Outgassing analysis on materials received resin bleed and lay-up

Purpose: To identify the out-gassing species on resin and lay-up materials.

Experimental:

Sample preparation:

One sample of each material was received approximately 2 x 0.5 inch pieces. Samples were massed using a Mettler Toledo Balance (±0.0001gm) and placed into cleaned glass vials (40 mL). The vials were evacuated and pressurized with UHP nitrogen to 20 psia and sat on the benchtop overnight to reach an equilibrium. Then the vials were heated at 70C for˚ one hour, cooled back to room temperature, and tested. No duplicate samples were tested and analyzed because one sample of each material was received.

Samples of a cured stack-up of prepreg material containing 3362 resin as well as a resin-only sample obtained from cure bleeding were submitted for analysis. Individual materials were received and analyzed using cryofocusing gas chromatography/mass spectrometry to qualitatively characterize their off-gassing constituents. The names of the samples, their masses, and pressures are listed in Table 1.

Table 1. Sample ID, mass, and final pressures.

Sample ID	**Mass (grams)**	**Pressure (psia)**
N_2 Blank	---	20.35
Lay-up	5.0038	20.28
Resin bleed	2.259	21.22

GC-MS Analysis:

The gas samples were pre-concentrated with an Entech 7650 cryofocuser. GC-MS was performed using an Agilent 7690B gas chromatograph (using a 60m Rxi-1ms column) in series with an Agilent 5977B MSD.

After injection onto the GC oven, the sample was held at -20ºC for 4 min, ramped to 230ºC at 10ºC/min, and then held for 2 mins, for a total GC run time of 31 minutes (see Figure 1).

Mass spectral data was collected in the range of m/z = 30-300. A TIC (total ion chromatogram) was generated for each sample, and major peaks were identified manually using NIST mass spectral library database (Figure 1-4). Mass spectras collected were analyzed using both NIST standard database with greater than 90% confidence and Chemometrics analysis. Chemometrics approach factors the data using multivariate curve resolution-alternating least squares. The resulting factors represent the chromatographic profile of each compound and the mass spectra, which are matched against the NIST standard database and identifications are reported by the highest reverse match score (perfect match = 999) among the top confidence identifications. Factor validity is assessed using metrics of smoothness, and the highest intensity peaks are reported here. The remainder are available as supplemental information.

GC Column: 60m Rxi-1ms (Restek)

Flow rate: 2 ml/min

Detector: Mass selective detector (MSD) Agilent 5977B.

Injection mode: Splitless

GC oven temperature: -20°C (4 mins) to 230 °C @ 10°C/min; hold for 2 min. for a single sample measurement of 31 minutes.

Instrument blanks were measured:

1) By running the GC-MS cycle with carrier gas only (helium) prior to running any samples or sample blanks.
2) Sample blanks (40mL glass vials) containing N_2 blank runs are collected to show no addition chemical species were introduced during sample preparation.
3) TO-15 at 100ppb is used as a calibration standard.

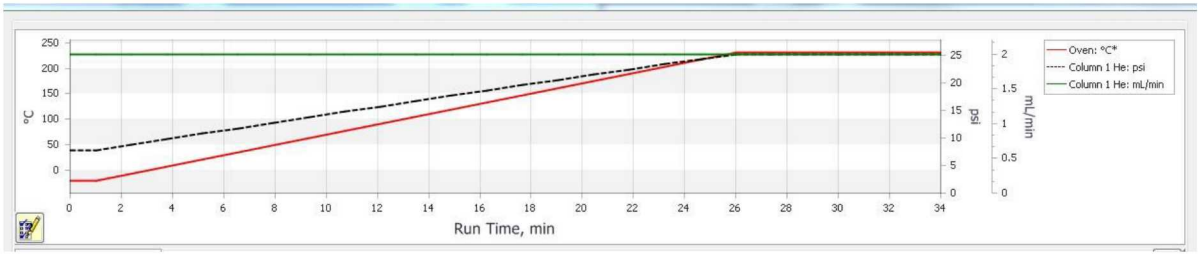

Figure 1. GC temperature profile used for analysis of samples received.

Results and Interpretations

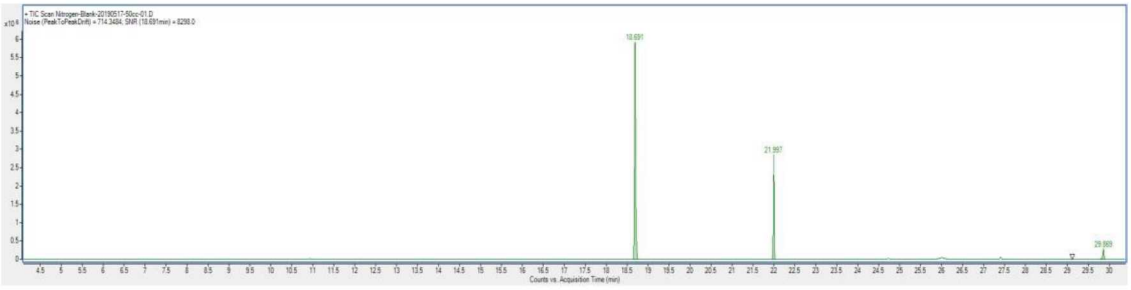

Figure 2. N_2 Blank TIC.

The peaks in the N_2 Blank originate from the instrument column. These siloxanes peaks appear in the sample TICs, but do not come from the sample itself.

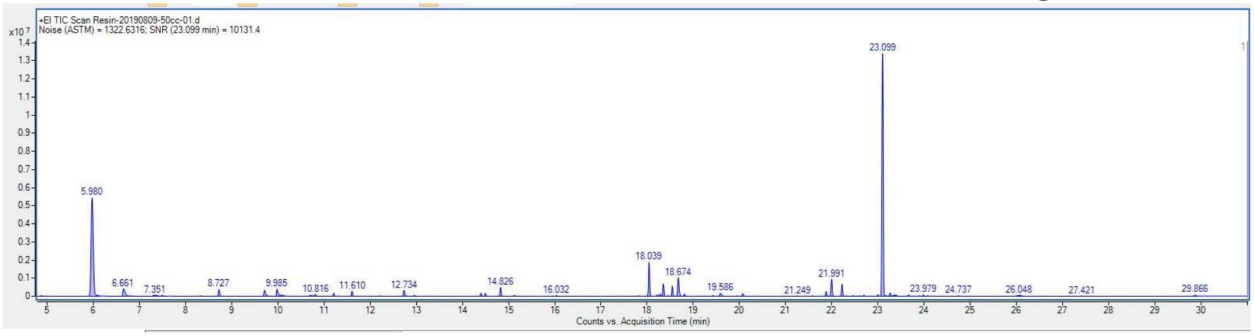

Figure 3. GC-MS TIC Resin bleed.

Table 2. Index of peaks identified in Resin bleed.

RT (min)	Match Statistic	Chemical Name	Estimated Concentration
5.98	92	chloromethane	513 ppb
6.661	94.4	Acetaldehyde	
7.351	66.32	MeOH	
7.501	93	1,3-Butadiene	
8.325	86.73	methyl formate	
8.727	97.15	ethyl chloride	
9.714	96.99	propenal	
9.985	92.95	propanal	
10.698	86.76	IPA	6 ppb
10.816	83.14	cyclopentene	
11.211	94.66	methylene chloride	4 ppb
11.61	96.04	1,3-cyclopentadiene	
12.221	85.02	Methacrolein	
12.734	94.35	silanol, trimethyl	
12.957	86.8	2-butanone	2 ppb
14.401	95.51	1,4-cyclohexadiene	
14.826	97.51	benzene	7 ppb
16.032	89.35	heptane	
17.82	89.54	hexanal	
18.039	97.88	1-octene	
18.216	95.62	4-octene E	
18.281	87.15	1-Octene, 3,4-dimethyl-	
18.35	97.66	2-octene, (E)	
18.448	89.48	Heptane, 3-methylene-	
18.543	97.79	4-octene, (E)	
18.808	94.77	heptane, 2,4-dimethyl-	
19.115	83.85	Benzene, 1-chloro-3-(trifluoromethyl)	
19.422	93.84	ethylbenzene	<1 ppb
19.586	89.89	p-xylene	<1 ppb
19.952	70.96	heptanal	
20.069	91.18	o-xylene	1 ppb
21.586	91.27	octane, 2,2,6-trimethyl-	
21.874	97.72	octanal	
22.22	97.97	octane, 2-chloro-	

22.308	86.92	heptane, 2,3,5-trimethyl-	
23.099	94.82	1-chloro-octane	

*Peaks at the following retention time correspond to contamination from the instrument's column itself and not originating from the sample: 18.67, 21.99 minutes.

A 100 ppb TO-15 calibration gas standard was run to quantify the concentration of the chloromethane from the resin bleed sample. TO-15 calibration gas is a 65-component mixture. The concentration of chloromethane was found to be 513 ppb from the resin bleed sample with mass of 2.259 gms. It should be noted that the chloromethane saturated the MS detector. This causes peak broadening and loss of mass accuracy. 2-Chloro octane and 1-chloro-octane could not be quantify because these chemicals are not part of the TO-15 calibration mix.

Chloromethane is identified using NIST library match, Mass Hunter, and Chemometrics which shows the molecular ion peaks (M+ and M+2) which can be either of the two chlorine isotopes, ^{35}Cl and ^{37}Cl. In addition the peak heights are in the ratio of 3:1 that indicated one chlorine atom.

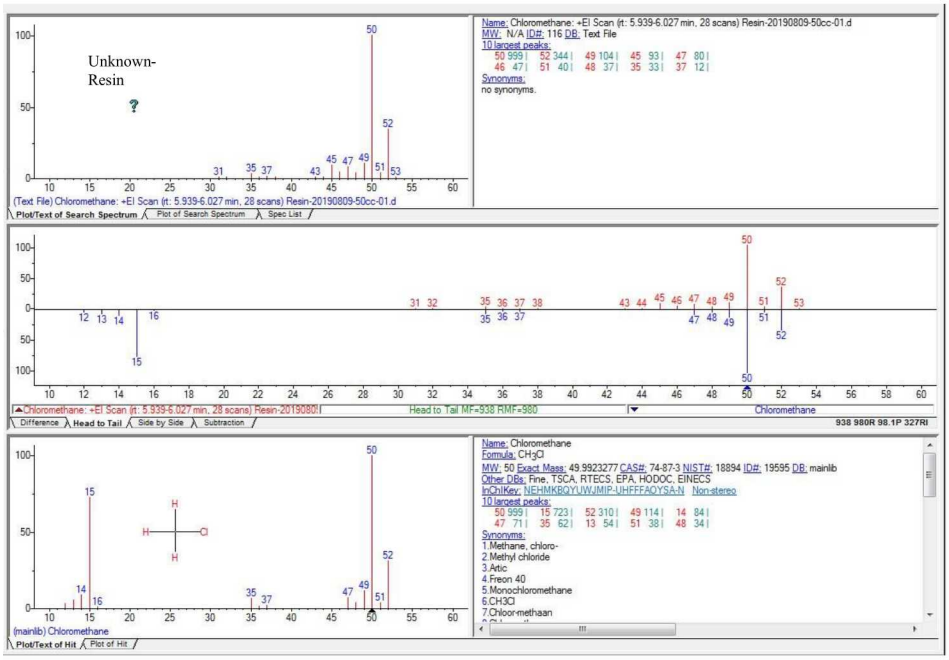

Figure 4. NIST library mass spectrum of unknown compound in resin and chloromethane. Mass spectral data was collected in the range of m/z = 30-300. m/z < 30 is not collected.

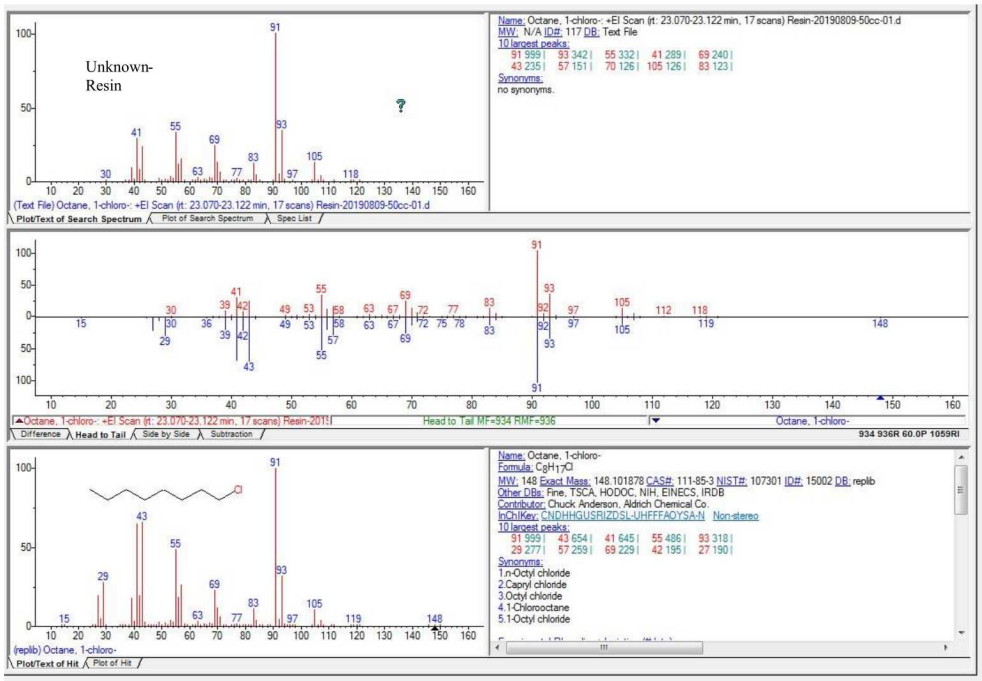

Figure 5. NIST library mass spectrum of unknown compound in resin and octane, 1-chloro. Mass spectral data was collected in the range of m/z = 30-300. m/z < 30 is not collected.

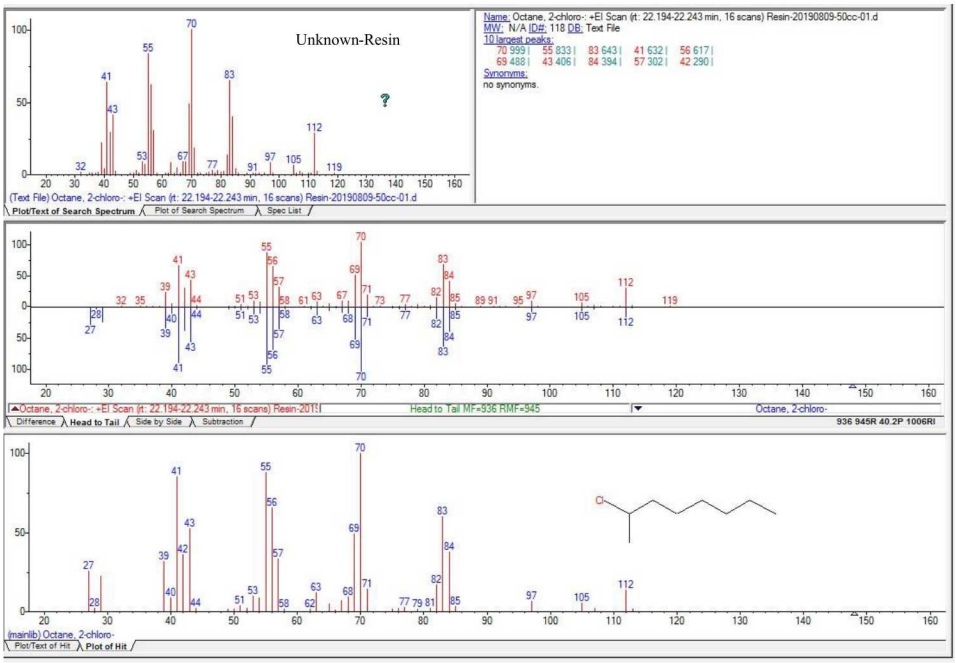

Figure 6. NIST library mass spectrum of unknown compound in resin and octane, 2-chloro. Mass spectral data was collected in the range of m/z = 30-300. m/z < 30 is not collected.

Table 3. Peak information for specific chemicals identified in resin bleed sample.

Identifcation	Peak Area	Peak Height	Saturated (S)
chloromethane	18105479	5437770	S
octane, 2-chloro-	1178030	670486.8	No
Octane, 1-chloro	26789486.68	13400126.37	No

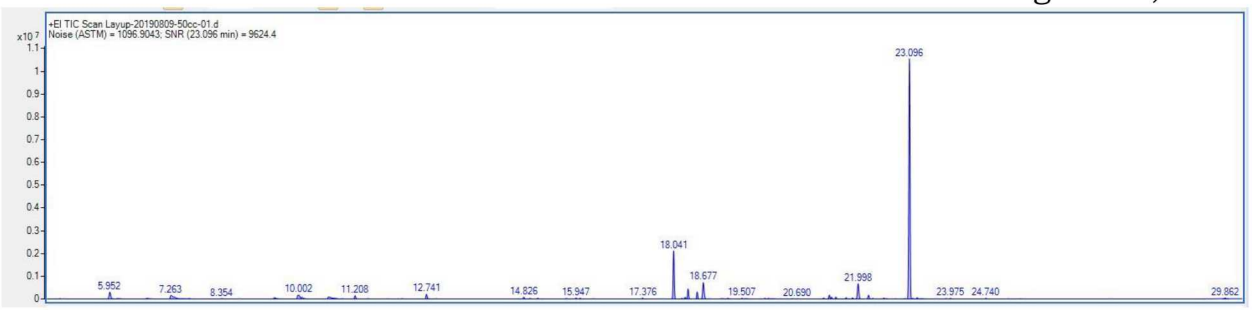

Figure 7. GC-MS TIC Lay-up.

Table 4. Index of peaks identified in Lay-up.

RT (min)	Match Statistic	Chemical Name	Concentration
5.952	97.21	chloromethane	24 ppb
7.263	82.43	MeOH	
7.655	73.7	butane	
9.479	90.1	EtOH	15 ppb
10.002	95.7	Acetone	7 ppb
10.639	90.82	IPA	15 ppb
11.208	94.98	Methylene Chloride	4 ppb
12.741	94.38	silanol, trimethyl-	
14.826	94.26	benzene	
14.954	76.17	1-butanol	
15.124	89.05	1,3-Cyclopentadiene, 1-methyl-	
15.745	80.47	disiloxane, hexamethyl-	
15.947	91.07	methyl methacrylate	
16.032	86.91	heptane	
16.317	76.4	1-pentene, 2,4,4-trimethyl-	
17.376	89.44	toluene	
18.041	97.81	1-octene	
18.216	83.06	2-octene	
18.288	91.32	octane	
18.35	97.47	4-octene	
18.808	76.66	hexane, 2,3,5-trimethyl-	
19.056	85.28	cyclohexane, 1,3,5-trimethyl-	
19.118	81.84	Benzene, 1-chloro-2-(trifluoromethyl)-	
19.2	89.96	cyclohexane, 1,1,3-trimethyl-	
19.507	89.94	cyclohexane, 1,2,4-trimethyl-	
20.001	90.72	cyclohexane, 1,2,4-trimethyl-	
20.069	65.72	p-xylene	<1ppb
20.135	86.06	cyclohexane, 1,2,4-trimethyl-	
20.197	84.79	1-ethyl-3-methyl-cyclohexane	
20.599	85.93	cyclohexane, 1-ethyl-2-methyl-	
20.69	85.13	benzene, (1-methylethyl)-	
21.259	92.06	benzene propyl-	
21.377	96.49	benzene, 1-ethyl-4-methyl-	
21.429	95.95	benzene, 1-ethyl-4-methyl-	

21.521	92.47	Mesitylene	
21.877	92.27	Octanal	
22.22	95.83	Octane, 2-chloro-	
23.096	95	Octane, 1-chloro	

*Peaks at the following retention time correspond to contamination from the instrument itself and not originating from the sample: 18.67 (cyclotrisiloxane hexamethyl-) and 21.99 (cyclotrisiloxane octamethyl-) minutes.

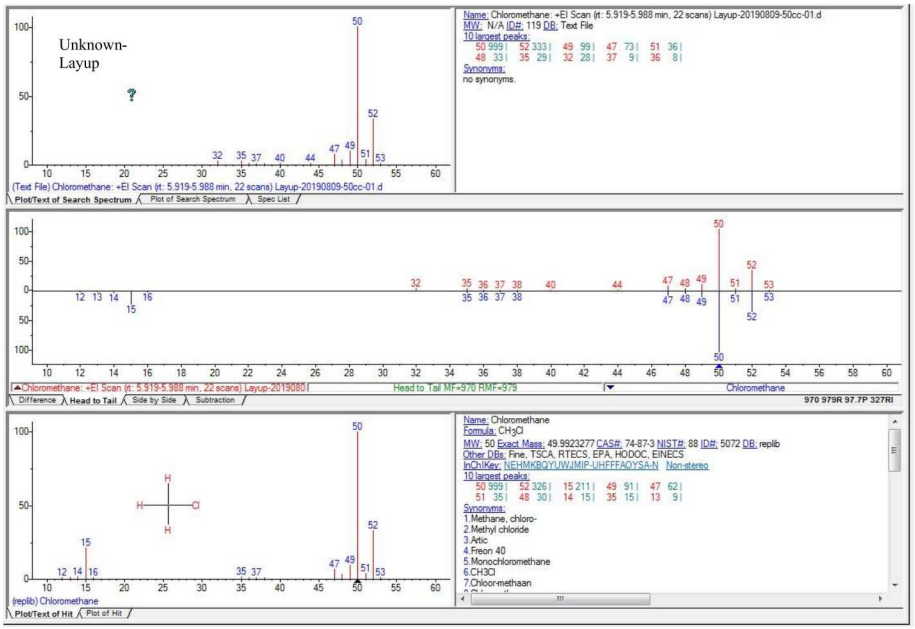

Figure 8. NIST library mass spectrum of unknown compound in lay-up and chloromethane. Mass spectral data was collected in the range of m/z = 30-300. m/z < 30 is not collected.

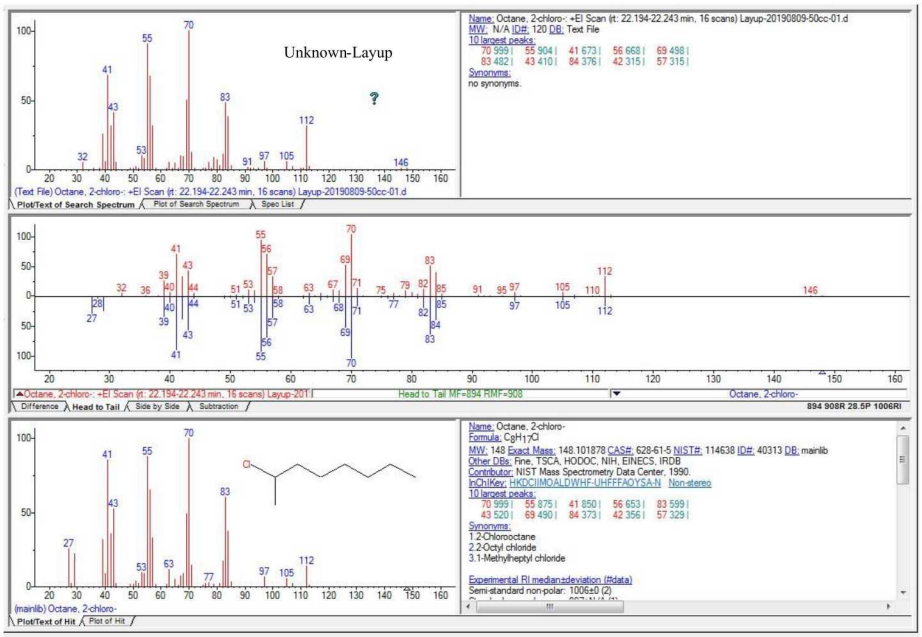

Figure 9. NIST library mass spectrum of unknown compound in lay-up and octane, 2-chloro. Mass spectral data was collected in the range of m/z = 30-300. m/z < 30 is not collected.

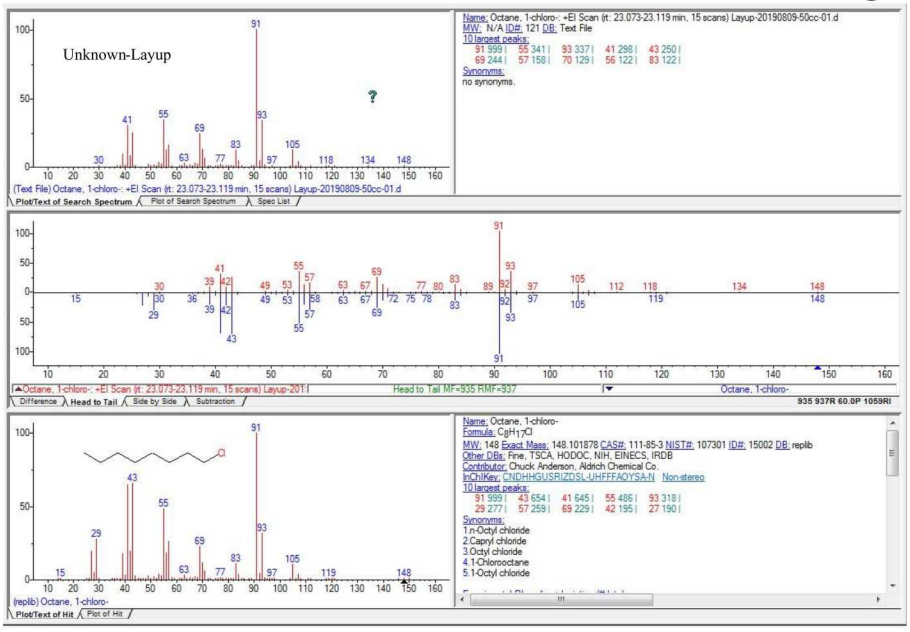

Figure 10. NIST library mass spectrum of unknown compound in lay-up and octane, 1-chloro. Mass spectral data was collected in the range of m/z = 30-300. m/z < 30 is not collected.

Table 5. Peak information for specific chemicals identified in Lay-up sample.

Identifcation	Peak Area	Peak Height	Saturated
chloromethane	754819.26	300027.53	No
octane, 2-chloro-	297221.06	170344	No
Octane, 1-chloro	19830564.31	10557039.08	No

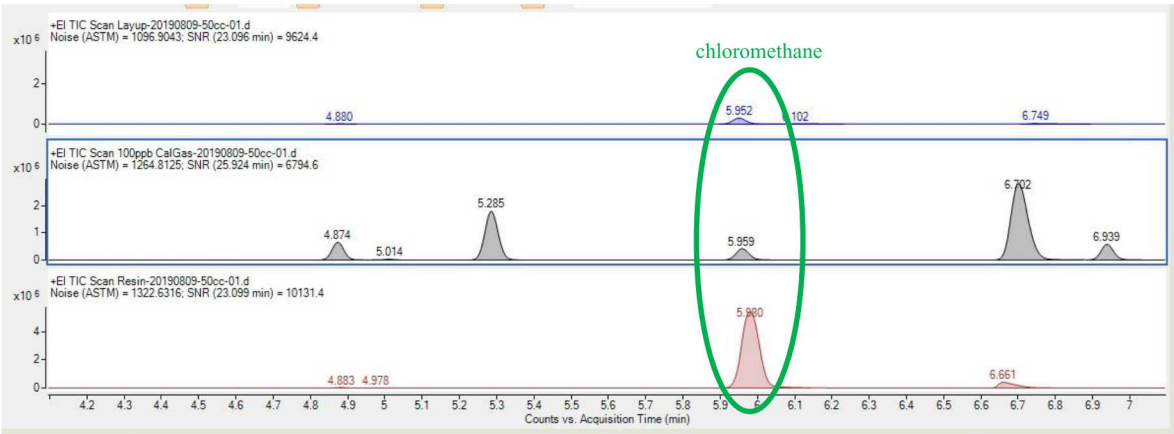

Figure 11. GC-MS TIC Overlay of Lay-up (blue), 100ppb calibration gas TO-15 mix (black) and resin bleed (red).

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