Automotive Paint Analysis Using Pyrolysis-GC-TOFMS and Pyrolysis-GCxGC-TOFMS

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1. Introduction

Pyrolysis (Py) is the analytical process that uses controlled temperature to produce smaller, more volatile compounds from large molecules. What makes this process even more attractive are the small sample sizes required and the fact that no sample preparation is needed. Paint analysis has traditionally been done using two different approaches: non-destructive (UV, IR, NMR, headspace GC), or destructive (Py-GC, Py-GC-MS) techniques. While the former approach provides information on functional groups, structural elements, and volatile compounds, the latter one can provide detailed information on polymeric sequences, cross-linking agents, etc.

Automotive paint formulation has continuously changed over the years according to automotive industry needs (cost, durability, ease of application) and, more recently, to meet environmental criteria (reduced use of solvents). It has evolved from simpler mixtures of BMA, MMA, and styrene copolymers to more complex mixtures of cross-linked polymers, plasticizers, additives, and other ingredients. Py-GC-MS of paint has been used for decades not only to help in process monitoring and quality control in industrial settings, but also to identify the origin of the paint in criminal cases where automobiles are involved.

The purpose of this analysis was to demonstrate the use of Py-GCxGC-TOFMS technology for the analysis of automotive paint samples and to compare the results obtained with one-dimensional (GC-TOFMS) analysis.

2. Experimental Conditions

Py-GC-TOFMS

Pyrolysis Unit:	CDS Pyroprobe 2000
Temp of the Coil Probe:	750°C
Time:	15 seconds
Sample Size:	~1 mg

GC:	Agilent 6890 GC
Column:	Rtx-1MS, 30 m, 0.25 mm id, 0.25 µm film thickness
Oven Program:	35°C (2 minute hold) to 250°C (10 minute hold) at 5°C/minute
Inlet Temp:	300°C
Split Ratio:	400:1
Carrier Gas:	He at a constant flow of 1.3 ml/minute

MS:	LECO Pegasus® GC-TOFMS
Ionization:	EI at 70eV
Mass Range (u):	35 to 500
Acquisition Rate:	10 spectra/second
Source Temperature:	200°C

Py-GCxGC-TOFMS

Pyrolysis Unit:	CDS Pyroprobe 2000
Temp of the Coil Probe:	750°C
Time:	15 seconds
Sample Size:	~1 mg

GCxGC:	Agilent 6890 GC equipped with a LECO Thermal Modulator
Primary Column:	Rtx-1MS, 30 m, 0.25 mm id, 0.25 µm film thickness
Main Oven Program:	35°C (2 minute hold) to 250°C (10 minute hold) at 5°C/minute
Secondary Column:	DB-WAX, 1 m, 0.1 mm id, 0.1 µm film thickness
Secondary Oven Program:	30°C offset from main oven
Inlet Temperature:	300°C
Split Ratio:	400:1
Carrier Gas:	He at a constant flow of 1.3 ml/minute
Modulator Temp:	30°C offset from main oven
Modulation Frequency:	6 seconds with a 1.2 second hot pulse time

MS:	LECO Pegasus® 4D GCxGC-TOFMS
Ionization:	EI at 70eV
Mass Range (u):	35 to 500
Acquisition Rate:	200 spectra/second
Source Temp:	200°C

Sample Description

Two samples were used for the experiment. The first sample consisting of paint chips from a black Pontiac Grand AM car was obtained from a local body shop. No separation of the layers was performed before this sample was analyzed. The second sample analyzed was a universal black touch-up paint obtained from a local automotive parts retail shop. This sample was dried prior to the analysis. About 1 mg of each sample was used for the analysis. Since quantitative comparison was not the purpose of the experiment, sample size varied slightly from one analysis to another.

3. Results

A. One-Dimensional Analysis (GC-TOFMS)

Results from the one dimensional-analysis of the two samples are displayed in Figure 1. Both chromatograms are presented as the total ion current (TIC) chromatogram.

The two samples were compared using the automated Compare algorithm available from the ChromaTOF® software. The paint chips sample was designated as the reference sample and the touch-up paint sample was compared against it. The algorithm allows the user to define specific parameters (concentration and concentration tolerance, S/N and match threshold, retention time deviation, and masses used for peak quantification) to be used for the comparison of the samples. At the end of the comparison the found peaks will be classified in one of four categories.

Match—Peaks that passed all the Compare criteria

Out of Tolerance—Peaks that pass all the criteria except the concentration tolerance

Not Founds—Peaks that were found in the reference sample but not in the compared sample

Contaminants—Peaks that were found in the compared sample but not in the reference sample

The processing of the paint chips sample resulted in 220 peaks being found and identified using the NIST library. About 25% of these peaks were also found in the touch-up paint sample at various concentration levels. Table 1 presents the analytes that were found to be present in both samples. The touch-up paint sample also contained about 25% unique peaks ("contaminants"). When cars are painted, multiple layers of paint and finishes are applied (primer, surfacer, base coat, clear coat, etc.). The larger number of analytes present in the paint chips sample can probably be explained by the fact that the analysis was performed on this sample without separation of these layers.

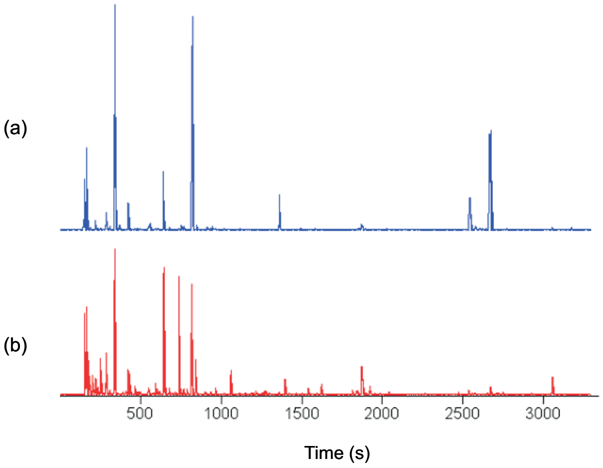

Figure 1. TIC chromatograms of the universal touch-up paint sample (a) and the black paint chips sample (b) obtained from one-dimensional analysis.

ChromaTOF software allows filtered display of both the chromatogram view and the peak table. The filtering can be done based on peak types and/or user-defined groups. This feature enables the analyst to perform faster data review. Figure 2 shows this feature applied to the chromatogram display of the touch-up paint sample.

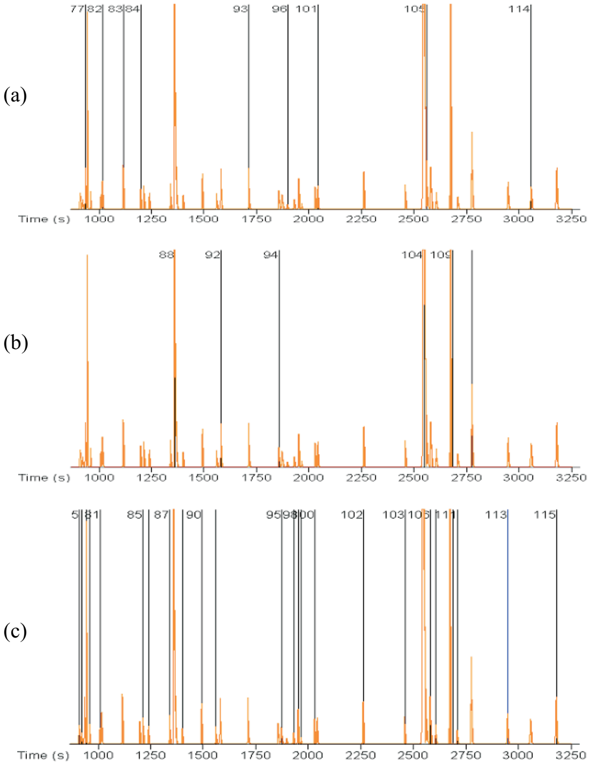

Figure 2. TIC chromatograms of the touch-up paint sample with the peak markers filter set to display the Match peaks (a), the Out of Tolerance Peaks (b), and the Contaminants (c).

Table 1. Analytes present in both paint samples at a S/N higher than 100.

Peak #	Name	R.T. (s)	Unique m/z	Match	Relative Concentration
3	Propene	154.0	41	891	54.5
5	1-Propene, 2-methyl-	161.4	57	978	102
8	Alpha-amino-gamma-butyrolactone	174.5	56	644	22.6
9	Propylene oxide	176.9	58	816	3.2
11	1-Butene, 3-methyl-	182.7	55	849	18.3
12	1,4-Pentadiene	186.0	40	900	28.2
13	Acetic acid, methyl ester	190.6	43	784	17.7
15	Methacrolein	206.9	39	908	10.9
16	Methyl vinyl ketone	214.6	70	879	94.8
17	Butanal	217.9	72	980	175
19	Cyclopropane, 1-ethyl-2-methyl-, cis-	227.6	42	959	48.2
20	2-Propenoic acid, methyl ester	236.7	55	901	17.7
21	1,3-Butadiene, 2-ethyl-	241.0	69	788	47.3
22	Acetic acid	245.7	45	924	56.3
25	3-Hexen-1-ol, acetate, (Z)-	272.5	43	839	60.6
26	Butanal, 2-methyl-	277.4	41	927	9.9
27	2-Butenal, 2-methyl-	282.0	78	669	112
28	2-Pentenal, (E)-	283.5	81	603	73.6
29	1-Butanol	284.5	56	960	57.0
31	Propanoic acid, 2-methyl-, methyl ester	307.1	43	955	133
32	2-Propenoic acid, 2-methyl-, methyl ester	341.1	40	985	312
34	Propanoic acid, 2,2-dimethyl-, methyl ester	358.7	56	836	146
37	Toluene	422.2	91	994	117
41	2-Undecanethiol, 2-methyl-	479.9	83	845	71.0
42	Acetic acid, butyl ester	494.9	43	970	120
45	Isocrotonic acid	558.2	45	927	49.6
46	Ethylbenzene	589.8	91	987	11.6
48	p-Xylene	606.2	91	937	36.5
50	Styrene	641.3	104	979	24.6
51	2-Cyclopenten-1-one, 2-methyl-	646.7	67	818	60.1
52	2-Propenoic acid, butyl ester	648.2	73	985	4.2
53	Propanoic acid, butyl ester	675.7	57	974	50.6
54	5-Hexenoic acid, methyl ester	678.6	68	766	173
55	2(3H)-Furanone, dihydro-3-methyl-	703.5	41	884	53.9
57	2-Propenoic acid, 2-methyl-, 2-methylpropyl ester	737.7	69	951	0.3
59	Benzaldehyde	752.1	77	919	439
62	2(5H)-Furanone, 3-methyl-	763.5	69	806	53.5
63	Propanoic acid, 2-methyl-, butyl ester	766.0	71	794	210
64	Benzene, propyl-	769.7	91	884	17.8
66	Benzonitrile	789.4	103	944	11.6
67	2-Propenoic acid, 2-methyl-, butyl ester:2	824.4	143	979	755
74	Benzene, 1-ethenyl-2-methyl-	852.5	118	826	363
77	Butanoic acid, 2-methyl-, propyl ester	936.4	57	905	127
78	Benzene, 3-butenyl-	937.1	91	964	18.3
83	Benzene, (3-methyl-3-butenyl)-	1115.7	91	886	56.9
84	3,5-Dimethyldihydropyran-2,6-dione	1198.8	56	969	24.0
88	Phthalic anhydride	1361.9	76	839	942
92	Diphenylmethane	1580.9	91	799	246
93	Bibenzyl	1714.3	91	878	138
94	2-(Butyliden-2-one)tetrahydrofuran	1856.5	68	770	309
96	Benzene, 4-hexenyl-	1897.3	92	615	13.5
101	1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	2042.9	149	804	43.9
104	Phenol, 4,4'-(1-methylethylidene)bis-	2546.3	213	974	1327
105	Unknown 63	2561.7	237	953	189
109	2-Hydroxy-3-allyl-5-t-butylbiphenyl	2684.7	91	970	289
112	Methanone(3,4-dimethylphenyl)(2,4,6-trimethylphenyl)	2776.0	91	943	380
114	Phenol-2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)	3058.2	322	974	9.90

B. Two-Dimensional Analysis (GCxGC-TOFMS)

The two paint samples were also analyzed using the Pegasus 4D GCxGC-TOFMS instrument. Two columns are connected in series by means of a thermal dual-stage modulator that uses cold N2 and hot air to trap and release the analytes in and out of the modulator. Tremendous increase in peak capacity (and peak separation as a result) is obtained by the use of the GCxGC technique.

Figure 3 shows the TIC chromatogram of the paint chips sample in a two-dimensional display. Peak intensity is represented on a color scale with red being the most intense and blue showing the baseline. More than 1500 peaks were found in each of the samples when the data was processed at a S/N of 1000.

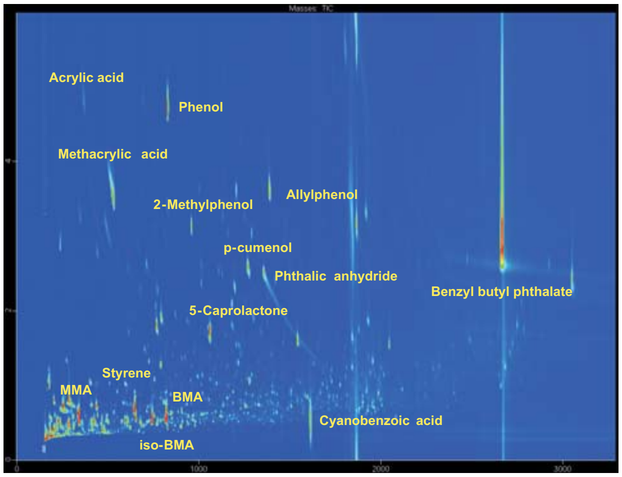

Figure 3. TIC chromatograms of the paint chips sample shown in a two-dimensional display. The x-axis represents retention time in the first dimension and y-axis represents retention time in the second dimension.

The increase in separation obtained from the GCxGC technique is better illustrated in Figure 4. The upper part of the figure shows the separation obtained from a one-dimensional analysis in a small region of the chromatogram. While a total of 9 peaks can be distinguished in this region, only 4 of them passed the set S/N criteria and were found by the software automatically. The same region of the chromatogram is presented in a two-dimensional analysis. This time the software was able to detect 28 peaks that pass the S/N criteria set in the data processing method at 1000.

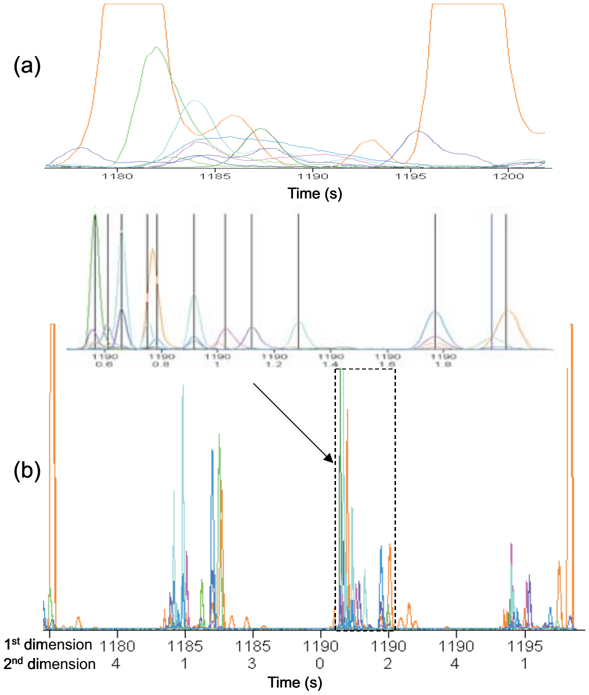

Figure 4. Extracted ion chromatograms in a selected region of the chromatogram obtained from the analysis of the paint chips sample by GC-TOFMS (a) GCxGC-TOFMS (b).

4. Conclusions

Comparison of the two samples resulted in big differences being found. The one-dimensional analysis resulted in about 200 analytes being found in the paint chips sample. The addition of separation in the second dimension resulted in a great increase in peak capacity and consequently peak separation. More than 1500 analytes were automatically found to be present in each of the samples when the data was processed at a S/N of 1000.