# FINAL REPORT

# DEVELOP A POST-MARKET TEST FOR RECYCLED FOOD CONTACT MATERIALS

## FS241007

## 11th March 2014


## SMITHERS RAPRA & SMITHERS PIRA LIMITED


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**DEVELOP A POST-MARKET TEST FOR RECYCLED FOOD CONTACT MATERIALS – FINAL PROJECT REPORT**


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# DEVELOP A POST-MARKET TEST FOR RECYCLED FOOD CONTACT MATERIALS – FINAL PROJECT REPORT

## 1. INTRODUCTION

### 1.1 Overview of Project FS241007

There can be problems with the quality of recycled materials for a number of reasons. For example, if the individual stages do not function as effectively as they should, if an attempt is made to eliminate individual stages to speed up the recycling process, or if the complete process does not function as effectively as it should. The latter could occur if attempts are made to increase the output of the process by increasing the quantity of recycled material going through it, or if the process is speeded up, reducing the amount of time that a unit mass of the recycled materials spends passing through each stage. A more extreme case is where the material has not been recycled using a process governed by good manufacturing practice. In all of these cases, the recycled material may contain contaminants and so it may not comply with Article 3 of the Framework Directive 1935/2004.

The FSA therefore required work to be done to establish a list of marker compounds (i.e. contaminants) that are specific to food contact materials manufactured from recycled paper and board (P&B) and polyethyleneterephthalate (PET). These marker compounds could then be used to indicate if a poor, or defective, recycling process has been used to generate recycled material intended for the manufacture of recycled food contact products. These marker compounds would also be of use to monitor the quality of recycled products (e.g. bottles) and to assist in the enforcement of the appropriate legislation.

The objectives of the project can be summarised as follows:

1) Identification of a suite of marker compounds for recycled PET and P&B that are inherent of the materials, and the compounds that they will have absorbed during use.

2) Development of analytical methods based on the technique of gas chromatography-mass spectrometry (GC-MS) for the detection and quantification of these Marker compounds in recycled PET and P&B, and food simulants.

3) Targeted analysis of selected Marker compounds in recycled PET and P&B food grade products, and food simulants that they have contacted under representative end-use conditions.

This is the final project report summarising all of the findings of the project on recycled P&B and PET for food contact use which ran from 1st March 2011 until 28th February 2013.

## 1.2 Project Objectives

The project had the following five research Objectives:

**Objective 01**

**Review in-house and industry information on the chemical compounds that represent first use conditions for both recycled PET, and paper and board. Select a suite of appropriate marker compounds to determine in recycled materials and products**

**Objective 02**

**Establish validated analytical methods for the identification and quantification of the selected marker compounds in the FCM's and food simulants**

**Objective 03**

**Determination of the selected marker compounds in recycled paper and board materials and products**

**Objective 04**

**Determination of the selected marker compounds in recycled PET and products**

**Objective 05**

**Verification by target analysis in a range of food simulants**

# 2. MARKER COMPOUNDS FOR P&B AND PET

## 2.1 Definition of Marker Compounds in Recycled Food Contact Materials

Marker compounds for recycled food contact materials such as P&B and PET are relatively low molecular weight compounds which have the ability to migrate from these materials into food when these are used for the packaging of food products. They vary in a number of ways, for example in their potential toxicity and whether they are single compounds or a mixture of isomeric forms of a compound. Another very important way in which they vary is in their origin, which is dependent on a number of factors, including the following:

a) The material itself and its chemical properties and resistance to influences such as thermal degradation.

b) The technology associated with the manufacture of the food contact packaging from a particular material.

c) The types of food products that they contact during their original use and the conditions under which they contact these food products.

## 2.2 Published maker compounds present in recycled P&B and PET

A literature search was undertaken at the start of this project to review the Smithers Rapra in-house information and the published information on the marker compounds for both recycled PET, and P&B. The results of this literature review is summarised in Appendix 1, and this information enabled a suite of appropriate marker compounds to be selected for both recycled PET and P&B. The summary list of principal marker compounds that were obtained from the literature search are shown this Section, with the final selection of five for each material that were used for this project provided in Section 2.3.

The complexity of the waste stream and the range of potential compositions of the P&B itself, mean that there is a much greater range of potential origins for contaminants in recycled P&B. Some examples are : inks, coatings, surface treatments, conventional paper additives, functional additives in certain specialist grades of paper etc.

A list of the principal marker compounds that originate from these various sources is shown below in Table 1.

**Table 1 Principal marker compounds in recycled P&B**

| **Potential Migrant** | **Range found in P&B (mg/kg)** |
|---|---|
| Benzophenone | Up to 3.1 mg/dm$^2$* |
| 4-methyl benzophenone | - |
| Michlers ketone | Up to 1.6 |
| DEAB | Up to 0.7 |
| Diisobutyl phthalate and Dibutyl phthalate | Up to ~6000 |
| Other phthalates (e.g. DEHP) | Up to 3000 |
| Diisopropylnaphthalenes | Up to 0.89 |
| Fluorescent whitening agents | Up to ~1100 |
| Pentachlorophenol | 0.1 |
| Hydrogenated terphenyls | - |
| Glycol ethers (e.g. diethylene glycol) | - |
| Polychlorinated biphenyls | Up to 0.33 |
| Alkanes | - |
| Abietic acid and Dehydroabietic acid | Up to 1,200 |
| Grease proofing agents (e.g. mono- and di - ammonium perfluoroalkyl phosphate salts)<br>FOSE alcohol breakdown product | <0.15 to 1.8 mg/dm$^2$*<br><0.01 to 0.8 mg/dm$^2$* |
| Mineral oil (<C24) | Up to ~900 (unprinted) ; ~2000 (printed) |

- Concentration range not provided in the literature, only qualitative information is available.

* mg/kg values not available

The studies that have been carried out on post-consumer PET samples have shown that the major species present originate from two principal sources:

1) The PET polymer.
2) Flavouring substances present in the food that has been packaged in the PET.

A list of the principal marker compounds that originate from these two sources is shown below in Table 2.

**Table 2 Principal marker compounds in recycled PET**

| **Potential Migrant** | **Range found in recycled PET (mg/kg)** |
|---|---|
| Acetaldehyde | 18.6 to 86.0 |
| Ethylene glycol | - |
| 2-methyl-1,3-dioxolane | - |
| Limonene | 0.1 to 20 |
| 4-iso-propyl toluene | ~0.02 to 4 |
| Numerous organic compounds (e.g. food compounds, polymer additives and breakdown products, misuse chemicals etc.) | ~0.05 to 0.5 |

- Concentration range not provided in the literature, only qualitative information is available.

## 2.3 Final Selection of Five Marker Compounds for recycled P&B and PET

A summary of the principal marker compounds that have been reported for recycled P&B and PET is provided in Sections 2.2.

For the purposes of this project, five of these marker compounds for each of the two materials were selected for determination. In order to be chosen they had to meet the following criteria:

1) They should be representative of the typical marker compounds that are present in recycled P&B and PET.

2) They should enable a cost effective and efficient analytical programme to be devised for the analysis of the following : post-consumer material, recycled material (removed from various stages within the process), and finished products made from recycled material.

3) They should be acceptable to the Foods Standards Agency.

For P&B there were a greater number of potential candidates and so, in addition to the criteria shown above, the following additional criteria were also used:

a) Compounds that have been detected in reasonably high concentrations in P&B.
b) Compounds that vary in their degree of water solubility.
c) Compounds that originate from at least four technological sources in P&B.
d) To satisfy point 2) above, only one example that is a multi-component species.

With these criteria in mind, the five marker compounds that were selected for recycled P&B and PET are shown below in Sections 2.3.1. and 2.3.2.

### 2.3.1 Five Marker compounds for Paper and Board

The following five marker compounds met the criteria for P&B:

1. Benzophenone
2. Diisobutyl phthalate
3. Diisopropyl naphthalenes
4. Di-2-ethylhexyl phthalate
5. Michlers ketone

These compounds are within the volatility range which will typically allow analysis by gas chromatography-mass spectrometry (GC-MS). An analytical method based on solvent extraction, followed by direct-injection GC-MS was therefore developed for them. An overview of these analytical methods is provided in Section 3.0, with the validation work that was carried out on them described in detail in Appendix 2.

### 2.3.2 Five Marker compounds for PET

The following five marker compounds met the criteria for PET:

1. Acetaldehyde
2. 2-methyl-1,3-dioxolane
3. Ethylene glycol (also called monoethylene glycol - MEG)
4. Limonene
5. 4-iso-propyl toluene

Being of lower volatility than the marker compounds chosen for P&B (especially acetaldehyde) an analytical method based on headspace gas chromatography-mass spectrometry (HS-GC-MS) was developed for these compounds. During the method development stage the MEG was found not to be suitable for this approach and so a solvent extraction, direct injection GC (gas-chromatography) based method was developed for it. An overview of these analytical methods is provided in Section 3.0, with the validation work that was carried out on them described in detail in Appendix 2.

## 3.0 ANALYTICAL METHODS FOR THE DETERMINATION OF MARKER COMPOUNDS IN RECYCLED P&B AND PET

A summary and overview of the analytical methods that were developed for the marker compounds is provided in this Section. The validation work that was carried out on the methods is described in detail in Appendix 2.

### 3.1 Overview of the experimental conditions used for the analysis of the marker compounds

#### 3.1.1 Sample preparation

**P&B Samples - Preparation for solvent extraction direct injection GC-MS analysis**

Whether the P&B samples were provided as post-consumer waste, consolidated material from areas within the paper mill (such as the pulper), flat sheet from mill, or as final coated card product; they were prepared for analysis as follows:

An accurately weighed amount of the sample (2 grams) is cut up into pieces that had an area of approximately 2 $cm^2$ and extracted in a Dichloromethane (DCM) internal standard solution for 24 hours at 35°C. Aliquots of the extracts are then transferred directly into autosampler vials, ready for analysis.

**Preparation of Calibration standards**

A stock solution of the five analytes of interest is prepared using DCM which contains the internal standard (an isotopically labelled version of the marker compound, or a chemically similar analogue). The stock is then diluted with DCM internal standard solution to provide a series of reference standards that are within a realistic concentration range. An example of the calibration range that was used is 0.01 µg/mL to 25 µg/mL; with the internal standard present at a concentration of 0.4 µg/mL.

The sample and calibration solutions are then analysed by direct injection GC-MS using the experimental conditions that are shown in Section 3.1.2.

**PET Samples – Preparation for headspace GC-MS analysis**

Whether the PET samples were provided as flake, granules or final product (e.g. bottles) they were prepared for analysis as follows:

As an initial step, the PET samples are cryogenically ground through a 2mm ring sieve at 16,000rpm. An accurate 1g portion of each ground sample is weighed directly into individual 22.5mL glass headspace vials and sealed with PTFE-lined Silicone septa and crimp caps. A 1µL aliquot of acetone is added to each vial prior to sealing to mimic the conditions in the calibration vials.

**Preparation of Calibration standard**

A stock solution containing known amounts of each of the four marker compounds is prepared in acetone.

A replicate vial containing 1g of the ground polymer under test is spiked with a 1µL aliquot of the calibration stock prior to sealing the vial to provide a matrix-matched calibration vial.

The sample and calibration vials are then analysed by HS-GC-MS under the instrumental conditions that are shown in Section 3.1.3.

**PET Samples – Preparation for solvent extraction direct injection GC analysis for the MEG marker compound**

It was not possible to accurately and precisely determine MEG by headspace GC-MS and so a solvent extraction and direct injection GC method was developed. To ensure that a high extraction efficiency was achieved an accelerated solvent extraction procedure (ASE) was employed as follows:

As an initial step, the PET samples were cryogenically ground through a 2mm ring sieve at 16,000rpm prior to analysis. This ground PET was then prepared for Accelerated Solvent Extraction (ASE) using a Dionex ASE 200 instrument as described below:

2.5 grams of sodium sulphate and 2 grams of Ottawa sand is weighed into a series of glass vials (the number of vials equivalent to the number of samples) and to this mixture 2.5 grams of the ground PET sample is added and mixed thoroughly. For each sample, a glass fibre filter is then added to the base of an ASE cell (with the bottom cap sealed securely), followed by a layer of Ottawa sand and then the contents of one of the vials containing the sand/sodium sulphate/ground PET mixture. Additional Ottawa sand is then added to fill the cell completely. Finally, the centre of each ASE cell is spiked with 5 µL of a 10 mg/mL butanediol solution (as an internal standard) and then the top is screwed on. The prepared cell is then placed into the Dionex ASE 200 and extracted using acetone under the conditions below.

**Preparation of Calibration standards**

A series of calibration standards are prepared in acetone, each containing known amounts of MEG and a constant amount of butanediol internal standard. The internal standard concentration is exactly equivalent to the amount present in the final sample extracts (assuming 100% recovery from the ASE cell).

**ASE extraction conditions**

The extraction of each PET sample was carried out using acetone with the following settings on the Dionex ASE instrument:

| | |
|---|---|
| Pressure | 2000 psi |
| Temperature | 150 °C |
| Pre-heat | 0 mins |
| Heat | 7 mins |
| Static | 5 mins |
| Flush | 60% volume of cell |
| Purge time | 60 minutes |

The sample solutions are then filtered into 25mL volumetric flasks and made up to volume using acetone. The sample and standard solutions are analysed by GC using the experimental conditions that are shown in Section 3.1.4.

### 3.1.2 Direct injection GC-MS method for the determination of the marker compounds in recycled P&B samples

**Table 3 GC-MS conditions used for the determination of marker compounds in recycled P&B samples**

| | |
|---|---|
| Instrument | Agilent Technologies 6890 Gas Chromatograph with a 5973 MSD |
| Column | 5% diphenyl, 95% PDMS 30m x 0.25mm 0.25 µm film |
| Injection | 1µL Splitless @ 280°C |
| Carrier Gas | Helium @ 1.2mL (constant flow) |
| Oven Program | 40°C for 2 minutes. 20°C/minute to 300°C.<br>Hold for 15 minutes |
| MS | Single Ion Monitoring (SIM) mode.<br>D-naphthalene (ISTD for DIPN) - (m/z 108, 136)<br>Benzophenone and ISTD - (m/z 105, 110, 182, 187)<br>DIPN - (m/z 197, 212)<br>DiBP and ISTD - (m/z 149, 153, 223, 227)<br>DEHP and ISTD - (m/z 149, 153, 167, 171)<br>Michlers Ketone - (m/z 148, 268) |

### 3.1.3 Headspace GC-MS method for the determination of four of the marker compounds in recycled PET samples

**Headspace GC-MS Conditions**

The HS-GC-MS conditions that were used to analyse four of the marker compounds (acetaldehyde, 2-methyl-1,3-dioxolane, limonene and 4-isopropyl toluene) in the PET samples are shown below in Tables 4 (GC-MS conditions) and 5 (headspace sampler conditions).

**Table 4 GC-MS conditions for the determination of four of the marker compounds in recycled PET samples**

| | |
|---|---|
| Instrument | Agilent Technologies 6890<br>Gas Chromatograph with a 5973 MSD |
| Column | 5% phenyl 95% PDMS<br>30m x 0.32mm 3µm film |
| Injection | Split 1:1 @ 200°C |
| Carrier Gas | Helium, @ 5 PSI (constant pressure) |
| Oven Program | 40°C for 2 minutes. 20°C/minute to 150 °C, hold for<br>4 mins; then 50°C/min to 300°C; finally hold for 2 mins. |
| MS | Single Ion Monitoring (SIM) mode.<br>(acetaldehyde m/z 29, 44); (methyl dioxolane m/z 58, 73);<br>(limonene and isopropyl toluene m/z 68, 93, 119, 134) |

**Table 5 Headspace sampler conditions for the determination of four of the marker compounds in recycled PET samples**

| | |
|---|---|
| Instrument | Perkin Elmer Static headspace sampler |
| Sample Temperature | 150°C |
| Needle Temperature | 160°C |
| Transfer Temperature | 170°C |
| Thermostat Time | 60 minutes |
| Pressurise Time | 1.0 minutes |
| Injection Time | 0.04 minutes |
| Withdrawal Time | 1.0 minutes |
| Head Pressure | ~22 PSI |

### 3.1.4 Direct injection GC-FID method for the determination of the MEG compounds in recycled PET samples

**GC-FID Conditions**

The GC-FID conditions that were used to analyse both calibrants and the PET extracts prepared using the ASE method are shown in Table 6 below (note that a GC-MS method based on similar parameters could be used, however, for the samples encountered in the duration of this study, the sensitivity of a GC-FID was easily sufficient).

**Table 6 GC-FID conditions used for the determination of MEG in recycled PET samples**

| | |
|---|---|
| Instrument | Agilent Technologies 6890 Gas Chromatograph with an FID detector |
| Column | SGE SolGel-WAX 30m x 0.25mm 0.25µm film |
| Injection | 1µL Splitless @ 280°C |
| Carrier Gas | Helium @ 1.2mL/min (constant flow) |
| Oven Program | 60°C for 2 minutes. 20°C/minute to 200°C.<br>Hold for 1 minute |
| FID | Temperature : 250°C<br>Hydrogen flow: 40 mL/min<br>Air flow: 450 mL/min |

### 3.2 Validation work carried out on the analytical methods

A full description of the validation work that was carried out on the analytical methods to determine the marker compounds in both recycled P&B and PET samples is provided in Appendix 2.

Consideration was given to the amount of development work that should be carried out on the properties and characteristics of the analytical methods to ensure that they were robust and fit for purpose. The areas that were included in the validation programme for the methods are summarised below in Sections 3.2.1 and 3.2.2. Some of these parameters were investigated more thoroughly than others.

#### 3.2.1 Recycled P&B samples – Solvent extraction/direct injection GC-MS

a) Influence of sample size/area
b) Extraction conditions – solvent, temperature and time
c) Recovery from sample matrix
d) Method verification
    a. Detection limit
    b. Limit of quantification
    c. Precision
    d. Linearity
    e. Accuracy

### 3.2.2 Recycled PET samples – HS-GC-MS and Solvent extraction/direct injection GC

a) Headspace conditions – time, temperature, injection parameters
b) Recovery from sample matrix
c) Method verification
    a. Detection limit
    b. Limit of quantification
    c. Precision
    d. Linearity
    e. Accuracy

## 3.3 Summary of the work on the analytical methods

Sections 3.1 and 3.2 have provided an overview of the analytical methods that were developed to identify and quantify the marker compounds in the recycled P&B and PET. A concise summary of the work carried out is provided below in Sections 3.3.1 and 3.3.2.

### 3.3.1 Method for the P&B samples

1) It was possible to develop and validate a single analytical method which was capable of the reliable separation, detection and quantitation of the five marker compounds shown in Section 2.3.1 in a typical P&B sample matrix.

2) The method that was developed is shown in Sections 3.1.1 and 3.1.2 was based on solvent extraction of the samples using DCM followed by GC-MS analysis.

3) This analytical method was used to identify and quantify the five marker selected compounds in samples of recycled P&B and the results that were obtained are shown in Section 5.1.

### 3.3.2 Method for the PET samples

1) The initial intention was to develop and validate a single analytical method which was capable of the reliable detection and quantitation of the five marker compounds shown in Section 2.3.2. in a typical PET sample matrix.

2) Due to the problems that can occur with the determination of volatile compounds, such as acetaldehyde, by solvent extraction based techniques (for example losses through volatilisation during extraction); headspace GC-MS was the preferred choice of analytical technique for this method. However, the initial development work using this method showed that the quantitative headspace analysis was unsuitable for the MEG marker compound. Therefore, a method based on HS-GC-MS was developed for four of the marker compounds, and a method based on Accelerated Solvent Extraction (ASE) using acetone followed by direct injection GC-FID was developed for MEG (see Sections 3.1.1, 3.1.3 and 3.1.4). Note that the method initially developed for MEG was based on reflux solvent extraction, however, it was later discovered that the method suffered from significant irreproducibility and was superseded by the ASE extraction method.

3) These two analytical methods were used to identify and quantify the five marker selected compounds in samples of recycled PET and the results that were obtained are shown in Section 5.2.

The methodology that has been employed to validate these three analytical methods is described in detail in Appendix 2.

## 4. SAMPLES OF RECYCLED P&B AND PET SAMPLES OBTAINED FOR ANALYSIS

Once the analytical methods for the determination of the marker compounds had been completed they were then used to analyse samples of P&B and PET that were obtained from recycling companies. The samples that were received for analysis are shown below in Section 4.1. and 4.2 and the results that were obtained on these samples are shown in Sections 5.1 and 5.2.

### 4.1 Sourcing of Industrial Samples of Recycled P&B

To enable samples of P&B to be obtained from recycling companies that supplied food grade recycled P&B products into the UK market, discussions took place between Smithers Rapra and Smithers PIRA (a company in the Smithers Group who have extensive experience of food contact products made from P&B). These discussion enabled sources of recycled P&B to be identified and samples were obtained from two recycling companies. These are described below in Sections 4.1.1 and 4.1.2. The total number of samples that were provided and analysed were 84; this was in excess of the target number (75 samples) for this part of the project.

It should be noted that all the P&B samples, from both of the suppliers (i.e. the first and second recyclers as described below), were supplied in a dry or dried form. The samples that started off wet when they were moved from various stages in the recycling process (e.g. samples from the pulper) were dried prior to being shipped to Smithers Rapra.

### 4.1.1 First P&B recycler to provide samples

This recycling company provided between 200 and 250 grams samples from each of these stages in different stages in their recycling system:

a) Shredded samples from the raw materials mix.
b) Samples out of the pulper which have been air dried.
c) Samples after a cleaning step has been used in the process.
d) Samples of card from the board machine after drying.
e) Samples of card after the pigment coating that were suitable for food contact use, e.g. pizza boxes.

Samples from these stages enabled any change in the concentration of the “marker compounds” to be monitored as the post-consumer P&B moved through the recycling process. These arrived during March and April 2012.

In addition, another request was also made for a daily collection of these five types of samples (i.e. a) over three consecutive days (21st, 22nd and 23rd of August 2012) to enable some measure of the day to day variability of the level of the marker compounds to be obtained. These were designated SR6675 (see below).

The final recycled P&B card samples (sample type e)) that were provided by the recycler were of a quality that is suitable for primary packaging that could contact both dry food (e.g. cereal) and food products having a fat content (such as frozen pizza).

The Smithers Rapra sample designations that were given to the samples from this recycler, and the dates that they were received, are shown below.

The following samples arrived at Smithers Rapra on 2nd March 2012 (SR5915) and 2nd April 2012 (Coated card only – SR6027) and were given the sample designations as shown below.

**1) SR5915 and SR6027 Series**

| SR number | Sample description |
|---|---|
| SR5915/1 | Raw material (i.e. shredded waste P&B) |
| SR5915/2 | Material from the Pulper |
| SR5915/3 | Material after a cleaning step |
| SR5915/4 | Uncoated card |
| SR6027 | Coated card |

The results that have been obtained on these samples are shown in Table 7.

In addition, the following two batches of samples that had been taken throughout the process were received on 27th July 2012 (SR6519 series) and 30th August 2012 (SR6675 series), respectively.

**2) SR6519 Series**

This batch has been designated using the SR number and a suffix as follows:

| SR number | Sample description |
|---|---|
| SR6519/1 | Raw material (i.e. shredded waste P&B) |
| SR6519/2 | Material from the Pulper |
| SR6519/3 | Material after a cleaning step |
| SR6519/4 | Uncoated card |
| SR6519/5 | Coated card |

The results that have been obtained on these samples are shown in Table 8.

**3) SR6675 Series (collected over three consecutive days)**

This batch has been designated using the SR number and a suffix as follows:

| SR number | Sample description |
|---|---|
| SR6675/1 | Raw material (i.e. shredded waste P&B) |
| SR6675/2 | Material from the Pulper |
| SR6675/3 | Material after a cleaning step |
| SR6675/4 | Uncoated card |
| SR6675/5 | Coated card |

The results that have been obtained on these samples are shown in Table 9.

**4) SR6805 Series**

The following samples of uncoated card (not normally for food use) and coated card for food use (all designated SR6805) manufactured using recycled P&B were received on 28th September 2012:

**Samples 1 to 16 were coated board for food use. The following food groups applied:**

| | |
|---|---|
| 1 to 5 | Dry and Fatty Food |
| 6 to 10 | Dry food only |
| 11 to 13 | Dry and Frozen Food (the dry will be in a plastic bag within the packaging) |
| 14 to 16 | Dry food only |

These board samples were of a sandwich construction containing different sources of recycled P&B in the centre, e.g. post-consumer waste and post industrial waste.

**Samples 17 to 21 in this fourth batch were uncoated board which is not normally used for food use**

These samples (which were designated SR6805/17 to SR6805/21) were provided for both the determination of marker compounds stage and, some of those that were coated samples for food use, were used for the food migration stage of the project.

These board samples were also of a sandwich construction containing different sources of recycled P&B in the centre, e.g. post-consumer waste and post industrial waste.

The results that have been obtained on these samples are shown in Table 10.

### 4.1.2 Second P&B recycler to provide samples

The samples from this recycler (approximately 200 grams each) were received in one batch on 26th September 2012.

**SR6796 Series (only batch from this P&B recycler)**

These samples were given the Smithers Rapra sample number SR6796. A duplicate of each sample type was supplied. The samples were designated as follows:

a) After pulper (SR6796/1 and SR6796/8)
b) After HD cleaner (SR6796/2 and SR6796/9)
c) Inlet Multifractor (MF) (SR6796/3 and SR6796/10)
d) Long fibre after MF (SR6796/4 and SR6796/11)
e) Short fibre after MF (SR6796/5 and SR6796/12)
f) Long fibre to Paper Factory (SR6796/6 and SR6796/13)
g) Paper (SR6796/7 and SR6796/14)

The duplicate set samples of a) to f) through the process were taken on two occasions in September 2012, separated by a week. The duplicate paper samples (sample g)) were taken on different days in the same month.

The results that have been obtained on these samples are shown in Table 11.

### 4.2 Sourcing of Industrial samples of recycled PET

There are a number of recyclers in the UK that recycle post-consumer PET into food grade PET product. It has been possible to obtain recycled samples for analysis from two of these PET recyclers and they are described below in Sections 4.2.1 and 4.2.2. The total number of samples that were analysed was 77, which was short of the target number (100 samples) for this part of the project. The project was brought to a conclusion before this figure could be reached.

#### 4.2.1 First PET recycler to provide samples

This company primarily recycles post consumer food grade PET for use in new, food grade PET bottles. The batches of samples that were received are described below.

**1) SR5914 Series**

A number of samples were collected from the companies' site on 28th February 2012. These were representative of different stages in the recycling process and were designated as follows:

1) Post consumer PET bottles which had gone through the following:
    a. Hot caustic pre-wash to remove labels and provide a general clean up.
    b. Grinding to flake.

2) Flake from b. which had then been treated with a hot wash/chemical clean-up process to remove contamination (this flake can be sold for non-food use applications).

3) Pellets that had been produced from the flake from 2) after they had been through a "super-clean" process to produce food-grade product.

4) PET bottle performs that had been produced from the pellets in 3) blended with 50% virgin PET – this practice is the industry norm.

5) Food grade PET Bottles which had been "blow moulded" from the bottle pre-forms in 4).

These samples were given the following Smithers Rapra sample numbers:

a) SR5914/1 1st sample of flake (been through a hot pre-wash with caustic).
b) SR5914/2 2nd sample of flake (been though a hot chemical wash).
c) SR5914/3 Superclean granulate.
d) SR5914/4 Bottle pre-forms from superclean granulate.
e) SR5914/5 Bottles blown from pre-forms of superclean granulate.

The results that were obtained on these samples are shown in Table 12.

**2) <u>SR6785 Series</u>**

An additional set of samples was provided to Smithers Rapra by this recycler on 24th September 2012. Samples were provided from the same stages ('a' to 'e') that are shown above for the SR5914 Series. To enable an evaluation of the day to day variation to be made, two samples were collected at stages a) to c) for each day over a 5 day period (17th September to 21st September 2012). Bottle preforms and bottles that had been manufactured from "superclean" pellets in Week 38 of 2012 were also provided. These samples were given the Smithers Rapra sample designations SR6785 – numbers 1 to 34.

The results that have been obtained on these samples are shown in Table 13.

**3) <u>SR6828 Series</u>**

To provide additional samples for the determination of marker compounds and samples for the food migration stage of the project, this recycler provided final products (32 PET bottles) that had been manufactured using 75% of their recycled PET.

The results that have been obtained on these samples are shown in Table 14.

### 4.2.2 Second PET recycler to provide samples

This company receives mixed bottle waste (i.e. HDPE, PET, LDPE etc.) for recycling into separate recyclate streams. It was hoped that HQWF flake from this recycler which had been through a "super cleaning" process to generate recycled food grade PET would also be available for analysis, but for various reasons this was not possible within the timeframe of the project.

The following samples were provided by this company for the marker compound analysis stage of the project, and they assisted us in obtaining non-bottle, recycled food grade products (SR6942 Series below) for the food migration stage.

**1) <u>SR6591 Series</u>**

In order to provide both a measure of how the "input stream" to the recycling site varied with time and to what degree the various stages in the process cleaned up the PET, this company provided sets of samples (one per week), as described below, for each week over a five week period.

1) PET from the stage in the process where the mixed bottle input stream has been separated into different polymer types (e.g. HDPE and PET), and the PET stream has been ground into 25mm flake and any metal removed.

2) PET that has been through the process to Stage 1) and then through a friction caustic hot wash, and sink-float and air clean up purification systems.

3) PET that has been through Stages 1) and 2) and then through a series of flake sorters and then a final metal sorter. This PET is HQWF grade and is then further treated to obtain food grade PET.

These five sets of samples were designated as follows:

| | |
|---|---|
| SR6591 (A) | Arrived at Smithers Rapra 10th August 2012 |
| SR6634 (B) | Arrived at Smithers Rapra 17th August 2012 |
| SR6665 (C) | Arrived at Smithers Rapra 28th August 2012 |
| SR6687 (D) | Arrived at Smithers Rapra 3rd September 2012 |
| SR6717 (E) | Arrived at Smithers Rapra 10th September 2012 |

The results that have been obtained on these samples are shown in Tables 15, 16, 17, 18 and 19.

**2) SR6942 Series**

To provide additional samples for the analysis stage, and samples for the food migration stage, this recycler provided the following final products that had been manufactured using recycled PET:

a) 20 circular “salad pots”
b) 20 pyramidal “deli trays”

The results that have been obtained on these samples are shown in Table 20.

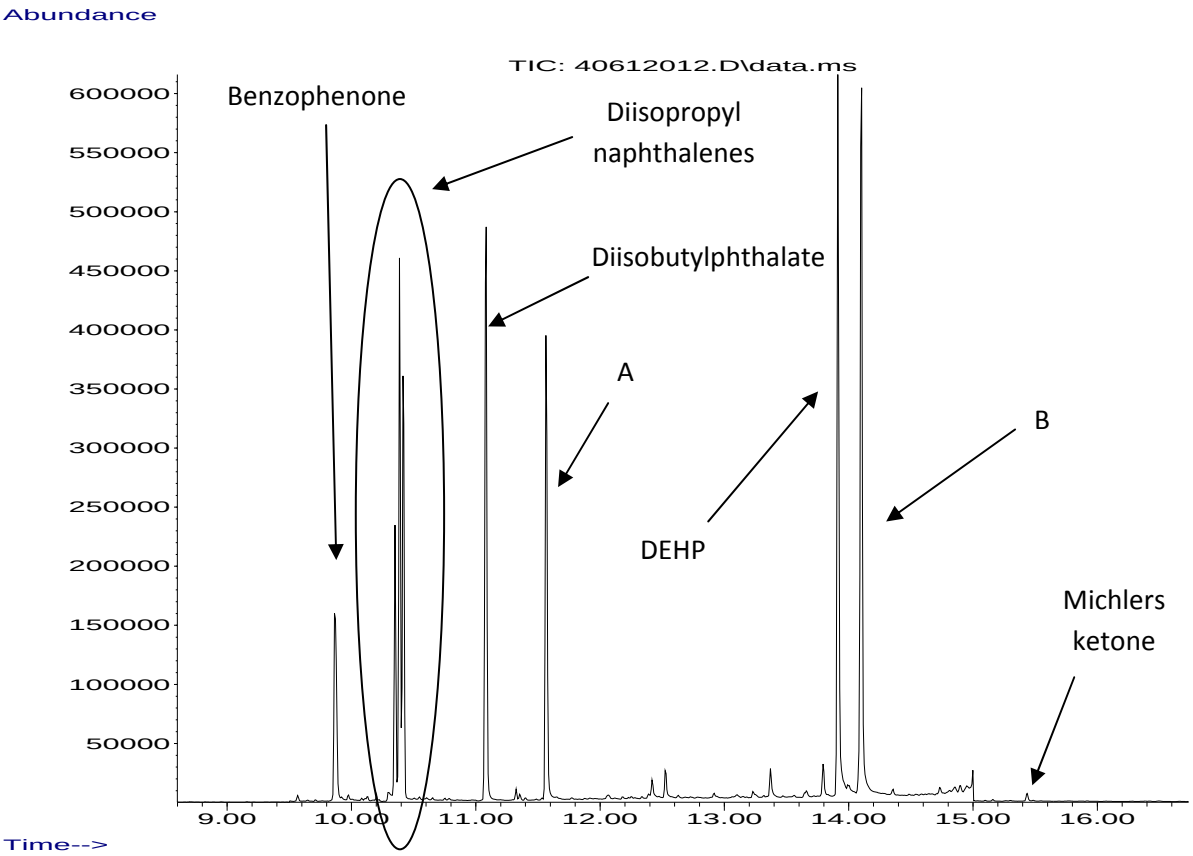
## 5. RESULTS OBTAINED ON THE DETERMINATION OF MARKER COMPOUNDS IN RECYCLED P&B AND PET

### 5.1 Results obtained on the marker compounds in P&B

A single method based on DCM solvent extraction of the samples followed by GC-MS was developed to allow all five marker compounds to be analysed simultaneously in samples of recycled P&B.

A typical chromatogram displaying the five marker compounds (and other co-extractants) that have been extracted from a recycled P&B sample is shown below in Figure 1.

**Figure 1 Five marker compounds extracted from a recycled P&B sample**




**Where :**

A= Di-n-butyl phthalate

B= Di-n-octyl phthalate

This section contains all of the data that has been obtained on the recycled P&B samples. For all of the results tables that are included in Sections 5.1.1 and 5.1.2 the following key applies:

**Key to Tables**

DIBP = Diisobutyl phthalate; DEHP = Di-2-ethylhexyl phthalate; BP = Benzophenone; DIPN = Diisopropyl naphthalenes; MK = Michlers ketone; <LOQ = Less than Limit of Quantification.

The values for the five Marker compounds that are in the Tables have been determined using the direct injection GC-MS analytical method that was specifically developed for the project.

For some of the determinations, the levels found were below the limit of quantification (LOQ) for the analytical method. The LOQ for the five Marker compounds were:

| | |
|---|---|
| Benzophenone | 0.08 ug/ml |
| Diisopropyl naphthalene | 0.04 ug/ml |
| Diethylhexylphthalate | 0.11 ug/ml |
| Michlers Ketone | 0.37 ug/ml |
| Diisobutylphthalate | 0.07 ug/ml |

**Note.** The LOQ figures are reported as weight per volume ('µg' of analyte per 'mL' of solvent). The sample masses and solvent volumes used for the method validation work (2g sample extracted in 25-mL solvent) will result in weight for weight (e.g. 'milligram' of analyte per 'kilogram' of P&B sample) values 12.5 times greater than the reported µg/mL values; however, concentration or dilution of the extract solutions prior to analysis can allow some adjustment of these limits to suit specific samples.

### 5.1.1 P&B samples obtained from the first recycler

The samples that were received from this recycler are described in Section 4.1.1. The results that were obtained on these four batches of P&B samples are shown in Tables 7 to 10. The samples in Tables 7 to 9 were provided in singular and prepared and analysed in duplicate in order to provide a measure of the homogeneity of the bulk sample. The samples in Table 10 were provided as multiple replicates and prepared and analysed in singular.

The results obtained on the first batch of samples (SR5915 and SR6027) from this recycler are shown below in Table 7.

**Table 7 Results obtained on the five marker compounds in the first batch of samples (designated SR5915 and SR6027)**

| SR Number | Sample Description | DiBP (µg/g) | DEHP (µg/g) | BP (µg/g) | DIPN (µg/g) | MK (µg/g) |
|---|---|---|---|---|---|---|
| SR5915/1 | Raw Material | 2.18 | 2.45 | 19.26 | 9.40 | <LOQ |
| SR5915/1 | Raw Material | 2.32 | 2.35 | 22.41 | 9.11 | <LOQ |
| SR5915/2 | Pulper Material | 7.23 | 9.08 | 2.56 | 33.89 | <LOQ |
| SR5915/2 | Pulper Material | 6.91 | 8.67 | 2.52 | 33.21 | <LOQ |
| SR5915/3 | Post cleaning | 6.78 | 6.92 | 2.04 | 27.87 | <LOQ |
| SR5915/3 | Post cleaning | 6.90 | 8.40 | 2.08 | 26.35 | <LOQ |
| SR5915/4 | Uncoated card | 4.62 | 6.77 | 1.48 | 36.57 | <LOQ |
| SR5915/4 | Uncoated card | 4.49 | 6.12 | 1.43 | 34.76 | <LOQ |
| SR6027/1 | Coated card | 6.15 | 7.19 | 1.85 | 39.92 | 5.11 |

The results obtained on the second batch of P&B samples (designated SR 6519) from this recycler are shown in Table 8.

**Table 8 Results obtained on the five marker compounds in the second batch of samples (designated SR6519)**

| SR Number | Sample Description | DiBP (µg/g) | DEHP (µg/g) | BP (µg/g) | DIPN (µg/g) | MK (µg/g) |
|---|---|---|---|---|---|---|
| SR6519/1 | Raw Material | 0.95 | 1.75 | 2.57 | 15.90 | <LOQ |
| SR6519/1 | Raw Material | 1.40 | 5.92 | 3.65 | 30.26 | <LOQ |
| SR6519/2 | Pulper Material | 8.31 | 18.04 | 2.25 | 67.81* | <LOQ |
| SR6519/2 | Pulper Material | 8.32 | 18.28 | 2.38 | 75.49* | <LOQ |
| SR6519/3 | Post cleaning | 8.21 | 20.32 | 2.11 | 78.85* | <LOQ |
| SR6519/3 | Post cleaning | 8.32 | 19.28 | 2.09 | 77.00* | <LOQ |
| SR6519/4 | Uncoated card | 5.76 | 10.86 | 3.20 | 48.97 | <LOQ |
| SR6519/4 | Uncoated card | 5.64 | 10.84 | 3.21 | 48.05 | <LOQ |
| SR6519/5 | Coated card | 10.46 | 16.31 | 2.25 | 85.64* | <LOQ |
| SR6519/5 | Coated card | 9.43 | 15.52 | 2.26 | 85.01* | <LOQ |

* Values in excess of the calibration range

The results obtained on the third batch of P&B samples (designated SR 6675) from this recycler are shown in Table 9.

**Table 9 Results obtained on the five marker compounds in the third batch of samples**

| SR Number | Sample Description | DiBP (µg/g) | DEHP (µg/g) | BP (µg/g) | DIPN (µg/g) | MK (µg/g) |
|---|---|---|---|---|---|---|
| SR6675/1 | Raw Material (21/8/12) | 1.13 | 5.29 | 1.66 | 3.16 | <LOQ |
| SR6675/1 | Raw Material (21/8/12) | 1.23 | 6.71 | 1.75 | 3.04 | <LOQ |
| SR6675/1 | Raw Material (22/8/12) | 1.06 | 2.38 | 36.95 | 3.81 | <LOQ |
| SR6675/1 | Raw Material (22/8/12) | 1.22 | 2.62 | 29.80 | 3.70 | <LOQ |
| SR6675/1 | Raw Material (23/8/12) | 0.83 | 3.90 | 2.74 | 6.19 | <LOQ |
| SR6675/1 | Raw Material 23/8/12 | 0.78 | 5.01 | 2.15 | 5.52 | <LOQ |
| SR6675/2 | Pulper Material 21/8/12 | 1.71 | 10.35 | 1.74 | 9.01 | <LOQ |
| SR6675/2 | Pulper Material 21/8/12 | 1.72 | 10.78 | 1.80 | 9.36 | <LOQ |
| SR6675/2 | Pulper Material 22/8/12 | 3.34 | 15.51 | 2.29 | 19.82 | <LOQ |
| SR6675/2 | Pulper Material 22/8/12 | 2.59 | 16.20 | 2.33 | 26.22 | <LOQ |
| SR6675/2 | Pulper Material 23/8/12 | 1.66 | 15.81 | 1.52 | 11.24 | <LOQ |
| SR6675/2 | Pulper | 1.48 | 9.50 | 1.45 | 9.89 | <LOQ |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Material 23/8/12 | | | | | |
| SR6675/3 | Post cleaning 21/8/12 | 2.20 | 12.46 | 1.74 | 17.83 | <LOQ |
| SR6675/3 | Post cleaning 21/8/12 | 2.12 | 11.99 | 1.74 | 17.85 | <LOQ |
| SR6675/3 | Post cleaning 22/8/12 | 1.94 | 7.11 | 1.82 | 23.77 | <LOQ |
| SR6675/3 | Post cleaning 22/8/12 | 1.79 | 4.34 | 1.76 | 23.44 | <LOQ |
| SR6675/3 | Post cleaning 23/8/12 | 2.88 | 11.40 | 2.04 | 15.83 | <LOQ |
| SR6675/3 | Post cleaning 23/8/12 | 2.80 | 11.30 | 1.97 | 15.96 | <LOQ |
| SR6675/4 | Uncoated card 21/8/12 | 6.24 | 12.37 | 2.52 | 27.27 | 5.27 |
| SR6675/4 | Uncoated card 21/8/12 | 6.87 | 12.40 | 2.48 | 26.59 | 7.04 |
| SR6675/4 | Uncoated card 22/8/12 | 6.95 | 13.01 | 2.63 | 39.36 | 5.67 |
| SR6675/4 | Uncoated card 22/8/12 | 7.40 | 13.24 | 2.68 | 39.84 | 5.88 |
| SR6675/4 | Uncoated card 23/8/12 | 6.70 | 10.41 | 2.19 | 24.78 | 7.53 |
| SR6675/4 | Uncoated card | 6.35 | 10.65 | 2.18 | 24.84 | 5.65 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 23/8/12 | | | | | |
| SR6675/5 | Coated card 21/8/12 | 8.21 | 12.82 | 2.52 | 31.70 | <LOQ |
| SR6675/5 | Coated card 21/8/12 | 7.65 | 12.31 | 2.47 | 32.08 | <LOQ |
| SR6675/5 | Coated card 22/8/12 | 8.49 | 14.07 | 2.68 | 47.75 | 5.72 |
| SR6675/5 | Coated card 22/8/12 | 8.44 | 11.74 | 2.64 | 47.47 | 4.85 |
| SR6675/5 | Coated card 23/8/12 | 7.94 | 10.42 | 2.07 | 29.53 | 5.80 |
| SR6675/5 | Coated card 23/8/12 | 7.64 | 10.05 | 2.06 | 28.54 | 5.10 |

The results obtained on the fourth batch of P&B samples (designated SR 6805) from this recycler are shown in Table 10.

**Table 10 Results obtained on the five marker compounds in the fourth batch of samples (uncoated card not normally for food contact, and coated card for food contact use)**

| SR Number | Sample Description | DiBP (µg/g) | DEHP (µg/g) | BP (µg/g) | DIPN (µg/g) | MK (µg/g) |
|---|---|---|---|---|---|---|
| SR6805/1 | Board for dry/fatty food | <LOQ | 3.01 | 1.81 | 4.47 | <LOQ |
| SR6805/2 | Board for dry/fatty food | <LOQ | 3.02 | 2.43 | 5.54 | <LOQ |
| SR6805/3 | Board for dry/fatty food | 1.20 | 3.04 | 12.86 | 4.46 | <LOQ |
| SR6805/4 | Board for dry/fatty food | <LOQ | 3.08 | 2.21 | 3.20 | <LOQ |
| SR6805/5 | Board for dry/fatty food | <LOQ | 3.02 | 2.40 | 3.48 | <LOQ |

| | | | | | | |
|---|---|---|---|---|---|---|
| SR6805/6 | Board for dry food | 5.25 | 8.80 | 1.65 | 43.41 | <LOQ |
| SR6805/7 | Board for dry food | 4.59 | 8.15 | 1.43 | 30.99 | <LOQ |
| SR6805/8 | Board for dry food | 4.80 | 9.80 | 1.97 | 46.01 | <LOQ |
| SR6805/9 | Board for dry food | 3.88 | 7.07 | 2.21 | 31.35 | <LOQ |
| SR6805/10 | Board for dry food | 4.35 | 9.29 | 2.23 | 28.82 | <LOQ |
| SR6805/11 | Board for dry frozen food | 3.80 | 8.35 | 2.47 | 30.10 | <LOQ |
| SR6805/12 | Board for dry frozen food | 4.06 | 7.54 | 1.54 | 43.43 | <LOQ |
| SR6805/13 | Board for dry frozen food | 4.37 | 7.22 | 2.19 | 31.12 | <LOQ |
| SR6805/14 | Board for dry food | 3.72 | 7.36 | 1.60 | 34.81 | <LOQ |
| SR6805/15 | Board for dry food | 4.26 | 7.23 | 1.44 | 40.35 | <LOQ |
| SR6805/16 | Board for dry food | 4.21 | 7.89 | 1.55 | 40.36 | <LOQ |
| SR6805/17 | Uncoated board* | 6.69 | 9.94 | 1.95 | 29.70 | <LOQ |
| SR6805/18 | Uncoated board* | 7.22 | 11.78 | 1.93 | 34.95 | <LOQ |
| SR6805/19 | Uncoated board* | 6.95 | 10.94 | 1.94 | 28.80 | <LOQ |
| SR6805/20 | Uncoated board* | 7.26 | 10.48 | 2.40 | 44.68 | <LOQ |
| SR6805/21 | Uncoated board* | 7.45 | 13.48 | 1.89 | 43.07 | <LOQ |

*Not normally used for food contact use

**Note**: Samples SR6805/1 to SR6805/16 can be used for direct food contact use and some of these were used in the food migration stage of this project which is reported in Section 6. of this report.

### 5.1.2 P&B samples obtained from the second recycler

The samples that were received from this recycler (designated SR6796) are described in Section 4.1.2. The results that have been obtained on these P&B samples are shown in Table 11. These samples were provided as duplicates and prepared and analysed in singular

**Table 11 Results obtained on the five marker compounds on the batch of samples from the second recycler**

| SR Number | Sample Description | DiBP (µg/g) | DEHP (µg/g) | BP (µg/g) | DIPN (µg/g) | MK (µg/g) |
|---|---|---|---|---|---|---|
| SR6796/1 | After Pulper (1st sample) | 3.43 | 11.54 | 1.55 | 10.31 | <LOQ |
| SR6796/2 | After HD Cleaner (1st sample) | 2.30 | 12.11 | 1.29 | 13.05 | <LOQ |
| SR6796/3 | Inlet Multifractor (MF) (1st sample) | 2.33 | 13.84 | 1.26 | 8.22 | <LOQ |
| SR6796/4 | Long Fibre after MF (1st sample) | 3.82 | 11.58 | 1.23 | 9.17 | <LOQ |
| SR6796/5 | Short Fibre after MF (1st sample) | 3.34 | 12.24 | 1.24 | 8.35 | <LOQ |
| SR6796/6 | Long Fibre to Paper Factory (1st sample) | 2.56 | 12.46 | 1.21 | 11.81 | <LOQ |
| SR6796/7 | Paper (1st sample) | 7.61 | 12.11 | 2.04 | 18.17 | <LOQ |
| SR6796/8 | After Pulper (2nd sample) | 1.31 | 10.37 | 1.28 | 6.30 | <LOQ |

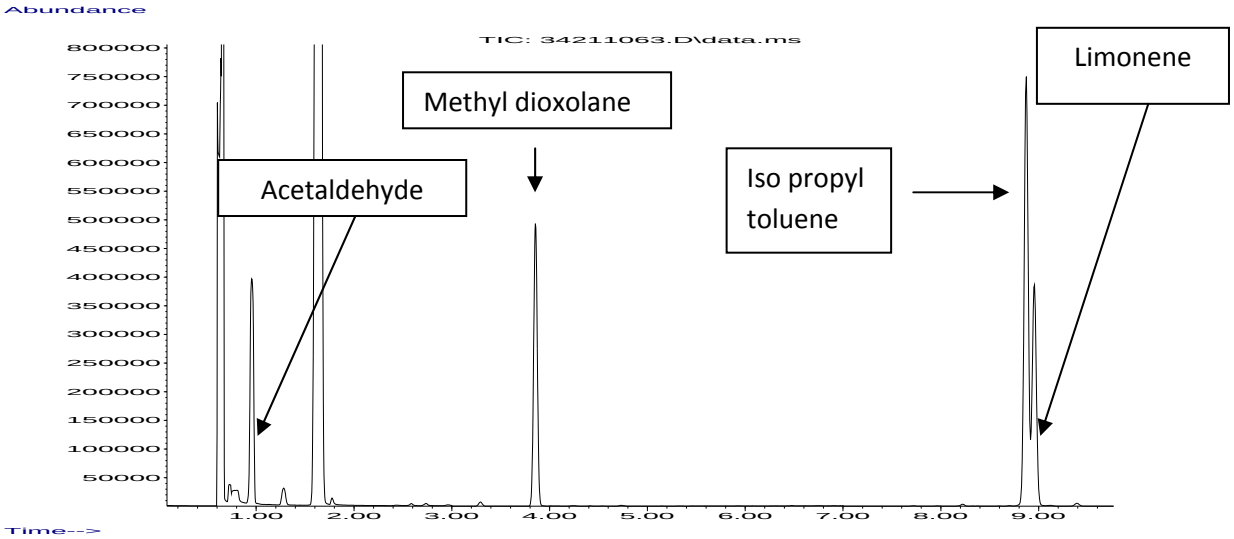
| | | | | | | |
|---|---|---|---|---|---|---|
| SR6796/9 | After HD Cleaner (2nd sample) | 2.42 | 10.97 | 1.70 | 8.82 | <LOQ |
| SR6796/10 | Inlet Multifractor (MF) (2nd sample) | 2.75 | 14.00 | 1.01 | 8.56 | <LOQ |
| SR6796/11 | Long Fibre after MF (2nd sample) | 3.37 | 16.30 | 1.09 | 10.28 | <LOQ |
| SR6796/12 | Short Fibre after MF (2nd sample) | 3.26 | 16.70 | 1.24 | 9.71 | <LOQ |
| SR6796/13 | Long Fibre to Paper Factory (2nd sample) | 2.22 | 11.55 | 1.32 | 15.67 | <LOQ |
| SR6796/14 | Paper (2nd sample) | 8.09 | 12.24 | 2.05 | 14.98 | <LOQ |

### 5.2 Results obtained on the marker compounds in recycled PET

Work carried out on the development of the analytical methods showed that the following four marker compounds in the recycled PET could be detected and quantified by headspace GC-MS: acetaldehyde, methyl dioxolane, iso-propyl toluene, and limonene.

An example of the headspace GC-MS chromatogram that was obtained on a recycled PET sample is shown below in Figure 2. The peaks due to the four marker compounds have been assigned.

**Figure 2 Example of the headspace GC-MS chromatogram obtained for a recycled PET sample**



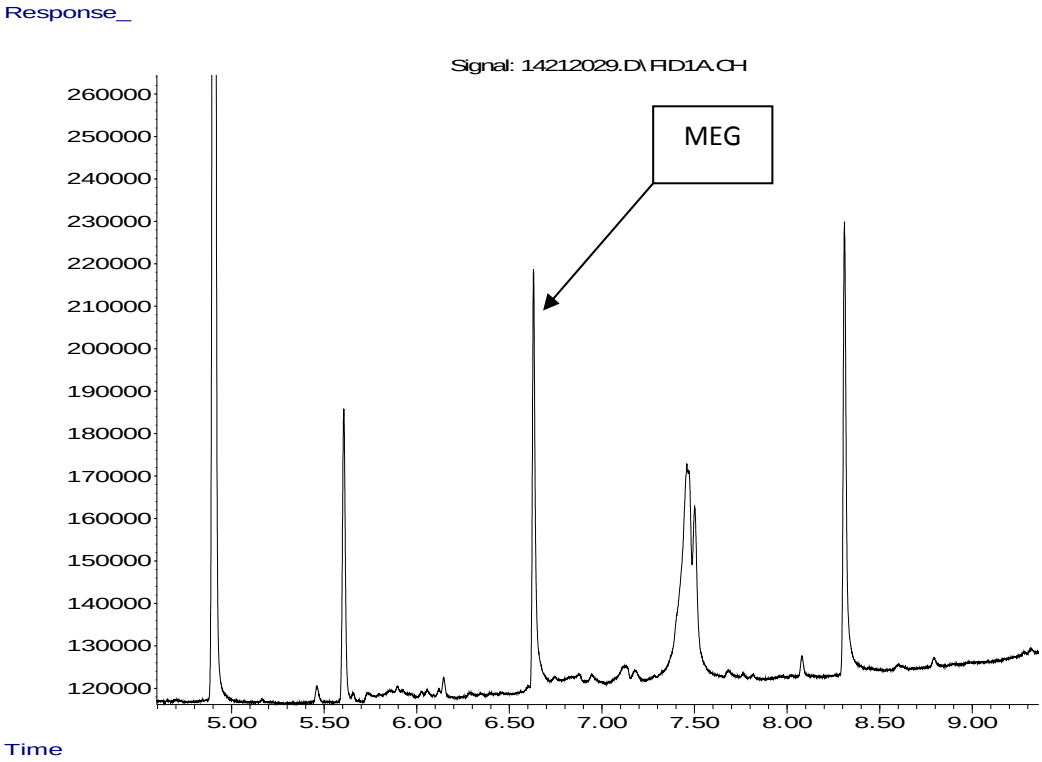

**Notes** :

(a) The large peak at a retention time of ~1.8 minutes is acetone

(b) The peak at ~0.7 minutes is the air peak

A direct injection Gas Chromatography method, based on Accelerated Solvent Extraction of the samples was developed for the other marker compound, monoethylene glycol (MEG). An example of the chromatogram that was obtained on a recycled PET sample is shown below in Figure 3. The peak due to MEG has been assigned.

**Figure 3 Example of the direct injection GC-FID chromatogram obtained on a recycled PET sample**




This section contains all of the data that has been obtained on the recycler PET samples. For all of the Tables that are included in Sections 5.2.1 and 5.2.2 the following key applies:

**Key**

AC = Acetaldehyde; MD = Methyl dioxolane; IT = Isopropyl toluene; Lim = Limonene; MEG = Monoethylene glycol; <LOQ = less than Limit of Quantification

For some of the determinations, the levels found were below the Limit of Quantification (LOQ) for the analytical method. The LOQ for the five Marker compounds were:

| | |
|---|---|
| Acetaldehyde | 0.15 ug/g |
| Methyl dioxolane | 0.07 ug/g |
| Isopropyl toluene | 0.08 ug/g |
| Limonene | 0.10 ug/g |
| MEG | 0.70 ug/g |

**Note.** The LOQ quoted for MEG was calculated using GC-MS in Single Ion Monitoring (SIM) mode during the initial validation work. The MEG determinations reported in this report were conducted using a GC-FID method (see Section 3.1.4) and therefore the sensitivity (and hence LOQ) is not as good.

The re-validation of the extraction method (i.e. the ASE method) for MEG (see Section 2 in Appendix 2) would have no effect on the suitability for the analysis of the samples by GC-MS in SIM mode; therefore, the stated LOQ of 0.70 µg/g is still valid. All samples the PET samples analysed during this study were comfortably within the sensitivity range for the GC-FID.

### 5.2.1 PET samples from the first recycler

The samples that were received from this recycler are described in Section 4.2.1. The data that has been obtained on these samples is shown below in Tables 12, 13 and 14. The samples designated SR5914 (Table 12) were provided in singular and prepared and analysed in duplicate in order to provide a measure of the homogeneity of the bulk sample. The samples designated SR6785 (Table 13) were supplied as multiple replicates and analysed in singular

**Table 12 Results obtained on the five marker compounds in the first batch of PET samples**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR 5914/1 | 1st Flake Caustic pre-washed | 8.21 | 4.07 | < LOQ | 0.85 | 19.00 |
| SR 5914/1 | 1st Flake Caustic pre-washed | 4.47 | 3.53 | < LOQ | 1.46 | 18.11 |
| SR 5914/2 | 2nd Flake Hot chemical wash | 4.05 | 3.60 | < LOQ | 0.79 | 17.57 |
| SR 5914/2 | 2nd Flake Hot chemical wash | 3.38 | 4.23 | < LOQ | 1.20 | 17.65 |
| SR 5914/3 | Granule from Vacurema Process | 5.34 | 0.81 | < LOQ | < LOQ | 18.87 |
| SR 5914/3 | Granule from Vacurema Process | 6.23 | 0.93 | <LOQ | <LOQ | 20.91 |
| SR 5914/4 | Pre-form from Vacurema granules | 6.15 | 1.24 | < LOQ | < LOQ | 21.94 |
| SR 5914/4 | Pre-form from Vacurema granules | 6.18 | 1.10 | <LOQ | <LOQ | 24.32 |
| SR 5914/5 | Bottle from Vacurema pre-forms | 2.80 | 1.83 | < LOQ | < LOQ | 23.97 |
| SR 5914/5 | Bottle from Vacurema pre-forms | 2.05 | 1.54 | <LOQ | <LOQ | 23.69 |

The samples shown in Table 13 below were collected over a five day period (17th September to 21st September) to provide an illustration of how the input stream for the recycling plant varied during a working week. The dates that the samples were collected by the recycler are shown in brackets.

**Table 13 Results obtained on the five marker compounds in the second batch of PET samples**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6785/1 | 1st Flake Caustic pre-washed (17th Sept '12) | 6.34 | 3.87 | <LOQ | 0.78 | 28.25 |
| SR6785/2 | 1st Flake Caustic pre-washed (17th Sept '12) | 5.33 | 3.63 | <LOQ | 0.95 | 28.68 |
| SR6785/7 | 1st Flake Caustic pre-washed (18th Sept '12) | 7.46 | 4.04 | 0.11 | 1.94 | 27.45 |
| SR6785/8 | 1st Flake Caustic pre-washed (18th Sept '12) | 7.18 | 4.33 | 0.12 | 1.35 | 26.07 |
| SR6785/13 | 1st Flake Caustic pre-washed (19th Sept '12) | 6.91 | 3.62 | <LOQ | 1.03 | 23.26 |
| SR6785/14 | 1st Flake Caustic pre-washed (19th Sept '12) | 7.47 | 4.08 | 0.13 | 2.20 | 21.85 |
| SR6785/19 | 1st Flake Caustic pre-washed (20th Sept '12) | 5.93 | 3.56 | 0.08 | 1.55 | 21.42 |
| SR6785/20 | 1st Flake Caustic pre-washed (20th Sept '12) | 6.32 | 4.18 | 0.13 | 2.22 | 19.40 |
| SR6785/25 | 1st Flake | 6.17 | 3.69 | <LOQ | 1.23 | 21.42 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Caustic pre-washed (21st Sept '12) | | | | | |
| SR6785/26 | 1st Flake Caustic pre-washed (21st Sept '12) | 6.09 | 3.81 | 0.08 | 1.11 | 20.83 |
| SR6785/3 | 2nd Flake Hot chemical wash (17th Sept '12) | 3.61 | 3.67 | 0.08 | 0.79 | 23.84 |
| SR6785/4 | 2nd Flake Hot chemical wash (17th Sept '12) | 3.81 | 3.97 | 0.08 | 1.21 | 25.69 |
| SR6785/9 | 2nd Flake Hot chemical wash (18th Sept '12) | 4.26 | 3.98 | 0.09 | 1.33 | 23.38 |
| SR6785/10 | 2nd Flake Hot chemical wash (18th Sept '12) | 4.36 | 3.61 | 0.12 | 1.47 | 25.59 |
| SR6785/15 | 2nd Flake Hot chemical wash (19th Sept '12) | 4.91 | 4.56 | 0.09 | 1.18 | 19.26 |
| SR6785/16 | 2nd Flake Hot chemical wash (19th Sept '12) | 3.74 | 3.75 | <LOQ | 1.23 | 20.08 |
| SR6785/21 | 2nd Flake Hot chemical wash (20th Sept '12) | 3.84 | 3.85 | <LOQ | 0.91 | 18.59 |
| SR6785/22 | 2nd Flake Hot chemical | 4.39 | 3.74 | <LOQ | 1.08 | 17.44 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | wash (20th Sept '12) | | | | | |
| SR6785/27 | 2nd Flake Hot chemical wash (21st Sept '12) | 4.17 | 3.60 | <LOQ | 0.81 | 19.34 |
| SR6785/28 | 2nd Flake Hot chemical wash (21st Sept '12) | 3.97 | 3.64 | <LOQ | 1.29 | 17.06 |
| SR6785/5 | Granule from Vacurema Process (17th Sept '12) | 7.03 | 0.97 | <LOQ | <LOQ | 21.42 |
| SR6785/6 | Granule from Vacurema Process (17th Sept '12) | 7.46 | 1.02 | <LOQ | <LOQ | 19.91 |
| SR6785/11 | Granule from Vacurema Process (18th Sept '12) | 5.13 | 0.97 | <LOQ | <LOQ | 21.41 |
| SR6785/12 | Granule from Vacurema Process (18th Sept '12) | 5.32 | 0.90 | <LOQ | <LOQ | 20.05 |
| SR6785/17 | Granule from Vacurema Process (19th Sept '12) | 4.58 | 0.95 | <LOQ | <LOQ | 15.70 |
| SR6785/18 | Granule from Vacurema Process (19th Sept '12) | 4.16 | 0.76 | <LOQ | <LOQ | 15.75 |
| SR6785/23 | Granule from Vacurema Process | 6.21 | 0.93 | <LOQ | <LOQ | 13.88 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | (20th Sept '12) | | | | | |
| SR6785/24 | Granule from Vacurema Process (20th Sept '12) | 6.55 | 0.91 | <LOQ | <LOQ | 16.06 |
| SR6785/29 | Granule from Vacurema Process (21st Sept '12) | 7.33 | 0.89 | <LOQ | <LOQ | 16.78 |
| SR6785/30 | Granule from Vacurema Process (21st Sept '12) | 6.67 | 0.86 | <LOQ | <LOQ | 16.21 |
| SR6785/31 | Bottle Pre-form | 6.28 | 1.09 | <LOQ | <LOQ | 18.56 |
| SR6785/32 | Bottle Pre-form | 7.27 | 1.05 | <LOQ | <LOQ | 18.67 |
| SR6785/33 | Bottle | 3.86 | 1.30 | <LOQ | <LOQ | 19.42 |
| SR6785/34 | Bottle | 3.96 | 1.44 | <LOQ | <LOQ | 20.14 |

**Marker data obtained on PET bottles received for the food migration stage of the project (covered in Section 6.)**

**Table 14 The data obtained on the final product samples**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6828 | Bottle | 4.89 | 1.27 | <LOQ | 0.10 | 16.43 |

### 5.2.2 PET samples from the second recycler

The samples that were received from this recycler are described in Section 4.2.2. The data that has been obtained on these samples is shown below in Tables 15 to 20.

These samples were provided in singular and prepared and analysed in duplicate in order to provide a measure of the homogeneity of the bulk sample.

**Table 15 The data obtained on the first batch of samples (SR6591 A)**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6591/1 | Post Granulator | 11.30 | 3.90 | 0.95 | 7.86 | 36.57 |
| SR6591/1 | Post Granulator | 10.78 | 4.00 | 0.84 | 7.28 | 37.83 |
| SR6591/2 | Post Hot Wash | 5.14 | 4.07 | 0.04 | 0.90 | 31.66 |
| SR6591/2 | Post Hot Wash | 4.63 | 3.94 | 0.05 | 1.17 | 29.45 |
| SR6591/3 | HQWF | 6.32 | 4.59 | 0.09 | 1.82 | 31.49 |
| SR6591/3 | HQWF | 5.47 | 4.07 | 0.07 | 1.47 | 30.26 |

**Table 16 The data obtained on the second batch of samples (SR6634 B)**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6634/1 | Post Granulator | 8.27 | 3.51 | 0.18 | 2.24 | 20.67 |
| SR6634/1 | Post Granulator | 10.12 | 3.39 | 0.25 | 6.99 | 20.51 |
| SR6634/2 | Post Hot Wash | 3.81 | 3.47 | 0.10 | 1.57 | 19.98 |
| SR6634/2 | Post Hot Wash | 4.73 | 4.23 | <LOQ | 1.50 | 20.58 |
| SR6634/3 | HQWF | 5.04 | 3.99 | 0.08 | 1.61 | 19.91 |
| SR6634/3 | HQWF | 5.04 | 3.75 | <LOQ | 1.46 | 19.85 |

**Table 17 The data obtained on the third batch of samples (SR6665 C)**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6665/1 | Post Granulator | 9.03 | 2.99 | 0.34 | 4.18 | 19.15 |
| SR6665/1 | Post Granulator | 9.16 | 3.05 | 0.27 | 7.27 | 20.06 |
| SR6665/2 | Post Hot Wash | 4.89 | 3.82 | <LOQ | 1.31 | 18.70 |
| SR6665/2 | Post Hot Wash | 4.96 | 3.71 | <LOQ | 1.27 | 18.18 |
| SR6665/3 | HQWF | 3.56 | 3.35 | <LOQ | 1.14 | 19.15 |
| SR6665/3 | HQWF | 5.00 | 4.37 | <LOQ | 1.49 | 19.20 |

**Table 18 The data obtained on the fourth batch of samples (SR6687 D)**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6687/1 | Post Granulator | 10.05 | 3.35 | 0.88 | 5.87 | 19.81 |
| SR6687/1 | Post Granulator | 9.40 | 3.17 | 0.66 | 5.64 | 20.34 |
| SR6687/2 | Post Hot Wash | 5.06 | 3.84 | 0.09 | 1.59 | 17.99 |
| SR6687/2 | Post Hot Wash | 4.49 | 3.63 | 0.10 | 1.64 | 18.20 |
| SR6687/3 | HQWF | 5.07 | 3.79 | 0.09 | 1.60 | 16.71 |
| SR6687/3 | HQWF | 4.68 | 3.78 | <LOQ | 0.88 | 17.96 |

**Table 19 The data obtained on the fifth batch of samples (SR6717 E)**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6717/1 | Post Granulator | 9.88 | 3.28 | 0.38 | 7.63 | 18.74 |
| SR6717/1 | Post Granulator | 8.68 | 3.22 | 0.40 | 5.00 | 18.46 |
| SR6717/2 | Post Hot Wash | 4.86 | 4.56 | 0.10 | 1.41 | 18.77 |
| SR6717/2 | Post Hot Wash | 4.00 | 3.55 | <LOQ | 1.06 | 16.93 |
| SR6717/3 | HQWF | 5.94 | 3.98 | 0.08 | 1.42 | 17.92 |
| SR6717/3 | HQWF | 5.14 | 3.77 | 0.12 | 2.41 | 18.00 |

**Marker data obtained on "Deli" trays received for the food migration stage of the project (covered in Section 6.0)**

**Table 20 The data obtained on the final product samples**

| SR Number | Sample Description | AC (µg/g) | MD (µg/g) | IT (µg/g) | Lim (µg/g) | MEG (µg/g) |
|---|---|---|---|---|---|---|
| SR6942 | Circular Pot | 4.84 | 1.61 | 0.01 | 0.03 | 15.59 |
| SR6942 | Pyramidal Pot | 5.67 | 0.74 | 0.02 | 0.08 | 20.03 |

## 5.3 Conclusions

In drawing conclusions from the data that has been obtained during the course of this project, care has to be taken as an important consideration is the very large amounts of waste, heterogeneous material that plastics recycling plants and, to an even greater extent, paper mills, process during a year. For example, a PET recycling plant can recycle over 30,000 tonnes of material, and a paper mill in excess of 500,000 tonnes of material. This means that even though a relatively large number of samples have been analysed during the course of this project, the mass of each sample involved was relatively small, between 1 and 2.5 grams, and so it represents a very small proportion of the material that was being processed at the time that it was taken.

Even allowing for the above, it is possible to see some trends in the data that are not only thought to relate to batch to batch feedstock variability, and the following conclusions can be made from the results that have been obtained on the marker compounds in the recycled P&B and PET samples.

### 5.3.1 Variation of the level of marker compounds through the recycling process

**Paper and Board Samples**

In the case of the P&B samples from the first recycler, the quantification data that has been obtained on the five marker compounds has shown one of three trends, depending upon the species examined. For example:

(1) There has been a steady decrease in the concentration as the P&B has moved through the recycling process, e.g. in the case of Benzophenone.

(2) The concentration has remained relatively constant throughout the process, e.g. in the case Michlers ketone[a]

(3) For the other three, the DEHP, DIBP and DIPN, their level through the process from raw material to post cleaning is quite variable, with no trend apparent, and this could relate to both their relative insolubility in the paper mill water-based medium and to the comment above regarding the small amount of sample (2 grams) that is being analysed compared to the very large amount of material that is passing through the paper mill [b]

**Note a** *A small but variable response was detected for MK in all samples analysed for (although the majority of them were below the LOQ), which prompted the question as to whether this may be an un-related interference masquerading as MK (i.e. having the same single ion monitoring fragment ion), particularly as it was noted by an industry source that MK had not been widely used in Europe for some time. An investigation was conducted by concentrating a selected sample extract by a factor of 20 and re-analysing it using full-scan GC-MS. The presence of MK was confirmed based on its mass spectrum and retention time match to the reference standard.*

*The Michlers Ketone (MK) response was also found to be variable in replicate samples and also in replicate standards analysed throughout the sequences. It was noted that the response was strongly influenced by 'conditioning' of the system as a result of successive injections of P&B sample extracts (which potentially contain a highly variable matrix). No suitable internal standard could be found for this compound during the method development and validation to correct for the conditioning effect so the decision was made to progress using external standard calibration.*

***Note b*** *: The data from the final board product samples cannot be included in this assessment of how the levels of marker compounds vary through the process, as it is a complex construction of recycled P&B and waste P&B (in the centre) and not just manufactured from the post cleaned P&B material.*

With respect to the final food contact product (i.e. the card) from this recycler, as mentioned above in Note b, it was of a sandwich construction containing different sources of recycled P&B in the centre (e.g. post-consumer waste and post industrial waste) and this is thought to be the reason why, given that a thorough solvent extraction was being performed, the values were higher for these samples than for some of the samples taken from earlier stages within the milling process which may had a less complicated composition.

In the case the second P&B recycler, it was difficult to observe any trends, but it should be borne in mind that only a relatively small number of samples were obtained from this source and, again the small mass of the samples relative to the very large amount of material being processed.

**PET Samples**

For the PET samples that were provided by the first supplier, the results obtained for the marker compounds have showed the following trends, which are to be expected:

(1) Substances that the PET has picked up during "first use" (e.g. limonene and isopropyl toluene) have decreased as the PET has moved through the recycling process.

(2) There is an initial downward trend for substances that are formed within the PET as a result of degradation, e.g. acetaldehyde and methyl dioxolane. With these species there is often an initial decrease as the PET is "cleaned up" by the process, but then an increase when the PET is re-processed into granules, pre-forms and bottles.

In addition to this, it is observed that the level of the highly volatile substance, acetaldehyde, reduces again once the pre-forms are processed into bottles. This is probably because it can diffuse more readily from within the polymer matrix due to the shorter path-length of a thin walled (blown) bottle than that of a granule or pre-form.

(3) The level of monoethylene glycol in the samples from the first recycler exhibits a gradual downward trend throughout the clean-up process, with a slight rise shown as the granules pre-forms and blown bottles are produced.

In the case of the second supplier, time did not allow for the provision of samples that completed the recycling process (e.g. super-clean granules, pre-forms or bottles), but the trends and comments stated above in (1) to (3) for the marker compounds were found to apply for the first three stages in the process (i.e. post-consumer waste to HQWF). Only two finished product samples (obtained from a third party) were analysed from this supplier (SR6942 – "Deli" pots) for the food migration stage and these showed levels of all five marker compounds that were comparable to the pre-forms and bottles obtained from supplier one.

### 5.3.2 Variation of the level of the marker compounds in the source material with time

**Paper and Board Samples**

Samples were received from the first recycler over a seven month period (March to September 2012). A series of samples were also received at the rate of one per day over a three day period. The results obtained on four of the marker compounds (at all stages in the recycling process) were reasonably consistent, showing that the post-consumer feedstock for the plant and its functioning were both reasonably stable. The exception was DIPN, as its level at various stages in the process showed some variation over the seven month period. No clear trend was apparent but this could be due to the relatively small samples that were taken (~200 grams) and analysed (duplicate sub-samples of 2.5 grams) compared to the daily throughput of the mill (>1,000 tonnes).

With respect to the second recycler, only two sets of samples were taken in very close proximity to each other, and so investigating any change over time was not possible in this case.

**PET Samples**

Samples were received from the first recycler over an eight month period (February to September 2012). A series of samples were also received at a rate of one per day over a five day period. The results obtained on all five marker compounds (at all stages in the recycling process) were reasonably consistent in all cases, showing that the post-consumer feedstock for the plant and its functioning were both reasonably stable.

In the case of the second recycler, batches of samples that had been taken over a five week period showed a reasonable level of consistency of the concentration for most of the marker compounds, the exception being limonene which showed some variation.

### 5.3.3 Samples of products for the Food Migration stage of the project

The results for all five marker compounds in the final products (i.e. PET bottles and “Deli” pots, and P&B card) that were used for the food migration work have been presented in this report (see Tables 10, 14 and 20). This is because the overall level of the two designated marker compounds for this stage (acetaldehyde and diisobutyl phthalate) had to be established in the products in the first instance, to determine what proportion migrated during the migration test. To achieve this, a full analysis of all five marker compounds was performed using the analytical methods which had been developed, with the additional benefit that it provided additional data for the food contact materials stage.

One observation that was made possible by carrying out a full analysis of all five marker compounds was that, although only a relatively few samples of finished board products have been analysed, as the principal reason for this activity was to provide data for the food simulant stage of the project (see Section 6), Table 10 does indicate that the board that was intended for dry/fatty food contact contains lower levels of marker compounds than that intended for dry foods. In fact the board intended for dry food had a similar level of contamination to the uncoated board that was not intended for direct food contact.

# 6. RESULTS OBTAINED ON THE DETERMINATION OF MARKER COMPOUNDS IN FOOD SIMULANTS THAT HAD CONTACTED PRODUCTS MADE FROM RECYCLED P&B AND PET

## 6.1 Introduction

Once the work to identify and quantify the five marker compounds in the recycled PET and P&B samples was complete, a targeted food migration study was performed on final, food grade PET and P&B products to determine how much of these marker compounds had migrated into food simulants under representative conditions.

## 6.2 Choice of Marker Compounds from the P&B and PET products

For this stage of the work, one marker compound was selected from the set of five that are reported in Section 2.3 for both P&B and PET. One of the principal criteria that was used in this selection process was toxicity. Other criteria were whether the compound was present at a reasonably high level in the FCM (i.e. and therefore able to migrate to a detectable level into the simulant), and whether it was present as a single compound, or a set of isomers (which was less desirable).

With these criteria in mind, the following two marker compounds were selected.

a) Diisobutyl phthalate (DiBP) was selected for P&B*
b) Acetaldehyde was selected for PET

*Note : After consulting the FSA, DiBP was chosen as a marker for this stage of the work instead of DEHP because of its higher toxicity (see below) and greater potential to migrate into food due to its lower molecular weight.

The specific migration limits into food for DiBP and DEHP, according to the Paper & Board Materials and Articles for Food Contact Guidelines published jointly by the Confederation of European Paper Industries (CEPI) and the International Confederation of Paper and Board Converters in Europe (CITPA) in March 2010, are :

| | |
|---|---|
| DiBP | 0.5 mg/kg food (baby food)/1.0 mg/kg food (other food) |
| DEHP | 1.5 mg/kg of food |

## 6.3 P&B and PET Products selected and choice of food simulants

Although this stage was a relatively minor one for the project as a whole, it was thought desirable to cover as many options (e.g. product type and food simulant type) as were practical within the available budget. Accordingly, the products that were selected are described in Sections 6.3.1 and 6.3.2 below.

### 6.3.1 P&B Products

The P&B products that were used for this stage of the project were selected from those that are listed in Section 4.1.1. The samples were designated SR 6805 “Coated, recycled card”. The particular samples within this group of products that were used for this food migration exercise were as follows:

1) Samples 1 to 5 (Coated card for Dry and Fatty food) – i.e. 5 samples
2) Samples 11 to 13 (Coated card for Dry and Frozen food) – i.e. 3 samples
3) Samples 14 and 15 (Coated card for Dry food only) – i.e. 2 samples

This gave a total of ten coated card samples, which would be immersed in two different food simulants (i.e. a total of 20 food simulant samples). The experimental conditions that were used to prepare the simulant samples for GC analysis are described in Section 6.4.3.

### 6.3.2 PET Products

The PET products that were used for this stage of the project were selected from those that are listed in Sections 4.2.1 and 4.2.2 (SR6828 and SR6942). The following samples from these batches were chosen for this food migration work:

**PET Bottles**

These samples were designated “SR6828 Recycled PET Bottles” and were used for packaging both carbonated and non-carbonated drinks, of all types (e.g. fruit juice, mineral water, alcoholic beverages etc.) at refrigerated and ambient temperatures. The time that the food contacts the bottles could vary from a couple of days to at least one year.

**PET "Deli" trays**

These samples were designated "SR 6942 Recycled PET Deli Tray samples – Circular and Pyramidal types" and were used to package aqueous and fatty type foods, between refrigerated and ambient temperatures, for relatively short periods of time, e.g. two to three days. They were either cold-filled or in-store filled with the foodstuff.

The experimental conditions that were used to prepare the simulant samples from both the bottle and "Deli" tray samples for GC analysis are described in Section 6.4.2.

## 6.4 Experimental methods for P&B and PET

### 6.4.1 Method for P&B products

#### 6.4.1.1 Preparation of food migration samples

Initially, an attempt was made to use a single sided migration cell (as, in use, the card will only contact food products on its coated side) of the type used for EU migration work to prepare the migration samples. Unfortunately, the simulant was found to "wick" out of the cell and the card disintegrated. It was therefore decided that the FDA "sandwich" method (described in the FDA Title 21 CFR, see below) would be an appropriate way to contact the card with the food simulants. The method was used to prepare samples for the determination of the marker compound, DiBP, as described below.

**Sample Preparation**

Two "FDA sandwiches" of each of the 10 samples listed in Section 6.3.1 using the method described in 21 CFR Section 176.170 (d), (3), (i). Each "sandwich" contained a total of 1 $dm^2$ of coated card (comprised of 16 x 2.5 $cm^2$ square pieces) with aluminium foil "dividers" and held together with a large metal paper clip. Although the FDA method of sample preparation was used, the simulants that were chosen and the contact conditions were taken from the EU list present in Directive 82/711/EEC. The FDA "sandwiches" were immersed in a pre-warmed, 100mL aliquot of each of the simulants shown below using a large boiling tube that could be fitted with a quick fit stopper to prevent evaporation of the simulant of analyte. The boiling tubes were placed in an oven set at the required temperature (see immersion conditions, below).

The total weight of the card used for each of the three product types that were tested was as follows:

SR6805 (Coated card for dry and fatty food) – weight of the 1 $dm^2$ portion = 2.52 grams
SR6805 (Coated card for dry and frozen food) - weight of the 1 $dm^2$ portion = 4.10 grams
SR6805 (Coated card for dry food only) - weight of the 1 $dm^2$ portion = 3.23 grams

**EU Simulants and immersion conditions that were used to prepare the samples**

From the potential end-use conditions of the card samples (see Section 6.3.1) the following simulants and immersion conditions were used:

**Simulants**

Iso-octane (fatty food simulant)
3% acetic acid (aqueous food simulant)

**Immersion Conditions**

a) Iso-octane - 2 days at 40°C (roughly equivalent to 10 days at 60°C in olive oil – which allows for relatively long term (e.g. 3 months) storage of fatty food in a freezer/refrigerated environment) – see Note below

**Note**: Two hours at 70°C with olive oil = 0.5 hours at 40°C with iso-octane. As we are trying to test to equivalent of 10 days at 60°C with olive oil, we have multiplied the test time with iso-octane to try and replicate this:
2 hours at 70°C = 0.5 hours at 40 °C, i.e. x 4 less
240 hours (10 days) = 60 hours at 40 °C (=2.5 days at 40 °C)
To account for the slightly higher test temperature in the olive oil test (70 °C) when the target temperature is 60 °C, the test time was reduced to 2 days at 40 °C with iso-octane instead of 2.5 days.

b) 3% acetic acid – 1 hour at 70°C (worse case aqueous scenario for relatively short term situations such as hot, take-away chips and vinegar).

**Note**: From information received from the supplier, it is not believed that there are any long term storage conditions for aqueous food. Also, vegetables etc. are usually packed initially in plastic bags and then placed in cardboard boxes to be frozen – and so do not contact the card.

#### 6.4.1.2 Analysis method to determine DiBP in the food simulant samples

The GC method that was used to determine DiBP in the food simulant samples is described below:

**Calibrants**

A set of calibrants ranging from 0.1µg/ml to 10µg/ml were made up in both 3% acetic acid and iso-octane, depending upon which simulants samples were being analysed.

**GC Conditions**

**Table 21 GC conditions for the analysis of DiBP in 3% acetic acid and isooctane**

| | |
|---|---|
| Instrument | Agilent Technologies 6890 Gas Chromatograph with an FID Detector |
| Column | Varian CP Wax 57CB wax 17.5m x 0.53mm |
| Injection | Cool-on-column |
| Carrier Gas | Helium @ 4.92 psi |
| Oven Program | 80°C for 1 minute; 25°C/minute to 170°C.<br>Hold for 15 minutes |
| FID Detector | Temperature : 220°C<br>Hydrogen @ 40 mL/min<br>Air @ 450 mL/min |

### 6.4.2 Method for the PET products

The experimental methods for the PET migration samples are described in Sections 6.4.2.1 and 6.4.2.2 below.

#### 6.4.2.1 Preparation of food migration samples

**PET Bottles**

The method used to prepare simulant samples from the PET bottles for the determination of the marker compound acetaldehyde is described below.

**Sample preparation**

The 20 gram bottles were filled to the neck with 530 ml of each simulant, which had been pre-warmed. To ensure that acetaldehyde was not lost from the bottles during the test, the bottles were securely closed using screw caps. The bottles were then placed in an oven that had been set at the appropriate temperature. The types of food simulant and the immersion conditions that were used are shown below.

1) Five bottles filled to the neck (i.e. as when full of drink) with 3% acetic acid for 10 days @ 60 °C.

2) Five bottles filled to the neck (i.e. as when full of drink) with 20% ethanol/80% distilled water for 10 days @ 60 °C.

The amount of acetaldehyde present in the food simulant samples that were prepared as described above was determined by GC using the method shown in Section 6.4.2.2. To ensure that any loss of acetaldehyde from the samples was minimised, they were stored in a refrigerator immediately after preparation and were analysed as soon as possible.

**PET "Deli" Trays**

The method used to prepare simulant samples from the PET "Deli" trays for the determination of the marker compound acetaldehyde is described below.

**Sample preparation**

In each case, a 1 $dm^2$ portion was removed from each of the "Deli" trays (Circular and Pyramidal) and mounted onto a stainless steel cruciform support. The sample was then placed into a large, glass test tube with 100ml of the appropriate simulant that had been pre-warmed. The test tubes were then placed into an oven set at the correct temperature for the appropriate time. The weight of this 1 $dm^2$ portion for each tray type was as follows:

Weight of 1 $dm^2$ of the Circular "Deli" trays = 3.37 grams
Weight of 1 $dm^2$ of the Pyramidal "Deli" trays = 3.82 grams

The types of food simulant and the immersion conditions used for the testing are shown below.

**EU Simulants and immersion conditions that were used to prepare the samples**

From the potential end-use conditions of the “Deli” trays (see Section 6.3.1.2) the following simulants and immersion conditions were used:

1) Two Circular Deli Pots immersed in olive oil for 10 days @ 40 °C
2) Three Pyramidal Deli Pots immersed in olive oil for 10 days @ 40 °C
3) Three Circular Deli Pots immersed in 3% acetic acid for 10 days @ 40 °C
4) Two Pyramidal Deli Pots immersed in 3% acetic acid for 10 days @ 40 °C

The amount of acetaldehyde present in the food simulant samples that were prepared as described above was determined by GC using 6.4.2.2 to ensure that any loss of acetaldehyde from the samples was minimised, they were stored in a refrigerator immediately after preparation and were analysed as soon as possible.

**6.4.2.2 Analysis method to determine acetaldehyde in the simulant samples**

**Preparation of Calibrants for analysis of PET bottle samples**

A series of twelve headspace vials were prepared, six containing 5ml of 20% ethanol and six containing 3% acetic acid. Into these volumes (between 0µL and 100µL) of acetaldehyde standard solution of known concentration was spiked.

**Preparation of Calibrants for analysis of PET “Deli” tray samples**

A series of olive oil standards were prepared by accurately weighing 5 grams of olive oil into six headspace vials and then injecting amounts (between 0µL and 50µL) of an acetaldehyde standard solution of known concentration. The 3% acetic acid standards were prepared using the same approach.

**Analysis Conditions for Calibrants and Samples**

**Headspace GC-MS Conditions**

The analysis conditions that were used to conduct the HS-GC-MS analysis of the 3% acetic acid and olive oil samples are shown below in Tables 22 and 23.

**Table 22 GC conditions for the analysis for acetaldehyde in 3% acetic acid and olive oil**

| | |
|---|---|
| Instrument | Agilent Technologies 6890 Gas Chromatograph with an FID detector |
| Column | J&W GS-Q 30m x 0.53 mm |
| Injection | Split 1:1 @ 200°C |
| Carrier Gas | Helium @ 9.07 psi (constant pressure) |
| Oven Program | 80°C for 0 minutes; 20°C/minute to 180°C;<br>hold for 4 mins. |
| FID Detector | Temperature : 250°C<br>Hydrogen @ 40 mL/min<br>Air @ 450 mL/min |

**Table 23 Headspace sampler conditions analysis for acetaldehyde in 3% acetic acid and olive oil**

| | |
|---|---|
| Instrument | Perkin Elmer Static headspace sampler |
| Sample Temperature | 80°C |
| Needle Temperature | 100°C |
| Transfer Temperature | 150°C |
| GC Cycle Time | 20.0 minutes |
| Thermostat Time | 60 minutes |
| Pressurise Time | 1.0 minutes |
| Injection Time | 0.1 minutes |
| Withdrawal Time | 0.2 minutes |
| Head Pressure | ~15 PSI set for a split flow of 30 mL/min |

## 6.5 Results obtained

### 6.5.1 DiBP from P&B products

The samples SR6805/1 to SR6805/5 and SR6805/11 to SR6805/15 (see Section 4.1.1) were used for this work. The results that were obtained when these samples were contacted with the two simulants as described in Section 6.4.2.1 follow:

**Results obtained in the 3% acetic acid simulant**

In the case of all the P&B samples tested, no DiBP was detected in the 3% acetic acid simulant above the detection limit of the analytical method (which was approximately 0.12 µg/ml). Assuming a density of 1 for the acetic acid this gives a migration value of 0.12 mg/kg.

**Results obtained in the Isooctane simulant**

The migration results that were obtained in the Isooctane simulant for these samples are shown below in Table 24.

**Table 24 Amount of DiBP in the samples of isooctane food simulant**

| Sample | Amount of Diisobutyl phthalate in simulant (ug/ml) | Amount of Diisobutyl phthalate in simulant (mg/kg)* | SML Limit in BfR XXXVI (mg/kg)**** |
|---|---|---|---|
| SR6805/1 | 0.07 | 0.07** | 0.3 |
| SR6805/2 | 0.10 | 0.10** | 0.3 |
| SR6805/3 | 0.09 | 0.09** | 0.3 |
| SR6805/4 | 0.09 | 0.09** | 0.3 |
| SR6805/5 | 0.08 | 0.08** | 0.3 |
| SR6805/11 | 0.50 | 0.50*** | 0.3 |
| SR6805/12 | 0.54 | 0.54*** | 0.3 |
| SR6805/13 | 0.45 | 0.45*** | 0.3 |
| SR6805/14 | 0.42 | 0.42*** | 0.3 |
| SR6805/15 | 0.40 | 0.40*** | 0.3 |
| **Average for all three card types** | **0.27** | **0.27** | **0.3** |

*Assuming a density of 1 for Isooctane

**The integrated peak in the FID response for samples SR6805/1 to SR6805/5 is not thought to be DiBP due to a small shift in retention time and the poor peak shape in comparison to the standards.

***The integrated peak in the FID response for samples SR6805/11 to SR6805/15 is thought to be the sum of DiBP co-eluting with the peak that also appears in the FID response for samples SR6805/1 to SR6805/5.

****BfR Recommendation XXXVI – Paper and Board for Food Contact Applications.

Unfortunately, to facilitate direct injection of the aqueous simulant, this analysis work was carried out using a GC-FID instrument rather than a GC-MS. The response of the mass spectrometer was therefore not available to support the comments made above in notes ** and ***.

### 6.5.2 Acetaldehyde from PET products

The samples SR6828 (see Section 4.2.1) and SR6942 (see Section 4.2.2) were used for this work. The results that were obtained when these samples were contacted with the two simulants as described in Section 6.4.2.1.

**Bottles samples – Results obtained for the 3% acetic acid and 20% Ethanol simulants**

The migration results that were obtained for these samples using the two simulants are shown below in Table 25.

**Table 25 Amount of acetaldehyde in the samples of 3% acetic acid and 20% ethanol food simulant that had contacted the PET bottle samples (SR6828)**

| Sample | Amount of acetaldehyde in 3% acetic acid (mg/kg) | Amount of acetaldehyde in 20% Ethanol (mg/kg) | SML Limit for acetaldehyde in (EU) 10/2011 (mg/kg |
|---|---|---|---|
| Bottle 1 Rep 1 | 0.037 | 0.108 | 6.0 |
| Bottle 1 Rep 2 | 0.033 | 0.109 | 6.0 |
| Bottle 2 Rep 1 | 0.038 | 0.106 | 6.0 |
| Bottle 2 Rep 2 | 0.034 | 0.111 | 6.0 |
| Bottle 3 Rep 1 | 0.033 | 0.090 | 6.0 |
| Bottle 3 Rep 2 | 0.035 | 0.100 | 6.0 |
| Bottle 4 Rep 1 | 0.035 | 0.105 | 6.0 |
| Bottle 4 Rep 2 | 0.036 | 0.100 | 6.0 |
| Bottle 5 Rep 1 | 0.034 | 0.083 | 6.0 |
| Bottle 5 Rep 2 | 0.031 | 0.111 | 6.0 |
| **Average Value** | **0.035** | **0.102** | **6.0** |

**“Deli” tray samples – Results obtained for the 3% acetic acid and olive oil simulants**

The migration results that were obtained for these samples using the two simulants are shown below in Table 26.

**Table 26 Amount of acetaldehyde in the samples of 3% acetic acid and 20% ethanol food simulant that had contacted the PET "Deli" tray samples (SR6942)**

| Sample | Amount of acetaledehyde in 3% acetic acid (mg/kg) | Amount of acetaledehyde in olive oil (mg/kg) | SML Limit for acetaldehyde in (EU) 10/2011 (mg/kg) |
|---|---|---|---|
| Pyr 1 Rep 1 | 0.039 | 0.028 | 6.0 |
| Pyr 1 Rep 2 | 0.040 | 0.031 | 6.0 |
| Pyr 2 Rep 1 | 0.040 | <LOD | 6.0 |
| Pyr 2 Rep 2 | 0.035 | <LOD | 6.0 |
| Pyr 3 Rep 1 | 0.029 | 0.031 | 6.0 |
| Pyr 3 Rep 2 | 0.030 | 0.033 | 6.0 |
| **Average for Pyr samples** | **0.030** | **0.019** | **6.0** |
| Cir 1 Rep 1 | 0.027 | 0.029 | 6.0 |
| Cir 1 Rep 2 | 0.031 | 0.023 | 6.0 |
| Cir 2 Rep 1 | 0.031 | <LOD | 6.0 |
| Cir 2 Rep 2 | 0.031 | <LOD | 6.0 |
| **Average for Cir samples** | **0.030** | **0.026*** | **6.0** |

Pyr = Pyramidal shaped tray

Cir = Circular shaped tray

<LOD = less than the limit of detection = 0.01 mg/kg

*Based on the two results above the LOD

## 6.6 Summary of results obtained on the food migration samples

### 6.6.1 DiBP

The results shown in section 6.5.1 for this marker compound show that the level of DiBP in the 3% acetic acid was below the detection limit of the analytical method used for the determination. For the isooctane simulant, they show that the levels of DiBP migrated from the card samples were close to the SML for this substance stated in the German BfR Recommendation XXXVI for Paper and Board. However, for all of the samples it was apparent that there was an enhancement of the DiBP peak in the sample chromatograms due to a co-eluting peak.

The results obtained on the card products that were used for this migration work showed that they contained up between <0.07 (LOQ) to around 4.3 µg/g of DiBP (Table 10). The weight of card that was immersed in the 100 ml of 3% acetic acid and 100 ml of isooctane are shown in Section 6.4.1.1. Taking the average of the values in Table 10 gives average total values for the total amount of DiBP in the three types of card of:

SR6805 (Coated card for dry and fatty food) – 0.75 µg
SR6805 (Coated card for dry and frozen food) – 16.11 µg
SR6805 (Coated card for dry food only) – 12.9 µg

The total amount of DiBP for each simulant/product combination and the proportion that this represented of the total amount in the products is shown in the Table 27 below. Because of the inaccuracies due to the limitations referred to above, it was inappropriate to look into all three card types separately and the results for all three types have been averaged

**Table 27 Proportion of DiBP that had migrated into the food simulants from the card samples**

| **Product Type** | **Simulant Type** | **Total amount of DiBP in the 100 ml of simulant** | **Proportion of DiBP that had migrated** |
|---|---|---|---|
| All three card types | 3% Acetic acid | <12 µg* | <46% |
| Coated card for dry and fatty food | Isooctane | 8.8µg** | >100%*** |
| Coated card for dry and frozen food | Isooctane | 49.6 µg** | >100%*** |
| Coated card for dry food | Isooctane | 41.0µg** | >100%*** |

**Less than the detection limit of the method
**Assuming an average level of DiBP in the Isooctane simulant taken from Table 24
*** >100% due to interference peak in the chromatogram

The data in Table 27 shows that a high proportion of the DiBP that is present in the recycled card migrates into the food simulants under test. The values in Table 27 are uncertain due to the limitations in the original analysis data. It is not surprising that the value for isooctane is over 80% due to the high affinity that DiBP has for this simulant.

### 6.6.2 Acetaldehyde

The results provided in Tables 25 and 26 show that the levels of acetaldehyde that have migrated from both the bottle and "Deli" tray samples are well below the SML for this substance (6.0 mg/kg) stated in the EU Plastics Regulation (EU) 10/2011.

It is possible to determine what proportion of the total amount of acetaldehyde that is present in the PET products has migrated into the two simulants under the test conditions that were used. The analysis work carried out on the bottles and "Deli" trays that were used for this work showed that the amount of acetaldehyde that was present in the PET bottles was around 5 µg/g (Tables 13 and 14), and 4.84 µg (Circular trays) and 5.67 µg (Pyramidal trays) - both in Table 20.

The bottles weighed a total of 20 grams, which gives a total amount of acetaldehyde in the bottle of around 100 µg, and they were completely filled with simulant. The total amount of simulant that was in the bottles was 530 ml. In the case of the "Deli" trays, 1 $dm^2$ section of tray that was used for the migration test weighed 3.37 grams (Circular trays) or 3.82 grams (Pyramidal trays), and this was immersed in 100 ml of simulant.

The amount of acetaldehyde that was detected in the PET tray samples is shown in Table 20, and the amount migrated into the simulants in Table 26. The amount of acetaldehyde that was detected in the PET bottle samples is shown in Tables 13 and 14, and the amount migrated into the simulants in Table 25.

The total amount of acetaldehyde for each simulant/product combination and the proportion that this represented of the total amount in the original PET products is shown in Table 28 below.

**Table 28 Proportion of acetaldehyde that had migrated into the food simulants from the PET bottles and "Deli" trays**

| Product Type | Simulant Type | Total amount of acetaldehyde in simulant (µg)* | Acetaldehyde migrated from the PET product into the simulant ** |
|---|---|---|---|
| Bottle | 3% Acetic acid | 18.55 µg | 19.0% |
| Bottle | 20% Ethanol | 54.06 µg | 55.3% |
| Pyramidal "Deli" Tray | 3% Acetic acid | 3.0 µg | 13.8% |
| Pyramidal "Deli" Tray | Olive oil | 3.3 µg | 15.2% |
| Circular "Deli" Tray | 3% Acetic acid | 3.0 µg | 18.4% |
| Circular "Deli" Tray | Olive oil | 2.6 µg*** | 16.0% |

*Average value based on the average result obtained during the migration testing (Table 25 and 26)

**Assuming following approximate levels of acetaldehyde in the PET product of :
Bottle – 97.8 µg per bottle; Pyramidal trays (1 $dm^2$) – 21.7 µg; Circular trays (1 $dm^2$) – 16.3µg
Based on a combination of the weights of the samples tested (Section 6.4.2.1) and the average amount of acetaldehyde in the PET (Tables 14 and 20)

***Approximate value based on the two results above the LOQ

## 7.0 OVERALL CONCLUSIONS

### 7.1 Marker compounds

It has been possible from the published literature and the work carried out during this project to select five marker compounds for both recycled P&B and PET that are consistently representative of these materials and which can be used to obtain a measure of their purity and the efficacy of the recycling processes that are used to produce material that is acceptable for food contact use.

### 7.2 Analytical methods

It has been possible to develop a single analytical method (based on solvent extraction with direct injection GC-MS) for the analysis and determination of five marker compounds in recycled P&B. In the case of PET, it was not possible to develop a single method that was applicable for all five marker compounds, and so they were covered by a combination of two methods: headspace GC-MS, and solvent extraction, direct injection GC-MS. In all cases, it has been possible to validate these methods and the results obtained have shown that they are fit for purpose.

### 7.3 Variation in the level of marker compounds through a recycling process

The results that have been obtained on the marker compounds have shown some trends for both recycled P&B and PET. In the case of P&B, all three possible trends have been shown - with particular marker compounds remaining consistent through a recycling process, diminishing or showing variations in concentration. For PET, markers that are associated with first use (e.g. flavouring compounds) have been found to reduce, whereas those that are associated with material itself show some variation depending upon the stage monitored.

### 7.4 Variation in the level of marker compounds in the post-consumer waste over time

The data obtained for both recycled P&B and PET over a seven to eight month period showed that, for most of the marker compounds, there was a measure of consistency with time, although for some (e.g. limonene in PET) more variation was noticeable.

### 7.5 Food migration data

A limited amount of food migration testing was carried out during this project. The results obtained on two marker compounds when food contact products made from recycled P&B and PET were contacted with food simulants using representative conditions showed that migration did occur, but that in the case of acetaldehyde this was below the SML in (EU) 10/2011.

For the marker DiBP, migration was below the SML in BfR Recommendation XXXVI for 3% acetic acid. In the case of isooctane, the results obtained were more variable (due to a co-eluting peak) and, for this reason, in some cases above the BfR SML.

# APPENDIX 1 TO CTR 55414
# RESULTS OF THE LITERATURE REVIEW – MARKER COMPOUNDS IN PET AND P&B

## RESULTS OF THE LITERATURE REVIEW – MARKER COMPOUNDS IN PET AND P&B

### 1. INTRODUCTION

### 1.1 Background to this literature review

This literature review was carried out for the FSA project FS241007 which was concerned with the potential contaminants and migrants (i.e. marker compounds) that are present in recycled paper and board (P&B) and polyethylene terephthalate (PET) for food contact applications. One of the principal objectives of this literature search was to correlate and assess the published information on the marker compounds that were present in these two materials. This enabled, in conjunction with discussions with the Foods Standard Agency (FSA), five primary markers for PET and P&B to be selected for which analytical methods were then developed for their determination in these materials as a means of monitoring their levels throughout recycling processes and in recycled products. It also enabled analytical methods to be developed for their determination in food simulants that had contacted these materials under representative conditions.

### 1.2 Scope of this literature review

This Appendix contains the results of an extensive literature and information search to identify marker compounds within recycled PET and recycled P&B.

A multi-faceted approach was used in order to maximise the extent and value of the information that was obtained. This approach had the following principal components:

A literature search was conducted using the following specialist databases:

1) Smithers Information Polymer Library Database.
2) Smithers Information PIRA/Paperbase Database

The information obtained from these searches was complemented and expanded by utilising the following sources:

(i) Food Standard Agencies archives (e.g. Foodbase)
(ii) Discussions with specialists at Smithers PIRA, FERA(CSL) and CEPI
(iii) EU Regulations, National Regulations and CoE Resolutions
(iv) General internet searches

The data and information obtained from all of these sources on the contaminants and potential migrants present in recycled PET and recovered P&B has been collated together in this literature search.

In addition to this information, some studies that have been carried out using “surrogate” compounds to spike PET and P&B recyclate in order to perform “Challenge” tests on recycling processes, or to perform migration studies (e.g. to test the performance of functional barriers), have also been included as they illustrate the types of species (i.e. molecular weight, polarity etc.) that experienced food contact material scientists expect to be present in these materials.

As well as correlating the qualitative information that is available on potential contaminants within PET and P&B, any information relating to the concentration of these species has also been included in this literature search so it can be used as a guide for the range of concentrations that may be expected in recycled PET and P&B.

## 1.3 Brief background to the use of recycled PET and Paper and Board for food contact

### 1.3.1 PET

Although recycling is not widespread at present in the EU for all food contact plastics, it is at an advanced stage for PET, particularly PET bottles.

At present, the main documents covering the recycling of plastics within in the EU are the recycled plastics Regulation (EU) 282/2008, which covers articles and materials in the Plastics Regulation (EU) 10/2011 that contain recycled plastic, and stipulates that the plastic must be sourced from a recycling process that meets the definitions in Regulation 282/2008, and that they are manufactured according to the Good Manufacturing Practice (GMP) Regulation (EC) 2023/2006.

The Regulation (EC) 282/2008 does not apply to:

i) Plastics made with monomers and starting substances derived from depolymerisation of plastic materials.

ii) Plastics made from in-process scrap that complies with (EU) 10/2011.

iii) Where recycled plastic is used behind a functional barrier as defined in (EU) 10/2011.

Regulation (EC) 282/2008 describes “challenge” tests which are used to determine if a particular recycling process for plastics is effective at removing contaminants from the waste feedstocks. These “challenge” tests involve “doping” the process using a series of chemical compounds that are representative (in terms of molecular weight, polarity, volatility etc.) of the types of compound which can contaminated post-consumer waste.

Both recycled plastics and paper and board materials and articles must comply with the Framework Regulation (EC) 1935/2004. Also, both plastics and P&B are covered by the EU Packaging Waste Directive 94/62/EC.

A number of researchers have looked into the migration of organic compounds from virgin and post-consumer recycled (PCR) PET into various contact media (e.g. Monteiro et al (1), Hinrichs and O Piringer (2). They have found that the diffusion laws governing migration are not affected by the recycling process.

For PET there are several “super-clean” processes that are used to recycle the material into food grade recyclate. Each of the processes will have key steps that involve deep cleansing (e.g. vacuum treatment, high temperatures, high surface areas etc.) in order to eliminate undesirable chemical compounds.

Franz et al (3 and 4) have published the results of work aimed at establishing a statistical overview of the nature and extent of post-consumer contaminants in PET that resulted from the European project FAIR-CT98-4318 ‘Recyclability’. Typical post-consumer substances were found to be:

Acetaldehyde, 2-methyl-1,3-dioxolane and ethylene glycol (from the PET)
Limonene and 4-iso-propyltoluene (common flavour substances)

One example of the information in the literature on the migration of oxidation species from PET is the paper by Mutsuga and Kawamura (5) on the migration of formaldehyde and acetaldehyde in mineral water from polyethylene terephthalate (PET) bottles.

For paper and board, comprehensive literature reviews on possible migrants occurring from recycled fibres have been prepared by Castle and Damant (7 and 8) and Soderhjelm and Sipilainen-Malm (9). A large number of classes of contaminants were covered, including: trace elements, waxes, fluorescent whitening agents, dyes, sizing agents, organochlorines, plasticisers, aromatic hydrocarbons, curing and grease proofing agents, amines, biocides and surfactants.

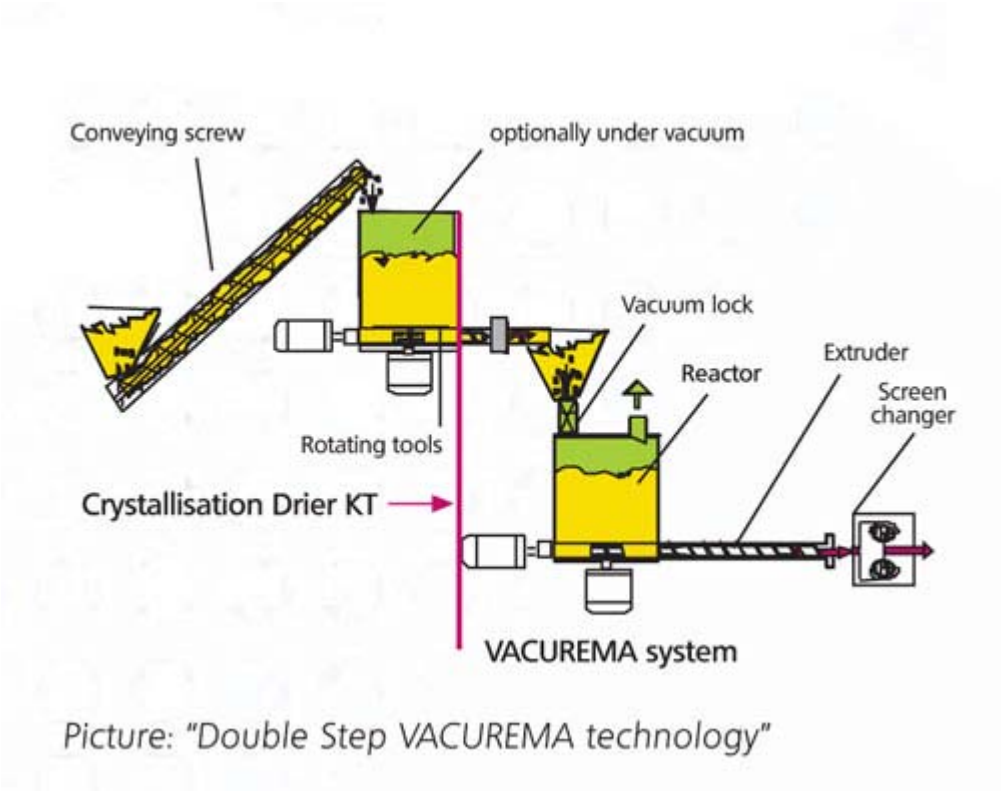
The Technical Document No 3 of the Council of Europe Resolution on Paper and Board Materials and Articles (10): intended to come into contact with foodstuffs has a list of 11 specific compounds (e.g. Michler's ketone and benzophenone) and classes of compound (e.g. primary aromatic amines, phthalates and azo colourants) which have the potential to be present in recycled fibre products and for which migration work should be carried out. This list also provides some guidance on test conditions, detection limits and migration limits. Analytical methods for these are also provided in Appendix A of Technical Document No 2 in this Resolution (10) There is also a "consolidated matrix" in this section of the Resolution, which assists in assessing potential risks to health by taking into account the nature of the recovered paper, the effectiveness and purpose of the recycling treatments, and the nature of the contact with foodstuffs for the end product.

Some specific migration work has also been reported in the literature for paper and board. For example, Castle et al (11) published work on residues of dialkylamino benzophenone UV-cure ink photoinitiators.

The recycling processes for food grade PET are complex and involve a number of key stages with thorough sorting and washing being essential. There are two main processes that are used for recycling food grade PET : the Buhler and Vacurema processes.

The Buhler process uses a long "ring extruder", but this can cause degradation and so the PET has to be re-condensed. Vacurema subjects the PET to high vacuum at ~230 °C which minimises degradation, and is therefore becoming the most popular process. The Vacurema process is also being used, with modifications, (e.g. lower temperature of 120 °C and longer process times) for HDPE. A schematic diagram of the Vacurema process for PET with an upstream crystallisation dryer is shown in Figure 1 below.

**Figure 1 Schematic diagram of the "double step" Vacurema process**




(Reproduced from http://www.petnology.com/profile.php?p_ID=2)

### 1.3.2 Paper and Board

Paper and Board for food contact use may essentially be composed of : Pulp - cellulose (40-45%), hemicellulose (20-30%) and lignin (25-30%).

Additives that may be present in Paper and Board:

a) *Fillers:* added to improve the optical properties and printability of the material. Clay, talc, calcium carbonate or titanium dioxide are the substances commonly used.

b) *Sizes:* pulp fibres are hydrophilic, but are rendered more hydrophobic by the use of sizes. The classic sizing agent is tall oil rosin, which consists of rosin acids. Rosin acids are fixed to paper fibres by aluminium sulphate. Other sizing agents which can be used include alkylketene dimers and paraffin waxes.

c) *Starch and starch derivatives:* used to give paper greater strength.

d) *Wet strength sizing agents:* added to improve paper strength when wet. Common wet strength agents include melamine formaldehyde, urea formaldehyde and polyamide resins.

e) *Retention aids*: used to prevent fillers and fine fibres from draining through the wire on the paper machine. Commonly used are polyamides, polyethyleneimines and bentonite..

f) *Biocides:* added to the water circuit of a paper machine to inhibit bacterial and fungal growth.

g) *Fluorescent whitening agents*: added to improve the 'whiteness' of the product. Substances typically used are derivatives of 4,4-diaminostilbene-2,2-sulphonic acid.

h) *Dyes*: most are organosulphur and organonitrogen substance.

i) *Grease-proofing agents*: added to improve resistance against fats. They are typically fluoroalkyl polymers.

Pigment coating:

a) *Binders:* starch, protein, polyvinyl alcohol, styrene-butadiene, styrene-acrylate copolymers.

b) *Additives:* dispersing agents, defoamers, lubricants and preservatives.

Polymer coating:

a) *Extrusion coating and lamination*: coating of paper and board with polyethylene is the largest application of extrusion coating.

b) *Hot melt coating*: a common coating agent is paraffin wax, which is composed of a mixture of straight-chain saturated hydrocarbons ($C_{23}$-$C_{35}$). Aluminium stearate is sometimes added to the wax as a plasticiser.

c) *Dispersion coating*

All P&B manufacturing process are based on a similar basic process, which is comprised of seven different sections: head box, wire section (wet end), press section, drier section, size press, calendar and reel-up. It is normal for a proportion of recovered fibres to be mixed with virgin fibres prior to the initial “head box” step.

Recycled fibres are used in some paper grades that are intended for food contact, mostly as inner layers in multi-layer materials intended for the packaging of dry, non-fatty food. A large volume of recycled fibre originates from recovered paper that has not been de-inked, and sometimes can be identified by its typical greyish colour. Once de-inked, recycled fibres lose this distinctive colour and are very difficult to distinguish from virgin fibres. Currently, Paper and Board is not regulated for food contact at the EU level despite the fact that it is used extensively in food contact situations – both as a primary and secondary packaging material.

There is, however, a Council of Europe Resolution (CoE) on Paper and Board (Resolution AP(2002)1) This also covers the use of recycled fibres for the manufacture of food contact products. It contains analytical methods for testing papers made from recycled fibres in Appendix A of Technical Document No 2; guidelines on paper and board made from recycled fibres in Technical Document No. 3; and the CEPI guide for Good Manufacturing Practice in Technical Document No 4 (Ref 10).

About one third of the world's P&B making fibre is recycled and a large proportion of the feedstock for paper and board production in Europe, is recycled fibres. Some countries have higher recycling rates than others. Statistics for the EU Member States suggest a range of 25 to 85% use of recycled fibres. Some examples, as shown in the ILSI report (Ref 12) are shown in Table 1 below:

**Table 1 Examples of P&B recycling rates in the EU**

| Country | Recycling Rate |
|---|---|
| Spain | 81% |
| The Netherlands | 77% |
| The United Kingdom | 66% |
| Germany | 61% |
| Italy | 54% |
| France | 50% |

The proportion of recycled fibres going into direct and indirect food contact applications is unknown but it will be lower than these figures for all applications. Nevertheless, the volume of recycled fibres used for food packaging is very significant.

Broadly speaking the final production process for recycled P&B is the same as the process used for P&B made from virgin fibres; the main difference being the contaminants picked up during "first use" have to be removed.

The major steps in the recycling process are:

- Collection and Transportation – recovered P&B is sorted, graded, formed into bales and delivered to a paper mill.

- Repulping and Screening – the recovered P&B is mixed with water and chemicals, which separates the P&B into individual fibres.

- Cleaning – the pulp is diluted with water and passes through a centrifugal cleaning process to remove the large (e.g. wood, stones, plastics, glass etc.) “first use” contaminants, as well as smaller contaminants (e.g. string, glue etc.).

- De-inking – this step is necessary for certain recovered papers such as newspaper. There are a number of variants to this process. For example, it can be carried out by flotation, with or without washing, with or without kneading, with or without bleaching (see below).

There is general agreement that waste paper from post-consumer domestic waste, hospital waste or non-food processing industrial waste, should not be used. During the cleaning step above, unwanted water-solubles (e.g. wet-strength agents, soluble glues and gums) are removed but, because water is a poor solvent for many organic substances that can be present in the recovered P&B, then special cleaning processes are needed to remove more completely chemical components such as printing inks, hot-melt adhesives, varnishes and lacquers. These washing processes include:- fractionation by washing, de-inking by washing with special floatation chemicals, bleaching with hydrogen peroxide or hydrosulphite, oxygen or ozone treatment, steam treatment and enzymatic treatment.

There are different grades of recovered P&B to satisfy the needs of the different users. More than 50 grades of recovered P&B are defined in the European List of Standard Grades of Recovered Paper and Board (EN643).

These grades can be categorised as follows:

- Low grades (mixed papers, old corrugated containers, board etc.) constitute the main part of the recovered paper consumed. These are used to produce secondary packaging papers and boards, and are not intended to be in direct contact with food.

- De-inking grades (newspapers and magazines, graphic papers etc.) are usually also considered as low grades because they need extensive recycling treatments. These are for graphic and sanitary papers.

- High grades (scraps, sheets, print off cuts etc.) require little or no cleaning. They can be used for the production of any paper product as pulp substitute. They may therefore be suitable for food contact packaging.

## 2. INFORMATION OBTAINED AND SEARCHED FOR THE LITERATURE REVIEW

### 2.1 Abstract Databases Searched

Literature searches for members of the Smithers Group of companies are performed by the Smithers Information group. The following Smithers Information databases were searched by this group for Smithers Rapra who were managing this FSA project:

3) Smithers Information Polymer Library Database.
4) Smithers Information PIRA/Paperbase Database

A brief description of these and the methodology that was used to search them is provided below:

#### 2.1.1 Background to the Smithers Polymer Library database

The Smithers Information Polymer Library Database covers published literature on plastics, rubber, polymeric composites, adhesives and other polymer-based systems. The majority of the articles within the database are taken from journals that are chosen according to technical merit, subject matter (i.e. polymers and polymer related), and are peer reviewed.

**a) The Database - Facts and figures**

- Around a million records dating back as far as 1972.
- This equates to approx. 2.5 million pages of original, published, literature.
- Approximately 22,000 new records added every year.
- Easy-to-use search interface.

**b) Source material for the Database**

The Polymer Library includes references from over 450 journals, together with conference papers, specifications and standards, books, reports, press releases, company literature, data sheets and directories. It also contains Patent records from 1994 - 2001. The coverage is fully international with source material in a wide range of languages from 30 different countries including North America, Australia, Europe, Japan and China.

**c) Subject Coverage**

All aspects of the science, technology and the business of polymers are covered for the industries that produce and use them.

(i) Science: Polymerisation and Synthesis; Processing and Treatment; Raw Materials and Monomers; Compounding Ingredients; Adhesives and Coatings; Properties and Testing; Composite Materials and Additives.

(ii) Technology: End-use Applications; Processing and Treatment; Machinery; Test Equipment; Intermediate & Semi-finished Products; Additives.

(iii) Business: Commercial Information; Health and Safety; Legislation Environmental Issues; Markets and Statistics; Trade Names; Product Announcements.

**d) Sources of Information for the Smithers Polymer Library Database**

Examples of the information sources that are included in the Smithers Information Database are shown below:

(i) High quality scientific journals which have been peer reviewed – a major source of the information used for the database and for this particular review*.

(ii) Books and industry relevant publications.

(iii) Conference proceedings.

(iv) Multi-client research projects and Government funded research projects.

(v) Rapra review reports, e.g. Silicone products for food contact applications.

(vi) Trade journals.

### 2.1.2 Background to the Smithers Information Pirabase/Paperbase databases

Pirabase is a complete information service for companies operating in the print, packaging, and paper supply chains. It is compiled and written by Pira's team of expert editors who scan a wide range of regular trade and technical journals, market reports, conference proceedings, magazines, press releases, newspapers, newsletters and websites translated from 20 languages into English.

The publications cover all major western European and Asian languages. The Pirabase team are briefed to find the most important global business and technical developments across the three industries and then summarise in easy-to-read articles of around 250 words.

Pulp and paper coverage is provided by Paperbase International, a partnership bringing together expertise from four leading pulp and paper institutes: CTP (France), KCL (Finland), PIRA International (UK) and STFI-Packforsk (Sweden).

Pirabase produces around 1800 new summarised articles per month across the supply chain. The web-based archive contains over half a million articles.

Around 500 publications are scanned worldwide during each year.

**Online archive for industry**

Access can be obtained to the complete Pirabase archive of more than 600,000 articles spanning over 30 years. This enables subscribers to search and retrieve all Pirabase articles, relating to a specific technology, company or market.

The database complements current awareness services and newsletters, as it provide scientists with a ready-made research device, which can be used to gain more detailed or historical knowledge of a company, technology or market. Information can be obtained on:

- markets and technologies
- year-on-year comparisons of installations, company results, new patents or market activity
- Find intelligence on specific target customers, suppliers or competitors
- Research legislation and amendments
- market or technical trends over variable periods of time

### 2.1.3 Approach used to search the Smithers Information Databases

The specialist knowledge of the Information Scientists in the Smithers Group were utilised to carry out a search of the databases from around the year 2000 to the present day. This was carried out in two stages, with the objectives of the project being used to put together an initial search strategy and, after some refining by running investigative searches and examining the results, this was used to compile a list of around 600 abstracts in total with around 400 originating from the Polymer Library database and around 200 abstracts from the PIRAbase/Paperbase database.

These lists of Abstracts were then reviewed in detail by the Principal Consultants at Smithers Rapra and a number of articles identified which were deemed to be of sufficient relevance to the project for the complete papers to be accessed for examination.

The information and data obtained from these two searches was complemented by information arising from a large number of sources, including discussions with leading organisations and professionals working in both the plastics and P&B recycling sectors. These additional sources of information are described in Section 2.2. below and the references provided in the General References section of this literature search.

## 2.2. Other Information Sources

### 2.2.1 Food Standard Agency Reports, MAFF Information Sheets and Other Information

#### 1) FSA Research Projects Reports and Information Summaries

Information from the following FSA research projects has been used in the writing of this literature review:

a) Determination of the potential for transfer from secondary packaging to foods and development of guidelines to reduce transfer to levels of no concern. Final report for FSA project A03027 April 2004 (13).

b) Migration from recycled paper and board to dry foods. Research into the factors involved leading to practical avoidance and emelioration measures. Final report for FSA project A03021 - September 2004 (14).

c) An investigation of functional barriers currently used by the food industry and an assessment of their efficacy. Final report for FSA project A03049 - March 2006 (15).

d) Study of packaging materials used for dietary staples. Final report for FSA project A04006 – March 2002 (16).

**2) MAFF Information Sheets from the MAFF Archive**

The following information was obtained from MAFF Archive:

| | | |
|---|---|---|
| a) | Number 26 , May 1994 | Formaldehyde in Tea Bag Tissue (17) |
| b) | Number 47, January 1995 | Fluorescent Whitening Agents (18) |
| c) | Number 60, May 1995 | Phthalates in P&B Packaging (19) |
| d) | Number 66, June 1995 | Grease Proofing Agents in P&B (20) |
| e) | Number 72, July 1995 | Curing agents in Carton Board Food Packaging* ( 21) |
| f) | Number 90, May 1996 | Survey of P&B – Residual Amine Monomers from Wet Strength Agents (22) |
| g) | Number 139, December 1997 | Pentachlorophenol In P&B Packaging (23) |
| h) | Number 169, January 1999 | Diisopropylnaphthalenes in Recycled P&B (24) |
| i) | Number 174, April 1999 | Polychlorinated Biphenyls in P&B (25) |

*MAFF Food Surveillance Sheet 72, shown above, cites the MAFF publication “Progress report of the working party on chemical contaminants from food contact materials: 1988 to 1992” that is published as Food Surveilance Paper No 38 by HMSO (26).

### 2.2.3 EU and German National Food Contact Regulations

**EU Food contact regulations**

Some of the principal EU food contact regulations that have relevance to this project are shown below:

- The Framework Regulation (EC) 1935/2004
- Good Manufacturing Practice Regulation (EC) 2023/2006
- Plastics Materials and Articles Regulation (EU) 10/2011
- The Recycled Plastics Materials and Articles Regulation (EC) 282/2008
- Packaging Waste Directive 94/62/EC

All food contact materials must comply with (EC) 1935/2004 and (EC) 2023/2006 and should not, according to Article 3 of the Framework Regulation (EC) 1935/2004:

a) Endanger human health
b) Bring about an unacceptable change in the composition of the food
c) Bring about a deterioration in the organoleptic characteristics of the food

Regulation (EU) 10/2011 for plastics contains a positive list for substances such as monomers and additives and also stipulates SML's for certain substances and compositional limits for plastics.

Regulation (EU) 282/2008 lays down the quality standard for the recycling of plastics material (PET in the case of this project), including a "Challenge Test", and specifies the procedure for achieving authorisation of a recycling process.

Recycled PET must be capable of passing the compositional requirements and migration criteria laid down in (EU) 10/2011, and it must be recycled using a recycling process that has met the criteria described in (EC) 282/2008 to ensure that it has been de-contaminated to a sufficient degree.

Directive 94/62/EC defines recycling targets for a wide range of packaging materials (plastic, metal, P&B etc.) and stipulates maximum limits for the following heavy metals : lead, cadmium, mercury and hexavalent chromium.

**German (BfR) Regulations**

- Paper and Board is regulated by the BfR using their Recommendation XXXVI (Paper and Board for Food Contact)

- PET is regulated by the BfR using their Recommendation XVII (PET for food contact)

### 2.2.5 Other sources of information

Examples of other sources of information that were obtained and examined for this project are listed in the General References section at the end of this literature review.

## 3. POTENTIAL MIGRANTS PRESENT IN RECYCLED PET

The literature search has provided the following information on the potential migrants present in recycled PET.

### 3.1 WRAP report on recycled PET

This report was published in February 2006 upon completion of a WRAP funded project, which has commenced in August 2004 (27). The recycling of the PET was carried out by the Closed Loop recycling company in London, and the recycled PET that was generated was incorporated into products that were marketed by the retailers Boots and Marks & Spencer.

The project sought to demonstrate the viability of using recycled PET in retail packaging and was regarded by WRAP as being successful. Prior to the project, no major retailer in the UK produced PET packaging containing a significant level of recycled material derived from post-consumer recyclate.

Two principal types of food packaging were produced from the recycled PET during the project:

- Thermoformed products – e.g. salad bowls and lids
- Injection blow moulded bottle – e.g. for containing juice

#### 3.1.1 Salad bowls and lids

As part of the due diligence process, migration testing and headspace measurements were carried out on some of the recycled PET finished items. This work was carried out at the Fraunhofer-Institute for Process Engineering and Packaging IVV.

Migration testing was carried out on thermoformed salad bowl products using 95% ethanol as a “worst case” food simulant, the presence of volatile substances was carried out by headspace gas chromatography. Products made from virgin PET were used as controls.

The headspace results for the virgin and recycled materials were similar, but the chromatograms for the recycled PET contained additional peaks at longer retention times where flavour molecules such as limonene and cineole are usually found. All of the peaks in this region were below a concentration of 1 ppm.

When it came to the migration tests, the results obtained with the thermoformed products containing 50% of recycled PET were significantly lower (16 times) than the maximum overall migration limit of 10 mg/$m^3$.

Overall, these analytical results showed that materials containing 50% of recycled PET adequately meet the standards of performance expected for food contact packaging.

In addition to this analytical work, recycled salad bowls and lids were delivered to Geest for filling with salads and shelf life stability tests. The products passed the storage and organoleptic tests with the only observation that there was some condensation on the lids, which was due to the absence of the anti-misting treatment for this trial.

Following these successful results M&S gave permission for the launch of the thermoformed packaging containing 50% recycled PET.

### 3.1.2 Juice Bottles

No headspace evaluations for carried out on these products, but bottles containing recycled PET were submitted to Fraunhofer for migration testing. Again, 95% ethanol was used as the simulant and the results obtained were low, the overall migration being 0.1 mg/$dm^3$ (100x lower than the limit of 10 mg/$dm^3$).

Instead of organoleptic testing, Orchard House Foods Ltd decided to measure the microbiological influence of the recycled PET in the juice bottles. The results obtained showed that all the bottles tested were free of contamination of yeasts and moulds.

These results enabled the introduction of food grade recycled PET into bottles at levels up to at least 30% for juice bottles.

## 3.2 ILSI Guidelines – recycling of plastics for food contact use and the “Challenge Test”

The ILSI guidelines for recycling food contact plastics were published in 1998 (28), and share many of the same scientific principals established by the US FDA, but also have some differences that have developed from new scientific knowledge and also differences in approach to the same problems.

These guidelines were initially developed for food grade plastics and use the concept of the “Challenge Test” conducted using surrogate chemical species. These species are listed below in Table 2 and are similar to those used in by the FDA.

**Table 2 Surrogate chemical species used in Challenge Test**

| Compound Class | Substance | Concentration (%) |
|---|---|---|
| Polar, volatile | trichloroethane | 1 |
| Polar, non-volatile | benzophenone | 1 |
| Non-polar, volatile | toluene | 10 |
| Non-polar, non-volatile | chlorobenzene | 1 |
| Non-polar, non-volatile | phenylcyclohexane | 1 |
| Organometallic | methyl palmitate (or methyl stearate) | 1 |

The report on PET that resulted from the FAIR-CT98-4318 “Recyclability” project (5) (see Section 3.3) recommended the same surrogates as these, but without the use of trichloroethane. The key difference from the US FDA protocol is the way the surrogates are mixed with the PET. The FDA uses a solvent based cocktail whereas the ILSI approach uses a direct mixing and sorption by mixing at 50 °C for 7 days which was found to be functionally equivalent but simpler to prepare. The level of surrogates in the PET flake should be between 50ppm to 350ppm for all except toluene which should approach 500 ppm. The contaminated flake is then directed straight into the systems that first undergo the washing and drying steps, before the “Supercleaning” takes place.

The normal requirements of the challenge test are that 100% of the test articles are contaminated with surrogates and the results from the cleaning process must demonstrate “not detectable migration” at the limit of detection of the analytical methodology. The limit of detection at which reliable analytical measurements can be made is stipulated to be 10 ug/kg.

Challenge tests to test the efficiency of recycling processes for food contact plastics are also mentioned in the EU Plastics Recycling Regulation (EC) 282/2008 and a number of papers in this literature review undertaken are concerned with migration studies undertaken using samples of PET that have been spiked with surrogate chemical compounds such as the one published by Widen et al (29).

a) Limonene
b) Benzaldehyde
c) Benzophenone
d) Anethole

Or, the use of cocktails of surrogates to determine the decontamination efficiency of new or modified recycling processes (30) and the TNO V663 Report published in 2005 (31).

### 3.3 The EU-Project FAIR-CT98-4318 “Recyclability” Project Report - Section I : PET Recyclability

The Fraunhofer Institute IVV was the task leader for the PET section (Section I) of this project (5) and this report was authored by Roland Franz and Frank Welle of the Institute, along with Forrest Bayer of the Coca-Cola company in the USA.

During the course of the project the workers at Fraunhofer developed analytical tests for flake, pellet and packaging products to detect the level of decontamination of the PET material and the migration of any species from PET packaging into food products. For the analysis of the PET itself, they used headspace gas chromatography, with the samples being heated and the volatile products being detected by their characteristic retention times.

The substances listed below were typically identified in post-consumer PET.

1. Acetaldehyde
2. 2-methyl-1,3-dioxolane
3. ethylene glycol
4. limonene

The first three of the compounds are found in all PET resins and originate from the polymer itself; the last substance is a common compound used to flavour soft drinks.

The results of the analysis work showed that after decontamination using a super clean process, all of the contaminant species had been removed from the recycled PET flake, and in fact it contained even fewer potential migrants that conventional virgin PET.

As mentioned above in Section 3.2., this report recommends a very similar range of surrogate chemicals for determining the effectiveness of the recycling processes that are used for PET. It also describes the migration modelling of substances based upon molecular weight and shows that the inverse relationship between the amount migrated after 10 days at 40 °C and molecular weight reaches a limit beyond 350 g/mol. Beyond this level substances are virtually immobilised in the PET matrix.

### 3.4 FSA Research Project A03049 : An investigation of functional barriers currently used by the food industry and an assessment of their efficiency (15).

The objectives of this project, which looked at the performance of functional barriers in food packaging, are outlined in section 3.2.4.3. A number of migration scenarios were studied during the lifetime of the project.

The one that had relevance for PET was use of a PET trimer (molecular weight : 576 g/mol) as a surrogate compound. PET was immersed into a “spiking “ solution containing this trimer and then this layer was placed against the PET film on the non-food contact side of the functional barrier and migration experiments carried out. In this set up in order to get into the food simulant, the PET trimer had to migrate out of the spiked layer, through the non-food contact side PET, through the functional barrier, and finally through the PET film on the food contact side. Experiments were also carried out without any functional barrier.

Sunflower oil (fatty food) and aqueous food stimulants were used, and the PET trimer determined by HPLC with a UV detector.

The results obtained with the PET trimer showed that very little migration occurred. The only positive result was obtained when it was in direct contact with sunflower oil at a high temperature (100 °C). When a functional barrier was present no migration occurred.

### 3.5 German BfR Recommendation XVII

In 2000, the German BfR issues a statement to ensure the safe mechanical recycling of plastics made from PET for the manufacture of articles for direct food contact. This statement has been incorporated into Recommendation XVII and introduces two criteria:

(i) an analytical assurance that post-consumer recycled PET must not be disadvantageously distinguishable from virgin PET.

(ii) a 10ppb migration limit for evaluating the performance of “superclean” recycling processes – but this limit is not to be used as a toxicological-based end parameter.

## 3.6 Information obtained by search of the Smithers Information Polymer Library Database

The following information on the potential migrants from recycled PET has been obtained by a search of the Smithers Polymer Library database.

An important general finding concerning migrants in PET and their potential to migrate has been commented on by Franz (3). This is that, owing to the extreme low diffusively of PET, substances with molecular weights higher than 350 g/mol are virtually immobilised in the PET matrix and so will only migrate very slowly.

This section has been ordered according to specific groups, or types, of compounds.

### 3.6.1 PET related compounds

Acetaldehyde is one of the most common thermal degradation products of PET. It can be found in both virgin PET and recycled PET, but it is normally at a higher concentration in recycled PET due to the fact that the product has been in service, and therefore subjected to degradation agencies such as UV light, and the bottles have been shredded, which will have resulted in some additional "heat history". Franz et al (3 and 4) have determined levels of acetaldehyde in recycled PET of between 18.6 and 86.0 mg/kg, and found that once this recycled materials was re-extruded the level could be reduced to between 1 and 20 mg/kg.

Two other compounds that originate from the PET polymer and which can be detected in both virgin and recycled PET (30) are 2-methyl-1,3-dioxolane (a condensation product of acetaldehyde and ethylene glycol), and ethylene glycol (a residual monomer).

### 3.6.2 Flavour compounds and other species from foodstuffs

A very common flavour compound that is detected in recycled PET is limonene. This has been found in the range 0.1 to 20 mg/kg by Franz et al (3 and 4)

In addition to limonene, p-Cymene has also been detected in a large number of samples by Nerin et al (32) This work was carried out qualitatively, but it was estimated that the concentration of p-Cymene was around five times lower than limonene.

Nerin also reports finding aliphatic aldehydes, such as 2-decenal and 1-octadecenal, in flavoured soft drink bottles.

Bayer (33) has reported finding flavour-like terpenoid compounds (e.g. beta-burbonene and (Z) beta-farnesene.

The differences in the extraction profiles that can be obtained from PET bottles that have been used to store different food products has been illustrated by Mancini et al (34) who compared post-consumer PET bottles that had been used to store oil and a soft drink. The PET container that had been used to store oil had a much more complicated profile of species, with a total of 35 organic species being detected, five of which were non-volatile, and seven metals.

### 3.6.3 Additives from other polymers

It is possible during the collection and sorting of PET bottles for other plastics to remain in the waste stream and these will then contaminant the PET flakes exiting the shredder. A number of other common plastics, such as PVC, contain a considerable number of additives that are introduced into the material for technological reasons and these will appear in the recycled PET as contaminants.

Two common examples of these are:

a) Plasticisers such as phthalates (DBP, DOP, BBP etc.) and adipates (e.g. DEHA).
b) Slip additives such as erucamide and oleamide – used extensively in polyolefin films.

Due to the random nature of their inclusion, their appearance in recycled PET is sporadic and they tend to be present at very low concentrations. Franz (3) suggests levels around the detection limits of analytical techniques, such as 0.05 to 0.2 mg/kg. Nerin has reported an example of the plasticiser dioctyl adipate being present at 0.5 mg/kg (32).

### 3.6.4 Chemicals from misuse of bottles

Examples of the types of chemicals that can be detected in recycled PET as a result of the misuse of bottles, for example the storage of household chemicals, prior to recycling include solvents. In common with the plastics additives mentioned above in section 3.6.3, these are intermittent contaminants and workers such as Franz (3) have reported that they are mostly present at low concentrations (1.4 to 2.7 mg/kg) although a substance thought to be toluene from its retention time was present in one flake sample at 450 mg/kg. In the same study, xylene isomers were also detected in a few samples of flake at concentrations between 50 and 200 mg/kg.

Two estimates of the frequency of misuse of PET are from Bayer et al (35) have reported that the frequency of misuse of PET bottles is one misused bottle per 10,000 uncontaminated bottles, and Franz (3) who estimated one in 3,000.

### 3.6.5 Other chemical compounds

Workers such as Nerin (32) and Bayer (33) have reported the results of screening studies on a number of recycled PET samples and a wide range of chemical compounds have been detected by sensitive analytical methods such as headspace GC-MS. For example, in addition to the classes of compound already covered in the sections above:

a) Aromatic aldehydes
b) Esters
c) Aliphatic acids
d) Alkanes
e) Ketones
f) Ethers

These studies tend to be carried out in a qualitative manner only due to the large number of samples and so concentrations per kilo of PET are not reported.

## 4.0 POTENTIAL MIGRANTS PRESENT IN RECYCLED PAPER AND BOARD

The literature search has provided the following information on the potential migrants present in recycled P&B.

### 4.1 Council of Europe Resolution on Paper and Board

This Resolution (10) provides important information associated with the production and use of recycled fibres for P&B packaging materials.

It list the following compounds which can be present in recycled paper and board and these are presented within Table 2 located in Technical Document No 3 (Guidelines for recycled fibres):

1) Benzophenone
2) Micher’s ketone (4,4’ bis(N,N-dimethylamino)benzophenone)
3) 4,4’(diethylamino)benzophenone (DEAB)
4) Diisopropylnaphthalene’s

5) Partially hydrogenated terphenyls
6) Phthalates
7) Azo colourants
8) Fluorescent whitening agents
9) Primary aromatic amines
10) Polycyclic aromatic hydrocarbons
11) Solvents

### 4.2. Information obtained from Confederation of European Paper Industries (CEPI)

#### 4.2.1 CEPI Industry Guideline – Compliance of Paper and Board Materials and Articles for Food Contact

This guideline was published in March 2010 (67) and listed the following compounds in Section 4 (Chemical Testing):

1) Heavy metals (e.g. cadmium, lead and mercury)
2) Pentachlorophenol
3) Antimicrobial substances
4) Michlers ketone
5) DEAB
6) Azo colourants
7) Fluorescent whitening agents
8) PAH's
9) Phthalates (DBP, DiBP, DEHP and benzylbutyl phthalate)
10) DINP
11) Benzophenone, hydroxyl benzophenone and 4-methyl benzophenone
12) Bisphenol A

#### 4.2.2 Good Manufacturing Practice Guide

This document was issued in September 2010 (68) and provides an informative, comprehensive overview of P&B manufacture for food contact and is intended to complement the CEPI Industry Guideline (see Section 4.2.1).

The principal section of the Guide that concerns recycled P&B is Annex 3 entitled "Guidelines for Responsible Sourcing and Supply of Recovered Paper".

In order to control contamination, this Guide uses the CoE Resolution guidelines for ruling out certain paper streams as the raw materials for recycling into food grade P&B. These are:

- Contaminated waste from Hospitals
- P&B that has been mixed with “garbage” and then sorted out
- Stained sacks which has contained products such as chemicals and foodstuffs
- Paper used to cover items, e.g. during repair and painting
- Batches consisting mainly of carbonless copy paper
- Waste paper from households that contains used hygiene paper (e.g. kitchen towels, facial tissues and handkerchiefs
- Old archives from libraries, offices etc., if they contain PCB’s

With respect to the testing of P&B produced from recycled fibres, there is no specific mention of the chemical species that should be targeted, but Section 4.4 “Testing Frequency” in the main document does mentions that “consideration must be given to the testing scheme intended to analyse the end product for compliance with regulatory and customer specifications”.

### 4.2.3 CEPI statement on 4-Methylbenzophenone in Food Contact Materials

This statement was published on the CEPI (The Confederation of European Paper Industries) web site (36) and was concerned with the recent conclusions of the European Commission Standing Committee on the Food Chain and Animal Health which established a specific migration limit for 4-benzophenone and benzophenone of 0.6 mg/kg of food. CEPI regarded the limit as achievable in most direct food contact applications by use of the current good manufacturing practice guidelines to avoid problems such as “set off”.

The statement also mentions the availability of new inks which are free of these substances, which may be alternatives in applications where low migration and low odour are required.

## 4.3 Information present in the KCL Science and Consulting report

This document was published in May of 2007 and deals with the application of correction factors to be used in testing P&B, which was a concept originally introduced by the EU FAIR project entitled “Recyclability” (37) and further explored in the joint EU Commission/Paper Industry project “Biosafepaper” (38).The reason for considered correction factors was that scientific work on chemical migration indicated that migration and extraction tests could overestimate migration.

The report cites the migration into food from P&B work carried out by Fabes Forschungs-GmbH in 2004. Fabes used the following surrogate to spike a range of P&B samples (some from recycle sources) and determine the migration into a wide range of foodstuffs (e.g. fatty, dry and peeled/washed):

- Benzosothiazole
- Benzophenone
- Diisobutyl phthalate
- Dibutyl phthalate
- Phenanthrene
- Diisopropyl naphthalene
- Dioctyl phthalate

In addition to the Fabes work, this report also covers some of the results obtained from the "Recyclability" project, and other published information, and compares the results obtained by these studies. The correction factors proposed by the "Biosafepaper" project are presented as are the correction factors proposed by the draft industry guidelines published by CEPI.

### 4.4 BfR Recommendation XXXVI – Paper and Board for Food Contact

1) Metal ions should not be present in paper above the following values (determined by cold water extraction):

   a. Cadmium 0.5 ug/g
   b. Lead 3 ug/g
   c. Mercury 0.3 ug/g

2) DIPN (due to its use as a solvent in carbonless copy paper) can be present in recycled paper and board and this BfR Recommendation states, without providing a reference, that experiments have shown that fat-containing foodstuffs and foodstuffs having a large surface area (e.g. nut biscuits and cocoa) can take up DIPN in large quantities. Therefore in packaging of such food special precautionary measures should be take, e.g. use of additional intermediate packaging. The amount of DIPN should be kept "as low as technologically possible".

3) Azo dyes must not be used in the manufacture of food contact paper or board.

In general, recycled fibres may be used for the manufacture of food contact packaging providing that they meet the requirements of this Recommendation. It is stipulated that “only rejects from manufacturing and processing, or recycled paper of equivalent quality may be used”.

### 4.5 Information obtained from the FSA

#### 4.5.1 FSA Research Project A03021. Migration from recycled paper and board to dry foods. Research into the factors involved leading to practical avoidance and emelioration measures (14).

This project was completed in 2004 and provided the FSA with an extensive literature search of information that was available on potential migrants from paper and board. This was based on an earlier review by Soderhjelm and Sipilanen (9).

The review of the literature that was carried out for this project is presented in detail in Annex 1 of the final report. The processes that recycled P&B undergo during the recycling process has already been mentioned in Section 1.3.2. The literature review carried out during this project covered the following thirteen principal groups of compounds/species:

- Trace elements
- Waxes
- Fluorescent whitening agents
- Sizing agents
- Organochlorine substances
- Plasticisers
- Aromatic hydrocarbons
- Volatiles
- Curing agents
- Grease proofing agents
- Extractable amines
- Biocides
- Surfactants

The main findings of the literature review can be summarised as follows:

1) The literature review confirmed the expectation that the most important source of low molecular weight residues in recycled paper and board is recovered printed material (39 and 11) because most printing processes use a liquid ink or a paste ink and fix the image onto the substrate by drying.

The three mechanisms for drying the ink film were:

- Use of volatile solvents which are evaporated by heating.

- Use of higher molecular weight, non-volatile solvents that sink into the printed paper or boards leaving behind a solid film of print.

- Chemical drying, in which a reactive solvent is used which is subsequently dried by autoxidation (e.g. drying oils) or by polymerisation initiated by ultra-violet or electron-beam radiation (e.g. benzophenone initiated with UV radiation).

All three of these drying mechanisms can give rise to low molecular weight residues.

In addition to residues due to the drying mechanism, low molecular weight additives such as plasticisers are commonly used to assist with the dispersion of the pigment. The contaminants most commonly for recycled P&B are reported are phthalates and benzophenone.

- The second most widely-reported low molecular weight organic contaminants found in P&B are additives that have been used in carbonless copy papers and thermal copy papers. Polychlorinated biphenyls (PCB) (40), diisopropylnaphthalenes (DiPN) (41) and hydrogenated terphenyl (HTP) (REF 42) isomer mixtures were reported as occurring widely in recycled cartonboard and can migrate into dry foods such as rice and pasta.

- Another contaminant that historically had been problematic but which was not so important (was pentachlorophenol (PCP) (23). Historically, this substance was used as a preservative for timber, and so was not a specifically recycling-derived contaminant, but its use was discontinued in the 1970's.

The report concluded that the five most commonly reported contaminants in recycled paper and board up to the early 2000's were:

(a) Benzophenone
(b) Phthalates
(c) DIPN's
(d) Polychlorinated biphenyls
(e) Pentachlorophenol

The report makes the following comments regarding this set of compounds:

- These substances are all low molecular weight, relatively non-polar, aromatic substances and may be reported so often because:

    - This class of chemicals is easy for analytical chemists to detect and measure using the tool of preference, GC-MS.

    - These substances share chemical and physical properties that make them resist washing (i.e. they are poorly water soluble and fibre retentive) and so they may carry-through to P&B made from recycled fibres.

The report also makes the following comments regarding the chemical natures of P&B and Paper and how they may influence the retention of contaminants:

- Paper and board consists mainly of fibres and fillers. The cellulose fibres have repeat units of glucose residues and are very hydrophilic but are largely non-ionic.

- The lignin component of paper has aromatic phenolic repeat units with hydrophilic and hydrophobic domains that are both anionic in character. This gives an overall negative charge to the surface of paper fibres due to the carboxy groups and the hydroxy groups of the lignins. The consequence of this, when considering the interactions of contaminant molecules with the paper surface, is that positively charged contaminant species (i.e. cationic) and also electron-deficient substances (e.g. certain aromatics) could experience a net attraction to the surface and will be fibre-retentive. This latter case applies for the five compounds listed above which persist in recycled paper because of electron interaction with the lignin surface.

### 4.5.2 FSA Research Project A03027. Determination of the potential for transfer from secondary packaging to foods and development of guidelines to reduce transfer to levels of non concern (13).

This project, which was also completed in 2004, was concerned with the potential migration from secondary packing into foods. The salient points that were established by this project were:

2) Alkanes (a wide range all at relatively low levels), phthalates and DIPN's were detected in virtually all cartonboard and corrugated board samples containing recycled fibres. The phthalates that were detected included:

- Diisobutyl phthalate
- Dibutyl phthalate
- Di(2-ethylhexyl)phthalate
- Benzyl butyl phthalate

3) Other substances detected commonly in paper and board included dehydroabietic acid, stigmastenol, fatty acids and squalene; these are naturally occurring compounds. 2-Methyl-1-(1,1-dimethylethyl)-2-methyl-1,3- propanediyl propanoate was detected in a number of materials, but this did not appear to be a substance used in the manufacture of paper and board. The only reference which could be found refers to finding it in glassine paper and it was assumed that it is a naturally occurring substance.

4) A variety of glycol ethers were found in some board materials. Ethylene glycol monophenyl ether is used as a surfactant and as a de-inker for flexographic inks. This may explain its presence in recycled materials. Similarly, diethylene glycol monobutyl ether is used as a de-inking compound for paper recycling and as a solvent for lacquers. It is also used in the developing solution for pre-sensitised lithographic plates. Any of these could be possible sources for this substance in recycled, litho printed cartonboard. Diethylene glycol ethyl ether is also used as a de-inking compound, as a detergent and as a wetting agent for inks.

5) A number of different photo-initiators were detected. Photo-initiators are used in UV cure inks and lacquers used in the lithographic printing of cartonboard. Of these, benzophenone (BP) was detected most frequently, often in combination with other photo-initiators such as 2,2-dimethoxy-2-phenylacetophenone (DMPAP); 2-benzoyl-methylbenzoate; 2-phenyl acetophenone; 2-ethylhexyl-4-(dimethylamino) benzoate; 4-(dimethylamino) ethyl benzoate; 4-phenyl benzophenone. Most of these substances are used in printing inks and hence are not listed in the EU synoptic document. The exception is BP.

In the analytical method used standards were only run phthalates, DIPN, bisphenol A and BP. For all other substances, identification was library matching only i.e. no standard has been run to check for retention time match and so there was the possibility of incorrect identification of substances.

### 4.5.3 FSA Research Project A03049. An investigation of functional barriers currently used by the food industry and an assessment of their efficiency (15).

This project was concerned with the functional barriers that are used in the food industry to prevent/reduce chemical migration from the following:

- An adhesive used in a laminate
- A non-food contact plastic layer
- A non-food contact P&B layer
- A printing ink or coating applied to the non-food contact surface of a packaging material

These sources can result in a wide range of chemical substances having the potential to migrate and the project established the ability of selected systems to act as functional barrier.

The performance of a wide range of functional barriers and food packaging/food combinations were investigated by the use of migration experiments involving spiking with surrogate compounds.

Examples of the functional barriers that were evaluated included :

(1) Aluminium foil
(2) Metallised plastic films
(3) Films with vacuum deposited ceramic coatings
(4) Plastic films, such as PET films

The surrogate compound that was used which is of particular relevance to P&B was benzophenone. In the case of PET it was a PET trimer.

The results obtained experimentally on the different barrier systems studied showed that all the systems investigated acted as a functional barrier to a certain extent dependent upon on the material type, food type and storage conditions. They also underlined the importance of considering the use efficiency of materials s functional barriers on a case-by-case basis.

### 4.5.4 FSA Research Project A04006. Study of packaging materials used for dietary staples (16).

This project looked at a range of possible packaging materials and packaging formats for a large (~100) number of dietary staples in the UK.
The results obtained concluded that although considerable efforts have been made by the packaging and food industries to reduce the migration hazards associated with packaging materials, a number of issues of potential migration interest remain.

The examples found that are of interest to this project are:

- Recycled board sandwiched between virgin materials for a wide range of foodstuffs.

- Cook in pack (oven or microwave) paperboard packaging for ready meals and convenience foods.

### 4.5.5 Information obtained from MAFF Information Sheets – now available from the FSA

The Information sheets that are listed in Section 2.2.1 have been examined and the potential migrants for Paper and Board that are discussed and highlighted in them are listed below:

(a) Formaldehyde from tea bag paper at a maximum level of 0.24 mg/kg of tea – Sheet number 26 (17).

(b) Fluorescent whitening agents. Most of the samples analysed contained FWA's at 50mg/kg of P&B. The highest concentrations of FWA's found were in the region of 430-1160 mg/kg P&B – Number 47 (REF 18).

(c) Phthalates – Dibutyl phthalate (DBP) and diethyl hexyl phthalate (DEHP) were found to be the most common. DBP was found at concentrations between 5 and 5860 mg/kg of packaging in 98% of samples, and DEHP in 95% of samples at 5 to 3030 mg/kg packaging. Analysis of food that had been in contact with this packaging showed DBP to be present at 0.04 to 62 mg/kg of food, and DEHP at 0.1 to 25 mg/kg food – Sheet Number 60 (19).

(d) Grease proofing agent (monoammonium and diammonium perfluoroalkyl phosphate salts) and its alcohol (FOSE) breakdown product. The grease proofing agent was found to be present in the paper at levels of <0.15 to 1.8 mg/dm$^2$. The concentration of FOSE increased when the paper was heated, being found in the range <0.01 to 0.8 mg/dm$^2$ – Sheet number 66 (20).

(e) Michlers ketone (MK) and DEAB. MK was detected in 29% of the paper and board samples at 0.1 to 1.6 mg/kg, and DEAB in 5% of the samples at 0.2 to 0.7 mg/kg – Sheet number 72 (21). These were similar reported levels to those in Food Surveillance Paper No 38, which also showed that there was no detectable migration of MK into food (26).

(f) Residual amine monomers from wet strength agents such as polyamine resins and melamine-formaldehyde resins. Ethylene diamine (EDA), hexamethylenediamine (HMDA) diethylenetriamine (DETA), N-(2-aminoethyl)-1,3-propanediamine (APDA), and melamine were determined and none were found to be above the detection limits of the method used : 0.05 mg/l (EDA and HMDA) and 0.1 mg/l (DETA, APDA and melamine). Sheet number 90 (22).

(g) Pentachlorophenol. This wood preservative chemical was detected in levels up to and above 100 ug/kg of packaging, but was not found to migrate into food – Sheet number 139 (23).

(h) Diisopropylnaphthalenes (DIPN) from recycled P&B. These were detected in all samples of board from mills (up to 33 mg/kg) and in most samples of retail packaging (up to 44 mg/kg). Food migration experiments were performed and DIPN detected at up to 0.89 mg/kg food – Sheet number 169 (24).

(i) Polychlorinated biphenyls (PCB's) from general environmental contamination. PCB's were detected in 24% of the P&B samples at up to 0.33 mg/kg – Sheet number 174 (25).

### 4.5.6 The EU-Project FAIR-CT98-4318 "Recyclability" Project Report – Section II : P&B Recylability

This project, which looked at P&B, in addition to PET and Plastics covered by functional barriers, ran for 40 months from 1st January 1999.

The P&B work was conducted as Section II of this project. A literature search of the contaminants in recycled fibres of paper and board food contact materials was conducted and the results obtained were presented in the consolidated report for Section II. This literature review was included in the work carried out on FSA Project number A03021 and the thirteen sections (i.e. chemical migrant types) that it is was comprised of are described above in Section 4.5.1.

## 4.6 Information obtained from the search of the Smithers Information PIRA/Paperbase Database

The following information on the potential migrants from recycled P&B has been obtained by a search of this database, which includes both Pirabase and Paperbase This section has been ordered according to specific groups, or types, of compounds.

### 4.6.1 Benzophenone, 4-methyl benzophenone and dialkylamino benzophenone

EFSA have reviewed chemicals in printing inks that have migrated into food in recent years and the most prominent example was breakfast cereal being contaminated by 4-methyl benzophenone in 2009 which prompted a Europe wide investigation (43).

Other potential migrants that can originate from UV-curable printing inks include benzophenone and the transfer of this, and other substances present in P&B into food at low temperatures, has been examined by Johns et al (44 and 66). In addition, Castle et al have published migration work that has been carried out on residues of dialkylamino benzophenone UV-cure ink photoinitiators (11). Also, Anderson and Castle have published a paper that considers the factors that influence the migration of benzophenone into food (65).

### 4.6.2 Phthalates

Phthalates have featured in a large number of published papers over the past 10 years. This is due to their widespread use as plasticisers in a number of products that are associated with P&B, for example glues (45), inks (46) and adhesives (47). Efforts are underway in European countries such as Germany to look for alternatives to low molecular weight phthalates such a DIBP (48). Work by the BfR has shown that DIBP can be found in food at concentrations of up to 5 mg/kg (49 and 47). Work has also been carried out in Italy to determine the amount of DIBP in foods such as pizzas that are packaged in P&B (Answer 17). A new evaluation of DBP by EFSA has resulted in an SML being set for it of 0.3 mg/kg of food, and Germany is intending to bring in the same SML for DIBP because of the similarity in the structures of these two substances (51).

### 4.6.3 Diisopropylnaphthalene isomers

DIPN ‘s are used as solvents in carbonless copy paper and this is a potential route for their way into recycled P&B. Mariani et al have studied the migration of DIPN from impregnated paperboard into dry foods such as rice and flour and found only low levels of migration into the foodstuffs (52). The MAFF Information Sheet (53) reported on the findings of the analysis work on 51 samples of recycled P&B (mill and retail) and 34 samples of food packaged in recycled P&B. Up to 33 mg/kg of DIPN was found in most of the P&B samples, and levels of up to 0.89 mg/kg in the foods.

### 4.6.4 Fluorescent whitening agents

Florescent whitening agents (also called optical brighteners) are possible contaminants that can migrate into food from P&B packaging (54). Milanova et al (55 and 56) have investigated the migration of FWA into both aqueous and fatty food simulants and concluded that the migration of such agents into non-aqueous foods would be extremely low and so barrier coatings (e.g. of polyethylene) would not be required in these cases. However in the case of the aqueous food stimulants containing at least 90% water, the migration of FWA's was extensive.

### 4.6.5 Dehydroabietic acid (DHA) and Abietic acid (AA)

These two compounds are present in the Rosins that are used as sizing agents in paper to increase its hydrophobicity and they can be present in both virgin fibres and recovered fibres. Ozaki et al (57) have found that the levels of DHA and AA in virgin samples varied between 14 and 500 ug/g and in recycled products at between 110 and 1,200 ug/g. However, when migration studies were performed using food stimulants, the highest level of migration for DHA was only found to be 0.853 ug/g, and for AA it was 3.14 ug/g.

### 4.6.6 Mineral oils

A recent study in Germany has highlighted the potential problems with mineral oils that are used in newsprint and printing in general remaining in recycled fibres (58 and 59). Mineral oils are also being addressed when the British Retail Consortium (BRC) publishing a new Global Standard for Packaging (60) in 2011 which contained extra safeguards to reduce the danger of chemicals migrating from packaging inks into food. The European Carton Makers Congress have also discussed the issue in 2010 (61), and research is on-going to eliminate mineral oils in packaged food by the introduction of mineral oil free newspaper inks (62).

## 4.7 Other information

### 4.7.1 Determination of Mineral Oil in Paper and Board

This paper published by Vollmer et al (59 and 62) describes how food samples from the German market that had been packaged for extended periods in P&B had been analysed for the presence of mineral oil. The levels were found often exceeded the 0.6 mg/kg WHO/JECFA limit by a factor of 10-100. Samples were predicted to contain up to and beyond 100 mg/kg after their 1 to 3 year shelf life was reached. It was estimated that around 25% of the migrating mineral oil came from the printing ink used to decorate the boxes.

The analytical method used to carry out the determination of the mineral oil (up to $C_{24}$) was based upon a normal phase HPLC on-line coupled to a GC-FID, with fractions being transferred to the GC-FID by partially concurrent eluent evaporation and the retention gap technique.

### 4.7.2 Study of the behaviour of model contaminants in P&B

This paper by Triantafyllou et al (64) was concerned with investigating the physicochemical behaviour of selected model contaminants (i.e. surrogates) on paper and board in contact with foodstuffs with a view to producing fundamental data about their mobility from recycled P&B into foods.

The following model compounds were used:

1) o-xylene
2) acetophenone
3) n-dodecane
4) naphthalene
5) diphenyl ether
6) 2,3,4-trichloroanisole
7) benzophenone
8) diisopropyl naphthalene – mixture of isomers
9) dibutyl phthalate
10) methyl stearate

The results obtained showed that the proportion of the surrogate compounds that migrated into a food was strongly dependent on: the nature of the paper samples, fat content of the food, and the chemical nature and volatility of the migrant. The highest levels of migration were observed with the foods that had the highest fat content, and the contact time and contact temperature also had an important influence.

## 5.0 SUMMARY OF POTENTIAL MIGRANTS FOR RECYCLED PET AND PAPER AND BOARD

Having examined all of the information that has been collated on the potential migrants that are present in post-consumer PET and recovered P&B, it was possible to provide a brief summary of these species and this is shown in the Sections 5.1 and 5.2 below.

## 5.1 Potential migrants from recycled PET

The studies that have been carried out on post-consumer PET samples have shown that the major species present originate from two sources:

3) The PET polymer
4) Flavouring substances present in the food that has been packaged in the PET

Some workers have detected a large range of other compounds (see Sections 3.6.3, 3.6.4 and 3.6.5) but these have all been present at very low levels and some have originated from small quantities of small amounts of contaminated PET (due to misuse of the containers), or small amounts of other polymer-based waste entering the PET waste stream. The low level and intermittent and sporadic nature of these compounds makes them unsuitable for use as marker compounds.

A summary of the potential migrants in recycled PET is shown in the Table 3 below.

**Table 3 Potential migrants in recycled PET**

| Potential Migrant | Range found in post-consumer PET flakes |
|---|---|
| Acetaldehyde | 18.6 to 86.0 mg/kg |
| Ethylene glycol | n/a |
| 2-methyl-1,3-dioxolane | n/a |
| Limonene | 0.1 to 20 mg/kg |
| p-Cymene | ~0.02 to 4 mg/kg |
| 4-iso-propyl toluene | ~0.02 to 4 mg/kg |
| Numerous organic compounds | ~0.05 to 0.5 mg/kg |

n/a = cited by Franz et al (3) as detected but a concentration not provided

## 5.2 Potential migrants from recycled Paper and Board

The large range of waste P&B products that can be used as a source of recovered fibres for the production of recycled P&B products, the complexity of the composition of these materials, and hence the corresponding large number of potential contaminants that can be present in these products, has meant that there is a much larger body of information available in this area than is the case for PET. This is reflected in the sizes of the respective section for these materials (i.e. Sections 3 and 4) in this review.

The various origins of the potential migrants that can be present in recycled P&B products has been described in Section 4.0. A summary of these species is given in the Table 4 below.

**Table 4 Potential migrants in recycled P&B**

| **Potential Migrant** | **Range found in P&B** |
|---|---|
| Benzophenone | Up to 3.1 mg/dm$^2$ |
| 4-methyl benzophenone | - |
| Michlers ketone | Up to 1.6 mg/kg |
| DEAB | Up to 0.7 mg/kg |
| Diisobutyl phthalate and Dibutyl phthalate | Up to ~6000 mg/kg |
| Other phthalates (e.g. DEHP) | Up to 3000 mg/kg |
| Diisopropylnaphthalenes | Up to 0.89 mg/kg |
| Fluorescent whitening agents | Up to ~1100 mg/kg |
| Pentachlorophenol | 100 ug/kg |
| Hydrogenated terphenyls | - |
| Glycol ethers (e.g. ethylene glycol) | - |
| Polychlorinated biphenyls | Up to 0.33 mg/kg |
| Alkanes | - |
| Abietic acid and Dehydroabietic acid | Up to 1,200 ug/g |
| Grease proofing agents (e.g. mono- and di - ammonium perfluoroalkyl phosphate salts)<br>FOSE alcohol breakdown product | <0.15 to 1.8 mg/dm2<br><br><0.01 to 0.8 mg/dm2 |
| Mineral oil (<C24) | Up to ~900 mg/kg (unprinted) ; ~2000 mg/kg (printed) |

- cited in the literature but a concentration range not provided

## 6. SELECTION OF MARKER COMPOUNDS FOR PET AND P&B

A summary of the potential migrants that have been reported for PET and P&B is provided in Section 5.

For the purposes of this project, five of these potential migrants for each of these two materials needed to be selected. In addition to being acceptable to the FSA, the five species had to meet the following criteria:

a) They should be representative of the typical potential migrants (contaminants) that are present in recycled PET and recovered fibres.

b) They should enable a cost effective and efficient analytical programme to be devised for the analysis of the following: pre-recycled material, post-recycled material, and finished products made from recycled material.

With these criteria in mind, and following discussions with the FSA, the following marker compounds were selected for PET and P&B.

### 6.1 Five marker compounds selected for PET

1. Acetaldedyde
2. 2-methyl-1,3-dioxolane
3. Ethylene glycol
4. Limonene
5. 4-iso-propyl toluene

### 6.2 Five marker compounds selected for P&B

1. Benzophenone
2. Diisobutyl phthalate
3. Diisopropyl naphthalenes
4. Di-2-diethylhexyl phthalate (DEHP)
5. Michlers ketone

The literature search revealed that there was a greater number of potential candidates for P&B and so, in addition to the criteria shown in above in the first paragraph of this section, to assist in the decision making process, this range of compounds were chosen because they provide:

a) Compounds that have been detected in reasonably high concentrations in P&B
b) Compounds that vary in their degree of water solubility
c) Compounds that originate from at least four technological sources in P&B
d) Only one example that is a multi-component species

## 7. CONCLUSION

This extensive literature review has provided a thorough overview of the work that has been carried out to identify and quantify potential contaminants and migrants (i.e. marker compounds) in recycled PET and P&B.

It enabled five marker compounds for recycled PET and P&B to be identified (see Sections 6.1 and 6.2) for the experimental phases of the project, during which analytical methods were developed for their determination in both the recycled materials and products, and in selected food simulants following migration tests carried out under representative conditions. The results of this work are shown in the main body of this report.

## 8. REFERENCES


1. M. Monteiro, C.Nerin and F.G.R.Reyes, Packaging Technology and Science, 12, pp241, 1999.

2. K. Hinrichs and O Piringer, Evaluation of Migration Models. Final Report of the Thematic Network EU Contract SMT4-CT98-7513, 2001.

3 Franz et al, Food Additives and Contaminants, 21(3), pp265-286, 2004

4 Franz, Food Additives and Contaminants, 19 (Suppl.), pp93-110, 2002

5. Report published on the EU-Project FAIR-CT98-4318 – Section I : PET Recyclability "Guidance and Criteria for Safe Recycling of Post-Consumer PET into New Food Packaging Applications"

6. M Mutsuga, Y Kawamura et al. National Institute of Health Sciences, Toyko. Food Additives and Contaminants, 23(2): pp 212, 2006.

7. Castle, "Surveillance results on residues in paper and board", paper presented at PIRA Conference on "Paper in contact with foodstuffs", Edinburgh, 1999.

8. A.Damant and L.Castle, Interim Report for the FAIR-CT98-4318 project (1/1/99 to 31/07/99)

9. L. Soderhjelm and T.Sipilainen-Malm, 'Paper and Board' Chapter in 'Migration from Food Contact Materials', ed. L.L.Katan 1996.

10. Council of Europe Resolution ResAP(2002)1 on Paper and Board Materials and Articles intended to come into Contact with Foodstuffs Version 4 – 12.02.2009

11. L.Castle, A.P.Damant, C.A.Honeybone, S.M.Johns, S.M.Jickells, M.Sharman and J.Gilbert, Food Additives and Contaminants, Vol 14, pp 45 -52, 1997.

12. The International Life Sciences Institute (ILSI) report Packaging Materials, No 6. Paper and Board for Food Contact Applications, published October 2004. International Life Sciences Institute

13. Determination of the potential for transfer from secondary packaging to foods and development of guidelines to reduce transfer to levels of no concern. Final report for FSA project A03037. Dated April 2004.

14. Migration from recycled paper and board to dry foods. Research into the factors involved. Leading to practical avoidance and emelioration measures. Final report for FSA project FD04/07. Dated September 2004.

15. An investigation of functional barriers currently used by the food industry and an assessment of their efficacy. Final report for FSA project A03049. Dated March 2006.

16. Study of packaging materials used for dietary staples. Final report for FSA project A04006 – July 1999 to March 2002.

17. MAFF Information Sheet : Number 26 , May 1994, Formaldehyde in Tea Bag Tissue

18. MAFF Information Sheet Number 47, January 1995, Fluorescent Whitening Agents

19. MAFF Information Sheet Number 60, May 1995, Phthalates in Paper and Board Packaging

20. MAFF Information Sheet Number 66, June 1995, Grease Proofing Agents in Paper and Board

21. MAFF Information Sheet Number 72, July 1995, Curing agents in Carton Board Food Packaging

22. MAFF Information Sheet Number 90, May 1996, Survey of Paper and Board – Residual Amine Monomers from Wet Strength Agents

23. MAFF Information Sheet Number 139, December 1997, Pentachlorophenol In Paper and Board Packaging

24. MAFF Information Sheet Number 169, January 1999, Diisopropylnaphthalenes in Recycled Paper & Board

25. MAFF Information Sheet Number 174, April 1999, Polychlorinated Biphenyls in Paper and Board

26. MAFF publication “Progress report of the working party on chemical contaminants from food contact materials: 1988 to 1992”. Published as Food Surveillance Paper No 38 by HMSO.

27. Waste Resources Action Programme (WRAP) Report published on 21st June 2006 entitled “Large-scale demonstration of viability of recycled PET (rPET) in retail packaging

28. ILSI Europe Report Series: Recycling of Plastics for Food Contact Use, ILSI Europe Packaging Material Task Force, May 1998)

29. Widen et al, Food Additives and Contaminants, 21(10), pp993-1006, 2004

30. Welle, Food Additives and Contaminants, 25(1), pp123-131, 2008

31. TNO Report, Challenge test of the PTP modified PET-M recycling system, published 25th October 2005.

32. Nerin et al Food Additives and Contaminants, Vol 20 (7), pp 668-677, 2003

33. Bayer, Food Additives and Contaminants, 19 (Suppl.), pp111-134, 2002

34. Mancini et al, Int, J. of Polym. Mats., 59(6), pp407-423, 2010

35. Bayer et al, Consideration of PET recycling for food use, 208th American Chemical Society National Meeting, Washington DC, 25 August 1994, pp 152-16

36. CEPI Statement, 28th July 2009

37. EU Project FAIR-CT98-4318 “Recyclability” 1/1/99 to 30/4/02: Section 2: Paper & Board

38. EU Project Biosafepaper 1/1/01 to 31/12/05 – Final report published in February 2006

39. Castle et al, Food Additives and Contaminants, 14, pp 35-44, 1997.

40. Brunner et al, Dtsch. Lebensm.-Rundsch, 85(6), pp 175, 1989.

41. Sturaro et al, International Journal of Food Science & Technology, 29, pp 593-603, 1994.

42. Sturaro et al, Chemosphere, 30, pp 687-694, 1995.

43. "Bag-in-box cereal liner now protects flavour and aroma", Byrne, Food Production Daily, 26th Oct, 2010.

44. Johns et al, Packag. Technol. Sci., 13(3), pp99-104. 2000.

45. "Scare over diisobutyl phthalate in packaging:BfR and UBA call for producers to sign agreement to stop use of diisobutyl phthalate", Eur. Environ. Packag. Law., number 85, pp7-8, 2007.

46. "New test finds diisobutyl phthalate in some cardboard food packaging", Packag. Tech. and Sci. press release, 15th Nov 2007.

47. "Putting the consumer first: new plasticiser-free adhesives for packaging", Int. Pap. Board. Ind., 51(3), pp36-37, 2008.

48. "Plasticiser-free paper and packaging adhesives from Henkel", Henkel press release, 18th April 2008.

49. "Putting the consumer first: new plasticiser-free dispersion adhesives from Henkel, Folding Carton Ind., 35(2), pp24-25, Mar-Apr 2008.

50. Bonoi and Tateo, "Identification of diisobutyl phthalate (DIBP) suspected as possible contaminant in recycled cellulose for take-away pizza boxes, Packag. Technol. Sci., 22(1), Jan-Feb 2009, pp53-58, 2009.

51. Traussnig, "Detection of contaminants : analytical and toxicological approach", paper presented at PIRA Conference "Paper in contact with foodstuffs", Brussels, 2008.

52. Mariani et al, Food Addit. Contam. 16(5), pp207-213, 1999.

53. “Diisopropylnaphthalenes in food packaging made from recycled paper and board – food surveillance information sheet number 169”, MAFF, UK, 1999.

54. Escabasse et al, “Fluorescent whitening agents in food contact paper and board”, paper presented at 11th VFV meeting in Aschaffenburg, Germany, 2004.

55. Milanova and Sithole, Pap. Film Foil Converter, 78(3), pp78-79, 2004.

56. Milanova and Sithole, “Migration of optical brighteners from recycled paper into food simulating solvents”, paper presented at International Symposium on Wood and Pulping Chemistry, Nice, France, 2001.

57. Ozaki et al, Food Addit. Contam., 23(8), pp854-860, 2006.

58. Article, “Ink Migration into Food”, Eur. Environ. Packag. Law. Number 229, pp 6-7, 2010

59. Vollmer et al. Migration of mineral oil from printed paperboard into dry foods: survey of the German market, Eur. Food. Res. Technol., 232, pp175-182, 2011.

60. Montague-Jones, “BRC reveals changes to global standard for packaging”, Food Production Daily, 11th June 2011.

61. Blery, Pap. Argus (English edition), 24, pp182-183, 2010.

62. Bitterman and Farkas, “Developments in innovations in recycled paperboard packaging”, paper presented at PIRA 1st Annual Paperboard Packaging Conference, Budapest, June 2010.

63. Vollmer et al, Eur.Food.Res.Technol. 232, pp 175-182, 2011.

64. V.I. Triantafyllou et al, “A study on the migration of organic pollutants from recycled paperboard packaging materials to solid food matrices”, Food Chemistry, 101, pp 1759-1768, 2007.

65. Anderson and Castle, Benzophenone in cartonboard packaging materials and the factors that influence its migration into food, Food Additives and Contaminants, Vol 20 (6), pp 607-618, (2003).

66. Johns et al, Studies on Functional Barriers to Migration 1. Transfer of Benzophenone from Printed Paperboard to Microwaved Food, Deutsche Lebensmittel-Rundschau, 91(3), pp 69-73, (1995).

67. CEPI Industry Guideline for the Compliance of Paper and Board Materials and Articles for Food Contact – published 18th May 2010.

68. CEPI Good Manufacturing Practice for the Manufacture of Paper and Board for Food Contact – published September 2010. This is an updated version of Technical Document No 5 in the CoE Paper and Board Resolution.

# APPENDIX TWO TO CTR 55414
# ANALYTICAL METHODS DEVELOPED FOR THE DETERMINATION OF THE MARKER COMPOUNDS IN RECYCLED PAPER AND BOARD AND PET

## ANALYTICAL METHODS DEVELOPED FOR THE DETERMINATION OF THE MARKER COMPOUNDS IN RECYCLED PAPER AND BOARD AND PET

A summary and overview of the analytical methods that were developed for the marker compounds in P&B and PET is provided in Section 3 of the main report.

Section 3 of the main report provides information on the following:

a) Preparation of the samples
b) The preparation of the calibration standards
c) The HS-GC-MS and GC-MS instrumental conditions

This Appendix provides detailed information of the approach that was used to develop and validate the analytical methods that were based on these experimental conditions, and the validation data that was generated.

Once the methods had been validated successfully, they were used to generate data on the recycled P&B and PET samples that were provided by industry and these results are shown in Section 5 of the main report.

### 1. PROPERTIES AND CHARACTERISTICS OF THE ANALYTICAL METHODS

Consideration was given to the amount of development work that would be carried out for each of the analytical methods to ensure that they were fit for purpose. These are summarised below in Sections 1.1 and 1.2.

### 1.1 Recycled PET samples – Headspace GC-MS

Headspace conditions – time, temperature, injection parameters
Recovery from sample matrix
Detection limit
Limit of quantification
Precision
Linearity
Accuracy

### 1.2 Recycled P&B samples – Solvent extraction/GC-MS

Influence of sample size
Extraction conditions – solvent, temperature and time
Recovery from sample matrix
Detection limit
Limit of quantification
Precision
Linearity
Accuracy

## 2. WORK CARRIED OUT TO DEVELOP THE ANALYTICAL METHODS FOR THE FIVE MARKER COMPOUNDS IN PET

The initial intention was to develop and validate a single analytical method which was capable of the reliable detection and quantitation of the five marker compounds shown in Section 2.3 of the main report in a typical PET sample matrix.

However, the initial development showed that quantitative headspace analysis for monoethylene glycol (MEG) was unsuitable; therefore a separate method was developed and validated for MEG involving solvent extraction followed by direct injection Gas Chromatography with Mass Spectrometry (GC-MS) analysis – see Section 2.2 in this Appendix. This method was then further refined, as described in section 2.3.

A further method based on Headspace Gas Chromatography with Mass Spectrometry (HS-GC-MS) was developed for the remaining four marker compounds and is described in Section 2.1 below.

### 2.1 Headspace GC-MS

#### 2.1.1 Cryogenic Grinding of the sample

The PET samples have been ground cryogenically through a 2mm ring sieve to decrease the path length for desorption of target analytes.

### 2.1.2 Thermostat time.

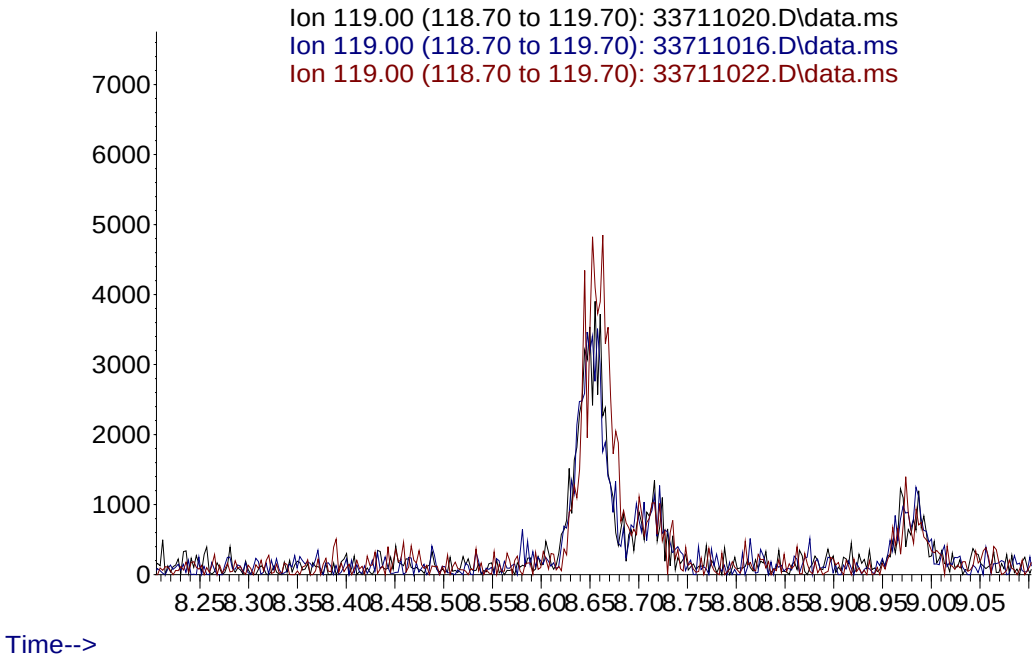
The experiment to assess thermostat times demonstrated that 60 minutes is sufficient to liberate the target compounds from the cryogenically ground PET matrix and there is no significant increase in response to extended thermostat times, see Table 1, below.

Table 1 - peak areas for replicate analyses of a ground PET sample using different thermostat times.

| Marker compound | Thermostat time | | |
|---|---|---|---|
| | 60 mins | 120 mins | 300mins |
| **acetaldehyde** | 6,067,770 | 6,126,628 | 6,965,427 |
| **methyl dioxolane** | 4,887,256 | 5,206,651 | 5,404,540 |
| **limonene** | 4,245,898 | 3,732,572 | 3,733,111 |

Note. Isopropyl toluene (IPT) has not been fully assessed due to it being present at a level which is barely detectable in this particular sample. Figure 4 shows the overlaid chromatograms displaying a diagnostic ion (m/z = 119) at the expected retention time for IPT, to demonstrate that it is detected at a constant level under the three chosen thermostat times.

**Figure 4 – overlays of IPT at different thermostat times**



### 2.1.3 Temperature

The thermostat temperature of 150°C for the method has been chosen based on the ASTM standard F2013-10 “Standard test method for the determination of residual acetaldehyde in polyethylene terephthalate bottle polymer” and the requirement to promote efficient desorption of the target compounds from the polymer matrix without causing degradation of the polymer. The ASTM standard F2013-10 states “the desorption conditions of 150°C for 60 minutes are such that no measurable AA [acetaldehyde] is generated by the sample during the desorption process”.

### 2.1.4 Injection parameters (time)

Because of the relatively wide boiling point range of the chosen PET marker compounds (more specifically the extremely high volatility of acetaldehyde with respect to the other compounds), optimal conditions with respect to column choice to suit all analytes was not possible on a single column, leading to use of alternative means of obtaining acceptable chromatographic performance. The short injection time setting chosen for the headspace sampler is a compromise between good chromatography (peak shape) for the low boiling compounds (particularly acetaldehyde) and analytical sensitivity.

### 2.1.5 Accuracy

The simplest choice of quantitative methodology using Headspace GC-MS is external standard calibration because this will allow a single vial of each sample to be analysed and quantified against a series of common standards prepared in separate vials, hence being quite efficient. However, it is usually the case that the response for a specific amount of a given compound in an otherwise empty vial will not be comparable to the response of the same amount of that compound in a vial which also contains sample material, therefore rendering the technique inaccurate. This was found to be the case for the four target compounds in a PET sample matrix and therefore external standard calibration was ruled out.

The next step was to assess standard addition calibration. The accuracy of the standard addition calibration method was initially assessed by performing Multiple Headspace Extraction (MHE) Static Headspace GC-MS on a selected sample, as well as ‘standard addition’ calibration Static Headspace GC-MS on the same sample and subsequently comparing the results.

MHE Static Headspace GC-MS is considered the gold standard for analysis by headspace, however it is quite inefficient for large sample numbers because the headspace from the same vial is analysed successively to provide an extrapolated 'total area', which, if the resulting curve can be described as linear, will negate the matrix effects associated with 'normal' headspace analysis. The intention of the comparison was to demonstrate that our standard addition Static Headspace GC-MS method did not suffer from adverse matrix effects and the results of our comparison of the techniques are shown in Table 2:

**Table 2 – comparison of quantitative headspace techniques**

| Compound | Amount (µg/g)* | | | % RSD |
|---|---|---|---|---|
| | MHE rep 1 | MHE rep 2 | Standard addition | |
| **acetaldehyde** | 4.21 | 3.90 | 3.87 | 4.7 |
| **methyl dioxolane** | 3.54 | 3.52 | 3.66 | 2.1 |
| **isopropyl toluene** | 0.05 | 0.05 | 0.05 | 2.5 |
| **limonene** | 0.80 | 0.77 | 0.84 | 4.6 |

* Reported to 2 D.P

An alternative method for assessment of accuracy involving dissolution and subsequent precipitation of the polymer, followed by analysis of the supernatant solution by direct injection GC-MS was also attempted (avoiding headspace analysis altogether). Unfortunately, a method and analytical column which could reliably separate and quantify all four target analytes, as well as the associated solvent peaks and impurities from the sample preparation, was not identified and so the assessment was reduced to comparison of the levels of limonene alone.

A freshly ground batch of sample was prepared and analysed both by the MHE Headspace GC-MS method and the dissolution/precipitation direct injection GC-MS method, the results are shown in Table 3:

**Table 3 – comparison of headspace GC-MS with direct injection GC-MS**

| Compound | Diss/precip. DI-GC-MS Amount (µg/g)* | MHE HS-GC-MS Amount (µg/g)* |
|---|---|---|
| limonene | 1.43 | 1.43 |

* Reported to 2 D.P

As can be seen, the dissolution/precipitation and MHE GC-MS method results for limonene agree. This, combined with the knowledge that the MHE results for all four compounds agree with the standard addition results for all four compounds suggests that the standard addition HS-GC-MS method is sufficiently accurate.

A further requirement was to provide a suitably efficient method, therefore the number of data points for the standard addition needed to be reduced (it is not efficient to prepare six separate vials for each sample, each with different levels of standard addition). The data for the standard addition method from only the lowest point (un-spiked sample) and the highest point (most concentrated addition) were used to calculate the level in the samples and then compared to the original results. The results obtained are shown in Table 4 and demonstrate that a 2-point standard addition HS-GC-MS method is acceptable.

**Table 4 – effect of reducing number of data points for standard addition quantification.**

| Compound | Amount (µg/g)* | |
|---|---|---|
| | **Std. Add. – 6 points** | **Std. Add – 2 points** |
| **acetaldehyde** | 3.87 | 4.02 |
| **methyl dioxolane** | 3.66 | 3.61 |
| **isopropyl toluene** | 0.05 | 0.04 |
| **limonene** | 0.84 | 0.95 |

* Reported to 2 D.P

### 2.1.6 Detection limit and Quantification limit

The detection limit (LOD) and quantification limit (LOQ) have been assessed via the calibration curves produced from the standard addition method with all 6 data points included.

LOD = 3.3 x SD/S
LOQ = 10 x SD/S
SD = Standard deviation of the slope
S = Slope of the calibration curve

**Table 5 – LOD and LOQ calculations**

| Compound | LOD (µg/g)* | LOQ (µg/g)* |
|---|---|---|
| acetaldehyde | 0.05 | 0.15 |
| methyl dioxolane | 0.02 | 0.07 |
| isopropyl toluene | 0.03 | 0.08 |
| limonene | 0.03 | 0.10 |

* Reported to 2 D.P

### 2.1.7 Precision

The precision of the method has not been fully investigated, however, three determinations on the same sample have been made comprising duplicates by the MHE technique, and a single replicate using the standard addition method, the results are summarised in table 2.

### 2.1.8 Linearity

The linearity of the method has been assessed by evaluation of the correlation coefficient ($R^2$) of the calibration curves produced by both the standard addition method and external standard method; the results are shown in table 6.

**Table 6 – linearity assessment**

| | correlation coefficient $R^2$ | |
|---|---|---|
| | **ext. std.** | **Std. Add.** |
| **acetaldehyde** | 1.000 | 0.999 |
| **methyl dioxolane** | 1.000 | 1.000 |
| **isopropyl toluene** | 0.999 | 1.000 |
| **limonene** | 0.999 | 1.000 |

## 2.2 Solvent Extraction GC-MS (for determination of MEG)

### 2.2.1 MEG analysis Background

The analysis of monoethylene glycol (MEG) in PET was initially intended to be carried out by Headspace Gas Chromatography with Mass Spectrometry (HS-GC-MS). However, it was soon identified that the accuracy and precision of the determination was unacceptable. Significant attempts were made to remedy the situation, involving derivatisation of the MEG into a more amenable form.

Common derivatisation (methylation) reactions for polar groups (e.g. using dimethyl sulphate) are known to be ineffective for ethylene glycol due to the close arrangement of the two hydroxyl groups, therefore derivatisation using phenylboronic acid was chosen to produce the volatile cyclic ester, ethylene glycol phenylboronate (phenyl-dioxaborolane). Unfortunately, after significant trial, the evidence obtained suggested that the derivatisation was incomplete as at times an underivatised MEG response was being detected alongside the derivatised compound.

A final decision was made to abandon analysis of the MEG by headspace and begin progress towards a direct injection method. In the first instance this was aimed at dissolution of the polymer, followed by subsequent precipitation and then analysis of the supernatant solution because of poor extraction characteristics of PET under normal solvent extraction conditions. However, it was soon discovered that the sample mass to solvent volume ratios required to achieve an acceptable method were difficult to handle for this kind of approach (i.e. dissolution/precipitation). Also, solvent choice was severely limited due to the fact that PET is insoluble at room temperature in almost all organic solvents with the exception of hexafluoroisopropanol, which brought its own challenges in the subsequent GC-MS analysis.

The next available option was to investigate the extraction of cryogenically ground PET under reflux in an aggressive organic solvent. Because the samples would already be cryogenically ground for the headspace analysis of the remaining four target compounds, there was no issue with the loss of efficiency in the sample preparation when including a grinding stage.

A sample known to contain residual MEG was selected and a ground portion was extracted under reflux in isopropanol (IPA) and then directly analysed by GC-MS using SIM detection targeting MEG. This approach appeared to be successful and was subsequently validated, as follows, however, it was later determined that the extraction of MEG from the PET sample was imprecise (See section 2.3).

### 2.2.2 Extraction time

The experiment to assess extraction time demonstrated that 7 hours is sufficient to liberate MEG from the cryogenically ground PET matrix in the extraction solvent to a state of equilibrium and there is no increase in response for extended extraction, as shown in Table 7.

**Table 7 – MEG response for replicate analyses of ground detergent bottle polymer sample using different extraction periods.**

| Value | 2hrs | 4hrs | 7hrs | 24hrs |
|---|---|---|---|---|
| Peak area | 836,446 | 942,147 | 1,034,978 | 1,014,385 |
| Percentage increase from 2hr extraction | N/A | 12.64% | 19.18% | 17.54% |

### 2.2.3 Accuracy

Five replicate samples of ground PET bottle were prepared and two of the replicates were spiked with known amounts of MEG. All five samples were subjected to equivalent reflux extractions and then analysed by GC-MS; the results are shown in Table 8 (the 'expected' column relates to the mean value determined in the triplicate un-spiked extracts, plus the known spike amount).

**Table 8 – Results of accuracy assessment for MEG**

| Sample ID | Amount (µg/mL)* | Expected (µg/mL)* | % recovery |
|---|---|---|---|
| Rep1 | 1.36 | N/A | N/A |
| Rep2 | 1.23 | N/A | N/A |
| Rep3 | 1.23 | N/A | N/A |
| Rep 4 (+ 1.29) | 2.34 | 2.56 | 91 % |
| Rep 5 (+ 6.47) | 6.90 | 7.74 | 89 % |

* Reported to 2 D.P

### 2.2.4 Precision

Replicate determinations (n=6) of the top, middle and bottom standard solutions were performed and the percent relative standard deviation (%RSD) was calculated for each, the results are shown in Table 9.

**Table 9 – Results of precision assessment for MEG**

| Value | 0.01 µg/mL Std. | 1 µg/mL Std. | 10 µg/mL Std. |
|---|---|---|---|
| **Mean area** | 19,915 | 570,922 | 5,903,184 |
| **STD DEV** | 527 | 8,524 | 114,587 |
| **%RSD** | 2.65% | 1.49% | 1.94% |

### 2.2.5 Linearity

The linearity of the method has been assessed by evaluation of the correlation coefficient ($R^2$) of the calibration curve ranging from 0.01 to 10-µg/mL. The calculated $R^2$ value is 0.9998.

### 2.2.6 Detection limit and Quantification limit

The lower detection limit (LOD) and lower quantification limit (LOQ) have been assessed via the calibration curve.

LOD = 3.3 x SD/S
LOQ = 10 x SD/S
SD = Standard deviation of the slope
S = Slope of the calibration curve

**Table 10 – LOD and LOQ assessment for MEG**

| Compound | LOD (µg/mL)* | LOQ (µg/mL)* |
|---|---|---|
| MEG | 0.02 | 0.07 |

* Reported to 2 D.P

**Note**. The LOD and LOQ figures are reported as weight per volume ('µg' of MEG per 'mL' of solvent). The sample masses and solvent volumes used for the validation herein (0.5g sample extracted in 50-mL solvent) will result in weight for weight (e.g. 'milligram' of MEG per 'kilogram' of PET sample) values ten-fold higher than the reported µg/mL values; however, concentration or dilution of the extract solutions prior to analysis will allow some adjustment of these limits to suit specific samples.

## 2.3 Revalidation of the Extraction methodology for MEG in PET

During the analysis of the first PET samples received for quantification of MEG, the method initially developed (which was based on reflux extraction of the PET samples in propan-2-ol - see section 2.2.1), was found to return irreproducible results. Significant efforts were made to amend the method in an attempt to control the imprecision, but to no avail.

An alternative approach was chosen based on Accelerated Solvent Extraction (ASE) of the samples, which involved sealing cryogenically ground sample in a stainless steel extraction cell and extracting with minimal solvent at significantly increased pressure and temperature than could be achieved using a traditional extraction technique. The results of the re-validation of the extraction are presented below.

### 2.3.1 Precision

The precision was initially found to be poor due to variations in the volume of the final extract produced by the ASE (the final volume is related to the overall void volume in the extraction cells and the integrity of the seals, which can vary sample to sample and cell to cell). It was found that inclusion of an internal standard in the extraction cell and adjustment of the extracts to a common volume before analysis improved the precision dramatically.

Six replicate extractions were performed using the ASE on a single, cryogenically ground and homogenised batch of ground PET. The six determinations were found to have a percent relative standard deviation (%RSD) of 1.8%.

### 2.3.2 Accuracy

The sample used for the n=6 precision determination was also used to determine the accuracy of the extraction.

Three replicate spiked extractions were prepared with a known amount of MEG added to the extraction cells immediately prior to sealing. Alongside this, three replicate extractions of Ottawa sand (i.e. no ground PET) were prepared, with an equivalent amount of MEG added as for the spiked extractions.

The mean result for the spiked sand was subtracted from the mean result of the spiked PET sample (to yield the amount of extractable MEG from the PET). The agreement between this value and the mean result from the n=6 precision determination was found to be 98.1%.

### 2.3.3 Calibration

The calibration was initially determined to be linear ($R^2$ = 0.998), however, upon injection of successive samples, the linearity deteriorated. It is thought that this was due to accumulation of semi- or non-volatile material in the GC inlet liner or column, leading to adsorption of the analyte. A good correlation could still be achieved by use of a $2^{nd}$ order polynomial calibration and calculating the response ratio to the internal standard, allowing accurate values to be derived for the calibration solutions when applied back to the curve.

It was found that more consistent results could be achieved by use of peak height measurement as opposed to peak area due to the assymetrical nature of the MEG peak. Use of peak height means that interferences eluting on the tail of the MEG peak are not contributing to the result and also, selection of the exact point at which the peak returns to baseline and subsequent placement of integration limits are not critical.

## 3. WORK CARRIED OUT TO DEVELOP THE ANALYTICAL METHODS FOR THE FIVE PAPER AND BOARD MARKER COMPOUNDS

The intention was to develop and validate a single analytical method which was capable of the reliable detection and quantitation of the five marker compounds, shown in Section 2.3 in the main report, in a typical P&B sample matrix.

A single method based on Solvent extraction of the samples followed by Gas Chromatography with Mass Spectrometry (GC-MS) was developed to allow all five marker compounds to be analysed simultaneously.

### 3.1 P&B Marker Compound Method Validation

#### 3.1.1 Solvent type

The best choice of solvent for extraction of the marker compounds from the paper and board (P&B) sample matrix was determined by extracting duplicate portions of a single cardboard sample into three 'GC amenable' solvents of differing polarities (namely propan-2-ol (IPA), dichloromethane (DCM) and hexane). The peak areas for each of the marker compounds detected in each of the extracts were mutually compared to reveal the best solvent choice. The results are shown in Table 11, below.

**Table 11 – Extraction solvent choice**

| | **(mean peak areas of duplicate determinations)** | | | | |
|---|---|---|---|---|---|
| **Solvent** | **BP** | **DIPN** | **DEHP** | **MK** | **DIBP** |
| DCM | 121,455 | 5,288,660 | 3,856,036 | 8,780 | 3,693,599 |
| IPA | 87,603 | 1,929,970 | 2,226,586 | 4,997 | 2,791,305 |
| Hexane | 24,613 | 1,154,542 | 3,264,856 | 6,840 | 2,789,648 |

BP = benzophenone
DIPN = diisopropyl naphthalene
DEHP = diethylhexyl phthalate
MK = Michlers Ketone
DIBP = diisobutylphthlate

It can be seen that DCM is the most effective solvent choice for all of the marker compounds.

### 3.1.2 Sample size

The particle size of the samples was investigated to assess the effect of surface area on the amount of each marker compound extracted from the P&B sample matrix. Duplicate extractions on three different sized sections of a single cardboard sample were performed using DCM as the extraction solvent. The results are shown in table 12.

**Table 12 – Effect of particle size on extraction efficiency**

| | **(mean peak areas of duplicate determinations)** | | | | |
|---|---|---|---|---|---|
| **Section size** | **BP** | **DIPN** | **DEHP** | **MK** | **DIBP** |
| Finely chopped | 231,507 | 3,272,116 | 3,976,369 | 15,967 | 3,008,287 |
| ~ 0.5cm$^2$ | 308,720 | 3,159,999 | 3,644,418 | 15,241 | 3,074,023 |
| ~ 2cm$^2$ | 169,482 | 3,294,911 | 3,773,305 | 14,494 | 2,909,907 |

BP = benzophenone
DIPN = diisopropyl naphthalene
DEHP = diethylhexyl phthalate
MK = Michlers Ketone
DIBP = diisobutylphthlate

It can be seen that there is no significant benefit to sectioning paper and board samples smaller than approximately 2cm$^2$.

**Note.** The apparently low response of benzophenone for the 2cm$^2$ sections is considered to be due to lack of precision in the determination (or possibly a lack of homogeneity of the distribution of benzophenone in the selected sample) as opposed to an effect of the section size. This is thought to be the case because the finely chopped sections do not also exhibit an increased response in comparison to the 0.5cm$^2$ sections.

### 3.1.3 Extraction conditions

Initially the temperature and time allowed to extract the marker compounds from the P&B sample matrix was investigated by preparing replicate vials containing a typical P&B sample immersed in solvent (DCM) and subjecting them to extraction at two temperatures for three different time periods; these were room temperature and 35°C for 1 hour, 6 hours and 24 hours, respectively. A maximum temperature of 35°C was chosen for safety reasons because the boiling point of the extraction solvent (DCM) is just under 40°C and the extraction is to take place in a sealed vessel.

In every case, the 35°C extracts showed a slightly increased response in comparison to the relevant room temperature extracts.

The diisopropylnaphthalene and two phthalate species had shown a plateau in their response after 6 hours at 35°C; however, the Michler's ketone and benzophenone responses were not constant, indicating that an investigation was required into longer extraction times.

Unfortunately, there was no sample of the same source used in the initial test remaining, so an alternative was collected and the revised extraction conditions of 35°C for 24 hours, 48 hours and 120 hours were investigated.

The initial results of the extended time test suggested that the responses for all compounds were not constant after 120-hours (contrary to the previous experiment which had shown a plateau after 6 hours for diisopropylnaphthalene and the two phthalate species). However, the response of the subsequent standard solutions (bracketing the sequence) showed a significant increase in response in comparison to the same standard solutions from the start of the sequence, indicating that the system (GC-MS) was being 'conditioned' by successive injection of sample extracts, leading to increasing sensitivity.

This effect had not been observed in previous development and validation work, and the most obvious change was the newly sourced sample material. Our suspicion was that there were components in the sample matrix of the new sample material that were dynamically affecting (increasing) the response for some target compounds throughout the sequence. Re-analysis of the extract solutions confirmed that the effect of increasing response throughout the sequence was still apparent upon analysis of the solutions in reverse order (long to short extraction times).

A series of compounds of similar characteristics to the target analytes were selected from Smithers Rapra's chemical store for use as internal standards in an attempt to control for the apparent conditioning effect, however, no compounds could be found which mimicked the behaviour of Michler's Ketone and benzophenone successfully.

The next step was to obtain isotopically labelled (deuterated) analogues of the target compounds. This was possible for all but Michler's Ketone and diisopropylnaphthalene. As alternatives, deuteronaphthalene was used for diisopropylnaphthalene, and deutero-aminoacetanilide was used for Michlers Ketone (aminoacetanilide and Michlers Ketone both contain similar functionality, comprising an amine, a ketone and an aromatic ring in their structure, so the assumption was that they would behave in a similar manner to each other).

The extraction conditions experiment was repeated a further time (with the inclusion of isotopically labelled internal standards) using the conditions of 35°C for 4, 24, 48 and 120 hours and the results are shown in Tables 13 to 17.

**Table 13 – Extraction conditions (Benzophenone)**

| Benzophenone | area (ISTD) | area (Analyte) | Ratio |
|---|---|---|---|
| 120hrs vial A | 464,950 | 1,045,414 | 2.25 |
| 120hrs vial B | 484,796 | 1,092,981 | 2.25 |
| 48hrs vial A | 433,529 | 967,848 | 2.23 |
| 48hrs vial B | 469,041 | 1,033,018 | 2.20 |
| 24hrs vial A | 422,216 | 911,074 | 2.16 |
| 24hrs vial B | 466,582 | 1,024,098 | 2.19 |
| 4hrs vial A | 319,237 | 633,552 | 1.98 |
| 4hrs vial B | 457,700 | 843,168 | 1.84 |
| Standard deviation | **52,690** | **148,813** | **0.15** |
| mean | **439,756** | **943,894** | **2.14** |
| % RSD | **11.98** | **15.77** | **6.92** |

**Table 14 – Extraction conditions (diisopropyl naphthalene)**

| diisopropyl naphthalene | area (ISTD) | area (Analyte) | Ratio |
|---|---|---|---|
| 120hrs vial A | 2,600,582 | 6,197,166 | 0.42 |
| 120hrs vial B | 2,573,688 | 6,191,735 | 0.42 |
| 48hrs vial A | 2,509,443 | 5,935,759 | 0.42 |
| 48hrs vial B | 2,546,343 | 6,030,252 | 0.42 |
| 24hrs vial A | 2,530,768 | 5,799,921 | 0.44 |
| 24hrs vial B | 2,547,412 | 6,208,017 | 0.41 |
| 4hrs vial A | 2,388,065 | 5,459,720 | 0.44 |
| 4hrs vial B | 2,578,601 | 5,915,329 | 0.44 |
| Standard deviation | **65,726** | **254,801** | **0.01** |
| mean | **2,534,363** | **5,967,237** | **0.43** |
| % RSD | **2.59** | **4.27** | **2.43** |

**Table 15 – Extraction conditions (diisobutylphthalate)**

| diisobutylphthalate | area (ISTD) | area (Analyte) | Ratio |
|---|---|---|---|
| 120hrs vial A | 917,796 | 4,051,990 | 0.23 |
| 120hrs vial B | 974,666 | 4,135,391 | 0.24 |
| 48hrs vial A | 867,668 | 3,784,361 | 0.23 |
| 48hrs vial B | 926,721 | 3,924,369 | 0.24 |
| 24hrs vial A | 862,376 | 3,596,312 | 0.24 |
| 24hrs vial B | 946,744 | 3,901,131 | 0.24 |
| 4hrs vial A | 707,289 | 2,977,974 | 0.24 |
| 4hrs vial B | 924,912 | 3,526,265 | 0.26 |
| Standard deviation | **83,122** | **370,819** | **0.01** |
| mean | **891,022** | **3,737,224** | **0.24** |
| % RSD | **9.33** | **9.92** | **4.56** |

**Table 16 – Extraction conditions (diethylhexyl phthalate)**

| diethylhexyl phthalate | area (ISTD) | area (Analyte) | Ratio |
|---|---|---|---|
| 120hrs vial A | 1,514,877 | 3,932,636 | 0.39 |
| 120hrs vial B | 1,628,258 | 4,197,880 | 0.39 |
| 48hrs vial A | 1,481,046 | 4,551,926 | 0.33 |
| 48hrs vial B | 1,605,886 | 4,101,504 | 0.39 |
| 24hrs vial A | 1,492,110 | 3,919,044 | 0.38 |
| 24hrs vial B | 1,610,790 | 5,236,101 | 0.31 |
| 4hrs vial A | 1,296,749 | 3,399,820 | 0.38 |
| 4hrs vial B | 1,569,144 | 3,992,773 | 0.39 |
| Standard deviation | **108,053** | **538,744** | **0.03** |
| mean | **1,524,858** | **4,166,461** | **0.37** |
| % RSD | **7.09** | **12.93** | **8.96** |

**Table 17 – Extraction conditions (Michler's Ketone)**

| Michler's Ketone | area (ISTD) | area (Analyte) | Ratio |
|---|---|---|---|
| 120hrs vial A | 131,676 | 38,610 | 3.41 |
| 120hrs vial B | 393,908 | 47,781 | 8.24 |
| 48hrs vial A | 334,145 | 32,136 | 10.40 |
| 48hrs vial B | 606,549 | 38,344 | 15.82 |
| 24hrs vial A | 378,771 | 24,089 | 15.72 |
| 24hrs vial B | 603,998 | 32,901 | 18.36 |
| 4hrs vial A | 1,067,914 | 14,671 | 72.79 |
| 4hrs vial B | 2,031,079 | 21,387 | 94.97 |
| Standard deviation | **606,920** | **10,722** | **34.14** |
| mean | **693,505** | **31,240** | **29.96** |
| % RSD | **87.51** | **34.32** | **113.92** |

It can be seen that no significant increase in response is obtained for any compounds by extracting for greater than 24 hours at 35°C, with the exception of Michler's Ketone, which exhibited a gentle increase in response with no plateau after 120 hours extraction. However, the increase in response is not considered significant in light of the poor precision observed for this compound.

It is apparent that the internal standard chosen for Michler's ketone is unsuitable. An isotopically labelled analogue of Michler's ketone could not be sourced; neither could a suitable, closely related compound be identified. Therefore, the final method will exclude an internal standard for Michler's ketone.

### 3.1.4 Linearity

The linearity of the method has been assessed by evaluation of the correlation coefficient ($R^2$) of the individual calibration curves, the results are shown in Table 18.

All calibration curves were constructed from peak area ratio (to the appropriate internal standard) versus solution concentration (µg/mL), except for Michler's ketone, which was constructed from raw peak area (no ratio to internal standard) versus solution concentration (µg/mL).

**Table 18 - linearity assessments for marker compounds in P&B**

| Compound | Linearity ($R^2$) | Range (µg/mL) |
|---|---|---|
| benzophenone | 0.9997 | 0.010 to 5.150 |
| diisopropyl naphthalene | 0.9999 | 0.010 to 5.050 |
| diethylhexyl phthalate | 0.9994 | 0.024 to 11.750 |
| Michlers Ketone | 0.9991* | 0.050 to 26.40 |
| diisobutylphthalate | 0.9998 | 0.015 to 7.450 |

*****The calibration curve for Michler's Ketone exhibited a second order polynomial regression. The square root of the acquired area values were taken to produce the linear calibration plot.

### 3.1.5 LOD and LOQ

The lower detection limit (LOD) and lower quantification limit (LOQ) have been assessed via the calibration curves.

LOD = 3.3 x SD/S
LOQ = 10 x SD/S
SD = Standard deviation of the slope
S = Slope of the calibration curve

**Table 19 – LOD and LOQ assessment for marker compounds in P&B**

| Compound | LOD (µg/mL)* | LOQ (µg/mL)* |
|---|---|---|
| benzophenone | 0.03 | 0.08 |
| diisopropyl naphthalene | 0.01 | 0.04 |
| diethylhexyl phthalate | 0.04 | 0.11 |
| Michler's Ketone | 0.21 | 0.37 |
| diisobutylphthalate | 0.02 | 0.07 |

* Reported to 2 D.P.

**Note.** The LOD and LOQ figures are reported as weight per volume ('µg' of analyte per 'mL' of solvent). The sample masses and solvent volumes used for the validation herein (2g sample extracted in 25-mL solvent) will result in weight for weight (e.g. 'milligram' of analyte per 'kilogram' of P&B sample) values 12.5 times greater than the reported µg/mL values; however, concentration or dilution of the extract solutions prior to analysis will allow some adjustment of these limits to suit specific samples.

### 3.1.6 Precision

The precision of the method was assessed by replicate (n=6) injections of the high, middle and low concentration standard solutions (standards 1, 4 and 7 respectively – see Section 3 of the Main Report) and calculating the percent relative standard deviation of the response for each compound.

The area ratio to the appropriate internal standard was used for each compound with the exception of Michler's ketone, where the raw peak area (no ratio to internal standard) was used.

The results of the precision assessment are shown in Table 20, below.

**Table 20 –precision of n=6 replicates of standards**

| Compound | Standard 1 | Standard 4 | Standard 7 |
|---|---|---|---|
| | (%RSD) | (%RSD) | (%RSD) |
| Michlers Ketone | 8.38 | 2.98 | 8.17 |
| diisobutyl phthalate | 1.01 | 1.14 | 6.62 |
| diethylhexyl phthalate | 0.86 | 1.74 | 21.59 |
| diisopropylnaphthalene | 1.29 | 0.86 | 3.01 |
| Benzophenone | 3.23 | 0.83 | 1.37 |

### 3.1.7 Accuracy

The accuracy of the method was assessed by preparing extracts of copier paper samples alongside further copier paper sample extracts, spiked with known amounts of the marker compounds at low and high concentrations within the linear range for each compound (as determined in Section 2.5). The extracts were all prepared in duplicate. Copier paper was chosen because it represents a typical paper and board sample matrix as well as being relatively free from the marker compounds.

The results of the accuracy assessments are shown in Tables 21 to 25.

**Table 21 – Accuracy assessment results for benzophenone**

| Sample ID | Expected Conc. (µg/mL) | Acquired Conc. (µg/mL) | % Error | Difference (µg/mL) |
|---|---|---|---|---|
| D-ISTD | N/A | 0.006 | N/A | N/A |
| D-ISTD | N/A | 0.004 | N/A | N/A |
| D-ISTD + 0.10µg/mL | 0.11 | 0.10 | -5.97% | -0.01 |
| D-ISTD + 0.10µg/mL | 0.11 | 0.10 | -7.93% | -0.01 |
| D-ISTD + 5.15µg/mL | 5.16 | 4.80 | -6.90% | -0.36 |
| D-ISTD + 5.15µg/mL | 5.16 | 4.67 | -9.42% | -0.49 |

**Table 22 – Accuracy assessment results for diisopropylnaphthalene**

| Sample ID | Expected conc. (µg/mL) | conc. (µg/mL) | % Error | Difference (µg/mL) |
|---|---|---|---|---|
| D-ISTD | N/A | - | N/A | N/A |
| D-ISTD | N/A | - | N/A | N/A |
| D-ISTD + 0.10µg/mL | 0.10 | 0.09 | -10.44% | -0.01 |
| D-ISTD + 0.10µg/mL | 0.10 | 0.09 | -9.97% | -0.01 |
| D-ISTD + 5.05µg/mL | 5.05 | 5.04 | -0.28% | -0.01 |
| D-ISTD + 5.05µg/mL | 5.05 | 5.10 | 1.03% | 0.05 |

**Table 23 – Accuracy assessment results for diisobutyl phthalate**

| Sample ID | Expected conc. (µg/mL) | Conc. (µg/mL) | % Error | Difference (µg/mL) |
|---|---|---|---|---|
| D-ISTD | N/A | 0.004 | N/A | N/A |
| D-ISTD | N/A | 0.002 | N/A | N/A |
| D-ISTD + 0.74µg/mL | 0.74 | 0.77 | 3.82% | 0.03 |
| D-ISTD + 0.74µg/mL | 0.74 | 0.77 | 3.68% | 0.03 |
| D-ISTD + 7.45µg/mL | 7.45 | 7.33 | -1.53% | -0.11 |
| D-ISTD + 7.45µg/mL | 7.45 | 7.21 | -3.14% | -0.23 |

**Table 24 – Accuracy assessment results for diethylhexyl phthalate**

| Sample ID | Expected conc. (µg/mL) | Conc. (µg/mL) | % Error | Difference (µg/mL) |
|---|---|---|---|---|
| D-ISTD | N/A | -0.06 | N/A | N/A |
| D-ISTD | N/A | -0.06 | N/A | N/A |
| D-ISTD + 1.18µg/mL | 1.12 | 1.11 | -0.73% | -0.01 |
| D-ISTD + 1.18µg/mL | 1.12 | 1.10 | -1.40% | -0.02 |
| D-ISTD + 11.75µg/mL | 11.69 | 10.66 | -8.85% | -1.04 |
| D-ISTD + 11.75µg/mL | 11.69 | 10.70 | -8.53% | -1.00 |

**Table 25 – Accuracy assessment results for Michler's ketone**

| Sample ID | Expected conc. (µg/mL) | Conc. (µg/mL) | % Error | Difference (µg/mL) |
|---|---|---|---|---|
| D-ISTD | N/A | 0.50 | N/A | N/A |
| D-ISTD | N/A | 0.50 | N/A | N/A |
| D-ISTD + 2.64µg/mL | 3.14 | 1.99 | -36.56% | -1.15 |
| D-ISTD + 2.64µg/mL | 3.14 | 2.12 | -32.61% | -1.02 |
| D-ISTD + 26.40µg/mL | 26.90 | 28.10 | 4.47% | 1.20 |
| D-ISTD + 26.40µg/mL | 26.90 | 29.31 | 8.98% | 2.41 |

## 4. CONCLUSIONS

### 4.1 PET

The work carried out has been successful in developing a headspace GC-MS method for the detection and quantification of the following four marker compounds in PET.

a) Acetaldehyde
b) 2-methyl-1,3-dioxolane
c) Limonene
d) 4-iso-propyl toluene

This headspace GC-MS method could not be used successfully for the remaining marker compound, MEG, and so a direct injection GC-MS method using Accelerated Solvent Extraction (ASE) has been developed for the detection and quantification of this compound in PET.

These two methods were used to identify and quantify these five marker compounds in samples of recycled PET.

### 4.2 Paper and Board

The work carried out during this project has been successful in developing a direct injection GC-MS method for the detection and quantification of the following five marker compounds in Paper and Board.

a) Benzophenone
b) Diisobutyl phthalate
c) Diisopropyl naphthalenes
d) Di-2-ethylhexyl phthalate (DEHP)
e) Michlers ketone

This method was used to identify and quantify these five marker compounds in samples of recycled Paper and Board.

End of Report

# Smithers Rapra

**CONDITIONS OF BUSINESS (the "Conditions")**

**DEFINITIONS**

**"Smithers Rapra"** means Smithers Rapra and Smithers Pira Limited (registration number: 5761324 and whose registered office is at Shrewsbury Road, Shawbury, Shropshire, SY4 4NR), trading as Smithers Rapra;
**"Client"** means the person(s), firm or company who purchases the Goods and/or Services from Smithers Rapra;
**"Conditions"** means the terms and conditions set out in this document as amended from time to time;
**"Contract"** means any contract between Smithers Rapra and the Client for the sale and purchase of Goods and/or provision of Services, incorporating these Conditions;
**"Goods"** means any goods agreed in the Contract to be supplied to the Client by Smithers Rapra (including any parts of them);
**"Intellectual Property Rights"** means any patent, registered design, copyright (including rights in software), design right, database right, moral right, trade mark, service mark, domain name, rights in confidential information and all similar property rights anywhere in the world in each case whether registered or not and including any application for registration of the foregoing;
**"Order"** means in the Client's purchase order form, the Client's written acceptance of Smithers Rapra's quotation or overleaf, as the case may be;
**"Services"** means any services agreed in the Contract to be supplied to the Client by Smithers Rapra;
**"Work"** means Goods and Services;
**"Working Day"** means a day (other than a Saturday or Sunday) on which the banks are ordinarily open for business in the City of London.

**FORMATION OF CONTRACT**

1.1 All quotations are made and all orders are accepted subject to the following conditions. All other terms, conditions or warranties whatsoever (including any terms or conditions which the Client purports to apply under any purchase order, confirmation, specification or other document whatsoever and whenever) are excluded from any contract between the parties unless expressly accepted by Smithers Rapra in writing.

1.2 Without prejudice to Smithers Rapra's right not to accept an order, quotations shall be available for acceptance for a maximum period of 20 Working Days from the dates thereof.

1.3 If any statement or representation has been made to the Client by Smithers Rapra, or its employees upon which the Client relies (other than in the documents enclosed with Smithers Rapra's quotation) then the Client must set out that statement or representation in a document to be attached to the return copy of the quotation and in any such case Smithers Rapra may accept or reject the same and/or submit a new quotation.

1.4 Each Order for Work by the Client from Smithers Rapra shall be deemed to be an offer by the Client to purchase Work in accordance with these Conditions. Smithers Rapra hereby objects to any additional, contradictory or different terms contained in any initial or subsequent order or communication from the Client pertaining to the Work. Any notice by the Client objecting to these Conditions must be in writing separate from any form purchase order. Smithers Rapra's failure to object specifically to provisions contained in any communication from the Client shall not be deemed a waiver of the provisions contained in these Conditions.

1.5 No Order placed by the Client shall be deemed accepted by Smithers Rapra until a written acknowledgement of order is issued by Smithers Rapra or the Client supplies materials, products or information pursuant to the quotation, whichever is the earlier at which point the Contract shall come into existence. The Client shall ensure that the terms of the Order and any relevant specification are complete and accurate.

**PRICES**

2.1 The price for the Goods is, unless otherwise stated, quoted exclusive of all costs or charges in relation to packaging, labelling, loading, unloading, carriage, freight and insurance all of which amounts the Client will pay, where appropriate, in addition when it is due to pay for the Goods.

2.2 The price for the Work is exclusive of amounts in respect of value added tax ("VAT") or other similar taxes or levies. The Client shall, on receipt of a valid VAT invoice from Smithers Rapra, pay to Smithers Rapra such additional amounts in respect of VAT as are chargeable on the supply of the Work.

2.3 All requests for variations or addition to the Work must be made by the Client in writing. In the event of any variation or addition being so requested and agreed to by Smithers Rapra, Smithers Rapra shall be entitled to make an adjustment to the contract price fairly reflecting such variation or addition.

2.4 Smithers Rapra may, by giving notice to the Client at any time up to 5 Working Days before delivery, increase the price of the Goods to reflect any increase in the cost of the Goods that is due to:
(a) any factor beyond Smithers Rapra's control (including foreign exchange fluctuations, increases in taxes and duties, and increases in labour, materials and other manufacturing costs);
(b) any request by the Client to change the delivery dates, quantities or types of Goods ordered; or
(c) any delay caused by any instructions of the Client or failure of the Client to give Smithers Rapra adequate or accurate information or instructions.

2.5 All prices quoted are valid for 20 Working Days from the date of the quote. For non Sterling quotes, Smithers Rapra reserves the right to adjust reasonably for changes in exchange rate.

2.6 The price for the Work shall be the price set out in the Order.

**DELIVERY AND ACCEPTANCE OF GOODS**

3.1 Unless otherwise agreed in writing by Smithers Rapra delivery of the Goods shall take place at Smithers Rapra's place of business in normal business hours and the Client shall collect the Goods within 5 Working Days of Smithers Rapra giving the Client notice that the Goods are ready for collection.

3.2 Any dates specified by Smithers Rapra for delivery of the Work are intended to be an estimate only and time for delivery shall not be of the essence. If no dates are so specified, delivery will be within a reasonable time. Delivery of the Goods shall be completed on the completion of the loading of the Goods at Smithers Rapra's place of business.

3.3 If for any reason the Client does not accept delivery of any of the Goods within 5 Working Days of Smithers Rapra giving the Client notice that the Goods are ready for collection, or Smithers Rapra is unable to deliver the Goods on time because the Client has not provided appropriate instructions, documents, licences or authorisations then:
(a) the Goods shall be deemed to have been delivered at 9.00am on the fifth Working Day following the day on which Smithers Rapra notified the Client that the Goods were ready for collection;
(b) risk in the Goods passes to the Client (including for loss or damage caused by the Client's negligence); and
(c) Smithers Rapra may: (a) store the Goods until actual delivery whereupon the Client will be liable for all related costs and expenses (including without limitations storage and insurance); or (b) sell the Goods at the best price readily obtainable and (after deduction of all reasonable storage and selling expenses) charge the Client for any shortfall below the Contract price.

3.4 Where applicable, the Client will provide at its expense at the place of delivery adequate and appropriate equipment and manual labour for loading the Goods.

3.5 If Smithers Rapra delivers to the Client a quantity of Goods of up to 5% more or less than the quantity ordered by the Client, the Client shall not be entitled to object to or reject the Goods or any of them by reason of the surplus or shortfall and shall pay for the Goods delivered at the pro rata Contract rate.

3.6 Smithers Rapra shall be entitled at its discretion to make delivery of the Goods by instalments and to invoice the Client for each instalment individually. Where the Goods are to be delivered in instalments, each delivery shall constitute a separate contract and failure by Smithers Rapra to deliver any one or more of the instalments in accordance with these Conditions or any claim by the Client in respect of any one or more of the instalments in accordance with these Conditions or any claim by the Client in respect of any one or more instalments shall not entitle the Client to treat the Contract as a whole as repudiated or to refuse to accept subsequent instalments.

3.7 The Client shall be deemed to have accepted the Goods as being in accordance with the Contract unless:
(a) within 14 days of the date of delivery of the Goods, the Client notifies Smithers Rapra in writing of any defect or other failure of the Goods to conform with the Contract (which would be apparent upon reasonable inspection and testing of the Goods within 14 days);
(b) or the Client notifies Smithers Rapra in writing of any defect or other failure of the Goods to conform with the Contract within a reasonable time where the defect or failure would not be so apparent within 14 days of the date of delivery, failing which the Client shall not be entitled to reject the Goods and Smithers Rapra shall have no liability for such defect or failure, and the Client shall be bound to pay the Contract price as if the Goods had been delivered in accordance within the Contract.

3.8 Goods, once delivered, may not be returned unless their return is agreed in advance in writing by the Client, and subject to the following conditions:
(a) Goods are returned in a new and unused condition;
(b) any packaging remains unbroken and in reasonable condition;
(c) returns are made within 3 weeks of delivery of the Goods, all transport and other redelivery costs of whatever nature are paid by the Client;
(d) returned Goods shall be accompanied by a written record of invoice number, date and a note of reasons for their return.

3.9 Smithers Rapra shall not be liable for any loss (including loss of profit), costs, damages, charges or expenses caused directly or indirectly by any delay in the delivery of the Goods (even if caused by Smithers Rapra's negligence), nor will any delay entitle the Client to terminate or rescind the Contract.

3.10 Smithers Rapra shall only be liable for the non-delivery of Goods (even if caused by Smithers Rapra's negligence) if the Client gives written notice to Smithers Rapra within 10 Working Days of the date when the Goods would, in the ordinary course of events, have been delivered.

3.11 If the Client gives notice to Smithers Rapra in accordance with Condition 3.10, the liability of Smithers Rapra for non-delivery of the Goods shall be limited to replacing the Goods within a reasonable time or issuing a credit note at the pro rata Contract rate against any invoice raised for such Goods.

**PASSING OF RISK AND LEGAL TITLE**

4.1 The Goods shall be at the risk of the Client on completion of delivery.

4.2 Full legal, beneficial and equitable title to and property in the Goods shall remain vested in Smithers Rapra (even though it has been delivered and risk has passed to the Client) until:
(a) payment in full, in cash or cleared funds, for all of the Goods has been received by Smithers Rapra; and
(b) all other money payable by the Client to Smithers Rapra on any other account or under the Contract or any other contract has been received by Smithers Rapra.

4.3 Until full legal, beneficial and equitable title to and property in the Goods passes to the Client:
(a) the Client shall hold the Goods on a fiduciary basis as Smithers Rapra's bailee;
(b) the Client shall keep the Goods at its premises in a proper manner in conditions which adequately protect and preserve the Goods and shall insure them against all risks for their full price from the date of delivery, without any charge to Smithers Rapra, and not tamper with any identification upon the Goods or their packaging and shall ensure that they are stored separately from any other Goods (whether or not supplied by Smithers Rapra) and are clearly identifiable as belonging to Smithers Rapra and Smithers Rapra shall be entitled to examine any such Goods in storage at any time during normal business hours upon giving the Client reasonable notice of its intention to do so;
(c) provided that the Client has not resold or irrevocably incorporated the Goods into another product as authorised to do so by Smithers Rapra, Smithers Rapra may at any time, on demand and without prior notice, require the Client to deliver the Goods up to Smithers Rapra and Smithers Rapra may repossess and resell the Goods if the Client fails to comply with the conditions specified in Condition 4.2 or becomes subject to any of the events listed in Condition 12;
(d) for the purposes of this Condition 4 Smithers Rapra, its employees, agents and subcontractors shall be entitled to free and unrestricted access to any premises owned, occupied or controlled by the Client and/or any other location where any of the Goods are situated at any time without prior notice;
(e) Smithers Rapra shall be entitled to maintain an action against the Client for the price of the Goods notwithstanding that legal, equitable and beneficial title to and property in the Goods has not passed to the Client; and
(f) Smithers Rapra hereby authorises the Client to use and/or sell the Goods in the normal course of the Client's business and to pass good title in the Goods to its clients, if they are purchasers in good faith without notice of Smithers Rapra's rights. This right shall automatically cease on the occurrence of any event set out in Condition 12 and/or if any sum owed to Smithers Rapra by the Client is not paid when due. If the Client sells the Goods prior to paying the full price thereof the Client shall hold the proceeds of sale on trust for Smithers Rapra and shall immediately pay the proceeds of the sale into a separate bank account. At Smithers Rapra's request, the Client shall assign to Smithers Rapra all claims that the Client may have against purchasers of the Goods from the Client.

4.4 Smithers Rapra's rights and remedies set out in this Condition 4 are in addition to and shall not in any way prejudice, limit or restrict any of Smithers Rapra's other rights or remedies under the Contract or in law or equity.

**PROVISION OF SERVICES**

5.1 Smithers Rapra shall provide the Services to the Client and shall use all reasonable endeavours to meet any performance dates for the Services specified in the Order, but any such dates shall be estimates only and time shall not be of the essence for the performance of the Services.

5.2 Where Smithers Rapra is to perform Services at the Client's premises, the Client shall procure safe access to the premises and the provision of adequate power, lighting, heating and other such facilities or supplies for Smithers Rapra's employees or agents in accordance with the demands of any applicable legislation and as Smithers Rapra shall reasonably require.

**PAYMENT**

6.1 Smithers Rapra may invoice the Client for the Goods on or at any time after the completion of delivery. Unless otherwise agreed by Smithers Rapra in writing the payment by the Client shall be due 20 Working Days from receipt of invoice by the Client, which shall be deemed to be two Working Days after posting. In respect of Services Smithers Rapra may submit interim invoices in respect of each stage of Work completed for the Client.

6.2 Time for payment shall be of the essence. No payment shall be deemed to have been received until Smithers Rapra has received cleared funds.

6.3 Notwithstanding any other provision, all payments payable to Smithers Rapra under the Contract shall become due immediately upon termination of this Contract for whatever reason.

6.4 The Client shall make all payments due under the Contract without any deduction whether by way of set-off, withholding, counterclaim, discount, abatement or otherwise unless the Client has a valid court order requiring an amount equal to such deduction to be paid by Smithers Rapra to the Client.

6.5 If payments received from the Client are not stated to refer to a particular invoice, Smithers Rapra may appropriate such payment to any outstanding invoice addressed to the Client from Smithers Rapra.

6.6 No indulgence granted by Smithers Rapra to the Client concerning the Client's obligations under this Clause 6 shall be or be deemed to be a credit facility but if any such facility is granted to the Client by Smithers Rapra, Smithers Rapra may withdraw it at its sole discretion at any time.

6.7 Smithers Rapra reserves the right to vary the payment terms of this Contract in the event that it considers payment in advance (in part or whole) is necessary.

6.8 No disputes arising under the Contract nor delays beyond the reasonable control of Smithers Rapra shall interfere with prompt payment in full by the Client.

6.9 In the event of default in payment by the Client Smithers Rapra shall be entitled at its option to treat the whole Contract as repudiated by the Client or to suspend all further Work on any contract or contracts between Smithers Rapra and the Client without notice and to charge interest on any amount outstanding at the rate of 8% per annum above the base rate of National Westminster Bank plc in force at the time when payment was due. Such interest shall accrue on a daily basis from the due date of actual payment of the overdue amount, whether before or after judgment. The Client shall pay the interest together with the overdue amount.

6.10 The Client shall also pay Smithers Rapra's cost of collection (including legal fees and disbursements). Payments received may be applied by Smithers Rapra against any obligation owed by the Client to Smithers Rapra. Smithers Rapra may refuse or delay further Services if the Client fails to pay promptly any amounts due to Smithers Rapra.

**COMPLETION/CANCELLATION**

7.1 Time for completion of Work for the Contract is not of the essence but is given as accurately as possible but is not guaranteed. The Client shall have no right to damages, to reject the Work and/or to cancel the Order for failure for any cause to meet any time stated for completion of Work.

7.2 Any estimate of the date of completion of Work shall in every case be dependent upon prompt receipt of all necessary information, samples, instructions or approvals from the Client. Variations or additions to the Work requested by the Client may result in delay in completion.

7.3 Either party may cancel the Contract on 30 days' written notice to the other on condition that all costs and expenses incurred by Smithers Rapra up to the time of cancellation and, where cancellation is at the insistence of the Client, all loss of profits and other loss or damage resulting to Smithers Rapra by reason of such cancellation, shall be paid forthwith by the Client to Smithers Rapra.

**WARRANTY AND WARRANTY LIMITATIONS**

8.1 Smithers Rapra warrants that all Services will be performed in a reasonable timely and workmanlike manner and in material conformity with the agreed upon specifications. If the Client establishes to Smithers Rapra's reasonable satisfaction that there is a defect in the materials or workmanship of the Services, if the Services have not been performed with reasonable care and skill, or there is some other failure by Smithers Rapra in relation to the Services the Client's sole and exclusive remedy shall be reperformance of the Services in question by Smithers Rapra at no additional cost to the Client. If re-performance is impossible or impractical, Smithers Rapra may, at its sole discretion, refund to the Client a proportion of the fees (to be determined at Smithers Rapra's sole discretion) attributable to the defective Services in question. This Condition 8.1 shall not apply unless the Client notifies Smithers Rapra in writing of the alleged defect within 7 days of the time when the Client discovers or ought to have discovered the defect and in any event within 3 months of the performance of Services to the Client or such other periods as agreed by Smithers Rapra in writing.

8.2 If Smithers Rapra elects to re-perform the Services pursuant to Condition 8.1, Smithers Rapra shall re-perform the Services for the Client at Smithers Rapra's own expense.

8.3 Smithers Rapra warrants that on delivery the Goods shall:

(a) conform in all material respects with their description and any applicable specification; and

(b) be free from material defects in design, material and workmanship.

8.4 Subject to Condition 8.5, if:

(a) the Client gives notice in writing to Smithers Rapra within a reasonable time of discovery that some or all of the Goods do not comply with the warranty set out in Condition 8.3;

(b) Smithers Rapra is given a reasonable opportunity of examining such Goods; and

(c) the Client (if asked to do so by Smithers Rapra) returns such Goods to Smithers Rapra's place of business at the Client's cost

Smithers Rapra shall, at its option, repair or replace the defective Goods, or refund the price of the defective Goods in full.

8.5 Smithers Rapra shall not be liable for Goods' failure to comply with the warranty set out in Condition 8.4, if:

(a) the Client makes any further use of such Goods after giving notice in accordance with Condition 8.5; or

(b) the defect arises because the Client failed to follow Smithers Rapra's oral or written instructions as to the storage, commissioning, installation, use and maintenance of the Goods or (if there are none) good trade practice; or

(c) the defect arises as a result of Smithers Rapra following any drawing, design or specification supplied by the Client; or

(d) the Client alters or repairs such Goods without Smithers Rapra's written consent; or

(e) the defect arises as a result of fair wear and tear, wilful damage, negligence, or abnormal storage or working conditions.

8.6 Except as provided in this Condition 8, Smithers Rapra shall have no liability to the Client in respect of the Goods' failure to comply with the warranty set out in Condition 8.3.

8.7 Conditions 8.4 to 8.7 shall apply to any repaired or replacement Goods supplied by Smithers Rapra.

8.8 Except as provided in this Condition 8, all warranties, conditions or other terms implied by statute or common law, whether written or oral, are to the fullest extent permitted by law excluded from the Contract.

8.9 Smithers Rapra shall be under no liability under the warranties contained in this Condition:

(a) in respect of any defect arising from fair wear and tear, wilful damage, negligence, abnormal working conditions, failure to follow Smithers Rapra's instructions (whether oral or in writing), misuse or alteration or repair of the Work without Smithers Rapra's approval;

(b) if the total price for the Work or Services has not been paid by the due date for payment;

(c) for any Work manufactured or appropriated to the Contract in accordance with any design, specification, instruction or recommendation made to Smithers Rapra by the Client or for any Services provided in accordance with specifications, instructions or recommendation issued by the Client;

(d) in respect of any type of defect, damage or wear specifically excluded by Smithers Rapra by notice in writing; or

(e) if the Client makes any further use of the Work after giving notice in accordance with Condition 8.1.

**LIABILITY/INDEMNIFICATION**

9.1 This Condition 9 together with Condition 3 and Condition 8 set out the entire liability of Smithers Rapra (including any liability for the acts or omissions of its subcontractors and any member of its group) in respect of any breach of these Conditions or the Contract and any representation, statement or tortuous act or omission including negligence arising under or in connection with the Contract.

9.2 Nothing in these Conditions shall exclude or limit Smithers Rapra's liability for:

(a) death or personal injury caused by Smithers Rapra's negligence, or the negligence of its employees, agents or sub-contractors (as applicable);

(b) fraud or fraudulent misrepresentation;

(c) breach of the terms implied by section 12 of the Sale of Goods Act 1979;

(d) any matter in respect of which it would be unlawful for Smithers Rapra to exclude or restrict liability.

9.2 Smithers Rapra is not responsible for the performance, adequacy, or safety of any material, product, or process of the Client being tested or evaluated by Smithers Rapra. Smithers Rapra is not responsible for the Client's use of the information or concepts generated as part of the Services, and shall not be liable for any loss or damage resulting from such use.

9.3 Subject to Condition 9.2 Smithers Rapra shall not be liable to the Client, whether in contract, tort (including negligence), breach of statutory duty, or otherwise, for any loss of profit or indirect or consequential loss arising under or in connection with the Contract.

9.4 The Client agrees to indemnify and hold harmless Smithers Rapra and each of its affiliates and their respective shareholders, directors, officers, employees, and agents (collectively the "Indemnified Parties") from and against any and all claims, liabilities, damages, and expenses, including, without limitation, legal fees, consultant's fees, costs of investigation and disbursements, incurred by any Indemnified Party as a result of or in connection with (a) the Client's breach of the Contract, (b) any attempt to impose upon an Indemnified Party any responsibility, liability, or obligation which under the terms of the Contract is not to be a

responsibility, liability, or obligation of Smithers Rapra and/or its affiliates, or (c) a product, service, process, operation, or activity of the Client.

9.5 Subject to Condition 9.2, Smithers Rapra's total aggregate liability to the Client arising out of, or in connection with the performance or contemplated performance of this Contract and any other agreements between the Client and Smithers Rapra whether in contract, tort (including negligence), breach of statutory duty or otherwise shall in no event exceed [£500,000] in any Year] [the Contract Price].

9.6 The price of the Work has been calculated on the basis that Smithers Rapra will exclude or limit its liability as set out in these Conditions and the Client by placing an Order agrees and warrants that the Client shall insure against or bear itself any loss for which Smithers Rapra has excluded or limited its liability in these Conditions and Smithers Rapra shall have no further liability to the Client.

**CONFIDENTIAL INFORMATION AND INTELLECTUAL PROPERTY RIGHTS**

10.1 All data, information and reports are produced for the benefit of the addressee only. Smithers Rapra accepts no liability arising from unauthorised use of such information or reports by a third party.

10.2 All Intellectual Property Rights belonging to or otherwise in the control of either party prior to entering into the Contract shall remain the property of the party owning such Intellectual Property Rights.

10.3 Unless expressly agreed in writing by Smithers Rapra and set out in the Order:

10.3.1 the Client shall not reproduce or abstract for the purpose of advertising or otherwise any report or other information from the Work or use the name of Smithers Rapra either expressly or by implication in any of its advertising or sales promotional material.

10.3.2 all title and ownership of, or relating to, any Intellectual Property Rights, including, but not being limited to, ideas, inventions, discoveries, creations, improvements or any other property subject to patent protection or Intellectual Property Rights in or arising out of or in connection with the Work under the Contract, shall be vested in and owned by Smithers Rapra.

10.3.3 all Intellectual Property Rights in all drawings, documents, confidential records, computer software and other information supplied by Smithers Rapra ("Documents") are vested in and shall remain the property of Smithers Rapra.

10.3.4 nothing in the Contract shall be deemed to have given the Client a licence or any other right to use any of Smithers Rapra's Intellectual Property Rights.

10.3.5 the Client will not give away, loan, exhibit, sell or in any way use any Documents or extracts therefrom or copies thereof.

10.4 For the avoidance of any doubt if Smithers Rapra agrees to an assignment of any of the Intellectual Property Rights owned by Smithers Rapra, Smithers Rapra shall be granted a royalty-free, irrevocable, non-exclusive, worldwide right to use such Intellectual Property Rights assigned under this Condition 10.3 by the Client.

10.5 Smithers Rapra's confidential and sensitive information including, but not limited to, information contained in any proposal, order acknowledgment, or invoice provided by Smithers Rapra to the Client shall be kept confidential and shall not be disclosed by the Client to any third party or otherwise made public the terms or existence of the Contract without Smithers Rapra's prior written consent, except as may be required by law in which case the Client shall notify Smithers Rapra of such disclosure, if legally possible, in good time prior to making the disclosure.

**CLIENT'S INFORMATION/SAMPLES**

11.1 The Client shall be solely responsible for ensuring that all drawings, information, advice and recommendations given to Smithers Rapra, either directly or indirectly by the Client or by the Client's agents, servants, consultants or advisers, are accurate and sufficient for completion of the Work. Examination or consideration by Smithers Rapra of such drawings, information, advice or recommendations shall in no way limit the Client's responsibility hereunder unless Smithers Rapra specifically agrees in writing to accept responsibility.

11.2 Smithers Rapra shall not disclose to any third party any knowledge or information relating to the Work which is, on receipt by Smithers Rapra, marked 'confidential' by the Client unless and until such information becomes public knowledge.

11.3 Smithers Rapra retains the right to return or dispose of the samples at the Client's cost after a period of 6 months unless otherwise agreed with the Client. Storage of the samples beyond the initial 6 month period will be charged for, invoiced in advance for the agreed period (minimum additional 6 months).

**TERMINATION**

12.1 Smithers Rapra may, as it thinks fit, (without prejudice to any other rights or remedies it may have against the Client) immediately suspend further performance of the Contract or cancel any outstanding provision of the Work by notice in writing to the Client or any other contract between the Client and Smithers Rapra without incurring any liability to the Client and all outstanding sums in respect of the Work delivered to the Client shall become immediately due if:

(a) the Client suspends, or threatens to suspend, payment of its debts or is unable to pay its debts as they fall due or admits inability to pay its debts or (being a company) is deemed unable to pay its debts within the meaning of section 123 of the Insolvency Act 1986, or (being a partnership) has any partner to who any of the foregoing apply;

(b) the Client commences negotiations with all or any class of its creditors with a view to rescheduling any of its debts, or makes a proposal for or enters into any compromise or arrangement with its creditors other than (where the Client is a company) these events take place for the sole purpose of a scheme for a solvent amalgamation of the Client with one or more other companies or the solvent reconstruction of the Client;

(c) a creditor or encumbrancer of the Client attaches or takes possession of, or a distress, execution, sequestration or other such process is levied or enforced on or sued against, the whole or any part of its assets and such attachment or process is not discharged within 14 days;

(d) an application is made to court, or an order is made, for the appointment of an administrator or if a notice of intention to appoint an administrator is given or if an administrator is appointed over the Client;

(e) a floating charge holder over the assets of the Client has become entitled to appoint or has appointed an administrative receiver;

(f) a person becomes entitled to appoint a receiver over the assets of the Client or a receiver is appointed over the assets of the Client;

(g) any event occurs, or proceeding is taken, with respect to the Client in any jurisdiction to which it is subject that has an effect equivalent or similar to any of the events mentioned in Condition 12(a) to 12(l) (inclusive);

(h) the Client suspends, threatens to suspend, ceases or threatens to cease to carry on all or substantially the whole of its business;

(i) the financial position of Smithers Rapra deteriorates to such an extent that in the opinion of the Client the capability of Smithers Rapra adequately to fulfil its obligations under the Contract has been placed in jeopardy;

(j) the Client commits a material breach of any of its obligations under the Contract which is incapable of remedy;

(k) any sum payable under the Contract is not paid within 7 days of its due date for payment in accordance with this Contract;

(l) the Client fails to remedy a breach of its obligations under the Contract (except as to payment) which is capable of remedy, or persists in any breach of any of its obligations under the Contract after having been requested in writing by Smithers Rapra to remedy of desist from such breach within a period of 14 days.

**FORCE MAJEURE**

13 Smithers Rapra shall not be in breach of this Contract or liable for delay in performing, or failing to perform any obligation under this Contract arising from or attributable to acts, events, omissions or accidents beyond its reasonable control, including but not being limited to any of the following: by direction of government, war, industrial dispute, strike, breakdown of machinery or plant, acts of God, terrorism, riot, flood, storms, earthquakes, extreme adverse weather conditions, lock-outs, accident, fire (any one a "Force Majeure Event"). If the Force Majeure Event prevails for a continuous period of more than 2 months, Smithers Rapra may terminate this Contract by giving 14 days' written notice to all the other parties. On the expiry of this notice period, the Contract will terminate. Such termination shall be without prejudice to the rights of the parties in respect of any breach of this Contract occurring prior to such termination. Smithers Rapra shall be entitled to recover all sums owing to it in respect of Goods provided and costs incurred prior to the date of termination.

**GENERAL/LEGAL**

14.1 All agreements contained herein shall apply to and bind the assignees and successors in interest of Smithers Rapra and the Client. Facsimile signatures or other reliable means of authentication by which the Client signifies its assent to this Agreement shall be effective to bind the Client to this Contract.

14.2 The waiver by Smithers Rapra of any right or remedy under the Contract is only effective if given in writing and shall not be deemed to be a waiver of any later breach or default. No failure or delay by Smithers Rapra to exercise any right or remedy provided under the Contract or by law shall constitute a waiver of that or any other right or remedy, nor shall it preclude or restrict the further exercise of that or any right or remedy. No single or partial exercise of such right or remedy shall preclude or restrict the further exercise of that or any other right or remedy.

14.3 If any court or competent authority finds that any provision or part provision of this Contract is invalid, illegal or unenforceable, that provision or part provisions shall to the extent required, be deemed to be deleted, and the validity and enforceability of the other provisions of the Contract shall not be affected. If any invalid, unenforceable or illegal provision of the Contract would be valid, enforceable and legal if some part of it were deleted, the provision shall apply with the minimum modification necessary to make it legal, valid and enforceable.

14.4 The headings are used for the convenience of the parties only and shall not affect the construction or interpretation of this Contract. Any clerical errors are subject to correction.

14.5 The Contract and any dispute or claim arising out of or in connection with it shall be governed and interpreted exclusively according to the Law of England and shall be subject to the exclusive jurisdiction of the English Courts to which the parties irrevocably submit.

14.6 Notwithstanding any different or additional terms or conditions contained in the Client's purchase order or other communication, Smithers Rapra accepts the Client's order only on the condition that the Client expressly accepts and assents to the terms and conditions contained in this Contract. The Client's acceptance of any Work shall be deemed to be acceptance of these Conditions.

14.7 Smithers Rapra may at any time assign, charge, subcontract, transfer or deal in any other manner with all or any of its rights or obligations under the Contract or any part of it to any person. The Client may not assign, charge, subcontract, transfer or deal in any other manner with all or any of its rights or obligations under the Contract without the prior written consent of Smithers Rapra.

14.8 A person who is not a party to the Contract (including without limitation any employee, officer, agent, representative or subcontractor or either party) shall not have any right to enforce any term of the Contract which expressly or by implication confers a benefit on that person without the express prior written agreement of Smithers Rapra and the Client.

14.9 All notices between the parties relating to this Contract must be in writing and sent pre-paid first class or sent by facsimile to:

(a) in the case of the Client the registered office of the addressee (if it is a company) or (in any other case) to any address of the Client set out in any document which forms part of this Contract or a Contract or such other address as shall be notified to Smithers Rapra by the Client in writing; and

(b) in the case of Smithers Rapra, the address set out below:

***Smithers Rapra and Smithers Pira Limited***
***Shawbury***
***Shrewsbury***
***Shropshire SY4 4NR***
***UK***

or other such address as shall be notified to the Client by Smithers Rapra in writing.

14.10 Notices shall be deemed to have been received: in the case of first class post, 2 days after posting (exclusive of the day of posting) and if sent by facsimile transmission, at 10:00 am local time on the first usual Working Day in the country of receipt following transmission, subject to being able to show that the notice was sent to the correct facsimile number.

14.11 Nothing in this Contract is intended to, or shall be deemed to, establish any partnership or joint venture between any of the parties, constitute any party the agent of another party, nor authorise any party to make or enter into any commitments for or on behalf of any other party.

14.12 The Contract constitutes the entire agreement between the parties. The Client acknowledges that it has not relied on any statement, promise or representation made or given by or on behalf of Smithers Rapra which is not set out in the Contract. Any samples, drawings, descriptive matter or advertising issued by Smithers Rapra and any descriptions or illustrations contained in Smithers Rapra's catalogues or brochures are issued or published for the sole purpose of giving an approximate idea of the Services described in them. They shall not form part of the Contract or any other contract between Smithers Rapra and the Client for the sale of the Goods.

14.13 In performing the Services, Smithers Rapra shall operate as, and have the status of, an independent contractor and shall not operate or have the status of agent, employee or representative of the Client.

**ANTI-BRIBERY**

15.1 The Client shall:

(a) comply with all applicable laws, statutes, regulations and codes relating to anti-bribery and anti-corruption including but not limited to the Bribery Act 2010 ("Relevant Requirements");

(b) not engage in any activity, practice or conduct which would constitute an offence under sections 1, 2 or 6 of the Bribery Act 2010 if such activity, practice or conduct had been carried out in the UK;

(c) comply with any Anti-Bribery Policy as Smithers Rapra may provide to it from time to time ("Relevant Policy");

(d) have and shall maintain in place throughout the term of this Agreement its own policies and procedures, including adequate procedures under the Bribery Act 2010, to ensure compliance with the Relevant Requirements, the Relevant Policy and Condition 15.1(b) and will enforce them where appropriate;

(e) promptly report to Smithers Rapra any request or demand for any undue financial or other advantage of any kind received by the Client in connection with the performance of this Agreement;

(f) immediately notify Smithers Rapra in writing if a foreign public official becomes an officer or employee of the Client or acquires a direct or indirect interest in the Client, and the Client warrants that it has no foreign public officials as officers, employees or direct or indirect owners at the date of this Agreement;

(g) the Client shall provide such supporting evidence of compliance as Smithers Rapra may reasonably request.

15.2 The Client shall ensure that any person associated with it who is performing services or providing goods in connection with this Agreement does so only on the basis of a written contract which imposes on and secures from such person terms equivalent to those imposed on the Client in this Condition 15 ("Relevant Terms"). The Client shall be responsible for the observance and performance by such persons of the Relevant Terms, and shall be directly liable to Smithers Rapra for any breach by such persons of any of the Relevant Terms.

15.3 For the purpose of this Condition 15, the meaning of adequate procedures and foreign public official and whether a person is associated with another person shall be determined in accordance with section 7(2) of the Bribery Act 2010 (and any guidance issued under section 9 of that Act), sections 6(5) and 6(6) of that Act and section 8 of that Act respectively. For the purpose of this Condition 15, a person associated with the Client includes but is not limited to any Sub-Contractor.