CHEMICAL CHARACTERIZATION OF THE AIRCRAFT CABIN ENVIRONMENT UTILIZING GCxGC-TOFMS AND HARD AND SOFT IONIZATION

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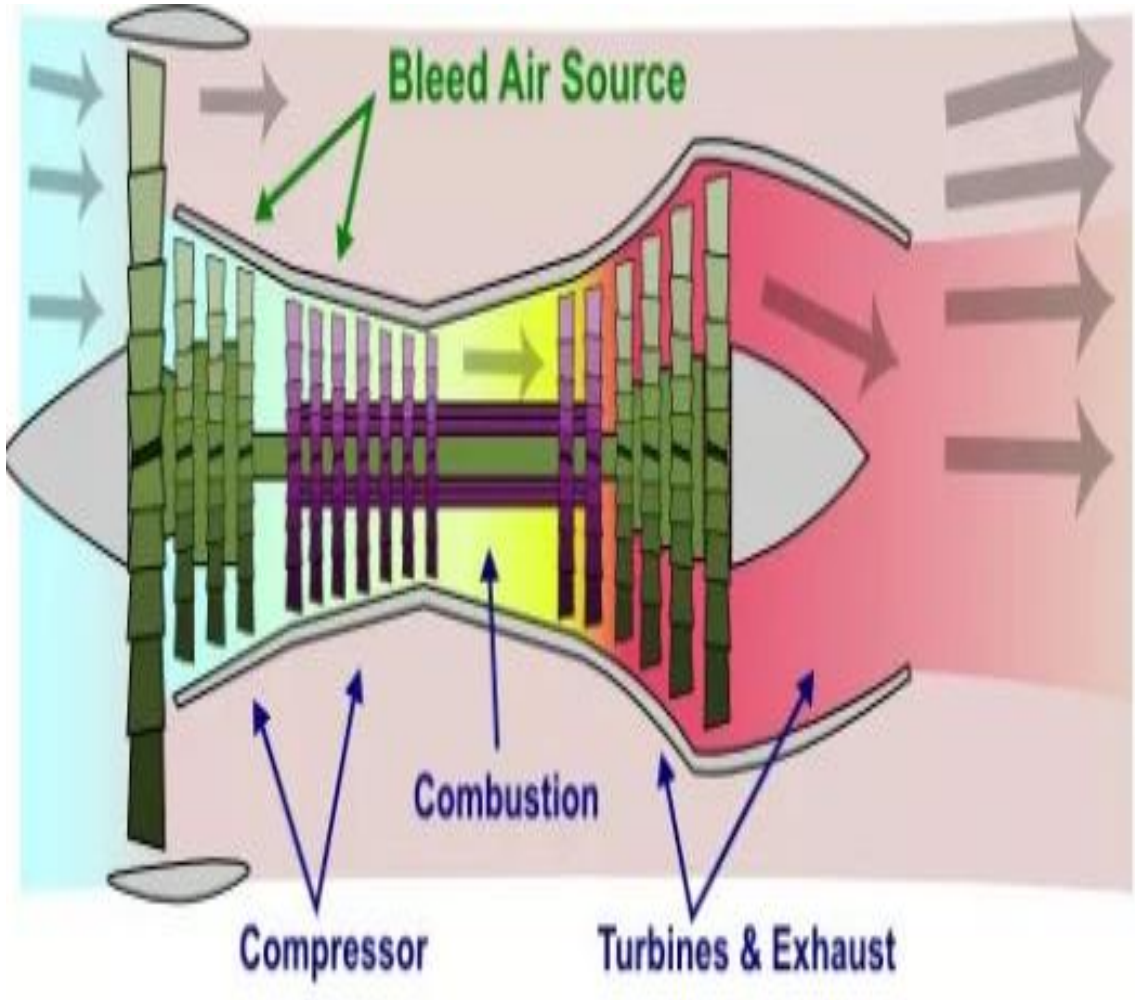
15th Multidimensional Chromatography Workshop

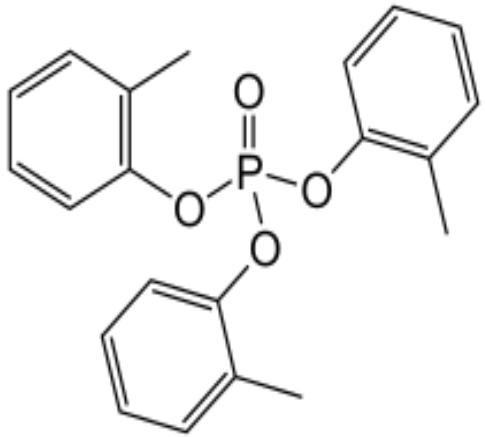
Aircraft Pressurization

- Atmospheric pressure drops to about 7.3 psi at 18,000 ft altitude, risking delirium or unconsciousness in unacclimated individuals, while commercial aircraft fly between 30,000 and 43,000 ft where the pressure is even lower.
- Aircraft pressurization is crucial for human safety, financial, and operational efficiency, allowing flights at higher altitudes where engines are more efficient and speeds are faster, despite lower atmospheric pressures.
- The aircraft fuselage is not sealed; it employs a controlled air exchange system where fresh air is pumped in and old air exits via outflow valves, refreshing cabin air every 2-3 minutes.
- Modern jet aircraft use bleed air from the engines for cabin pressurization and other essential functions, a system developed in the 1950s for its efficiency over heavy electric compressors, with the Boeing 787 Dreamliner being a notable exception using non-bleed air methods.



Bleed Air Contamination of the Cabin

- Contaminants may enter cabin air through bleed air systems from engine leaks or failure of components designed to manage extreme operating conditions.
- Fume events (resultant from major leaks) are rare but significant incidents where cabin air is contaminated, potentially leading to emergency landings and health issues.
- These events are challenging to study due to their infrequency, but even without visible signs, some level of contamination associated with bleed air is thought to be present in aircraft cabins.
- Air quality in aircraft cabins can also be affected by various external and internal factors, which are not associated with pressurization by the engines, including other aircraft, on-ground operations, cleaning chemicals, and cabin materials.



Tri-o-cresyl Phosphate

Human Health Implications

AEROTOXIC SYDROME: ADVERSE HEALTH EFFECTS FOLLOWING EXPOSURE TO JET OIL MIST DURING COMMERCIAL FLIGHT

July 2001 · Toxicology · 164(1-3)

Chris Winder · Jean Christo

Cognitive impairment and associated loss in brain white microstructure in aircrew members exposed to engine oil fumes

Original Research | Open access | Published: 12 June 2015

Volume 10, pages 437–444, (2016) Cite this article

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Amyotrophic Lateral Sclerosis Among Veterans Deployed in Support of Post-9/11 U.S. Conflicts FREE

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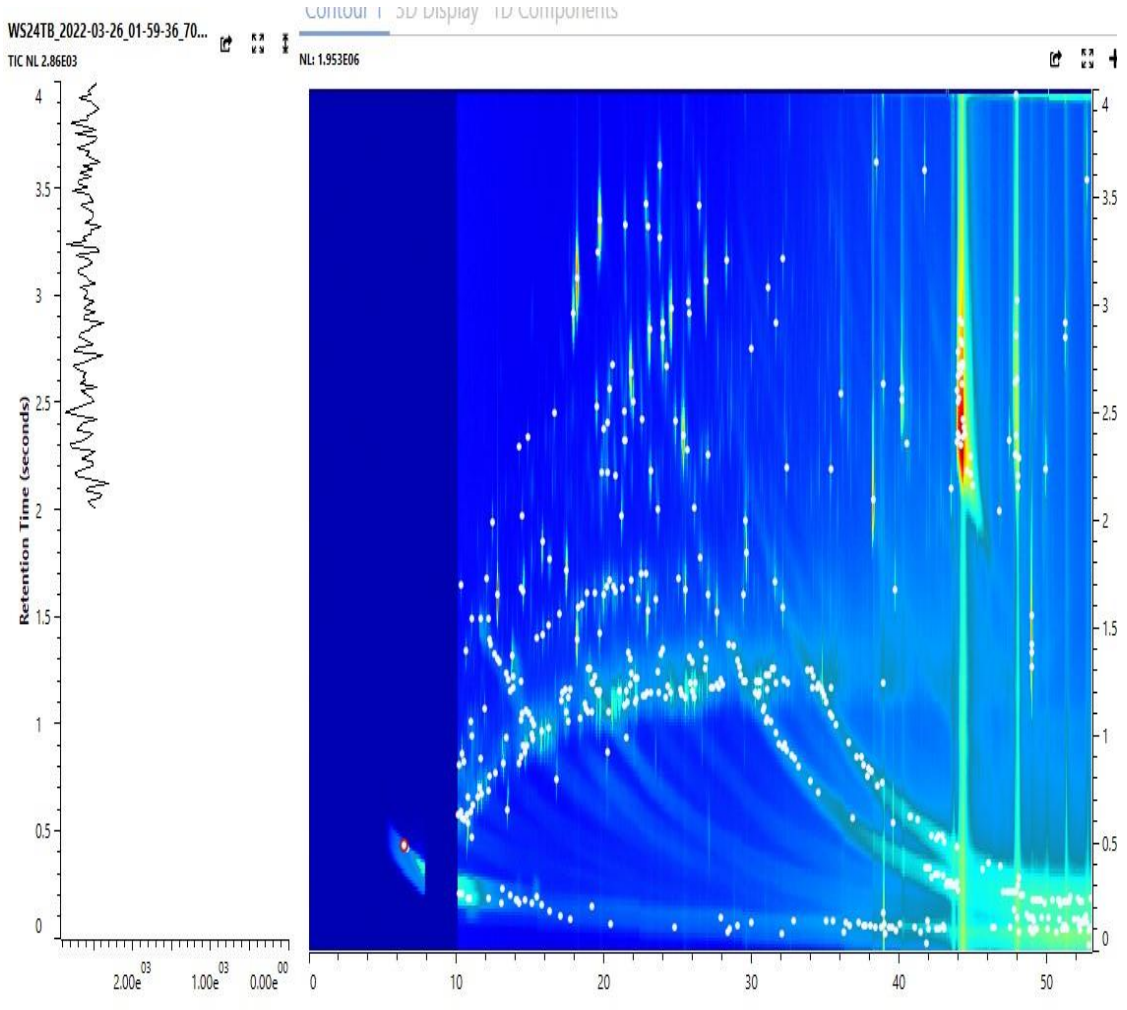
Military Medicine, Volume 185, Issue 3-4, March-April 2020, Pages e501–e509, https://doi.org/10.1093/milmed/usz350

Published: 23 October 2019

Our study

- Utilizing a citizen science initiative, 98 wipe samples from 62 unique flights across various durations and aircraft types were collected for analysis.
- Instrumental analysis was conducted using two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC ToFMS).
- The samples were run with concurrent tandem ionization to achieve a balance of the benefits of hard and soft ionization.
- A pseudo- non-targeted analytical approach was taken to assess what chemical contaminants, if any, can be identified to be exclusive or enhanced in bleed air pressurized aircraft as compared to non-bleed air pressurized aircraft.



Instrument Parameters and Operation

- Modulator – 4 seconds.
- Non-polar 1-D (25m); Semi-polar 2-D (5m).
- Hard ionization = 70eV ; Soft ionization = 16eV.
- Each trip blank (and all other blanks) and sample were injected in triplicate.
- Instrument drift was monitored using a daily Deuterated Kovats-Lee Retention index mix injection.

GCxGC-ToF Parameters	
Modulation Frequency	4 Seconds
Injection Volume	2 µL
Inlet Temperature	300°C
Split Ratio	5 to 1
Flow Rate	0.5000mL/min
Initial Oven Temperature	60°C
Ramp	10°C per minute to 150°C
Ramp 2	4°C per minute to 310°C
Ramp 3	Hold at 310°C for 5 minutes
Total Run Time	54 minutes
Transfer Line Temperature	280°C
Ion Source Temperature	280°C
Filament Voltage	1.70
Filament Delay	600 seconds
Mass Range	30 - 568.8
Hard Ionization (eV)	70
Soft Ionization (eV)	16

Data Processing

- Parameters were chosen to provide adequate peak identification while minimizing the identification of false or absent peaks. (Huge thanks for the assistance of John and Scott at SpectralWorks for this!)
- One important consideration is the minimum number of masses for peak ID. While identification confidence can be improved by increasing this number, a low number is necessitated if the same method is to be used to process both 70eV and 16eV sample data due to decreased fragmentation occurring with soft ionization.

AnalyzerPro Data Processing Parameters	
1D-2D Matching	80%
Mass Range	40-5000
Min Masses for Peak ID	4
Area Threshold	50
Height Threshold	0
Signal to Noise	5 to 1
Gaussian Smoothing	3
Minimum Peak Width	0.001 minutes
Library Searching	NIST-Main Library
Min Match Confidence	60%

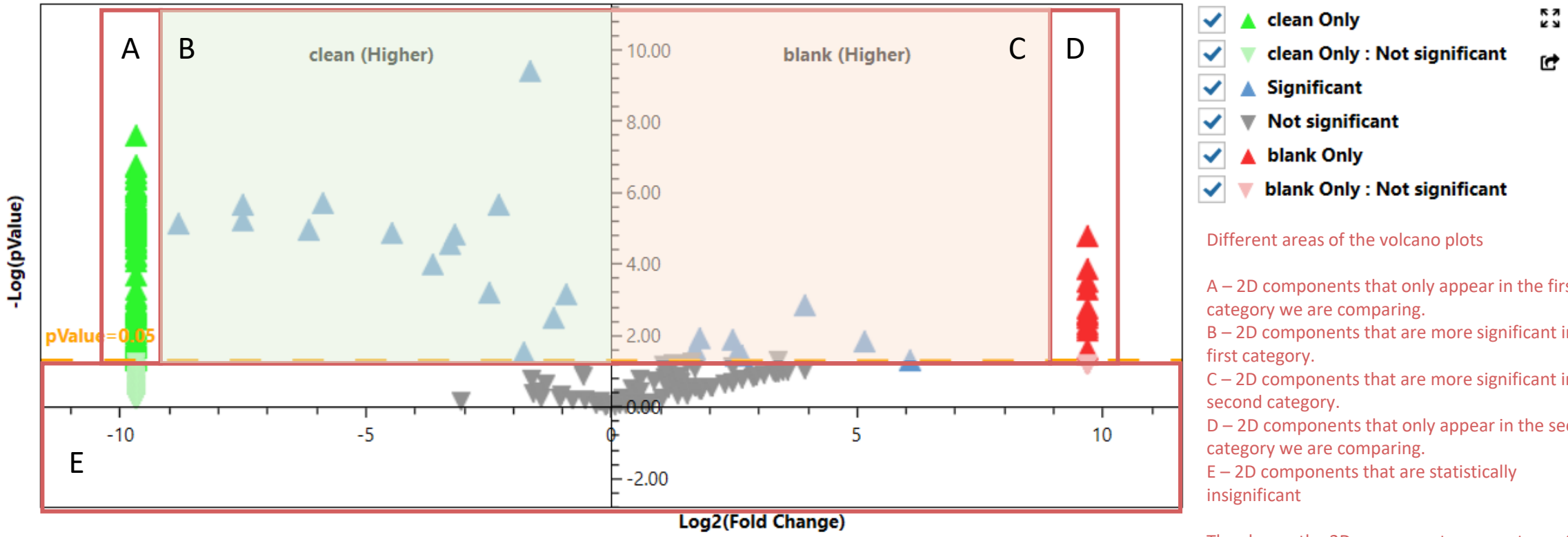
How does AnalyzerPro XD work?

- AnalyzerPro XD works using a proprietary chromatographic deconvolution algorithm developed by SpectralWorks.
- Deconvolution is performed on the data as it would for a typical GC-MS or LC-MS data file.
- The results from this is a list of components.
- When processing GCxGC-MS data, the components are then ‘clustered’ together to create a list of 2D components.
- The ‘clustering’ algorithm is again proprietary, but it based on spectral comparison and retention time information to ensure components repeating over multiple modulations are correctly clustered together.

Statistics – Volcano Plot

PCA | Volcano Plot | Spectra | Chromatograms | QC Samples

Volcano Plot - blank / clean

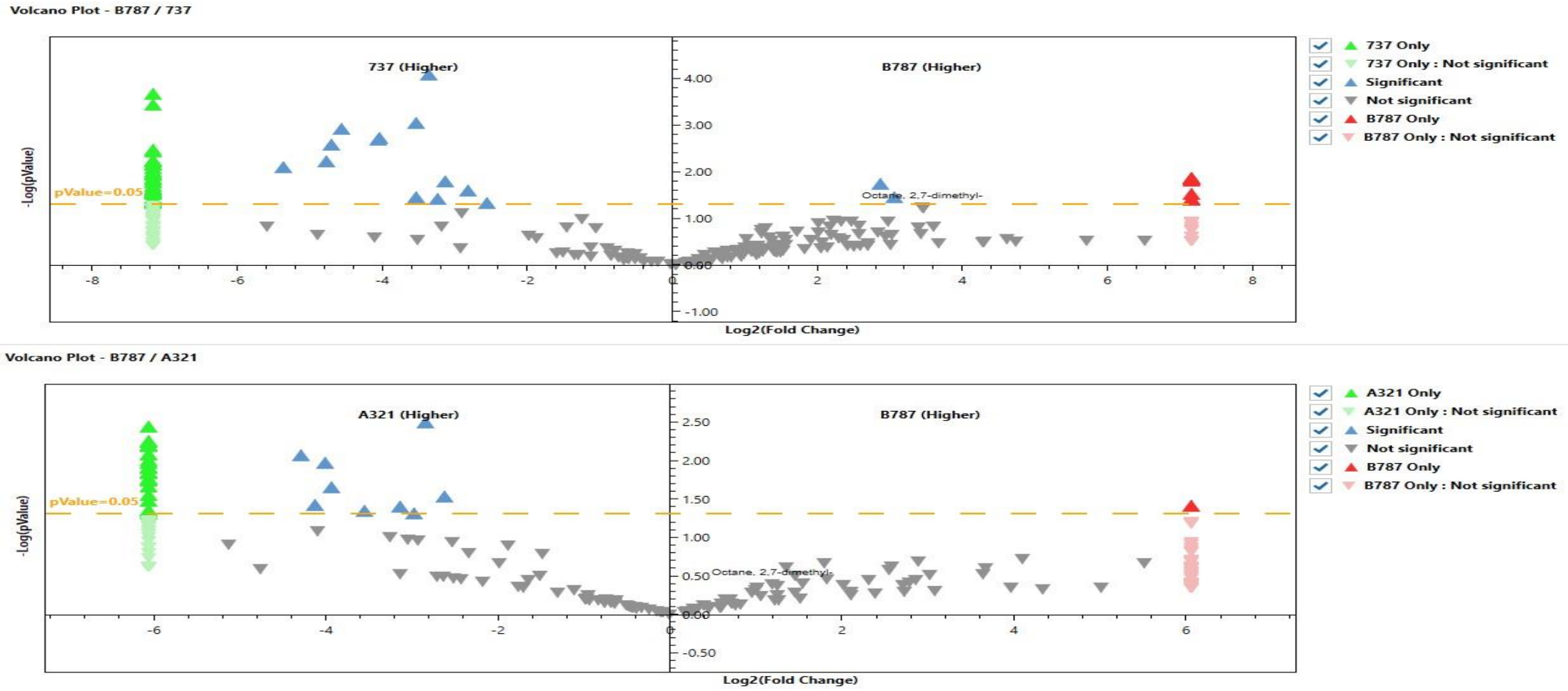


Different areas of the volcano plots

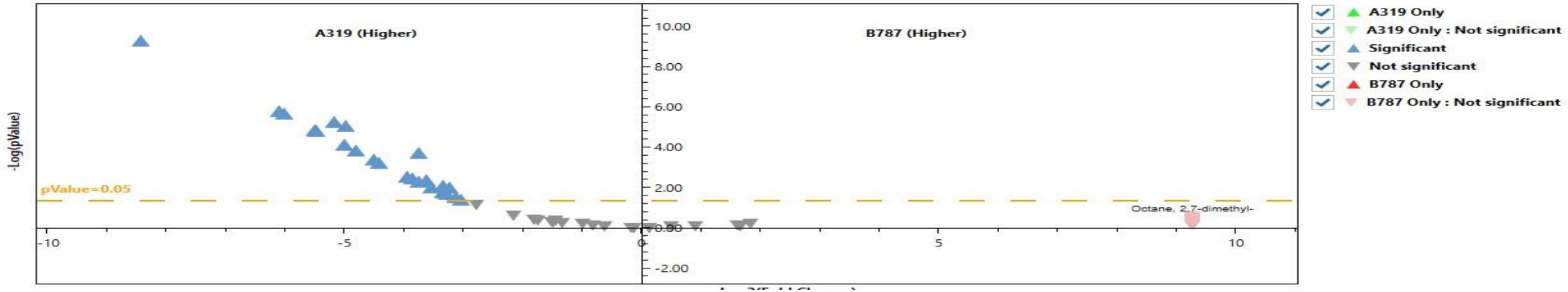
A – 2D components that only appear in the first category we are comparing.
B – 2D components that are more significant in the first category.
C – 2D components that are more significant in the second category.
D – 2D components that only appear in the second category we are comparing.
E – 2D components that are statistically insignificant

The closers the 2D components appear to y = 0, the more common the component is two each category.

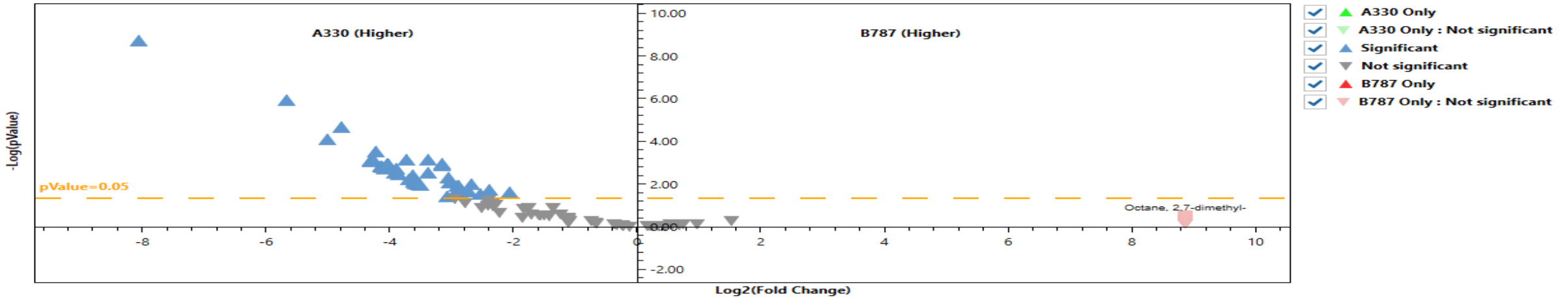
Bleed VS Non-Bleed Volcano Plots



Volcano Plot - B787 / A319



Volcano Plot - B787 / A330



Volcano Plot Summary

Aircraft	Bleed Air Higher	Bleed Air Unique	Non-Bleed Air Higher	Non-Bleed Air Unique
Boeing 737-600	13	40	2	10
Airbus A321	9	36	0	19
Airbus A319	23	0	0	0
Airbus A330	42	0	0	0

Data base Creation

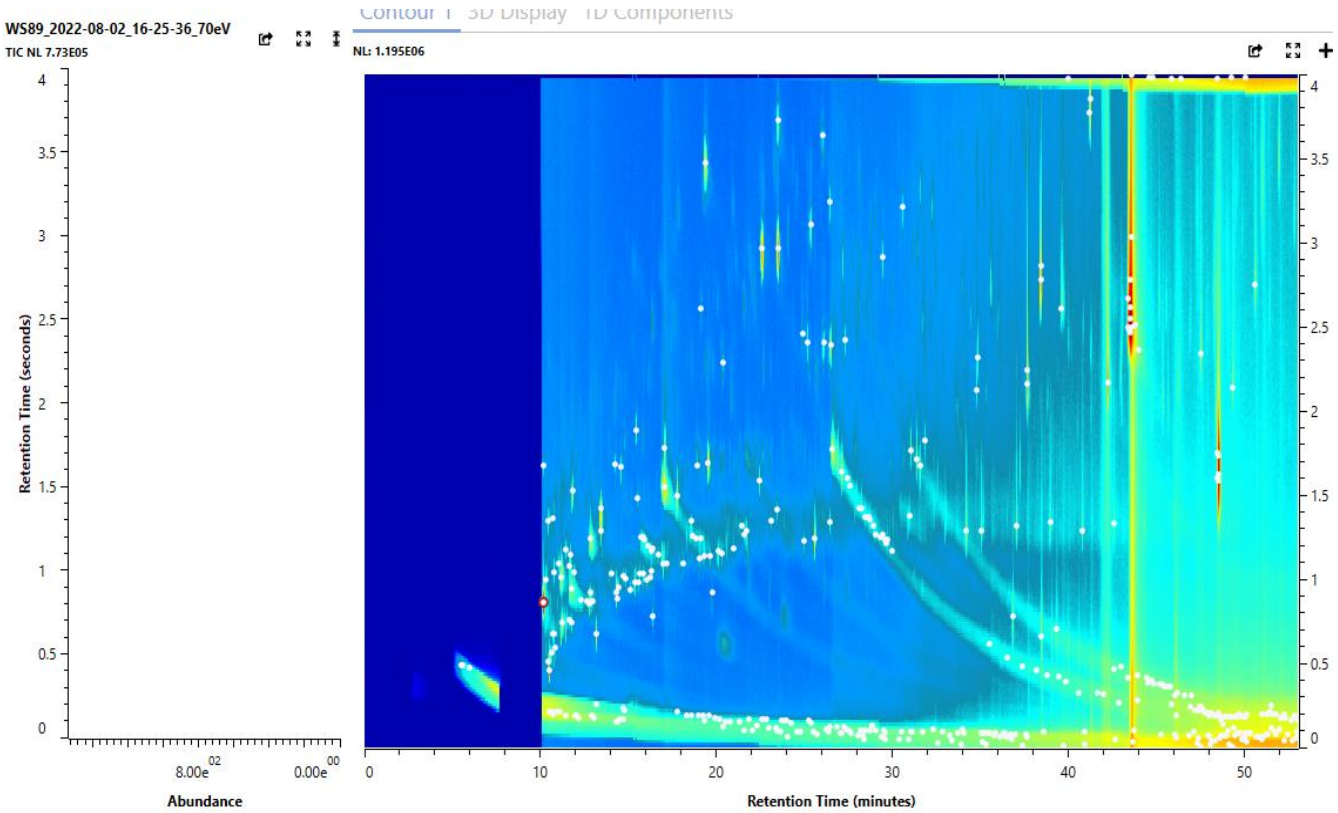
Peak tables generated by software from chromatographic data were prepared in Excel and imported into Microsoft Access.

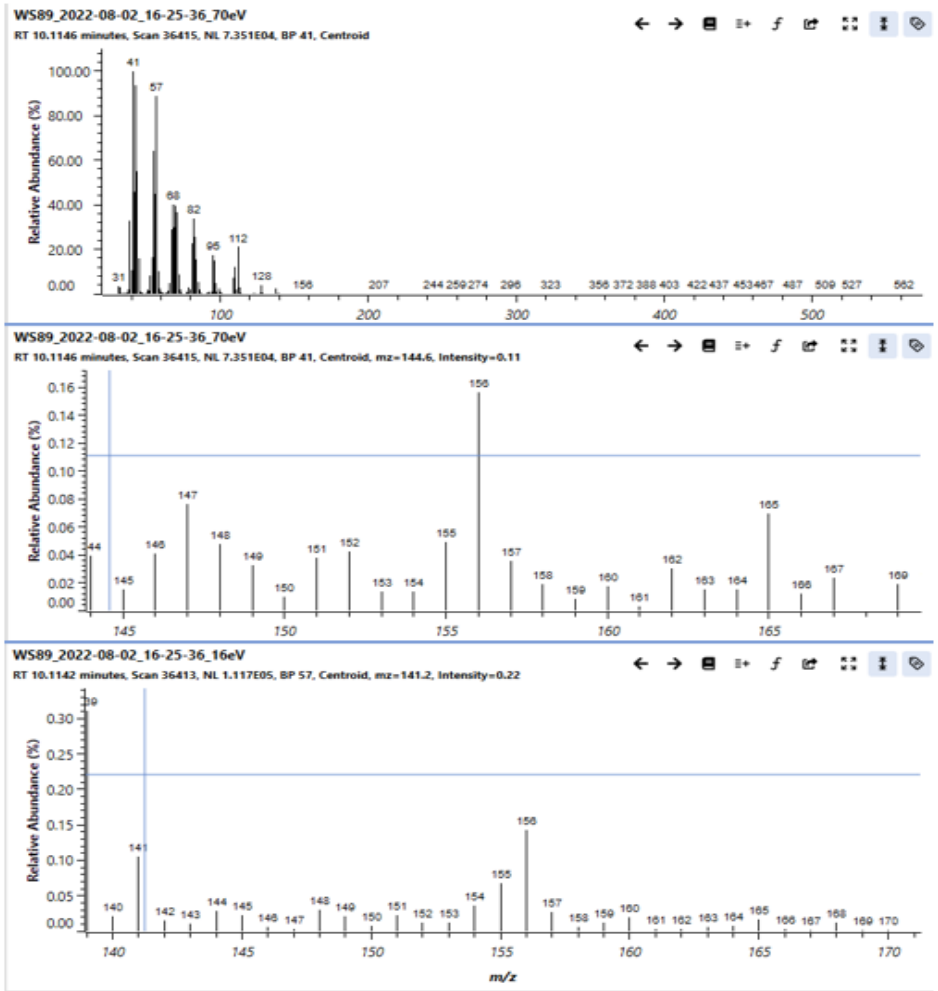
Database Queries:

- Matched Data:
    - Identifies peaks in both wipe samples and trip blanks, with a peak area in samples at least 10 times that of the blank.
    - Retention time windows established for matching peaks and verified visually.
- Unmatched Data:
    - Identifies unique peaks present in wipe samples but not in trip blanks, with specific retention time criteria.
- Only Bleed:
    - Filters compounds found in at least two bleed air aircraft samples but absent in bleed-free aircraft and trip blanks.
- RT Window:
    - Isolates data that does not match with retention times of trip blanks and falls within a visually determined retention time window.

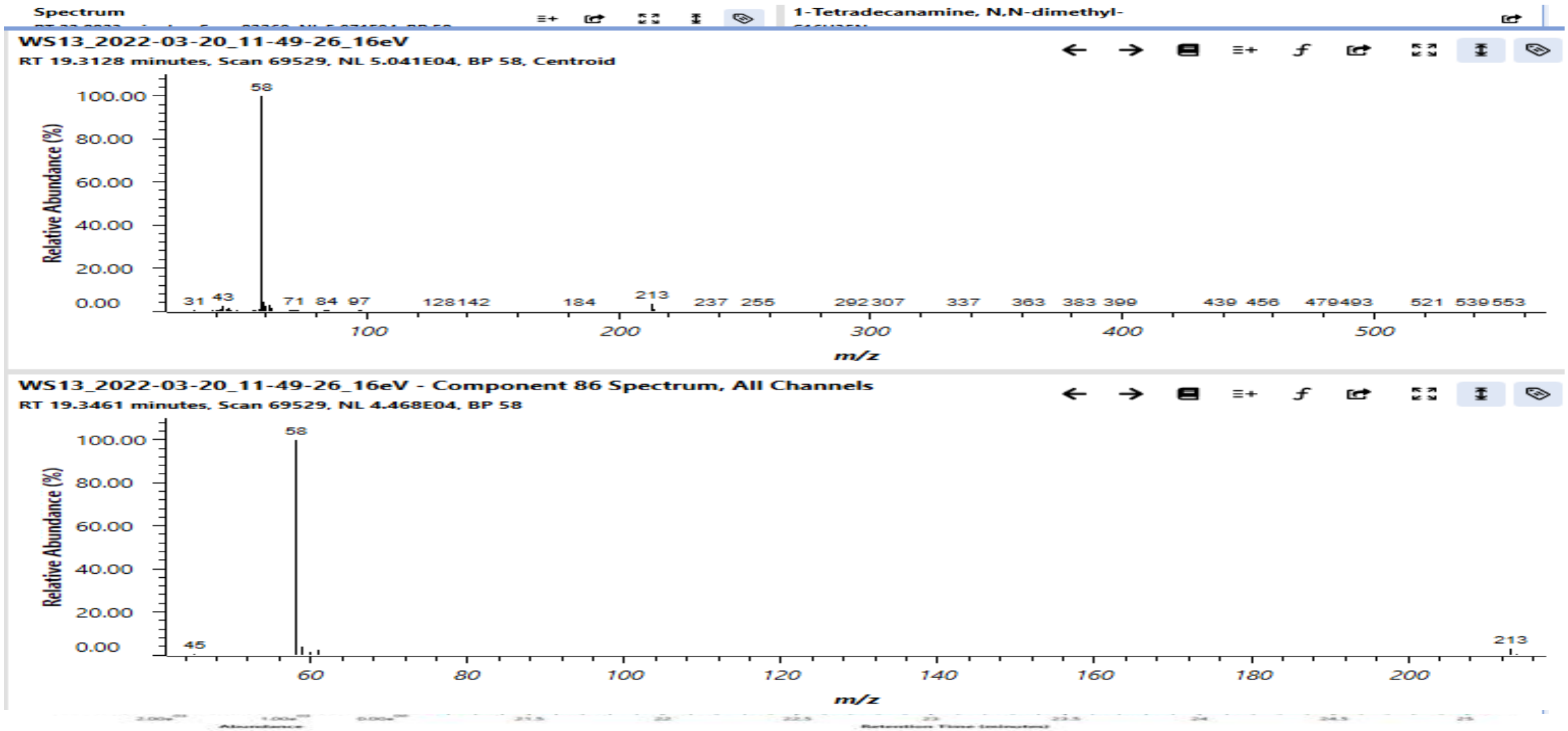
Compounds Present in Sample and TB

Decanal





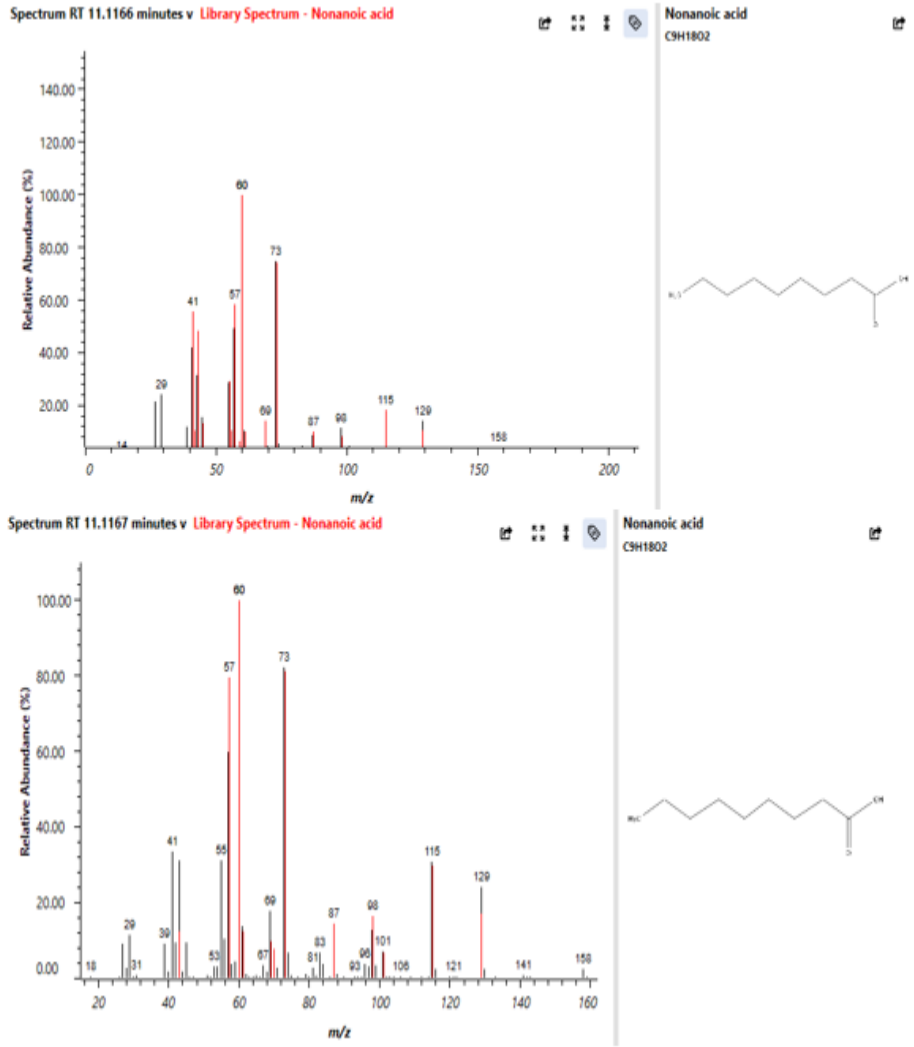
Compounds Present in a Sample but not TB



Compounds Present in Only Bleed Aircraft

A database query identified unique chemical compounds present in bleed air pressurized aircraft by excluding duplicates on a per sample basis and cross-referencing against non-bleed aircraft and trip blanks.

- Initial results yielded 94 compounds, narrowed down to 12 distinct chemical identities after applying a confidence threshold and excluding irrelevant data (peaks that appeared in solvent band, poor chromatography, etc.).
- Spectral analysis using 16eV ionization provided clearer molecular ion peaks for certain compounds, refining the potential matches and identifying likely chemical identities.
- Although no compounds met the highest confidence criteria for identification, several were deemed significant enough to merit targeted analysis in future studies (e.g. Nonanoic Acid).



Conclusions

- GCxGC ToFMS utilizing tandem ionization is a very useful for inclusion or elimination of non-targeted compounds from future suspect/targeted lists.
- While meeting the criteria of the Schymanski scale is not technically possible with this instrumentation, this type of analysis is believed to be the equivalent of describing Level 5: Masses/ Compounds of Interest.
- The bleed air pressurized aircraft cabin appears to exhibit a greater variety of chemical compounds at significant levels than its non-bleed air pressurized counterparts.

Acknowledgements

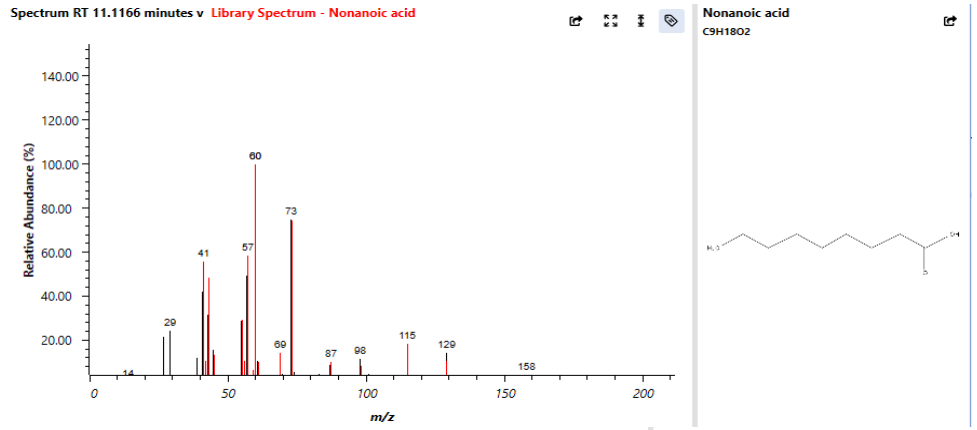
I would like to thank,

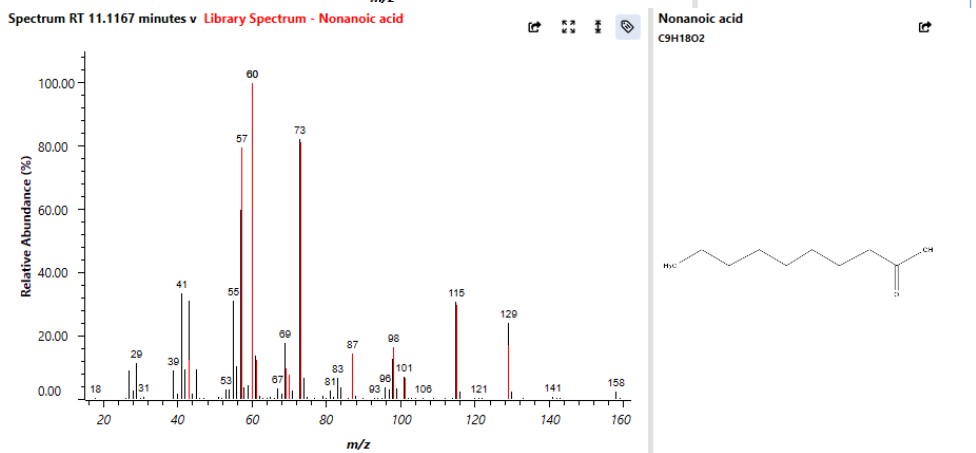
My supervisory team - Dave Megson, Gwen O'Sullivan, and Aidan Doyle.

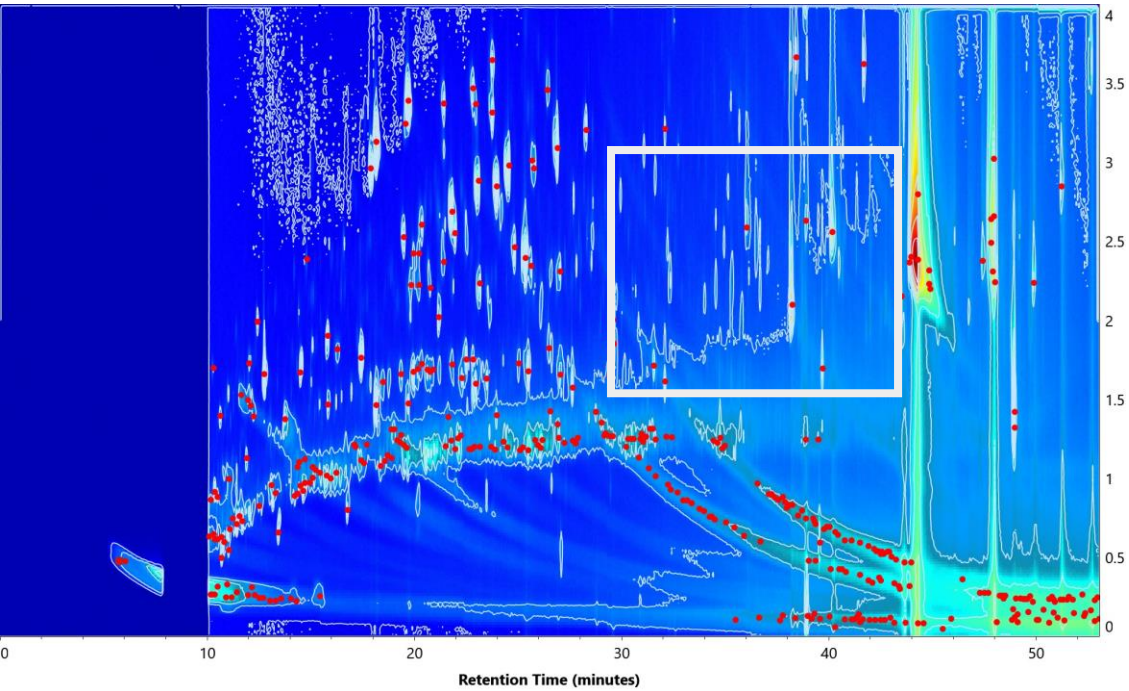
Fellow lab members of the Environmental Forensics and Arson Lab - Emily Carroll, Caleb Marx, and James Walker

John Moncur and Scott Campbell from SpectralWorks

Sample	RT	RTm	Area	Base Peak	Base Peak	Classifier	ChemName	Mol Ion	MI in 16EV	Notes
WS49	15.5161	0.9662	173015	57	71	211	1-Iodo-2-methylundecane	296	Raw Spec	Not likely based on surrounding spectra
WS21	15.7169	1.0157	32860	57	43	169	1-Iodo-2-methylundecane	296	Raw Spec	Not likely based on surrounding spectra
WS1	21.7842	1.0511	56263	71	57	155	1-Iodo-2-methylundecane	296	Raw Spec	Not likely based on surrounding spectra
WS56	21.4536	1.2186	11811	57	71	153	1-Nonene, 4,6,8-trimethyl-	168	Raw Spec	
WS89	11.7157	0.9417	28639	55	56	112	1-Octanol	130	Raw Spec	158 more prominent likely decanol
WS49	11.5832	0.9934	6597	55	56	97	1-Octanol	130	Raw Spec	158 more prominent likely decanol
WS24	13.0481	0.8888	19760	43	41	196	1-Tetradecene	196	Comp Spec	Extra peaks in 16 that are useful
WS21	13.4492	0.9545	8791	55	43	196	1-Tetradecene	196	Comp Spec	
WS56	44.9435	2.6122	2113	149	71	293	Di-isononyl phthlate	418	Raw Spec	
WS49	44.9427	2.5622	4719	149	150	293	Di-isononyl phthlate	418	Raw Spec	
WS42	45.0094	2.5622	14233	149	43	294	Di-isononyl phthlate	418	Raw Spec	
WS41	44.4116	2.6965	3086	149	71	293	Di-isononyl phthlate	418	Raw Spec	
WS54	44.1438	2.6305	8384	149	43	294	Di-isononyl phthlate	418	Raw Spec	
WS41	43.4764	2.5821	19364	149	71	294	Di-isononyl phthlate	418	Raw Spec	
WS42	42.7434	2.601	12057	149	71	293	Di-isononyl phthlate	418	Raw Spec	
WS54	43.4103	2.6155	20493	149	57	294	Di-isononyl phthlate	418	Raw Spec	
WS49	43.41	2.5992	13085	149	71	294	Di-isononyl phthlate	418	Raw Spec	
WS56	27.1962	1.7717	103994	43	73	257	n-Hexadecanoic acid	256	Comp Spec	
WS41	36.7886	1.3148	1743	57	71	127	Nonane, 1-iodo-	254	Comp Spec	
WS1	11.1166	0.9934	6027	60	73	129	Nonanoic acid	158	Comp Spec	
WS1	14.4473	0.8354	3137	57	71	85	Sulfurous acid, 2-ethylhexyl isohexyl ester	278	Absent	Probably Trimethyl decane or similar '184' present
WS14	25.786	1.1582	20266	71	43	127	Sulfurous acid, 2-ethylhexyl isohexyl ester	278	Absent	Probably Trimethyl decane or similar '184' present
WS56	20.3195	1.1713	117638	57	71	211	Sulfurous acid, hexyl pentadecyl ester	376	Absent	
WS13	20.7201	1.2039	141779	43	57	169	Sulfurous acid, hexyl pentadecyl ester	376	Absent	Probably nonadecane '268' present
WS41	26.3207	1.2399	45896	71	57	169	Tridecanol, 2-ethyl-2-methyl-	242	Raw Spec	
WS42	25.8551	1.3081	146243	57	71	211	Tridecanol, 2-ethyl-2-methyl-	242	Raw Spec	
WS39	24.3208	1.2451	51198	57	71	155	Undecane, 3,8-dimethyl-	184	Raw Spec	
WS41	19.5862	1.1727	64928	57	71	196	Undecane, 3,8-dimethyl-	184	Raw Spec	
WS21	11.9796	0.7747	7838	43	71	141	Undecane, 4,7-dimethyl-	184	Raw Spec	Lots of unaccounted spectra in 70ev, no software match in 16
WS24	11.9121	0.7249	12069	43	57	169	Undecane, 4,7-dimethyl-	184	Raw Spec	Lots of unaccounted spectra in 70ev, no software match in 16
WS56	16.4511	1.0639	23446	57	71	127	Undecane, 4,7-dimethyl-	184	Raw Spec	


Spectrum RT 11.1166 minutes v Library Spectrum - Nonanoic acid
Relative Abundance (%)
m/z
Nonanoic acid
C9H18O2


Spectrum RT 11.1167 minutes v Library Spectrum - Nonanoic acid
Relative Abundance (%)
m/z
Nonanoic acid
C9H18O2


4
3.5
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1
0.5
0
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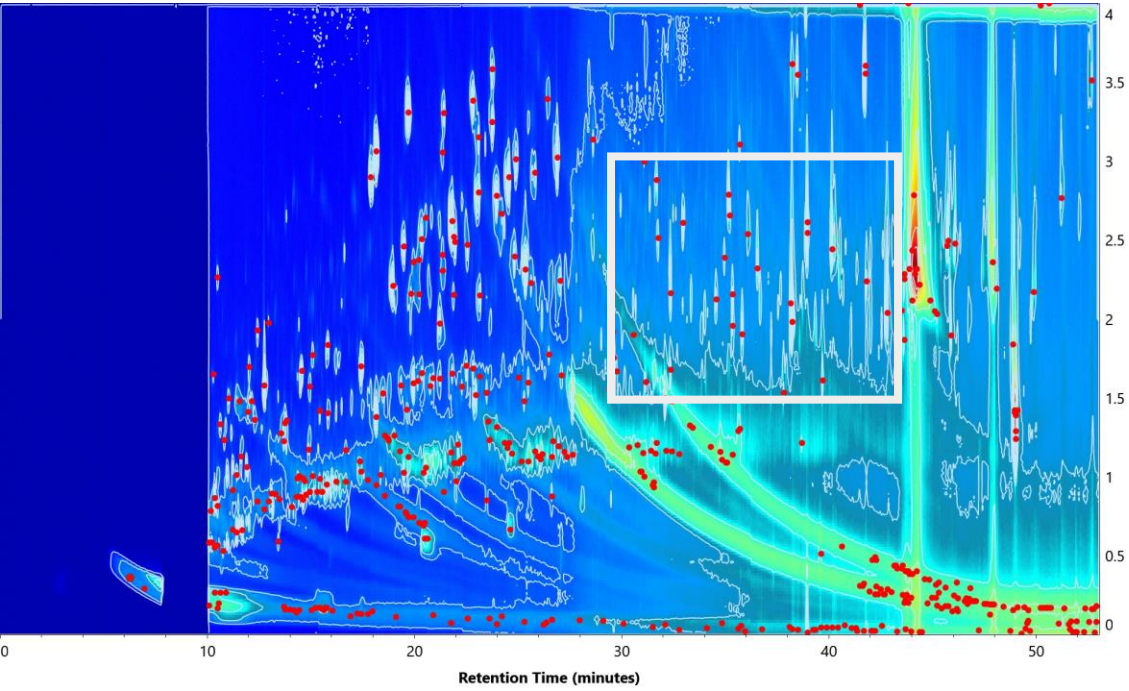
50
Retention Time (minutes)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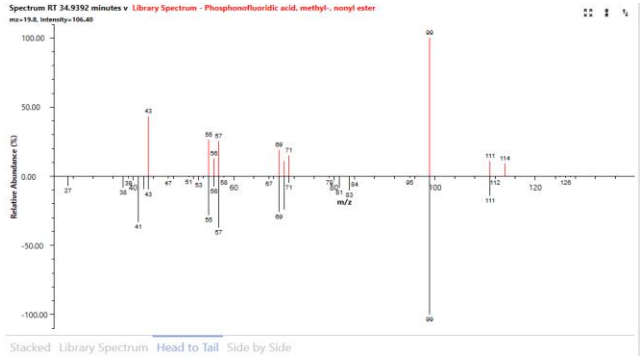
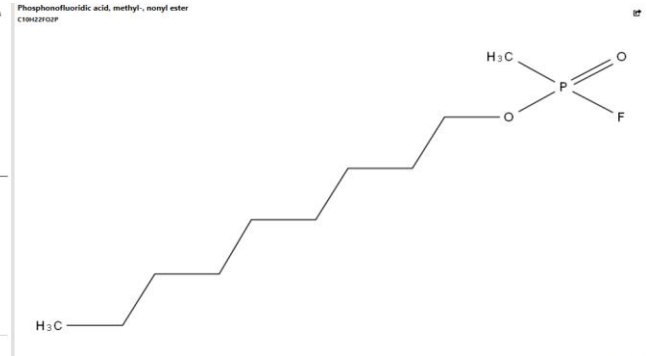
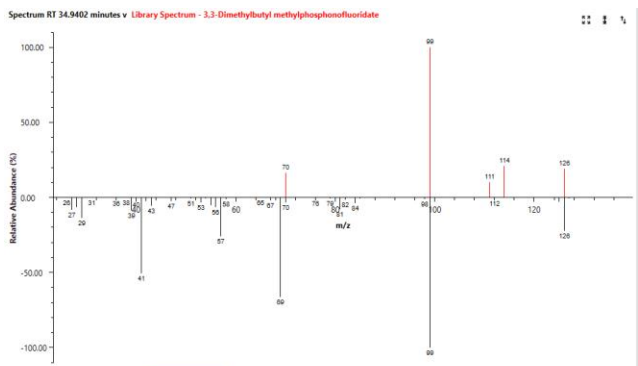
Retention Time (minutes)

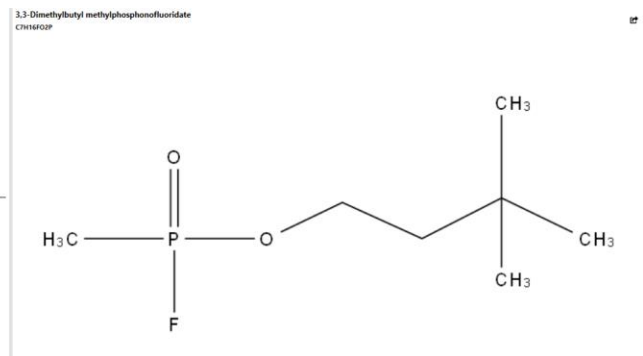




Library Results

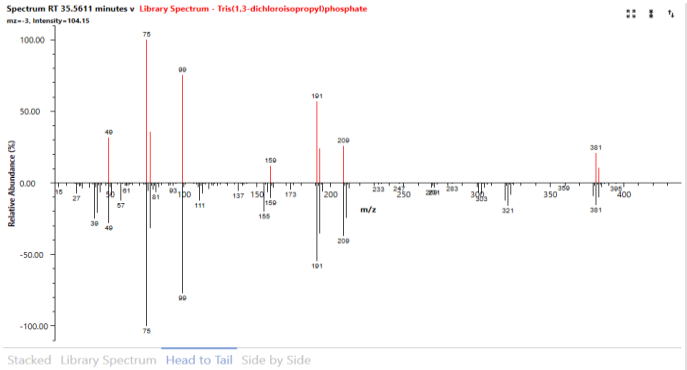
	Selected Hit	Name	Confidence %	Forward	Reverse	Formula	Mol. Weight	CAS #	Library	Synonyms
1	●	2(3H)-Furanone, 5-butyldihydro-4-methyl-, cis-	76.32	752	782	C9H16O2	156	55013-32-6	mainlib	9
2	○	Phosphonofluoridic acid, methyl-, nonyl ester	74.18	731	760	C10H22FO2P	224	211192-74-4	mainlib	3
3	○	5-Hexyl-5-methyloxolan-2-one	72.87	728	728	C11H20O2	184	7011-83-8	mainlib	0
4	○	trans-3-Methyl-4-octanolide	73.28	722	751	C9H16O2	156	39638-67-0	replib	7
5	○	Phosphoric acid, monododecyl ester	72.71	717	744	C12H27O4P	266	2627-35-2	mainlib	6
6	○	Hexanoic acid, 4-hexadecyl ester	71.27	712	712	C22H44O2	340	4294684-45-8	mainlib	1
7	○	2(3H)-Furanone, dihydro-5-methyl-5-(2-methylpropyl)-	71.27	712	712	C9H16O2	156	10200-21-2	mainlib	1
8	○	Phosphoric acid, tris(2-ethylhexyl) ester	71.07	710	710	C24H51O4P	434	78-42-2	replib	19
9	○	2(3H)-Furanone, 5-butyldihydro-4-methyl-, cis-	71.61	706	733	C9H16O2	156	55013-32-6	replib	9
10	○	2(3H)-Furanone, 5-butyldihydro-4-methyl-, cis-	70.27	702	702	C9H16O2	156	55013-32-6	replib	9

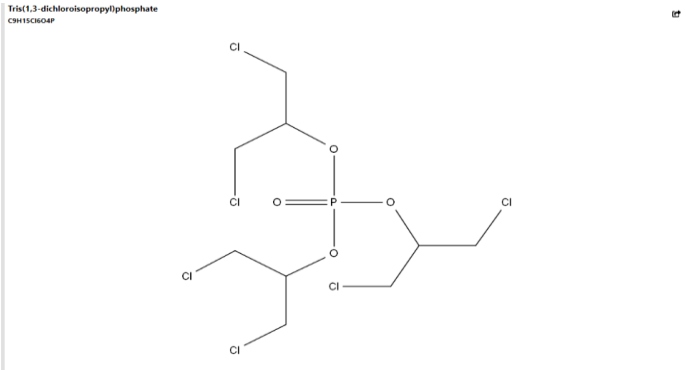




Library Results

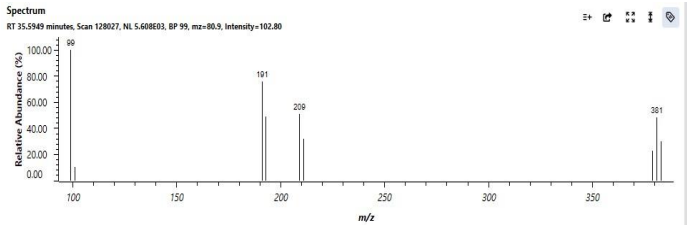
	Selected Hit	Name	Confidence %	Forward	Reverse	Formula	Mol. Weight	CAS #	Library	Synonyms
1	●	Acetaldehyde, diethylhydrazone	77.23	707	892	C6H14N2	114	7422-91-5	replib	1
2	○	3,3-Dimethylbutyl methylphosphonofluoridate	73.21	692	805	C7H16FO2P	182	660-21-9	mainlib	4
3	○	3,3-Dimethylbutyl methylphosphonofluoridate	71.54	676	787	C7H16FO2P	182	660-21-9	replib	4
4	○	3,3-Dimethylbutyl methylphosphonofluoridate	72.57	665	837	C7H16FO2P	182	660-21-9	replib	4
5	○	Acetamide, N-[(dimethylamino)methylidene]-	72.54	664	838	C5H10N2O	114	4294770-19-8	mainlib	1
6	○	3,5,5-Trimethyl-1-hexyl methylphosphonofluoridate	70.23	664	772	C10H22FO2P	224	4294668-84-7	mainlib	2
7	○	2-Propanone, (1-methylethyl)hydrazone	73.75	651	897	C6H14N2	114	7423-01-0	replib	1

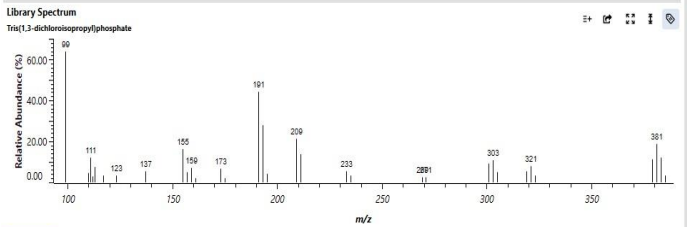


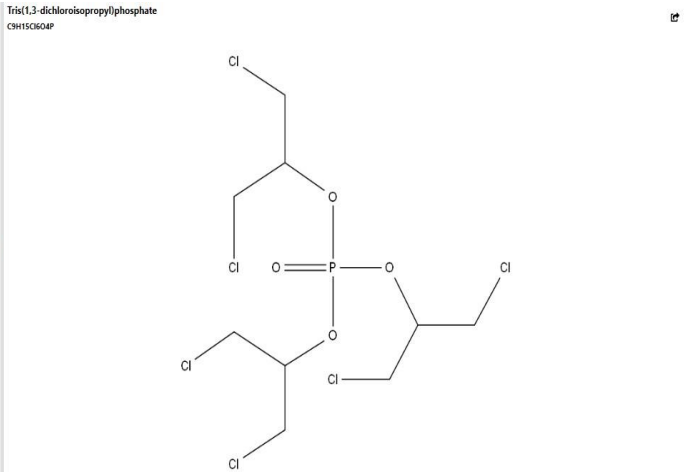


Library Results

	Selected Hit	Name	Confidence %	Forward	Reverse	Formula	Mol. Weight	CAS #	Library	Synonyms
1	◉	1-Propanol, 2,3-dichloro-, phosphate (3:1)	54.25	542	542	C9H15Cl6O4P	428	78-43-3	mainlib	9
2	○	Tris(1,3-dichloroisopropyl)phosphate	50.25	502	502	C9H15Cl6O4P	428	13674-87-8	mainlib	17
3	○	Phosphoric acid, bis[2-chloro-1-(chloromethyl)ethyl] 2,3-dichloropropyl ester	42.84	428	428	C9H15Cl6O4P	428	68460-03-7	mainlib	4
4	○	2-Fluoro-3-trifluoromethylbenzoic acid, cyclohexyl ester	35.22	329	405	C14H14F4O2	290	4294609-65-4	mainlib	0
5	○	2-Fluoro-6-trifluoromethylbenzoic acid, cyclohexyl ester	34.95	327	401	C14H14F4O2	290	4294609-60-3	mainlib	0
6	○	4H-1-Benzopyran-4,8(5H)-dione, 6,7-dihydro-3,5-dihydroxy-2-methyl-	32.74	316	353	C10H10O5	210	35942-09-7	mainlib	1
7	○	3-Fluoro-4-trifluoromethylbenzoic acid, cyclohexyl ester	31.84	298	365	C14H14F4O2	290	4294609-36-0	mainlib	0
8	○	Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid mono-(2-chloro-allyl) ester	30.91	295	341	C12H13ClO4	256	4294671-42-7	mainlib	1
9	○	4-Fluoro-2-trifluoromethylbenzoic acid, cyclohexyl ester	31.37	293	361	C14H14F4O2	290	4294609-63-6	mainlib	0
10	○	3,4-Dichlorobutane nitrile	34.37	290	468	C4H5Cl2N	137	34362-21-5	mainlib	0

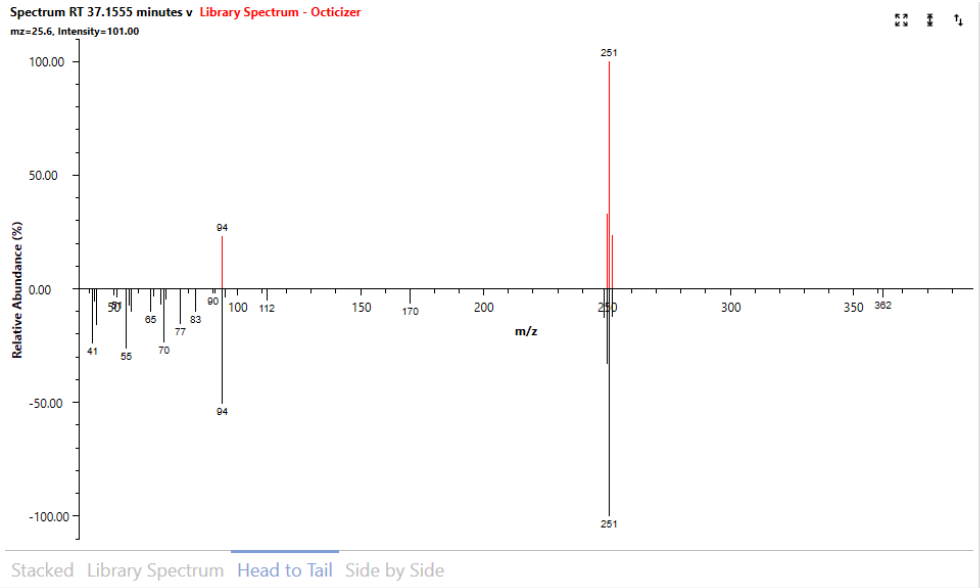




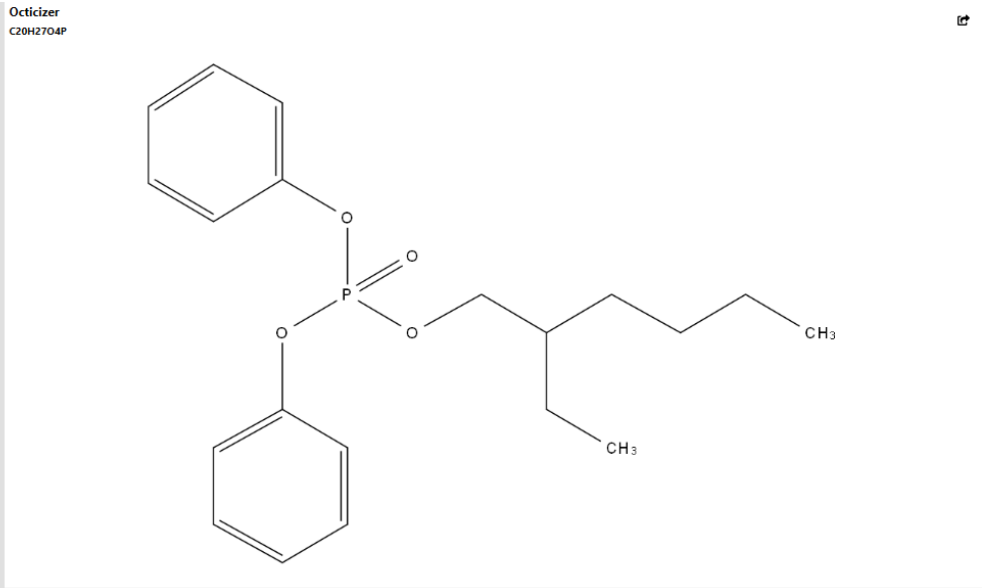


Library Results

	Selected Hit	Name	Confidence %	Forward	Reverse	Formula	Mol. Weight	CAS #	Library	Synonyms
1	◉	Tris(1,3-dichloroisopropyl)phosphate	71.05	708	713	C9H15Cl6O4P	428	13674-87-8	replib	17



Stacked Library Spectrum Head to Tail Side by Side



Library Results

	Selected Hit	Name	Confidence %	Forward	Reverse	Formula	Mol. Weight	CAS #	Library	Synonyms
1	●	Octicizer	84.88	848	848	C20H27O4P	362	1241-94-7	replib	12
2	○	Phosphoric acid, isodecyl diphenyl ester	78.88	788	788	C22H31O4P	390	1346599-15-2	mainlib	5
3	○	Phosphoric acid, isodecyl diphenyl ester	78.58	785	785	C22H31O4P	390	1346599-15-2	replib	5
4	○	7H-Pyrazolo[4,3-E][1,2,4]triazolo[1,5-c]pyrimidine, 7-methyl-2-pyridin-4-yl-	76.58	765	765	C12H9N7	251	4294657-28-0	mainlib	0
5	○	2-(5-Methyl-2-phenyl-1,2,4-triazol-3-yl)phenyl acetate	76.35	754	779	C17H15N3O2	293	4294530-86-2	mainlib	0
6	○	Octicizer	74.27	742	742	C20H27O4P	362	1241-94-7	replib	12
7	○	2-Methyl-3-(2-chloro-5-hydroxyphenyl)-4(3H)-quinazolinone	78.67	734	883	C15H11ClN2O2	286	51837-91-3	mainlib	1
8	○	6H-Indolo[2,3-b]quinoxaline, 9-fluoro-6-methyl-	72.07	720	720	C15H10FN3	251	4294647-69-4	mainlib	0
9	○	Phosphoric acid, octyl diphenyl ester	71.27	712	712	C20H27O4P	362	115-88-8	mainlib	3
10	○	trans-4-(Dimethylamino)chalcone	71.60	709	727	C17H17NO	251	22965-98-6	mainlib	1