TNO Report

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Identification of chemicals specific to active and intelligent packaging on the European market and the extent to which they migrate into food

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SUMMARY

A thorough literature/internet search was performed to identify active and intelligent materials on the market. Initially, the search was focussed on the UK market but since only a few examples were identified, the search was extended to encompass the European and US markets. Examples of 25 active or intelligent packaging materials were obtained. Of the samples obtained those that were selected for analysis included; oxygen scavengers (sachets, labels and crown caps), a moisture absorber, ethylene scavengers, antimicrobial systems, anti-mould systems, a heat releaser, flavour releasers, a heat sensitive monitoring system and a food freshness indicator monitoring system. The samples were subjected to an analytical screening procedure to identify the chemicals that made up the active or intelligent component. It was not always possible to separate the active or intelligent component from the bulk of the sample and in the absence of control samples these screening procedures also detected any substances associated with the primary packaging and the active/intelligent delivery system. A larger number of substances remained either unidentified or with an ambiguous identification only. As a result these findings support the need for an 'authorised list' of active and intelligent ingredients as required by the EU Regulation (EC) No. 450/2009 on these materials.

Based on the screening experiments and on the levels of active/intelligent substances observed, the worst case exposure of those active/intelligent substances for which identities were proposed was calculated and compared with any specific migration limits or other restrictions that have been assigned to them. For those substances for which the migration limit (or other restriction) had the potential to be exceeded, migration tests using food simulants and real foods were performed. As not all packaging materials were suitable for standard migration tests, alternative migration tests were performed where required. One of the oxygen scavenging systems tested (a label) under the test conditions used, transferred the active component, iron, to acidic food simulant and tomato sauce at a level which could lead to an exceedance of the Tolerable Daily Intake (TDI). No conditions of use were supplied with this packaging format but these results would indicate that there should be restrictions on the use of this sort of material.

An important aspect of active or intelligent materials is that they should be efficacious so that the consumer is not misled regarding their use. Therefore a selection of active and intelligent materials were chosen to test their efficacy and investigate whether the materials work as described by the manufacturer. Ten samples were studied: an oxygen scavenging label, an oxygen scavenging sachet, an antimicrobial film, an antimicrobial food storage liner, an anti-mould pad, an anti-mould bag, an absorbent pad, an ethylene scavenging sachet, a heat sensing spoon and a time indicator. Seven of the ten samples behaved in the way claimed by the suppliers/manufacturers. Neither the antimicrobial film nor the antimicrobial food storage liner reduced the microbial growth on their food contact surfaces and on the surface of a meat sample compared to a material without antimicrobial properties. The mould growth on cheese stored in the anti-mould bag did not differ from that of the control sample stored in a polyethylene bag with no anti-mould properties. For these samples detailed instructions of how the materials should be used were not given. Therefore it is recommended that these are provided to allow the claimed activity of these materials to be achieved.

Signature

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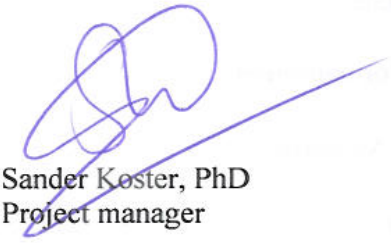

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LIST OF ABBREVIATIONS

AES	Atomic emission spectroscopy
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
b.w.	body weight
CEN	Comité Européen de Normalisation
Da	Daltons
EFSA	European Food Safety Authority
EI	Electron impact
ESI	Electrospray ionisation
FDA	Food and Drug Administration
Fera	The Food and Environment Research Agency
FSA	Food Standards Agency
FT-IR	Fourier transform-infra red
GC	Gas chromatography
HPLC	High performance liquid chromatography
ICP	Inductively coupled plasma
JECFA	Joint FAO/WHO Expert Committee on Food Additives
LC	Liquid chromatography
LIMS	Laboratory information management system
LOD	Limit of detection
LTQ	Linear ion trap
MS	Mass spectrometry
NIOD	Non invasive oxygen detection
PET	Polyethylene terephthalate
ppb	Parts-per-billion
ppm	Parts-per-million
PIM	Plastics Implementation Measure
PTWI	Provisional tolerable weekly intake
RF	Radio frequency
RODAC	Replicate organisms detection and counting
SML	Specific migration limit
TIC	Total ion chromatogram
TNO	Toegepast Natuurwetenschappelijk Onderzoek
TOF	Time-of-flight
TSA	Tryptic soy agar
TVC	Total viable counts
UV	Ultra-violet
VRBG	Violet red bile glucose

Contents

1 Introduction 7

2 Legislation 8

3 Aims and objectives of the project 10

4 Active and intelligent packaging materials presently on the market (or expected to be in the near future) 11

5 Description of the test samples obtained 13
5.1 Oxygen scavengers 14
5.1.1 Samples obtained 15
5.2 Moisture absorbers 15
5.2.1 Samples obtained 15
5.3 Ethylene scavengers 16
5.3.1 Samples obtained 16
5.4 Acetaldehyde scavengers 16
5.4.1 Samples obtained 17
5.5 Antimicrobial releasing systems 17
5.5.1 Samples obtained 18
5.6 Anti-mould systems 18
5.6.1 Samples obtained 18
5.7 Heat releasers 18
5.7.1 Samples obtained 19
5.8 Flavour releasers 19
5.8.1 Samples obtained 19
5.9 Monitoring systems 19
5.9.1 Samples obtained 20
5.10 Other active and intelligent packaging samples 20
5.10.1 Amine scavengers 20
5.10.2 Aldehyde scavengers 20
5.10.3 Sulphide scavengers 20
5.10.4 Bitter taste removers 20
5.10.5 Lactose and cholesterol removers 21
5.10.6 Carbon dioxide regulating systems 21
5.10.7 Nitrogen releasers ('beer widget') 21
5.10.8 Anti-oxidant releasers 21
5.10.9 Tin releasers 21

6 Screening experiments 22
6.1 Screening experiments – TNO 23
6.1.1 Sample logging 23
6.1.2 Sample preparation for headspace GC-MS analysis 23
6.1.3 Sample preparation for GC-MS analysis 23
6.1.4 Sample preparation for LC-MS analysis 24
6.1.5 Sample preparation for elemental screening 24
6.1.6 Analysis by headspace GC-MS 24
6.1.7 Analysis by GC-MS 24
6.1.8 Analysis by LC-MS 24

6.1.9 Results screening 25
6.1.10 Active/intelligent ingredients 29
6.2 Screening experiments – Fera 31
6.2.1 Sample logging 31
6.2.2 Sample preparation for headspace GC-MS 31
6.2.3 Sample preparation for GC-MS 31
6.2.4 Sample preparation LC-TOF-MS 31
6.2.5 Sample preparation ICP-MS 31
6.2.6 Analysis by headspace GC-MS 31
6.2.7 Analysis by GC-MS 32
6.2.8 Analysis by LC-TOF-MS 32
6.2.9 Analysis by ICP-MS 32
6.2.10 Results screening 33
6.2.11 Active/intelligent ingredients 35

7 Migration experiments 40
7.1 Migration experiments TNO 40
7.1.1 Oxygen scavengers; label (0939-03-0471-OxS3) and sachet (0939-03-0472-OxS4) 40
7.1.2 Flavour releaser (0939-02-0227-FlavR1) 42
7.1.3 Anti-mould SO_2 emitter (0939-02-1737-AntiM2) 44
7.2 Migration experiments Fera 46
7.2.1 Antimicrobial food storage liner (0939-03-0269-AntiM3) 46
7.2.2 Antimicrobial cling film (S07-024123-AntiM4) 48
7.2.3 Ethylene scavenging sachet (S07-024128-EthS3) 49
7.2.4 Moisture absorber (S07-024129-MoistA) 50

8 Efficacy experiments 52
8.1 Efficacy experiments TNO 52
8.1.1 Oxygen scavengers; label (0939-03-0471-OxS3) and sachet (0939-03-0472-OxS4) 52
8.1.2 Efficacy antimicrobial materials (food storage liner 0939-03-0269-AntiM3 and film S07 024123-AntiM4) 52
8.1.3 Efficacy anti-mould SO_2 emitter (0939-02-1737-AntiM2) 54
8.2 Efficacy experiments Fera 55
8.2.1 Absorbent pads (S07-024129-MoistA) 55
8.2.2 Ethylene scavenging sachet (S07-024128-EthS3) 55
8.2.3 Anti-mould cheese bag (S08-003221-AntiM5) 56
8.2.4 Heat sensitive weaning spoons (S08-000164-HeatS) 56
8.2.5 Time indicator (S07-024306-TimeS) 56

9 General conclusions 57
9.1 Screening for substance responsible for active/intelligent function 57
9.2 Migration into foods versus simulants 57
9.3 Efficacy tests 58

10 Reference List 60

11 Appendices 61

1 Introduction

One of the most innovative developments in food packaging in recent years is the application of active and intelligent packaging. The development of these new food packaging systems has mainly been initiated by the continuing increasing demands for improved quality and extended shelf-life for packaged foods. Today's consumers want to be assured that packaging is fulfilling its function of protecting the integrity, quality, freshness and safety of foods. A current trend in the food industry is the development of mildly preserved, wholesome and easy-to-prepare products in anticipation of consumer demands for fresh 'natural' convenience foods. Centralisation of activities and the search for cost reduction while maintaining food safety and quality are trends in retail. In addition, international markets are being extended by harmonisation and globalisation, resulting in longer distribution distances. These changes have encouraged the development of a wide range of active and intelligent food packaging systems in recent years. Active packaging is intended to influence the packed food. It is intended to change the condition of the packed food, to extend shelf-life or improve sensory properties while maintaining the freshness and the quality of the food. To do this, the packaging should absorb food-related chemicals or should release substances such as preservatives, antioxidants, flavourings or colours. For intelligent packaging, the food is intended to influence the packaging so that the packaging gives information about the current condition of the food and/or its storage history. These active and intelligent food packaging systems enable either a further extension of shelf-life or the monitoring of food quality and safety.

2 Legislation

With the advent of active and intelligent materials and articles, the European legislation has been amended to permit their use in contact with food. The Framework Regulation (EC) 1935/2004 allows the introduction of active and intelligent packaging on the European market. Article 3 of the Framework Directive, which is applicable to all food contact materials including active and intelligent packaging, states that food contact materials shall not transfer constituents to food in quantities which could:

- endanger human health
- bring about an unacceptable change in the composition
- bring about a deterioration in organoleptic characteristics thereof.

Furthermore, labelling, advertising and presentation of the material or article should not mislead the consumer.

The Framework Regulation also empowers the European Commission to set requirements for specific materials. In the past food contact materials were considered to act in such a way that they offer protection to the foodstuff within. However the advent of novel technologies such as active and intelligent packaging may make it possible to assign new functions to packaging, i.e. the packaging could interact with the food by releasing or adsorbing/absorbing substances or it could inform consumers of the state of the packaged food. Provisions have been introduced in the Framework Regulation to account for these developments.
Article 4, which provides specific requirements for active and intelligent materials and articles, includes the following provisions:

- Active materials and articles may bring about changes in the composition or organoleptic characteristics of food on condition that the changes comply with the food legislation.
- Substances deliberately incorporated into active materials and articles to be released into the food or the environment surrounding the food shall be authorised and used in accordance with the relevant Community provisions applicable to food (*this means, should be authorised as direct food additives*).
- Active materials and articles shall not bring about changes in the composition or organoleptic characteristics of food, for instance by masking the spoilage of food, which could mislead consumers.
- Intelligent materials and articles shall not give information about the condition of the food which could mislead consumers.
- Active and intelligent materials and articles already brought into contact with food shall be adequately labelled to allow identification by the consumer of non-edible parts.
- Active and intelligent materials and articles shall be adequately labelled to indicate that the materials or articles are active and/or intelligent.

In Article 5 (Specific measures for groups of materials and articles) of the same Regulation the need to label active and intelligent packaging materials is repeated. Information should be provided throughout the packaging chain as well as to the consumer to ensure the correct use of these materials and articles and articles, such that, for example, sachets should be labelled as non-edible.

The Framework Regulation also recommends that a specific measure to regulate active and intelligent packaging should be introduced. This measure is now published as Commission Regulation (EC) No. 450/2009.

The provisions listed in the Framework Regulation specific to active and intelligent packaging are not repeated in this Regulation. The additional specific provisions included in this Regulation include:

- The individual substance or combination of substances which make up the active or intelligent component should be evaluated to guarantee that they are safe and comply with the requirement in the Framework Regulation.
- Substances should undergo a safety assessment before they are authorised for use. This should be carried out by the European Food Safety Authority (EFSA).
- A community list of active and intelligent components should be drawn up following authorisation of these substances by EFSA. The information that should be included in this list is defined.
- Active releasing materials should comply with any restrictions in the existing food law (e.g. as authorised food additives).
- The overall migration from active releasing materials can exceed the overall migration limits described in EU or national legislation as long as the levels transferred to the food comply with restrictions in the existing food law (e.g. as authorised food additives). The transfer of these active substance/substances should not be included in the calculation of the overall migration limit.
- As well as complying with the Framework Regulation the passive parts of the active and intelligent packaging materials must also comply with the rules applicable to the same materials and articles when they do not contain the active component, such as the Plastics Directive 2002/72/EC, as amended. For materials such as paper and board that are not regulated at Community level any national legislation should be applied. This is the case for all existing and future legislation. The existing national legislation is summarised in document: http://ec.europa.eu/food/food/chemicalsafety/foodcontact/eu_nat_laws_en.pdf.
  For example, if an active or intelligent component is present within a plastic containing material or article then the plastic component must be in compliance with Directive 2002/72/EC, as amended.
- If intelligent systems are on the non-food contact surface of the package then they may be separated from the foodstuff by a functional barrier, i.e. a barrier to any migration. If it is demonstrated that the packaging material acts as a functional barrier to migration then non-authorised substances can be used providing they meet specific criteria defined in the Regulation.

The Regulation on active and intelligent materials and articles states that EFSA should publish detailed guidance concerning the preparation and submission of the application for the inclusion of a substance/or combination of substances in the authorised Community list. The public consultation on the ‘Guidelines on the submission of a petition for safety evaluation by the EFSA of active or intelligent substance(s) present in active and intelligent materials and articles intended to come into contact with food’ closed in April 2009.

3 Aims and objectives of the project

In a previous FSA funded study [1] a report entitled 'Active packaging – current trends and potential for migration' summarised that the UK market for active and intelligent applications was small. This report was prepared in 2003.

The aims of this new project were to advance the knowledge on these materials and articles through the provision of a review document describing the current status of the use of active and intelligent packaging materials (and to update the information reported in 2003), by identifying the ingredients present in active and intelligent systems that are currently available on the market and assessing the migration of these substances into food simulants and foods using conventional and, where applicable, dedicated migration tests. An important aspect of active or intelligent materials is that they should be efficacious so that the consumer is not misled regarding their use. Little information on efficacy testing is publicly available and therefore this project sought to address this information gap. These aims were achieved by addressing the objectives listed below.

Objective 01. Survey study about the active and intelligent packaging materials and articles presently on the market (or expected to be in the near future). Collect and describe test samples from UK market (or if not possible from world-wide markets or manufacturers)

Objective 02. Define a set of test samples representative of the market

Objective 03. Identify the chemicals that are specific to active and intelligent packaging and assess the potential risk of migration

Objective 04. Determine the specific migration of selected active and/or intelligent chemicals from relevant samples into food simulants using dedicated tests

Objective 05. Determine the specific migration of the selected active and/or intelligent chemicals from relevant samples into food

Objective 06. Evaluate the effectiveness of the active and intelligent packaging systems

Objective 07. Draw conclusions and prepare the final project report

4 Active and intelligent packaging materials presently on the market (or expected to be in the near future)

To establish the different active and intelligent packaging systems that are presently on the market information was sought from existing in-house knowledge (through previous research projects including Actipak – TNO and FSA funded project A03039 – FERA), packaging magazines, trade journals and the internet. From these sources as well as the scientific literature and our contacts with food manufacturers, food packaging manufacturers and food retailers the following classes of active and intelligent packaging types were identified:

- Active absorbers and scavengers
- Active releasers
- Monitoring systems

Examples of active absorbers and scavengers include:

- Oxygen scavengers
- Moisture absorbers
- Ethylene scavengers
- Acetaldehyde scavengers
- Amine scavengers
- Aldehyde scavengers
- Sulphide scavengers
- Bitter taste removers
- Carbon dioxide regulating systems (oxygen emitting and carbon dioxide scavenging)
- Lactose and cholesterol removers
- UV light absorbers

Examples of active releasers include:

- Carbon dioxide regulating systems (oxygen emitting and carbon dioxide scavenging)
- Antimicrobial releasing systems
- Nitrogen releasers
- Heat releasers
- Antioxidant releasers
- Sulphur dioxide releasers
- Chlorine dioxide releasers
- Flavour releasers
- Ethylene inhibitor releasers

Examples of monitoring systems include:

- Time-temperature indicators
- Time indicators
- Freshness and ripening indicators
- Oxygen indicators
- Carbon dioxide indicators
- Heat indicators

Active and intelligent packaging materials have been extensively reviewed elsewhere [2-6] and this information is not duplicated in this report.

To identify the types of materials and articles used in the UK and subsequently throughout Europe and the rest of the world the information sources listed below were searched.

Internet search engine:
www.google.co.uk

Keywords included in the search:
Active packaging; Intelligent packaging; Active packaging manufacturers; Intelligent packaging manufacturers; Oxygen scavenger; Moisture absorber; Ethylene scavenger; Off-flavour scavenger; Aldehyde scavenger; Amine scavenger; Sulphide scavenger; Bitter taste remover; Lactose scavenger; Cholesterol scavenger; Carbon dioxide regulator; Antimicrobial releasing systems; Antimicrobial packaging; Nitrogen releaser; Heat releaser; Antioxidant releaser; Sulphur dioxide releaser; Chlorine dioxide releaser; Flavour releaser; Ethylene inhibitor releaser; Time-temperature indicator; Time indicator; Freshness and ripening indicator; Oxygen indicator; Carbon dioxide indicator; Heat indicator.

Packaging magazines and trade journals searched:

Packaging News	www.packagingnews.co.uk
Packaging Today	www.packagingtoday.co.uk
Retail packaging magazine	www.retailpackagingmag.co.uk
The Packaging Professional	www.iom3.org/content/packaging-professional
Packaging Europe	www.packagingeurope.com/
Packaging Digest	www.packagingdigest.com
Flexible packaging	www.flexpackmag.com

Scientific literature search engine:
Web of science

Keywords included in the search were the same as those listed above along with:
Migration; Safety; Food contact

An overview of all of the systems identified in the information gathering exercise for which commercial applications were established is provided in Table 1.

Following this exercise the manufacturers of the systems identified (Table 1) were contacted to establish whether or not their products were currently used in packaging materials that may come into contact with foodstuffs that are available to UK consumers. Few samples were identified so subsequently information was sought on the use of these materials and articles throughout the EU and world-wide.

In addition potential users of active and intelligent packaging materials (e.g. food packers and supermarkets) were contacted and information requested to establish whether or not these systems are in use in their products.

5 Description of the test samples obtained

The original aim defined in the project proposal was to try to obtain at least three samples of each of the main active and intelligent packaging material types: water absorbers, oxygen scavengers, ethylene scavengers and monitoring systems. From the literature study more than 20 different classes of active and intelligent packaging were identified (Table 1) however not all of these were confirmed as having commercial application in the UK. Only a small number of samples with a limited range of applications were confirmed as being used in the UK. Potter *et al*. [6] reported that the consumer's lack of understanding with respect to the benefits of active and intelligent packaging has limited its use in the UK. It could of course be equally true that some consumers do understand but that they are not convinced of the benefits. Other hurdles include cost and a lack of clarity in the legislation – although this has now been resolved with the specific Regulation that was published in 2009. Therefore to ensure that an appropriate number and range of samples were obtained the scope of the project was widened to include European and American markets.

Twenty five samples and one control sample were obtained either directly from manufacturers or from retail outlets (Table 2). These included: seven oxygen scavenging systems (and one a reference material, i.e. the material type but with none of the scavenger present), one water absorber, three ethylene scavengers (one of which is also described as preventing moisture formation and therefore may also fall into the water absorbing category), one acetaldehyde scavenging system, two antimicrobial systems, three anti-mould containing materials, one heat-releasing system, three flavour releasers and three monitoring systems (including a freshness indicator, a heat sensing material and time indicators suitable for various storage temperatures). Seven oxygen scavenging samples (and one control) were obtained as these represented the majority of the systems present on the market at the time the samples were obtained. Only one water absorber was included (contrary to the three initially proposed). This change in the proposed sampling plan allowed a greater range of active and intelligent applications to be included.

Further classification was made as to which materials should be considered to be active and which as passive. Passive packaging provides protection from external elements such as air and moisture compared to active packaging which actively changes the condition of the packaged food. Two of the oxygen scavengers obtained (the polyethylene terephthalate (PET) bottles with the integral oxygen absorber) are considered passive rather than active as the role of the oxygen absorber is to prevent diffusion of external oxygen through the packaging whereupon it would come into contact with the food. Furthermore the role of the acetaldehyde scavenger is to mop up the acetaldehyde in the PET bottle in which it is contained and is also considered passive rather than active.

In addition to the passive materials not being considered as active, food contact materials and articles that have an antimicrobial effect on the surface of the packaging but not on the food are not regarded as active packaging. Therefore it may be considered that, for example, the silver containing cling film should not be classed as active packaging. However according to information from the manufacturers, the anti-microbial activity provided by these materials is designed to extend the shelf life of the foodstuff. Therefore the samples obtained are classified as active materials.

Therefore of the 25 samples obtained, 22 were classed as containing active or intelligent components.

Information on each of the applications, as derived in the literature study, is given below. Any non-confidential information received from the supplier is also provided.

5.1 Oxygen scavengers

Oxygen scavenging active packaging materials and articles contain chemicals which remove residual oxygen from the atmosphere surrounding the foodstuff or from the foodstuff itself. Exposure to oxygen may result in microbiological growth on the food (e.g. mould and aerobic bacteria), chemical changes to the food (e.g. rancidity, changes in the nutritional composition or a change in the appearance of the food) or physiological changes (e.g. the rate of respiration). Therefore the inclusion of an oxygen scavenger in the pack will reduce these effects thereby prolonging the shelf-life of the foodstuff.

Oxygen scavengers may be used in the form of a sachet, a label, a closure or by incorporation into a polymer film or bottle. Examples of working principles include iron or iron complexes, nylon film with a cobalt catalyst, ascorbic acid, sulphite salts and enzymes such as glucose oxidase and alcohol oxidase.

Iron based oxygen scavengers are the most commonly used. Iron scavenges oxygen by its reaction to form iron oxide ($Fe + O_2 \rightarrow Fe_xO_y$). The iron has a greater affinity for oxygen than most foodstuffs and therefore the oxygen preferentially reacts in this way reducing the oxidation of the food.

The oxidation of sulphite salts to form sulphates is an active mechanism for scavenging headspace oxygen used in crown caps used to seal glass bottles.

An active film that absorbs oxygen uses meta-xylene diaminoadipic acid nylon to which between 50 and 200 ppm of a cobalt carboxylic acid salt has been incorporated. The cobalt catalyses the reaction between the nylon and oxygen reducing the free oxygen levels in the package. As mentioned above incorporation of such films into PET bottles is considered to be passive rather than active.

Ascorbic acid is a powerful scavenger of oxygen. It is active in the presence of a transition metal such as copper. In its role as an antioxidant, ascorbic acid reacts with the oxygen releasing a molecule of water and forming dehydroascorbic acid.

Glucose oxidase is an oxidoreductase enzyme which acts by transferring two hydrogen atoms from the $-CH_2OH$ functionality of the glucose to oxygen forming glucone-delta-lactone and hydrogen peroxide $2H + O_2 \rightarrow H_2O_2$. In the presence of another enzyme, catalase, the hydrogen peroxide is broken down to form water and oxygen $H_2O_2 \rightarrow \frac{1}{2}O_2 + 2H_2O$. The net effect is to reduce the oxygen concentration in the pack.

Alcohol oxidase scavenges oxygen by reaction with the ethanol to form acetaldehyde although this may not be favourable given the low sensory threshold for the acetaldehyde thus formed.

Other reported mechanisms include the reaction of the oxygen with unsaturated fatty acids in the presence of a transition metal catalyst and replacing the air in the pack with hydrogen and nitrogen such that any residual oxygen reacts with the hydrogen (in the presence of a palladium catalyst) thus eliminating the oxygen.

For all of the scavenging mechanisms the oxygen scavenging substance is converted into an oxidation product. Since the oxidation product is not intended to be released this substance does not need to be listed. As with any starting substance, additive, reaction or breakdown product migration into foods will depend on the laws of diffusion.

5.1.1 Samples obtained

A total of seven oxygen scavenging systems (and one reference sample) were received. As described previously, on reflection two were considered to be passive materials with respect to their action on food rather than active packaging and therefore these were not considered further. Four iron based absorbers in the form of sachets and labels were received. Only two were included in the study (one label and one sachet) to avoid duplication. All four samples were from the same supplier. A crown cap in which the active ingredient was described, by the supplier, as being based on sulphite was also obtained (along with a reference material, i.e. the same crown cap but with none of the scavenger present).

5.2 Moisture absorbers

Moisture absorbers are used to control the humidity of moisture sensitive foods. The presence of a moisture absorber reduces the condensation that forms on the surface of materials used to pack respiring foods such as fruit and vegetables and foodstuffs with a high water content.

Moisture absorbers may take the form of absorbent pads, sachets or they may be incorporated into polymer films.

Absorbent pads are very widely used in contact with fish and meat. They are also known as drip pads. Their construction is usually a laminate of plastic gauze, adhesive and either a cellulose fibre pad or a water absorbent acrylate polymer.

Sachets containing salt or silica gels have also been reported to act as dessicants for use with moisture sensitive foodstuffs.

Moisture absorbers may also be incorporated into polymer films or between layers in a polymer construction. Examples include clays, glucose, and propylene glycol.

5.2.1 Samples obtained

One sample, a meat pad, was obtained and included in the study. This was described, by the manufacturer, as made from a mix of pure cellulose and super absorbent fibres.

5.3 Ethylene scavengers

Ethylene, a natural plant growth hormone, is a key to the ripening process of fruits and vegetables, being liberated during respiration and then driving the ripening process itself. Therefore it is important to prevent an excess of the gas in order to extend shelf life of packaged produce.

Ethylene scavengers may be used in sachets or incorporated into a polymer film. Mechanisms of action include the use of potassium permanganate or adsorption onto activated carbon, zeolites, clays and other minerals.

Potassium permanganate oxidises ethylene first to acetaldehyde and then to acetic acid. Further oxidation can ultimately form carbon dioxide and water. It is expected, although it is not clear from the literature, that the oxidation products are trapped on the silica or alumina on which the potassium permanganate is immobilised.

Ethylene gas can be adsorbed onto the surface of activated carbon, zeolites and clays all of which have a large surface area and are highly porous. Activated carbon with a palladium catalyst has been used in sachet form. The ethylene is adsorbed by the carbon and broken down. Clays, zeolites and carbon incorporated into polyethylene bags have also been used as ethylene scavengers for the aforementioned application. These systems may also be used to absorb other volatile substances that may be present as off-flavours.

5.3.1 Samples obtained

Three ethylene scavengers were obtained, of which one was a sachet and two were food bags.

The manufacturers of the ethylene scavenging sachets stated that their product produces nascent oxygen that oxidises ethylene gas. They explained that the active ingredient does not come into direct contact with the foodstuff and that the sachet material and the ink are both FDA approved. Specific information on the active ingredient(s) was not provided however from the appearance of the sachets it was expected that the active ingredient is potassium permanganate adsorbed onto silica gel.

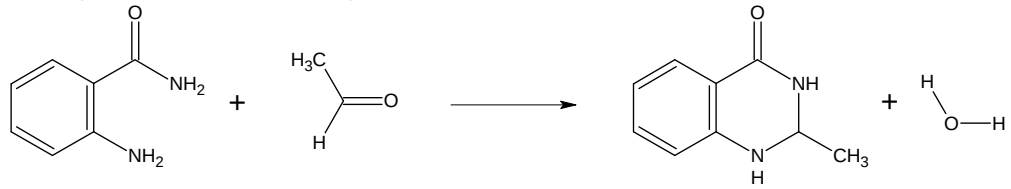
No information was provided by the suppliers of either of the food bags. The labelling on one of the packs states that “the bags allow the food to breathe, contain a very porous, entirely safe and natural Japanese stone powder suspended in the polyethylene film. This adsorbs the ageing hormones present in fruit and vegetables and therefore increases the storage life. The surface is treated to prevent moisture and bacteria forming.”

The two examples of the ethylene scavenging food bags are similar in appearance. The labelling on the external packaging also claimed that the product maintains vitamin C levels.

5.4 Acetaldehyde scavengers

Degradation of PET polymers results in the formation of acetaldehyde. Because of the low sensory threshold of this substance acetaldehyde scavengers are incorporated into

PET polymers used to package flavour sensitive foods and beverages such as bottled water. Examples of chemicals that can act as acetaldehyde scavengers are listed in the various patents available on-line. Typically they follow one of two mechanisms. The first involves the reaction of the acetaldehyde with an amine, amide or imine functionality. The mechanism of action of one of the most commonly described scavengers, anthranilamide, is given below.



The second utilises an oxidation catalyst such as cobalt octanoate or cobalt naphthalate which acts by oxidising the acetaldehyde to acetic acid (the flavour threshold of acetic acid is more than 1000 higher than that of acetaldehyde). Oxygen is consumed in the same reaction.

5.4.1 Samples obtained

One sample was obtained. No information was received from the supplier on the active ingredient(s). As the acetaldehyde is derived from the polymer rather than the food then this system is considered passive rather than active (as described above) and it was not considered further.

5.5 Antimicrobial releasing systems

Antimicrobial action may be imparted from films or sachets emitting ethanol, silver ions, organic acids such as propionic [7], sorbic [8] and benzoic [9] acid, sulphur dioxide, plant extracts e.g. allyl isothiocyanate from horseradish/mustard [10] or from other bio-based sources e.g. the bacteriocin nisin, a protein with activity against gram-negative bacteria which is an approved food additive in some countries [11, 12]. Other substances reported to have antimicrobial properties include enzymes, bacteriocins, chlorine dioxide, ozone, carbon dioxide, fatty acids, proteins, antibiotics, parabens and natural plant extracts. These are reported in detail by Potter *et al*. [6]. Although many examples are provided there is little information on commercial applications.

Sachets containing ethanol adsorbed onto silica release ethanol vapour which imparts a preservative effect on the packaging headspace preventing microbial spoilage of intermediate moisture foods. To mask the flavour of the ethanol, flavour releasers such as vanilla are often also included in the product.

Silver antimicrobials function in contact with microorganisms via an ion exchange mechanism that releases ionic silver in the presence of moisture (silver ions exchange with sodium ions in the environment/moisture). The silver ions released interact with the bonding sites on the microbe surface to prevent bacteria from reproducing. Some silver containing materials are not classed as active materials as their function is to inhibit the growth of microbes on the surface of the food contact material rather than preventing growth on the foods itself.

The use of organic acids as food preservatives is well documented [7-9] which includes the use of sorbic acid as an antimycotic in dry foods.

Sulphur dioxide may be used as a gas or in the form of its sulphite, bisulphite or metabisulphite salts which are powders and therefore easier to handle.

Most natural antimicrobials function to interrupt the metabolic pathway by interference in the cell wall membrane/structure. Nisin, for example, interacts with the sulphur containing compounds in the bacterial membrane disrupting their semi-permeable function and causing lysing of the cells.

5.5.1 Samples obtained

Two samples were obtained; one cling-film and one food storage liner. No information was provided on the source of the antimicrobial activity in the cling-film. The supplier of the food storage liner said that the active ingredient is silver zeolite based. According to information from the manufacturer, the anti-microbial activity of these materials extends the shelf life of the foodstuff. Therefore these samples can be classed as active materials and included in this study.

5.6 Anti-mould systems

Little information is available on the use of anti-mould agents on packaging materials. Sodium carbonate, sodium sorbate and potassium carbonate have been reported to act as anti-mould agents on wood. Sodium metabisulphite may be incorporated into a material or article releasing sulphur dioxide which will prevent any mould growth. Biphenyl in paper has been classified as a biocide for citrus fruits.

5.6.1 Samples obtained

Two anti-mould samples were obtained. One was described as a cheese preserving bag and the other was a paper bag.

The cheese preserving bag was described as incorporating an anti-mould treatment however the identity of the anti-mould treatment was not known.

Paper bags containing sodium metabisulphite crystals were obtained. These release sulphur dioxide gas in humid conditions. The sulphur dioxide reduces the growth of moulds. The bags were made of paper and intended to be used as an anti-mould system for grapes.

5.7 Heat releasers

Heat releasers include self-heating beverages and microwave susceptors. The two mechanisms of action are quite different and are described below.

Self-heating beverages are available, which generate an exothermic reaction upon mixing water with a salt. The heat generated in this process is used to heat the beverage.

Microwave susceptors are materials used for crisping and browning foods in microwave ovens. Under the definitions of active packaging they modify the foodstuff and therefore fall into this category. Examples of their use include packaging for pizzas,

chips and popcorn. Microwave susceptors in current use are bi- or tri- laminate in structure. Bi-laminate materials comprise a PET film as the food contact surface which is vacuum deposited with a thin layer of aluminium. This is glued onto a paperboard backing. Tri-laminate materials also comprise metallised film with a paper backing but have an overlying layer of paper as the food contact surface. Microwave susceptors are intentional 'releasing' systems but the high temperature generated (ca. 200ºC or more) can give rise to thermal breakdown of their constituents and accelerated migration.

5.7.1 Samples obtained

One microwave susceptor was obtained. The susceptor comprised a PET film coated with a thin layer of aluminium applied to a paperboard backing.

5.8 Flavour releasers

Wooden barrels are very widely used for the storage and maturation of whisky, wine and other alcoholic drinks and this has been practiced for a very long time. This packaging application has both releasing and adsorbing character, to change and improve the organoleptic qualities of the stored drink. To help do this, the barrels may be pre-treated by flaming to char the interior of the wood. The barrels may also be used first with e.g. sherry wine to incorporate flavour, aroma and colour components that may subsequently re-migrate into the spirit. It should be noted that this traditional application for the release of natural ingredients into specific food types during the process of their manufacture is not included in the EU Regulation on active and intelligent materials. This is stated in whereas clause (5) of the Framework Regulation (EC) No. 1935/2004.

Encapsulation can be used to hold flavours within a product. When the packaging is opened or the food contact material/article is used the flavours are released. Examples include flavour encapsulated straws, films and sports bottle caps. These intentionally release flavour compounds when the milk (straws), bread/cereal/snack bags (film) or bottled beverage (sports caps) is consumed and therefore are also considered to be active food contact materials.

5.8.1 Samples obtained

Three samples were obtained. One foil and two sports cap closures. The foil was described as releasing a cinnamon flavour and the two caps as lemon and orange flavoured.

5.9 Monitoring systems

Monitoring systems may provide information on the freshness of a foodstuff or on the time for which it has been stored (again related to product freshness). They may also provide information on the temperature of a foodstuff. Many of the consumer goods on shelves today rely totally on the ubiquitous "use-by" or "best-before" date to indicate when perishable goods are no longer fit to eat. It is generally agreed that these are always based on conservative estimates and that this can result in considerable food waste. A comprehensive review of these systems is provided in the report 'Smart and active packaging to reduce food waste' which can be found at [13] and in [6]. This information is not repeated here.

5.9.1 Samples obtained

Three classes of samples were obtained, including indicators of time, heat and freshness.

Several time indicators were obtained. However, since these are used on the external surface of the food packaging and the intelligent components were behind an aluminium barrier which would serve as a functional barrier to migration, it was decided not to include these materials to determine the migration in this study. However one of the examples received was investigated in the efficacy studies carried out (see section 8).

One freshness indicator was obtained. The intelligent ingredient was described as a 'metal coordinated complex in a medium'. In this way food spoilage is detected (a colour change is observed) following the reaction of the complex with, for example, sulphur compounds or amines.

A heat sensing weaning spoon was obtained. The elastomeric part of the spoon changes colour at elevated temperature. The intelligent ingredient is not known.

5.10 Other active and intelligent packaging samples

Several other classes of active and intelligent packaging materials were identified in the information gathering exercise however no samples were obtained. This may be due to there being no commercial application of the active/intelligent functions described (to date), that it was not possible to get hold of samples within the timeframe of the project or that it was decided that no testing was required as the active ingredient is known to be inert (e.g. nitrogen releasing beer widgets).

5.10.1 Amine scavengers

The removal of amines, which impart an undesirable off-flavour to foodstuffs, can occur by reaction of the alkaline amine with an acid such as citric acid incorporated into polymers. Other reports describe a film containing iron salts with organic acids such as citric and ascorbic acid. The organic acid reacts with the amines and the reaction products (salts) are adsorbed by the polymer.

5.10.2 Aldehyde scavengers

The oxidation of fats and oils forms aldehydes which can result in off-flavours in high fat foods. Aldehydes can be removed by the inclusion of sodium sulphate or other inorganic sulphates in the packaging. Tocopherols such as vitamin E and synthetic aluminosilicate zeolites are also effective aldehyde adsorbers. Acetaldehyde adsorbers have been considered separately (Section 5.4).

5.10.3 Sulphide scavengers

Sulphide scavengers are reported to be active in the removal of hydrogen sulphide off-flavours generated from the spoilage of poultry.

5.10.4 Bitter taste removers

An active packaging to reduce bitterness in grapefruit juice which comprises a thin cellulose acetate layer containing the fungal derived enzyme naringinase has been described [14]. The naringinase enzyme consists of α-rhamnosidase and β-glucosidase

which hydrolyses the bitter naringin to form naringenin and prunin. Neither of these are bitter tasting compounds. The cellulose acetate also absorbs limonin which is another bitter substance present in fruit juices.

5.10.5 Lactose and cholesterol removers

The incorporation of the enzyme lactase into a packaging material hydrolyses lactose to form glucose.

Incorporation of cholesterol reductase converts cholesterol to coprosterol which is not absorbed by the intestine and is so excreted from the body.

5.10.6 Carbon dioxide regulating systems

Carbon dioxide is formed in some foods due to deterioration and respiration reactions. The carbon dioxide produced has to be removed from the package to avoid food deterioration and/or package destruction. Carbon dioxide adsorbers can contain calcium hydroxide, sodium hydroxide or potassium hydroxide, calcium oxide and silica gel. Active minerals have also been reported to adsorb gases such as carbon dioxide.

In other cases, however, high carbon dioxide levels (10–80%) are desirable, e.g. for foods such as meat and poultry because these high levels inhibit surface microbial growth and thereby extend shelf-life. Fresh meat, poultry and cheese can benefit from packaging in a high carbon dioxide atmosphere. Removal of oxygen from a package by use of oxygen scavengers creates a partial vacuum which may result in a collapse of flexible packaging. Also, when a package is flushed with a mixture of gases including carbon dioxide, the carbon dioxide dissolves partly in the product and creates a partial vacuum. In such cases, the simultaneous release of carbon dioxide from inserted sachets which consume oxygen is desirable. Such systems are based on either ferrous carbonate or a mixture of ascorbic acid and sodium bicarbonate. The oxygen scavengers / carbon dioxide generators are intended for use in products where package volume and package appearance are critical e.g. peanuts or potato crisps [15].

5.10.7 Nitrogen releasers ('beer widget')

The purpose of the widget is to release the gas into the beer in the can to create the foam ‘head’. The widget may take several forms but essentially releases either carbon dioxide or nitrogen gas. When the can is opened the gas is released into the beer creating the foam.

5.10.8 Anti-oxidant releasers

The release of antioxidants such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) has been reported to retard the ageing of cereals and snack food products. Vitamin E (α-tocopherol) is considered to be a natural viable alternative to BHT/BHA impregnated packaging. Antioxidants react with free radicals and peroxides to retard or block the oxidation reactions that result in staling of the foodstuff.

5.10.9 Tin releasers

The quality of many canned tomato products benefits from tin migration from tinplate and there are special (elevated) levels of tin permitted in such products. This intentional migration of tin may be considered to be a form of active packaging.

6 Screening experiments

The main aim of the analytical screening experiments was to identify the active and intelligent components present in the samples. Different analytical strategies were pursued to identify trace elements, volatile, semi- and non-volatile compounds. The experiments were performed in two laboratories; TNO Quality of Life in Zeist, the Netherlands and The Food and Environment Research Agency (Fera) in York, UK. The analytical methods used at both laboratories were essentially the same. However, some of the experimental details, such as the MS system used and the acid used in the elemental screening varied. This is because the screening methods used are not standardised and each laboratory will have developed small variations in the method for the same type of analyte. For this reason the methodology used and the results obtained by the two laboratories are described separately. Despite these small differences, the results of the screening would be expected to yield similar results if the same sample was analysed by both laboratories.

Information on the active components of the oxygen scavenging sachet, label and crown cap, one of the anti-mould samples (the paper bag) and the antimicrobial food storage liner was provided by the suppliers. Therefore an analysis to screen for these compounds specifically was not performed. A general non-target screening for the presence of other substances was however carried out. For the remaining samples information on the active compound was not provided and a non-target screening experiment was carried out to:

1) identify the active and/or intelligent substances

2) (where possible) to determine which other compounds related to the active/intelligent substance(s) are present in the material or article and which have the potential to migrate to packaged food. This was only possible when control samples (the same materials or articles but without the active of intelligent component(s)) were provided. Where possible where control samples were not available, alternative representative reference materials were used.

An analytical screening test protocol was followed. This protocol contains a suite of complementary analytical methods to identify and estimate the concentrations of potential chemical migrants in the samples obtained. The techniques used were:

- Headspace gas chromatography (GC) – mass spectrometry (MS) for the analysis of volatile substances
- GC-MS for the analysis of semi-volatile substances
- Liquid chromatography (LC) – linear ion trap (LTQ)/time-of-flight (TOF) – MS for the analysis of polar non-volatile substances
- Inductively coupled plasma (ICP) – MS / (atomic emission spectroscopy AES) for elemental analysis

Where possible the analysis was carried out on extracts of the active and intelligent parts of the packaging only.

6.1 Screening experiments – TNO

6.1.1 Sample logging

The samples obtained and analysed by TNO were assigned unique identifying codes. The sample numbers and descriptions are provided in Table 2. Each code contains an abbreviation indicating the type of active/intelligent material. OxS stands for oxygen scavenger, CC for crown cap, AntiM for anti-mould or antimicrobial, FlavR for flavour releaser, EthS for ethylene scavenger, HeatR for heat releaser, FreshI for freshness indicator, MoistA for moisture absorber, TI for time indicator, AS for acetaldehyde scavenger and HeatS for heat sensor.

6.1.2 Sample preparation for headspace GC-MS analysis

A piece from the following samples was cut with scissors into small pieces (approximately 4 × 4 mm); oxygen absorbers (0939-02-1731-OxS3, label, 0939-02-1735-OxS4, sachet, 0939-02-1729-CC1, Crown cap), SO_2 emitter (0939-02-1737-AntiM2), flavour releasers (0939-03-0227–FlavR1 blown film, 0939-03-0228-FlavR2 closure green, 0939-03-0229-FlavR3, closure orange) and antimicrobial food storage liner (0939-03-0269-AntiM3). The test sample was transferred to a 10 mL headspace vials and the mass recorded (Table 3). Internal standard, 10 µL of a 0.03-1 mg/mL solution of fluorobenzene (for analysis using a polar column) or dodecane (for analysis using an apolar column) in methanol, was added to the vial. The experiment was performed in duplicate. Blanks (no samples) were also prepared in duplicate.

6.1.3 Sample preparation for GC-MS analysis

Different sample preparation strategies were needed since different types of samples were obtained and tested. The mass of each material used is shown in Table 3. A worst-case extraction was performed for all materials in 95% ethanol and in iso-octane.

Oxygen scavenger containing crown cap and control; three inlays of the crown caps 0939-02-1729-CC1 and 0939-02-1730-CC2 were removed using a scalpel and extracted with 5 mL 95% ethanol or 5 mL iso-octane.

Oxygen scavenging sachet; the sachet containing the oxygen scavenger 0939-02-1735-OxS4 was emptied in a vial and the contents were extracted with either 5 mL 95% ethanol or 5 mL iso-octane.

Oxygen scavenging label; the label 0939-02-1731-OxS3 contains a packaged pad to which the iron powder is added. Four of these were transferred to a vial and extracted with either 5 mL 95% ethanol or 5 mL iso-octane. It was difficult to isolate the oxygen scavenger from the packaging. Therefore part of the packaging was also extracted.

Anti-mould containing paper bag; the $Na_2S_2O_5$ crystals were removed from the bag (0939-02-1737-AntiM2). The crystals were extracted with either 5 mL 95% ethanol or 5 mL iso-octane.

Flavour releasers; the flavour releasing film (5.0 g, 10 dm^2) 0939-03-0227-FlavR1 was extracted with 50 mL 95% ethanol or 50 mL iso-octane. The two flavour releasing closures 0939-03-0228-FlavR2 and 0939-03-0228-FlavR3 (5 g) were extracted with 50 mL 95% ethanol or 90 mL iso-octane.

Antimicrobial food storage liner; the antimicrobial food storage liner 0939-03-0269-AntiM3 (4.8 g) was extracted with 150 mL 95% ethanol or 150 mL iso-octane.

All samples were extracted for 1 day at 60°C after which time a portion of the solvent layer was transferred to a GC vial. 5 µL internal standard (0.847 mg/mL dodecane in methanol) was added to the vial. All experiments were performed in duplicate. Blanks (no sample) were also prepared in duplicate.

6.1.4 Sample preparation for LC-MS analysis

The extracts of 0939-03-0227-FlavR1, 0939-03-0228-FlavR2, 0939-03-0228-FlavR3, 0939-03-0269-AntiM3, 0939-02-1729-CC1, 0939-02-1730-CC2, 0939-02-1731-OxS3, 0939-02-1735-OxS4 and 0939-02-1737-AntiM2 obtained under 6.1.3 were used for LC-MS analysis. Internal standards were not added for LC-MS analysis as the response would be difficult if not impossible to correlate with the peaks observed since the response is far more substance specific than GC-MS.

6.1.5 Sample preparation for elemental screening

Samples 0939-02-1729-CC1 and 0939-02-1730-CC2 were digested with sulphuric acid and hydrogen peroxide under reflux temperature. In the resulting solutions the trace element levels were determined using ICP-AES. To cover all elements listed in Table 10, the samples were ashed at 550°C and the residues were dissolved in diluted hydrochloric acid. In the resulting solutions the trace element levels were determined using ICP-AES. In total 60 elements were screened for.

Screening of the antimicrobial food storage liner (0939-03-0269-AntiM3) was performed by Fera, see 6.2.9 for experimental details. For the other materials tested by TNO the active substance was known and elemental screening was not performed.

6.1.6 Analysis by headspace GC-MS

The headspace vial was incubated for 30 minutes at 100°C and 1 mL of the headspace gas was injected onto a CP-Porabond Q column (25 m, 320 µm internal diameter, 5 µm film thickness) or an AT1000 column (30 m, 320 µm internal diameter, 0.30 µm film thickness). Detection was performed with electron impact (EI)-MS.

A similar experiment was performed on an apolar column AT-5MS (30 m, 250 µm diameter, 1 µl film thickness) or a DB-5HT column (30 m, 250 µm diameter, 0.1 µm film thickness). The temperature program was 40°C for 2 minutes followed by a temperature ramp to 250°C at 15°C/min. The temperature was held constant at 250°C for 1 minute.

6.1.7 Analysis by GC-MS

All samples were analysed using an Agilent GC-MS fitted with an HP5973 mass selective detector. The oven temperature was 100°C for 1 minute after which the temperature increased to 320°C at a rate of 15°C/min. The temperature was held for 5 minutes at 320°C. The injection volume was 1 µL splitless. The column used was an AT-5MS (30 m, 250 µm diameter, 1 µm film thickness) or a DB-5HT (30 m, 250vµm diameter, 0.1 µm film thickness).

6.1.8 Analysis by LC-MS

A Vision HT C18 column (50 x 2 mm with 1.5 µm particle size) was used for LC separation. The mobile phase was the same for both positive and negative electrospray

ionisation. A gradient of 5 mM ammonium acetate, pH5 (A) and acetonitrile + 1 mM ammonium acetate (B) was used with a flow rate of 300 µL/min. The starting mixture was 90%A and 10% B and was held for 1 minute, the gradient increased to 100% B over 4 minutes, held at 100% B for 1 minute after which it changed to 90% A and 10% B over a period of 0.1 minutes and was held for 5 minutes. The injection volume was 5 µL.

The MS analyses were performed in positive and negative electrospray mode with the sheath gas flow on. The capillary temperature was 275°C, source voltage was 3.5 kV, capillary voltage 44 V (in negative mode -35 V), tube lens 95 V (in negative mode -80 V).

The mass range selected was m/z 125-1250. The data were handled and interpreted manually. Ions that were selected were above at least 5% of the most abundant ion present. Further only the ions that were greater than ~ 10 times higher than in the background signal were considered.

6.1.9 Results screening

Active and intelligent packaging materials concern materials to which chemicals are added to give the packaging material a desirable property. It is unknown if and which compounds can migrate from such materials. The migration was performed under worst-case conditions to ensure that all potential migrants were extracted from the material.

The main aim of this analytical screening process was to identify the active and intelligent components present in the samples. These components are expected to be present at a high level. However any impurities, reaction or breakdown products associated with the active and intelligent components are also of interest and these are expected to be present at much lower levels, hence it is important to consider all substances that are present in the samples above a defined cut-off concentration. This cut-off concentration is product specific but is equivalent to a migration of 10 µg/kg in the foodstuff. This is generally used as a margin below which compounds are considered to be safe (with the exception of a few compound classes such as carcinogens). The levels in the sample that are equivalent to a worst case migration, i.e. a total transfer, of 10 ppb are calculated below. As defined in CEN standards (for plastics but here as a guide for all material types) for migration testing, where the surface-to-volume ratio to be used in contact with food is known, e.g. a bottle of defined volume, this is used in the calculation. Where the surface-to-volume ratio to be used in contact with foodstuff is not known, conventional exposure conditions have been used, i.e. 6 dm² of surface area in contact with 1 kg of foodstuff. For products such as sachets and labels for which the ratio is not known but the conventional ratio is clearly incorrect then the assumptions made are described in the calculation. It should be noted that these concentrations do not take into account any barrier layers present between the active/intelligent components and the foodstuff and therefore they represent the worst case food contact conditions. The methods used were capable of detecting substances in the molecular weight range 125-1250 Da at levels below the cut-off concentrations calculated below.

0939-02-1731-OxS3 Oxygen scavenger, label
One label can be in contact with at least 50 g of food (information from the supplier) which means that 1 kg of food that is consumed at maximum each day can be in contact with 20 labels.

- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg / 20 = 0.5 µg per label.
- The mass of each label is 0.25 g
- A concentration of 0.5 µg per label is equivalent to **2.0 mg/kg** label.

0939-02-1735-OxS4 Oxygen scavenger, sachet
One sachet can be in contact with at least 50 g of food (information from the supplier) which means that 1 kg of food that is consumed at maximum each day can be in contact with 20 bags or labels.

- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg / 20 = 0.5 µg per sachet.
- The mass of each sachet is 4.6 g
- A concentration of 0.5 µg per sachet is equivalent to **0.11 mg/kg** label.

0939-02-1729-CC1, 0939-02-1730-CC2 Oxygen scavengers, crown cap and control
The crown caps are applied to bottles of volume ≥ 250 mL. Therefore the surface-to-volume ratio is known.

- The volume of the bottle is taken as 250 mL (the worst-case ratio).
- The insert containing the active ingredient is 0.55 g.
- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg / 4 = 2.5 µg/crown cap or **4.5 mg/kg** insert.

0939-02-1737-AntiM2 Anti-mould emitter, paper bag
From a technical report received from the supplier, it can be concluded that 24 sachets containing ~ 0.4 g $Na_2S_2O_5$ each will be in contact with 4.5 kg of grapes. The SO_2 emitters are placed on-top of the grapes during storage.

- The mass of each emitter is 1.25 g.
- 24 sachets will be in contact with 4.5 kg grapes = 5.3 sachets in contact with 1 kg of grapes.
- One emitter is in contact with 0.19 kg of grapes.
- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg / 5.3 = 1.89 µg/emitter or **1.5 mg/kg** sachet.

0939-03-0227-FlavR1 Flavour releaser, blown film
The product has the potential to come into contact with a broad range of foods and therefore the surface-to-volume ratio is not known. Under these circumstances the conventional area to mass of food ratio of 6 dm^2 /kg food is applicable.

- The mass of the film is 0.6 g/dm^2.
- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg/6 dm^2 (1.7 $µg/dm^2$) of film or to **2.8 mg/kg** film.

0939-03-0228-FlavR2, 0939-03-0228-FlavR3 Flavour releaser, closures
The closures are applied to bottles of volume ≥ 250 mL. Therefore the surface-to-volume ratio is known.

- The volume of the bottle is taken as 250 mL (the worst-case ratio).
- One closure weighs 5 g

- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg / 4 = 2.5 µg/closure or **0.50 mg/kg** closure.

0939-03-0269-AntiM3 Antimicrobial food storage liner
The product has the potential to come into contact with a broad range of foods and therefore the surface-to-volume ratio is not known. Under these circumstances the conventional area to mass of food ratio of 6 dm^2/kg food is applicable.

- One food storage liner weighs 0.36 g/dm^2.
- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg per 6 dm^2 (1.7 µg/dm^2) or **4.7 mg/kg** food storage liner.

6.1.9.1 Results volatile substances

The best library matches (based on the library fit and a visual consideration of the ions present) and estimated concentrations of the substances detected in the headspace GC-MS analysis above the cut-off concentrations described above are shown in Tables 4 and 5. For most of the samples none or very few volatile substances were detected. The exceptions were the flavour releasing materials in which many volatile substances were observed however most were below the cut-off concentration of 10 µg/kg. Interesting is the presence of BHT in film sample 0939-02-0227-FlavR1, which is probably added as an antioxidant. This is the only substance in this material that is above the cut-off concentration described above. It is not expected that this antioxidant will have an effect on the foodstuff however it may be present to impart its properties on the flavouring compounds and therefore would be present as a consequence of the active ingredient and so is relevant in this study. According to the manufacturer of the flavour releaser, BHT was probably added during the manufacturing of the film (this was supplied by a different manufacturer). It was not added during the process where the flavour was encapsulated in the film. Compounds that were observed below the threshold level of 10 µg/kg are not listed in Table 5.[1] Among these substances, i.e. below 10 µg/kg, are the substances that cause the flavour; 2-acetylpyridine with a tobacco like aroma and cyclotene with a sweet flavour somewhat similar to liquorice.

The flavour releasers 0939-03-0228-FlavR2, 0939-03-0229-FlavR3 contain many flavours of which most are related to lemon or orange flavour, see Tables 4 and 5.[2] Compounds that could not be related in sample 0939-03-0228-FlavR2 to a natural flavour were; 4-methyl-octane (CAS No 2216-34-4), 4-methyl-1-(1-methylenethyl)-bicyclohexane (CAS No 58037-87-9), 1,5-cyclooctadiene, 1,5-dimethyl- (CAS No 3760-14-3), 2,6-octadienal, 3,7-dimethyl- (CAS No 5392-40-5), 2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol (CAS No 10482-56-1). For 0939-03-0229-FlavR3 these are; bicyclo[3.1.0]hexane,4-methylene-1(1-methylethyl)- (CAS No 28634-89-1) and benzoic acid, 2-(methylamino)-, methylester (CAS No 85-61-6). However, since it was difficult to separate the active material from the packaging and a reference was not provided, it is not known whether or not these substances are related to the active ingredient or the packaging material.

From the oxygen scavenging label 0939-02-1731-OxS3, toluene, methylester of acetic acid, dimethoxymethane and 4-methyl octane were detected, see Tables 4 and 5. However, as above, since it was difficult to separate the active material from the packaging and a reference was not provided, it is not known whether or not these substances are related to the active ingredient or the packaging material.

[1] Fenaroli's Handbook of Flavour Ingredients Volume II, sec. ed. CRC press, 1975
[2] Volatile compounds in food (www.vcf-online.nl)

6.1.9.2 Results semi-volatile substances

The best library matches and estimated concentrations of the substances detected above the cut-off concentration in the iso-octane and 95% ethanol extracts of the samples by GC-MS analysis are shown in Table 6 for the ethanolic extracts and Table 7 for the iso-octane extracts. No GC-MS detectable semi-volatile substances were detected above the cut-off concentrations defined above in either the ethanolic or iso-octane extracts of samples 0939-02-1729-CC1, 0939-02-1730-CC2, 0939-02-1737-AntiM2 or 0939-03-0269-AntiM3. Only octadecyl-3,5-di-(tert)-butyl-4-hydroxyhydrocinnamate was detected above the cut-off concentration in the 95% ethanol extracts of sample 0939-02-1735-OxS4. Many compounds were observed in the 95% ethanol and iso-octane extracts of the flavour releasers 0939-02-0227-FlavR1, 0939-02-0228-FlavR2 and 0939-02-0229-FlavR3. Most of these compounds have been reported as natural flavours.[3] Compounds that could not be related to a natural flavour were:
For 0939-02-0227-FlavR1; 1,4-benzenedicarboxylic acid, diethyl ester (CAS 636-09-9) and about 16 further substances for which the identities could not be proposed with a total content of approximately 100 mg/kg.
For 0939-02-0228-FlavR2 bicyclo[3.1.1]hept-2-ene, 3,6,6-trimethyl (CAS 4889-83-2), cyclohexene 1-methyl-4-(1-methylethenyl)- (CAS 7705-14-8), 3-cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)- (CAS 20126-76-5) and benzoic acid, 4-ethoxy-, ethyl ester (CAS 23676-09-7) could not be related to a natural flavour. A further 48 peaks that could not be identified were observed in the TIC chromatograms with a total content of approximately 1900 mg/kg.
For 0939-02-0229-FlavR3 1,5-cyclooctadiene, 1,5-dimethyl (CAS 3760-14-3), 6-octenal, 3,7-dimethyl-,R- (CAS 2385-77-5), tritetracontane (CAS 7098-21-7), benzoic acid, 4-ethoxy-, ethyl ester (CAS 23676-09-7, 1,4-benzenedicarboxylic acid, diethyl ester (CAS 636-09-9 and cyclopropanenonanoic acid, 2-[(2-butylcyclopropyl)methyl]-, methyl ester (CAS 152-69-9) could not be related to a natural flavour. Another 68 unidentified compounds were detected with a total content of approximately 2500 mg/kg.

6.1.9.3 Results polar and non-volatile substances

The LC-LTQ-MS data acquired have a mass accuracy of about 0.1 Da. All data was analysed using a Microsoft Excel macro containing mass information about additives and their reaction/degradation products. A mass range of 0.5 Da was used. The information in this Microsoft Excel macro was prepared as a part of another FSA funded project (A03054, An investigation into the reaction and breakdown products from starting substances used to produce food contact plastics, 2007). As mentioned previously quantification was not possible due to the difficulty of finding a suitable internal standard for electrospray ionisation (ESI)-MS.

A number of compounds were detected for the ions that were observed in positive ESI mode (Table 8) and in the negative ESI mode (Table 9). The identity of many ions could be related to additives and reaction/breakdown products thereof and clusters of salt. As is usually the case for LC-MS data where no spectral libraries are available several substances were detected for which no identity could be proposed.

For samples 0939-02-1728-OxS1 and 0939-02-1738-OxS2 direct infusion-MS was performed. All other samples were analysed by LC-MS. For the substances tested by LC-MS it may be the case that different ions appearing at the same retention time in the chromatogram originate from the same substance. On the other hand, because there is

no chromatographic separation with direct infusion, ions may appear in the same spectrum but originate from different substances.

6.1.9.4 Results elemental screening

Only the oxygen scavenger 0939-02-1729-CC1 (and the reference sample 0939-02-1730-CC2) were subjected to the elemental screening (Table 10) by TNO.

The crown caps (0939-02-1729-CC1/1730-CC2) were screened for the presence of sulphur (the active ingredient is known to be a sulphite). An approximately 100 times higher level of sulphur was found in the material containing the active ingredient (0939-02-1730-CC2) compared to the reference material (0939-02-1729-CC1). This confirms the presence of the sulphite as the active component.

6.1.10 Active/intelligent ingredients

From the data generated in the analytical screening exercise and information provided by the manufacturer/supplier, the following active/intelligent ingredients have been identified:

0939-02-1731-OxS3 Oxygen scavenger, label

The active ingredient is known to be iron powder. This information was provided by the supplier. The iron reacts with oxygen to form iron oxide. A provisional maximum tolerable daily intake for man of 0.8 mg of Fe/kg body weight was assigned by JECFA (http://www.inchem.org/documents/jecfa/jecmono/v18je18.htm). Applying a body weight of 60 kg (as is the convention) this equates to 48 mg/kg of food. Since the labels contain up to a few grams of pure iron powder, such a high migration into the food is a possibility and further migration testing was carried out.

0939-02-1735-OxS4 Oxygen scavenger, sachet

The active ingredient is known to be iron powder. This information was provided by the supplier. The iron reacts with oxygen to form iron oxide. A provisional maximum tolerable daily intake for man of 0.8 mg/kg body weight was assigned by JECFA (http://www.inchem.org/documents/jecfa/jecmono/v18je18.htm). Applying a body weight of 60 kg (as is the convention) this equates to 48 mg/kg of food. Since the sachets contain up to a few grams of pure iron powder, such a high migration into the food is a possibility and further migration testing was carried out.

0939-02-1729-CC1 0939-02-1730-CC2 Oxygen scavenger, crown cap

The active component is based on sulphite. The elemental screening of the crown caps gave a 100 times higher level of sulphur (15 g/kg) for the material containing the active ingredient compared to the reference material. As a guide sodium sulphite has an SML of 10 mg/kg food. Since the concentration of sulphur in the crown caps was in the range of 15 g sulphur/kg crown cap corresponding to 38 g sulphite/kg crown cap, it can be estimated that the sulphate concentration that can potentially transfer to the beverage is below 0.08 g/person/day (four bottles containing 250 mL beverage consumed per person per day, mass one crown cap insert is 0.55 g). Therefore, in principle migration testing should be performed. However, it was demonstrated in section 7.1.3.3. for the anti-mould emitter that sulphite is unstable in 3% acetic acid. Therefore, no further migration tests were performed with the crown caps.

0939-02-1737-AntiM2 Anti-mould emitter, paper bag
The active material is known to be sodium metabisulphite ($Na_2S_2O_5$). $S_2O_5^{2-}$ exists in equilibrium with sulphite ions and SO_2 gas. The total specific migration limit (SML(T)) of $NaHSO_3$ and Na_2SO_3 is 10 mg/kg food expressed as SO_2. The amount of $Na_2S_2O_5$ in the anti-mould emitter is 400 mg. From a technical report received from the supplier, it can be concluded that 24 sachets each will be in contact with 4.5 kg of grapes. Therefore the potential exists for the migration to exceed the SML(T) and migration testing was carried out.

0939-03-0227-FlavR1 Flavour releaser, blown film
The results of the screening studies suggest that the active components are a range of naturally occurring flavours. No restrictions were found relating to these flavouring substances. BHT, proposed to be associated with the active ingredient (see earlier), was detected in the film at a concentration of ~ 5 mg/kg film. BHT has been assigned an SML of 3.0 mg/kg food and migration testing is proposed. Applying the conventional area to mass of food ratio of 6 dm^2 / kg food a concentration of 5 mg/kg in the film is equivalent to a worst case migration of 0.018 mg/kg food (the mass of the film is 0.6 g/dm^2). Though the SML could not be exceeded migration testing was carried out because BHT is a permitted food additive controlled under Directive 95/2/EC. The substance is however permitted for use in a resticted number of foods in case the technological function of BHT in foods were demonstrated.

0939-03-0228-FlavR2 0939-03-0229-FlavR3 flavour releasers, closures
The screening studies identified numerous naturally occurring compounds that are also present in lemons and oranges. It was therefore concluded that the flavour released from the closures has a natural origin and therefore no migration testing was carried out.

0939-03-0269-AntiM3 Antimicrobial food storage liner
Information on the active component was provided by the manufacturer, which is silver zeolite. The material may contain up to 10% silver zeolite corresponding to a maximum percentage of 0.5% Ag in the material. ICP-MS analysis measured silver at a concentration of 17 mg/kg in the liner. Applying the conventional contact area to mass of food ratio and the mass of food storage liner, it can be reasoned that 6 dm^2 may release up to 0.04 mg of Ag to food. Since this approaches the Group restriction of 0.05 mg/kg food (given in the Synoptic Document) and that the results of the ICP-MS analysis were only semi-quantitative, migration testing was carried out.

For all samples the aim was to identify the active/intelligent ingredient(s) and any other potential migrants associated with them. In most cases it was not possible to isolate the active/intelligent component from the rest of the packaging and therefore the potential migrants derived from these components could not be differentiated from those derived from the packaging itself. The identities of the substances other than those listed above that were detected in the samples have been considered. One sample 0939-03-0227-FlavR1 the blown film flavour releaser contained BHT at a level between 3.8 and 5 mg/kg film which is probably added as an anti-oxidant. At this level in the film the SML for this substance (3 mg/kg) will not be exceeded. The other substances for which identities are proposed are expected, based on our experience of testing food contact materials and articles, to be derived from the materials and articles themselves rather than specifically from the active components.

6.2 Screening experiments – Fera

6.2.1 Sample logging

The samples obtained and analysed by FERA were assigned a unique identifying code using the Fera LIMS system. The sample numbers are provided in Table 2.

6.2.2 Sample preparation for headspace GC-MS

The samples were cut into small pieces and the pieces were mixed. 10 mL headspace vials were half-filled with test sample and the masses of the samples were recorded (Table 11). Internal standard, 10 µl of a 1 mg/mL solution of fluorobenzene in methanol, was added. Triplicate samples were prepared. Blanks (no test sample) were also prepared in triplicate.

6.2.3 Sample preparation for GC-MS

The samples were cut into small pieces (~ 5 x 5 mm) and the pieces were mixed. Sub-samples were weighed into glass vials (masses of each sample are given in Table 12). 40 µl of a mixed solution of d_{10}-benzophenone and 1-fluorononane each at a concentration of 1 mg/mL in either ethanol or iso-octane was added and allowed to infuse into the samples. The samples were then extracted with iso-octane or 95% aqueous ethanol (20 mL) for 24 hours at 60°C. A portion of the extract (0.5 mL) was removed and transferred to a vial for analysis. Triplicate samples were prepared. Blanks were prepared in the same way but in the absence of the test samples.

6.2.4 Sample preparation LC-TOF-MS

The samples were cut into small pieces (~ 5 x 5 mm) and the pieces were mixed. Sub-samples were weighed into glass vials (masses of each sample are given in Table 13). 40 µl of a mixed solution of d_{10}-benzophenone and 1-fluorononane each at a concentration of 1 mg/mL in either ethanol or iso-octane was added and allowed to infuse into the samples. The samples were then extracted with iso-octane or 95% aqueous ethanol (20 mL) for 24 hours at 60°C. A portion of the ethanol extract (0.5 mL) was removed and transferred to a vial for analysis. A portion of the iso-octane extract (0.5 mL) was removed and transferred to a 2 mL glass vial. Isopropanol (0.5 mL) was added to the vial and the contents mixed prior to analysis by LC-TOF-MS. The remainder of the solvent extract was evaporated to dryness under a gentle stream of nitrogen. The residue was reconstituted in acetonitrile and transferred to a vial for analysis. Triplicate samples were prepared. Blanks were prepared in the same way but in the absence of the test samples.

6.2.5 Sample preparation ICP-MS

Portions (0.1-0.5 g) of the sample were digested in a nitric and hydrochloric acid mixture using quartz high pressure closed vessels and microwave heating prior to quantification by ICP-MS. Reagent blanks, a reagent blank spiked with a known amount of each analyte, and a certified reference material, were analysed with the test samples to estimate recovery and accuracy.

6.2.6 Analysis by headspace GC-MS

The samples were incubated for 30 minutes at 100°C. The resulting volatiles were analysed using an Agilent 6980 gas chromatograph (Agilent, Palo Alto, CA, USA) coupled with an Agilent 5973 inert mass selective detector by splitless injection (splitless time 1 minute) of 1 mL of the headspace gas onto a DB-VRX capillary

column (60 m x 0.25 mm i.d. x 1.4 µm film thickness; J & W Scientific, Folson, Ca, USA). Following injection, the oven was held at 40°C for 2 minutes and then raised at 10°C/minute to 320°C and held for 10 minutes. The inlet was held at 250°C. Helium (1 mL/min constant flow) was employed as the carrier gas. The MS was operated in electron impact mode with scanned monitoring between 50 - 450 amu.

6.2.7 Analysis by GC-MS

The ethanol and iso-octane extracts were analysed by GC-MS using an Agilent 6980 gas chromatograph (Agilent, Palo Alto, CA, USA) coupled with an Agilent 5973 inert mass selective detector. Splitless injection (splitless time 1 minute) of 1 µl of extract was carried out into a ZB-5MS capillary column (30 m x 250 µm i.d., 0.25 µm film thickness; Phenomonex, USA). Following injection the oven was held at 60°C for 5 minutes and then raised at 10°C/minute to 320°C and held for 10 minutes. The injector was held at 250°C. Helium (1 mL/min constant flow) was employed as the carrier gas. The MS was operated in electron impact mode with scanned monitoring between 50 - 450 amu.

6.2.8 Analysis by LC-TOF-MS

The extracts were analysed by LC-TOF-MS using an Agilent 6210 LC/MS TOF (Agilent, Santa Clara, California, USA) consisting of a 1200 Series LC and a time of flight mass spectrometer. Two separate LC-MS methods were used in order to increase the coverage of compounds that could be detected in this way. In both cases separation used an Agilent ZORBAX Eclipse XDB-C18 (100 x 2.1 mm, 3.5 µm) column. For positive mode electrospray the mobile phase consisted of 0.1% aqueous acetic acid (channel A) and acetonitrile (channel B). For negative mode electrospray the mobile phase was 5 mM ammonium formate at pH 5.5 (channel A) and 0.1% 5 mM ammonium formate at pH 5.5 in acetonitrile (channel B). The mobile phase gradient for both positive and negative mode electrospray was the same: a starting mixture of 80% A and 20% B that changed to 50% B over 25 minutes. This was held for 20 minutes and increased to 100% B over a period of 15 minutes. This was held for a further 10 minutes before returning to 20% B over a period of 10 minutes. The flow rate was 0.2 mL/min with an injection volume of 5 µl.

TOF-MS analysis was carried out in positive and negative mode electrospray with nebuliser pressure 45 psi, capillary 4000 V, gas temperature 325^{o}C, drying gas flow at 10 l/min, skimmer 60 V, fragmentor 150 V and octopole RF voltage 250 V. The mass range measured was 100 – 1100 m/z. The TOF-MS data produced was processed using Agilent Molecular Feature Editor software with signal to noise threshold 50, minimum relative volume 5% and a mass accuracy of 10 ppm. The elements used in the Molecular Formula Database along with the potential number of atoms (in brackets) were C (1-100), H (0-200), O (0-20), N (0-20), P (0-10), S (0-5), Cl (0-5), Si (0-10), Na (0-5) and K (0-1). This elemental profile was selected based on the composition of known packaging additives. If elements such as bromine were present then these would have been identified based on the isotope pattern.

6.2.9 Analysis by ICP-MS

All digests were measured by flow injection using an Elan6000 ICP-MS, operating with a nebuliser flow rate 1.3-1.5 l/min argon, R.F. power (for the ICP) 1250 Watts. Peak jump acquisition. The instrument was optimised to achieve < 3% oxide formation (based on CeO) and < 1% double charged species (based on Ba^{2+}).

6.2.10 Results screening

As mentioned previously (Section 6.1.9) the analytical screening process should identify the active and intelligent components and any related impurities, reaction or breakdown products present in the samples above a defined cut-off concentration. The calculated cut-off concentrations are given below.

S07-024123-AntiM4 – Antimicrobial cling film

The product has the potential to come into contact with a broad range of foods and therefore the surface-to-volume ratio is not known. Under these circumstances the conventional area to mass of food ratio of 6 dm^2/kg food is applicable.

- Therefore a concentration of 10 µg/kg in the food is equivalent to 10 µg in 6 dm^2 (1.7 µg/dm^2) of cling film.
- The cling film weighs 0.13 g/dm^2.
- Therefore a concentration of 10 µg in 6 dm^2 is equivalent to **13 mg/kg** film.

S07-024124-EthS1 – Ethylene scavenging bag

The product has the potential to come into contact with a broad range of foods and therefore the surface-to-volume ratio is not known. Under these circumstances the conventional area to mass of food ratio of 6 dm^2/kg food is applicable.

- Therefore a concentration of 10 µg/kg in the food is equivalent to 10 µg in 6 dm^2 (1.7 µg/dm^2) of bag.
- The bag weighs 0.40 g/dm^2.
- Therefore a concentration of 10 µg in 6 dm^2 is equivalent to **4.2 mg/kg** bag.

S07-024125-HeatR – Heat releasing microwave susceptor

Typically the contact area : mass of food ratio is 100 g : 2 dm^2 (ratio obtained from consideration of actual use on the UK market).

- Therefore a concentration of 10 µg/kg in the food is equivalent to 0.5 µg/dm^2 of susceptor.
- The susceptor weighs 1.2 g/dm^2.
- Therefore a concentration of 0.5 µg/dm^2 is equivalent to **0.42 mg/kg** susceptor.

S07-024126-EthS2 – Ethylene scavenging bag

The product has the potential to come into contact with a broad range of foods and therefore the surface-to-volume ratio is not known. Under these circumstances the conventional area to mass of food ratio of 6 dm^2/kg food is applicable.

- Therefore a concentration of 10 µg/kg in the food is equivalent to 10 µg in 6 dm^2 (1.7 µg/dm^2) of bag.
- The bag weighs 0.44 g/dm^2.
- Therefore a concentration of 10 µg in 6 dm^2 is equivalent to **3.8 mg/kg** bag.

S07-024127-FreshI – Food Freshness indicators

It is assumed that 1 indicator is in contact with ≥ 50 g of fruit/vegetables which means that 1 kg of food that is consumed at maximum each day can be in contact with 20 indicators.

- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg/20 = 0.5 µg per indicator.
- The mass of each label is 0.17 g
- Therefore a concentration of 0.5 µg per indicator is equivalent to **2.9 mg/kg** label.

S07-024128-EthS3 – Ethylene scavenging sachets
Information on the supplier website states that 1 sachet should be used with 30 lbs (~ 14 kg) of fruit or vegetables (these sachets are sold for use in bulk transport rather than individual packs).

- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 140 µg per sachet.
- The mass of each sachet is 9 g.
- Therefore a concentration of 10 µg per sachet is equivalent to **15.5 mg/kg** sachet.

S07-024129-MoistA – Water absorbing pads
It is assumed that 1 pad comes into contact with 250 g of food (ratio obtained from consideration of actual use on the UK market).

- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 2.5 µg per pad.
- The pad weighs 1.2 g/dm^2.
- Therefore a concentration of 2.5 µg per pad is equivalent to **2.1 mg/kg** pad.

S08-000164-HeatS – Heat sensitive weaning spoons
Spoons are repeat use food contact articles and therefore when considering exposure the contact over the lifetime of the article should be considered. As a conservative estimate a spoon may be used to feed a total of 1 kg of foodstuff until it is disposed of.

- Therefore a concentration of 10 µg/kg in the food is equivalent to a worst case migration of 10 µg per spoon.
- The mass of the feeding portion of the spoon is 0.3 g.
- Therefore a concentration of 10 µg per spoon is equivalent to **33 mg/kg** of the feeding portion of the spoon.

S08-003221-AntiM5 – Anti-mould cheese preserving bags
The product has the potential to come into contact with any mass/volume of cheese and therefore the surface-to-volume ratio is not known. Under these circumstances the conventional area to mass of food ratio of 6 dm^2/kg food is applicable.

- Therefore a concentration of 10 µg/kg in the food is equivalent to 10 µg in 6 dm^2 (1.7 µg/dm^2) of bag.
- 1 dm^2 of the polyethylene food contact layer of the bag weighs 0.65 g.
- A concentration of 10 µg in 6 dm^2 is equivalent to **2.6 mg/kg** bag.

6.2.10.1 Results volatile substances

The best library matches (based on the library fit and a visual consideration of the ions present) and estimated concentrations of the substances detected in the headspace GC-MS analysis above the cut-off concentrations described above are shown in Table 14. No good library matches were obtained for several substances detected in the headspace gas. Given the low estimated concentrations it is likely that many of the substances detected are not present at levels that have the potential to give rise to high migration levels. Volatile substances were detected in five of the ten samples tested. The substances observed in the headspace gas, or structurally similar substances, have all previously been detected in non-active/intelligent packaging materials and therefore, in the absence of any control samples, it cannot be concluded whether or not they derive from the active/intelligent components, but is felt to be unlikely.

6.2.10.2 Results semi-volatile substances

The best library matches and estimated concentrations of the substances detected in the iso-octane and 95% ethanol extracts of the active and intelligent packaging samples by GC-MS analysis above are shown in Table 15. Numerous semi-volatile substances were detected in the solvent extracts of all of the materials tested. As for the headspace analysis the substances for which good library matches were obtained could not be assigned specifically to the active or intelligent components as they, or structurally similar substances, have previously been detected in non-active/intelligent packaging.

6.2.10.3 Results polar and non-volatile substances

The TOF-MS data produced was processed using Agilent Molecular Feature Editor and Masshunter software. These packages examined the data, extracted the chromatographic peaks and generated mass spectra for those peaks. Some of the chromatographic peaks seen in the total ion chromatograms (TIC) obtained from the analysis of the extracts were very small, but were elucidated nevertheless, highlighting the power of TOF-MS. Many of the peaks were not visible from the TICs but were extracted from the raw data by the data processing software and their mass spectra were generated. A user-prepared database was searched. A database of potential structures was prepared as a part of another FSA funded project [16]. These structures were produced based on known additives and predicted reaction/breakdown products. This database was used to assign the identities of the chromatographic peaks that were detected. Searches of scientific literature and the Internet were also carried out to propose possible identities for the substances detected in the extracts that could not be assigned from the knowledge of additives and/or reaction/breakdown products. Quantification of the substances detected could not be estimated as the internal standard used (d_{10}-benzophenone) was not seen in the TIC of the sample extracts. The substances detected are described in Table 16. As for the volatiles and semi-volatiles the substances detected in the solvent extracts could not be specifically assigned as being derived from the active/intelligent components of the packaging.

6.2.10.4 Results elemental screening

The concentrations of the trace elements detected in the samples following acid digestion are given in Table 17. The samples were analysed in three batches hence the differences in the detection limits reported. From our knowledge of the materials studied and the likely ingredients that may provide the active or intelligent function we were able to propose the identities of several active ingredients:

S07-024123-AntiM4 – Antimicrobial film – silver
S07-024124-EthS1 and S07-024126-EthS2 – active ethylene adsorbing mineral (sodium, magnesium, aluminium, potassium, calcium, titanium, iron, copper, zinc and barium)
S07-024125-HeatR – Microwave susceptor - aluminium
S07-024127-FreshI – Freshness indicators – palladium (complex)
S07-024128-EthS3 – Ethylene scavenging sachets – potassium permanganate

6.2.11 Active/intelligent ingredients

No control samples, i.e. samples of the same composition but without the active/intelligent component(s), were available. As a result it was not possible to identify the active/intelligent component(s) in the samples by comparing differences in chromatograms between the two sets of samples. Instead the active/intelligent component(s) in the samples have been proposed based on in-house knowledge gained

from our previous experience of testing food contact materials and articles. The following active/intelligent ingredients were proposed:

S07-024123-AntiM4 – Antimicrobial film
Silver was detected in the acid digests of the film. Silver is known to impart antimicrobial properties and therefore this is proposed to be the antimicrobial ingredient. No restriction could be found for silver itself. However several silver containing zeolites are listed in the Synoptic Document along with a restriction of 0.05 mg silver/kg food based on the human no-observed effect level of about 10 g of silver for a total lifetime oral intake allocated for drinking water by the World Health Organisation. Given that other trace elements (including sodium, aluminium, calcium, titanium and zinc) were detected at high levels (greater than 5 mg/kg) then it is expected that the antimicrobial silver is in this form. The film contains 6.6 mg silver/kg film. The mass of 1 dm^2 of film is 0.13 g and therefore the maximum amount of silver that could migrate into 1 kg of food is 5.1 µg. Although the restriction could not be exceeded this sample was included because it may not be intended that such products effect the food and therefore any transfer of the silver from the surface where it is intended that it will impart its effect to the food is of interest.

S07-024124-EthS1 and S07-024126-EthS2 – ethylene scavenging bags
High levels (greater than 5 mg/kg) of sodium, magnesium, aluminium, potassium, calcium, titanium, iron, copper, zinc and barium were detected in the acid digests of both samples. These elements are consistent with the presence of a mineral as the active ingredient. Labelling on one of the samples states that a Japanese stone powder (a mineral) is part of the product and acts as an ethylene scavenger.

The proposed Plastics Implementation Measure (PIM) includes restrictions for a small number of trace elements. The measure states, that ‘ Plastic materials and articles shall not release the following substances in quantities exceeding the limits set below.

Zinc = 25 mg/kg
Copper = 5 mg/kg
Barium = 1 mg/kg
Cobalt = 0.05 mg/kg
Lithium = 0.6 mg/kg
Iron = 0.48 mg/kg
Manganese = 0.6 mg/kg

Limits for sodium, magnesium, aluminium, potassium, calcium and titanium are not defined (or proposed for inclusion) in EU legislation for plastic food contact materials. However salts of these materials are permitted for use in food contact plastics without restriction. For such substances the overall migration limit of 60 mg/kg applies.

JECFA have recently revised the provisional tolerable weekly intake (PTWI) for aluminium as 1 mg/kg body weight. Assuming a body weight of 60 kg this is equivalent to 60 mg of aluminium per week [17].

For sample S07-024124-EthS1 the trace element concentrations detected in the ethylene scavenging bags (> 5 mg/kg) are equivalent to worst case migration values of:

Sodium = 0.25 mg/kg
Magnesium = 0.12 mg/kg
Aluminium = 1.22 mg/kg

Potassium = 0.41 mg/kg
Calcium = 3.12 mg/kg
Titanium = 0.12 mg/kg
Iron = 0.26 mg/kg
Copper = 0.02 mg/kg
Zinc = 0.25 mg/kg
Barium = 0.02 mg/kg

For sample S07-024126-EthS2 the trace element concentrations detected in the ethylene scavenging bags (> 5 mg/kg) are equivalent to worst case migration values of:
Sodium = 0.67 mg/kg
Magnesium = 0.02 mg/kg
Aluminium = 0.11 mg/kg
Potassium < 0.13 mg/kg
Calcium = 0.05 mg/kg
Titanium = 0.03 mg/kg
Iron < 0.13 mg/kg
Copper = 0.02 mg/kg
Zinc = 0.22 mg/kg
Barium < 0.01 mg/kg

Comparing these values with the limits given above and the PTWI for aluminium (it is assumed that a 60 kg adult consumes 1 kg of food per day) all meet the restrictions given.

Although sample S07-024124-EthS1 also contained lead, the concentration present does not have the potential to exceed the restriction of 100 µg/kg (given in the Dutch legislation, Verpakkingen en gebruiksartikelen, chapter IV metals, 4.3) or 1.5 mg/L for cookware as given in Directive 84/500/EEC relating to ceramic articles intended to come into contact with foodstuffs as amended by Directive 2005/31/EC. Both are used here as a guide.

Sample S07-024124-EthS1 is also described as being surface treated to prevent moisture and bacteria from forming. In the absence of control samples the identities of the chemicals that are responsible for this action could not be determined. The presence of diatomaceous micropores adsorbing water by capillary condensation has been reported therefore it is possible that the mineral/clay also fulfils this action.

It is also claimed that sample S07-024126-EthS2 maintains vitamin C levels in the foods. If true this could be simply that the film gives some UV barrier protection and this function would not fall into the definition of active packaging. Alternatively, if ethylene is scavenged then the fruit will ripen less quickly and vitamin C levels could be maintained. Only in the case where vitamin C was protected using a released antioxidant would the rules on active packaging come into play and there was no evidence for this from the chemical analysis. Since all applicable restrictions for the levels of trace elements found would be met, these materials were not selected for the migration studies.

S07-024125-HeatR – Microwave susceptor
The thin aluminium layer in the susceptor provides the browning action.

As mentioned above aluminium has a PTWI of 1 mg/kg bw. Assuming a body weight of 60 kg this is equivalent to 60 mg per week. Aluminium was detected in the sample at a concentration of 0.75 mg/kg which is equivalent to 0.9 µg/dm^2. Assuming the conventional food contact ratio this is equivalent to a weekly exposure of 0.04 mg per week, i.e. much lower than the PTWI for this element. Therefore this material was not selected for the migration studies.

S07-024127-FreshI – Freshness indicators
Palladium was detected in the acid digests. In the patent received from the manufacturers this element is described as being used as part of a metal co-ordinated complex in a medium, e.g. a palladium-fluorophore, may be used to detect food spoilage by preferential binding of the metal to, for example, sulphur compounds or amines. Pd has no restriction. Considering the low concentration of Pd in the sample, it can be calculated that the migration of Pd into a food will be low (less than 1 µg/kg food). Therefore this material wasn't selected for the migration studies.

S07-024128-EthS3 – Ethylene scavenging sachets
High levels (greater than 5 mg/kg) of several elements were detected in the sachet contents. Potassium and manganese were two of the elements detected at high levels providing evidence that the adsorbent is the known ethylene scavenger potassium permanganate. The restriction of manganese is 0.6 mg/kg food (given in the proposed PIM and in the existing Plastic Directive – 2002/72/EC, as amended). The sachet contains 11.7 g of manganese/kg. Each sachet weighs 9 grams. Therefore up to 100 mg Mn could migrate into the 14 kg of food with which the sachet will come into contact which is above this restriction. Therefore migration tests were carried out to assess the safety of this sachet for contact with food (Section 7.2.3).

S07-024129-MoistA – Absorbent pads
The pads are known to be made from cellulose fibres, this information was provided by the supplier. The substances detected in the extracts are expected in such fibres. Conventional migration tests have been shown to be unsuitable in the Aktipak [3] project for materials such as these and therefore although migration limits were not expected to be exceeded for this sample suitable test methods were investigated.

S08-000164-HeatS – Heat sensitive weaning spoons
No information was provided as to the intelligent ingredient in these samples. From the analysis carried out the identity of the intelligent component could not be confirmed. None of the substances detected in the extracts could be assigned to the intelligent component and therefore no migration testing was carried out.

S08-003221-AntiM5 – Cheese preserving bags
No information was provided as to the active ingredient in these samples. Lead was detected in the acid digests of the sample although it is not expected that this would act to preserve the cheese. Although sample S08-003221-AntiM5 contained lead, the concentration present does not have the potential to exceed the restriction of 100 µg/kg (given in the Dutch legislation, Verpakkingen en gebruiksartikelen, chapter IV Metals, 4.3) or 1.5 mg/L for cookware as given in Directive 84/500/EEC relating to ceramic articles intended to come into contact with foodstuffs as amended by Directive

2005/31/EC. Both are used here as a guide. Therefore no migration testing was carried out.

As mentioned previously the aim was to identify the active/intelligent ingredient(s) and any other potential migrants associated with them. In most cases it was not possible to isolate the active/intelligent component from the rest of the packaging and nor were any control samples received. As a result the potential migrants derived from these components could not be differentiated from those derived from the rest of the packaging. The identities of the substances other than those listed above that were detected in the samples have been considered. In all cases the other substances for which identities are proposed may be derived from the materials themselves rather than the active/intelligent components or systems.

7 Migration experiments

Based on the screening experiments described in chapter 6, a selection of active materials was taken forward for further migration experiments. The choice for the selection of these materials is explained in sections 6.1.10 and 6.2.11.

7.1 Migration experiments TNO

7.1.1 Oxygen scavengers; label (0939-03-0471-OxS3) and sachet (0939-03-0472-OxS4)

The migration experiments with the oxygen scavengers were carried out into food simulants and foods (cheese and tomato sauce). The foods chosen for the migration experiments were cheese and tomato sauce that represent fatty and acidic foods, respectively.

7.1.1.1 Migration into food simulants

The migration experiments with the oxygen scavenging label (0939-03-0471-OxS3) and the oxygen scavenging sachet (0939-03-0472-OxS4) could not be performed with conventional migration tests, since these rely on a total immersion of the material in the food simulant. This does not represent the actual conditions of use and would overestimate the migration since during use the materials will not come into contact with liquid foods. The scavenger may be expected to come into contact with moist and/or fatty foods such as cheese, ham, etc. The migration test was performed using tissues soaked in food simulant to mimic this contact. The food simulants 3% acetic acid, 95% ethanol and olive oil were selected as these represent the acid and fatty foodstuffs with which the sachet or the label may be used. The food contact conditions were not defined therefore the worst foreseeable use was considered. In the worst case it was expected that the sachet and the label may be exposed to foods at room temperature for more than 24 hours. Equivalent test conditions for conventional simulants given in EU legislation for plastics are 10 days at 40ºC. Therefore all experiments were performed in duplicate at 40ºC for 10 days.

The migration tests for the sachet were performed as shown in Figure 1B. Standard laboratory filter paper was cut into pieces of 9 x 6 cm. A square hole, the size of the sachet (4.5 x 3.5 cm), was cut into ten of these pieces. Five pieces of the paper without the square hole were placed on top of a glass plate. Ten pieces of the paper with hole were placed on top and the sachet was positioned in the centre of the hole. An additional five pieces of paper without the hole were placed on top. A glass plate was positioned at the top and bottom of the stack. All of the papers were soaked with simulant and the excess of simulant was allowed to drip from the tissue such that the paper was saturated with the simulant. A standard operating procedure was prepared to ensure that tissues with repeatable simulant content were obtained each time this set-up was carried out. The entire stack was placed in a plastic bag to avoid evaporation of the simulant during the migration experiments.

The migration tests for the label were performed as shown in Figure 1C. Four oxygen scavenger labels were attached to a glass plate. The glass plate was positioned between a stack of laboratory filter paper soaked with simulant (as described above) and glass plates.

Overspiking experiments were set up to allow the recovery of iron through the entire procedure to be determined. Samples were spiked with $FeCl_3.6H_2O$ in 3% acetic acid or 95% ethanol at a concentration equivalent to the maximum tolerable daily intake of iron (48 mg of iron/kg of food). The iron solution was spiked onto the simulant soaked tissues as described set up as described above and these overspiked samples were treated in the same way as the migration test samples.

After the migration experiments were complete, the samples were removed from the plastic bags and the sachets/labels removed. Acid digestion of the simulant soaked tissues was performed by boiling in nitric acid for 1 hour. Inductively coupled plasma (ICP) - Atomic emission spectroscopy (AES) (Iris Intrepid, Thermo) was used at a wavelength of 259 nm to determine the concentration of iron in the digests which was then used to calculate the migration from the labels/sachets. The internal standard rhodium was used. Calibration was performed with external iron standards.

7.1.1.2 Migration into foods

Slices of cheese containing 48% fat were cut into parts slightly larger than the sachet and label to be tested. For the sachet, two slices of cheese were placed on top of each other in a Petri dish (9 cm diameter). The sachet was placed on top of the second slice which was then covered with a third slice of cheese. The system was sealed with the lid of the Petri-dish. For the label, two labels were placed on a glass plate and three slices of cheese were placed on top. The system was sealed with a Petri-dish (9 cm diameter). All samples were stored in a plastic bag. Overspiking experiments were set up to allow the recovery of iron through the entire procedure to be determined. Samples were spiked with $FeCl_3.6H_2O$ in 95% ethanol at a concentration equivalent to the maximum tolerable daily intake of iron (48 mg of iron/kg of food). The iron solution was spiked between the first and second slices of cheese for the sachet experiments and between the second and third slices for the label experiments. The overspiked samples were treated in the same way as the migration test samples. All experiments were performed in duplicate at 40ºC for 10 days. After the migration experiments were complete, the samples were removed from the plastic bags and the sachets/labels removed. Acid digests of the foods were performed and analysed as described above.

Tomato sauce (~ 35 g) was placed in a Petri dish (9 cm diameter). The label and sachet was placed on top of the tomato sauce. The Petri-dishes were sealed. Overspiking experiments were set up to allow the recovery of iron through the entire procedure to be determined. Samples were spiked with $FeCl_3.6H_2O$ in 95% ethanol at a concentration equivalent to the maximum tolerable daily intake of iron (48 mg of iron/kg of food). The iron solution was spiked directly into the tomato sauce. The overspiked samples were treated in the same way as the migration test samples. All experiments were performed in duplicate at 40ºC for 10 days. After the migration experiments were complete, the samples were removed from the plastic bags and the sachets/labels removed. Acid digests of the foods were performed and analysed as described above.

7.1.1.3 Iron migration

Table 18 presents the results for the migration of the label 0939-03-0471-OxS3, Table 19 gives the results for the sachet 0939-03-0472-OxS4. The maximum tolerable daily intake of iron is 48 mg of iron/kg of food. Assuming as is the convention that 1 kg of food is consumed a day then the migration calculated from the iron transferred from the label (0939-03-0471-OxS3) to the paper soaked in 3% acetic acid (235 mg/kg) and the

tomato sauce (211 mg/kg) exceeds this limit. These results indicate that the label should not be used for direct contact with acidic foodstuffs.

Measurable migration was also observed from the sachet to the paper soaked in 3% acetic acid (11 mg/kg) and the tomato sauce (10.8 mg/kg) but the levels were less than the daily intake value. No detectable or a low migration was observed in 95% ethanol and cheese, which may have been caused by a low solubility of iron in ethanol and fat and hence a low migration. The results have not been corrected for the recovery. The results obtained indicate that the sachet is suitable for direct contact with all foodstuffs with respect to the migration of iron.

Tables 20 and 21 present the results of the recovery tests for the label and sachet, respectively. In general recoveries were low. The recovery in olive oil was just 4% for the sachet. However the recovery of iron from highly organic liquids such as olive oil and iso-octane is known to be low. Therefore 95% ethanol should be considered as an appropriate simulant for fatty foods for this metal. Only the sachet in combination with tomato sauce and cheese gave good recoveries (89 and 94% respectively). It is unclear where the large difference in recovery between sachet and label originates from. For example, in 3% acetic acid a recovery of 77% and 24% for the label and sachet were measured, respectively. Whether this effect was sample related or related to the concentration of iron was not further investigated. Even applying the low recovery corrections (Tables 20 and 21) would not result in the migration of iron exceeding the daily intake value.

Importantly the dedicated migration tests used in this experiment overestimated the migration into acidic foods. This is an essential requirement of any migration test in order to ensure consumer protection. The migration into cheese was greater than that observed into the paper soaked in the fatty simulants. However it is recognised in EU legislation for plastics that some cheeses are acidic and in these cases 3% acetic acid should also be used as a simulant and therefore the migration was overestimated. This also highlights that in some instances it may be necessary to take into account the properties of the migrant as well as the food when selecting the appropriate simulant.

7.1.2 Flavour releaser (0939-02-0227-FlavR1)

The migration experiments with the flavour releasing film were carried out into food simulants (3% acetic acid to mimic contact with acidic foods, 50% ethanol for milk products and olive oil for fatty foods) and foods (cheese and tomato sauce). The intended use of the film is bread/cereal snack bags and beverage pouches. The real food types chosen for the migration experiments were cheese and tomato sauce to represent fatty and acidic food, respectively. Cheese was chosen as cheese may be in contact with the film. Tomato sauce was chosen as a representative acidic liquid food which may be to mimic contact with the proposed use in beverage pouches.

7.1.2.1 Migration into food simulants

The film (0939-02-0227-FlavR1) has a clear and a dull side. FT-IR measurements confirmed that the clear side was polyethylene. In the FT-IR spectrum of the dull side additional peaks probably due to a coating appeared. This coating was most probably used to apply the active ingredient and therefore single-sided migration experiments were carried out using a migration test cell (capacity 100 mL, contact area 2.34 dm^2) with the coating in direct contact with the simulant or foodstuff. The food contact conditions were not defined by the supplier of this sample. In the worst case it was

expected that the flavour releasers may be exposed to foods at room temperature for more than 24 hours. Equivalent test conditions for conventional simulants defined in EU legislation are 10 days at 40ºC. The film was exposed to the food simulants 3% acetic acid, 50% ethanol and olive oil. The concentration of BHT in the 3% acetic acid and 50% ethanol exposed simulant samples was determined following direct analysis by HPLC with UV detection. Following the exposure the olive oil was mixed and 0.5 g was transferred to a 20 mL volumetric flask and made up to the mark with iso-octane. The oil/iso-octane mixture was analysed directly by GC-MS. All experiments were performed in duplicate.

Overspiking experiments were carried out to determine the recovery of BHT in the migration experiment. Simulant was spiked with BHT (in ethanol or iso-octane) at a concentration equivalent to its SML of 3 mg/kg. The BHT was spiked onto the film and was allowed to infuse into the test sample prior to the addition of the simulant.

7.1.2.2 Migration into foods

Slices of cheese containing 48% fat were cut into 6 x 11 cm pieces. Two slices of cheese (~ 20 g) were placed on top of each other and packed in-between two pieces of sample 0939-02-0227-FlavR1. The contact surface area was approximately 1.3 dm^2. It was not possible to remove all air in the packages reducing the contact surface by approximately 10%. The films were sealed with a sealer to form a pouch containing the cheese and were stored at 40°C for 10 days. A glass sheet was placed on top of the packages to maximise the contact between the film and the foodstuff. Once the migration phase was complete, the cheese was transferred to a Soxhlet thimble and refluxed for 6 hours with 230 mL iso-octane. The iso-octane was transferred to a 250 mL volumetric flask and made up to 250 mL. The iso-octane extract was analysed directly by GC-MS. Overspiking experiments were carried out to allow the recovery of the BHT to be calculated. Cheese samples were spiked at a concentration of 3 mg BHT (in iso-octane) per kg cheese. The spike was added in-between the two slices of cheese in contact with the film.

Two pieces of 0939-02-0227-FlavR1 were sealed together to form a pouch. Tomato sauce (~ 50 g) was packed inside and the pouch was sealed. The contact was approximately 2.0 dm^2. The exposure was carried out for 10 days at 40°C. After this time the BHT was extracted from the tomato sauce with iso-octane (100 mL) using a separating funnel. The iso-octane extract was analysed directly by GC-MS. Overspiking experiments were carried out to allow the recovery of the BHT to be calculated. The tomato sauce was spiked with BHT in ethanol at 3 mg/kg tomato sauce.

7.1.2.3 BHT migration

The recoveries obtained from the analysis of the overspiked samples were low (< 30%) in all matrices except 50% ethanol (83% recovery). The explanation for this effect can be found in the intrinsic properties of the BHT molecule. BHT is an antioxidant and its activity relies on its instability; BHT is easily oxidised in the presence of reducing substances. Reducing substances can be acetic acid (present in tomato sauce) or fatty acids present in olive oil and cheese. This explanation for the low recovery of BHT is confirmed by a publication [18] where the stability of antioxidants in food simulants was studied. The recovery of BHT was low in all simulants under exposure conditions of 10 days at 40°C (around 50%). The recovery reported [18] was much lower at 70°C. Another factor may be the partitioning of the BHT between the film and the simulant/foodstuff during the exposure period.

Table 22 gives the BHT concentrations detected in the exposed food simulants and foodstuffs. All BHT migration experiments resulted in concentrations in the food of less than the SML of 3 mg/kg. As might be expected the highest migration was into 50% ethanol in which BHT was most stable (as above). However, a correction for the recovery was not made as was demonstrated that BHT is not stable in the various simulants. A low recovery is therefore caused by the instability of BHT rather than poor analytical sample work-up.

The maximum level of BHT that is permitted in a restricted number of foods as a food additive under Directive 95/2/EC is 100 mg/kg. It was however not possible to demonstrate whether the level of BHT found will have a technological function in the food and should therefore comply with this legislation.

7.1.3 Anti-mould SO_2 emitter (0939-02-1737-AntiM2)

The migration experiments with the anti-mould SO_2 emitter were carried out into a food simulant and foods (grapes).

7.1.3.1 Migration into food simulants

The SO_2 emitter is not suitable for direct contact with liquid food simulants. This would wet the active $Na_2S_2O_5$ crystals packed inside the paper bag and may overestimate the migration. Therefore a dedicated migration test to mimic moist contact was used. The food simulant selected for the migration studies was 3% acetic acid intended to mimic the acidic nature of the grapes. The SO_2 emitter is intended for use with grapes that are normally stored at chilled conditions for a few months. However, it can be expected that the packed grapes will be exposed to room temperature for more than 24 hours during e.g. transport. Equivalent test conditions for conventional simulants defined in EU legislation for plastics are 10 days at 40ºC. The migration tests for the simulants were performed as shown in Figure 1A. Standard laboratory filter paper was cut into pieces of 9 x 6 cm. The paper was soxhlet refluxed in simulant (3% acetic acid) for 24 hours prior to use to remove any residues of sulphuric acid salts. The experimental set up was similar to the experimental set up of the oxygen scavenging sachet although a hole was not cut, the SO_2 emitter was simply sandwiched between the simulant soaked papers. All experiments were in carried out in duplicate.

Overspiking experiments were set up to allow the determination of the recovery of sulphite in the analytical procedure (migration, sample work-up, analysis). During the migration experiments performed with the tissue approach described above, the recovery was determined by spiking with a sulphite solution containing Na_2SO_3 in 3% acetic acid at a concentration equivalent to the SML(T)(10 mg/kg, expressed as SO_2, applying the assumption that four SO_2 emitters come into contact with 1 kg of grapes). The Na_2SO_3 solution was spiked onto the simulant soaked paper with the test specimen in-between the layers set up as described above and these overspiked samples (test samples spiked with sulphite at a concentration equivalent to the SML(T)) were treated in the same way as the migration test samples (i.e. without the spike). Additional samples were spiked with Na_2SO_4 to achieve a similar level (10 mg/kg) for SO_4. The sulphite and sulphate spiking experiments were performed separately on different migration experiments as SO_3 may be converted into SO_4. All experiments were in carried out in duplicate.

After the migration period the stack of paper was removed from the plastic bag under an atmosphere of nitrogen. The SO_2 emitter was removed and the paper was transferred to a tube and 15 mL eluent (3.5 mM Na_2CO_3 + 1 mM $NaHCO_3$ solution) was added. Sulphate/sulphite was extracted from the tissues for 30 minutes at 300 strokes/minute. The resulting extracts were diluted with eluent by a factor of 100 prior to analysis by ion chromatography. The spiked samples were diluted 1000 times with the eluent. Sulphite and sulphate were analysed using a Dionex ion chromatography system with a conductivity detector. The column used was an AS14 anion exchange column with an AG14 guard column. The eluent was a 3.5 mM Na_2CO_3 + 1 mM $NaHCO_3$ solution at a flow rate of 1.2 mL/min.

7.1.3.2 Migration into food

Both red and white grapes were investigated. Grapes were packed with and without the SO_2 emitters for 1 month at 7°C in a sealed plastic bag. A few grapes were sampled after this migration period for analysis. The rest of the grapes remained packed for the efficacy tests (see Section 8.1.3). One grape of each type was used for each experiment. Sample work-up started on the same day. Two different approaches were followed for the analysis. The first was by washing the skin of the grape in 6 mL eluent (as above) for 30 minutes at 300 strokes/minute, the second involved crushing the grape in 5 mL eluent (30 minutes at 300 strokes/minute) followed by filtration through a 0.45 µm filter.

7.1.3.3 Sulphite migration

The results of the sulphite dedicated migration experiment from the bag containing the SO_2 emitter (0939-02-1737-AntiM2) into the 3% acetic acid soaked paper are presented in Table 23. The repeatability of the migration experiments was poor. On average, a migration of 152 mg/kg sulphite was determined. This exceeds the SML(T) for sulphite, which is 10 mg/kg (expressed as SO_2), by a factor of 15. Data on the stability and recovery of the sulphite under these test conditions and in this matrix could not be determined as the mass of sulphite spiked onto the simulant soaked paper was not significantly greater than that of the unspiked sample. In separate studies sulphite was converted (~87% conversion) into sulphate on storage for 1 month in 3% acetic acid (equivalent to the migration test conditions). Given the issues with the stability of the sulphite and no recovery data being generated the results obtained could not be used to assess compliance with the migration limit. Further the simulant was selected to represent the worst case of contact between the acid of the grape and the emitter. Although grapes are acidic the acid is contained within the fruit and the SO_2 emitter would therefore be separated from the acidic portion of the fruit. Therefore the simulant and dedicated test selected is likely to significantly overestimate any migration that occurs and as such it may not be appropriate for this application.
The results of the sulphite and sulphate migration into grapes are presented in Table 24. As mentioned above two different approaches were followed. The first extracted the sulphite from the entire grape, the second just from the skin of the grapes. This was carried out to test the hypothesis that the sulphite accumulates mostly on the apolar skin of the grapes which functions as a barrier for water and water soluble substances.

A response was observed at the retention time associated with the sulphite in the chromatograms obtained from the analysis of all samples. No confirmatory method was available and therefore it could not be confirmed that this response was due to the presence of sulphite in the grapes. One possible explanation is that the peak observed is

from another unknown substance that is present naturally in the grapes. There was no difference between the response observed from the analysis of the grapes with and without the emitter. Due to these high background levels it was not possible to establish whether or not sulphite migration had occurred in this test. However no response was observed at the retention time associated with the sulphite in either skin sample. If migration had occurred then the highest concentration would have been expected to be present at the food contact surface interface, i.e. on the grape skin.

A response at the retention time of the sulphate was observed in the extracts of the whole grapes. Again a confirmatory method was not available so it was not possible to prove that this reponse was due to the presence of this substance. As for the sulphite there was no significant difference between the grapes stored with or without the SO_2 emitter. The level of sulphate detected on the skin of the grapes was higher for the grapes stored in contact with the SO_2 emitter than without. Therefore the source of the sulphate in the grape skin could be the SO_2 emitter. Whether sulphate has migrated directly from the SO_2 emitter or by migration of sulphite which has subsequently broken down into sulphate cannot be deduced from these experiments.
Given the many uncertainties with the sulphite/sulphate data described above, firm conclusions on the migration behaviour of the SO_2 emitter could not be drawn.

7.2 Migration experiments Fera

7.2.1 Antimicrobial food storage liner (0939-03-0269-AntiM3)

The migration experiments with the antimicrobial food storage liner were carried out into food simulants and foods (meat and fish – the two classes of foods with which the liner may be expected to come into contact).

7.2.1.1 Migration into food simulants

The food contact conditions were not defined. In the worst case it was expected that the liner may be exposed to foods at room temperature for more than 24 hours. Equivalent test conditions for conventional simulants defined in EU legislation (for plastics but used here as a guide) are 10 days at 40°C. Triplicate portions of the liner (1 dm^2) were exposed, by total immersion, to 30 mL of:

- 10% ethanol
- 3% acetic acid
- 95% ethanol for 10 days at 40°C (equivalent simulant D substitute test media and test conditions)
- iso-octane 2 days at 20°C (equivalent simulant D substitute test media and test conditions)

Duplicate control samples (no test specimen) were also prepared alongside the samples.

The concentration of silver in the simulant samples was determined by ICP-MS. The 3% acetic acid and 10% ethanol simulant samples were analysed directly. The 95% ethanol and iso-octane samples were evaporated to dryness and reconstituted in 10 mL of 2% HNO_3 and 0.1% HCl, by roller mixing for 1 hour and then subjecting to ultrasonication for 30 minutes. The resulting extracts were cloudy so to ensure the dissolution of any silver salts (e.g. silver chloride) 1 mL of a 50% solution of concentrated HCl in water was added. The samples were analysed by ICP-MS

following a further ten-fold dilution with 2% HNO_3 and 0.1% HCl containing rhodium/indium internal standards. A certified reference material, NIST 1640, trace elements in water, was analysed alongside the test samples.

The concentration of silver detected in the exposed simulant samples is shown in Table 25. To calculate the migration values the instructions provided in the CEN standard EN13130 Part 1 were followed. "When the surface-to-volume ratio in actual use is not known the results obtained under the test conditions shall be reported in milligrams per square decimetre (mg/dm^2)". The concentration of silver detected in the exposed simulant was used to calculate the migration value taking into account the surface area and volume of simulant used in the test. EN13130 Part 1 states that "where results are expressed in milligrams per square decimetre (mg/dm^2) they should be compared to the any specific migration limits recalculated in milligrams per square decimetre (mg/dm^2) obtained by dividing the substance limits in milligrams per kilogram (mg/kg) by the conventional conversion factor of 6". Therefore for silver which has been assigned a Group restriction limit of 50 µg/kg (Synoptic Document) this equates to a migration of 8.3 $\mu g/dm^2$. Although this restriction is not a specific migration limit we have used it as a guide to calculate the equivalent migration from the test material.

As expected the highest migration was into the 3% acetic acid simulant. The analysis of the certified reference material, NIST 1640, trace elements in water gave satisfactory results with 100% recovery (our result 6.66 µg/L, certified value 6.70 µg/L). The migration of silver was, in all cases, less than the Group restriction for this substance.

7.2.1.2 Migration into foods

The migration of silver into meat and fish following exposure for 5 days at 5°C (the shelf-life of the foods) was determined in triplicate. Approximately 50 g of salmon and 130 g of beef steak were each exposed to 1 dm^2 of liner. Exposures were carried out in sealed glass Petri-dishes overwrapped with cling film to avoid moisture losses from the foods. Triplicate blank samples (no liner) were prepared alongside the samples. Certified reference materials DOLT-2, dogfish liver, and NIST1566a, oyster tissue, were analysed with each batch.

Following the exposure the foodstuffs were homogenised and the silver concentrations in the foods (and the corresponding migration values) were determined by ICP-MS. Aliquots (1 g) of the homogenised foodstuff plus certified reference materials were digested in a mixture of nitric acid and hydrochloric acid (4:1 ratio, 5 mL) using quartz high pressure closed vessels and microwave heating. Digests were transferred to plastic test tubes and diluted to 10 mL with water. A further ten-fold dilution was performed using dilute nitric acid containing rhodium/indium internal standards prior to analysis by ICP-MS. Reagent blanks and a reagent blank spiked with a known amount of the analyte were analysed with the test samples for recovery estimate purposes. The recovery of the added silver was 109%, and the CRM results were acceptable (DOLT-2; our result 489 µg/kg, certified value 608 µg/kg. NIST 1566a; our result 1383 µg/kg, certified value 1680 µg/kg).

No silver was detected in any of the samples. The limit of detection was 5 µg/kg of food which is equivalent to a migration of 0.25 $\mu g/dm^2$ for the salmon and 0.65 $\mu g/dm^2$ for the beef steak, i.e. much lower than the Group restriction limit which would be equivalent to 8.3 $\mu g/dm^2$.

7.2.2 Antimicrobial cling film (S07-024123-AntiM4)

The migration experiments with the antimicrobial cling film were carried out into food simulants and foods (apple sauce and tomato sauce selected as acidic foodstuffs to represent the worst case for the migration of metal ions).

7.2.2.1 Migration into food simulants

The food contact conditions were not defined. In the worst case it was expected that the liner may be exposed to foods at room temperature for more than 24 hours. Equivalent test conditions for conventional simulants defined in EU legislation (for plastics but used here as a guide) are 10 days at 40°C. Triplicate portions of the film (1 dm^2) were exposed, by total immersion, to 30 mL of:

- 10% ethanol
- 3% acetic acid
- 95% ethanol for 10 days at 40°C (equivalent simulant D substitute test media and test conditions)
- iso-octane 2 days at 20°C (equivalent simulant D substitute test media and test conditions)

Duplicate control samples (no test specimen) were also prepared alongside the samples.

The concentration of silver in the exposed simulant was determined by ICP-MS. The 3% acetic acid and 10% ethanol simulant samples were analysed directly. The 95% ethanol and isooctane were evaporated to dryness and reconstituted in 10 mL of 2% HNO_3, 0.1% HCl, by roller mixing for 1 hour and then subjecting to ultrasonication for 30 minutes. The resulting extracts were cloudy so to ensure the dissolution of any silver salts (e.g. silver chloride) 1 mL of a 50% solution of concentrated HCl in water was added. The samples were analysed by ICP-MS following a further ten-fold dilution with 2% HNO_3, 0.1% HCl containing rhodium/indium internal standards.

There was no detectable migration of silver into the food simulants. In-house quality assurance samples analysed alongside these test samples were satisfactory (as above).

7.2.2.2 Migration into foods

The migration of silver into apple sauce and tomato sauce following exposure for 10 days at 40°C was determined in triplicate. Approximately 20 g of sauce was exposed to 1 dm^2 of film. Exposures were carried out in sealed glass vials with the cling film immersed in the liquid foodstuffs. Triplicate blank samples (no film) were prepared alongside the samples. As for the antimicrobial liner analytical quality assurance samples were analysed with each batch.

Following the exposure the foodstuffs were homogenised and the silver concentrations detected in the foods (and the corresponding migration values) were determined by ICP-MS. Aliquots (1 g) of the homogenised foodstuff plus certified reference materials were digested in a mixture of nitric acid and hydrochloric acid (4:1 ratio, 5 mL) using quartz high pressure closed vessels and microwave heating. Digests were transferred to plastic test tubes and diluted to 10 mL with water. A further ten-fold dilution was performed using dilute nitric acid containing rhodium/indium internal standards prior to analysis by ICP-MS. Reagent blanks and a reagent blank spiked with a known amount of the analyte were analysed with the test samples for recovery estimate purposes. The recovery of the added silver was 109%.

No silver was detected in any of the samples. The limit of detection was 5 µg/kg of food which is equivalent to a migration of 0.1 µg/dm^2, i.e. much lower than the Group restriction limit which is equivalent to 8.3 µg/dm^2.

7.2.3 Ethylene scavenging sachet (S07-024128-EthS3)

The migration experiments with the ethylene scavenging sachet were carried out into food simulants and foods (apples – selected as they are ethylene producing and ethylene sensitive fruits and strawberries – selected as they form a moist contact between the fruit and the sachet and may be considered to represent the worst case).

7.2.3.1 Migration into food simulants

The food contact conditions were not defined. In the worst case it was expected that the ethylene scavenging sachets may be exposed to foods at room temperature for more than 24 hours. Equivalent test conditions for conventional simulants defined in EU legislation (for plastics but used here as a guide) are 10 days at 40°C. Sachets (n = 3) were exposed to:

- 10% ethanol soaked onto filter paper (see below)
- 3% acetic acid soaked onto filter paper (see below)
- olive oil soaked onto filter paper (see below)

It was expected that immersion of the ethylene scavenging sachet into the aqueous food simulants would overestimate the migration into foods as the foods with which these articles are intended to come into contact are dry (i.e. fruit and vegetables). Moist contact may be envisaged if the fruits/vegetables perspire. Tenax, often used as a simulant for dry foods, was not used as it was not expected to have a high affinity for the inorganic manganese. Instead an approach previously proposed in the EU Actipak project [3], and by TNO in this report (see section 7.1.3.1) was investigated. The experimental set up was similar to that described for the oxygen scavenging sachet although a hole was not cut, the sachet was simply sandwiched between the simulant soaked papers (Figure 1A). Duplicate control samples (no test specimen) were also prepared alongside the samples. Following the exposure, the simulant soaked papers plus certified reference materials NIST 1515, apple leaves, and NIST 1547, peach leaves, were digested under high pressure in quartz vessels using nitric acid and microwave heating prior to analysis by ICP-MS. Reagent blanks and a reagent blank spiked with a known amount of the analyte were analysed with the test samples for recovery estimate purposes. Recovery of added manganese was 70% and CRM results were acceptable (NIST 1515; our result 47 mg/kg, certified value 54 mg/kg. NIST 1547; our result 96 mg/kg, certified value 98 mg/kg).

The concentration of manganese detected in the digested paper samples was used to calculate the migration value. The mass of manganese transferring from one sachet to the simulant soaked paper was calculated along with the migration. Information available on the suppliers website states that 1 sachet should be used per box of 30 lbs (14 kg) of fruit or vegetables. The levels of manganese detected in the paper soaked in simulant and the corresponding migration values are given in Table 26.

As expected the highest migration was into the 3% acetic acid simulant soaked paper. The migration was variable. Although care was taken to prevent losses due to evaporation by overwrapping in cling film these differences in concentration are proposed to be due to differing levels of moist contact. In all cases the calculated migration was less than the SML (0.6 mg/kg) for this metal.

7.2.3.2 Migration into foods

The migration of manganese into strawberries following exposure for 2 days at 40°C (the shelf-life of the foods) and apples following exposure for 10 days at 40°C was determined in triplicate. The foodstuffs were placed in direct contact with the sachets. Approximately 60 g of strawberries and 125 g of apples were exposed to each sachet within a sealed polyethylene bag. Triplicate blank samples (no sachet) were prepared alongside the samples. Analytical quality assurance samples were analysed with each batch. Following the exposure the foodstuffs were homogenised (the apples were first cored to aid the homogenisation). Aliquots (1 g) of the homogenised foodstuff plus certified reference materials (DOLT-2, dogfish liver, and NIST1566a, oyster tissue) were digested in a mixture of nitric acid and hydrochloric acid (4:1 ratio, 5 mL) using quartz high pressure closed vessels and microwave heating. Digests were transferred to plastic test tubes and diluted to 10 mL with water. A further ten-fold dilution was performed using dilute nitric acid containing rhodium/indium internal standards prior to quantification by ICP-MS. Reagent blanks and a reagent blank spiked with a known amount of the analyte were analysed with the test samples for recovery estimate purposes. Recovery of added manganese was 110% and CRM results were acceptable (DOLT-2; our result 5.4 mg/kg, certified value 6.9 mg/kg. NIST 1566a; our result 10.8 mg/kg, certified value 12.3 mg/kg).

The manganese concentrations detected in the exposed foods were the same as those in the blank foods, i.e. no migration was observed. Manganese was detected in the blank unexposed foodstuffs (an average of 2.5 mg/kg in the strawberries and 0.4 mg/kg in the apples). Taking into account the standard deviation of the results and the low mass of food exposed to the sachet a migration equivalent to 0.6 mg/kg would have been detected.

Comparing the migration from the sachet into the simulant soaked papers with that into the foods demonstrates that the migration tests used did overestimate the migration and could be used to demonstrate the compliance of such materials.

7.2.4 Moisture absorber (S07-024129-MoistA)

The migration experiments with the absorbent pads were carried out into food simulants and foods (meat and fish – the foods with which these materials are intended to come into contact).

7.2.4.1 Migration into food simulants

The food contact conditions were not defined. In the worst case it was expected that the absorbent pads may be exposed to foods at chilled temperature (< 5°C) for more than 24 hours. Equivalent test conditions for conventional simulants defined in EU legislation (for plastics but used here as a guide) are 10 days at 5°C. Triplicate portions of the absorbent pads were exposed to:

- 10% ethanol soaked onto paper (see below)
- 3% acetic acid soaked onto paper (see below)
- olive oil soaked onto paper (see below)

Duplicate control samples (no test specimen) were also prepared alongside the samples. It has previously been demonstrated that immersion of the absorbent pads into food simulants overestimates the migration that occurs into foods (EU Actipak project). Instead test methods proposed in this project were used as described above. Following the exposure the simulant soaked paper was solvent extracted. 1 dm^2 was extracted

with 20 mL of acetonitrile containing d_4-diisobutyl phthalate as an internal standard and the concentrations of diisobutyl phthalate, di-(2-ethylhexyl) fumarate and di-(2-ethylhexyl) maleate were determined by GC-MS. As the food contact ratio (area to mass of food ratio) was not defined the migration was calculated from these concentration values in units of mg/dm^2.

The concentrations of di-(2-ethylhexyl) fumarate and di-(2-ethylhexyl) maleate in the papers and the corresponding migration values are shown in Table 27. Both were quantified against the response of the di-(2-ethylhexyl) maleate and therefore the uncertainty in the concentration of the di-(2-ethylhexyl) fumarate is not known. Diisobutyl phthalate was not detected in any sample above the limit of detection of 3.4 mg/kg of absorbent pad which is equivalent to a migration of 17.2 µg/dm^2.

7.2.4.2 Migration into foods

The migration of diisobutyl phthalate, di-(2-ethylhexyl) fumarate and di-(2-ethylhexyl) maleate into beef steak and salmon following exposure for 5 days at 5°C (the shelf-life of the foods) was determined in triplicate. The foodstuffs were placed in direct contact with the absorbent pads. Approximately 50 g of salmon and 130 g of beef steak were each exposed to 1 dm^2 of absorbent pad. Exposures were carried out in sealed glass Petri-dishes overwrapped with cling film to avoid moisture losses from the foods. Blank samples (no absorbent pads) were prepared alongside the samples. Samples were overspiked with diisobutyl phthalate and bis-(2-ethylhexyl) maleate each at a concentration of 0.5 mg/kg in the food.

Following the exposure the foodstuffs were homogenised. Aliquots (5 g) of the homogenised foodstuff were solvent extracted with 10 mL of acetonitrile:dichloromethane 1:1 (v/v) and shaken for 18 hours. Following centrifugation the solvent was decanted from the sample residue and held at –20^{o}C for 4 hours to precipitate the fat. The solvent was removed and evaporated to dryness, The residue was redissolved in 1 mL of acetonitrile and the diisobutyl phthalate, di-(2-ethylhexyl) fumarate and di-(2-ethylhexyl) maleate concentrations (and the corresponding migration values) were determined by GC-MS. Quantification was against solvent standards containing known amounts of analytes and internal standard.

No diisobutyl phthalate was detected in any of the food samples. The limit of detection was 0.18 mg/kg (calculated as 3 times the concentration of diisobutyl phthalate detected in the procedural blank sample). This is equivalent to a migration of 9 µg/dm^2 for salmon and 23 µg/dm^2 for the beef steak. The overspiked samples gave acceptable recoveries in the range 83 – 93%. No di-(2-ethylhexyl) maleate was detected in any food samples. The limit of detection was 6.1 mg/kg (calculated as 3 times the concentration of di-(2-ethylhexyl) maleate detected in the procedural blank sample). This is equivalent to a migration of 0.31 mg/dm^2 for salmon and 0.8 mg/dm^2 for the beef steak. The high limit of detection was caused by a co-eluting compound in the GC-MS chromatograms. Di-(2-ethylhexyl) fumarate was detected in the food samples and results are given in Table 28.

Comparing the migration from the pad into the simulant soaked papers with that into the foods demonstrates that the migration tests used did overestimate the migration and could be used to demonstrate the compliance of such materials.

8 Efficacy experiments

8.1 Efficacy experiments TNO

8.1.1 Oxygen scavengers; label (0939-03-0471-OxS3) and sachet (0939-03-0472-OxS4)

The efficacy of the oxygen scavengers was tested using OXYDOT oxygen sensitive sensors developed by TNO. A dot a few millimetres across containing an oxygen sensitive material is attached to the inside of the packaging material. The oxygen concentration inside the packaging material can be monitored using a non-invasive oxygen determination (NIOD) set-up. The principle is that the fluorescence life-time of the oxygen sensitive material depends on the oxygen concentration in the air. A picture of the set-up is presented in Figure 2. The yellow dot inside the packaged food exhibits fluorescence upon irradiation (with the probe shown in Figure 2). Detection of the fluorescence life-time is performed simultaneously with the same probe. All experiments were performed in duplicate.

The sachet and label containing oxygen scavengers were tested inside 210 mL glass bottles closed with an airtight stopper. According to the provider of the oxygen scavengers, the sachets have an oxygen capacity of 100 mL and the label of 5 mL. The 210 mL glass bottles were filled with atmospheric air containing ~ 21% oxygen. This corresponds to a total of 44 mL oxygen. The sachets are normally used in cold or frozen conditions and the label used at room temperature. Therefore, the experiments with the sachets were performed at 7-10°C. As a comparison, the experiment was also performed at room temperature. Experiments with the labels were performed at room temperature only.

Figures 3 and 4 present the oxygen concentration inside the glass bottles as a function of time (hours). The sachets show a clear decrease of the oxygen concentration to 0% in 4.5 hours. The highest oxygen absorption rate during the first hour is observed at low temperatures, whereas the time required to reduce the oxygen concentration to <<1% is shortest at room temperature. The labels also show a clear decrease of the oxygen concentration until ~ 1% in ~ 110 hours. This slower oxygen absorption rate can be explained by the lower oxygen capacity of the labels. The experiments demonstrate the efficacy of the oxygen absorbers sachet and label.

8.1.2 Efficacy antimicrobial materials (food storage liner 0939-03-0269-AntiM3 and film S07 024123-AntiM4)

The antimicrobial activity of the two materials 0939-03-0269-AntiM3 and S07 024123-AntiM4 was tested by means of two different tests:

- Method A: Artificial contamination of the materials with meat drip
- Method B: Microbiological monitoring of meat contact surfaces

Since a reference material was not provided by the manufacturers, standard laboratory paper was used as a reference.

8.1.2.1 Method A: Artificial contamination of products and surfaces with meat drip

Pieces of the antimicrobial materials and standard laboratory paper (5 x 5 cm) were placed in the centre of sterile Petri dishes. The standard laboratory paper (Tork

Premium Facial Tissues) did not contain added antimicrobial substances and was used as a reference. One droplet of meat sap that had been artificially contaminated with approximately 10.000 cfu/ml *Escherichia coli* was spread on the top of each tissue. This is presented schematically in Figure 5a. After 4 and 24 hours, two contaminated pieces from each type of tissue were transferred into sterile physiological salt and were vortexed for 1 minute. All measurements were performed in duplicate. Microbial dilutions were made and microbiological analysis was performed to investigate the following parameters:
1. Total Viable Counts (TSA incubation for 3 days at 30^{o}C). This is a general indicator of the microbial quality.
2. Enterobacteriaceae (VRBG, incubation for 2 days at 37^{o}C). Enterobacteriaceae is an indicator of the hygienic condition of the investigated sample. The *Escherichia coli* with which the drip has been inoculated, belongs to the group of Enterobacteriaceae.

Table 29 presents the results of the experiments performed with meat drip. The total counts and Enterobacteriaceae counts found in the inoculated sheets of 0939-03-0269-AntiM3 and S07 024123-AntiM4 were higher than the counts found in kitchen paper after 4 hours and 24 hours. This indicates that the standard lab paper has a higher anti-microbial function under the conditions of the experiment.

A slight reduction in the total viable counts (TVC) was observed after 24 hours in all three tissues. The reduction of the Enterobacteriaceae was significant in all three products after 24 hours. This reduction should not be attributed to antimicrobial activity but to a failure of the microorganisms to retain viability after 24 hours under the pure conditions on the paper strips and the absence of nutrients.

Under the test conditions investigated the efficacy of the antimicrobial materials was not demonstrated using this test.

8.1.2.2 Method B: Microbiological monitoring of contact surfaces with and without RODAC plates

Small pieces of pork meat were homogenised to obtain microbiologically homogeneous pork pieces. The pieces of pork were transferred to Petri dishes on top of the antimicrobial samples and references tissues. Samples were taken after 5 minutes and after 4 hours of contact of the meat with a piece of tissue. All experiments were performed in duplicate. The experiment is schematically presented in Figure 5b.

RODAC (replicate organisms detection and counting) was used to sample the tissue that was in contact with the meat. The Petri dish was gently pressed onto the rounded agar surface of the RODAC plate to ensure that the entire surface of the agar has contacted the sample surface. After removing the tissue from the Petri dish, the surface of the Petri dish was sampled in a similar manner. The pieces of pork were analysed directly without using RODAC.

The scoring system to rate the results of the RODAC plates is internationally recognised:
• 0-5 colonies: (considered excellent)
• 6-15 colonies: (considered good)
• 16-30 colonies: (considered borderline acceptable)
• 31-50 colonies: (considered poor)

The results of the anti-microbial efficacy tests with real meat are shown in Table 30. In the first column the microbiological results of the meat are presented. The second column presents the results from the tissues that were in contact with the meat. In the last column the microbiological data from the surface of the Petri dish are shown. This experiment was performed to see whether the antimicrobial tissues prevent microbiological contamination of the surface underneath.

Microbiological activity on the meat
No reduction of the total microbial counts on the meat cuts was observed after contact with the tissues compared to the control. The TVC did not change significantly between the samples and reference material for 5 minutes and 4 hours. The Enterobacteriaceae counts did not change after contact for 5 minutes. An effect may be present after a contact time of 4 hours.

Microbiological activity on tissues
Investigation of cultures on the tissue after a contact time with meat for 5 minutes and 4 hours demonstrated a high microbiological activity on the surface of all tissues. It is remarkable that no Enterobacteriaceae counts were detected on the samples after 5 minutes. In contrast, the number of Enterobacteriaceae on both tissues was very high after contact with the meat cut for 4 hours. The efficacy of the anti microbial materials to reduce microbial growth on the surface of the tissues was therefore not demonstrated under the conditions investigated.

Microbiological activity on surface Petri dish
The microbiological quality of the Petri dish surface in contact with the reference tissue after 4 hours was very poor. This poor quality can be attributed to diffusion of meat juice through the paper tissue onto the surface of the Petri dish. The microbiological quality of the Petri dish in contact with the two antimicrobial tissues was very good both after 5 minutes and after 4 hours, showing that a possible contamination due to diffusion of the meat drip is probably retarded under these conditions. These experiments demonstrate that microbial growth on the surface of the Petri dish was prevented by using the anti-microbial tissues. Whether this can be attributed to the anti-microbial properties or due to the barrier properties of the materials can not be concluded. The efficacy could therefore not be confirmed.

Therefore the tests used to assess the efficacy of the antimicrobial materials did not demonstrate their efficacy in improving the antimicrobial properties of the foods or of the food contact surfaces of the materials themselves.

8.1.3 Efficacy anti-mould SO_2 emitter (0939-02-1737-AntiM2)

To test the efficacy of the anti mould product, two different batches of white grapes were purchased at a two different local supermarkets. Five SO_2 emitters were packed with 1 kg of grapes. Grapes from the same batch were packed without SO_2 emitters as reference. Additional mould cultures were not added to the grapes i.e. the naturally occurring moulds were used instead. The experiments were performed at room temperature.

8.1.3.1 Results

The grapes were stored at room temperature in the laboratory. After two weeks, slight discoloration of the grapes stored without the SO_2 emitter was apparent. After one

month, a clear difference in the grapes packed with and without SO_2 emitter was evident.

Figure 6 shows the results for the grapes from two different sources. For the first brand it can clearly be seen that some moulds have started to grow on the grapes packed without the SO_2 emitter, see Figure 6a. The grapes with SO_2 emitter do not show the growth of moulds (Figure 6b). This effect is more apparent for the second brand, see Figures 6c and 6d.

Therefore the efficacy of the SO_2 emitter has been demonstrated.

8.2 Efficacy experiments Fera

8.2.1 Absorbent pads (S07-024129-MoistA)

Absorbent pads are used in contact with meat and fish to absorb water released from the products during storage.

To establish the absorbency the pads were saturated with water and the difference in the mass of the dry and saturated pads was determined. This was carried out at two temperatures (5°C and ambient). The mean mass of the water taken up by the pads (triplicate specimens were tested) was:

5°C	mean mass of water held by pad = 19.5 g
Room temp	mean mass of water held by pad = 20.0 g

Using cuts of salmon and beef, the absorbency of the pads was measured to assess the efficacy. A known amount of sample was placed on a pad of known mass, covered and refrigerated at ~5°C for 5 days. The pad was then re-weighed. The results were:

Salmon (193g)	salmon loss on refrigeration	= 9.6 g	Pad take up = 7.8 g
Beef (240g)	beef loss on refrigeration	= 7.4 g	Pad take up = 4.1 g

The pads have been shown as being capable of absorbing up to ~ 20 g of water. Therefore over the shelf-life of the foods the pads do not become saturated with water and therefore the efficacy is demonstrated.

8.2.2 Ethylene scavenging sachet (S07-024128-EthS3)

The sachets are described as scavenging ethylene to prolong the freshness of ethylene sensitive fruits. Bananas were selected as they produce relatively high levels of ethylene, are ethylene sensitive and can easily be observed when they start to age.

Green, unripe, bananas were used. There were 2 bunches of bananas, each having 4 bananas per bunch. Each bunch was broken in half to give 2 bananas of roughly comparable sizes (weights were noted). Bunches labelled “a” were exposed to the packaging under test (sat on a scavenger sachet), and “b” bunches were the corresponding controls. The four samples were put into labelled resealable food bags (Figure 7) according to the following:

Description	Bunch size	Active packaging	Conditions
Bunch 1a	2 bananas	+ scavenger sachet	25°C
Bunch 1b	2 bananas		25°C
Bunch 2a	2 bananas	+ scavenger sachet	25°C + moist atmosphere
Bunch 2b	2 bananas		25°C + moist atmosphere

The moist atmosphere was achieved by putting a dish of water into the relevant sealed bags. The bananas were placed in an oven at 25°C (± 5°C). To increase the rate of ageing at Day 14, the bananas were moved from a glass-fronted oven where daylight could reach the bananas to an incubator set at the same temperature but in the dark. By day 5 the bananas in a moist atmosphere (Bunches 2a & 2b) were visibly ripening faster than those stored in the absence of the water (Bunches 1a & 1b): variation seen for different moisture conditions. The presence of the ethylene scavenging sachet had no visible effect. By day 18 the effect of the presence of the ethylene scavenging sachet was starting to be visible to the eye. Figure 8 shows the samples after 21 days storage at 25°C. The bananas stored in the presence of the ethylene scavenger had not aged to the same extent as those in the absence of the sachet and therefore the efficacy is demonstrated.

8.2.3 Anti-mould cheese bag (S08-003221-AntiM5)

A single block of English medium mature cheddar was purchased. The cheese block (19.5 x 9 x 14 cm) was cut with a knife into 10 smaller blocks (approximately 3.8 x 7 x 9 cm), labelled A to J. The weight of each block was recorded. No use instructions were provided with the anti-mould cheese bag and therefore one block of cheese (~ 250 g) was placed directly inside a labelled bag, the drawstring pulled tight and toggled shut. Triplicate samples were stored in this way in a temperature controlled incubator set to 8°C. Triplicate control samples were stored in resealable polyethylene bags in the same way. The samples were stored for 2 weeks and were examined daily. One of the samples stored in the anti-mould cheese bag was the first to show mould growth (by eye). By day 14 two of the samples stored in the anti-mould cheese bag and one of the control samples had visible mould growth and therefore under the experimental conditions used the efficacy could not be demonstrated.

8.2.4 Heat sensitive weaning spoons (S08-000164-HeatS)

The efficacy of the heat sensitive weaning spoons was tested by immersing the spoon in water at temperatures of 20, 40, 60 and 80°C. The elastomeric portion of the spoon changed from a red colour at 20°C to an orange colour at 40°C and was yellow at 60°C and 80°C (Figure 9). Therefore the efficacy was demonstrated.

8.2.5 Time indicator (S07-024306-TimeS)

The efficacy of one of the time indicators was tested. The strip was activated by forcing a liquid through a membrane and into the time monitoring chamber. Activation was confirmed by the presence of a black line appearing in the centre of the indicator (Figure 10a). The indicator was intended for use to monitor 2 and 4 hours at room temperature. Photographs were taken at these timepoints after storage at ambient temperature of approximately 20°C (Figures 10b and c). The photographs demonstrate that after both 2 and 4 hours the indicator had reached the appropriate point. Therefore the efficacy was demonstrated.

9 General conclusions

Over 60 companies were identified in Europe and the USA that are marketing active and intelligent packaging materials. The following types of active and intelligent materials were identified; oxygen scavengers, moisture absorbers, ethylene scavengers, amine/aldehyde and/or sulphide scavengers, carbon dioxide regulators, antimicrobial releasing systems, nitrogen releasers, heat releasers, flavour releasers and monitoring systems.

A selection of materials acquired from these companies was tested to investigate whether migration of the active/intelligent substances into food simulants and real food is of interest. Additionally, the efficacy of the active materials was tested to establish whether the consumer could be misled.

9.1 Screening for substance responsible for active/intelligent function

Analytical screening experiments were performed to identify the active and intelligent components present in the samples. In general it was very difficult to identify the active and intelligent ingredients without knowledge of product formulation. The materials tested and the active/intelligent substances identified were:

- oxygen scavenger, sachets; iron.
- oxygen scavenger, labels; iron.
- oxygen scavenger, crown cap; sulphite based (information provided by the manufacturer).
- moisture absorber; cellulose fibres.
- ethylene scavenger, sachet; potassium permanganate.
- ethylene scavengers, bags; natural clay/mineral.
- antimicrobial releasing systems; silver.
- anti-mould systems, food liner; $Na_2S_2O_5$ based (information provided by the manufacturer).
- anti-mould systems, bag; the active substance could not be identified in the screening studies.
- microwave susceptor; aluminium.
- flavour releasers; natural flavours were identified.
- heat sensitive monitoring system; the active substance could not be identified in the screening studies.
- food freshness indicator monitoring system; palladium complex (information provided by the manufacturer).

9.2 Migration into foods versus simulants

Active/intelligent packaging materials are often not suitable for direct contact with liquid food simulants. This would wet the packaging materials to such an extent that migration into foods would be overestimated. Therefore, dedicated migration tests, as developed in the EU Actipak project, were performed where the liquid simulant is replaced by a tissue soaked in simulant. The tissue is considered to better represent the morphology and wetness of real foods.

Most of the migration experiments performed using the tissue soaked in simulant showed higher migration than into real foods. This is an essential requirement of any migration test in order to ensure consumer protection. The only exception was for the oxygen absorbing label for which the migration into cheese was greater than that observed into the paper soaked in the fatty simulants. However it is recognised in EU legislation for plastics that some cheeses are acidic and in these cases 3% acetic acid should also be used as a simulant and therefore the migration was overestimated. This also highlights that in some instances it may be necessary to take into account the properties of the migrant as well as the food when selecting the appropriate simulant.

The migration of silver into food simulants was tested using conventional migration test conditions. There was no detectable migration into foods.

BHT was detected in the flavour releasing film. A low recovery in all but 50% ethanol due to the reactivity of BHT was observed. All migration results in food simulants and foods were below the specific migration limit for BHT. The migration in to real foods was higher than the migration into the food simulants. This is believed to be related to the stability of BHT in the different media, rather than a consequence of higher migration.

For only one of the oxygen scavengers tested (the label) the migration of iron measured in the acidic foodstuff (in the 3% acetic acid simulant soaked tissues) exceeded the restriction set (the maximum tolerable daily intake of iron is 48 mg of iron/kg of food). The results obtained indicate that the label should not be used for direct contact with acidic foodstuffs. For the substances tested migrating from all of the other materials, the migration does not exceed any levels or restrictions established to protect the consumer.

9.3 Efficacy tests

The efficacy of ten samples was investigated: an oxygen scavenging label, an oxygen scavenging sachet, an antimicrobial film, an antimicrobial food storage liner, an anti-mould pad, an absorbent pad, an ethylene scavenging sachet, an anti-mould bag, a heat sensing spoon and a time indicator. Seven of the ten samples behaved in the way claimed by the suppliers/manufacturers.

A consumption of about 44 mL of oxygen in less than 5 hours was observed for the oxygen scavenging sachet whereas three labels required approximately 100 hours to consume the 44 mL oxygen under the experimental conditions used. This can be explained by the lower oxygen capacity of the labels. The experiments demonstrate that the sachet and label are efficient oxygen absorbers.

Under the conditions tested microbial growth on the surface of the antimicrobial materials and meat in contact with these materials was not reduced compared to a material without antimicrobial properties. This would indicate that these materials should therefore not be used to prevent growth on the antimicrobial materials or foodstuffs. The materials did however demonstrate to be effective in preventing surfaces underneath the anti-microbial materials from becoming contaminated with microbes. Whether this can be attributed to the antimicrobial properties or due to the barrier properties of the materials can not be concluded. The efficacy could therefore not be confirmed.

The SO_2 emitter was shown to be capable of inhibiting mould growth on white grapes.

The absorbent pads had a capacity of ~20 g of water. The pads were shown to be capable of absorbing the water (up to 8 g) released from fish and meat throughout their shelf-lives and are therefore efficient water absorbers.

The efficacy of the ethylene scavenger sachet was demonstrated using bananas aged in the presence and absence of the sachet. Those bananas stored without the scavenger aged more quickly and more completely than those stored with the scavenger.

There was no difference between cheese stored in the anti-mould bag and that stored in a sealable plastic bag under the test conditions investigated. Therefore the efficacy was not demonstrated.

The two indicators tested both behaved as expected. The heat sensor clearly changed colour above 40°C and the time indicators gave the correct reading after both 2 and 4 hours.

10 Reference List

[1] L. Castle, Report FD 03/28. Active packaging-Current trends and potential for migration, 2004.

[2] R. Rijk, Chemical migration from active and intelligent packaging materials into food, in: Chemical migration and food contact material, K. A. Barnes, R. Sinclair, and D. Watson (eds), Woodhead Publishing, 2006.

[3] Aktipak final report, 2001. Evaluating safety, effectiveness, economic-environmental impact and consumer acceptance of active and intelligent packaging.

[4] A. L. Brody, E. R. Stupinsky and L. R. Kline, Active packaging for food applications. CRC Press, 2001.

[5] R. Ahvenainen, New food packaging techniques. Woodhead Publishing, 2003.

[6] L. Potter *et al*. Active and intelligent packaging – a review, Review No. 62, Campden & Chorleywood Food Research Association Group, 2008

[7] N. F. F. Soares, D. M. Rutishauser, N. Melo, R. S. Cruz and N. J. Andrade, Inhibition of microbial growth in bread through active packaging. *Packaging Technology and Science*, 2002, **15**, 132.

[8] F. Devlieghere, L. Vermeiren, A. Bockstal and J. Debevere, Study on antimicrobial activity of a food packaging material containing potassium sorbate. *Acta Alimentaria*, 2000, **29**, 137.

[9] Y. M. Weng, M. J. Chen and W. Chen, Benzoyl chloride modified ionomer films as antimicrobial food packaging materials. *International Journal of Food Science and Technology*, 1997, **32**, 229.

[10] P. V. Nielsen and R. Rios, Inhibition of fungal growth on bread by volatile components from spices and herbs, and the possible application in active packaging, with special emphasis on mustard essential oil. *International Journal of Food Microbiology*, 2000, **60**, 219.

[11] D. S. Cha, J. Chen, H. J. Park and M. S. Chinnan, Inhibition of Listeria monocytogenes in tofu by use of a polyethylene film coated with a cellulosic solution containing nisin. *International Journal of Food Science and Technology*, 2003, **38**, 499.

[12] A. G. M. Scannell, C. Hill, R. P. Ross, S. Marx, W. Hartmeier and E. K. Arendt, Development of bioactive food packaging materials using immobilised bacteriocins Lacticin 3147 and Nisaplin(R). *International Journal of Food Microbiology*, 2000, **60**, 241.

[13] P. LeGood and A. Clarke, http://amf.globalwatchonline.com/epicentric_portal/binary/com. epicentric. contentmanagement. servlet. ContentDeliveryServlet/AMF/smartmat/Smartandactivepackagingtoreducefoodwaste. pdf , Smart and Active Packaging to Reduce Food Waste, 2006.

[14] Del Nobile *et al*. *Journal od Food Science,* 2006, **68**, 2046

[15] L. Vermeiren, F. Devlieghere, M. van Beest, N. de Kruijf and J. Debevere, Developments in the active packaging of foods. *Trends in Food Science & Technology*, 1999, **10**, 77.

[16] FSA report A03054, An investigation into the reaction and breakdown products from starting substances used to produce food contact plastics, 2007

[17] http://www.who.int/ipcs/food/jecfa/summaries/summary67.pdf

[18] Dopico-Garcia *et al*. *Journal of Applied Polymer Science*, 2006, **100**, 656.

11 Appendices

Tables

Table 1. Active and intelligent packaging materials identified in the literature survey

Oxygen scavengers

Supplier	Amcor Flexibles	Amoco Chemicals / Colormatrix	Bericap UK Ltd	Ciba Specialty Chemicals	Constar International Inc.
Trade name	Bind-Ox+™	Amosorb® 2000 Amosorb® 2000	BO2S® Double seal O2S®	Shelfplus® O2	Oxbar™ MonOxbar™ DiamondClear™
Application	Layer in PET bottle	PET bottles and films	Closures/liners	PE or PP layers or flexible packaging	PET bottles
Active ingredient / working principle	Not known	Not known	Probably sodium sulfite or sodium ascorbate	Iron	Nylon polymer with cobalt salt catalyst
Applications	Juice/beer	Juice	Juice/beer	Soup, ready meals, meat etc	Juice/beer
Website	www.amcor.com	www.bpppetrochemicals.com	www.bericap.com	www.cibasc.com	www.constar.net

Some of these systems scavenge oxygen preventing diffusion of external oxygen through the packaging whereupon it would come into contact with the food. As such they are considered passive rather than active materials.

Table 1 continued.

Oxygen scavengers

Supplier	Chevron Phillips	Cryovac Sealed Air Corp	Didai Tecnologia[1]	Drypak	Everfresh
Trade name	OSP®	OS 2000®	O Buster	Drypak Oxygen Absorber	Everfresh BC Everfresh H Everfresh E
Application	Multilayer	Multilayer film	Sachet	Sachet	Sachets
Active ingredient / working principle	Polymer based (ethylene methyl acrylate cyclohexene methyl acrylate)	Polymer based	Iron and zeolite	Not known	Air or moisture
Applications	Wet and dry food	Wet end dry foods	Various foods	Dry/solid foods	Dry/solid foods
Website	www.cpchem.com	www.sealedair.com	www.didai.com.br/_ingles	www.drypak.com	www.everfreshusa.com

[1] Also intelligent packaging

Some of these systems scavenge oxygen preventing diffusion of external oxygen through the packaging whereupon it would come into contact with the food. As such they are considered passive rather than active materials.

Table 1 continued.

Oxygen scavengers

Supplier	Grace Darex	Honeywell Seelze Gm	M & G Polymers	Mitsubishi Gas Chemical Co. Inc	Multisorb
Trade name	DARABLEND® ASK1G	Aegis™ Ox-OXCE	ActiTUF	Ageless® (various codes)	Freshpax™, Freshmax®, Freshcard
Application	Crown cap	Bottles	Polymer based	Sachet/label	Sachet/label/card
Active ingredient / working principle	Not known	Moisture	Not known	Iron or iron and moisture component	Iron
Applications	Beverages	Beer/juice	Beer/juice	Dry/solid foods	Dry/solid foods
Website	www.gracedarex.com	www.honeywellplastics.com	www.mgpolymers.com	www.mgc.co.jp/eng	www.multisorb.com

Some of these systems scavenge oxygen preventing diffusion of external oxygen through the packaging whereupon it would come into contact with the food.
As such they are considered passive rather than active materials.

Table 1 continued.

Oxygen scavengers

Supplier	Nutricepts Inc	Standa Industries	Toyo Seikan	Valspar
Trade name	Oxyvac™	ATCO	Oxyblock, Oxyguard™ Sirius 101	ValOR Active 100
Application	Powder	Sachet/label	Containers, lidding, PET bottle	PET bottles
Active ingredient / working principle	Enzyme system	Iron	Not known	Nylon polymer with cobalt salt catalyst
Applications	Meat	Dry/solid foods	Various wet/moisture foods	Juice/beer
Website	www.nutricepts.com	www.atmosphere-controle.fr	www.toyo-seikan.co.jp.e/	www.valsparglobal.com

Some of these systems scavenge oxygen preventing diffusion of external oxygen through the packaging whereupon it would come into contact with the food. As such they are considered passive rather than active materials.

Table 1 continued.

Oxygen scavengers

Supplier	Bioka Ltd	EMCO Packaging Systems	Freund Industrial Co.	Ohe Chemicals Inc.	W. R. Grace & Co.
Trade name	Bioka	ATCO Oxycaps	Negamold® (also an ethanol emitter)	Tamotsu Sanso-cut Sequl	Pureseal Celox™
Application	Sachet	Self adhesive label	Sachet	Sachets	Crown cap
Active ingredient / working principle	Enzyme	Iron	Not known	Active carbon and an oxygen-absorbing component contained in green tea or iron	Ascorbate / metal salts
Applications	Various	Sliced meats	Not known	Various types for different foodstuffs	Beverages
Website	www.bioka.fi	www.emcouk.com	www.freund.co.jp	www.ohe-chem.co.jp	www.grace.com

Some of these systems scavenge oxygen preventing diffusion of external oxygen through the packaging whereupon it would come into contact with the food. As such they are considered passive rather than active materials.

Table 1 continued.

Moisture absorbers

Supplier	Cryovac Sealed Air Corporation	Elliot absorbency products	GTM converting Ltd	Humidipak Inc.	Multisorb Technologies
Trade name	Supa-Loc® Dri-Loc® Lite-Loc® Plus	Dryline®	HiSorb, Unisorb	Humidipak®	Minipax® Strippax® Natrasorb® Desimax®
Application	Pad	Pad	Pad	Pouch	Sachets
Active ingredient / working principle	Not known	Not known	Not known	Saturated solution of e.g salt or sugar	Silica gel or molecular sieve or clay
Activation	None	None	None	Not known	Not known
Applications	All food types	Fresh meat, fish	Fish	Dried fruits, dried meats, cheese	Various food types
Website	www.sealedair.com	www.elliottabsorbents.co.uk	www.gtmconverting.co.uk	www.humidipak.com	www.multisorb.com

Table 1 continued.

Moisture absorbers

Supplier	Showa Denka	Sirane Limited	EverFresh USA
Trade name	Pichit®	Dri-Fresh® Inflex® Eat-Fresh® Roast-it®	EverDri
Application	Wrapping film	Pad	Sachet
Active ingredient / working principle	Not known	Not known	Water is absorbed into diatomaceous micropores
Applications	Fresh meat, fish	Fresh meat, fish, beetroot, sandwiches and bakery products, ovenable foods	Sweets, flour, crisps, seaweed, and ‘other foodstuffs’
Website	http://www.sds.com.sg	www.sirane.co.uk	www.everfreshusa.com

Table 1 continued.

Ethylene scavengers

Supplier	Dennis Green Ltd.	Ethylene Control, Inc	Grofit Plastics	Lakeland	EverFresh USA
Trade name	ExtraLife	EC Power	Bio-Fresh	Stayfresh longer	EverFresh ET
Application	Disk	Sachets and filters	Bags	Bags	Sachet
Active ingredient / working principle	Potassium permanganate	Potassium permanganate	Not known	Minerals	Potassium permanganate
Applications	Household products used in refrigerator bin	Fruits, vegetables	Agriculture products	Fruits, vegetables	Fruit and vegetables
Website	www.dennisgreenltd.com	www.ethylenecontrol.com	www.grofitpl.com	www.lakeland.co.uk	www.everfreshusa.com

Table 1 continued.

Ethylene scavengers

Supplier	Peakfresh	Evert-fresh Corporation
Trade name	HOW PEAK*fresh* ®	Evert-Fresh Green bags®
Application	Bags	Bags
Active ingredient / working principle	Minerals	Minerals
Applications	Fruits and vegetables	Fruit and vegetables
Website	www.peakfresh.com	www.evertfresh.com

Table 1 continued.

Amine, aldehyde and/or sulphide scavengers

Supplier	Colormatrix	Anico Co.	EKA AkzoNobel	Multisorb Technologies	United Desiccants-Gates
Trade name	Triple A *	Anico bags	Not found	Minipax® Strippax®	Desi Pak® Getter® 2-in-1
Application	PET bottle	Bag	Paper based	Sachet	Sachet
Active ingredient / working principle	Not known	Ferrous salt and organic acid – absorbs amines	Aluminosilicate zeolites – adsorbs odourous gases	Activated carbon - adsorb mercaptans and hydrogen sulphide	Clay or activated carbon
Applications	Beverages	Fish	Meat	Not known	Not known
Website	www.colormatrix.co.uk	Not found	Not found	www.multisorb.com	www.sphinxadsorbents.com

***** This acetaldehyde scavenger is intended to scavenge the acetaldehyde released by the PET and as such is considered a passive material.

Table 1 continued.

Carbon dioxide regulating systems

Supplier	CSP Technologies	Landec Intelligent materials	Long life Solutions	Mitsubishi Gas Chemical Co. Inc	Mitsubishi Gas Chemical Co. Inc
Trade name	Activ-Pak	Intelimer, Breatheway technology	Smartpunnet®	Freshlock Ageless E	Ageless G
Absorber / emitter or permeation	Emitter	Permeation	O_2 absorber and CO_2 emitter	O_2 and CO_2 absorber	O_2 scavenger and CO_2 emitter
Application	Polymer material	Film	Film	Sachet	Sachet
Active ingredient / working principle	Carbonates or bicarbonates	Polymer responds to temperature change. Permeable above certain temperature	Not known	Not known	Not known
Applications	Bottles and cap liners	Not known	Fruits, Vegetables	Low moisture products	Rice cakes, nuts and dried fish
Website	www.csptechnologies.com	www.landec.com	www.longlifesolutions.com	www.mgc.co.jp/eng	www.mgc.co.jp/eng

Table 1 continued.

Carbon dioxide regulating systems

Supplier	EMCO Packaging Systems	EverFresh USA	Evert-fresh Corporation
Trade name	OxyFresh	EverFresh type G	Evert-Fresh Green bags®
Absorber / emitter or permeation	O_2 emitter and CO_2 absorber	O_2 and CO_2 absorber	CO_2 absorber (and ethylene absorber)
Application	sachet	Sachet	Sachet
Active ingredient / working principle	Not known	Not known	Minerals
Applications	Not known	Coffee, Kimchi, Soybean sauce, etc.	Fruit and vegetables
Website	www.emcouk.com	www.everfreshusa.com	www.evertfresh.com

Table 1 continued.

Antimicrobial releasing systems

Supplier	Freund Industrial Co. Ltd	IMAL Ltda	Lakeland	Kontek	Microbeguard
Trade name	Antimold® Negamold® Ethicap®	UVAS Grape guard	Not known	Kontroll UVA	Foodtouch, SurfaceGlove
Application	Sachets	Pad	Cling film	Pad	Paper liner
Active ingredient / working principle	Ethanol emitter (Negamold® is also an oxygen scavenger)	Sulphur dioxide	Silver ions	Sulphur dioxide	AgION silver containing ceramic
Applications	Not known	Grapes	Overwrapping foodstuffs	Grapes	Meat
Website	www.freund.co.jp	www.uvasquality.com/	www.lakeland.co.uk	Not found	www.microbeguard.com

Note: some food contact materials and articles that contain antimicrobial releasing systems are only intended to have an antimicrobial effect on the surface of the packaging, i.e. not on the food. These are not regarded as active packaging unless the claim is made that they extends the shelf life of the foodstuff through their antimicrobial action.

Table 1 continued.

Antimicrobial releasing systems

Supplier	Mitsubishi Gas Chemical Co. Inc	Ohe Chemicals Inc.	Sinanen Zeomic Co. Ltd	AgION Technologies	Microban International Ltd
Trade name	Ageless SE	Oyteck L	Zeomic	AgION	Microban
Application	Ethanol emitter (also an oxygen scavenger)	Ethanol emitter	Silver zeolite	Silver containing ceramic	Food preparation and processing products
Active ingredient / working principle	Sachet	Sachet	Film	Film	Triclosan
Applications	Not known	Sponge cakes, savoury delicacies, uncooked noodles	Not known	Not known	All foods
Website	www.mgc.co.jp/eng	www.ohe-chem.co.jp	www.zeomic.co.jp	www.agion-tech.com	www.microban.com

Note: some food contact materials and articles that contain antimicrobial releasing systems are only intended to have an antimicrobial effect on the surface of the packaging, i.e. not on the food. These are not regarded as active packaging unless the claim is made that they extends the shelf life of the foodstuff through their antimicrobial action.

Table 1 continued.

Antimicrobial releasing systems

Supplier	Mitsubishi Kagaku Foods Corporation
Trade name	
Application	Sheets/labels
Active ingredient / working principle	Allylisothiocyanate
Applications	Rice cakes, bakery products and delicatessaen foods
Website	http://www.mfc.co.jp/wasaouro

Note: some food contact materials and articles that contain antimicrobial releasing systems are only intended to have an antimicrobial effect on the surface of the packaging, i.e. not on the food. These are not regarded as active packaging unless the claim is made that they extends the shelf life of the foodstuff through their antimicrobial action.

Table 1 continued.

Nitrogen releasers

Supplier	Heineken
Trade name	Widget
Application	Balls
Active ingredient / working principle	Carbon dioxide
Applications	Beer
Website	www.heineken.com

It is expected that other nitrogen releasing widgets are available in the UK but further information was not sought.

Table 1 continued.

Heat releasers

Supplier	Alert packaging	API laminates	BCP Fluted Packaging Ltd	Sirane	OnTech
Trade name	M'wave+®	Not known	Not known	Crisp-it® Cook-it®	Hillside
Application	Laminate	Laminate	Laminate	Pad	Can
Active ingredient / working principle	Microwave susceptors for browning foods	Microwave susceptors for browning foods	Microwave susceptors for browning foods	The Crisp-it® susceptor pad is both an absorbent pad and microwave susceptor designed to crispen food as well as remove liquid and fat before and during cooking The Cook-it® microwave pad absorbs fat and liquid during cooking so that the food remains crisp	Self-heating can
Applications	Microwaveable foodstuffs	Microwaveable foodstuffs	Microwaveable foodstuffs	Microwaveable foodstuffs	Coffee, cocoa, tea and soup
Website	www.alertpackaging.com	www.apigroup.com	www.bcpflute.com	www.sirane.co.uk	www.ontech.com

Table 1 continued.

Heat releasers

Supplier	Nouva Bit SRL	Food Brand Ltd	Operational Support Ltd
Trade name	Caldo caldo	Rocketfuel	Hotcan®
Application	Container/cup	Container/cup	Container/cup
Active ingredient / working principle	Self-heating container	Self-heating container (water added to salt)	Self-heating container (water added to salt)
Applications	Coffee, cocoa and tea	Coffee based beverage	Ready meals
Website	www.caldocaldo.it	www.rocketfuel.uk.com	www.hotcan.com

Table 1 continued.

Flavour releasers

Supplier	ScentSational Technologies	Nutrisystems
Trade name	CompelAroma®	Aquaescents
Application	Film/closures	Bottle sports cap
Active ingredient / working principle	Encapsulated Aroma Release™ technology	Flavour released from bottle cap, intentional migration into water to deliver flavour
Applications	All foodstuffs	Water
Website	www.scentsationaltechnologies.com	www.nutrisystem.com

Table 1 continued.

Monitoring systems – Time and/or temperature indicators

Supplier	3M	Smart Lid Systems	Timestrip	Vitsab
Trade name	Monitor Mark™	Smart Lid systems™	timestrip®	CheckPoint®
Application	Label	Lid	Label	Label
Intelligent system	Diffusion of a coloured fatty acid ester along a porous wick to monitor the shelf-life of a foodstuff	Color changing additive that changes its color under influence of temperature	Irreversible colour change basedon enzymatic lipase colour change to monitor the shelf-life of a foodstuff	Irreversible colour change to monitor the shelf-life of a foodstuff
Applications	Meat and fish	Coffee	Customer activated, various foodstuffs	Meat and fish
Website	www.3m.com	www.smartlidsystems.com/	www.timestrip.com	www.vitsab.com

Table 1 continued.

Monitoring systems – Freshness indicators

Supplier	Cox Technologies	Lakeland	Lifelines	Ripesense	Toxin Alert
Trade name	FreshTag®	It's Fresh	Fresh-Check®	Ripesense	Toxin Guard™
Application	Not known	Label	Label	Label	Film
Intelligent system	Colour indicators that sense the production of volatile amines	Colour indicators that sense the production of sulphur compounds and amines	Irreversible colour change based on a polymerization reaction to demonstrate freshness of a foodstuff	Colour changing sensor spot	Bio-sensor
Applications	Fish	Meat, fish and vegetables	Fresh meat, vegetables, milk	Fruit and vegetables	Various food types
Website	www.meatandpoultryonline.com/storefronts/coxtechnologies.html	www.ismyfoodfresh.com	www.lifelinetechnology.com	www.ripesense.com	www.toxinalert.com

Table 2. Samples obtained.

Sample code	Sample description
0939-02-1728-OxS1	Oxygen scavenger, PET bottle ^
0939-02-1738-OxS2	Oxygen scavenger, PET bottle ^
0939-02-1731-OxS3 0939-03-0471-OxS3^{+}	Oxygen scavenger, label Label with an adhesive on one side and a perforated plastic film on other side. The active metal powder is immobilised in a 'tissue like structure' in-between. The label is 2.2 × 3.2 cm with a thickness of ~ 0.8 mm. The labels is intended for use with with a variety of products including dairy, meat, fish and dry foods. Samples were stored under vacuum and at room temperature prior to analysis.
0939-02-1735-OxS4 0939-03-0472-OxS4^{+}	Oxygen scavenger, sachet Plastic sachet. The plastic is peforated and coated from the inside with a plastic coating to prevent iron powder from falling out of the sachet. The sachet is 4.5 × 5 cm and contains ~ 3.8 g of iron powder. The sachets is intended for use with a variety of products including dairy, meat, fish and dry foods. Samples were stored under vacuum and at room temperature prior to analysis.
0939-02-1733-OxS5	Oxygen scavenger, label ^
0939-02-1734-OxS6	Oxygen scavenger, sachet ^
0939-02-1729-CC1	Crown cap reference Standard crown cap. Information on the beverages with which the crown cap may come into contact was not provided. Samples were stored at room temperature prior to analysis.
0939-02-1730-CC2	Crown cap with oxygen scavenger Standard crown cap. Information on the beverages with which the crown cap may come into contact was not provided. Samples were stored at room temperature prior to analysis.
0939-02-1736-AntiM1	Anti-mould SO_2 emitter ^

Table 2 continued. Samples obtained.

Sample code	Sample description
0939-02-1737-AntiM2	Anti-mould SO_2 emitter Paper bag. The bag is 5 x 8 cm and contains ~ 0.4 g $Na_2S_2O_5$. The samples are intended for use with grapes. Samples were stored at room temperature prior to analysis.
0939-03-0227-FlavR1	Flavour releaser, blown film Semi-opaque film with thickness of ~ 50 µm. The film is intended for use with a variety of foods including bread, beverage pouches, candy bars, etc. Samples were stored in a sealed bag at room temperature prior to analysis.
0939-03-0228-FlavR2	Flavour releaser, sports drink bottle closures green Green sports drink screw cap for PET bottles. The caps are intended for use with water, sports drinks and fruit juices. Samples were stored in a sealed bag at room temperature prior to analysis.
0939-03-0229-FlavR3	Flavour releaser, sports drink bottle closure orange Green sports drink screw cap for PET bottles. The caps are intended for use with water, sports drinks and fruit juices. Samples were stored in a sealed bag at room temperature prior to analysis.
0939-03-0269-AntiM3	Antimicrobial food storage liner White paper with a ribbed surface. The liner is 20 x 2.5.5 cm with a thickness of ~ 70 µm. The liner is intended for use with fish and meat. Samples were stored at room temperature prior to analysis.
S07-024123-AntiM4	Antimicrobial film Roll of transparent plastic film with green appearance The film was 30 cm wide with a thickness of ~ 25 µm The film is intended for use in the home and therefore may come into contact with any food type. Samples were stored at room temperature prior to analysis.

Table 2 continued. Samples obtained.

Sample code	Sample description
S07-024124-EthS1	Ethylene scavenger, bag Green plastic bag. The bag is 20.5 * 22.5 cm. The bag is intended for use with fruits and vegetables. Samples were stored at room temperature prior to analysis.
S07-024125-HeatR	Heat releaser, microwave susceptor PET/aluminium/paper laminate received as A4 sized sheets. Information on the foods with which the microwave susceptor may come into contact was not provided. Samples were stored at room temperature prior to analysis.
S07-024126-EthS2	Ethylene scavenger, bag Green plastic bag. The bag is 30.5 * 42 cm. The bag is intended for use with fruits and vegetables. Samples were stored at room temperature prior to analysis.
S07-024127-FreshI	Freshness indicator, label Paper/plastic laminate. The label is 3.8 ax 3.8 cm. The label is intended for use with deli meats, beef, chicken, pork and seafood. Samples were stored at room temperature prior to analysis.
S07-024128-EthS3	Ethylene scavenger, sachet Paper/plastic sachet. The sachet is 6 × 6 cm. The sachet is intended for use with fruits and vegetables. Samples were stored at room temperature prior to analysis.
S07-024129-MoistA	Moisture absorber, pad Fibre/plastic laminate pads. The pads are10 x 8 cm with a thickness of 1.5 mm. The pad is intended for use with meat and fish. Samples were stored at room temperature prior to analysis.
S07-024306-TimeI	Time indicator, label ^ #
S08-000157-AcetS	Acetaldehyde scavenger, PET bottle ^

Table 2 continued. Samples obtained.

Sample code	Sample description
S08-000164-HeatS	Heat sensor, weaning spoons Elastomeric spoons. The serving portion is oval shaped with maximum dimensions of 3.5 x 2.5 cm and a thickness of 2.5 mm. The spoons are intended for use in the home and therefore may come into contact with any food type. Samples were stored at room temperature prior to analysis.
S08-003221-AntiM5	Anti-mould, cheese bag Plastic bag inside a cloth outer and sealed with a drawstring. The bag id 20 x 33 cm. The polyethylene inner layer is 150 µm. The bags are intended for use with cheese. Samples were stored at room temperature prior to analysis.

^ samples not tested

^ # samples not tested but the efficacy was assessed

[+] a new batch of the same oxygen scavengers was provided by the manufacturer for the migration experiments since the first batch was exposed to air following the first screening studies.

Table 3. Amount of sample used for determination volatiles, semi-volatiles and non-volatiles compounds.

	Volatiles	**Semi-volatiles**	**Non-volatiles**
TNO code	**Mass (g)**	**Mass (g)**	**Mass (g)**
0939-02-1731-OxS3	0.5	0.5	0.5
0939-02-1735-OxS4	4.1	3.9	3.9
0939-02-1729-CC1	0.6	0.6	0.6
0939-02-1730-CC2	0.6	0.6	0.6
0939-02-1737-AntiM2	1.2	1.4	1.4
0939-03-0227-FlavR1	1.0	5.2	5.2
0939-03-0228-FlavR2	1.0	5.1	5.1
0939-03-0229-FlavR3	1.0	5.0	5.0
0939-03-0269-AntiM3	0.5	4.8	4.8

Table 4. Volatile substances detected by headspace GC-MS using a non-polar column

Retention time (minutes)	***Best library match***	***Estimated concentration (mg/kg)***
0939-02-1731-OxS3, Oxygen scavenger, label.**		
12.7	Toluene	11
0939-02-1735-OxS4, Oxygen scavenger, sachet		
	-	
0939-02-1729-CC1, Crown cap, reference material		
	-	
0939-02-1729-CC1, Crown cap, material with oxygen scavenger		
	-	
0939-02-1737-AntiM2 SO2 emitter		
	-	
0939-03-0227-FlavR1 Flavour releaser, blown film*		
16.5	Butylated hydroxytoluene	5
0939-03-0228-FlavR2Flavour releaser, closure green *		
5.7	2,4-Dimethyl-heptane	4
6.4	4-Methyl-octane	2
7.6	Bicyclo[3.1.0]hexane, 4-methyl-1-(1-methyl)-didehydroderiv.	2
7.8	alpha-Pinene	9
8.45	Cyclohexene, 4-methylene-1-(1-methylethyl)-	10
8.7	beta Pinene	33
9.1	alpha-Phellandrene	26
9.2	1,3-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	0.5
9.4	1-Methyl-2-(1-methylethyl)- benzene	7
9.5	1,5-Dimethyl-1,5-cyclooctradiene	87
9.6	1-Methyl-4-(1-methylethyl)-1,4-cyclohexadiene	79
9.9	3-Carene	19
10.4	1-Methyl-4-(1-methylethylidene)-cyclohexene	19
10.9	2,4,6-Octatrene, 2,6-dimethyl-,E,Z0-	2

Table 4 continued.

Retention time (minutes)	***Best library match***	***Estimated concentration (mg/kg)***
12.2	3-Cyclohexene-1-methyanol, .alpha.,.alpha.,4-trimethyl-, (S)-	5
13.1	2,6-Octadienal,3,7-dimethyl-	6
15.6	Bicyclo[3.1.1]hept-2-ene, 2,6-dimethyl-6-(4-methyl-3-pentenyl)-	1
15.7	Caropyllene	0.7
16.6	Cyclohexene, 1-methyl-4-(5-methyl-methylene-4-hexenyl)-,(S)-	0.9
16.7	Benzoic acid, 4-ethoxy-, ethylester	0.5
0939-03-0229-FlavR3 Flavour releaser, closure orange*		
5.2	Butanoic acid, ethyl ester	0.8
5.4	Butanoic acid, ethyl ester	35
5.8	Heptane, 2,4-dimethyl-	3
6.4	Octane, 4-methyl-	2
7.8	alpha.-Pinene	4
8.5	Bicycle[3.1.0]hexane,4-methylene-1(1-methylethyl)-	2
8.6	beta.-Myrcene	16
8.8	Octanal	2
9.1	3-Carene	0.5
9.3	1-Methyl-3-(1-methylethyl)-benzene	3
9.9	1-Methyl-4-(1-methylethyl)-1,4-cyclohexadiene,	4
10.5	1,6-Octadien-3-ol, 3,7-dimethyl-	4
12.1	Decanal	0.8
15.3	Benzoicacid, 2-(methylamino)-, methylester	2
0939-03-0269-AntiM3 Antimicrobial food storage liner*		
-	-	-

* Analysed using a DB-5 column.

** Analysed using an AT-5MS column

Table 5. Volatile substances detected by headspace GC-MS using a polar column

Retention time (minutes)	***Best library match***	***Estimated concentration (mg/kg)***
0939-02-1731-OxS3, Oxygen scavenger, label.**		
9.9	Methylester acetic acid	2
10.1	Dimethyoxymethane	2
14.4	Toluene	10
16.6	4-Methyl octane	3
0939-02-1735-OxS4, Oxygen scavenger, sachet**		
9.3	Acetone	0.4
0939-02-1729-CC1, Crown cap, reference material**		
	-	
0939-02-1730-CC2, Crown cap, with active substance**		
	-	
0939-02-1737-AntiM2 Anti-mould emitter **		
	-	
0939-03-0227-FlavR1 Flavour releaser, blown film **		
11.7	Butylated hydroxytoluene	4
0939-03-0228-FlavR2 Flavour releaser, closure green **		
4.5	beta–Pinene	34
5.2	beta–Myrcene	7
5.6	d-Limonene	88
6.1	1,4-Cyclohexadiene, 1-methyl-4-1-methylethyl)-	27
6.3	Benzene, 1-methyl-2-(1-methylethyl)-	13
6.4	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	2
8.8	1,6-Octadien-3-ol,3,7-dimethyl	0.6
9.1	3-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-	0.5
10.0	2,6-Octadienal,3,7-dimethyl,(Z)-	2
10.1	3-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-	6
10.3	2,6-Octadien-1-ol,3,7-dimethyl-,acetate,(Z)-	2

Table 5 continued.

Retention time (minutes)	***Best library match***	***Estimated concentration (mg/kg)***
10.4	2,6-Octadienal,3,7-dimethyl,	4
10.5	2,6-Octadien-1-ol,3,7-dimethyl-,acetate,€-	1
0939-03-0229-FlavR3 Flavour releaser, closure orange**		
4.7	Sabinen Bicyclo[3.1.0]ehexane,4-methylene-1-(1-methylethyl)-	1
5.2	beta.-Myrcene 1,6-octadiene, 7-methyl-3-methylene-	13
5.6	dl-Limonene cyclohexene, 1-methyl-4-(1-methylethyenyl)-	105
6.1	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	3
6.3	Benzene, 1-methyl-3-(1-methylethyl)-	7
8.5	Decanal	2
8.8	Linalool	2
12.9	Methyl N-methyl anthranilate	1
0939-03-0269-AntiM3 Antimicrobial food storage liner**		
-	-	

* Analysed on a C-porabond Q column.

** Analysed on a AT-1000 column.

Table 6. Semi-volatile substances detected by GC-MS. Extracts in 95% ethanol

Retention time (minutes)	*Substance*	*Estimated concentration (mg/kg)*
0939-02-1731-OxS3, Oxygen scavenger, label.		
-	-	
0939-02-1735-OxS4, Oxygen scavenger, sachet		
23.1	Octadecyl-3,5-di-(tert)-butyl-4-hydroxyhydrocinnamate	0.2
0939-02-1729-CC1, Crown cap, reference material		
-	-	
0939-02-1730-CC2, Crown cap, material with active substance		
-	-	
0939-02-1737-AntiM2 SO2 emitter		
-	-	
0939-03-0227-FlavR1 Flavour releaser, blown film		
5.6	1,2-Cyclopentanedione, 3-methyl-	3
9.9	Triacetin	28
10.9	Tetradecane	5
11.2	Vanillin	9
12.5	Butylated hydroxytoluene	630
13.1	Phenol, 2,5-bis(1,1-dimethylethyl)-4-ethyl-	6
13.5	Hexadecane	6
15.8	Octadecane	5
17.9	Eicosane	3
21.4	9-Octadecenamide. (Z)-	22
10.8	Unknown	7
13.4	Unknown	3
15.1	Unknown	7
15.6	Unknown	10.
19.7	Unknown	11
19.8	Unknown	3
20.8	Unknown	12

Table 6 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the 95% ethanol extracts (mg/kg)*
0939-03-0228-FlavR2Flavour releaser, closure green		
4.5	Bicyclo[3.1.1]hept-2-ene. 3,6,6-trimethyl	35
5.0	Bicyclo[3.1.1]hexane, 4-methylene-1-(1-methylethyl)-	100
5,7	Benzene, 1-methyl-3-(1-methylethyl)-	102
5.8	D-Limonene	2089
5.9	Cyclohexene 1-methyl-4-(1-methylethenyl)-	2448
6.2	alpha Phellandrene	448
6.6	Cyclohexene 1-methyl-4-(1-methylethylidene)-	26
8.0	Octanoic acid, ethyl ester	7
8.1	3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-	19
8.3	beta Pinene	160
8.9	2,6-Octadienal, 3,7-dimethyl- (Z)	78
9.2	2,6-Octadienal, 3,7-dimethyl- (E)	16
10.3	2,6-Octadien-1-ol, 3,7-dimethyl-, acetate, (Z)-	56
10.6	2,6-Octadien-1-ol, 3,7-dimethyl-, acetate, (Z)-	40
10.8	Decanoic acid, ethyl ester	8
10.9	Tetradecane	7
11.4	Bicyclo[3.1.1]hept-2-ene, 2,6-dimethyl-6-(4-methyl-3-pentenyl)-	5
11.7	Bicyclo[3.1.1]hept-2-ene, 2,6-dimethyl-6-(4-methyl-3-pentenyl)-	65
11.7	Caryophyllene	35
12.1	Tetratetracontane	18
12.4	alpha Farnesene	30
12.6	Cyclohexene, 1-methyl-4-(5-methyl-1-methylene-4-hexenyl- (S)-	115
12.7	Benzoic acid, 4-ethoxy-, ethyl ester	50
13.5	Octadecane	9
15.2	Docosane	14
15.8	Octadecane	10

Table 6 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the 95% ethanol extracts (mg/kg)*
17.1	Docosane	10
18.2	2H-1-Benzopyran-2-one, 5,7-dimethoxy-	24
19.2	Eicosane	6
19.8	Docosane	6
20.1	Glycerol tricaprylate	693
20.6	7H-Furo[3,2-g][1]benzopyran-7-one, 4,9-dimethoxy-	4
	48 unknown peaks with concentration between 1-700 mg/kg	Total 1880 mg/kg
0939-03-0229-FlavR3 Flavour releaser, closure orange		
4.5	alpha Pinene	17
5.0	Bicyclo[3.1.0]hexane, 4-methylene-1-(1-methylethyl)-	97
5.7	Benzene, 1-metyl-2-(1-methylethyl)-	61
5.8	1,5-Cyclooctadiene, 1,5-dimethyl	4513
5.9	Limonene	5776
6.67	1,6-Octadien-3-ol, 3,7-dimethyl-	32
7.4	6-Octenal, 3,7-dimethyl-,R-	7
7.9	Benzoic acid, ethyl ester	2
8.2	Decanal	21
9.2	Tritetracontane	24
10.9	Tetradecane	6
11.4	Benzoic acid, 2-(methylamino)-, methyl ester	156
12.6	NaphtHalene, 1,2,3,4,5,6,7,8,8a-octahydro-1,8a-dimethyl-7-(1-methylehtenyl)-	5
12.7	Benzoic acid, 4-ethoxy-, ethyl ester	40

Table 6 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the 95% ethanol extracts (mg/kg)*
13.5	Hexadecane	8
14.3	1,4-Benzenedicarboxylic acid, diethyl ester	3
15.8	Octadecane	10
19.8	Eicosane	5
22.7	Cyclopropanenonanoic acid, 2-[(2-butylcyclopropyl)methyl]-, methyl ester	11
	68 unknown peaks with concentration between 1-1900 mg/kg	Total 2500 mg/kg
0939-03-0269-AntiM3 Antimicrobial food storage liner		
-	-	

Table 7. Semi-volatile substances detected by GC-MS. Extracts in iso-octane

Retention time (minutes)	*Substance*	*Estimated concentration in the iso-octane extracts (mg/kg)*
0939-02-1731-OxS3, Oxygen scavenger, label.		
-	-	
0939-02-1735-OxS4, Oxygen scavenger, sachet		
0939-02-1729-CC1, Crown cap, reference material		
-	-	
0939-02-1730-CC2, Crown cap, material with active substance		
-	-	
0939-02-1737-AntiM2 SO2 emitter		
-	-	
0939-03-0227-FlavR1 Flavour releaser, blown film		
9.9	Triacetin	22
10.9	Tetradecane	5
12.5	Butylated hydroxytoluene	555
13.1	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl	6
13.5	Hexadecane	8
15.8	Octadecane	10
17.9	Pentacosane	8
19.8	Docosane	9
21.	Octadecanamide	67
23.1	Eicosane	14
	16 unknown peaks with concentration between 1-20 mg/kg	Total 105 mg/kg
0939-03-0228-FlavR2Flavour releaser, closure green		
5.3	Bicyclo[3.1.1]heptane, 6,6-dimethyl-2-methylene-, (1S)-	684
5.9	Limonene	3102

Table 7 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the iso-octane extracts (mg/kg)*
8.3	3-Cyclohexene-1-methanol, 44-trimethyl-,(S)-	111
9.2	2,6-Octadienal, 3,7-dimethyl-,(E)-	98
9.9	Dodecane, 2,6,11-trimethyl-	17
10.6	2,6-Octadien-1-ol, 3,7-dimethyl-, acetate, (E)-	19
10.9	Tetradecane	3
11.7	Bicyclo[3.1.1]hept-2-ene, 2,6-diemethyl-6-(4-methyl-3-pentenyl)-	39
11.7	Caryophyllene	26
12.1	Tetradecane	13
12.6	Cyclohexene, 1-methyl-4-(5-methyl-1-methylene-4-hexenyl)-,(S)-	52
12.7	Benzoic acid, 4-ethoxy-, ethyl ester	24
13.5	Hexadecane	3.4
14.7	Docosane	10
15.3	Eicosane	2
15.8	Heneicosane	3
	27 unknown peaks with concentration between 1-820 mg/kg	Total 1420 mg/kg
0939-03-0229-FlavR3 Flavour releaser, closure orange		
5.2	beta Myrcene	142
5.9	D-limonene	8042
9.9	Docosane	15
10.1	Heptadecane, 2,6,10,15-tetramethyl	5
10.9	Eicosane	3
11.0	Copaene	2
11.4	Benzoic acid, 2-(methylamino), methyl ester	73
12.1	Tetradecane	16
12.7	Bozoic acid, 4-ethoxy-, ethyl ester	24
13.5	Hexadecane	3
14.7	Hexadecane	12

Table 7 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the iso-octane extracts (mg/kg)*
15.8	Eicosane	4
17.1	Heneicosane	8
17.5	Nonadecane	7
19.2	Heneicosane	5
	26 unknown peaks with concentration between 1-305 mg/kg	Total 695 mg/kg
0939-03-0269-AntiM3 Antimicrobial food storage liner		
-	-	

Table 8. Polar and non-volatile substances detected in the LC-MS analysis of the solvent extracts. Migrated compounds (m/z values) measured under various extraction conditions with positive ESI.

Retention time (minutes)	***Positive ESI m/z***	***Proposed identity***
0939-02-1731-OxS3, Oxygen scavenger, label.		
	95% ethanol	
0.5	708.3	
0.6	350.8	Oligomer of polymer with 82 monomer mass
0.6	426.8	
0.6/7.1/5.2	492.1	Thermal oxidation product of Irganox 1076 + NH_4^+
0.6	187.0	Oligomer of polymer with 82 monomer mass
0.6	145.8	
0.7	269.0	Oligomer of polymer with 82 monomer mass
0.7	240.7	
0.7	221.7	
5.8/7.8	259.8	
7.9	680.1	Oxidised irgafos 168+NH_4^+
	Iso-octane	
5.9/7.8	708.1	Oxidised irgafos 168+NH_4^++ 2×14
5.9/7.8	694.1	Oxidised irgafos 168+NH_4^++ 14
5.9/7.9	371.4	Oxidised erucamide +H^+
6.0/7.8	663.4	Oxidised irgafos 168+H+
7.3/8.7	492.2	Thermal oxidation product of Irganox 1076 + NH_4^+
7.5	548.2	Irganox 1076+NH_4^+
7.5	1077.5	
7.8	680.1	Oxidised irgafos 168+NH_4^+
7.8	1209.5	
0939-02-1735-OxS4, Oxygen scavenger, sachet		
	95% ethanol	
0.6/5.1	182.1	
0.8	196.1	
0.9/9.5	221.6	Reaction/breakdown product Irganox 1010 + H^+

Table 8 continued.

Retention time (minutes)	***Positive ESI m/z***	***Proposed identity***
0.9	240.5	Thermal oxidation product of Irganox 1076 + NH_4^+
0.9	259.7	
1.6	284.1	
6.8	934.4	
7.4	1194.6	Irganox 1010+NH_4^+?
7.8	680.1	Oxidised irgafos 168+NH_{4+}
7.8	708.3	
	Iso-octane	
6.1	402.0	
6.4	530.1	
6.6	458.1	
6.8	934.4	
6.8	586.1	
7.3	624.7	
7.4	570.2	
7.4	1194.6	Irganox 1010+NH_4^+?
7.7	757.9	
7.8	680.0	Oxidised irgafos 168+NH_4^+
0939-02-1729-CC1, Crown cap, reference material		
	-	
0939-02-1730-CC2, Crown cap, material with active substance		
	95% ethanol	
6.9	647.6	Irgafos 168 +H^+
7.2/7.5	474.6	
7.3/7.8	1135.8	
	Iso-octane	
	-	

Table 8 continued.

Retention time (minutes)	***Positive ESI m/z***	***Proposed identity***
0939-02-1737-AntiM2 SO_2 emitter		
	95% ethanol	
0.6	269.0	H_2SO_3 cluster with m/z spacing 82. Many related ions present.
0.6	145.8	
0.6	205.6	
0.6/7.9	680.1	Oxidised irgafos 168+NH_4^+
0.6	722.7	H_2SO_3 cluster with m/z spacing 82. Many related ions present.
0.6	164.9	
0.6	664.8	H_2SO_3 cluster with m/z spacing 82. Many related ions present.
4.1/5.0/5.5	311.9	
6.8	934.5	
7.4	1194.6	Irganox 1010+NH_4^+
	Iso-octane	
5.0	311.9	
5.9	419.7	Thermal oxidation product of Irganox 1076 + NH_4^+
6.7	385.7	
7.6	548.3	Irganox 1076+NH_4^+
7.4	1194.6	Irganox 1010+NH_4^+
0939-03-0227-FlavR1 Flavour releaser, blown film		
	95% ethanol	
7.0	284.3	
7.2	962.9	
7.3	488.2	Reaction/breakdown product Irgafos P-EPQ+NH_4^+
7.5	1019.0	
7.5	516.2	
7.6	1012.6	
8.0	544.2	
Broad peak	236.0	

Table 8 continued.

Retention time (minutes)	***Positive ESI m/z***	***Proposed identity***
1.2	144.1	
7.1	284.3	
	Iso-octane	
7.5	516.2	
7.5	488.2	Reaction/breakdown product Irgafos P-EPQ+NH_4^+
7.5	1012.5	
8.0	544.2	
0.9	144.1	
2.6	236.0	
7.0	284.3	
7.1	934.4	
7.2	962.9	
7.2	493.4	
7.5	338.3	Erucamide +H^+ or Tinuvin 622 + Na^+
7.5	675.3	
7.5	1018.9	
0939-03-0228-FlavR2 Flavour releaser, closure green		
	95% ethanol	
6.1/8.0	544.2	
7.2	956.7	
7.2	488.2	Reaction/breakdown product Irgafos P-EPQ+NH_4^+
7.5	680.1	Oxidised irgafos 168+NH_4^+
7.5	516.2	
7.5	1013.7	
8.0	1070.0	
7.5	1177.4	Irganox 1010 + H^+
8.0	1068.5	Reaction/breakdown product Irgafos P-EPQ+NH_4^+

Table 8 continued.

Retention time (minutes)	***Positive ESI m/z***	***Proposed identity***
	Iso-octane	
4.8	247.1	
6.7	1194.6	Irganox 1010 + NH_4^+
7.2	488.2	Reaction/breakdown product Irgafos P-EPQ+NH_4^+
7.2	957.6	
7.5	1177.3	Irganox 1010 + H^+
7.5	516.2	
7.5	1013.1	
0939-03-0229-FlavR3 Flavour releaser, closure orange		
	95% ethanol	
5.1	166.1	
5.2	403.2	
5.4	373.3	
6.0	460.2	
6.0/8.0	544.1	
7.0	558.2	
7.3	572.3	
7.5	338.4	Erucamide +H^+
	Iso-octane	
	343.0	NH_4 adduct 329.2 or acetate adduct 283.5
	315.1	Uvitex OB +NH_4^+
6.5	255.4	
6.9	283.5	Reaction/breakdown product Irgafos P-EPQ +H^+ or glycerol monooleate +H^+
6.9	329.2	
0939-03-0269-AntiM3 Antimicrobial food storage liner		
	95% ethanol	
0.6	212.1	Breakdown/reaction product of Erucamide +H^+
0.8	217.1	Breakdown/reaction product of irganox 1010 +NH_4^+

Table 8 continued.

Retention time (minutes)	***Positive ESI m/z***	***Proposed identity***
4.8	442.2	
4.9	854.4	
4.9	436.1	Breakdown/reaction product of irganox 1076 $+NH_4^+$
4.9	500.3	
5.1/6.1	496.3	
5.1	558.3	
5.2	332.1	
5.3	376.1	PEG oligomer
5.3	332.1	PEG oligomer
5.3	616.3	
5.4	420.2	PEG oligomer
5.4/5.6	464.1	PEG oligomer
5.6/6.3	732.4	
5.7	790.4	
5.8	848.4	
6.2	402.2	
6.2	402.4	
6.3	644.4	
6.4	864.4	Breakdown/reaction product of Irgafos P-EPQ $+NH_4^+$
7.7	613.4	
6.7	537.5	
7.1	582.3	
7.2	766.3	
7.5	927.5	
7.8	662.6	
	909.8	Dimer 516-H2O
	516.2	
	909.8	

Table 8 continued.

Retention time (minutes)	***Positive ESI m/z***	***Proposed identity***
	508.3	PEG oligomer
	552.4	PEG oligomer
	Iso-octane	
0.5	152.0	
4.7/5.4	442.2	
5.1	558.3	
5.3	616.3	
5.4	191.1	
5.4	674.4	
5.5	596.3	
5.6	732.4	
5.7	790.4	
5.8	848.4	
6.0	906.4	
6.4/6.9	688.5	
7.0	782.6	
7.5	620.3	
7.5	680.1	
7.6	926.4	
7.9	984.8	

* direct infusion was performed. Two experiments were performed, one where the 95% ethanol was directly infused and the other where the 95% ethanol was evaporated followed by reconstitution in acetonitrile. Results from both experiments are presented in this table.

Table 9. Polar and non-volatile substances detected in the LC-MS analysis of the solvent extracts. Migrated compounds (m/z values) measured under various extraction conditions with negative ESI.

Retention time (minutes)	***Negative ESI m/z***	***Proposed identity***
0939-02-1731-OxS3, Oxygen scavenger, label.		
	95% ethanol	
0.6	141.1	Breakdown/reaction product of Erucamide $-H^+$
0.6/6.0	633.2	
0.7	217.1	Glycerol monooleate – acetate
0.8	203.1	
0.8	375.0	
5.7	383.8	
6.1	625.5	
6.3	529.1	Irganox 1076 – H+
6.6	389.6	
	Iso-octane	
6.9/7.8	527.7	
7.5	529.6	Iraganox 1076 – H+
0939-02-1735-OxS4, Oxygen scavenger, sachet		
	95% ethanol	
5.7	383.3	
6.0	633.2	
6.2	714.7	
6.2	635.2	
6.8	687.1	
6.8	343.1	
6.8	974.5	
7.4	1234.4	
7.4	1175.8	Irganox 1010 – H+
7.5	529.6	Irganox 1076 – H+
	Iso-octane	
6.8	974.6	

Table 9 continued.

Retention time (minutes)	***Negative ESI m/z***	***Proposed identity***
7.4	1175.8	Irganox 1010 – H+
7.4	1234.3	
0939-02-1729-CC1, Crown cap, reference material		
	95% ethanol/iso-octane	
	-	
0939-02-1730-CC2, Crown cap, material with active substance		
	95% ethanol	
6.1	625.5	
	Iso-octane	
	-	
0939-02-1737-AntiM2 SO_2 emitter		
	95% ethanol	
0.5/6.8	974.6	
0.5/6.4	587.2	Irgafos 168 $-H^+$
0.5/5.9	641.3	
0.6/6.8	687.2	
0.6	223.0	H_2SO_3 cluster with m/z spacing 82. Many related ions present.
5.7	383.4	
6.1/7.6	456.9	Breakdown/reaction product of Irgafos 168-H^+
6.8	343.2	
7.4	1175.7	Irganox 1010 $-H^+$
7.5	529.6	Irganox 1076 – H+
	Iso-octane	
6.9/7.8	527.6	
7.4	1175.8	Irganox 1010 $-H^+$
0939-03-0227-FlavR1 Flavour releaser, blown film		
	95% ethanol	
1.9	151.1	

Table 9 continued.

Retention time (minutes)	***Negative ESI m/z***	***Proposed identity***
4.3/6.2/7.	227.1	Breakdown/reaction product of glycerol monooleate-H^+
6.1	219.2	Breakdown/reaction product of Irganox 1010 -H^+ or - acetate
8.3	195.0	
	Iso-octane	
6.1	219.3	Breakdown/reaction product of Irganox 1010 -H^+ or - acetate
6.2	286.9	
6.9	687.1	
7.0	974.5	
7.6	1191.7	
0939-03-0228-FlavR2 Flavour releaser, closure green		
	95% ethanol	
5.8	327.4	Irgaclear DM - acetate
5.8	1019.7	
5.9/7.3	201.1	
5.9	337.4	
6.6	587.2	Irgafos 168 -H^+
6.9	283.5	Breakdown/reaction product of glycerol monooleate-H^+
7.2/7.5	691.3	
7.5	529.5	Irganox 1010 – H+
	Iso-octane	
4.3	782.9	
5.7	327.4	Irgaclear DM - acetate
7.1	564.4	
0939-03-0229-FlavR3 Flavour releaser, closure orange		
	95% ethanol	
5.8	469.0	
6.9	283.4	

Table 9 continued.

Retention time (minutes)	***Negative ESI m/z***	***Proposed identity***
6.9	329.1	
6.6	255.5	
6.2	287.1	
5.8	327.5	
6.6	287.2	
6.4	611.2	
6.9	615.2	
6.9	687.1	
6.6	918.4	
6.9	929.3	
6.9	1001.3	
	Iso-octane	
5.8	327.4	
6.6	315.1	
6.6	255.4	
6.9	283.5	
7.1	827.5	
7.1	564.4	
8.5	209.0	
9.8	217.0	
7.1	895.8	
5.5	700.2	
5.6	233.4	
0939-03-0269-AntiM3 Antimicrobial food contact liner		
	95% ethanol	
5.6	505.0	
5.6	777.1	
5.9	299.4	Glycerol monooleate - acetate
6.6	301.4	

Table 9 continued.

Retention time (minutes)	***Negative ESI m/z***	***Proposed identity***
6.6	281.4	Breakdown/reaction product of Irgafos P-EPQ -H^+ or Glycerol monooleate -H^+
	Iso-octane	
5.7	445.0	
5.7	1061.6	
5.9	632.2	
5.9	962.1	
5.9/6.2	964.5	
5.9	299.4	
6.2	633.2	
6.2	301.4	
6.4	279.4	

Table 10. Results elemental screening in mg/kg (ppm). Elements that were screened for and were measured below the detection limit were; As, Ba, Be, Bi, Cd, Ce, Cr, Cu, Dy, Er, Eu, Gd, Ge, Hf, Ho, In, Ir, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, U, V, W, Y and Yb. For 0939-03-0269-AntiM3 low levels of Li, Be, Sc, Ti, V, Cr, Cu, Ga, Rb, Sr, Y, Nb, Mo, Pd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Tl, Pb, Bi, Th, U and Ti were observed but not considered relevant. Samples 0939-02-1729-CC1/1730-CC2 were screened at TNO. The other samples were screened at Fera. NA is not analysed.

		Anti-bacterial food storage liner	Crown cap without oxygen scavenger	Crown cap with oxygen scavenger
		0939-03-0269-AntiM3	0939-02-1729-CC1	0939-02-1730-CC2
Ca	[mg/kg]	380	NA	NA
Co	[mg/kg]	0.17	NA	NA
Fe	[mg/kg]	120	NA	NA
K	[mg/kg]	40	NA	NA
Mg	[mg/kg]	116	NA	NA
Na	[mg/kg]	222	NA	NA
P	[mg/kg]	< 50	NA	NA
S	[mg/kg]	NA	180	15000
Sb	[mg/kg]	NA	NA	NA
Zn	[mg/kg]	108	NA	NA
Al	[mg/kg]	4840	<	<
Ti	[mg/kg]	485	NA	NA
Zr	[mg/kg]	1	NA	NA

Table 11. Masses of samples prepared for analysis by headspace GC-MS

Sample code	**Mass (g)**
S07-024123-AntiM4	0.4
S07-024124-EthS1	0.4
S07-024125-HeatR	1.0
S07-024126-EthS2	0.4
S07-024127-FreshI	0.2
S07-024128-EthS3 *	4.0
S07-024129-MoistA	0.2
S08-000164-HeatS	1.2
S08-003221-AntiM5	0.3

* Only the active component (the absorbent held within the sachet) was analysed

Table 12. Masses of samples prepared for analysis by GC-MS

	Extraction solvent	
	Isooctane	**Ethanol**
Sample code	**Mass (g)**	**Mass(g)**
S07-024123-AntiM4	1.0	0.9
S07-024124-EthS1	0.4	0.5
S07-024125-HeatR	1.0	1.0
S07-024126-EthS2	0.5	0.5
S07-024127-FreshI	0.2	0.2
S07-024128-EthS3 *	8.0	8.0
S07-024129-MoistA	0.2	0.2
S08-000164-HeatS	0.3	0.3
S08-003221-AntiM5	0.4	0.4

* Only the active component (the absorbent held within the sachet) was analysed

Table 13. Masses of samples prepared for analysis by LC-TOF-MS

	Extraction solvent	
	Isooctane	**Ethanol**
Sample code	**Mass (g)**	**Mass (g)**
S07-024123-AntiM4	1.0	1.0
S07-024124-EthS1	0.4	0.4
S07-024125-HeatR	1.0	1.0
S07-024126-EthS2	0.5	0.5
S07-024127-FreshI	0.2	0.2
S07-024128-EthS3 *	8.0	8.0
S07-024129-MoistA	0.3	0.3
S08-000164-HeatS	0.3	0.3
S08-003221-AntiM5	0.4	0.4

* Only the active component (the absorbent held within the sachet) was analysed

Table 14. Volatile substances detected by headspace GC-MS

Retention time (minutes)	***Best library match***	***Estimated concentration (mg/kg)***
S07-024123-AntiM4 – Antimicrobial film No peaks observed in the chromatogram above the cut-off concentration that were not in the blank samples		
S07-024124-EthS1 – Ethylene scavenging bags No peaks observed in the chromatogram above the cut-off concentration that were not in the blank samples		
S07-024125-HeatR – Microwave susceptor		
8.7	Acetic acid	3
10.5	1-Butanol	1
13.7	Hexanal	0.7
S07-024126-EthS2 – Ethylene scavenging bags No peaks observed in the chromatogram above the cut-off concentration that were not in the blank samples		
S07-024127-FreshI –Freshness indicator		
12.5	4-Methyl-2-pentanol	19
17.9	2-Ethyl-1-hexanol	12
S07-024128-EthS3 – Ethylene scavenging sachets - adsorbent only No peaks observed in the chromatogram above the cut-off concentration that were not in the blank samples		
S07-024129-MoistA – Absorbent pads		
8.0	Methyl acetate	2
S08-000164-HeatS – Heat sensing weaning spoons No peaks observed in the chromatogram above the cut-off concentration that were not in the blank samples		
S08-003221-AntiM5 – Cheese storage bag No peaks observed in the chromatogram above the cut-off concentration that were not in the blank samples		

Table 15. Semi-volatile substances in the solvent extracts detected by GC-MS

Retention time (minutes)	*Substance*	*Estimated concentration in the material as measured in the isooctane extracts (mg/kg)*	*Estimated concentration in the material as measured in the ethanol extracts (mg/kg)*
S07-024123-AntiM4: antimicrobial film			
7.8	2-Ethyl-1-hexanol	38	80
12.5	2-(1,1-Dimethylethyl) cyclohexanol	#	20
16.5	Ethyl dodecanoate	#	21
16.6-19.0	Isomeric mix - nonylphenols	7100	7900
19.2	No good library match	18	36
19.4	Diisobutyl phthalate	350	670
19.5	No good library match	#	20
19.7	No good library match	#	440
19.8	No good library match	#	13
20.4	Dibutyl phthalate	#	37
20.5	Ethyl-9-hexadecenoate	#	28
20.7	Ethyl hexadecanoate	#	380
21.2	No good library match	#	17
21.4	Hexanoic acid, 2-ethyl-, dodecyl ester	318	710
21.5	Hexanedioic acid, bis(2-methylpropyl) ester	37	80
22.1	Bis(2-ethylhexyl) maleate	#	18
22.3	Ethyl linoleate	#	73
22.3	Ethyl oleate	#	864
22.4	Ethyl oleate (isomer)	#	58
22.6	Ethyl octadecanoate	#	102
22.7	3,4-Dihydroxy benzeneacetic acid	190	360
23.0	Di(oct-4-yl) adipate	38	190
23.2	No good library match	8	35
23.2	No good library match	15	28

Table 15 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the material as measured in the isooctane extracts (mg/kg)*	*Estimated concentration in the material as measured in the ethanol extracts (mg/kg)*
23.3	No good library match	27	44
23.4	No good library match	26	50
23.5	4-Methyl-2-tert-octylphenol	27	51
23.6	No good library match	48	84
23.7	No good library match	#	36
23.7	No good library match	#	20
23.8	Diisooctyl adipate	300	480
24.0	No good library match	#	400
24.4	Di-(2-ethylhexyl) adipate	37000	70000
24.8	No good library match	15	29000
24.9	No good library match	74	141
25.2	No good library match	34	310
25.4	Di-(2-ethylhexyl) phthalate	950	1900
25.7	Dodecyl dodecanoate	990	2000
27.1	No good library match (mixture of isomers)	160000	410000
29.6	Unspecified fatty acid ester	13	31
29.8	No good library match	#	27
31.2	No good library match	20	39
31.3	Tri(2-ethylhexyl) trimellitate	37	56
31.8	No good library match	33	74
32.5	No good library match	14	#
35.6	Didodecyl phosphate	17	#
36.1	No good library match	49	#
39.2	No good library match	91	#
Alkanes - *sum per sample*		330	710
S07-024124-EthS1: ethylene scavenging bags			
15.4	2,4-Bis(1,1-dimethylethyl) phenol	73	55

Table 15 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the material as measured in the isooctane extracts (mg/kg)*	*Estimated concentration in the material as measured in the ethanol extracts (mg/kg)*
16.3	No good library match	42	43
20.7	Ethyl hexadecanoate	#	92
22.6	Ethyl octadecanoate	#	14
27.2	13-Docosenamide	14	150
27.3	Unspecified alkene	13	#
27.4	No good library match	8.2	130
31.1	Siloxane	190	190
32.3	No good library match	63	66
32.6	No good library match	250	270
Alkanes - *sum per sample*		470	710
S07-024125-HeatR: microwave susceptors			
20.8	Ethyl hexadecanoate	#	5
21.9	No good library match	#	6
22.4	No good library match	#	2
22.6	Ethyl octadecanoate	#	3
26.4	No good library match	0.7	#
27.4	No good library match	#	2
31.8	No good library match	5	6
33.3	No good library match	140	140
Alkanes - *sum per sample*		3	#
S07-024126-EthS2: ethylene scavenging bags			
12.2	No good library match	5	#
17.8	2-Ethylhexyl benzoate	5	#
18.7	Unspecified alkene	5.8	6
20.7	Ethyl hexadecanoate	#	270
21.4	No good library match	13	12
22.6	Ethyl octadecanoate	#	267
23.3	Docosene	5	7

Table 15 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the material as measured in the isooctane extracts (mg/kg)*	*Estimated concentration in the material as measured in the ethanol extracts (mg/kg)*
24.9	No good library match	110	240
25.1	No good library match	140	180
25.2	2-Hydroxy-1-(hydroxymethyl)ethyl hexadecanoate	670	1500
26.4	No good library match	95	160
26.6	No good library match	78	130
26.8	2-Hydroxy-1-(hydroxymethyl)ethyl octadecanoate	250	380
27.0	No good library match	5	7
27.4	Squalene	11	10
28.0	Unspecified alkene	12	#
32.3	No good library match	280	370
36.4	No good library match	120	#
Alkanes - *sum per sample*		4100	3600

S07-024127-FreshI: freshness indicator

The chromatogram obtained showed three broad peaks. Due to the co-elution of the peaks it was not possible to get good library matches for the substances present in the extracts. A typical chromatogram is shown below.

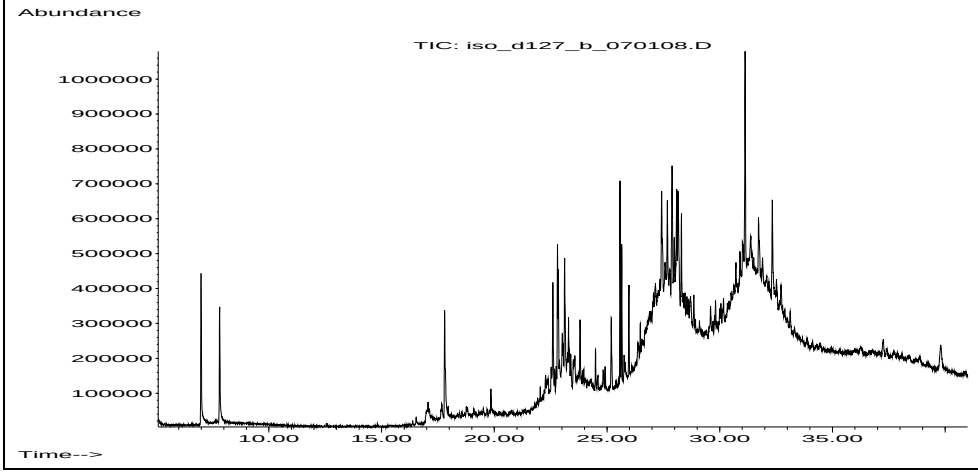


Table 15 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the material as measured in the isooctane extracts (mg/kg)*	*Estimated concentration in the material as measured in the ethanol extracts (mg/kg)*
S07-024128-EthS3: ethylene scavenging sachets – adsorbent only No peaks observed in the chromatogram above the cut-off concentration that were not in the blank samples			
S07-024129-MoistA: moisture absorbent pads			
6.6	Tetraethyl silicate	#	9
17.7	Unspecified alkene	#	3
17.8	2-Ethylhexyl benzoate	9	18
19.4	Diisobutyl phthalate	#	50
20.3	Dibutyl phthalate	#	2
21.4	Siloxane	12	18
22.0	Bis(2-ethylhexyl) maleate	#	81
22.1	Unspecified alkene	#	3
22.8	Bis(2-ethylhexyl) fumarate	#	1300
25.3	Bis(2-ethylhexyl) phthalate	#	3
26.4	No good library match	6	16
27.4	Squalene	3	9
31.1	Siloxane	#	4
32.3	No good library match	19	33
32.5	No good library match	#	36
Alkanes - *sum per sample (expressed as average value obtained from three sample replicates)*		240	290

Table 15 continued.

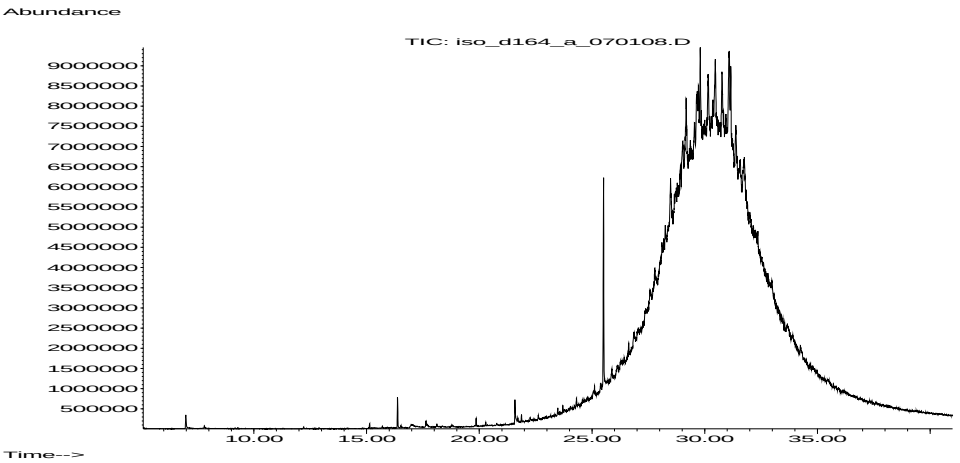
Retention time (minutes)	*Substance*	*Estimated concentration in the material as measured in the isooctane extracts (mg/kg)*	*Estimated concentration in the material as measured in the ethanol extracts (mg/kg)*
S08-000164-HeatS: heat sensitive weaning spoons			
The chromatogram obtained showed a broad peak with ions typical of an alkene or an alcohol (this peak was not integrated). It is possible that other substances were present but were masked by this large broad peak. 			
16.37	Propanoic acid, 2-methyl-, 1-(1-dimethylethyl)-2-methyl-1,3-propanediyl ester	340	*
17.05	Benzophenone	54	*
21.58	Heptadecanal	360	*
25.51	Bumetrizole	2200	*
29.17	28-Nor-17.B(H)-hopane	1500	*
31.15	No good library match	640	*
Alkanes - *sum per sample (expressed as average value obtained from three sample replicates)*		18000	*
S08-003221-AntiM5: cheese preserving bag			
11.00	No good library match	13	#
13.20	Triethylphenylsiloxane	#	15
20.69	Ethyl hexadecanoate	15	230
21.36	Eicosene	#	14
22.27	Ethyl-9-octadecenoate	5	100
22.49	Ethyl octadecanoate	12	260

Table 15 continued.

Retention time (minutes)	*Substance*	*Estimated concentration in the material as measured in the isooctane extracts (mg/kg)*	*Estimated concentration in the material as measured in the ethanol extracts (mg/kg)*
23.20	Docosene	6	35
23.36	Unspecified alkene	23	47
24.16	1,1'-(1,3-propanediyl)biscyclohexane	6	#
24.81	No good library match	7	150
24.98	No good library match	37	150
25.28	Di-(2-ethylhexyl) phthalate	4.6	#
26.36	No good library match	12	190
26.50	Unspecified alkene	40	70
27.21	13-Docosenamide	220	350
27.90	Unspecified alkene	51	63
29.23	Unspecified alkene	43	47
32.18	No good library match	140	210
32.40	No good library match	100	140
Alkanes - *sum per sample (expressed as average value obtained from three sample replicates)*		270	910

* no data – the internal standard response was not satisfactory. The substances detected in the isooctane extract were also present in the ethanolic extracts

not detected or present at concentration less than the cut-off concentration

Table 16. Polar and non-volatile substances detected in the LC-TOF-MS analysis of the solvent extracts

Peak	Retention time (minutes) in ethanol extract	Retention time (minutes) in isooctane extract	Molecular Formula	Proposed Identity
S07-024123-AntiM4 - ESI +				
1	47.6	46.9	C16H22O4	Diisobutyl phthalate
2	57.9	nd	C20H36O4	2-Ethylhexyl maleate
3	58.2	nd	C16H30O4	Hexadecanedioic acid
4	nd	58.7	Not identified	
5	59.0	nd	C21H38O4	1-Linoleoyl-rac-glycerol
6	62.3	61.0	C21H40O4	Glycerol monooleate
7	62.4	61.4	C18H34O4	Dibutyl sebacate
8	63.6	nd	Not identified	
9	66.6	66.7	C22H42O4	Di-(2-ethylhexyl) adipate
10	71.9	72.0	C26H48O4	2-Ethylhexyl ester of epoxidized soybean oil
S07-024123-AntiM4 - ESI -				
1	59.0	nd	Not identified	
2	61.5	nd	C20H40O6	Dodecanoic acid (tetraethoxy) ester
3	61.7 and 62.3	nd	C22H42O6	Glycerol monooleate
4	63.6	nd	Not identified	
S07-024124-EthS1 ESI +				
1	60.9	nd	C16H33NO	Hexadecanamide
2	62.5	nd	C18H35NO	Octadecanamide
S07-024124-EthS1 ESI -				
No peaks/masses different than those in blanks were found				
S07-024125-HeatR ESI +				
No peaks/masses different than those in blanks were found				
S07-024125-HeatR ESI -				
No peaks/masses different than those in blanks were found				

Table 16 continued.

Peak	Retention time (minutes) in ethanol extract	Retention time (minutes) in isooctane extract	Molecular Formula	Proposed Identity
S07-024126-EthS2 ESI+				
60.6	60.7 and 61.5	60.6	C19H38O4	2,3-Dihydroxypropyl hexadecanoate
60.9	nd	60.9	Not identified	
60-66	60.0-66.0	nd	C22H47NO2	PEG-2 stearamine
S07-024126-EthS2 ESI-				
1	60.7 and 61.4	61.3	C20H40O6	Dodecanoic acid (tetraethoxy) ester
2	64.6 and 65.2	65.3	C22H44O6	Diglycerol monopalmitate
S07-024127-FreshI ESI+				
1	33.0	32.8	Not identified	
S07-024127-FreshI ESI -				
No peaks/masses different than those in blanks were found				
S07-024128-EthS3 ESI +				
No peaks/masses different than those in blanks were found				
S07-024128-EthS3 ESI -				
No peaks/masses different than those in blanks were found				
S07-024129-MoistA ESI +				
No peaks/masses different than those in blanks were found				
S07-024129-MoistA ESI -				
1	1.6	nd	Not identified	
S08-000164-HeatS ESI+				
1	56.8	nd	C16H33NO4	N-Tris(hydroxyl)methyl lauramide
2	64.5	nd	Not identified	
S08-000164-HeatS ESI-				
No peaks/masses different than those in blanks were found				

Table 16 continued.

Peak	Retention time (minutes) in ethanol extract	Retention time (minutes) in isooctane extract	Molecular Formula	Proposed Identity
S08-003221-AntiM5 ESI+				
No peaks/masses different than those in blanks were found				
S08-003221-AntiM5 ESI-				
1	65.2	nd	C22H4406	Diglycerol monopalmitate

nd = not detected

Table 17. Trace element concentrations (µg/kg) in the samples detected by ICP-MS

	LoD	S07-024123-AntiM4	S07-024124-EthS1	S07-024125-HeatR	S07-024126-EthS2	S07-024127-FreshI
Li	200	<LoD	<LoD	<LoD	<LoD	2900
Be	200	<LoD	200	<LoD	<LoD	<LoD
B	5000	<LoD	<LoD	<LoD	<LoD	<LoD
Na	5000	91000	103000	221000	252000	176000
Mg	2000	2000	52000	296000	9000	23000
Al	10000	50000	510000	750000	40000	150000
P	20000	200000	<LoD	100000	<LoD	<LoD
K	50000	<LoD	170000	<LoD	<LoD	<LoD
Ca	10000	260000	1310000	40300000	20000	80000
Sc	500	<LoD	<LoD	<LoD	<LoD	<LoD
Ti	10000	20000	50000	50000	10000	<LoD
V	100	1300	200	200	1200	1100
Cr	1000	<LoD	<LoD	<LoD	<LoD	<LoD
Mn	5000	<LoD	<LoD	48000	<LoD	<LoD
Fe	50000	<LoD	110000	100000	<LoD	190000
Co	20	<LoD	30	900	<LoD	1030
Ni	2000	<LoD	<LoD	<LoD	<LoD	<LoD
Cu	200	2000	6400	1500	7700	12700
Zn	1000	302000	106000	3000	85000	2000
Ga	20	40	140	130	<LoD	30
Ge	50	<LoD	<LoD	280	<LoD	<LoD
As	100	800	<LoD	100	<LoD	<LoD
Se	500	<LoD	<LoD	<LoD	<LoD	<LoD
Rb	20	40	590	120	<LoD	<LoD
Sr	200	200	1300	86000	200	<LoD
Y	10	<LoD	360	810	15	<LoD
Zr	50	50	1070	210	300	<LoD
Nb	5	37	100	20	8	<LoD
Mo	20	<LoD	140	<LoD	280	<LoD
Ru	20	<LoD	<LoD	<LoD	<LoD	<LoD

Table 17 continued.

	LoD	S07-024123-AntiM4	S07-024124-EthS1	S07-024125-HeatR	S07-024126-EthS2	S07-024127-FreshI
Rh	1000	<LoD	<LoD	<LoD	<LoD	<LoD
Pd	10	60	50	<LoD	<LoD	960
Ag	500	6600	<LoD	<LoD	<LoD	<LoD
Cd	5	<LoD	8	22	36	<LoD
Sn	100	4200	<LoD	<LoD	<LoD	400
Sb	10	30	<LoD	5710	10	21200
Te	100	<LoD	<LoD	<LoD	<LoD	<LoD
Cs	5	6	41	17	<LoD	<LoD
Ba	200	1800	9300	2100	500	1400
La	10	10	160	820	20	<LoD
Ce	50	<LoD	400	920	<LoD	<LoD
Pr	5	<LoD	50	161	<LoD	<LoD
Nd	10	<LoD	170	610	10	<LoD
Sm	5	5	35	92	<LoD	<LoD
Eu	2	2	8	26	<LoD	<LoD
Gd	5	<LoD	51	131	<LoD	<LoD
Tb	2	<LoD	9	17	<LoD	<LoD
Dy	5	<LoD	55	103	<LoD	<LoD
Ho	2	3	13	23	<LoD	<LoD
Er	5	<LoD	36	59	<LoD	<LoD
Tm	2	<LoD	6	7	<LoD	<LoD
Yb	1	2	36	41	1	<LoD
Lu	2	<LoD	8	9	<LoD	<LoD
Hf	5	9	38	6	7	<LoD
Ta	5	7	6	<LoD	<LoD	<LoD
W	10	20	30	10	10	<LoD
Re	1	3	1	<LoD	<LoD	<LoD
Os	2	<LoD	<LoD	<LoD	<LoD	<LoD
Ir	10	40	<LoD	<LoD	<LoD	<LoD
Pt	5	8	<LoD	<LoD	<LoD	<LoD

Table 17 continued.

	LoD	S07-024123-AntiM4	S07-024124-EthS1	S07-024125-HeatR	S07-024126-EthS2	S07-024127-FreshI
Au	200	10400	200	<LoD	<LoD	<LoD
Hg	100	100	<LoD	<LoD	<LoD	<LoD
Tl	2	7	7	2	<LoD	<LoD
Pb	50	<LoD	350	290	<LoD	<LoD
Bi	2	4	6	13	39	<LoD
Th	50	<LoD	60	<LoD	<LoD	<LoD
U	10	<LoD	30	30	<LoD	<LoD

LOD = limit of detection

Table17 continued.

	LoD	S07-024128-EthS3	S07-024129-MoistA
Li	50	2300	<LoD
Be	50	1800	<LoD
B	1000	66000	<LoD
Na	1000	5690000	25200000
Mg	500	2030000	12000
Al	2000	20000000	40000
P	5000	50000	90000
K	5000	17200000	<LoD
Ca	2000	4840000	60000
Sc	100	1200	<LoD
Ti	2000	40000	40000
V	20	3200	<LoD
Cr	200	<LoD	<LoD
Mn	1000	11700000	<LoD
Fe	10000	3120000	<LoD
Co	5	460	30
Ni	500	<LoD	<LoD
Cu	50	9100	300
Zn	200	23000	7000
Ga	5	6010	<LoD
Ge	10	60	<LoD
As	20	1600	<LoD
Se	100	<LoD	<LoD
Rb	5	29500	<LoD
Sr	50	448000	300
Y	2	29600	<LoD
Zr	10	15400	70
Nb	1	155	23
Mo	5	430	<LoD
Ru	5	<LoD	<LoD

Table 17 continued.

	LoD	S07-024128-EthS3	S07-024129-MoistA
Rh	200	<LoD	<LoD
Pd	2	180	<LoD
Ag	100	<LoD	<LoD
Cd	1	38	<LoD
Sn	20	<LoD	<LoD
Sb	2	10	<LoD
Te	20	<LoD	<LoD
Cs	1	1490	<LoD
Ba	50	369000	300
La	2	36900	<LoD
Ce	10	88900	<LoD
Pr	1	9299	<LoD
Nd	5	32700	<LoD
Sm	1	6420	<LoD
Eu	1	779	<LoD
Gd	1	7390	<LoD
Tb	1	1054	<LoD
Dy	1	6120	<LoD
Ho	1	1180	<LoD
Er	1	3200	<LoD
Tm	1	444	<LoD
Yb	1	2720	<LoD
Lu	1	381	<LoD
Hf	1	376	<LoD
Ta	1	9	<LoD
W	2	30	<LoD
Re	1	<LoD	<LoD
Os	1	<LoD	<LoD
Ir	2	<LoD	<LoD
Pt	1	6	<LoD

Table 17 continued.

	LoD	S07-024128-EthS3	S07-024129-MoistA
Au	50	<LoD	<LoD
Hg	20	<LoD	<LoD
Tl	1	695	<LoD
Pb	10	4220	50
Bi	1	317	<LoD
Th	5	16300	<LoD
U	2	6880	<LoD

Table 17 continued.

	LoD	S08-000164-HeatS	S08-003221-AntiM5
Li	100	<LoD	<LoD
Be	200	<LoD	<LoD
B	5000	<LoD	<LoD
Na	5000	146000	25000
Mg	2000	366000	50000
Al	500	37700	311600
P	50000	<LoD	70000
K	10000	<LoD	<LoD
Ca	20000	<LoD	30000
Sc	500	500	<LoD
Ti	500	74700	373200
V	100	<LoD	<LoD
Cr	500	600	184500
Mn	100	<LoD	100
Fe	20000	<LoD	<LoD
Co	20	<LoD	<LoD
Ni	1000	5000	<LoD
Cu	1000	<LoD	<LoD
Zn	5000	<LoD	43000
Ga	20	<LoD	50
Ge	50	<LoD	<LoD
As	100	<LoD	69200
Se	50000	<LoD	<LoD
Rb	20	<LoD	<LoD
Sr	20	30	120
Y	10	<LoD	<LoD
Zr	20	260	2000
Nb	20	<LoD	<LoD
Mo	20	<LoD	<LoD
Ru	5	<LoD	<LoD

Table 17 continued.

	LoD	S08-000164-HeatS	S08-003221-AntiM5
Rh	500	<LoD	<LoD
Pd	10	<LoD	20
Ag	50	<LoD	<LoD
Cd	1	<LoD	7
Sn	100	<LoD	<LoD
Sb	20	<LoD	<LoD
Te	20	<LoD	<LoD
Cs	5	<LoD	<LoD
Ba	50	90	580
La	5	8	<LoD
Ce	5	12	6
Pr	5	<LoD	<LoD
Nd	5	<LoD	<LoD
Sm	5	<LoD	<LoD
Eu	2	<LoD	<LoD
Gd	2	<LoD	<LoD
Tb	2	<LoD	<LoD
Dy	1	<LoD	<LoD
Ho	1	<LoD	<LoD
Er	2	<LoD	<LoD
Tm	1	<LoD	<LoD
Yb	2	<LoD	<LoD
Lu	1	<LoD	<LoD
Hf	5	<LoD	52
Ta	10	<LoD	<LoD
W	10	<LoD	<LoD
Re	1	<LoD	<LoD
Os	1	<LoD	<LoD
Ir	5	<LoD	<LoD
Pt	5	<LoD	<LoD

Table 17 continued.

	LoD	S08-000164-HeatS	S08-003221-AntiM5
Au	400	<LoD	<LoD
Hg	50	<LoD	<LoD
Tl	1	<LoD	<LoD
Pb	50	<LoD	583000
Bi	2	9	200
Th	2	2	<LoD
U	5	5	<LoD

Table 18. Migration of iron from the oxygen scavenging label (0939-03-0471-OxS3)

	Mass of Fe detected (mg) - no label	Mass of Fe detected (mg) - with labels	Mass of Fe migrating from the labels (mg)	Equivalent Fe migration into food (mg/kg)
3% acetic acid soaked paper	0.004	44		
3% acetic acid soaked paper	0.003	50		
Average	**0.0035**	**47**	**47**	**235**[1]
95% ethanol soaked paper	0.21	0.014		
95% ethanol soaked paper	0.007	0.014		
Average	**0.11**	**0.014**	**< 0.007**	**< 0.035**[1]
Olive oil	<0.005	0.038		
Olive oil	<0.005	0.034		
Average	**<0.005**	**0.036**	**0.036**	**0.18**[1]
Tomato sauce	0.23	14		
Tomato sauce	0.21	16		
Average	**0.22**	**15**	**15**	**211**[2]
Cheese	0.036	0.55		
Cheese	0.034	0.51		
Average	**0.035**	**0.53**	**0.50**	**12**[2]

[1] Migration of Fe (mg/kg) was calculated as; (Mass of Fe measured in the simulant soaked tissues (mg) with label - Mass of Fe measured in simulant soaked tissues (mg) no label) × 5. The factor 5 originates from the fact that 1 label can be used to pack with 50 g of food and the migration experiment was performed with 4 labels.

[2] Migration of Fe (mg/kg) was calculated as; (amount Fe in food (mg) with label – amount Fe in food (mg) no label)/2*amount food used in experiment (kg). 0.0356 kg tomatosauce and 0.0208 kg cheese was used on average for the experiments. The factor 2 originates from the fact that 2 labels were used in the migration experiment.

Table 19. Migration of iron from the oxygen scavenging sachet (0939-03-0472-OxS4)

	Mass of Fe detected (mg) - no label	Mass of Fe detected (mg) - with labels	Mass of Fe migrating from the labels (mg)	Equivalent Fe migration into food (mg/kg)
3% acetic acid soaked paper	0.006	0.75		
3% acetic acid soaked paper	0.004	0.37		
Average	0.005	0.56	0.555	**11.1**[1]
95% ethanol soaked paper	0.014	0.012		
95% ethanol soaked paper	0.007	0.013		
Average	0.010	0.0125	0.0025	**0.05**[1]
Olive oil	<0.005	0.041		
Olive oil	<0.005	0.034		
Average	<0.005	0.038	0.038	**0.76**[1]
Tomato sauce	0.23	0.54		
Tomato sauce	0.21	0.64		
Average	0.22	0.59	0.37	**10.8**[2]
Cheese	0.036	0.14		
Cheese	0.034	0.093		
Average	0.035	0.12	0.085	**3.6**[2]

[1] Migraton of Fe (mg/kg) was calculated as; (Mass of Fe measured in the simulant soaked tissues (mg) with label - Mass of Fe measured in simulant soaked tissues (mg) no label) ×20. The factor 20 originates from the fact that 1 sachet can be used to pack 50 g of food.

[2] Migration of Fe (mg/kg) was calculated as; (amount Fe in food (mg) with label – amount Fe in food (mg) no label)/amount food used in experiment (kg). 0.0343 kg tomato sauce and 0.0238 kg cheese was used on average for the experiments.

Table 20. Recovery of iron for the migration experiment performed with the oxygen scavenging label (0939-03-0471-OxS3) in simulants and foods. The spike level was 9.7 mg Fe for the 3% acetic acid, tomato sauce and olive oil and 9.8 mg Fe for the 95% ethanol and cheese.

	Mass of Fe detected (mg) – with labels	Mass of Fe detected (mg) - with labels and spike	Mass of Fe recovered (mg)	Recovery (%)
3% acetic acid soaked paper	44	58		
3% acetic acid soaked paper	50	51		
Average	**47**	**54.5**	**7.5**	**77[1]**
95% ethanol soaked paper	0.014	5.3		
95% ethanol soaked paper	0.014	5.9		
Average	**0.014**	**5.6**	**5.5**	**57[1]**
Olive oil soaked paper	0.038	2.9		
Olive oil soaked paper	0.034	2.8		
Average	**0.036**	**2.85**	**2.81**	**29[1]**
Tomato sauce	14	19		
Tomato sauce	16	17		
Average	**15**	**18**	**3**	**31[2]**
Cheese	0.55	5.0		
Cheese	0.51	5.4		
Average	**0.53**	**5.2**	**4.7**	**48[3]**

[1] Recovery (%) was calculated as (Mass of Fe detected in simulant soaked tissues with Fe spike (mg) - Fe concentration in simulant soaked tissues no spike (mg))/amount spiked (mg) x 100%.

2 Recovery (%) was calculated as (mass of Fe detected in tomato sauce with label and spike (mg) – mass Fe detected in tomato sauce with label)/9.7 mg Fe.

3 Recovery (%) was calculated as (mass of Fe detected in cheese with label and spike (mg) – mass Fe detected in cheese with label)/9.8 mg.

Table 21. Recovery of iron for the migration experiment performed with the oxygen scavenging sachet (0939-03-0472-OxS4) in simulants and foods. The spike level was 2.4 mg Fe for the soaked papers. The spike level was 2.43 mg Fe for tomato sauce and cheese.

	Mass of Fe detected (mg) – with labels	Mass of Fe detected (mg) - with labels and spike	Mass of Fe recovered (mg)	Recovery (%)
3% acetic acid soaked paper	0.75	1.0		
3% acetic acid soaked paper	0.37	1.3		
Average	0.56	1.15	0.59	**24**[1]
95% ethanol soaked paper	0.012	1.2		
95% ethanol soaked paper	0.013	1.0		
Average	0.0125	1.1	1.09	**45**[1]
Olive oil soaked paper	0.041	0.13		
Olive oil soaked paper	0.034	0.14		
Average	0.038	0.135	0.097	**4**[1]
Tomato sauce	0.54	2.8		
Tomato sauce	0.64	2.7		
Average	0.59	2.75	2.16	**89**[2]
Cheese	0.14	2.3		
Cheese	0.093	2.5		
Average	0.12	2.4	2.28	**94**[2]

[1] Recovery (%) was calculated as (Mass of Fe detected in simulant soaked tissues with Fe spike (mg) - Fe concentration in simulant soaked tissues no spike (mg))/amount spiked (mg) x 100%.

[2] Recovery (%) was calculated as (Mass of Fe detected in food with Fe spike (mg) - Fe concentration in food without spike (mg))/amount spiked (mg) x 100%.

Table 22. Migration of BHT from the flavour releaser (0939-02-0227-FlavR1)

	BHT concentration in blank sample (µg/mL)	BHT concentration in exposed sample/sample extract (µg/mL)	Migration BHT (µg/mL) [1]	Migration BHT (mg/kg)
3% acetic acid	<0.03	0.024	0.024	0.01 [2]
3% acetic acid	<0.03	0.024	0.024	0.01 [2]
Average	**<0.03**	**0.024**	**0.024**	**0.01 [2]**
50% ethanol	<0.03	9.50	9.50	2.43 [2]
50% ethanol	<0.03	10.94	10.94	2.81 [2]
Average	**<0.03**	**10.22**	**10.22**	**2.62 [2]**
Olive oil	<0.03	<0.03	<0.03	<0.03 [2]
Olive oil	<0.03	<0.03	<0.03	<0.03 [2]
Average	**<0.03**	**<0.03**	**<0.03**	**<0.03 [2]**
Tomato sauce	<0.03	1.73	1.73	0.52 [3]
Tomato sauce	<0.03	1.60	1.60	0.48 [3]
Average	**<0.03**	**1.66**	**1.66**	**0.50 [3]**
Cheese	<0.03	0.22	0.22	0.25 [4]
Cheese	<0.03	0.28	0.28	0.32 [4]
Average	**<0.03**	**0.25**	**0.25**	**0.29 [4]**

[1] Migration BHT (µg/mL) was calculated as (BHT concentration in exposed sample/sample extract (µg/mL) - BHT concentration in blank sample (µg/mL)).

[2] Migration BHT (mg/kg) was calculated as (migration BHT (µg/mL) x 100 mL x ($6dm^2$/2.34 dm^2)/1000)

[3] Migration BHT (mg/kg) was calculated as (migration BHT (µg/mL) x 100 mL x ($6dm^2$/2.0 dm^2)/1000

[4] Migration BHT (mg/kg) was calculated as (migration BHT (µg/mL) x 250 mL x ($6dm^2$/1.3 dm^2)/1000

Table 23. Migration of sulphite from the SO_2 emitter (0939-02-1737-AntiM2) into 3% acetic acid soaked paper

	Mass of SO_3 meaured in the blank simulant soaked paper (mg)	Mass of SO_3 meaured in the simulant soaked paper exposed to the SO_2 emitter (mg)	Migration of SO_3 corrected for the blank (mg/kg) [1]
3% acetic acid soaked paper	<0.001	51	204
3% acetic acid soaked paper	<0.001	25	100
Average	**<0.001**	**38**	**152**

[1]Migration was calculated as (Mass of SO_3 meaured in the simulant soaked paper exposed to the SO_2 emitter (mg)- mass of SO_3 meaured in the blank simulant soaked paper (mg)) x 4. The factor 4 originates from the fact that 4 SO_2 emitters can be in contact with 1 kg of grapes.

Table 24. Concentrations calculated from the responses observed in the ion chromatograms at the retention times associated with sulphite and sulphate in studies on the migration of sulphite from the SO_2 emitter (0939-02-1737-AntiM2) into white and red grapes.

	SO_3 concentration (mg/kg)	SO_4 concentration (mg/kg)	SO_3 migration from the SO_2 emitter (mg/kg)	SO_4 migration from the SO_2 emitter (mg/kg)
Red grapes total no emitter	1988	1842		
Red grapes total +SO_2 emitter	1513	2191	*	*
Red grapes skin no emitter	< LOD	4.6		
Red grapes skin +SO_2 emitter	< LOD	24.7	< LOD	20
White grapes total no emitter	2570	2097		
White grapes total +SO_2 emitter	2505	2095	*	*
White grapes skin no emitter	< LOD	10.7		
White grapes skin +SO_2 emitter	< LOD	24.1	< LOD	13.4

* The difference in the concentrations calculated from the ion chromatogram responses of the grapes stored with and without the emitter was within the error associated with the measurement.

Table 25. Concentration of silver measured in the food simulants exposed to the antimicrobial liner (0939-03-0269-AntiM3) and the migration from the liner calculated taking into account the surface area of the liner and volume of simulant used in the test

	Exposed simulant (µg/L) *	Migration (µg/dm^2)
3% acetic acid	156.4	4.7
3% acetic acid	143.6	4.3
3% acetic acid	175.9	5.3
Average		**4.8**
10% ethanol	11.9	0.4
10% ethanol	10.0	0.3
10% ethanol	8.8	0.3
Average		**0.3**
95% ethanol	6.6	0.2
95% ethanol	7.1	0.2
95% ethanol	6.9	0.2
Average		**0.2**
Isooctane	< LOD	< LOD
Isooctane	< LOD	< LOD
Isooctane	< LOD	< LOD
Average		**< LOD**

LOD = 1 µg/L (equivalent to a migration of 0.03 µg/dm^2)

* The concentration detected in the blanks was subtracted from that detected in the exposed simulant.

Table 26. Migration of manganese from the ethylene scavenging sachets (S07-024128-EthS) to the paper soaked in the food simulants and the corresponding migration value for the foodstuff

	Migration (mg/sachet)	Migration (mg/kg) #
3% acetic acid	4.1	0.30
3% acetic acid	2.1	0.15
3% acetic acid	5.4	0.39
Average	**3.9**	**0.28**
10% ethanol	< LOD	< LOD
10% ethanol	< LOD	< LOD
10% ethanol	< LOD	< LOD
Average	**< LOD**	**< LOD**
Olive oil	< LOD	< LOD
Olive oil	< LOD	< LOD
Olive oil	< LOD	< LOD
Average	**< LOD**	**< LOD**

LOD = 0.2 µg/kg

Applying the information on the suppliers website that 1 sachet is used with 14 kg of fruit or vegetables

Table 27. Concentration of di-(2-ethylhexyl) maleate and di-(2-ethylhexyl) fumarate measured in the food simulant soaked tissues exposed to the absorbent pads (S07-024129-MoistA) and the migration calculated taking into account the surface area of the pad and volume of simulant used in the test.

	Di-(2-ethylhexyl) maleate detected in the simulant soaked tissue (mg/kg)	Di-(2-ethylhexyl) maleate migration ($\mu g/dm^2$)	Di-(2-ethylhexyl) fumarate detected in the simulant soaked tissue (mg/kg) *	Di-(2-ethylhexyl) fumarate migration ($\mu g/dm^2$) *
3% acetic acid	2.51	12.5	78.2	391
3% acetic acid	2.59	12.9	89.2	446
3% acetic acid	4.69	23.1	159	793
Average	**3.24**	**16.2**	**109**	**543**
10% ethanol	8.07	40.4	257	1290
10% ethanol	8.86	44.3	323	1610
10% ethanol	9.18	45.9	345	1730
Average	**8.70**	**43.5**	**308**	**1540**
Olive oil	0.902	4.51	8.02	40.1
Olive oil	3.11	15.6	22.8	114
Olive oil	1.70	8.48	15.5	77.6
Average	**1.90**	**9.52**	**15.5**	**77.3**

* Quantified based on the response of the di-(2-ethylhexyl) maleate

Table 28. Concentration of di-(2-ethylhexyl) fumarate measured in the foods and the migration calculated taking into account the surface area of the pad and mass of food used in the test

Sample	Di-(2-ethylhexyl) fumarate detected in the food (mg/kg) *	Di-(2-ethylhexyl) fumarate migration (µg/dm^2) *
Beef 1	0.32	42
Beef 2	0.23	30
Beef 3	0.38	49
Average	**0.31**	**40**
Salmon 1	0.30	15
Salmon 2	0.34	17
Salmon 3	0.43	22
Average	**0.36**	**18**

* Quantified based on the response of the di-(2-ethylhexyl) maleate

Table 29. Results of the microbiological analysis performed whole on whole strips after contamination with meat drip. The results are means of two samples 0939-03-0269-AnitM3 and S07024123-AntiM4.

	0939-03-0269-AntiM3 *(cfu/g)*		S07 024123-AntiM4 *(cfu/g)*		Reference lab paper *(cfu/g)*	
Microbiol. parameters	4 hours	24 hours	4 hours	24 hours	4 hours	24 hours
TVC[1]	740000	440000	600000	440000	196000	29000
Entero's	56000	70	270000	45	25000	<10

[1]TVC (Total viable counts).

Table 30. Results of the microbiological analysis performed on the contact surfaces. The results are means of two samples 0939-03-0269-AnitM3 and S07024123-AntiM4.

Conditions	Meat surface in contact with the tissues (cfu/g)		Surface tissues in contact with the meat cut (colonies/RODAC)		Petri dish surface in contact with the material (colonies /RODAC)	
Microbial parameters	5 minutes	4 hours	5 minutes	4 hours	5 minutes	4 hours
0939-03-0269-AntiM3						
TVC	54000	121000	>50	>50	0	0
Entero's	260	110	0	10	0	0
Evaluation			**Poor**	**Poor**	**Excellent**	**Excellent**
S07 024123-AntiM4						
TVC	310000	54000	>50	>50	0	0
Entero's	55	180	0	2	0	0
Evaluation			**Poor**	**Poor**	**Excellent**	**Excellent**
Lab paper						
TVC	280000	88000	>50	>50	5	>50
Entero's	90	850	0	11	0	11
Evaluation			**Poor**	**Poor**	**Excellent**	**Excellent**

Figure 1. Schematic overview of the dedicated migration tests performed.
A) an SO_2 emitter is positioned between a stack of laboratory filtration paper soaked with simulant and glass plates.
B) an oxygen scavenger sachet positioned between a stack of laboratory filtration paper soaked with simulant and glass plates.
C) Four oxygen scavenger labels are attached to a glass plate. The glass plate is positioned between a stack of laboratory filtration paper soaked with simulant and glass plates.

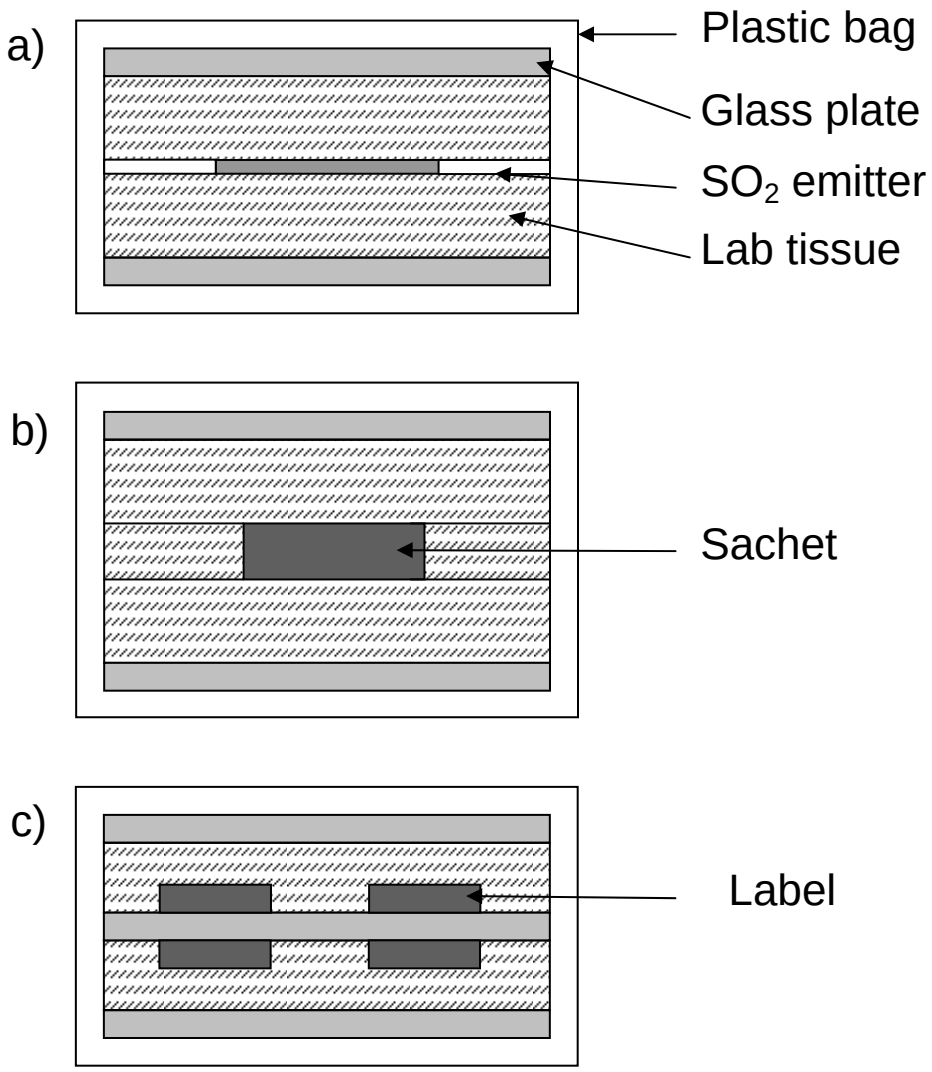


Figure 2. Set-up of the non-invasive oxygen determination. The yellow dot packed in the glass bottle contains the oxygen sensitive material.

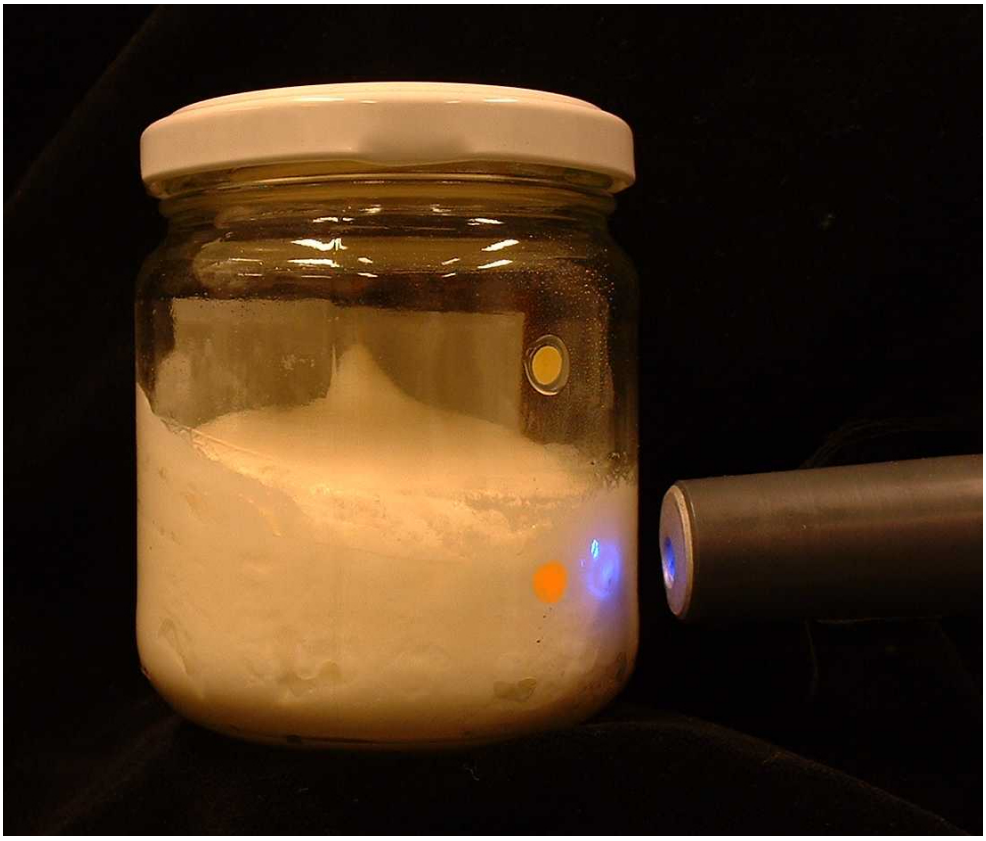


Figure 3. Decrease in the percentage of oxygen in a 210 mL glass bottle containing an oxygen absorbing sachet (0930-03-0471-OxS3).

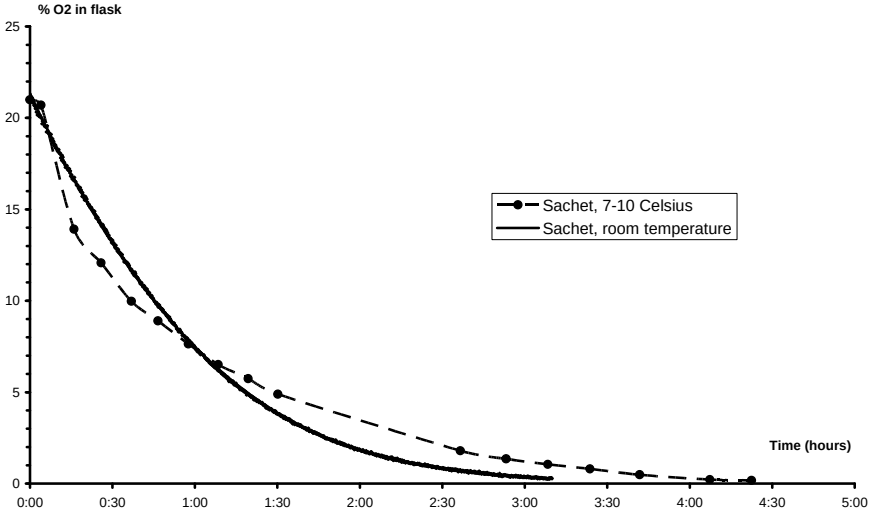


Figure 4. Decrease in the percentage of oxygen present in a 210 mL glass bottle containing three oxygen absorbing labels (0930-03-0471-OxS3) tested at room temperature.

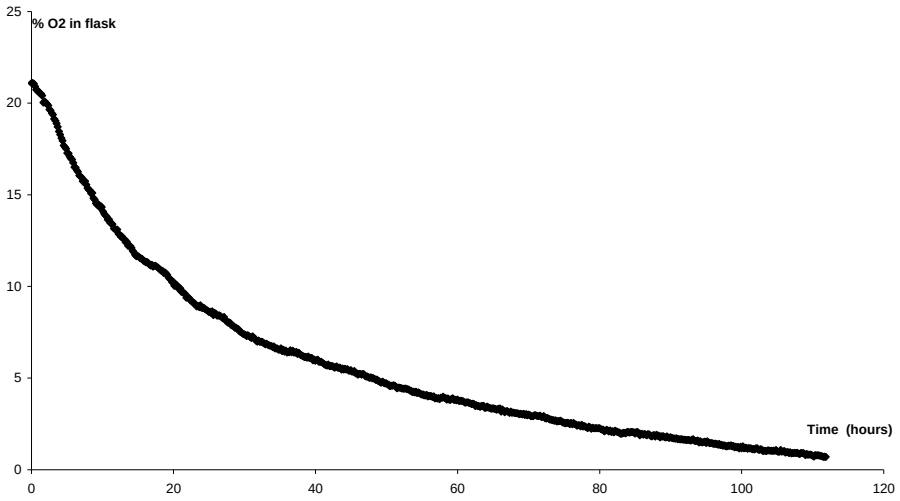


Figure 5. Schematic of the efficacy test of the antimicrobial tissue and test samples.
a) Method A: where the tissues were wetted with meat-drip,
b) Method B: where pieces of meat were placed on top of a tissue in a Petri dish.
The surface of the meat, tissue and Petri dish was analysed for microbes.

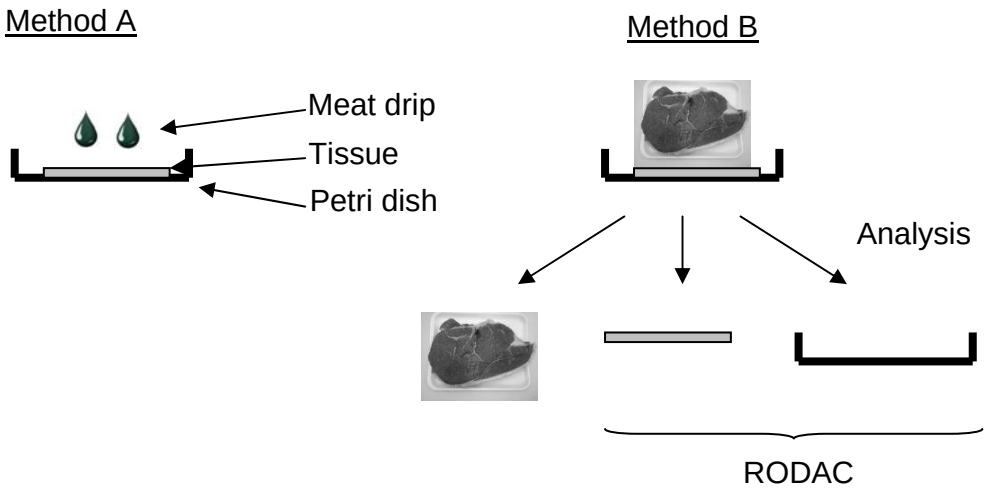
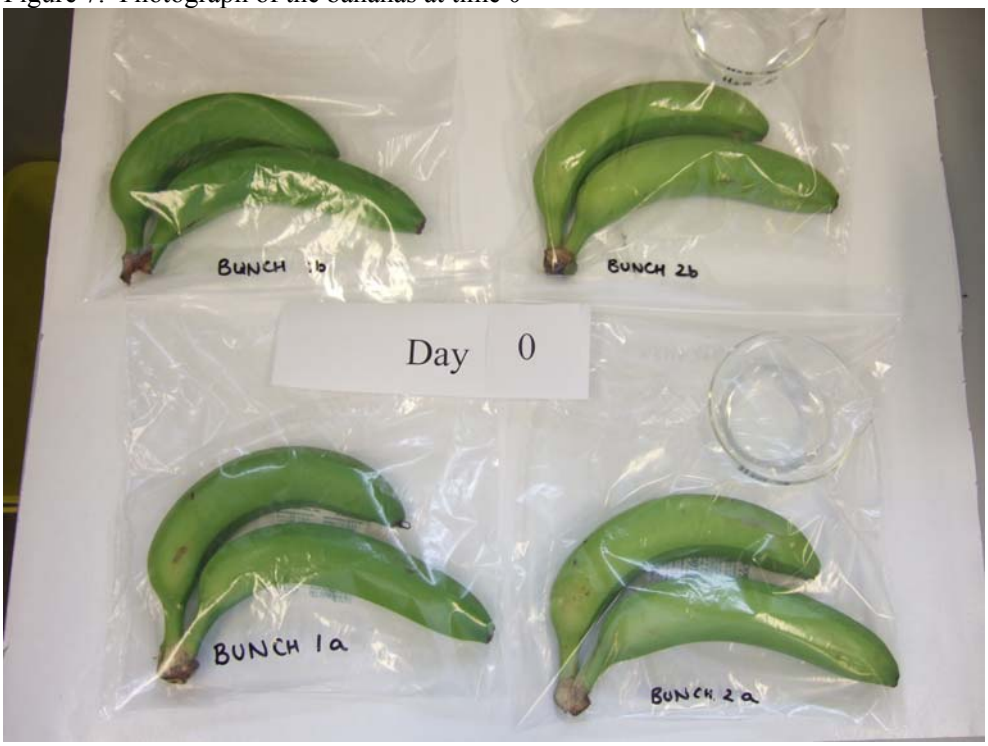


Figure 6. White grapes from supplier 1 without (a) and with (b) an SO_2 emitter and white grapes from supplier 2 without (c) and with (d) an SO_2 emitter.

Figure 7. Photograph of the bananas at time 0



Code
Bunch 1a = bananas only
Bunch 1b = bananas + ethylene scavenging sachet
Bunch 2a = bananas in a moist atmosphere
Bunch 2b = bananas + ethylene scavenging sachet in a moist atmosphere

Figure 8. Photograph of the bananas after storage for 21 days at 25°C

Code
Bunch 1a = bananas only
Bunch 1b = bananas + ethylene scavenging sachet
Bunch 2a = bananas in a moist atmosphere
Bunch 2b = bananas + ethylene scavenging sachet in a moist atmosphere

Figure 9. Photographs demonstrating the efficacy of the heat sensing spoons (S08-000164-HeatS)

Control at room temperature | After contact at 40°C

Control at room temperature | After contact at 60°C

Control at room temperature | After contact at 80°C

Figure 10. Photographs demonstrating the efficacy of the time indicators (S07-000306-TimeI)

A

B

C