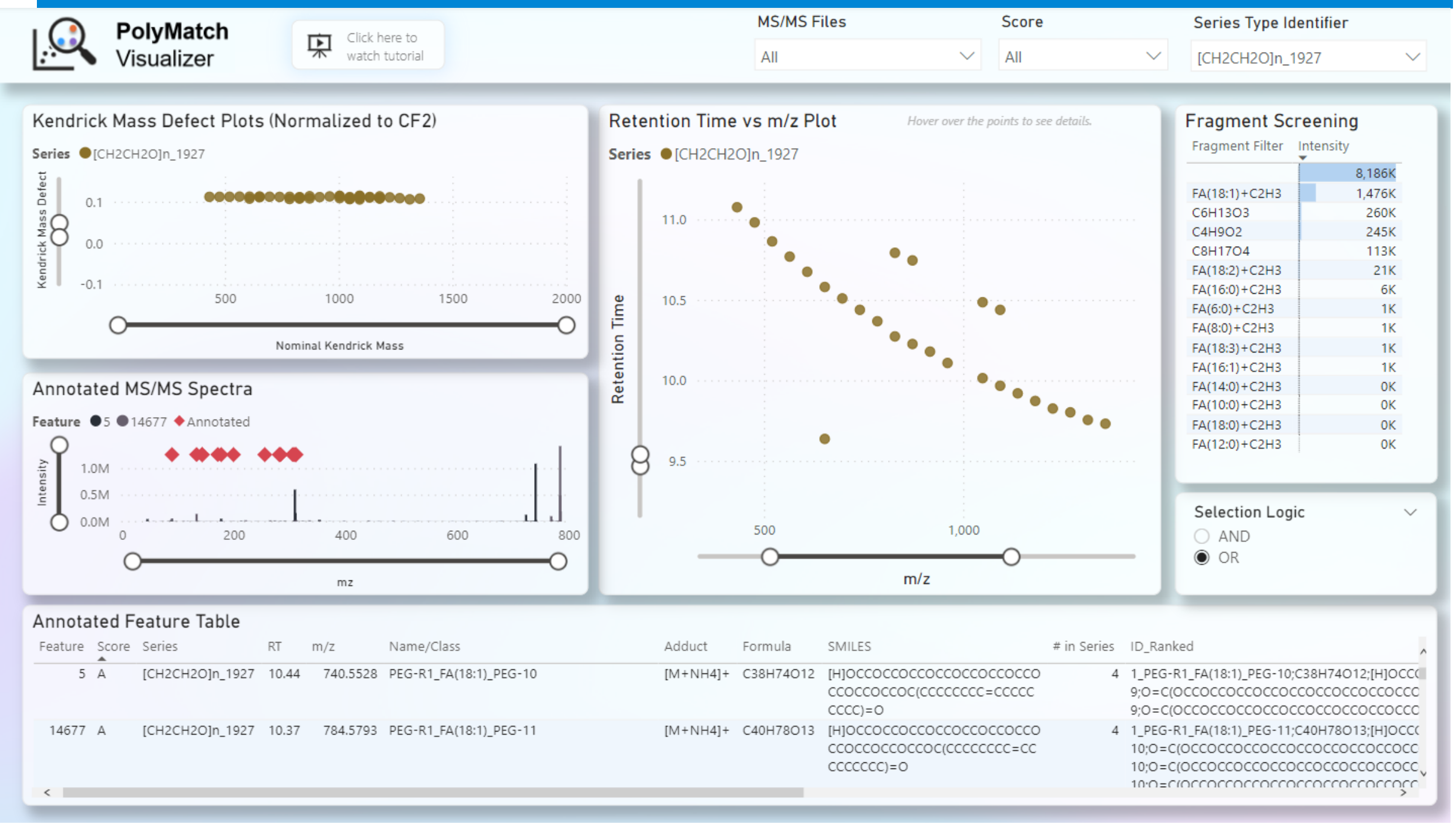


Visualization of the Results

PolyMatch Visualizer

A graphical interface (below) allows users to validate annotations and can be used to explore features using mass defect plots normalized to repeating units, retention time vs mass plots, annotated MS/MS spectra, fragment trace filters and other filters, and tables providing all annotation evidence. All plots cross-filter and are dynamic, allowing users to see all evidence for a feature(s) simultaneously.

Visualizer Interface: Example for PEG-R1 (18:1)



Feature	Score	Series	RT	m/z	Name/Class	Adduct	Formula	SMILES	# in Series	ID_Ranked
5	A	[CH2CH2O]n_1927	10.44	740.5528	PEG-R1_FA(18:1)_PEG-10	[M+NH4]+	C38H74O12	[H]OCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOC(CCCCCCCC=CCCCCCCCC)=O	4	1_PEG-R1_FA(18:1)_PEG-10;C38H74O12;[H]OCCC 9;O=C(OCCOCCOCCOCCOCCOCCOCCOCCOCCC 9;O=C(OCCOCCOCCOCCOCCOCCOCCOCCOCCC
14677	A	[CH2CH2O]n_1927	10.37	784.5793	PEG-R1_FA(18:1)_PEG-11	[M+NH4]+	C40H78O13	[H]OCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOCCOC(CCCCCCCC=CCCCCCCCC)=O	4	1_PEG-R1_FA(18:1)_PEG-11;C40H78O13;[H]OCC 10;O=C(OCCOCCOCCOCCOCCOCCOCCOCCOCCC 10;O=C(OCCOCCOCCOCCOCCOCCOCCOCCOCCC

Conclusions

PolyMatch, LipidMatch and FluoroMatch can be used to classify mixtures, identify compounds, and determine unknowns, for PFAS, Polysorbates, Lipids and other polymer-like species

- Incorporates MS/MS, homologous series, and retention time and displays all information in a user-friendly visualization
- Has over 200,000 species with fragmentation in libraries, as well as employing fragment screening and substructure assignment for unknowns
- Future work on EIC visualization, isotopic pattern matching, and statistics will enable even more comprehensive coverage of the non-targeted workflow for polymers and other chemical class with repeating motifs
- Please contact jeremykoelmel@gmail.com from Innovative Omics for more details.
- Other applications of this software framework include PFAS and Lipidomics

https://explore.agilent.com/asms

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