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

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Key Words: GCxGC-TOFMS, Pyrolysis, Deconvolution

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 crosslinked 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: Temp of the Coil Probe Time: Sample Size:	CDS Pyroprobe 2000 e: 750°C 15 seconds ~1 mg
GC:	Agilent 6890 GC
Column:	Rtx-1MS, 30 m, 0.25 mm id,
	0.25 μ m 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: Ionization: Mass Range (u): Acquisition Rate: Source Temperature:	LECO Pegasus® GC-TOFMS El at 70eV 35 to 500 10 spectra/second 200°C

Py-GCxGC-TOFMS Pyrolysis Unit: Temp of the Coil Pro Time: Sample Size:	CDS Pyroprobe 2000 obe: 750°C 15 seconds ~1 mg				
GCxGC:	Agilent 6890 GC equipped with a LECO Thermal Modulator				
Primary Column:	Rtx-1MS, 30 m, 0.25 mm id, 0.25 μ m film thickness				
Main Oven Program	35°C (2 minute hold) to 250°C				
Secondary Column	 (10 minute hold) at 5°C/minute DB-WAX, 1 m, 0.1 mm id, 0.1 μm film thickness 				
Secondary Oven Pro	ogram: 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: Ionization: Mass Range (u): Acquisition Rate: Source Temp:	LECO Pegasus [®] 4D GCxGC-TOFMS El at 70eV 35 to 500 200 spectra/second 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.

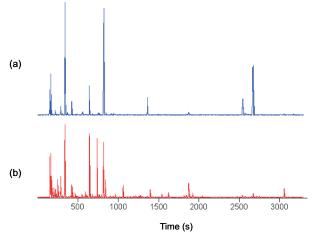


Figure 1. TIC chromatograms of the universal touch-up paint sample (a) and the black paint chips sample (b) obtained from one-dimensional analysis.

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.

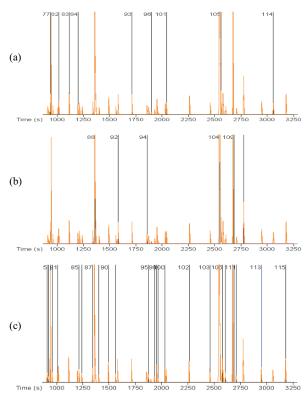


Figure 2. TIC chromatograms of the touch-up paint sample with the peak markers filter set to display the Match peaks (a), the Out of Tolerance Peaks (b), and the Contaminants (c).

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

5 1- 8 Al 9 Pr 11 1- 12 1,' 13 AA 15 M 16 M 17 B 20 2- 21 1,' 22 Ad 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 32 7 34 Pr	ropene 2. Progene 2	R.T. (s) 154.0 161.4 174.5 176.9 182.7 186.0 190.6 206.9 214.6 227.6 236.7 241.0 245.7 277.4 283.5 277.4 283.5 284.5 307.1 358.7	Unique m/z 41 57 56 58 55 40 43 39 70 72 42 55 69 43 42 55 69 43 41 78 81 56 81 56 43 40 56	Match 891 978 644 816 849 900 784 908 879 960 959 901 788 924 839 927 669 603 960 955 985	Concentration 54.5 102 22.6 3.2 10.9 28.2 17.7 10.9 94.8 17.7 47.3 56.3 60.6 9.9 112 77.6 57.0 57.0 57.0 113
5 1- 8 Al 9 Pr 11 1- 12 1,' 13 AA 15 M 16 M 17 B 20 2- 21 1,' 22 Ad 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 32 7 34 Pr	Propene, 2-methyl- pha-amino-gamma-butyrolactone ropylene oxide Butene, 3-methyl- 4-Pentadiene celic acid, methyl ester ethyl vinyl ketone utanal yclopropane, 1-ethyl-2-methyl-, cls- Propencia acid, methyl ester 3-Butadiene, 2-ethyl- celic acid Hexen-1-ol, acetate, (2)- utanal, 2-methyl- Butenal, 2-methyl- Butenal, 2-methyl- Pentenal, (E)- Butanol Propencia acid, 2-methyl-, methyl ester Propencia acid, 2-methyl-, methyl ester ropanoic acid, 2-dimethyl, methyl ester puene	161.4 174.5 176.9 182.7 186.0 190.6 206.9 214.6 217.9 227.6 236.7 241.0 245.7 241.0 245.7 277.4 282.5 277.4 282.5 284.5 307.1 358.7	57 56 58 55 40 43 39 70 72 42 55 69 45 43 41 78 81 56 43 40	978 644 816 849 900 784 908 879 980 959 901 788 929 901 788 927 669 927 669 927 669 955	102 22.6 3.2 18.3 28.2 17.7 10.9 94.8 175 48.2 17.7 48.2 17.7 56.3 56.3 56.6 9.9 9.9 112 73.6 57.0 133
8 All 9 Pr 11 1-1 12 1, 13 Ad 15 M 16 M 17 Bu 20 2- 21 1, 22 Ac 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	Ipha-amino-gamma-butyrolactone roykene oxide Butene, 3-methyl- 4-Pentadiene ositic acid, methyl ester lethacrolein danaf dyboropane, 1-ethyl-2-methyl-, cis- Propenoic acid, methyl ester 3-butadene, 2-ethyl- cetic acid Hexen-1-d, acetate, (2)- utanal, 2-methyl- Butenal, (E)- Butenal, 2-methyl- Pentenal, (E)- Butanol Propenoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester propanoic acid, 2-methyl-, methyl ester propanoic acid, 2-methyl-, methyl ester	174.5 176.9 182.7 186.0 190.6 206.9 214.6 217.9 227.6 236.7 241.0 245.7 241.0 245.7 241.0 245.7 241.0 245.7 277.4 282.0 283.5 277.4 282.0 283.5 277.4 284.5 307.1 358.7	56 58 55 40 39 70 42 55 43 69 45 43 41 78 81 56 43 40	644 816 849 900 784 908 879 980 959 901 788 929 901 788 924 839 927 669 900 955	22.6 3.2 18.3 28.2 17.7 10.9 94.8 175 48.2 17.7 48.2 17.7 48.2 48.2 17.7 56.3 60.6 9.9 112 73.6 57.0 133
9 Pr 11 1- 12 1,1 13 Ac 15 M 16 M 17 Bi 19 C; 20 2- 21 1,' 22 Ac 25 3- 26 Bi 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	ropylene oxide Butlene, 3-methyl- 4-Pentadiene eetiacrotein ethacrotein ethyl vinyl ketone utanal yclopropane, 1-ethyl-2-methyl-, cis- Propenoic acid, methyl ester 3-Butadiene, 2-ethyl- ecis acid Hexen-1-ol, acetate, (Z)- utanal, 2-methyl- Butenal, 2-methyl- Butenal, 2-methyl- Butenal, 2-methyl- Pentenal, (E)- Butanol Propenoic acid, 2-methyl-, methyl ester Propenoic acid, 2-dimethyl-, methyl ester popanoic acid, 2-dimethyl-, methyl ester popanoic acid, 2-dimethyl-, methyl ester	176.9 182.7 186.0 190.6 206.9 214.6 227.9 227.6 236.7 241.0 245.7 272.5 277.4 282.0 283.5 284.5 307.1 358.7	55 40 39 70 72 42 55 69 43 41 78 81 56 43 40	849 900 784 908 879 980 959 901 788 924 839 927 669 927 6603 960 955	32 18.3 28.2 17.7 10.9 94.8 17.7 48.2 17.7 48.2 17.7 47.3 56.3 60.6 9.9 9.9 112 73.6 57.0 133
11 1- 12 1, 13 Ac 15 M 16 M 17 B 19 C; 20 2- 21 1; 22 Ac 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	Butene, 3-methyl- 4-Pentadiene cetic acid, methyl ester lethyr vinyk ketone utanal ydopropane, 1-athyl-2-methyl-, cis- Propencia caid, methyl-seter 3-butadene, 2-athyl- cetic acid Hexam-1-di, acetate, (2)- utanal, 2-methyl- Butenal, 2-methyl- Butenal, (E)- Butanal Propencia caid, 2-methyl-, methyl ester Propencia caid, 2-methyl-, methyl ester ropancia caid, 2-methyl-, methyl ester propancia caid, 2-methyl-, methyl ester propancia caid, 2-methyl-, methyl ester propancia caid, 2-methyl-, methyl ester propancia caid, 2-methyl-, methyl ester	182.7 186.0 190.6 206.9 214.6 217.9 227.6 236.7 241.0 245.7 277.4 245.7 277.4 282.0 283.5 284.5 307.1 341.1 358.7	55 40 39 70 72 42 55 69 43 41 78 81 56 43 40	849 900 784 908 879 980 959 901 788 924 839 927 669 927 6603 960 955	18.3 28.2 17.7 10.9 94.8 175 48.2 17.7 47.3 56.3 60.6 9.9 9.9 112 73.6 57.0 133
12 1, 13 Ad 15 M 16 M 17 B 19 C) 20 2-2 21 1, 22 Ad 25 3- 26 BL 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 <tal< td=""> Tal</tal<>	4-Pentadiene -6cic acid, methyl ester lethacrolein ethyl vinyl kelone utanal ydopropane, 1-ethyl-2-methyl-, cis- Propenoic acid, methyl ester -8-Butadiene, 2-ethyl- ecic acid Hexen-1-ol, acetate, (Z)- utanal, 2-methyl- Butenal, 2-methyl- Butenal, 2-methyl- Butenal, (E)- Butanol Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2-methyl-, methyl ester ropanoic acid, 2-methyl-, methyl ester propenoic acid, 2-methyl-, methyl ester propenoic acid, 2-methyl-, methyl ester suene	186.0 190.6 206.9 214.6 217.9 227.6 236.7 241.0 245.7 272.5 277.4 282.5 283.5 284.5 307.1 341.1 358.7	40 43 39 70 72 42 55 69 45 43 41 78 81 56 43 40	784 908 879 980 959 901 788 924 839 927 669 603 960 955	28.2 17.7 10.9 94.8 175 48.2 17.7 47.3 66.3 60.6 9.9 112 73.6 57.0 133
13 Ad 15 M 16 M 17 BL 19 Cj 20 2- 21 1,- 22 Ad 25 3- 26 BL 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 Tot	cetic acid, methyl ester tethyz rolein tethyz innyk ketone utanal yciogropane, 1-ethyl-2-methyl-, cis- Propencic acid, methyl ester 3-Sutadieme, 2-ethyl- cetic acid Hexm-1-di, acetate, (Z)- utanal, 2-methyl- Butenal, 2-methyl- Pentenal, (E)- Butanal Propencic acid, 2-methyl-, methyl ester Propencic acid, 2-methyl-, methyl ester ropancic acid, 2-dimethyl-, methyl ester propanci acid, 2-dimethyl-, methyl ester propanci acid, 2-dimethyl-, methyl ester propanci acid, 2-dimethyl-, methyl ester	190.6 206.9 214.6 217.9 227.6 236.7 241.0 245.7 277.4 282.0 283.5 284.5 307.1 341.1 358.7	39 70 72 42 55 69 45 43 41 78 81 56 43 40	908 879 980 959 901 788 924 839 927 669 903 960 955	17.7 10.9 94.8 175 48.2 17.7 47.3 56.3 60.6 9.9 112 73.6 57.0 133
15 M 16 M 17 Bi 19 Cy 20 2-2 21 1,1,2 22 Ac 25 3- 26 Bu 27 27 27 27 29 1- 31 Pr 32 2- 34 Pr 37 To	lethacrolein lethyl vinyl ketone Judanal ydopropane, 1-ethyl-2-methyl-, cis- Propencia caid, methyl ester 3-Butadiene, 2-ethyl- celic acid Hexen-1-ol, acetate, (Z)- utanal, 2-methyl- Butenal, 2-methyl- Butenal, 2-methyl- Butenal, (E)- Sutanol Propencia caid, 2-methyl-, methyl ester Propencia caid, 2-methyl-, methyl ester propanoic acid, 2-methyl-, methyl ester propanoic acid, 2-dimethyl-, methyl ester ponence acid, 2-methyl-, methyl ester	214.6 217.9 227.6 236.7 241.0 245.7 272.5 277.4 282.0 283.5 284.5 307.1 341.1 358.7	70 72 42 55 69 45 43 41 78 81 56 43 40	879 980 959 901 788 924 839 927 669 603 960 955	10.9 94.8 175 48.2 17.7 47.3 56.3 60.6 9.9 112 73.6 57.0 133
17 Bi 19 Cj 20 2- 21 1; 22 Ac 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	utanat	217.9 227.6 236.7 241.0 245.7 272.5 277.4 282.0 283.5 284.5 307.1 341.1 358.7	72 42 55 69 45 43 41 78 81 56 43 40	980 959 901 788 924 839 927 669 603 960 955	175 48.2 17.7 47.3 56.3 60.6 9.9 112 73.6 57.0 133
19 C) 20 2- 21 1,: 22 Ac 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	ydopropane, 1-ethyl-2-methyl-, cis- Propencia caid, methyl ester 3-Butadiene, 2-ethyl- celic acid Hexan-1-ol, acetate, (Z)- Hazma1, -z-methyl- Butenal, 2-methyl- Pentenal, (E)- Butanol Propencia caid, 2-methyl-, methyl ester Propencia caid, 2-methyl-, methyl ester ropanoic acid, 2-methyl-, methyl ester polene	227.6 236.7 241.0 245.7 272.5 277.4 282.0 283.5 284.5 307.1 341.1 358.7	42 55 69 45 43 41 78 81 56 43 40	959 901 788 924 839 927 669 603 960 955	48.2 17.7 47.3 56.3 60.6 9.9 112 73.6 57.0 133
20 2- 21 1, 22 Ac 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	Propencia acid, methyl ester 3-Butadiene, 2-ethyl- Selic acid Hexen-1-ol, acetate, (2)- tutanal, 2-methyl- Butanal, 2-methyl- Pentenal, (E)- Butanol ropanoic acid, 2-methyl-, methyl ester Propencia acid, 2-methyl-, methyl ester ropanoic acid, 2-dimethyl-, methyl ester propencia acid, 2-dimethyl-, methyl ester Juene	236.7 241.0 245.7 272.5 277.4 282.0 283.5 284.5 307.1 341.1 358.7	55 69 45 43 41 78 81 56 43 40	901 788 924 839 927 669 603 960 955	17.7 47.3 56.3 60.6 9.9 112 73.6 57.0 133
21 1, 22 Ac 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	3-Butadiene, 2-ethyl- celic acid Hexen-1-ol, acetate, (Z)- utanal, 2-methyl- Sutenal, 2-methyl- Pentenal, (E)- Sutanol Torpanoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2-dimethyl-, methyl ester Juene	241.0 245.7 272.5 277.4 282.0 283.5 284.5 307.1 341.1 358.7	69 45 43 41 78 81 56 43 40	788 924 839 927 669 603 960 955	47.3 56.3 60.6 9.9 112 73.6 57.0 133
22 Ac 25 3- 26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	cetic acid Hexen-1-ol, acetate, (Z)- Hexen-1-ol, acetate, (Z)- Butenal, 2-methyl- Pentenal, (E)- Butanol Pontenal, (C)- Butanol Propenoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester propanoic acid, 2-dimethyl-, methyl ester Juene	245.7 272.5 277.4 282.0 283.5 284.5 307.1 341.1 358.7	45 43 41 78 81 56 43 40	924 839 927 669 603 960 955	56.3 60.6 9.9 112 73.6 57.0 133
25 3- 26 Bi 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	Hoven-1-ol, acetate, (2)- utanal, 2-methyl- Butenal, 2:-methyl- Butenal, (E)- Sutanol Sutanol Propenoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2-dimethyl-, methyl ester Juene	272.5 277.4 282.0 283.5 284.5 307.1 341.1 358.7	43 41 78 81 56 43 40	839 927 669 603 960 955	60.6 9.9 112 73.6 57.0 133
26 Bu 27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	utanal, 2-methyl- Butenal, 2-methyl- Pentenal, (E)- Butanol goganoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2-dimethyl-, methyl ester Juene	277.4 282.0 283.5 284.5 307.1 341.1 358.7	41 78 81 56 43 40	927 669 603 960 955	9.9 112 73.6 57.0 133
27 2- 28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	Butenal, 2-methyl- Pentenal, (E)- Butanol Butanol copanoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2-dimethyl-, methyl ester Juene	282.0 283.5 284.5 307.1 341.1 358.7	78 81 56 43 40	669 603 960 955	112 73.6 57.0 133
28 2- 29 1- 31 Pr 32 2- 34 Pr 37 To	Pentenal, (E)- Butanol organoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2,2-dimethyl-, methyl ester Juene	283.5 284.5 307.1 341.1 358.7	81 56 43 40	603 960 955	73.6 57.0 133
29 1- 31 Pr 32 2- 34 Pr 37 To	Butanol ropanoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2,2-dimethyl-, methyl ester Juene	284.5 307.1 341.1 358.7	56 43 40	960 955	57.0 133
31 Pr 32 2- 34 Pr 37 To	ropanoic acid, 2-methyl-, methyl ester Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2,2-dimethyl-, methyl ester Juene	307.1 341.1 358.7	43 40	955	133
32 2- 34 Pr 37 To	Propenoic acid, 2-methyl-, methyl ester ropanoic acid, 2,2-dimethyl-, methyl ester oluene	341.1 358.7	40		
34 Pr 37 To	ropanoic acid, 2,2-dimethyl-, methyl ester bluene	358.7		985	
37 To	pluene				312
				836	146
		422.2	91	994	117
	Undecanethiol, 2-methyl-	479.9	83	845	71.0
	cetic acid, butyl ester	494.9	43	970	120
	ocrotonic acid	558.2	45	927	49.6
	thylbenzene	589.8	91	987	11.6
	-Xylene	606.2	91	937	36.5
	tyrene	641.3	104	979	24.6
	Cyclopenten-1-one, 2-methyl-	646.7	67	818	60.1
	Propenoic acid, butyl ester	648.2	73	985	4.2
	ropanoic acid, butyl ester	675.7	57	974	50.6
	Hexenoic acid, methyl ester	678.6	68	766	173
	(3H)-Furanone, dihydro-3-methyl-	703.5	41	884	53.9
	Propenoic acid, 2-methyl-, 2-methylpropyl ester	737.7	69	951	0.3
	enzaldehyde	752.1	77 69	919	439
	(5H)-Furanone, 3-methyl-	763.5		806	53.5
	ropanoic acid, 2-methyl-, butyl ester	766.0	71 91	794	210
	enzene, propyl- enzonitrile	769.7 789.4	91 103	884 944	17.8 11.6
		824.4	103	944	755
	Propenoic acid, 2-methyl-, butyl ester:2 enzene, 1-ethenyl-2-methyl-	852.5	143	826	363
		936.4	57	905	127
	utanoic acid, 2-methyl-, propyl ester enzene, 3-butenyl-	936.4	57 91	905 964	127
	enzene, (3-methyl-3-butenyl)-	1115.7	91	904 886	56.9
	5-Dimethyldihydropyran-2,6-dione	1115.7	91 56	969	24.0
	hthalic anhydride	1361.9	76	839	942
	iphenylmethane	1580.9	91	799	942 246
	ibenzyl	1714.3	91	878	138
	-(Butyliden-2-one)tetrahydrofuran	1856.5	68	770	309
	enzene. 4-hexenvl-	1897.3	92	615	13.5
	2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	2042.9	149	804	43.9
	henol, 4,4'-(1-methylethylidene)bis-	2546.3	213	974	1327
	nknown 63	2540.3	213	953	189
	Hydroxy-3-allyl-5-t-butylbiphenyl	2684.7	91	970	289
	lethanone(3,4-dimethylphenyl)(2,4,6-trimethylphenyl)	2004.7	91	943	289
	henol-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.

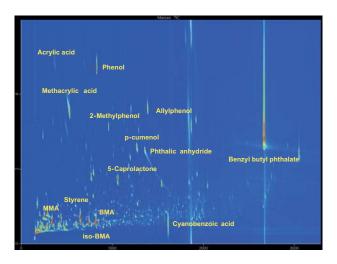


Figure 3. TIC chromatograms of the paint chips sample shown in a twodimensional display. The x-axis represents retention time in the first dimension and y-axis represents retention time in the second dimension.

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 onedimensional 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.

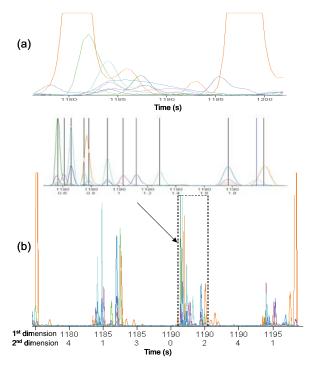


Figure 4. Extracted ion chromatograms in a selected region of the chromatogram obtained from the analysis of the paint chips sample by GC-TOFMS (a) GCxGC-TOFMS (b).

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.



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