

Harpur Hill, Buxton  
Derbyshire, SK17 9JN  
T: +44 (0)1298 218000  
F: +44 (0)1298 218590  
W: [www.hsl.gov.uk](http://www.hsl.gov.uk)



**Analysis of Weld-Thro' Primers  
Laboratory tests using pyrolysis-gas  
chromatography-mass spectrometry**

**HSL/2007/16**

Project Leader: **Alan Howe**

Author(s): **Ian Pengelly**

Science Group: **Health Improvement**

## **ACKNOWLEDGEMENTS**

Thanks are due to:-

Graham Carter of TWI, Cambridge for his technical input and for his coordination and leadership of the project.

Bernt Engstrom, Peter Backlund and their colleagues at FIOH, Finland for hosting a meeting at their laboratory facilities in Turku, preparation/supply of three of the test products and laboratory testing of the products.

Erik Beck Hansen and his colleagues at FORCE Technology, Denmark for hosting a meeting in Copenhagen and supply of two of the test products.

Philippe Legros and his colleagues at Arcelor, Belgium for laboratory testing of the products.

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# EXECUTIVE SUMMARY

## Objectives

The objective of the work is to provide information on test methods, analytical methods and sampling procedures for the determination of thermal degradation products generated during welding processes involving weld-thro' products and coatings. The information is, amongst other things, intended to aid completion of European Standard prCEN/ISO/TS 15011-5.

## Main Findings

Five weld thro- primer products were tested at HSL using a pyrolyser interfaced to a gas chromatograph-mass spectrometer (GC-MS). Similar tests were also carried out by FIOH, Finland and Arcelor, Belgium.

The tests at HSL were carried out at pyrolysis temperatures of 450°C, 650°C and 850°C. The major components at all three test temperatures were very similar, but the amounts of material generated generally increases with temperature and the number of trace/minor also tends to increase quite markedly. Tests at FIOH produced similar findings. One of the additional HSL/FIOH results show any reason to deviate from a standard test temperature of around 800°C.

The laboratory tests identified a number of significant components which will be targeted in future welding tests to be carried out using the same five products.

An inter laboratory comparison of the results obtained by HSL, FIOH and Arcelor showed generally good agreement with regard to the main components generated, although there were some anomalies in each of the five products. HSL and FIOH were using very similar pyrolysis (Pyrola) and GC-MS (Agilent) equipment, and, not unexpectedly, obtained the best agreement. This provided a good illustration of the level of inter laboratory agreement which might be expected from a 'best case' scenario, ie two independent laboratories examining the same sample using similar equipment and conditions. Agreement between the HSL/FIOH and Arcelor results, which although not as good, was still encouraging, particularly for the more volatile components. This gives an indication of the level of inter laboratory agreement for a 'worst case' scenario where the two laboratories are examining the same sample, but using different equipment and conditions. The main difference between the HSL/FIOH and Arcelor results was the absence of some semi- volatile components in the latter, in particular bisphenol-A in Product B and benzoic acid and phthalic anhydride in Product C. The reasons for this difference remain unclear.

## Recommendations

It is recommended that a pyrolysis temperature of 800°C be adopted as the standard test temperature.

The pyrolysis products identified in these laboratory tests should be compared with those collected during welding tests to be carried out at TWI, Cambridge using the same five products.

# 1 INTRODUCTION

This project was carried out in partnership with The Welding Institute (TWI), Cambridge, the Finnish Institute of Occupational Health (FIOH), Turku, Finland, FORCE Technology, Denmark and Arcelor, France/Belgium.

The objective of the work is to provide information on test methods, analytical methods and sampling procedures for determination of thermal degradation products generated during welding involving weld-thro' products and coatings. The information is, amongst other things, intended to aid completion of European Standard prCEN/ISO/TS 15011-5.

This report describes testing of a selection of products using the pyrolysis-based test procedure detailed in Project Report OMS/05/15. This forms part of Work Package 2 (WP2) of the project.

The objectives for WP2 are:

- To use various pyrolysis techniques to identify components produced by heating of weld-thro products.
- To examine and compare the results obtained by different test procedures and equipment on the amounts and composition of the thermal degradation products.
- To produce recommendations for a standard test procedure for testing of weld-thro products.

The products for these tests were provided by FIOH and FORCE Technology and comprised five weld-thro' shop primers. FIOH supplied samples of one shop primer and two top paints as thin films on aluminium foil and one shop primer in the form of small solid flake. FORCE supplied samples of three shop primers as bulk products, two of which were two-component types. These products were coated on aluminium foil at HSL (after mixing in the case of the two-component types). In the case of the FIOH samples, the film thickness was 100  $\mu\text{m}$ , which reduces to around 50  $\mu\text{m}$  when dry. The film thickness of the samples prepared as HSL is not known, but, when dry, is probably around 30 – 50  $\mu\text{m}$ .

The samples were tested using a pyrolyser interfaced to a gas chromatograph (GC) equipped with a mass spectrometer (MS) detector. Some of these products will also be subject of similar testing by FIOH and Arcelor.

## 2 TESTING PROCEDURE

The testing protocol and equipment is described more fully in Project Report OMS/05/15, but is basically as follows:-

Samples of the various primers are heated in a Pyrola 2000 pyrolyser interfaced to an Agilent HP5890 GC equipped with an HP5971 MS detector. This particular pyrolyser is mounted directly on to the 'normal' split-splitless injector of the GC and is capable of heating samples to over 1000°C. The sample is placed on a calibrated platinum filament assembly, which is placed inside the body of the pyrolyser surrounded by a heated (175°C) glass liner. When the GC is ready, the pyrolyser is started and an electrical current is passed through the filament. This heats up to the test temperature in just a few milliseconds (ms) and maintains it at that temperature for two seconds. Thermal degradation products are carried by the GC carrier gas (helium) from the pyrolysis chamber to the GC via a short heated transfer line. The rapid heating process focuses the degradation products at the front end of the chromatographic column producing good resolution of even the most volatile components.

### 2.1 CHROMATOGRAPHIC CONDITIONS

The chromatographic conditions used for the tests were as follows:-

**Column:-** 30 m × 0.25 mm HP-5 (0.25 µm film thickness);

**Carrier gas:-** Helium

**Carrier flow rate:-** 2 ml/min (initial pressure = 16.9 psi);

**Injector:-** Split-splitless (split on);

**Injector temperature:-** 250°C;

**Temperature program:-** 50°C for 5 minutes; 5°C/min to 75°C; 12.5°C to 200°C; 25°C/min to 300°C; 300°C for 6 minutes;

**Run time:-** 30 minutes;

**Detector 'Solvent' delay:-** 30 seconds;

**Detector range:-** 20 – 400 amu.

### 2.2 PYROLYSIS

Prior to the tests, the platinum filament was calibrated over a temperature range of 350°C to 1000°C using the calibration procedure described in the manufacturers literature.

Each product was pyrolysed, using a heating duration of 2 seconds, at 450°C, 650°C and 850°C. In all cases the heated glass liner and transfer line were maintained at 175°C.

### 3 TEST SAMPLES

The five weld-thro' primers examined in the tests were as follows:-

- i) **Product A** – This is a red two-component low zinc ethyl silicate shop-primer supplied as a bulk paint by FORCE Technology;
- ii) **Product B** – This is a red two-component epoxy polyamide shop-primer supplied as a bulk paint by FORCE Technology;
- iii) **Product C** – This is a red one-component alkyd shop-primer supplied as a bulk paint by FORCE Technology;
- iv) **Product D** – This is a grey two-component water-based ethyl silicate shop-primer supplied as small solid flakes by FIOH, Turku;
- v) **Product E** – This is a grey two-component solvent-based ethyl silicate shop-primer supplied coated onto aluminium foil by FIOH, Turku.

The three bulk paint samples were mixed (as per the manufacturers instructions), applied to aluminium foil and allowed to dry thoroughly at room temperature for at least 24 hours before testing. Paint thickness was not measured, but was estimated to be between 30 and 100  $\mu\text{m}$ .

The foil mounted sample were placed on a quartz filter and 1.4 mm circles were punched out using a metal borer. The quartz filter acts as backing material to prevent contact/reaction between the aluminium foil and the platinum filament.

Assuming a sample thickness of 0.03 – 0.1 mm and a sample density of around 2  $\text{g}/\text{cm}^3$ , a 1.4 mm diameter sample would equate to a mass of around 100 – 300  $\mu\text{g}$ .

In the case of the sample supplied as a solid flake, a small amount (*ca.* 100 – 500  $\mu\text{g}$ ) of the material was deposited directly on the platinum filament for testing.

## 4 PYROLYSIS TESTS

The tests carried out on the five test products were as follows:-

### 4.1 PRODUCT A

- *Sample A1:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 650°C for 2 seconds;
- *Sample A2:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 850°C for 2 seconds;
- *Sample A3:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 450°C for 2 seconds.

### 4.2 PRODUCT B

- *Sample B1:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 650°C for 2 seconds;
- *Sample B2:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 850°C for 2 seconds;
- *Sample B3:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 450°C for 2 seconds.

### 4.3 PRODUCT C

- *Sample C1:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 650°C for 2 seconds;
- *Sample C2:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 850°C for 2 seconds;
- *Sample C3:-* 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 450°C for 2 seconds.

### 4.4 PRODUCT D

- *Sample D1:-* Flakes placed directly on platinum filament and pyrolysed at 650°C for 2 seconds;
- *Sample D2:-* Flakes placed directly on platinum filament and pyrolysed at 850°C for 2 seconds;
- *Sample D3:-* Flakes placed directly on platinum filament and pyrolysed at 450°C for 2 seconds.

#### 4.5 PRODUCT E

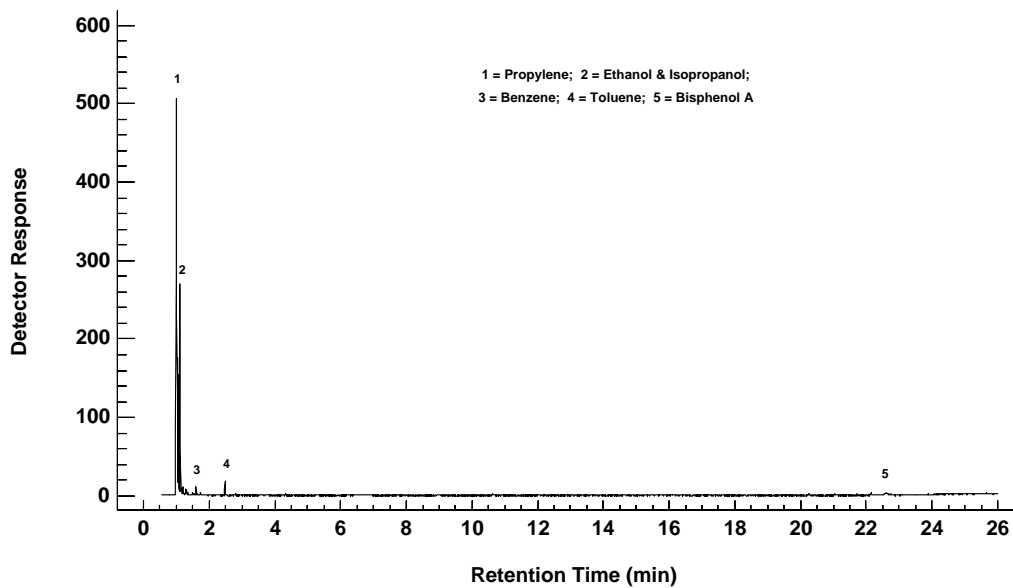
- *Sample E1*:- 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 650°C for 2 seconds;
- *Sample E2*:- 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 850°C for 2 seconds;
- *Sample E3*:- 1.4 mm circle punched from quartz/foil-mounted sample and pyrolysed at 450°C for 2 seconds.

## 5 TEST RESULTS

### 5.1 PRODUCT A

The chromatograms obtained from the three samples of Product A were generally found to contain around a dozen components, however many of these were present in amounts of rather less than 1%. The main components in the three samples were propylene, isopropanol, acetone, ethanol and acetaldehyde.

The chromatogram obtained from Sample A2, heated to 850°C, is shown in Figure 1.



**Figure 1: Product A – Heated to 850°C**

Table 1 shows the peak areas for the eleven largest components in the Total Ion Chromatogram (TIC) for each of the three tests. In Table 2, these peak areas have been converted to a percentage of the total peak area. The data in Table 2 are based on the assumption that all components give an equal detector response, and, while this is not strictly the case, the data are still useful as an estimate of the proportions of each compound present.

The data in Tables 1 and 2 produced the following observations:-

- The main components in all three samples were very similar;
- The total peak area for the sample heated to 450°C was significantly lower than for the corresponding samples heated to 650°C and 850°C;
- The sample heated to 450°C showed significantly fewer components than the corresponding samples heated to 650°C and 850°C;
- Overall, the three samples of Product A produced fewer components on heating than was the case for the other four products.

**Table 1: Product A – TIC Peak Areas**

COMPONENT	RT (min)	SAMPLE A3 450°C	SAMPLE A1 650°C	SAMPLE A2 850°C	MEAN VALUE
Propylene	1.00	450	13500	8300	7415
Acetaldehyde	1.06	-	800	1600	800
Ethanol	1.07	500	2000	1200	1235
Isopropanol + Acetone	1.11	1000	2900	2750	2215
Cyclopentadiene	1.19	-	-	90	30
Hexane	1.30	-	-	60	20
Benzene	1.60	-	220	130	115
Toluene	2.48	15	150	240	135
Indene	10.63	-	20	30	15
Bisphenol-A	22.56	-	130	170	100
TOTAL PEAK AREA		1965	19720	14570	12085

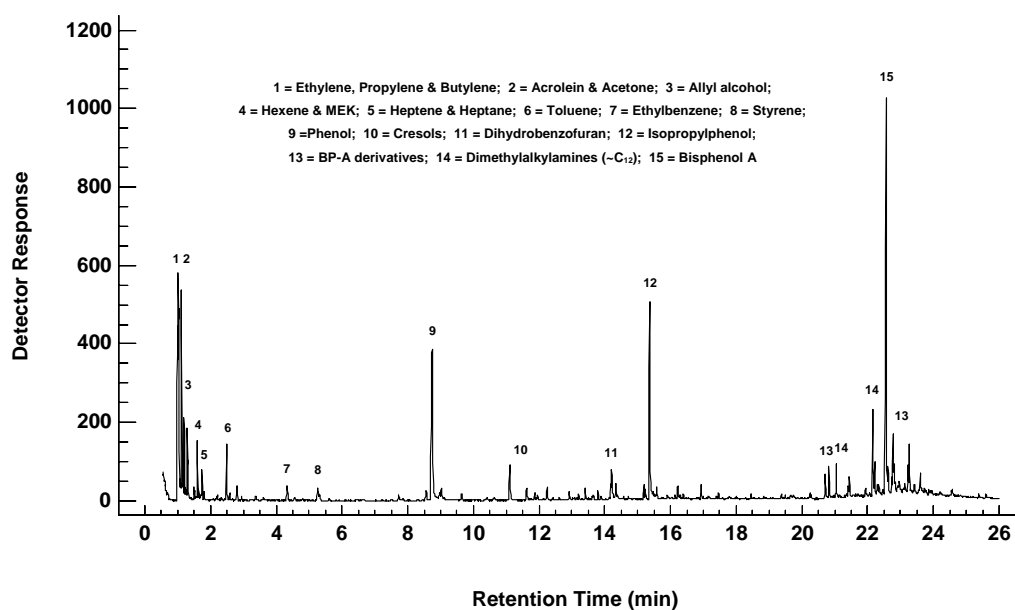
**Table 2: Product A – Main Components (%)**

COMPONENT	RT (min)	SAMPLE A3 450°C	SAMPLE A1 650°C	SAMPLE A2 850°C	MEAN VALUE
Propylene	1.00	22.9%	68.5%	57.0%	61.4%
Isopropanol + Acetone	1.11	50.9%	14.7%	18.9%	18.3%
Ethanol	1.07	25.4%	10.1%	8.2%	10.2%
Acetaldehyde	1.06	-	4.1%	11.0%	6.6%
Toluene	2.48	0.8%	0.8%	1.6%	1.1%
Benzene	1.60	-	1.1%	0.9%	1.0%
Other	-	-	0.8%	2.4%	1.4%
TOTAL PERCENTAGE		100%	100%	100%	100%

## 5.2 PRODUCT B

The chromatograms obtained from the three samples of Product B were generally found to contain in excess of 50 components, but many of these were present in amounts of rather less than 1%. The main components in the three samples were bisphenol-A (and related compounds), phenol, C<sub>2-4</sub> alkenes, C<sub>10-12</sub> dimethylalkylamines, isopropenylphenol and acetone.

The chromatogram obtained from Sample B2, heated to 850°C, is shown in Figure 2.



**Figure 2: Product B – Heated to 850°C**

Table 3 shows the peak areas for the forty or so largest components in the TIC for each of the three test samples. Table 4 shows the ten main components converted to a percentage of the total peak area and listed in order of abundance.

The data in Tables 3 and 4 produced the following observations:-

- The main components in all three samples were fairly similar, particularly in the case of the samples heated to 650°C and 850°C;
- The total peak area for the sample heated to 850°C was around twice that of the sample heated to 650°C and eight times that of the sample heated to 450°C;
- Increasing pyrolysis temperature from 450°C to 650°C produces a significant increase in the number of components generated;
- Further increasing pyrolysis temperature from 650°C to 850°C results in a number of additional minor/trace components being generated (including naphthalene and other aromatics);
- The ten most abundant components in the sample heated to 450°C account for around 90% of the total chromatographic peak area. This decreases to around 88% for the sample heated to 650°C and to around 79% for the sample heated to 850°C.

**Table 3: Product B – TIC Peak Areas**

COMPONENT	RT (min)	SAMPLE B3 450°C	SAMPLE B1 650°C	SAMPLE B2 850°C	MEAN VALUE
Ethene/Propene/Butene	1.00	-	5000	10000	5000
Acetaldehyde	1.06	-	1600	-	535
Acrolein	1.10	160	1500	100	585
Acetone	1.11	160	2200	5000	2455
Acrylonitrile	1.13	-	-	300	100
Allyl alcohol	1.16	80	1200	1500	925
Cyclopentadiene	1.18	-	-	500	165
Hexene	1.30	-	330	1600	645
Methyl ethyl ketone	1.31	20	220	960	400
Cyclohexadienes	1.49/1.64	-	-	650	215
Benzene	1.60	-	30	1400	475
Heptene	1.74	-	170	660	275
Heptane	1.80	-	120	200	105
Toluene	2.48	370	350	1900	875
Allyl acetone	2.58	-	120	230	115
Octene	2.80	-	120	490	205
Octane	2.94	-	80	140	75
Ethylbenzene	4.33	-	50	820	290
m/p-Xylene	4.57	-	15	190	70
Styrene	5.26	-	30	730	255
o-Xylene + Nonene	5.31	-	100	360	155
Nonane	5.61	-	60	70	45
Benzaldehyde	7.73	60	50	300	135
$\alpha$ -Methylstyrene	8.56	-	70	660	245
Phenol	8.74	-	5400	12900	6100
Benzofuran	9.03	-	-	630	210
Indane	9.11	-	80	110	65
Benzyl chloride	9.65	570	240	370	395
Benzyl alcohol	10.41	100	-	140	80
Indene	10.63	-	50	140	65
<i>o/p</i> -Cresol	11.1/11.6	-	320	2400	585
Methylbenzofuran	12.25	-	-	720	240
Ethylphenols	12.9/13.4	-	40	840	295
Ethylindene	14.19	-	50	500	185
Dihydrobenzofuran	14.21	-	-	1400	465
Isopropylphenol	14.34	-	200	540	245
t-Butylphenol	15.24	-	90	390	160
Isopropenylphenol	15.36	-	3700	9000	4235
Allylphenol	16.22	-	50	760	270
Bisphenol-A fragments	20 - 24	-	4000	8600	4200
Dimethylalkylamines (~C <sub>12</sub> )	21.0/22.2	7500	3400	4000	4965
Bisphenol-A	22.56	1100	10100	16200	9135
<b>TOTAL PEAK AREA</b>		<b>10120</b>	<b>41135</b>	<b>88410</b>	<b>88465</b>

**Table 4: Product B – Main Components (%)**

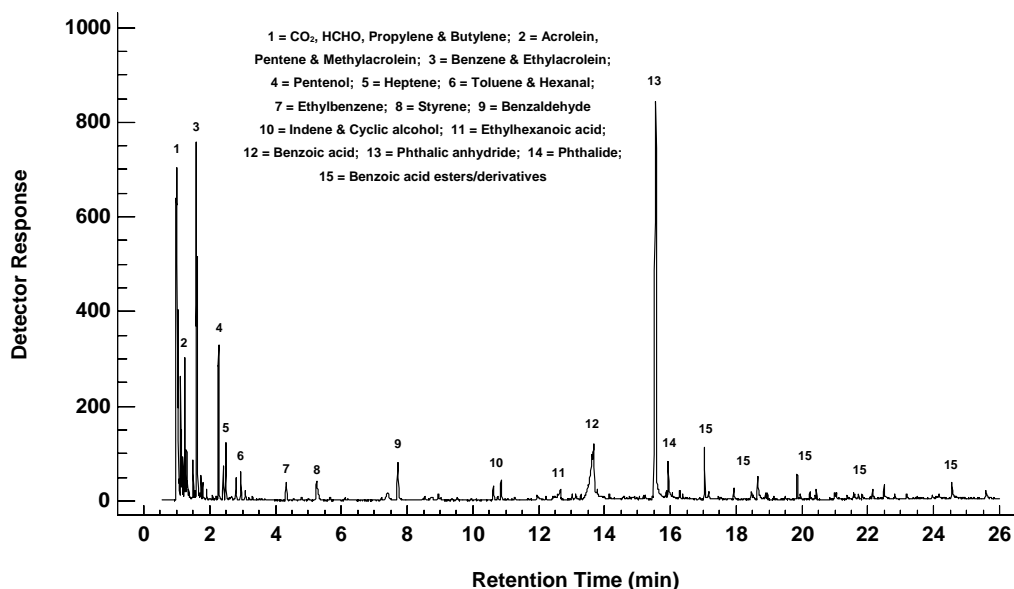
COMPONENT	RT (min)	SAMPLE B3 450°C	SAMPLE B1 650°C	SAMPLE B2 850°C	MEAN VALUE
Bisphenol-A	22.56	10.7%	24.6%	18.3%	19.6%
Phenol	8.74	-	13.1%	14.6%	13.1%
Ethene/Propene/Butene	1.00	-	12.2%	11.3%	10.7%
Dimethylalkylphenols (-C <sub>12</sub> )	21.0/22.2	72.9%	8.3%	4.5%	10.7%
Isopropenylphenol	15.36	-	9.0%	10.2%	9.1%
Bisphenol-A fragments	20 - 24	-	9.7%	9.7%	9.0%
Acetone	1.11	1.6%	6.6%	4.1%	4.6%
Allyl alcohol	1.16	0.8%	2.9%	1.7%	2.0%
o/p-Cresol	11.1/11.6	-	0.7%	2.7%	2.0%
Toluene	2.48	3.6%	0.9%	2.1%	1.9%
Other*	-	10.4%	12.0%	20.8%	17.3%

\* = Sum of remaining components

### 5.3 PRODUCT C

The chromatograms obtained from the three samples of Product C were generally found to contain in excess of 50 components, but many of these were present in amounts of rather less than 1%. The main components in the three samples were phthalic anhydride, alkenes (in particular propylene and butylene), aldehydes (in particular formaldehyde, ethylacrolein and methylacrolein), benzoic acid (and derivatives) and pentenol.

The chromatogram obtained from Sample C2, heated to 850°C, is shown in Figure 3.



**Figure 3: Product C – Heated to 850°C**

**Table 5: Product C – TIC Peak Areas**

COMPONENT	RT (min)	SAMPLE C3 450°C	SAMPLE C1 650°C	SAMPLE C2 850°C	MEAN VALUE
CO <sub>2</sub> /HCHO/Propylene	1.00	1800	16000	15400	11067
Butylene	1.04	-	1200	4800	2000
Acrolein	1.11	30	120	250	123
Methylbutene	1.12	100	1100	2200	1100
Isoprene	1.16	-	260	1200	487
Cyclopentadiene	1.19	-	120	680	267
Methylacrolein	1.25	170	1400	2400	1323
Hexene	1.30	80	490	950	507
Cyclohexadienes	1.50/1.65	-	330	1000	443
Benzene	1.60	-	250	4600	1617
Ethylacrolein	1.62	1300	6800	6100	4733
Heptene	1.75	-	220	500	240
Pentanal	1.79	30	370	410	270
Pentenol	2.27	490	4100	4300	2963
Heptenes	2.4/2.8	220	2000	1600	1273
Toluene	2.48	30	230	1500	587
Hexanal	2.95	400	840	900	713
Ethylbenzene	4.31	-	310	730	347
m/p-Xylene	4.54	-	-	85	28
Phenylacetylene	4.79	-	-	110	37
Styrene	5.25	-	180	1200	460
o-Xylene + Nonene	5.31	80	310	300	230
Heptanal	5.65	80	150	110	113
Pentyl formate	7.40	180	1500	800	827
Methylstyrenes	7 - 10	-	-	420	140
Benzaldehyde	7.72	130	1600	2000	1243
Indene	10.61	-	-	740	247
Unknown	10.76	-	140	180	107
Cyclopentanol	10.85	450	2300	830	1193
Acetophenone	11.28	-	90	100	63
Ethylhexanoic acid	12.65	270	500	520	430
Methylindenes	13.0/13.3	-	-	400	133
Naphthalene	13.62	-	-	380	127
Benzoic acid	13.68	750	9700	9200	6550
Methylnaphthalenes	15.2/15.5	-	-	250	83
Phthalic anhydride	15.56	9600	27000	26000	20867
Phthalide	15.93	270	1600	1500	1123
Benzoic acid derivatives	16 - 26	1700	10600	6100	6133
Biphenyl	16.29	-	10	250	87
Acenaphthylene	17.17	-	-	210	70
Fluorene	18.46	-	-	400	133
Dibutyl phthalate	22.49	370	760	400	510
TOTAL PEAK AREA		18520	102055	92560	71045

**Table 6: Product C – Main Components**

COMPONENT	RT (min)	SAMPLE C3 450°C	SAMPLE C1 650°C	SAMPLE C2 850°C	MEAN VALUE
Phthalic anhydride	15.56	51.8%	29.2%	25.5%	29.4%
CO <sub>2</sub> /HCHO/Propylene	1.00	9.7%	17.3%	15.1%	15.6%
Benzoic acid	13.68	4.0%	10.5%	9.0%	9.2%
Benzoic acid derivatives	16 - 26	9.2%	11.5%	6.0%	8.6%
Ethylacrolein	1.62	7.0%	7.3%	6.0%	6.7%
Pentenol	2.27	2.6%	4.4%	4.2%	4.2%
Butylene	1.04	-	1.3%	4.7%	2.8%
Benzene	1.60	-	0.3%	4.5%	2.3%
Methylacrolein	1.25	0.9%	1.5%	2.4%	1.9%
Methylbutene	1.12	0.6%	1.3%	2.4%	1.8%
Other*	-	14.2%	15.4%	20.2%	17.5%

\* = Sum of remaining components

Table 5 shows the peak areas for the forty or so largest components in the TIC for each of the three test samples. Table 6 shows the ten main components converted to a percentage of the total peak area and listed in order of abundance.

The data in Tables 5 and 6 produced the following observations:-

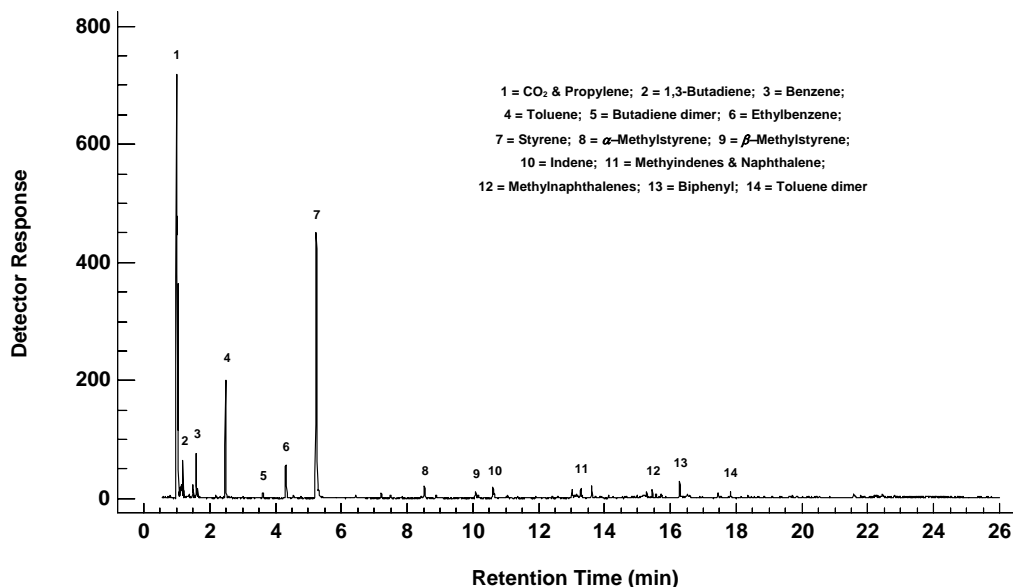
- The main components in all three samples of Product C were fairly similar, particularly in the case of the samples heated to 650°C and 850°C;
- The total peak areas for the samples heated to 650°C and 850°C were fairly similar, and around five times that of the sample heated to 450°C;
- In the sample heated to 450°C, the most prevalent component by far (at almost 52% of the total chromatographic peak area) is phthalic anhydride;
- Increasing pyrolysis temperature from 450°C to 650°C results in a reduction in the proportion of phthalic anhydride present (to around 30%) and in the generation of a number of additional minor and trace components;
- Further increasing pyrolysis temperature from 650°C to 850°C results in a significant increase the proportion of aromatic compounds present, in particular benzene, and an increase the amounts number of additional minor/trace components being generated (including naphthalene and other aromatics);
- The ten most abundant components account for around 86% of the total chromatographic peak area in the sample heated to 450°C. This decreases to 85% for the sample heated to 650°C and to around 80% for the sample heated to 850°C.

#### 5.4 PRODUCT D

The chromatograms obtained from the three samples of Product D were generally found to contain in excess of 20 components, but many of these were present in amounts of rather less

than 1%. The main volatile organic components in the three samples were styrene, propylene, butadiene and toluene.

The chromatogram obtained from Sample D2, heated to 850°C, is shown in Figure 4.



**Figure 4: Product D – Heated to 850°C**

Table 7 shows the peak areas for the twenty or so largest components in the TIC for each of the three test samples. Table 8 shows the ten main components converted to a percentage of the total peak area and listed in order of abundance.

The data in Tables 7 and 8 produced the following observations:-

- The main components in all samples of Product D were very similar, particularly in the case of the samples heated to 650°C and 850°C;
- The total peak area for the sample heated to 850°C was around three times that of the sample heated to 650°C and over 40 times that of the sample heated to 450°C;
- In the sample heated to 450°C, there were only six components present;
- Increasing pyrolysis temperature from 450°C to 650°C results in an increase in the number of components to over twenty;
- Further increasing pyrolysis temperature from 650°C to 850°C results in few additional components, but does result in a general increase in the proportion of the minor/trace components. This is accompanied by a significant fall in the proportion of styrene present from just over 45% of the total chromatographic peak area at 650°C to around 30% at 850°C;
- The ten most abundant components account for around 98% of the total chromatographic peak area in the sample heated to 450°C. This falls to around 93% in the sample heated to 650° and 91% in the sample heated to 850°C.

**Table 7: Product D – TIC Peak Areas**

COMPONENT	RT (min)	SAMPLE D3 450°C	SAMPLE D1 650°C	SAMPLE D2 850°C	MEAN VALUE
CO <sub>2</sub> /Propylene	1.00	480	2200	12500	5060
Butadiene	1.04	60	1300	3700	1687
Isoprene	1.16	-	30	280	103
Cyclopentadiene	1.19	-	60	450	170
Cyclohexadienes	1.50/1.65	-	130	480	203
Benzene	1.60	-	160	890	350
Toluene	2.48	40	900	2500	1147
Butadiene dimer	3.62	20	90	180	97
Ethylbenzene	4.31	-	310	1200	503
m/p-Xylene	4.54	-	10	90	33
Styrene	5.25	280	5200	11500	5660
o-Xylene	5.31	-	70	260	110
Trimethylbenzenes	6.45/7.49	-	90	280	123
Methylstyrenes	7 - 10	-	220	840	353
Indane	10.09	-	120	280	133
Indene	10.61	-	50	410	153
Methylindenes	13.0/13.3	-	100	520	207
Naphthalene	13.62	-	50	300	117
Methylnaphthalenes	15.2/15.5	-	40	250	97
Biphenyl	16.29	-	130	400	177
Diphenylmethane	17.47	-	60	140	67
Toluene dimer	17.82	-	30	150	60
Phenylnaphthalene	21.56	-	60	150	70
<b>TOTAL PEAK AREA</b>		<b>880</b>	<b>11410</b>	<b>37750</b>	<b>16680</b>

**Table 8: Product D – Main Components**

COMPONENT	RT (min)	SAMPLE D3 450°C	SAMPLE D1 650°C	SAMPLE D2 850°C	MEAN VALUE
Styrene	5.25	31.8%	45.6%	30.5%	33.9%
CO <sub>2</sub> /Propylene	1.00	54.5%	19.3%	33.1%	30.3%
Butadiene	1.04	6.8%	11.4%	9.8%	10.1%
Toluene	2.48	4.5%	7.9%	6.6%	6.9%
Ethylbenzene	4.31	-	2.7%	3.2%	3.0%
Methylstyrenes	7 - 10	-	1.9%	2.2%	2.1%
Benzene	1.60	-	1.4%	2.4%	2.1%
Methylindenes	13.0/13.3	-	0.9%	1.4%	1.2%
Cyclohexadienes	1.50/1.65	-	1.1%	1.3%	1.2%
Biphenyl	16.29	-	1.1%	1.1%	1.1%
Other*	-	2.4%	6.7%	8.4%	8.1%

\* = Sum of remaining components

## 5.5 PRODUCT E

The chromatograms obtained from the three samples of Product E were generally found to contain in excess of 20 components, but many of these were present in amounts of rather less than 1%. The main components in the three samples were propylene, other higher molecular weight alkenes, isopropanol, butyraldehyde, acetaldehyde and ethanol.

The chromatogram obtained from Sample E2, heated to 850°C, is shown in Figure 5.

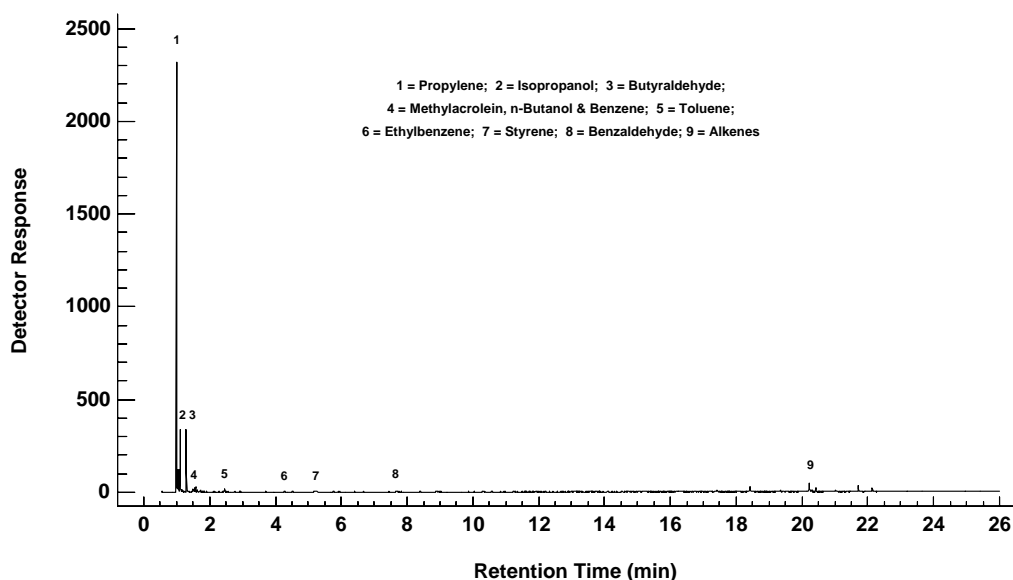


Table 9 shows the peak areas for the twenty or so largest components in the TIC for each of the three test samples. Table 10 shows the ten main components converted to a percentage of the total peak area and listed in order of abundance.

The data in Tables 9 and 10 produced the following observations:-

- The main components in all three samples of Product E were very similar, particularly in the case of the samples heated to 650°C and 850°C;
- The total peak area for the sample heated to 850°C was around 50% higher than that of the sample heated to 650°C and around 4 times that of the sample heated to 450°C;
- Increasing pyrolysis temperature from 450°C to 650°C results in a significant rise in the proportion of propylene present from 27% to 45%. This is accompanied by falls in the proportions of most of the other components;
- Further increasing the temperature to 850°C results in a further increase in propylene to almost 55% of the total chromatographic peak area;
- The ten most abundant components account for around 97% of the total chromatographic peak area in the sample heated to 450°C, falling slightly to around 96% in the sample heated to 650°C and to around 95% in the sample heated to 850°C.

**Table 9: Product E – TIC Peak Areas**

COMPONENT	RT (min)	SAMPLE E3 450°C	SAMPLE E1 650°C	SAMPLE E2 850°C	MEAN VALUE
Propylene	1.00	1850	7650	14500	8000
Acetaldehyde	1.02	-	850	1350	733
Ethanol	1.06	610	700	870	727
Isopropanol	1.10	1800	2100	2500	2133
Isoprene	1.14	5	15	60	27
Cyclopentadiene	1.18	2	25	70	32
Butyraldehyde	1.29	1400	1850	2600	1950
Ethyl acetate	1.36	15	30	65	37
Cyclohexadienes	1.47/1.62	25	50	140	72
Methylacrolein	1.51	65	140	220	142
Butanol	1.56	150	180	120	150
Benzene	1.57	55	100	260	138
Toluene	2.46	20	120	230	123
Ethylbenzene	4.29	-	55	85	47
Styrene	5.25	-	60	120	60
Butoxyethanol	5.73	100	160	170	143
Benzaldehyde	7.68	60	160	120	113
Indene	10.58	-	65	110	58
Naphthalene	13.60	-	45	80	42
Methyl naphthalenes	15.2/15.4	-	25	130	52
Alkenes	17 - 22	630	2400	2700	1910
Tertiary amines	21.0/22.1	40	400	370	270
<b>TOTAL PEAK AREA</b>		<b>6827</b>	<b>17180</b>	<b>26870</b>	<b>14683</b>

**Table 14: Product E – Main Components**

COMPONENT	RT (min)	SAMPLE E3 450°C	SAMPLE E1 650°C	SAMPLE E2 850°C	MEAN VALUE
Propylene	1.00	27.1%	44.5%	54.0%	47.2%
Isopropanol	1.10	26.4%	12.2%	9.3%	12.6%
Butyraldehyde	1.29	20.5%	10.8%	9.7%	11.5%
Alkenes	17 - 22	9.2%	14.0%	10.0%	11.3%
Acetaldehyde	1.02	-	4.9%	5.0%	4.3%
Ethanol	1.06	8.9%	4.1%	3.2%	4.3%
Tertiary amines	21.0/22.1	0.6%	2.3%	1.4%	1.6%
Butanol	1.56	2.2%	1.0%	0.4%	0.9%
Butoxyethanol	5.73	1.5%	0.9%	0.6%	0.9%
Methylacrolein	1.51	1.0%	0.8%	0.8%	0.8%
Other*	-	2.6%	4.5%	5.6%	4.6%

\* = Sum of remaining components

## 6 TOXICITY OF COMPONENTS

The data in Tables 2, 4, 6, 8 and 10 take no account of the toxicity of the individual compounds. Consequently, and in order to get a better estimate of the relative importance of the organic components generated by the five primers, the data were modified to take into account their toxicity, expressed in terms of a suitable exposure limit, eg their Workplace Exposure Limit (WEL) or Threshold Limit Value (TLV). The resulting data, obtained by dividing the peak area by the exposure limit (in mg/m<sup>3</sup>), are shown in Tables 11 to 14.

Many of the compounds do not have exposure limits and therefore do not give a 'toxicity' adjusted value. However, in certain cases, the exposure limit for a related compound has been used to obtain a value, for example the WEL for acrolein has been used for the methylacrolein and ethylacrolein observed in some of the samples.

### 6.1 PRODUCT A

The modified data for Product A are shown in Table 11. These indicate that, when toxicity is taken into account, benzene and acetaldehyde are probably the two most important components present, despite making up only around 8% of the total chromatographic peak area. The total 'toxicity' values for the components generated at 650°C and 850°C are very similar and over a hundred times greater than that at 450°C.

Most of the components generated by Product A have relatively high exposure limits or are only present in quite small amounts. Consequently, the total 'toxicity' values in Table 11 are fairly low compared with those of the other four primers.

**Table 11: Product A – 'Toxicity' Data**

COMPONENT	WEL (mg/m <sup>3</sup> )*	SAMPLE A3 450°C	SAMPLE A1 650°C	SAMPLE A2 850°C	MEAN VALUE
Benzene	3.2	-	70	40	35
Acetaldehyde	37	-	20	45	20
Bisphenol A†	5	-	25	35	20
Other*	-	1	5	6	3
TOTAL		1	120	120	80

\* = Sum of remaining components; † = Based on exposure limit for related compound

### 6.2 PRODUCT B

The modified data for Product B are shown in Table 12. These data indicate that, when toxicity is taken into account, acrolein is probably the most important component present, despite making up only around 1% of the total chromatographic peak area. Phenol (and substituted phenols), benzene and allyl alcohol emerge as secondary components.

The data in Table 12 show the total 'toxicity' value for the components generated at 850°C to be approximately twice that at 650°C and ten times that at 450°C.

**Table 12: Product B – ‘Toxicity’ Data**

COMPONENT	WEL (mg/m <sup>3</sup> )*	SAMPLE B3 450°C	SAMPLE B1 650°C	SAMPLE B2 850°C	MEAN VALUE
Acrolein	0.23	700	4400	6100	3700
Bisphenol A <sup>†</sup>	5	220	2000	3200	1800
Bisphenol A fragments <sup>†</sup>	5	-	800	1700	840
Phenol	7.7	-	700	1700	790
Benzene	2.3	-	15	610	210
Allyl alcohol	4.8	15	250	310	190
Isopropenylphenol <sup>†</sup>	27	-	140	330	160
Benzyl chloride	2.6	220	90	140	150
Other*	-	-	80	300	130
<b>TOTAL</b>		<b>1200</b>	<b>8400</b>	<b>14000</b>	<b>8000</b>

\* = Sum of remaining components; † = Based on exposure limit for related compound

### 6.3 PRODUCT C

The modified data for Product C are shown in Table 13. These indicate that, when toxicity is taken into account, ethylacrolein is probably the most important component present, with phthalic anhydride, methylacrolein, benzene and acrolein as secondary components.

The data in Table 13 show the total ‘toxicity’ value for the components generated at 850°C to be only slightly higher than the figure at 650°C, but around five times that at 450°C.

Several of the components generated by Product C have relatively low exposure limits or are present in quite high amounts. Consequently, the total ‘toxicity’ values in Table 13 are noticeably higher than those of the other four primers.

**Table 13: Product C – ‘Toxicity’ Data**

COMPONENT	WEL (mg/m <sup>3</sup> )	SAMPLE C3 450°C	SAMPLE C1 650°C	SAMPLE C2 850°C	MEAN VALUE
Ethylacrolein <sup>†</sup>	0.34	3800	20000	18000	13000
Phthalic anhydride	4	2400	6800	6500	4400
Methylacrolein <sup>†</sup>	0.29	590	4800	8300	4400
Benzoic acid <sup>†</sup>	5	150	1900	1800	1300
Benzoic acid derivatives <sup>†</sup>	5	340	2100	1200	1100
Benzene	2.3	-	110	2000	700
Acrolein	0.23	130	520	1100	540
Other*	246	75	170	330	170
<b>TOTAL</b>		<b>7500</b>	<b>36000</b>	<b>39000</b>	<b>25000</b>

\* = Sum of remaining components; † = Based on exposure limit for related component

## 6.4 PRODUCT D

The modified data for Product D are shown in Table 14. These data indicate that, when toxicity is taken into account, biphenyl, benzene and butadiene are probably the most important components present.

The data in Table 14 also indicate that the total ‘toxicity’ of the components generated at 850°C to be around four times that at 650°C and over two hundred times that at 450°C. Since most of the components generated by Product D have relatively low exposure limits or are only present in small amounts, the total ‘toxicity’ values in Table 14 are fairly low when compared with those of Products B and C.

**Table 14: Product D – ‘Toxicity Ratings’**

COMPONENT	WEL (mg/m <sup>3</sup> )	SAMPLE D3 450°C	SAMPLE D1 650°C	SAMPLE D2 850°C	MEAN VALUE
Biphenyl†	1	-	130	400	180
Benzene	3.2	-	50	280	110
1,3-Butadiene	22	3	60	170	75
Styrene	430	1	10	25	15
Others*	382	-	15	55	25
<b>TOTAL</b>		<b>4</b>	<b>260</b>	<b>930</b>	<b>400</b>

\* = Sum of remaining components; † = TLV

## 6.5 PRODUCT E

The modified data for Product E are shown in Table 15. These data indicate that, when toxicity is taken into account, methylacrolein is probably the most important component present, despite making up less than 1% of the total chromatographic peak area. Of the other components present, only benzene and acetaldehyde contribute significantly to the total figure.

The data in Table 15 also indicate the total ‘toxicity’ of the components generated at 850°C to be around twice that at 650°C and four times that at 450°C. Once again, most of the components generated by Product E have relatively low exposure limits or are only present in small amounts. Consequently, the total ‘toxicity’ values in Table 15 are fairly low when compared with those of Products B and C.

**Table 15: Product E – ‘Toxicity’ Data**

COMPONENT	WEL (mg/m <sup>3</sup> )	SAMPLE E3 450°C	SAMPLE E1 650°C	SAMPLE E2 850°C	MEAN VALUE
Methacrolein†	0.29	220	485	760	410
Benzene	2.3	25	45	110	50
Acetaldehyde	37	-	25	35	20
Ethyl acetate	720	4	9	15	7
<b>TOTAL</b>		<b>250</b>	<b>560</b>	<b>920</b>	<b>490</b>

\* = Sum of remaining components; † = Based on exposure limit for related component

## 7 INTER LABORATORY COMPARISON

Similar laboratory testing of the five products was carried out by FIOH and Arcelor (Products A to D only). The testing protocols, equipment and conditions used by the other two test laboratories are, briefly, as follows:-

Samples of the various primers are heated in a pyrolyser interfaced to a GC-MS system via a standard split-splitless injector. In the case of the Pyrola 2000 used by FIOH (and HSL) the sample is placed on an electrically heated platinum filament inside a glass liner, whilst the SGE Pyrojector used by Arcelor employs a quartz tube held in an electrically heated furnace. In both systems the samples are heated in a flow of helium carrier gas and the pyrolysis products pass from the pyrolyser to the GC-MS system via a short heated capillary transfer line. The components are then separated and identified. Both laboratories used an HP-5 (or equivalent) column, but with different column dimensions and film thicknesses.

A summary of the tests carried out by HSL, FIOH and Arcelor is shown in Table 16.

**Table 16: Summary of Inter Laboratory Pyrolysis Tests**

	HSL	FIOH	ARCELOR
<b>Pyrolyser</b>	Pyrola 2000	Pyrola 2000	SGE Pyrojector
<b>GC-MS</b>	Agilent	Agilent	Finnegan DSQ
<b>Product A</b>	450°C; 650°C; 850°C	800°C	800°C
<b>Product B</b>	450°C; 650°C; 850°C	450°C; 550°C; 800°C	800°C
<b>Product C</b>	450°C; 650°C; 850°C	450°C; 550°C; 800°C	800°C
<b>D</b>	450°C; 650°C; 850°C	800°C	800°C
<b>E</b>	450°C; 650°C; 850°C	800°C	-

A brief summary of the results obtained with the five test products is given below.

## 7.1 PRODUCT A

A summary of the test results obtained from Product A by HSL, FIOH and Arcelor is given in Table 17.

**Table 17: Product A – Top Ten VOCs by Abundance**

	HSL*	HSL**	FIOH†	Arcelor‡
1	Propene (61.4%)	Propene (57.0%)	Ethene/Propene (59.8%)	Propene (40.3%)
2	IPA/Acetone (18.3%)	IPA/Acetone (18.9%)	IPA/Acetone (8.6%)	CO <sub>2</sub> /Ethene (11.1%)
3	Ethanol (10.2%)	Acetaldehyde (11.0%)	Acetaldehyde (8.0%)	Acetone (10.5%)
4	Acetaldehyde (6.6%)	Ethanol (8.2%)	Toluene (2.0%)	2-Butene (7.0%)
5	Toluene (1.1%)	Toluene (1.6%)	Ethanol (1.1%)	Toluene (4.3%)
6	Benzene (1.0%)	Bisphenol-A (1.2%)	Benzene (0.5%)	Acetaldehyde (2.9%)
7	Bisphenol-A (0.8%)	Benzene (0.9%)	Octadecene (0.5%)	1,3-Butadiene (2.5%)
8	Cyclopentadiene (0.3%)	Cyclopentadiene (0.6%)	Diethylphthalate (0.4%)	Propyne (2.1%)
9	Hexane (0.2%)	Toluene (0.4%)	Indene (0.4%)	Benzene (2.0%)
10	Indene (0.1%)	Acrolein (0.2%)	Cyclopentadiene (0.3%)	Ethylbenzene (1.5%)
<b>Total</b>	<b>100.0%</b>	<b>100.0%</b>	<b>81.6%</b>	<b>84.2%</b>

\* = Average of 450°C, 650°C & 850°C; \*\* = 850°C; † = 800°C; ‡ = 800°C

The results obtained from Product A produced the following observations:-

- The amounts of material produced by Product A, measured as total chromatographic peak area, were amongst the lowest of the five products tested.
- The main components observed by all three laboratories were generally very similar, with propylene the major component present.
- Visually, the chromatograms obtained by HSL and FIOH were very similar.
- Because of the low amounts of material generated, components with relative abundances of less than 5% were present at very low levels. This may account for some of the variations and anomalies observed amongst the minor components. For example, Bisphenol-A was only observed by HSL, diethylphthalate only by FIOH and butadiene only by Arcelor.

## 7.2 PRODUCT B

A summary of the test results obtained from Product B by HSL, FIOH and Arcelor is given in Table 18.

**Table 18: Product B – Top Ten VOCs by Abundance**

	HSL*	HSL**	FIOH†	Arcelor‡
1	Bisphenol-A (19.6%)	Bisphenol-A (18.3%)	'N-Organic' (23.3%)	Phenol (11.3%)
2	Phenol (13.1%)	Phenol (14.6%)	Bisphenol-A (21.1%)	Isopropenylphenol (10.2%)
3	C <sub>2-4</sub> alkenes (10.7%)	C <sub>2-4</sub> alkenes (11.3%)	CO <sub>2</sub> (10.2%)	CO <sub>2</sub> /Ethane/Ethene (6.8%)
4	Dimethylalkylamines (10.7%)	Isopropenylphenol (10.2%)	Tetramethylbenzene (7.2%)	BP-A fragments (5.2%)
5	Isopropenylphenol (9.1%)	BP-A fragments (9.7%)	Phenol (4.3%)	Dihydrobenzofuran (4.1%)
6	BP-A fragments (9.0%)	Acetone (5.7%)	Dimethylalkylamines (2.8%)	Toluene (3.7%)
7	Acetone (5.3%)	Dimethylalkylamines (4.5%)	BP-A fragments (2.6%)	Butene (3.0%)
8	Allyl alcohol (2.0%)	Toluene (2.1%)	Butene/Butadiene (2.0%)	o-Cresol (2.7%)
9	Toluene (1.9%)	o-Cresol (1.9%)	Acetone/Acrolein (2.0%)	1,3-Butadiene (2.4%)
10	Acrolein (1.3%)	Hexene (1.8%)	Diethyl phthalate (1.0%)	Styrene (2.2%)
<b>Total</b>	<b>82.5%</b>	<b>80.1%</b>	<b>76.5%</b>	<b>51.6%</b>

\* = Average of 450°C, 650°C & 850°C; \*\* = 850°C; † = 800°C; ‡ = 800°C

The results obtained from Product B produced the following observations:-

- The amounts of material produced by Product B, measured as total chromatographic peak area, were significantly greater than those from Product A.
- Whilst the main components identified by all three laboratories were generally fairly similar, there were some significant anomalies.
- The FIOH results show the presence of a large peak, identified as an organo-nitrogen compound. This component was not detected by HSL or Arcelor.
- A second anomaly concerns the identity of one of the other main components, identified as tetramethylbenzene by FIOH and isopropenylphenol by HSL and Arcelor. However, a visual inspection of the chromatograms suggests that the component detected by all three laboratories is the same, and it therefore seems likely, given the similarity of the mass spectra of these two compounds, that this particular anomaly is due to limitations in the spectral search software.
- Whilst both HSL and FIOH identified bisphenol-A as one of the main components generated by Product B, this component was not observed by Arcelor. The reasons for this difference are unclear, but may be due to chromatographic conditions. Those used by Arcelor produce significantly longer retention times and show evidence of column bleed at retention times over 40 minutes, possibly leading to problems with semi-volatile components such as bisphenol-A.

### 7.3 PRODUCT C

A summary of the test results obtained from Product C by HSL, FIOH and Arcelor is given in Table 19.

**Table 19: Product C – Top Ten VOCs by Abundance**

	HSL*	HSL**	FIOH <sup>†</sup>	Arcelor <sup>‡</sup>
1	Phthalic anhydride (29.4%)	Phthalic anhydride (25.5%)	Phthalic anhydride (32.8%)	C <sub>18</sub> Aldehydes (36.9%)
2	CO <sub>2</sub> /HCHO/Propene (15.6%)	CO <sub>2</sub> /HCHO/Propene (15.1%)	Benzoic acid (15.8%)	Benzene (11.6%)
3	Benzoic acid (9.2%)	Benzoic acid (9.0%)	CO <sub>2</sub> /Propane (6.3%)	CO <sub>2</sub> /Ethene (7.5%)
4	B/A derivatives (8.6%)	B/A derivatives (6.0%)	Benzene (3.8%)	Propene (2.8%)
5	Ethylacrolein (6.7%)	Ethylacrolein (6.0%)	Ethylacrolein (3.5%)	Butene (2.1%)
6	Pentenol (4.2%)	Butene (4.7%)	Ethylhexanoic acid (2.9%)	Toluene (1.7%)
7	Butene (2.8%)	Benzene (4.5%)	Pentenol (2.4%)	1,3-Butadiene (1.7%)
8	Benzene (2.3%)	Pentenol (4.2%)	Phthalide (2.2%)	Styrene (1.5%)
9	Methylacrolein (1.9%)	Methylacrolein (2.4%)	Hexadecanoic acid (2.1%)	Naphthalene (1.1%)
10	Methylbutene (1.8%)	Methylbutene (2.2%)	Benzaldehyde (1.8%)	Ethylbenzene (1.1%)
<b>Total</b>	<b>82.3%</b>	<b>79.6%</b>	<b>73.6%</b>	<b>68.0%</b>

\* = Average of 450°C, 650°C & 850°C; \*\* = 850°C; † = 800°C; ‡ = 800°C

The results obtained from Product C produced the following observations:-

- The amounts of material produced by Product C, measured as total chromatographic peak area, were significantly greater than those from Product A.
- Whilst the pyrolysis products observed by HSL and FIOH show good agreement, there are significant differences with those observed by Arcelor.
- The major difference in the data is that while HSL and FIOH identified phthalic anhydride and benzoic acid as major pyrolysis products, neither of these components was observed by Arcelor. The reason for the absence of these components is unclear, although, as previously stated with Product B, differences in chromatographic conditions is one possibility.
- A second difference concerns the relative ratios of benzene and ethylacrolein, two potentially harmful components which elute with similar retention times. At a pyrolysis temperature of around 800°C, HSL and FIOH detected similar, quite significant, amounts of both compounds, whereas Arcelor detected significant levels of benzene, but relatively little ethylacrolein. At lower pyrolysis temperatures, HSL still observed significant levels of ethylacrolein, but these were accompanied by much lower amounts of benzene. However, whilst this indicates that levels of benzene increase with temperature, the reason for the lack of ethylacrolein observed by Arcelor remains unknown.

## 7.4 PRODUCT D

A summary of the test results obtained from Product D by HSL, FIOH and Arcelor is given in Table 20.

**Table 20: Product D – Top Ten VOCs by Abundance**

	HSL*	HSL**	FIOH†	Arcelor‡
1	Styrene (33.9%)	CO <sub>2</sub> /HCHO/Propene (33.1%)	Styrene (38.3%)	CO <sub>2</sub> (45.0%)
2	CO <sub>2</sub> /Propene (30.3%)	Styrene (30.5%)	CO <sub>2</sub> (10.9%)	Styrene (12.1%)
3	1,3-Butadiene (10.1%)	1,3-Butadiene (9.8%)	Toluene (6.0%)	Benzene (5.5%)
4	Toluene (6.9%)	Toluene (6.6%)	1,3-Butadiene (5.9%)	Toluene (5.1%)
5	Ethylbenzene (3.0%)	Ethylbenzene (3.2%)	Methylnaphthalene (2.3%)	1,3-Butadiene (4.6%)
6	Methystyrenes (2.1%)	Benzene (2.4%)	Ethylbenzene (2.0%)	Propene (3.2%)
7	Benzene (2.1%)	Methystyrenes (2.2%)	Biphenyl (1.9%)	2-Butene (2.8%)
8	Methyindenes (1.2%)	Methyindenes (1.4%)	α-Methylstyrene (1.7%)	Cyclopentadiene (2.2%)
9	Cyclohexadienes (1.2%)	Cyclohexadienes (1.3%)	Dimethylnaphthalene (1.3%)	Pentene (2.0%)
10	Biphenyl (1.1%)	Cyclopentadiene (1.2%)	Benzene (1.2%)	Ethylbenzene (1.9%)
<b>Total</b>	<b>92.0%</b>	<b>91.7%</b>	<b>71.5%</b>	<b>84.4%</b>

\* = Average of 450°C, 650°C & 850°C; \*\* = 850°C; † = 800°C; ‡ = 800°C

The results obtained from Product D produced the following observations:-

- In the case of HSL and FIOH, the amounts of material produced by Product D, measured as total chromatographic peak area, were significantly greater than those from Product A. However, the Arcelor data show levels of material generated by Product D to be the lowest of any of the four products tested by them.
- With regard to the identities of the main components present there is quite good agreement between all three laboratories, although there are some differences in the relative amounts of these components.
- Probably the main difference in the data is that the proportions of styrene in the HSL and FIOH data are somewhat higher than those observed by Arcelor.

## 7.5 PRODUCT E

A summary of the test results obtained from Product E by HSL and FIOH is given in Table 21 (Product E was not examined by Arcelor).

**Table 21: Product E – Top Ten VOCs by Abundance**

	HSL*	HSL**	FIOH†	Arcelor‡
1	Propene (47.2%)	Propene (54.0%)	Ethene/Propene (23.8%)	-
2	Isopropanol (12.6%)	Alkenes (10.0%)	Butyraldehyde (11.6%)	-
3	Butyraldehyde (11.5%)	Butyraldehyde (9.7%)	Isopropanol/Acetone (8.5%)	-
4	Alkenes (11.3%)	Isopropanol (9.3%)	Acetaldehyde/Butene (7.2%)	-
5	Acetaldehyde (4.3%)	Acetaldehyde (5.0%)	Octadecene (6.3%)	-
6	Ethanol (4.3%)	Ethanol (3.2%)	Hexadecene (3.7%)	-
7	Tertiary amines (1.6%)	Tertiary amines (1.4%)	Benzene (2.7%)	-
8	Butanol (0.9%)	Benzene (1.0%)	Ethanol (2.5%)	-
9	Butoxyethanol (0.9%)	Toluene (0.9%)	Dimethylalkylamines (2.5%)	-
10	Methylacrolein (0.8%)	Methylacrolein (0.8%)	Octadecanal (2.4%)	-
<b>Total</b>	<b>95.3%</b>	<b>95.3%</b>	<b>71.2%</b>	-

\* = Average of 450°C, 650°C & 850°C; \*\* = 850°C; † = 800°C; ‡ = Not analysed

The results obtained from Product E produced the following observations:-

- The amounts of material produced by Product E, measured as total chromatographic peak area, were significantly greater than those from Product A.
- The two laboratories show good agreement in the identities of the main components present.
- Agreement on the relative amounts of the main components observed by the two laboratories is also quite good, the main difference probably being that FIOH observed rather higher levels of semi-volatile material (alkenes, alkylamines, etc).

## 8 SUMMARY & CONCLUSIONS

A comparison of the results obtained by the three laboratories shows generally good agreement with regard to the main components present, although there were some anomalies in each of the five products. The best agreement was seen with the HSL and FIOH results, although this is only to be expected given that the two laboratories were using very similar pyrolysis (Pyrola) and GC-MS (Agilent) equipment. Nonetheless, such a comparison of the HSL and FIOH data provides a good illustration of the level of agreement which might be expected for a 'best case' scenario, ie results obtained by two independent laboratories on the same sample using similar equipment and instrument conditions. However, perhaps of more interest is the comparison between the HSL/FIOH results and those of Arcelor, which gives an indication of the level of agreement which might be expected from two independent laboratories on the same sample, but using different equipment and instrument conditions. This is what might be regarded as a 'worst case' scenario. In addition, other pyrolysis devices which can be similarly interfaced to a GC-MS system, in particular Curie-point pyrolysers, are also available.

A comparison of the HSL and FIOH results shows only two major anomalies, both with Product B. The first is the presence in the FIOH data of a large organo-nitrogen component which is not present in the HSL data. The second is a disagreement over the identity of a major component – isopropenylphenol or tetramethylbenzene. The reason for the first anomaly is unknown, although it was noted that the component in question was not as prominent in the first set of pyrolysis results obtained by FIOH, so it is possible that this component varies from sample to sample. The second anomaly is almost certainly due to a combination of similarities in the mass spectra of different compounds and limitations of spectral search routines. HSL identified the peak in question as isopropenylphenol, FIOH as tetramethylbenzene. Both these compounds have very similar mass spectra (as do several other aromatic compounds of the same molecular weight) and it is therefore difficult for a library search to distinguish between them. One solution is to run standards to check retention times, but this highlights one commonly encountered problem with pyrolysis products, namely that they are often obscure compounds which are not readily available as pure materials, or may not even be present in all search libraries. Under these circumstances, it may be necessary for the analyst to make an informed choice based on a combination of the results of the library search, physical data (eg boiling points) and the other pyrolysis products present. However, such a scenario will inevitably lead to differences between analysts and/or laboratories in identification of components – as seen in the example above.

Agreement between the HSL/FIOH and Arcelor results, whilst not as good, is still generally encouraging, particularly for the more volatile components. The main difference between the two sets of data is the general lack of less volatile components in the Arcelor chromatograms, in particular significant components such as bisphenol-A in Product B and phthalic anhydride and benzoic acid in Product C. The reasons for these differences are unclear as all three laboratories used a similar pyrolysis temperature. However, it was noted that the chromatographic conditions used at Arcelor result in much longer retention times than is the case with the HSL/FIOH data, and also produce some evidence of column bleed and/or deterioration in baseline quality at retention times beyond 40 minutes. It is therefore possible that some of the semi-volatile components in the Arcelor samples have been 'lost' in this region of the chromatogram. Another possibility is that the different design of the two pyrolysers is causing the differences. When using the Pyrojector equipment in the past at HSL, it has been noted that longer heating times are sometimes required to generate some higher boiling point components. This, in turn, requires the use of a cooled zone on the GC in order to re-focus the more volatile components on the GC column. This may indicate differences in the heat input to the sample using the two pyrolyser systems, differences which could be the cause of the lack of

semi-volatiles in the Arcelor data. Ideally, given the available time and resources, it would be useful to carry out additional testing using a combination of pyrojector and HSL/FIOH chromatographic conditions (or Pyrola with Arcelor chromatographic conditions). However, as mentioned above, there is generally good agreement on the more volatile pyrolysis products identified by HSL/FIOH and Arcelor in Products A to D, which is quite encouraging given the differences in equipment.

The comparison above is based on results obtained at around 800°C, however both HSL and FIOH carried out additional tests at lower temperatures - HSL at 450°C and 650°C and FIOH at 400/450°C and 550°C. Comparison of the HSL results shows the main components generated at all three test temperatures to be very similar. The main differences are that the total peak area increases with temperature and the number of minor/trace components also tends to increase quite markedly at higher temperature. The tests at FIOH arrived at similar conclusions. Subsequent, very brief, tests at 1000°C at HSL showed this trend to continue at higher temperatures. None of the additional HSL/FIOH test results show any reason to deviate from a standard test temperature of 800°C. Consequently, it is recommended that a pyrolysis temperature of 800°C be adopted as the standard test temperature.

## 9 REFERENCES

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Ian Pengelly