MIGRATION OF SUBSTANCES FROM PAPER AND BOARD FOOD PACKAGING MATERIALS

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Academic Dissertation

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ABSTRACT

There are three basic requirements for food contact materials: substances that might endanger human health must not transfer from the packaging into food, the packaging must not impair the composition of the packaged product nor must it impair its sensory properties. The purpose of this work was to determine what potentially hazardous substances are present in paper and board packaging materials and whether these can migrate into food itself. For this purpose, it was necessary to develop several new methods of analysis for fiber materials, all of which were based on gas chromatography.

Initially, several combinations of packaging/foodstuff were tested for compounds likely to migrate into food. Whenever significant amounts of such compounds were found, a test was performed to see whether the compounds could be transferred to a solid food simulant (Tenax, registered trademark for modified polyphenylene oxide resin). The final step was then to test whether the compounds migrated into the food wrapped in the packaging in question.

Phthalates originating from adhesives and alkylbenzenes originating from printing inks showed significant migration into both Tenax and the foods tested. The migration test developed using Tenax and a closed migration vessel proved both feasible and useful, as the results corresponded well with real life migration of phthalates and alkylbenzenes.

It is well known that migration accelerates with increasing temperature. Ovenable boards, which are used in microwave or conventional ovens at very high temperatures (up to around 200°C), demand migration tests different from those used for room temperature. Migration tests using Tenax at high temperature were easy to perform and satisfactorily simulated the actual use of food trays based on ovenable board. Both gravimetric overall migration and specific migration were determined. The overall migration from the samples was quite low. Consequently, it seemed that overall migration was not a limiting factor for high temperature use of the board. Compounds originating from the sizing agents used in the board's manufacture were the main migrants.

In addition to migration tests, methods were developed for testing barriers in food packaging materials. Spiking with model compounds followed by migration testing proved a promising way of developing a routine method for testing barriers. However, it is clear that a solid food simulant would be more feasible than the liquid simulants used at that time.

Predictive migration models for polymers are already quite well established, but the inhomogeneity of fiber-based materials makes modeling difficult. Experiments on the diffusion of certain volatile compounds through laboratory kraft pulp sheets were compared with computer simulations. These simulations were based on random walk, and the fiber network structure was modeled explicitly. For each compound, diffusion constants in air were determined before studying diffusion through the sheets. These diffusion experiments were carried out using equipment built in-house in conjunction with gas chromatography.

The major advantage of the random walk simulation created here is that it gives an estimate of the effective diffusion constant for the fiber network. For most of the compounds, experimental and simulation results agreed well. Both suggest that gas diffusion rate is very sensitive to sheet porosity.

CONTENTS

PREFACE

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LIST OF ORIGINAL PAPERS

This dissertation is based on the following six articles, hereafter referred to by their Roman numerals (I-VI).

I Residual Solvent Content in Heatset Offset Print, B. Aurela and T. Räisänen, *J. High Resol. Chromatogr.* 16, 1993, 422-424.

II Development of Methods for Testing Barriers in Food Packaging Materials, B. Aurela, T. Tapanila, R-M. Osmonen and L. Söderhjelm, *J. High Resol. Chromatogr.* 20, 1997, 499-502.

III Phthalates in paper and board packaging and their migration into Tenax and sugar, B. Aurela, H. Kulmala and L. Söderhjelm, *Food Addit. Contam.*, 16(12), 1999, 571-577.

IV Migration of alkylbenzenes from printing ink to food and Tenax, B. Aurela, T. Ohra-aho and L. Söderhjelm, *Packag. Technol. Sci.*, 14(2), 2001, 71-77.

V Migration from ovenable boards at high temperatures, B. Aurela, M. Vuorimaa and H. Lindell, *Nord. Pulp Pap. Res. J.*, 15(2), 2000, 124-128.

VI Diffusion of volatile compounds in fiber networks: experiments and modelling by random walk simulation, B. Aurela and J. A. Ketoja, accepted to *Food Addit. Contam*.

The author has written publications I-V and the experimental part of publication VI.

ABBREVIATIONS

ADI	Acceptable Daily Intake
ATR	attenuated total reflectance spectroscopy
AKD	alkylketene dimer (sizing agent)
BBP	benzylbutyl phthalate
BgVV	Bundesinstitut für Gesundlichen Verbraucherschutz und Veterinärmedizin
Butyrate	2,2,4-trimethyl-1,3-pentanediol diisobutyrate (CAS 6846-50-0)
CEN	Committee Européen de Normalisation (European Standardisation Organisation)
CH	hydrocarbons
CoE	Council of Europe
EC	European Commission
D	dispersion coating
DEP	diethyl phthalate
DEHP	diethylhexyl phthalate
DIBP	diisobutyl phthalate
DIPNs	diisopropylnaphthalenes
FAO	Food and Agriculture Organization
FDA	Food and Drug Administration
FID	flame ionization detector
FTIR	fourier transform infrared spectroscopy
GC	gas chromatography
GMP	Good Manufacturing Practise
HACCP	Hazard Analysis of Critical Control Points
HYSBS	board containing high yield pulp and solid bleached sulfate pulp
ISO	International Standardisation Organisation
MOS	Margins of Safety
MPPO	modified polyphenylene oxide
NC	nitrocellulose
NOEL	No Observed Adverse Effect Level
LC	liquid chromatography
MS	mass spectrometry
QM	Quantity in Material

PE	polyethylene
PET	polyethylene terephthalate
PP	polypropylene
PS	polystyrene
LAB	linear alkylbenzenes (CAS 67774-74-7)
SB	styrene-butadiene
SCF	EU Scientific Committee for Food
SML	Specific Migration Limit
TDI	Tolerable Daily Intake
SBS	board containing solid bleached sulfate pulp
ToR	Threshold of Regulation
TTC	Threshold of Toxicological Concern

SHORT GLOSSARY OF PAPER TERMINOLOGY

Beating — Any laboratory pulp refining (i.e. mechanical treatment of papermaking fibers to develop their optimum properties) or milling process.

Binder (in pigment coating) — Component of coating dispersion that serves to bind the pigment particles together in the coating, bind the coating to the raw stock, reinforce the raw stock, and fill the pores in the pigment structure.

Chemical pulp — Any pulp obtained from wood (or other plant raw material) principally by chemical means. The two major types of chemical pulp are kraft pulp and sulfite pulp.

Dispersion coating — Coating for functional purposes with less pigment than in pigment coating (or no pigment at all).

Folding boxboard — Paperboard suitable for conversion into folding cartons. In addition to general requirements of stiffness and durability, it must possess strength properties that permit scoring and folding. Contains usually mechanical pulp in the middle ply.

Mechanical pulping — Any pulping process relying primarily on mechanical energy and/or mechanical methods to separate the fibers.

Paperboard — Fundamentally, any thick, heavyweight papermaking product. The distinction between paper and paperboard is based on product thickness. Nominally, all sheets above 0.3 mm are classed as paperboard, but there are enough exceptions to blur the exact line of demarcation. Also commonly referred to simply as board (as in this text).

Pigment coating — Coating consisting of fine mineral particles (usually clay) along with binders and other components.

Sizing agent — Any material used for sizing (i.e. reducing liquid penetration), for example rosin with alum, starch, AKD, etc.

Solid board — Paperboard made on the paper machine with the same material throughout, usually chemical pulp.

1 INTRODUCTION

Packagings are needed to ensure a reliable supply of safe and high-quality food for the world's population. The requirements placed on packagings in modern urban society differ from those in societies in less developed countries. Demand for ready-to-eat meals and take-away foods is rising explosively in urban communities, and consequently new packaging designs are needed. Among other things, packaging is a powerful marketing tool designed to be attractive to the eye and to provide information about its contents. However, the main purpose of a packaging – to protect its contents – is global.

Total annual production of packaging paper and board in the EU is around 30 million tonnes. It has been estimated that half of this packaging paper and board comes into contact with food. Although paper and board as packaging materials have major environmental advantages, the consumption of paperboard in comparison with other packaging materials has decreased in the last five years. It is clear that packagings must not endanger human health or impair the product they are intended to protect, for example by tainting the packed foods.

Both the food industry and consumers are putting increasing pressure on the regulatory bodies to improve the safety of food packaging. Many competing materials, like plastics, are already subject to EU legislation, something that facilitates business in these products. However, there is so far no specific EU directive about paper and board in contact with foodstuffs. On the other hand, Council Directive 89/109/EEC, which covers all food contact materials, states that substances that are hazardous to human health must not be transferred (migrate) from the packaging into the packed food.

The safety of food contact plastic materials has been studied extensively for several decades, whereas extensive research into fiber-based food contact materials has been conducted only for the last ten years. As a result, legislation on plastic materials is much more specific than that on fiber-based materials. However, recommendations for paper and board intended for food contact have recently been adopted. These recommendations are based very much on recent scientific evidence. More scientific data is still needed to form the basis for future recommendations and legislation [1, 2].

As it is not always possible to use foodstuffs for testing food contact materials, food simulants have been introduced. They are classified by convention as having the character of one or more food types. Food types and simulants are indicated in the directives or technical documents issued by the Council of Europe [3, 4, 5].

2 AIMS OF THE STUDY

Materials intended for contact with food must not transfer any constituents to the food that might endanger human health, change the composition of the food, or cause a deterioration in its organoleptic properties. These stipulations contained in Council Directive 89/109/EEC issued by European Commission concern all materials and articles coming into contact with food. In the case of paper and board materials, however, little research is being carried out to determine whether these stipulations are fulfilled. The purpose of this study was to determine what potentially hazardous substances are present in paper and board packaging materials and whether these can migrate into food itself.

More specifically, the aims were:
- to develop methods for testing barriers in food packaging materials (II)
- to investigate what potentially hazardous substances are present in paper and board packaging materials (I, III-V)
- to develop methods using a solid food simulant (Tenax) for testing migration from fiber-based materials (III, V)
- to compare the results of migration tests using Tenax with migration into foods (III, IV)
- to develop the simplest experimentally verifiable model for migration through a fiber network (VI)

3 BACKGROUND

3.1 Interactions between packaging materials and food

Food packaging interactions can be defined as chemical and/or physical reactions between a food, its packaging and the environment which alter the composition, quality or physical properties of the food and/or packaging [6]. Earlier, most research was focused on the adverse effects of such interactions, but more recently there has been growing interest in how such interactions might improve food quality. Examples of this are selective absorption of undesirable aromas and use of antimicrobial polymers (active packagings).

In general, food-packaging interactions can be divided into three groups [7]

- Migration: the transfer of packaging components into food
- Sorption: the transfer of food components to the packaging
- Permeation: the transfer of components through the packaging in either direction

Sorption can also be called negative migration [8].

Examples of these interactions are [6]:

1. Migration

This can result in safety concerns and flavor degradation. The transfer of desirable functional components such as antimicrobial agents, on the other hand, may be beneficial.

2. Sorption:

The transfer of desirable aromas from food to packaging can result in flavor alteration and/or loss of packaging performance. Sorption of undesirable flavors or reduction in the oxygen content of a packaging could be beneficial.

3. Egress permeation:

Loss of aroma volatiles, moisture etc. can result in changes in food quality.

4. Ingress permeation:

Ingress of oxygen, moisture, light and components that may cause tainting or endanger the safety of food can be detrimental.

Migration has become a major factor in regulations regarding the safety and quality of packaged food. Diffusion is the main mechanism underlying migration [8, 9]. Diffusion is caused by concentration gradients, i.e. mass transfer of components from regions of high concentration to regions of low concentration will take place within the food and within the packaging material. The rate of mass transfer is proportional to the concentration gradient. The factor of proportionality is known as the ”diffusion coefficient” or “diffusivity”. Diffusion exists for substances in the gaseous, liquid and solid states. In migration, the commonest regimes comprise gas or liquid moving through and out of a solid. A typical example is vinyl chloride (gas) in the respective polymer (solid). Diffusion depends on a number of factors, i.e. the properties of the penetrating molecule, the temperature, the concentration gradient and the nature of the matrix in which the diffusion takes place.

The rate of migration is diffusion-controlled, which is further complicated by the fact that food components that have penetrated the packaging material may accelerate the diffusion of packaging components. Three different types of migration can be distinguished [10]. In Class I the diffusion coefficient is close to zero; hence little migration takes place. In Class II migration the diffusion coefficient is constant and independent of time and type of food in contact with the material. Class III systems refer to those where migration is controlled by food contact, with the implication that in these systems migration is negligible in the absence of food contact [11]. For example, food components penetrate the plastic, causing it to swell and thereby affect migration.

3.2 Current legislation

There is currently no global or regional legislation governing paper and board packagings for foodstuffs. In fact, many countries do not have their own specific regulations on paper and board food packagings. Many of these countries model their requirements on the regulations of other countries, in particular the American FDA (Food and Drug Administration) [12] and the German BgVV (Bundesinstitut für GesundlichenVerbrauchershutz und Veterinärmedizin) regulations [13]. The American FDA regulations are quoted globally, whereas German BgVV appear more often as European references.

The aim of regulations for food packaging materials is consumer protection. Food safety is a priority for the European Commission. Article 2 of Council Directive (89/109/EEC) states the following [14]:
Materials and articles must be manufactured in compliance with good manufacture practise so that, under their normal or foreseeable conditions of use, they do not transfer their constituents to foodstuffs in quantities which might endanger human health, bring about an unacceptable change in the composition of the foodstuffs or a deterioration in the organoleptic characteristics thereof.

This Directive is usually referred to as a Framework directive. Although at the moment there are different kinds of national regulations for food contact paper and board within Europe, it should be noted that the Framework Directive covers all food contact materials, including paper and board.

3.3 Future EU legislation on paper and board food packaging

The Council of Europe (Committee of Experts on Materials Coming into Contact with Food, hereafter called Committee of Experts) has worked on a resolution concerning paper and board in food contact applications since 1987. Finally, in March 2001, the draft of the resolution was published on the Internet (http:/www.coe.fr/soc-sp)[15]. The resolution will, in all likelihood, form the basis of future European legislation, for example a directive on paper and board intended for food contact. However, the resolution is only a recommendation that a member state may, if it wishes, include in its legislation

3.3.1 Forms of restrictions

Specific migration limits (SMLs) are the main form of restriction for plastics. The SML is a value assigned by the EU Scientific Committee for Food (SCF) to a substance as the maximum amount that is allowed to migrate into food from food contact material. An SML is usually expressed in mg/kg of food or food simulant. For years the general consensus has been that where restrictions for specified substances are listed in EU Directives for plastics,

the same restrictions will be adopted for the substances in the Index list of the Paper resolution [16], and this principle is indeed included in a footnote to the Paper resolution [15]. The restrictions placed on the substances are based on toxicological assessments. The extent of the assessment depends on the level of migration of the particular substance: the less migration, the fewer toxicological tests [17]. Toxicological assessments result in values such as Tolerable Daily Intake (TDI) or Acceptable Daily Intake (ADI) expressed in mg/kg body weight/day (mg/kg bw/d). When this is issued or endorsed by the United Nations (FAO/WHO) the standard abbreviation is ADI, whereas for the European Union Commission (SCF) it is TDI [8].

Quantity of Material (QM) is the maximum permitted quantity of the substance in the finished material or article. QM may be expressed in mg/dm^2 of the surface in contact with food or in mg/kg in the material.

Both SML and QM values can be derived from TDI or ADI values using conventions adopted by SCF. One convention is that an average person weighs 60 kg and can consume up to 1 kg of food per day, all wrapped in packaging containing the substance under evaluation. The QM value also requires the convention that 6 dm^2 of material comes into contact with 1 kg of food, plus the assumption of 100% migration [16]. Thus, for a substance with a TDI of 0.01 mg/kg bw/d, the corresponding SML would be 0.6 mg/kg food (or food simulant).

It should be remembered that TDIs and ADIs are estimated for consumption over the lifetime of an individual. Therefore, setting an SML on the assumption that all food consumed is always packaged in a particular packaging material containing a particular substance is certainly an overestimate of the true consumer exposure. In some cases, these overestimated SML values are far too severe. Attempts are therefore being made to establish more realistic exposure estimates in setting SML restrictions, such as the use of food consumption factors and packaging usage factors [18].

In the USA, packaging materials are regulated under food legislation. Potential migrants from packaging materials are considered as “indirect food additives”. The US Food and Drug Administration (FDA) has developed an abbreviated process for evaluating packaging materials instead of the extensive investigation normally required for food additives. This

process is used to determine “when the likelihood or extent of migration to food of a substance used in a food-contact article is so trivial as not to require regulation of the substance as a food additive”. This trivial level, known as the “Threshold of Regulation” (ToR), was based on a large database of carcinogenic potencies and was determined to be 1.5 µg/person/ day. This value was defined as being “low enough to ensure that the public health is protected, even in the event that a substance exempted from regulation as a food additive is later found to be a carcinogen”. Substances not having structural alerts or that are not known carcinogens and are below the threshold value are considered by the FDA to be exempted from regulation as food additives [19, 20, 21].

In the EU, there is growing support for the inclusion of the same kind of approach in the harmonized legislation on food contact materials. This concept is called “Threshold of Toxicological Concern” (TTC) [22].

3.3.2 Functional barrier

In the “Field of application” of the Paper resolution it is stated that, “When the materials and articles consist of two or more layers, exclusively or not exclusively made of paper and board, any layer which is composed of paper and board must fulfill the requirements of this resolution, unless separated from the foodstuffs by a *functional barrier* to migration”.

The concept of a functional barrier is defined in the Resolution as “Any integral layer which under normal or foreseeable conditions of use reduces all possible material transfer (permeation or migration) from any layer beyond the barrier into food to a toxicologically and organoleptically insignificant and to a technologically unavoidable level”.

Thus the efficiency of a functional barrier is eventually defined by a concentration of no concern (that is a conventional value) in a food or a food simulant. However, the above definition is quite difficult to interpret, and a new definition is therefore being discussed within the EU [22].

It is known from experience that only a few materials can be considered to be universal barriers. Packaging research, which is focused mainly on the barrier properties towards oxygen and water vapor or on how to retain the flavors of certain foodstuffs, provides numerous examples of the need to combine several barrier layers in order to achieve an absolute barrier [23, 24, 25, 26].

Only a few studies have been published on migration from a fiber material behind a barrier layer into food [27, 28, 29, 30, 31]. The functional barrier concept is being investigated more intensively in plastic materials and in articles where the virgin plastic layer separates the recycled material from food [32, 33, 34]. For example, three-layered polypropylene (PP) cups with recycled PP material in the middle layer have been studied to test the PP food contact layer for its functional barrier behavior [35].

3.3.3 Recycled fibers

During preparation of the Paper resolution, one of the most difficult issues to be decided was the use of recycled fibers in food contact materials. In many European countries recycled fibers are widely used for food packagings, while in other countries there are tight restrictions on the use of recovered material in contact with foods. The Paper resolution states that certain grades of recycled fiber can be used in the manufacture of paper and board intended for food contact. The details are given in the CoE document “Guidelines on paper and board made from recycled fibers intended to come into contact with foodstuffs”. Guidelines are less formal than resolutions; the Guidelines will be amended, as necessary, by the Committee of Experts to take into account technological developments in the processing of recovered paper, improvements in analytical techniques and increasing knowledge of the toxicology of chemical substances [36].

Paper and board made in part or in full from recycled fibers are subject to certain requirements in addition to those specified in the Paper resolution to ensure their safety. The source of recovered paper and board, the processing technologies applied to remove contaminants, and the intended end use of the product all have to be considered together. These aspects are linked to each other in a consolidated matrix.

The specific requirements imposed on end products depend on the nature of the food that will be in contact with the material or article under study. Foods are divided into three types: fatty and/or aqueous foods (all the requirements), dry non-fatty foods (some of the requirements) and foods that need to be washed, shelled or peeled (none of the requirements). In contrast to plastic materials, end product testing is also required when the product comes into contact with dry foods. This is because migration from packaging materials into dry foods has been demonstrated in a number of studies [37, 38, 39, 40, 41, 42, 43, 44, 56].

Most of the specific requirements deal with contaminants originating from printing inks or adhesives, for example Michler's ketone, 4,4'-bis(diethylamino)benzophenone (DEAB), phthalates, solvents, azo colorants, primary aromatic amines (suspected to be carcinogenic), benzophenone and polycyclic aromatic hydrocarbons (PAH). In addition to these substances, there are restrictions on fluorescent whitening agents (FWAs), diisopropylnaphthalenes (DIPNs) and partially hydrogenated terphenyls (HTP) in the end product. It is thought that these substances could be present in paper made from recycled fibers, and that they might migrate into foods at levels which may pose a risk to health [45, 46, 47, 48, 49, 50, 51, 52, 53]. However, it should be noted that this list of substances is only an example; tests should be carried out for other toxic substances whenever there are grounds to suspect their presence in the end product. Although the recovered paper grades suitable as raw material for manufacturing food packaging paper and board are specified in the Guidelines, the raw material is still very heterogeneous. Other potentially toxic substances may therefore arise from new studies [54].

3.3.4 Future EU resolution on packaging inks

The Committee of Experts is working on a resolution on the printing inks, primers, colored lacquers and overprint varnishes applied to the non-food contact surface of food packagings and articles intended to come into contact with foodstuffs (packaging inks). Although the draft of the resolution on packaging inks is still preliminary, it is quite similar in structure to the Paper resolution. At present, there are seven Technical documents related to the draft resolution on packaging inks: Glossary, Index List, GMP, Exclusion List, Specifications for

Colorants, Analytical Methods and Literature References. However, the Index List of packaging inks covers only the following substances: dyes, additives used in organic pigments, plasticizers, solvents and dryers. Consequently, not all the ingredients of the ink are included in the list. Photoinitiators, for example, are not listed, although some of them are known to be toxic.

3.4 Migration from paper and board food packaging materials

Migration from paper and board packaging materials has not been as extensively studied as migration from plastic materials. However, it has been demonstrated that migration from paper and board packagings does occur [44, 55, 56, 57, 58, 59, 60, 61]. Most of the migrants detected originated from the printing inks or adhesives used in the manufacture of the finished packaging. Diisopropylnaphthalenes (DIPNs) are an exception, because although they are used as solvents in some printing inks, they are also widely employed in the paper industry in the manufacture of carbonless copy paper and thermal paper.

The risks of contamination of food from printing ink components in packaging materials are associated with two mechanisms: transfer through the packaging material and set-off phenomena. The latter means that printing ink components are transferred from the printed to the non-printed surface by direct contact during the material's manufacture, storage or use. It should be noted that these phenomena usually involve substances other than dyes, and are therefore not visible. The use of recycled materials such as fibers from recovered paper may also result in direct contact between ink components and food, or at least the route through the material might be shorter. Castle has published an extensive review of potential contaminants in recycled paper and board food contact materials [62]. Migration to dry foods was reported for phthalates, diisopropylnaphthalenes (DIPNs), and certain volatile compounds. The adhesives used for food packaging applications have been tested for overall and specific migration using Tenax as a food simulant. Overall migration was well below the recommended limit in both studies [63, 64].

Residues of dialkylaminobenzophenone UV-cure ink photoinitiators and their possible migration into foods were investigated by Castle *et al.* [65]. One of these

dialkylaminobenzophenones, namely Michler's ketone (4,4'-bis(dimethylamino) benzophenone), is a suspected carcinogen. The concentrations of dialkylaminobenzophenones found in paper and board packagings were low and migration into foods was not detectable. It was concluded, therefore, that the concentrations of Michler's ketone present in the packaging samples analyzed were unlikely to pose a risk to human health.

3.5 Migration in high temperature applications

The use of microwave ovens at home and in offices around the world will continue to grow, and this will increase the demand for compatible packaging. Packages need to be suited for baking and for preparation of semi-cooked dishes. Often the materials are deep frozen, defrosted and reheated. Most ovenable boards today are extrusion coated with either polypropylene (PP) or polyethylene terephthalate (PET). In some new applications boards are coated with dispersion coatings [V].

The migration behavior of PET at high temperatures has been studied fairly extensively because PET is used in microwave susceptors [66, 67, 68, 69, 70]. Microwave susceptor packaging is designed to brown and crisp food in the microwave oven. These susceptors are usually made of a metallized PET film laminated to paperboard with an adhesive. Some of the studies are based on model compounds incorporated into susceptors [67, 68, 70].

The compounds in the studies just mentioned are in most cases typical of the PET or adhesive layer, but little attention has been given to the compounds originating from paperboard. Back in 1989, Booker and Friese developed a method for analyzing volatile compounds generated from microwave interactive paperboard materials [71]. The volatiles were collected in Tenax adsorbent and desorbed into the injector of a gas chromatograph. The compounds detected were divided into two classes: thermally desorbed compounds, which are indigenous to the material, and products produced from the pyrolysis of the material analyzed. This classification can be made by examining the quantity of volatiles released in a given time at several temperatures. Volatiles originally present in the material are easily desorbed and assayed because they are present in limited amounts, whereas true pyrolysis products are

continuously generated without achieving their stoichiometric limit. No migration tests were performed during the study.

Calvey *et al.* used supercritical fluid chromatography to analyze potential migrants in solvent extracts of several microwave susceptor packaging materials [72]. In addition to common aliphatic and aromatic plasticizers they found long-chain alkyl ketones that may arise from the alkyl ketene dimers used as sizing agents. No migration tests were performed.

In a recent study, Tenax was used to trap volatiles formed in PET-containing packaging materials during prolonged heating (50 min) in a closed vessel at temperatures up to 230°C [73]. The majority of compounds released by these PET-containing materials probably originated from the other layers containing paper, adhesives or printing inks. The concentrations found were generally very low. Several paper degradation products were detected.

Migrant transfer routes can be more complicated when the foods are heated in the packaging than when they are only stored at room temperature, because of possible transient contact with splashed food. The photoinitiator benzophenone has been studied as an indicator migrant. Migration to foods microwaved in a paperboard packaging was up to 1 mg/kg 74. It was concluded that the mechanism of migration depended on the design of the packaging, occurring by direct food contact, transient contact with splashed food, or by gas-phase diffusion through an air gap. In a later study, it was shown that migration into foods heated in trays with cartonboard splashguards was some 10 times higher when there was direct contact between the food and the lid than in a situation where there was no direct contact [75].

3.6 Testing of migration

As mentioned in Chapter 3.3.1, specific migration limits (SMLs) are the main form of restriction placed on plastics. At present, there are approximately one hundred SMLs in the EU directives. There is therefore an urgent need for analytical methods with which to test the compliance for all these SMLs. It is recommended that internationally recognized and validated methods of analysis be applied in testing to ensure compliance with the legislation

and recommendations. Analytical methods are the responsibility of the appropriate body within the CEN (Comité Européen de Normalisation) or ISO (International Standardisation Organisation). Unfortunately, the work within these international organizations is quite slow.

As there is as yet no uniform EU legislation on food contact paper and board, it is only natural that there are no standardized migration tests for paper and board either. It was quite quickly shown that the official liquid simulants used for plastic materials are not suitable for testing paper and board. Olive oil, which is used as a fat simulant, was unsuitable even for plastic coated paper and board [76, 77]. However, the alternative fatty food simulants, iso-octane and ethanol, were found to be suitable for overall migration testing of paperboard in a migration cell.

As most paper and board for food contact is intended for packaging of dry, non-fatty food, it has been important to define a suitable simulant for this kind of food. Tenax is recognized by the CoE Committee of Experts as a potential simulant for dry food. Tenax is a registered trademark for modified polyphenylene oxide (MPPO). It is a porous polymer which efficiently traps volatiles. Tenax is recognized by the European Commission in the "2nd amendment of Directive 82/711/EEC" for testing plastics as a substitute test medium for fatty food. Because of its thermal stability, Tenax is used for migration testing at elevated temperatures [78]. Thus, Tenax is mentioned in Directive 97/48/EEC for testing plastics, albeit only as a substitute for olive oil for high temperatures [79].

There are no standardized methods for migration testing using Tenax. However, there is a test method for overall migration in the form of a European pre-standard for plastics used at high temperature [80] and a proposed method for the determination of overall and specific migration from microwave susceptors [81]. These methods use Tenax as food simulant. Tenax is the preferred absorbent for testing microwave susceptors, although a reduction factor is said to be needed to relate migration results to those expected for foods [70].

In summary, it is somewhat anomalous that Tenax is recognized on the one hand as a dry, non-fatty food simulant for testing fiber materials, and on the other as a substitute fatty food simulant for testing plastic materials. It was therefore necessary to study Tenax as a food simulant and to develop migration tests for paper and board.

Just recently, Summerfield and Cooper studied methods for testing migration from paper and board into food [82]. They carried out migration tests using many foods (icing sugar, flour, rice, cakes, pastries and pizza), Tenax and a so-called semi-solid simulant (40% celite, 35% water and 25% olive oil). The migrants studied were phthalates (DBP and DIBP) and DIPN. Tenax was found to be a suitable food simulant for dry foods and dry "fatty foods" such as pastries and cakes. It was also found to be a suitable simulant for pizza base at higher temperatures for short contact times. However, the migration was in some cases a little higher in food than in Tenax. For example, phthalate migration was higher in rice than in Tenax tested similarly in a migration vessel. The tests used are therefore not appropriate for regulatory purposes.

3.7 Migration modeling

In many cases, compliance testing for plastic materials is time consuming and expensive due to the many existing specific migration limits. Migration modeling has been studied for years with the aim of reducing the number of migration tests. These investigations indicate that migration from polymers obeys Fick's diffusion law [83] and that migration is predictable. A reasonable prediction of migration in many practical cases is achieved when two fundamental constants are known: the partition coefficient ($K_{P/L}$) of the migrant between the plastic (P) and the food or simulating liquid (L) and the diffusion coefficient (Dp) of the migrant in the plastic. However, there is some discussion over the assumptions made concerning partition coefficients and how to take into account the swelling of the polymer. These models are discussed elsewhere [84, 85, 86, 87, 88, 89, 90, 91, 92, 93].

Predictive migration models for polymers are already so well established that the European Commission intends to allow their use as one quality assurance tool for plastics. Consequently, in the Practical Guide, which is an informative document of regulations on all food contact materials published by the European Commission, it is stated that "*when it can be demonstrated by generally recognized diffusion models that the amount of substance in the material is such that the limit(s) cannot be exceeded in any foreseeable conditions"* the migration tests can be avoided [94].

As migration from paper and board has been studied much less than migration from plastics, the modeling of migration from fiber materials is only just starting. Models created for plastic materials are based on a large database of the diffusion constants of additives in polyolefins and on assumed partition coefficients. The same approach was recently applied to fiber materials and for the study of functional barriers, for example plastic-coated board [95, 96, 97].

A different approach was used when the gas diffusion rate was investigated in model fiber networks which closely resembled real paper [98, 99]. In these studies, molecular diffusion was simulated by letting random walkers move through the uncoated pulp sheet.

Experimental studies of high-density papers used as barrier materials have shown that pinholes, even in small numbers, increase the gas transmission rate through uncoated greaseproof paper. When the pinholes are blocked with coating, the fibers' contribution to barrier formation becomes significant [100]. It is therefore important to understand how the fiber network itself slows down gas diffusion.

4 EXPERIMENTAL

Materials, instrumentation and analytical procedures are described briefly in this section. More detailed information can be found in papers I-VI.

4.1 Materials

All chemicals and solvents used were analytical grade in purity and obtained from commercial sources like Merck (Germany) and Rathburn (UK). All compounds used for quantification were purchased from commercial sources and are listed in papers I-VI. The Tenax used in the migration tests was Tenax TA 60-80 mesh (Chrompack, the Netherlands).

Samples for developing the determination of the total content of hydrocarbons in printed paper were heat-set offset printed at KCL. Initially, the pure mineral oil solvent of the ink was

obtained from the ink manufacturer and used as a reference, but later a straight chain alkane series with the same boiling point range was used, for example Florida TRPH Standard (Restek, USA) (I).

The samples used to develop methods for testing barriers were commercial paper plates. In one case the food contact layers was made of bleached pulp, while in the others it was plastic. The surfaces of the plastic layers were identified by IR using the ATR technique to be polyethylene (PE), polystyrene (PS) and nitrocellulose (NC). The thicknesses of the plastic layers were not known (II).

Samples to study what potentially hazardous substances paper and board packagings might contain and to develop migration tests using Tenax and/or foods at near ambient temperature were obtained from packaging manufacturers. The packagings to be used in the study were chosen together with the manufacturers. Packagings were not obtained from the store, because the necessary information would then have been missing. In addition, it was convenient to have empty, unused packaging. The brands, printing methods and varnishes (if any) were known for all samples. Working together with the manufacturers was very important as it enabled additional samples (packagings, inks, adhesives, etc.) and additional information to be obtained when needed during the study. The packaging samples studied are listed in Table 1 (III, IV).

The two foodstuffs studied were purified and crystallized refined extra white sugar with a fine grain size (0.35—0.41 mm) obtained from a sugar factory (III) and bread rolls made of wheat flour purchased from a grocery store (IV).

Table 1. Empty packaging samples studied in papers III and IV.

	Printing method	Material	Intended use	Supplier
1	4*offset, varnish	boxboard	cereals	A
2	5*offset, varnish	boxboard	cereals	A
3	6*flexo	paper	flour	A
4	5*offset, varnish	boxboard	rice	A
5	2*flexo	corrugated	pasta	A
6	6*flexo	paper	cereals	A
7	1*flexo	kraft paper	flour	A
8	4*offset, varnish	boxboard	chocolate	B
9	2*offset, varnish	boxboard	chocolate	B
10	5*offset, varnish	boxboard	chocolate	B
11	flexo	paper	sugar	C
12	flexo	paper	sugar	C
13	flexo	boxboard	sugar	C
14	offset, varnish	boxboard	chocolate	D
15	offset, varnish	boxboard	chocolate	D
16	offset, varnish	boxboard	hamburger	D
17	flexo, PE-coated	paper	pet food	E
18	offset, varnish, PE	solid board	ice cream	F
19	offset, varnish	boxboard	hamburger	G
20	offset, varnish	boxboard	hamburger	G
21	offset, varnish	boxboard	apple pie	G
22		paper plate	paper plate	G
23	varnish	paper plate	paper plate	G
24	varnish	paper plate	paper plate	G
25		paper plate	paper plate	G
26	3*flexo, wax	corrugated	strawberry	H
27	2*flexo	corrugated	pizza	H
28	3*offset	corrugated	fatty	H
29	4*offset	corrugated	liquorice	H

n* = n color printing

boxboard = folding boxboard (board containing mechanical and bleached sulfate pulp)

Samples to investigate what potentially hazardous substances ovenable boards might contain and to develop a migration test using solid food simulant (Tenax) for high temperature applications were obtained from the board manufacturer. The ovenable boards had either a plastic coating or a dispersion coating and are listed in Table 2 (V).

Table 2. Ovenable board samples studied in paper V.

Code	Board grade	Clay coating	Binder in clay coating	Plastic or dispersion coating (g/m^2)
SBS/PET40	SBS	no	no	40 PET
SBS/PET22	SBS	no	no	22 PET
SBS(coat)/PET40	SBS	yes	acetate	40 PET
HYSBS1/PET35	HYSBS 1	yes	acetate	35 PET
HYSBS2/PET35	HYSBS 2	yes	SB	35 PET
HYSBS1/D1	HYSBS 1	yes	acetate	SB-based dispersion
HYSBS2/D2	HYSBS 2	yes	SB	acrylate-based dispersion
SBS/PP1	SBS	no	no	20 PP
SBS/PP2	SBS	no	no	20 PP/PP

SBS = board containing solid bleached sulfate pulp

HYSBS = board containing high yield pulp and solid bleached sulfate pulp

SB = styrene-butadiene

PET = polyethylene terephthalate

Samples for migration modeling were laboratory pulp sheets made at KCL. The sheets were made of birch kraft pulp beaten in a PFI beater. The beating degree (number of revolutions) was varied in order to produce sheets with different porosities. Sheet grammage was 130 g/m^2. The sheets studied are listed in Table 3 (VI).

Table 3. Laboratory pulp sheets studied in paper VI.

Batch	Number of revolutions in PFI beater	Porosity measured by oil absorption method
A	2000	0.308±0.011
B	2000	0.320±0.006
C	1000	0.382±0.017

4.2 Instrumentation

Gas chromatography using both flame ionization (GC/FID) and mass spectrometric (GC/MS) detection were used in this work. Liquid injections were performed by automatic liquid samplers, but gas injections in experiments for migration modeling were performed manually. Three different GC/FID and GC/MS instruments were used, and the instruments and columns are presented in Table 4. The detailed GC and MS parameters can be found in papers I-VI.

Infrared spectroscopy was used for characterization of some extracts or evaporation residues. Spectra of extracts were obtained from a thin film cast on a KBr window. The surfaces of some samples were analyzed by IR using the ATR technique, for example to identify the plastic layers or to check whether the board had a varnish layer or not.

Table 4. Instrumentation used in the study.

Instrument	**Column length x i.d. x film thickness**	**Analyses**
HP 5890A GC FID	DB-1 15 m x 0.25 mm x 0.25 μm (J&W Scientific)	Quantification of mineral oil (I) Quantification of model compounds (II)
HP 5890 Series II Plus GC HP 5972 Series Mass Selective Detector	HP-5 30 m x 0.25 mm x 0.25 μm (Agilent Technologies)	Identification of unknowns and quantification of model compounds (II) Screening of potentially hazardous substances (III, V) Quantification of alkylbenzenes (IV)
HP 5890 Series II Plus GC VG 70/250 SEQ MS (low resolution mode)	Ultra-2 25 m x 0.20 mm x 0.11 μm (Agilent Technologies)	Quantification of phthalates (III)
HP 5890A GC FID	HP-1 30 m x 0.25 mm x 0.25 μm (Agilent Technologies)	Quantification of model compounds' diffusion through pulp sheet (VI)
FTIR Nicolet 740 ATR and KBr		Characterization of extracts (KBr) (I,V) Identification of samples' surfaces (ATR) (II)

4.3 Methods for testing barriers in food packaging materials

The basic rules necessary for testing migration, including simulants, are given in the 1982 directive for plastics (82/711/EEC). The simulants given in the directive are water, 3% acetic acid, 15% ethanol and olive oil [101]. However, alternative test media for olive oil were being studied back in the 1980s because of the difficulties related to the use of olive oil. These more powerful test media included iso-octane and ethanol (95%) [102, 103, 104, 105, 106, 107, 108, 109, 110]. In 1997, Commission Directive 97/48/EC was published, introducing the above mentioned volatile test media and MPPO (modified polyphenylene oxide) as alternative fatty food simulants [76]. In this study the test media used were 94% ethanol and iso-octane. Later in the text the word "simulant" is used for these test media.

As stated in directive 93/8/EEC, "*Verification of compliance of migration into foodstuffs with the migration limits shall be carried out under the most extreme conditions of time and temperature foreseeable in actual use*" [111]. For paper plates, the test conditions chosen were 2 hours at 70^{o}C, because it was considered that the paper plates may be employed for periods of more than one hour at temperatures between 40°C and 70°C, for example with hot soup. However, a later directive 97/48/EC states that the maximum temperature for volatile test media is 60°C, but this was not known at the time this study was carried out.

Tests were performed using commercial migration cells (Calipac cells manufactured by TECHPAP, France) in which the food contact surface of the specimen was exposed to the food simulant (Figure 1). This is known as a single side migration test. Solutions of model compounds were spiked onto the non-food contact layer of the paper plates, which were then placed into the migration cells. The amounts of model compounds added ranged from 3 mg to 10 mg. The total volume of the spike solution was 100 µl, and several spots were made on each plate. Pre-heated migration cells were set up and pre-heated simulant was added (200 ml). On completion of the test, 10 ml of simulant was taken for GC analysis. Before the GC analyses the simulant was concentrated by gentle evaporation under nitrogen. Blank tests were carried out with the migration cells without samples.

The model compounds were chosen to represent different molecular sizes and polarities. The model compounds selected were those that may originally be present in fiber material and which are also easy to determine by gas chromatography.

The most suitable compounds seemed to be vanillin, docosane and abietic acid. Abietic acid is a resin acid, and represents wood extractives and/or resin glue used as sizing agent. Docosane represents a paraffin hydrocarbon, such as may originate from recycled fibers (e.g. printing inks) and/or chemicals used in the pulp and paper industry (e.g. anti-foaming agents). Vanillin represents a low molecular mass aldehyde, such as may be present in fiber material (e.g. from degradation of lignin) (II).

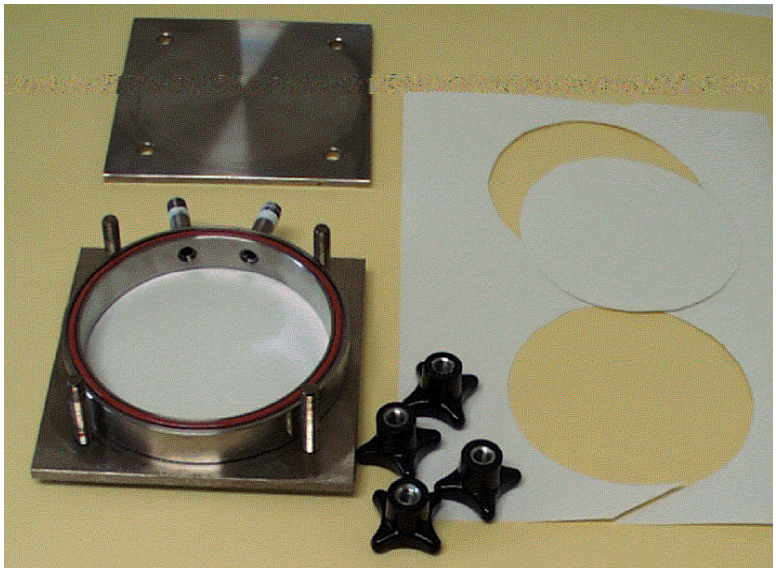


Figure 1. Commercial migration cell used in the test. A round sample is cut from the paper plate (or from the board as in the figure). The cell is put together and simulant is introduced.

4.4 Screening for potentially hazardous substances in fiber-based packagings

At least 50 g of the paper or board packaging (Table 1) was cut into small pieces (about 1 cm × 1 cm), which were then mixed. In the case of large packagings, samples were taken from the heavily printed area and from joints including adhesives. Small packagings were cut up completely. Five gram amounts of the cut pieces were used in the analysis. A mixture (100 µl)

of internal standards (BHT and C_{21} or C_{22}) in hexane was added to the cut pieces of packaging. The amount of internal standard was approximately 500 µg, corresponding to 100 mg/kg in the sample. Extraction was performed by shaking in a conical flask with hexane (45 ml) for half an hour. The hexane extract was transferred to a volumetric flask (50 ml) and used for compositional analysis of packages as well as for quantification of selected substances, for example phthalates, alkylbenzenes and hydrocarbons (see 4.5).

For compositional analysis, 1 ml of the hexane extract was evaporated under a stream of nitrogen to a volume of 50 µl (approximately) and analyzed by GC/MS in scan mode. Electron impact (EI) spectra were recorded at 70 eV and the scanning range was 40 to 600 amu.

Compositional analysis screens for potentially hazardous substances thought likely to migrate into food. The main criterion in compositional analysis was the content of the substance in the packaging: the higher the content, the more likely that the substance will migrate into food. The contents of the substances were estimated by comparing their peak areas with the internal standards' peak areas. Generally, the "limit of interest" was 1 mg/kg in the packaging material. On the other hand, the substances assumed to originate from the fiber material on the basis of the tentative GC/MS identification were of greater interest than substances originating from printing inks or adhesives.

Most of the chromatographic peaks from the extracts could not be identified from the commercial mass spectra library (Wiley). However, the exact identification of the substances was not essential at this stage. The next step was to study whether these known or unknown substances migrated into the food simulant (Tenax). For these migration tests, a user library of mass spectra was built up. Chromatographic peaks regarded as interesting because of their high content and/or tentative GC/MS identification were included in the user MS library. Those unknown peaks in the user MS library that were found again from the Tenax were studied in more detail. This approach significantly reduced the number of unknown peaks that had to be identified. Identification of the unknowns was based on the commercial MS library suggestions and mass spectra, but the main aid was information on substances possibly present in fiber-based packaging materials. Finally, the unknown was identified, if possible, using a model compound.

4.5 Quantification of selected compounds

In Paper I, a method was developed for determining the residual mineral oil solvent content of print. The method was later adapted for the quantification of selected compounds in packaging samples.

Packaging samples were extracted with hexane as described above (4.4).

Phthalates were determined in the hexane extracts by GC/MS using SIM detection. The following specific ions were monitored: m/z 220 (BHT), 163 (dimethylphthalate), 149 (other phthalates) and 129 (adipates, especially diethylhexyladipate). Phthalates were determined quantitatively using a one-point calibration. The calibration mixture contained DIBP, DBP, DEHP and DEHA (10 µg/ml) with BHT (50 µg/ml) as internal standard (III).

Hydrocarbons were determined in the hexane extract by GC/FID after aluminum oxide purification. An aliquot of hexane extract (10 ml) was transferred to a test tube and a spoonful of dry aluminum oxide was added. After shaking (30 sec), the extract was evaporated under a stream of nitrogen to approximately 1 ml. Hydrocarbons were determined quantitatively using one-point calibration (I). The commercial calibration mixture contained alkanes with even number of carbon atoms from C_8 to C_{40} (50 µg/ml).

Alkylbenzenes were determined in the hexane extract by GC/MS using scan detection. The total content of alkylbenzenes was the sum of the 18 homologous alkylbenzenes. As no model compounds or mixtures were available at the beginning of the study, the quantification was based on docosane, assuming that the response factor for alkylbenzenes was one. Heneicosane was chosen as the basis for quantification, as it eluted shortly after the alkylbenzenes. Later, the alkylbenzene mixture used in the printing ink was obtained from the ink manufacturer, and it was confirmed that the compounds quantified as alkylbenzenes were the same as in the ink (IV).

4.6 Migration test using Tenax at low temperature

As large a sample as possible and practical (0.4 dm^2 or 0.07 dm^2) was used for the migration test. The amount of Tenax was 4 g per square decimeter, as described in the draft prCEN method for overall migration at high temperatures [112]. Tests were performed in triplicate. A method blank (migration test without sample) was prepared alongside the samples. A simulant blank (extraction of Tenax without the migration step) was tested occasionally.

Samples were exposed to the simulant using single-side contact. The migration vessel was a closed glass jar considered to be gas-tight (Figure 2). Internal standard (BHT and C_{21} or C_{22}) solution was added to the migration vessel simultaneously with the sample.

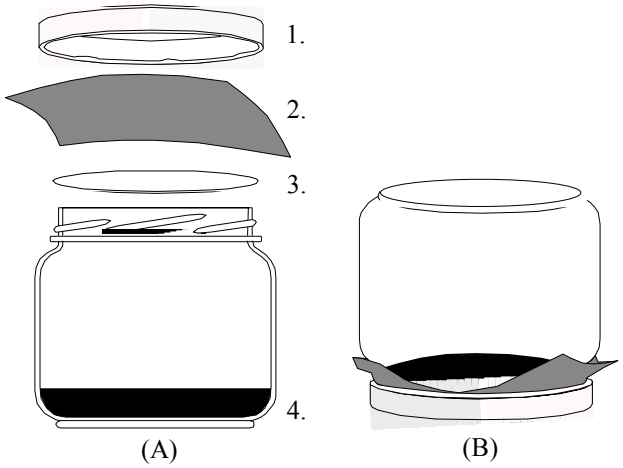


Figure 2. Experimental set-up for migration test with Tenax. (A) Preparation for test: 1. Lid, 2. Aluminum foil, 3. Sample, and 4. Tenax. (B) Exposure to Tenax: glass jar upside down.

Exposure temperature and time were based on the Commission Directive 97/48/EC "2nd amendment of Directive 82/711", see Appendix 1. The tests were performed in triplicate and a method blank (migration test without the sample) was prepared alongside the samples. After exposure, Tenax was extracted with ethyl acetate using an ultrasonic bath (2 min) and the extract transferred to a volumetric flask. The ethyl acetate extract was analyzed by GC/MS in scan mode (III, IV).

4.7 Migration test using Tenax at high temperature

4.7.1 Exposure to Tenax

Ovenable trays were constructed manually from A4 board samples. A collar from a commercial migration cell was placed on the sample to outline an area of 1 dm². Tenax (4 g) was poured onto the outlined area of the food contact surface (Figure 3). As a blank, the Tenax was placed on a migration mount (metal plate) and the contact area was outlined with a migration cell collar as when samples were used.

The sample was placed in an oven and heated under the appropriate test conditions (temperature and time). The sensor of a digital thermometer was placed in the oven to measure the air temperature slightly above the sample. The oven reached the pre-set temperature a few minutes after introduction of the sample. The temperature tolerance was ±5 °C. After the predetermined exposure time, the Tenax was divided into two vials: one for gravimetric determination of the overall migration and the other for GC/MS analysis of specific migration (V).

Figure 3. Experimental set-up for migration test using Tenax at high temperature. The migration collar outlines an exact area of 1 dm^2, which is covered by the Tenax. The steel rack makes sample handling easier.

4.7.2 Overall migration test gravimetrically

Tenax was extracted twice with diethyl ether as described in the method proposal for CEN [113]. Diethyl ether (20 ml) was added to a vial followed by manual shaking for one minute. After centrifugation the diethyl ether was transferred to constant weighed vials. The extraction and centrifugation were repeated with a 15 ml portion of diethyl ether. The extracts were then combined and evaporated to dryness under a stream of nitrogen. The evaporation residue from the extract was taken as the overall migration. Constant weight was considered to be achieved when the difference between two consecutive weighings was equal to or less than 0.5 mg.

The area of the board sample in direct contact with Tenax was 1 dm². The overall migration into the Tenax via the gas phase from the board was negligible. The overall migration was therefore calculated using the board area 1 dm^2.

The overall migration into Tenax is given by

$$M = m_r \times \frac{m_t}{m_v} \times 1000 \qquad (1)$$

where: M = overall migration into Tenax (mg/dm^2)

m_r = residue after evaporation (g)

m_t = amount of Tenax in contact with the sample during testing (g)

m_v = amount of Tenax in the vial after the oven test (g)

The blank determination was carried out in three replicates and the average of these was subtracted from each individual test result. The test result for each test specimen was the average of three replicates. No reduction factors were used (V).

4.7.3 Specific migration test with GC/MS

Tenax was extracted using a similar diethyl ether extraction as described for overall migration. An internal standard (cyclohexylbenzene) was added to the extract for specific migration testing. The extract was evaporated under a stream of nitrogen at room temperature

to a volume of 5 ml and analyzed by GC-MS. The concentration criterion used to distinguish between the different substances was based on the following assumptions: EC legislation on the specific migration limits (SML) for carcinogenic compounds (10 µg/kg food), the conventional ratio of 1 kg food in contact with 6 dm^2 packaging, and a chromatographic response factor of one for both the internal standard and the substances that migrated into Tenax [73] (V).

4.8 Methods for studying migration into foods

4.8.1 Migration tests with rolls

Hamburger collars were tested using rolls as simplified hamburgers. The tests were carried out in triplicate and a method blank (roll without collar) was prepared alongside the samples. The collar was put tightly around the roll and wrapped with aluminum foil (Figure 4). The test conditions were the same as for Tenax (30 min, 70°C). After exposure, the rolls were cut into small pieces and extracted twice with hexane using an ultrasonic bath. The quantification of alkylbenzenes in rolls was performed as for board (IV).

Figure 4. Experimental set-up for migration test with roll. The hamburger collar was put around the roll and this was wrapped in aluminum foil.

4.8.2 Migration into sugar under real conditions

Migration of phthalates from sugar packs was investigated under real conditions. Phthalate levels in the sugar were determined before and after packaging. Sugar before packaging was received from the sugar factory, as were the sugar packagings, which were stored at room temperature at the factory. After storage a paper bag containing 1 kg of sugar was emptied into a glass jar and the sugar was mixed carefully. Two replicates of the sugar (10 g) were taken for analysis. A solution (50 µl) of internal standard (BHT) in hexane was added to the sample. Extraction was performed in a conical flask with hexane (10 ml) for half an hour, and the hexane extract was transferred to a volumetric flask (10 ml). Phthalates were determined in the hexane extract by GC/MS. The quantification of phthalates in sugar was carried out as for the packaging samples, although the concentration of the calibration sample was adjusted (III).

4.9 IR analyses

FTIR was used for characterization of some extracts or evaporation residues. Spectra of the extracts were obtained from a thin film cast on a KBr window with an FTIR instrument (I, V). The surfaces of the samples were identified by IR using the ATR technique (II).

4.10 Migration modeling

4.10.1 Porosity measurement

The porosity of the sheets was measured by weighing them before and after immersion (60 s) in silicone oil (viscosity 10 mPas). After immersion, the sheet surfaces were wiped until the gloss disappeared (VI).

4.10.2 Diffusion rate in air

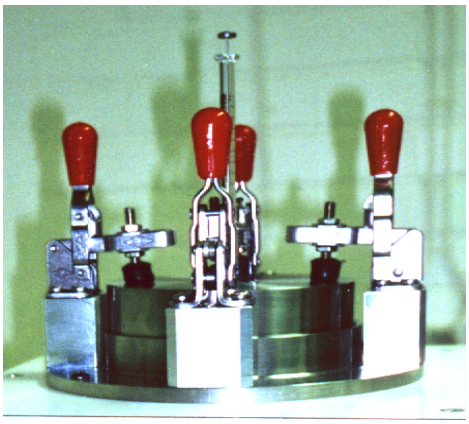
The diffusion rates for the model compounds in air were measured using a specially made tube (length 25 cm, internal diameter 6 mm) and gas chromatography. The tube ends were plugged with gas-tight septa. The model compound was introduced into the tube by piercing the septum with the needle of a syringe filled with the compound. The model compound was allowed to evaporate freely from the needle tip. Gas samples were taken from the other end of the tube with a gas-tight syringe. These samples (50 µl) were injected into the GC/FID. Samples were taken at intervals varying from 5 to 20 minutes (more frequent sampling was applied at the beginning) and this continued until a steady concentration of the model compound in the tube was achieved. This was double checked by removing the application syringe and taking gas samples from this end too. Areas of the chromatographic peaks were used to plot the curve describing the concentration increase within the tube (VI).

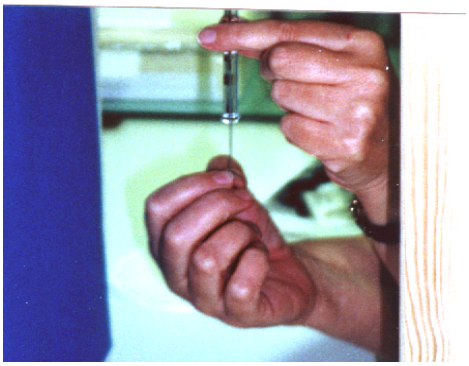
4.10.3 Diffusion rate through kraft pulp sheets

The diffusion of model compounds through kraft pulp sheets was measured using a specially constructed test cell (Figure 5) and gas chromatography. For these experiments, specimens of size 1 dm^2 were cut from the laboratory sheets. The edges of the specimens were treated with silicone glue in order to prevent leakage. Eight sheets were stacked together in order to slow down diffusion and make the measurement easier.

The test cell was made of stainless steel and was divided into two subcells of equal volume (ca. 200 ml). After placing the model compound in the eight small weighing boats in the lower subcell, the two subcells were pressed together tightly with the barrier (i.e. stack of eight kraft sheets) in between. Similar gas samples (50 µl) were taken from both subcells at almost equal times with a gas-tight syringe. This avoided any pressure gradient across the barrier and allowed any leakage to be observed. The samples were injected into the GC/FID. Sampling at intervals varying between 3 and 20 minutes was continued until equilibrium was reached between the bottom and top subcells. The areas of the chromatographic peaks at

about ten different time points were used to plot the curve of increasing concentration in the top subcell as compared to the concentration in the bottom subcell (VI).





A **B**

Figure 5. A) Preparation for the test to determine the diffusion of model compound through pulp sheets using a specially constructed test cell. B) Performing the test.

5 RESULTS AND DISCUSSION

5.1 Testing barriers in food packaging materials (II)

Four paper plate samples were tested using model compounds. The results obtained for the transfer of these model compounds through the barrier layer are presented in Table 5.

Table 5. Results for transfer of model compounds through the barrier layer. Tests were carried out in the migration cell for 2 hours at 70°C.

Sample	Docosane		Vanillin		Abietic acid	
	ethanol	iso-octane	ethanol	iso-octane	ethanol	iso-octane
1 PE	++	+++	+	-	++	-
2 PS	++	+	++	+	+	+
3 NC	+	-	++	+	+	-
4	++	+++	++	-	++	+

Samples:

1: Polyethylene coated, virgin fiber paper plate

2: Polystyrene coated paper plate, virgin fiber paper plate

3: Nitrocellulose coated paper plate, virgin fiber paper plate

4: Recycled fiber paper plate, food contact surface virgin fibre

- = not detected in simulant

+,++,+++ = increasing concentration in simulant indicating increasing transfer of model compounds through the barrier layer

In nearly all tests the paper plates became completely wetted and in some cases some of the simulant evaporated off. This wetting may be due to pinholes in the plastic layer, to the thinness of the plastic, or to the type of plastic concerned. Nevertheless, wetting of the samples indicates that the barrier layers did not resist penetration completely.

Spiking with model compounds like vanillin and docosane is a very simple method and does not need expensive instruments. Reliable identification of the model compounds from the GC/FID chromatograms requires addition of a suitable internal standard.

Injection is always critical in GC, especially when several different solvents are used. With fast automatic injection vanillin was split into two peaks when the solvent was ethanol, but not with non-polar solvents like hexane and iso-octane. Splitting also occurred with the slightly polar column (HP-5). This splitting was avoided by using a glass wool plug in the liner, which improves evaporation of the sample in the injector.

Most of the unknown peaks in the chromatograms were impossible to identify by commercial MS library search. Phthalates, antioxidants and hydrocarbons were identified only as a groups of compounds. It was therefore clear that the identification of compounds in future work has to be based on additional aids, for example on a user MS library and on expertise in fiber-based materials.

5.2 Potentially hazardous substances present in fiber-based packagings (III, IV)

5.2.1 Qualitative analyses

All packaging samples received from the manufacturers (Table 1) were extracted with hexane and analyzed by GC/MS for potentially hazardous substances. The GC/MS chromatograms of concentrated hexane extracts could be grouped quite nicely according to fiber material and printing method. Actually, many of the chromatograms had only a few major peaks and these were identified. Figure 6 presents some of the typical chromatograms. Folding boxboards that contain mechanical pulp usually had more peaks due to the extractives present in the mechanical pulp. Offset printed packagings all had high peaks due to plasticizers – either phthalates or adipates – but the hydrocarbon contents varied considerably. Some of the folding boxboards were sized with AKD (alkyl ketene dimer), which produced three high peaks, namely distearic ketone (stearone), dipalmitic ketone (palmitone) and stearicpalmitic ketone. These compounds have high molecular masses and high boiling points, which means they were unlikely to migrate at room temperature. Similarly, some quite high peaks were

seen at the ends of some chromatograms of boxboards which, though originating from fiber material (extractives), were not of interest because of their high boiling points.

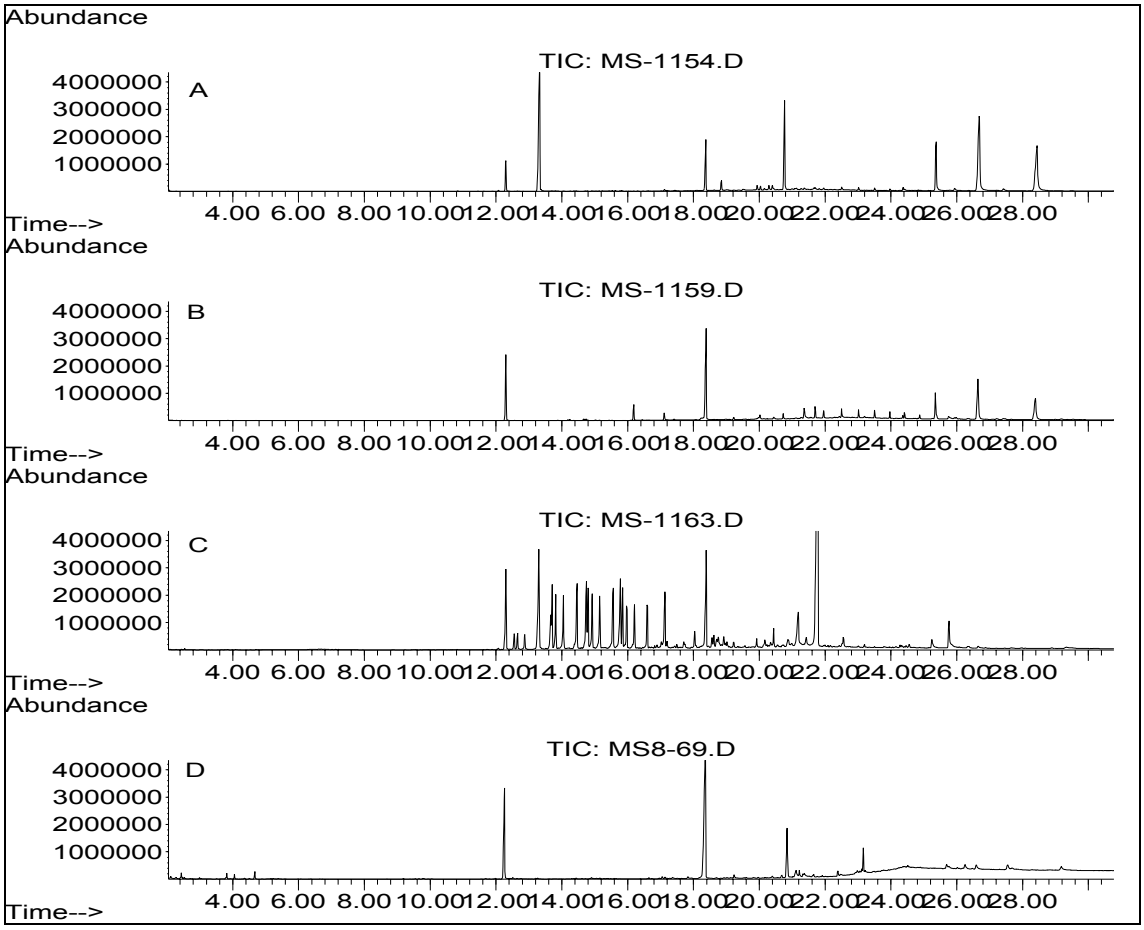


Figure 6. Typical GC/MS chromatograms of the hexane extracts of the four different kinds of packaging sample. A) offset printed solid board (contains only chemical pulp), B) flexo printed corrugated board (contains recycled fibers), C) offset printed folding boxboard (contains chemical and mechanical pulp) and D) flexo printed paper (contains only chemical pulp).

As described earlier, a user library of mass spectra was established. In this library, the peaks were named as follows: retention time, sample name and name of MS datafile. There are more than 40 entries in the user MS library at the moment. This user library was utilized when the chromatograms from the migration test with Tenax were examined. Many of the distinct peaks present in the chromatograms of packagings did not migrate into Tenax. This further reduced the number of peaks of interest for this study.

It was already known that offset printed packagings contain phthalates (used as a plasticizers in inks) and hydrocarbons (mineral oil used as ink solvent) (I). It was also known that both phthalates and hydrocarbons may migrate from packaging material into foods [l, 43, 39, 40, 41, 42, 44], and these compounds were therefore quantified in all samples (Table 6). Screening analysis, however, revealed that the most interesting compounds were phthalates and alkylbenzenes. In addition to these, another compound found in packagings was identified as 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (CAS 6846-50-0, hereafter called butyrate, but in paper IV TMPDiB). This identification was verified with a model compound after it was found to migrate significantly into Tenax. Butyrate is used in offset inks as a plasticizer or solvent component.

5.2.2 Quantitative analyses

Phthalates in packagings

18 out of the 30 samples studied had phthalate contents exceeding 5 mg/kg (Table 6). The most common phthalates were DEHP and DBP, which is in agreement with previous findings [42]. In addition, DIBP was found in many samples originating from several different suppliers. Diethylphthalate (DEP) was identified in one sample. No butylbenzylphthalate (BBP) was found in these samples (III).

Table 6. Contents of phthalates (DBP, DEHP and DIBP), alkylbenzenes (LAB), butyrate and hydrocarbons (CH) in unused packaging samples obtained from the manufacturers (mg/kg).

No.	Printing process	Material	DBP	DEHP	DIBP	LAB	Butyrate	CH
1	offset, varnish	boxboard	-	-	41	-	+	80
2	offset, varnish	boxboard	-	210	+	+	-	780
3	flexo	paper	-	-	-	-	-	10
4	offset, varnish	boxboard	-	-	30	+	+	610
5	flexo	corrugated board	-	-	-	-	-	80
6	flexo	paper	-	-	+	-	-	7
7	flexo	kraft paper	-	-	-	-	-	n.a.
8	offset, varnish	boxboard	43	81	-	+	+	80
9	offset, varnish	boxboard	-	20	-	-	+	230
10	offset, varnish	boxboard	-	-	-	+	+	n.a.
11	**flexo**	**paper**	**65**	**-**	**360**	-	-	60
12	**flexo**	**paper**	**100**	**-**	**450**	-	-	30
13	flexo	boxboard	-	-	-	-	-	20
14	offset, varnish	boxboard	-	260	-	+	+	830
15	offset, varnish	boxboard	-	9	-	+	+	400
16	offset, varnish	boxboard	7	31	-	+	+	270
17	flexo, PE-coated	paper	12	-	-	-	-	1290
18	offset, varnish, PE	solid board	-	-	-	+	+	500
19	offset, varnish	boxboard	38	430	-	670	+	790
20	offset, varnish	boxboard	31	400	-	+	+	230
21	offset, varnish	boxboard	130	170	-	+	+	580
22		paper plate	-	8	-	-	-	n.a.
23	varnish	paper plate	-	-	-	-	-	20
24	varnish	paper plate	-	-	-	-	-	5
25		paper plate, recycled	16	21	-	-	-	470
26	flexo, wax	corrugated board	-	-	-	-	-	n.a.
27	flexo	corrugated board	-	-	-	-	-	260
28	offset	corrugated board	-	-	-	-	+	n.a.
29	offset	corrugated board	-	-	-	-	+	250

- = below 5 mg/kg
\+ = identified but not quantified
n.a. = not analyzed

In most cases the origin of the phthalates was assumed to be offset printing. However, two of the flexo-printed samples (samples 11and 12 in Table 6) contained significant amounts of phthalates, and these packagings, which were intended for sugar, were studied in more detail. Both packagings had been manufactured in the same place using the same printing inks and adhesives but different papers. The unprinted and printed papers were analyzed separately, and were found not to contain phthalates (well below 5 mg/kg). It was therefore assumed that the phthalates originated from adhesives, which were analyzed semi-quantitatively for DIBP and DBP. The adhesive used for the bottom joint contained about 0.5% of DIBP and that for the side joint about 0.5% of DBP. Another of these sugar packs (sample 12 in Table 6) was studied further by migration testing (III).

Alkylbenzenes in packagings

Alkylbenzenes were identified in 10 out of 15 offset printed packaging samples (Table 6). Most samples contained only traces of alkylbenzenes, but one hamburger collar had an exceptionally high content of alkylbenzenes. More samples of that type of collar were obtained from the producer and analyzed, and these too were found to have high alkylbenzene contents (Table 7). One of these collars (C wide) was also subjected to migration testing (IV).

Table 7. Total contents of alkylbenzenes (LAB) and butyrate in the hamburger collars (mg/kg).

Sample	LAB	Butyrate
A (lightly printed)	70	35
B (lightly printed)	130	160
C narrow (heavily printed)	460	160
C wide (heavily printed)	500	190

5.2.3 Uneven distribution of compounds in packagings hampers migration testing (III)

For several practical reasons that are explained later, the migration testing of finished packagings cannot be carried out using the whole packagings, and smaller samples must be used instead. However, the distribution of substances in the packagings might be uneven, as was the case in the sugar packs studied.

Because it had already been found that adhesives were the source of phthalates, it was presumed that their distribution in the packaging was uneven. Five different samples were analyzed to investigate the distribution of phthalates in packaging. The size of the sample corresponded to the sample used later for the migration test. The results are presented in Figure 7. The bottom contained the bottom adhesive with the DIBP, the side joints contained DBP, but the lower (near bottom) also contained DIBP.

The sample chosen for the migration test was cut from the heavily printed area and did not contain any joints. Before analysis, a pile of packagings had been stored in aluminum foil with the surface of the sample taken for the migration test against the bottom of another packaging. Thus, the high concentration of phthalates in the migration sample was obviously caused by the set-off effect. At the sugar factory the packagings are either filled immediately or stored; consequently, the same set-off could take place in real life.

The results show that, in this case, the distribution of phthalates throughout the sample was extremely uneven. In fact, the lowest concentration differs from the highest by a factor of almost 1000. This makes it virtually impossible to obtain a sample from this sugar packaging that would be representative and thus suitable for migration testing.

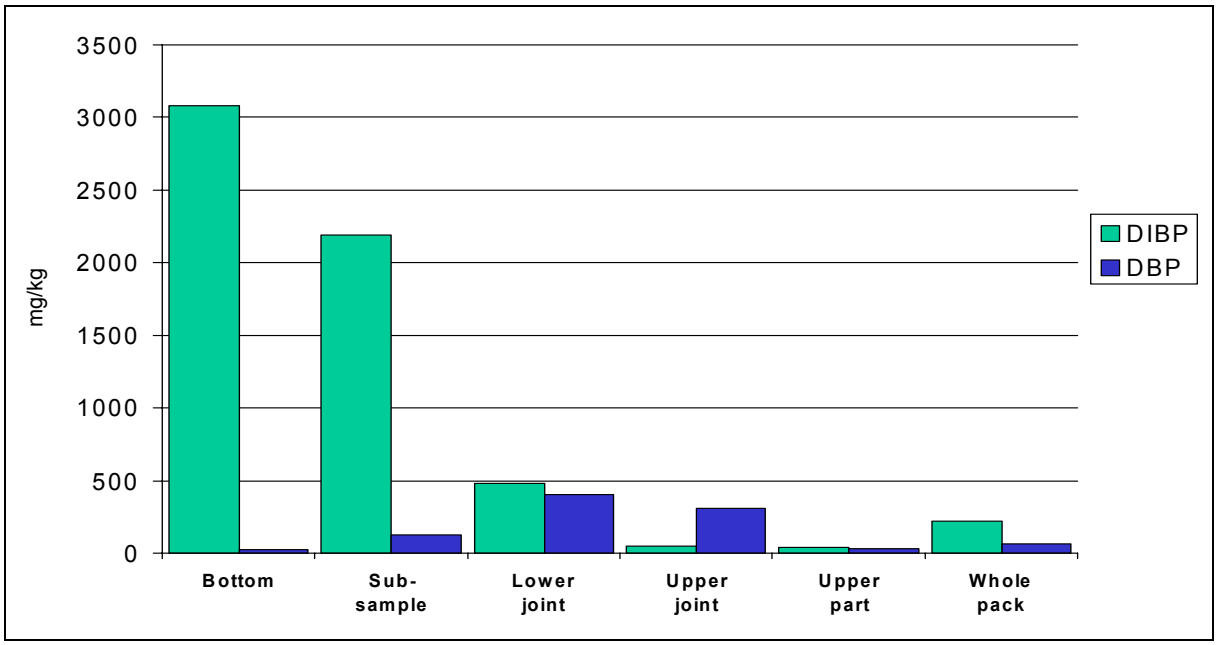


Figure 7. Contents of phthalates in different samples cut from sugar packagings and in a homogenized sample of several packagings (Whole pack). Sub-sample is the sample used later for migration testing.

5.3 Migration into Tenax and foods at low temperature (III, IV)

5.3.1 Migration tests using Tenax

The best way of performing a migration test would be to fill the entire packaging with a food simulant such as Tenax. In practice, however, samples normally have to be taken from the packaging. The samples chosen should contain the highest concentration of those components whose migration is to be tested (e.g. compact printed area).

The second best way of performing a migration test with food simulant would be to use the EU convention of 1 kg of food in contact with 6 dm^2 of food contact material in a migration vessel. The convention of 1 kg/6dm^2 corresponds well with the food packaging used in practices for products like sugar, flour, butter and ice cream. However, there are examples in which the ratio of food to packaging material differs significantly from the convention. Besides, even the convention is not practical because of the lightness and the extremely high price of Tenax (1 g costs 20 euros). For example, a sample of 0.4 dm^2 would require 67 g of

Tenax, which would cost about 1000 euros; also, its volume would be approximately 250 ml which is also impractical.

A more practical suggestion is to use a ratio of 4 g of Tenax in contact with 1 dm^2 [80]. This suggestion is mainly based on the fact that 4 g just covers 1 dm^2. There is some evidence that even smaller amounts of Tenax will trap compounds satisfactorily [82].

Tenax has the advantage that it can be regenerated and used again several times, although levels of impurities and decomposition products increase with time, ultimately rendering it no longer usable.

As stated earlier, the sample for the migration test should be chosen in such a way as to represent the highest possible content of different substances, for example compact printing or joints containing adhesives. The migration of phthalates from a sugar pack and alkylbenzenes from a hamburger collar are presented in Table 8 (III, IV).

Table 8. Migration into Tenax of phthalates from a sugar pack and alkylbenzenes from a hamburger collar.

Packaging	**Substance**	**QM**	**Migration into Tenax (mg/kg)**		
		mg/kg	% of QM	Ratio 4 g/dm^2 (migration test)	Ratio 1 kg/6dm^2 Calculated using EU convention
Sugar pack	DIBP	2190	91%	540	12.2
Sugar pack	DBP	125	69%	23	0.5
Hamburger collar	LAB	460	15%	52	(1.4)

QM = concentration in the packaging sample used for migration testing
% of QM values calculated by dividing the levels found in Tenax by the total quantities of constituents present in packaging sample used for the migration test

Table 8 shows quite clearly that the results from migration tests are not unambiguous. The ratio of Tenax to packaging sample used in the test was 4 g/dm^2. The migration test therefore

seems to give very high results. In the case of the sugar packs, the ratio of sugar to packaging material was very close to the EU convention, thus the calculated results for phthalates should be reasonable. However, with the sugar packs there was another reason why the results of the migration test were debatable. This was the extremely high content of phthalates, especially DIBP, in the sample used for the test (see Figure 7) (III).

In the migration testing of hamburger rolls, the collar was placed around the roll to simulate the actual use in hamburger restaurants. The contact conditions were 24 g/dm^2 of roll, as the rolls were very spongy. This differed significantly from the EU convention ratio of 1 kg/6 dm^2. For this reason, the value calculated using the EU convention does not apply to hamburger collar and LAB (the value 1.4 in Table 8) (IV).

There was only one sample that contained recycled fibers. This packaging, made of corrugated board and intended for pizzas, contained 8.2 mg/kg of DIPNs (diisopropylnaphthalenes). DIPNs are well-known contaminants of recycled fibers and have been shown to migrate into foods [56,57,58,59]. Testing of this sample with Tenax for 30 min at 100°C showed significant migration of DIPNs. The total content of hydrocarbons in the pizza packaging was 260 mg/kg, corresponding to alkanes C_{17}-C_{44} (Table 6). It was estimated that the migration of the hydrocarbons into Tenax was less than 10% of the original content in the packaging. Of the hydrocarbons found to have migrated, the one with the highest boiling point was tritriacontane (C_{33}). Tritriacontane has roughly the same boiling point as the ketones originating from the AKD sizing agent present in the packaging. The migration of these ketones from the same pizza box was very small, but nevertheless detectable.

5.3.2 Migration of phthalates into sugar (III)

Migration of phthalates into sugar was studied in a real life situation using blank sugar obtained from the sugar factory. Consequently, no migration tests were performed on the sugar. Before packing, the sugar was found to be phthalate-free (less than 0.5 mg/kg). Three identical packs of sugar were stored for four months at room temperature at the sugar factory. After storage, the sugar and its packaging were analyzed for phthalates. The packed sugar contained 2.2—2.6 mg/kg of DIBP and 0.5—1.0 mg/kg of DBP. The corresponding

packagings contained 95—98 mg/kg of DIBP and 56—64 mg/kg of DBP. Because the sugar from the factory storage was phthalate-free, it was assumed that the phthalates in the sugar had all migrated from the packaging. The weight of the paper wrap was 8.7 g. Consequently, migration from packaging into sugar was 74% for DIBP and 57% for DBP. Migration percentage values are calculated by dividing the levels found in food by the total quantities of constituents present in the packaging sample used for migration testing (III).

The above figures indicate that there is significant migration into packed sugar of phthalates originating from adhesives. It has been reported that impregnated low molecular mass model substances migrate readily from plastic materials into dry foods such as powdered milk and cereals, but not into sugar [114]. As migration is affected, among other things, by the partition coefficient of the migrant between material and food, it is clear that conclusions cannot be made about migration from fiber materials based on results obtained with plastics.

5.3.3 Migration of alkylbenzenes and butyrate into rolls (IV)

Hamburger rolls were used as simplified food simulants instead of whole hamburgers. Migration of alkylbenzenes (LAB) and butyrate into the roll was studied in the migration test, which was designed to simulate as closely as possible the actual situation in hamburger restaurants. After the migration test, the rolls and collars were analyzed for LAB and butyrate. The roll contained 2 mg/kg of LAB and 1 mg/kg of butyrate, while the corresponding collar contained 460 mg/kg of LAB and 160 mg/kg of butyrate. The weight of the collar was 0.23 g. Consequently, migration from collar into roll was 4% of LAB and 6% of butyrate. Hence, the migration percentages for these printing ink components were very similar (IV).

The total LAB content varied from collar to collar depending on the amount of printing ink used (Table 7). However, the relative contents of individual LAB compounds were similar in different collar samples. The alkylbenzenes also migrated similarly into Tenax and rolls. Consequently, the pattern of the LAB profile in the chromatograms was quite identical.

5.3.4 Risk assessment for the migration studied

In order to get any idea of the possible risk that the migration of the substances studied might pose to consumer health, the toxicological properties of the substances have to be known. Migration of all these substances was between 0.5 and 5 mg/kg, and SCF therefore requires only a limited testing of toxicity. This reduced testing includes three types of data, namely bioaccumulation (for which the octanol/water partition coefficient can be used as a surrogate measure), three mutagenicity tests and a 90-day oral study. The rationale for this reduced set of tests is that, for this low migration range, intakes from food would not exceed 0.1 mg/kg bw/d, and at this relatively low level of exposure, long-term, reproductive or teratogenic effects are extremely unlikely to occur [17].

The specific migration limit (SML) for phthalates is suggested to be 3 mg/kg based on their Tolerable Daily Intake (TDI) of 0.05 mg/kg bw/d and the conventions described earlier (3.3.1). Migration of DIBP into sugar was as high as 2.2 mg/kg. For calculation of SML it is assumed that an average person consumes up to 1 kg of the food in question per day, all wrapped in the packaging in question. In reality, it is estimated that one person consumes less than 30 g per day of sugar packed in the one kilogram sugar pack studied. Consequently, the SML value is clearly overestimated.

In the risk assessment report published by the European Commission for LAB, the margin of safety (MOS) for oral exposure is calculated for consumers using a NOAEL (no observed adverse effect level) value of 50 mg/kg/d derived from reproductive toxicity. The consumer exposure used in the report comes from the LAB traces present in detergents. The oral exposure is estimated to be 0.00019 mg/kg/d due to deposits on dishes. The calculated oral exposure based on the migration results from this study (2 mg/kg) is 0.03 mg/kg/d The calculation is based on the widely used assumption that a 60 kg person consumes daily 1 kg of food packed in the material in question. However, the margin of safety (MOS) for this higher oral exposure is still 1656, which is very acceptable (IV).

5.3.5 Comparing migration into Tenax with migration into foods

As mentioned earlier, migration of phthalates into sugar was studied under real conditions, while migration of LAB into rolls was studied by migration testing. The test with the rolls was performed by putting the collar around the roll to simulate the actual situation in hamburger restaurants. While this particular test was easily performed, it is impossible to develop different migration tests for all foods and use of packagings. Migration tests using migration vessels and food simulants therefore have to be developed. The main criterion for migration testing with a food simulant is that migration into the simulant must be consistent with migration into the food. In fact, if the test is used for regulatory purposes, migration should be overestimated to some extent. Naturally, the test with simulant has to be more feasible than the test with food. The latter criterion is quite obvious in the case of Tenax, but the first criterion has to be evaluated carefully. Figure 8 presents the results for the migration of phthalates and LAB into Tenax and food. For LAB compounds, the relative standard deviation of three replicates was 14% in both migration tests. For phthalates, the repeatability of the quantification in sugar and the migration test with Tenax ranged from 7% to 21% (five replicates).

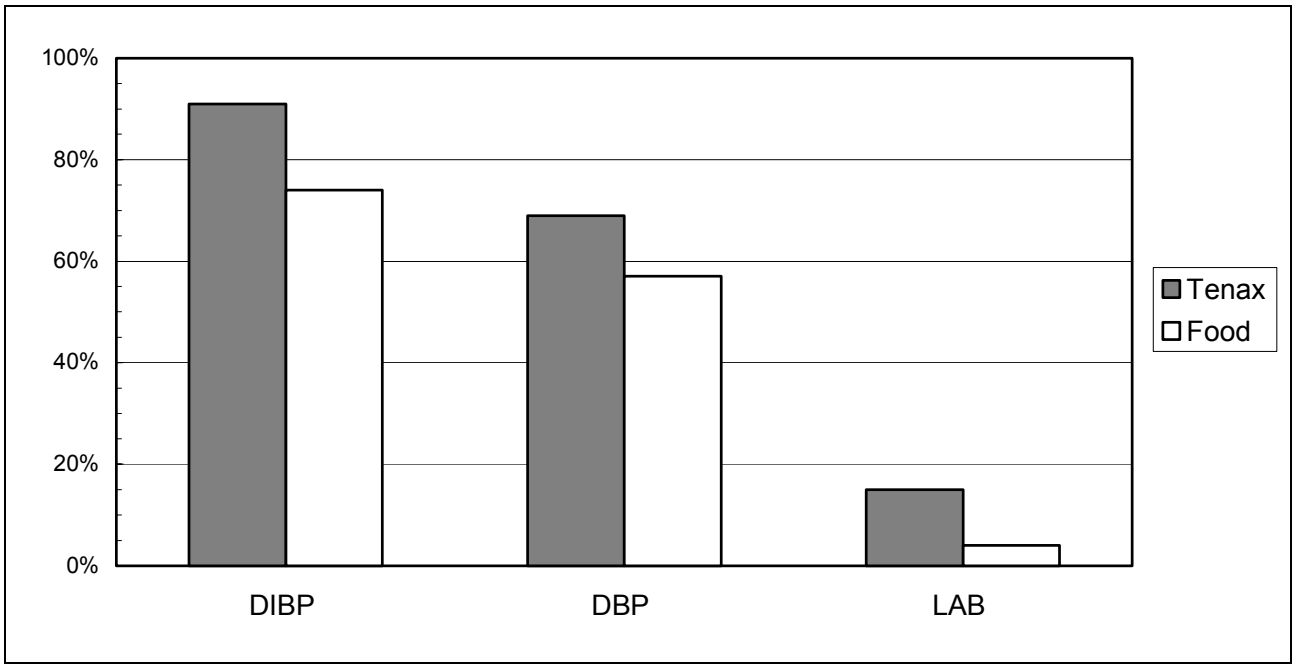


Figure 8. Comparing the migration percentages of phthalates and LAB into Tenax and food.

The percentage transfer of phthalates into Tenax corresponds well with migration during storage at the factory for four months. A migration test using Tenax for 10 days at 40°C is more severe than factory storage of real sugar packs for four months. This is quite interesting, in view of the fact that the content of phthalates in the sample used for migration testing was much higher than the average content in the sugar pack (Chapter 5.2.3). It is understandable that the migration of substances from a real, three-dimensional packaging is much higher than that in a single-sided migration test. For this reason, the results of migration testing using a food simulant should be compared with the results of migration from real packagings, and not with the results obtained from a migration test using food instead of food simulant in the migration vessel.

The percentage migration of LAB compounds is twice as high into Tenax as into rolls. Thus, the overestimation of migration is high. It would be more practical if the migration into simulant were less overestimated so to avoid any reduction factors. However, in both cases the migration into Tenax was higher than into foods, and migration testing using Tenax might therefore be further developed to yield standardized methods for migration from fiber-based food packagings.

5.4 Migration into Tenax at high temperature (V)

5.4.1 Overall migration

The plastic and dispersion coated ovenable boards listed in Table 2 were tested at high temperature. The overall migration results are shown in Figure 19. All results were below 10 mg/dm^2, which is the limit given in the EU directives for plastic. There were, however, some substantial differences between different board grades.

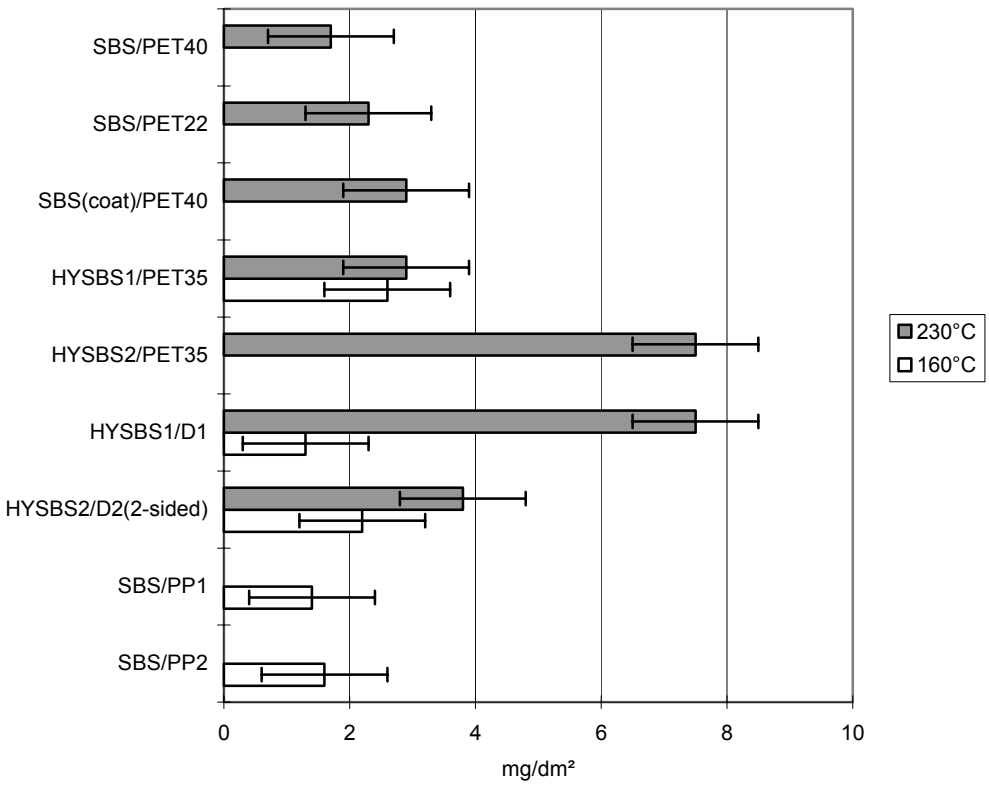


Figure 9. Overall migration results of ovenable boards.

All SBS-based grades gave similar results (1.4 - 2.9 mg/dm²), which were quite low. The thickness of the PET layer made no difference. It was of no significance whether the SBS-based board was clay coated or not. Migration from the PP-coated grades was also low.

HYSBS-based grades had a higher variation. The only known difference between the PET-coated HYSBS grades was the binder in the coating clay, although the specific migration results indicated that the binder was not the reason for the difference in the overall migration results between the HYSBS1 and HYSBS2 samples. Thus, it is unclear why the two HYSBS grades differed so much.

The other dispersion-coated board had a two-sided acrylate-based dispersion coating and the base board was HYSBS 2. The overall migration values were lower than those for the PET-coated HYSBS 2 (3.8 vs. 7.5 mg/dm²). The lower value was explained by the two-sided coating, which prevented migration from the base board.

In the gravimetric determination of overall migration, special attention was given to weighing the vials to constant weight because the amount of residue involved was only a few milligrams.

5.4.2 Specific migration

Compounds originating from the board

Small amounts of extracts or compounds originating from lignin were found in each sample. Vanillin and coniferyl aldehyde, products of the pyrolytic decomposition of lignin, were found in both types of HYSBS board. More fatty acids and resin acids were found in SBS-based samples than in HYSBS-based samples. The compounds found in the SBS board evidently originated from the rosin sizing agent (V).

The migration into the Tenax of three compounds originating from the other sizing agent, alkyl ketene dimer (AKD), was significant at 230°C. These ketones (stearone, palmitone and stearicpalmitic ketone) were identified using model compounds. They have high molecular masses (approx. 500 amu) and high boiling points. However, some transfer of these ketones to Tenax took place via the air at 230°C because they were also found in the Tenax that had not been in direct contact with materials but only with air in the oven. At 160°C their migration into Tenax was insignificant.

Compounds originating from the coatings

No compounds originating from PET coating were found by GC/MS analysis. Evaporation residues from the determination of overall migration were analyzed by FTIR. Although compounds originating from PET were not detected in GC/MS analyses, PET was identified by FTIR in all PET-coated samples. Hydrocarbons originating from the PP coating were found in both PP-coated samples. The SB-based dispersion coating had a high content of aromatic compounds.

Thermodesorption of compounds from Tenax

It is clear that thermodesorption of volatile compounds from Tenax is much greater at 230°C than 160°C. In this study, all compounds eluting before the internal standard

(cyclohexylbenzene, boiling point 240°C), were considered as volatile. The thermodesorption of volatile compounds from Tenax was clearly seen in the chromatograms of the samples exposed at 230°C. There were no volatile compounds in the samples exposed at 230°C. Moreover, a few interesting compounds were found originating from same samples at 160°C, but not at 230°C. For instance, 2-ethylhexyl acrylate, and many compounds originating from the SB coating, such as benzaldehyde, acetophenone, 4-phenylcyclohexene together with many hydrocarbons in the boiling point range of undecenes and dodecenes, were detected. As benzaldehyde and acetophenone are also known artefacts from Tenax, their non-existence in the blank determination was established [115].

5.5 Migration modeling (VI)

5.5.1 Experiments

Diffusion constants in air

The diffusion constants determined with this method were in good agreement with the values found in the literature. The values determined in this study were used in the calculations and simulations because they were more consistent than the values taken from different literature sources and determined with different methods. Besides, values could not be found for all model compounds studied [116, 117].

The experimental set-up for measuring diffusion constants for model compounds in air was very simple. The most critical factor was the way in which the liquid model compound was introduced into the tube. It was essential that the compounds were allowed to evaporate freely from the needle tip, because in many cases the liquid phase moved more rapidly along the inner tube surface than the gas phase through air.

Effective diffusion constants

Experimental results for the diffusion of model compounds through the pulp sheet fitted quite well with the continuous diffusion model for the test cell. The diffusion curve for butanol obtained from the cell experiment is presented in Figure 10. The experimental set-up is also suitable for testing different materials and their barrier properties against various substances.

Volumes under and above the pulp sheet were so large (200 ml) that several gas samples (50 µl) could be taken without disturbing the diffusion. To improve the precision we took three replicate samples and used their average in plotting the concentration curve. A few injections were rejected as outliers. The repeatability of manual gas injections into the GC/FID depends significantly on the gas tightness of the syringe used. Unfortunately, the performance of the syringes varied greatly and was difficult to predict. The best way to ensure successful injections during the test was to check the syringe just before the experiment. With a good gas-tight syringe the repeatability of the manual gas injection was determined to be approximately 5% (relative standard deviation for seven injections).

The tightness of the test cell was checked with tetrahydrofuran using aluminum foil as test specimen. The concentration of tetrahydrofuran was stable in the bottom of the cell for at least 24 h (relative standard deviation for fifteen injections was below 10%).

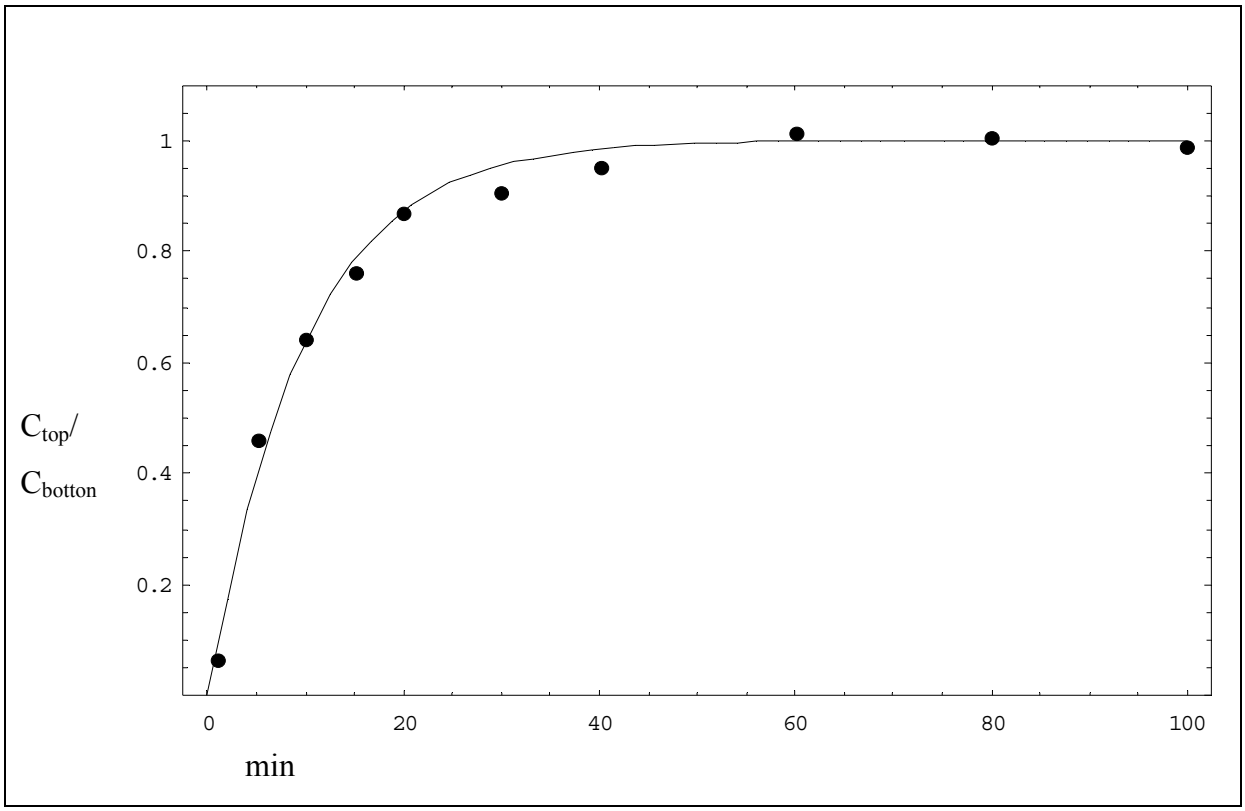


Figure 10. Increasing butanol concentration obtained from the cell experiment (dots). The solid curve shows the corresponding concentration obtained from the continuous diffusion model with fitted effective diffusion constant $D_e = 5.0 \cdot 10^{-8}$ m^2/s.

5.5.2 Comparison with simulations

Examples of experimental and calculated effective diffusion constants for the model compound (butanol) are presented in Table 9. The agreement is quite good considering that there were no tunable parameters in the simulation. It is noteworthy that the diffusion of molecules like butanol and butyl acetate, which differ in both size and polarity, was quite predictable (VI, Table 3). The deviations between the experiments and simulations for these compounds were within the error caused by the inaccuracy in the porosity measurement. On the other hand, we could not explain the underestimation of the diffusion for ethanol and tetrahydrofuran. It is possible that in these cases diffusion along the fiber surfaces and walls is significant (this was not included in our simulation model). The experimental diffusion times were long enough to allow the sorption and inhomogeneity effects to be ignored.

Table 9. Experimental and calculated effective diffusion constants for butanol.

Porosity of the kraft pulp sheets (oil absorption measurement)	**Effective diffusion constant for butanol (m^2/s)**	
	Experimental	Calculated
0.308 ± 0.011	$5.0 \cdot 10^{-8}$	$2.5 \cdot 10^{-8}$
0.382 ± 0.017	$9.1 \cdot 10^{-8}$	$12 \cdot 10^{-8}$

6 CONCLUSIONS

Migration tests using liquid simulants on paper products are in fact extractions rather than migration tests. This was true even with the plastic-coated paper plates investigated in Paper II. It was therefore clear that a solid food simulant (Tenax) had to be used for testing migration from paper and board packaging materials.

There were large variations in phthalate content within the packaging samples, but the phthalates found were the most common ones. Phthalate migration into sugar was high, which demonstrates that migration takes place even into dry food. The test conditions used with Tenax (10 days at 40°C) seemed to be appropriate for sugar packagings, because the percentage transfer of phthalates into Tenax corresponded well with real life migration. An uneven distribution of substances in the packagings is a serious drawback for migration tests employing only a small sample of packaging.

Some components of the inks used for printing board may migrate into food, even though there is no direct contact between the printed surface and the foodstuff. Alkylbenzenes from offset printing inks migrated from printed hamburger collars into rolls in migration tests performed at 70°C for 30 min.

Overall migration from the plastic or dispersion-coated ovenable boards was quite low, even though the samples were exposed to high temperatures. Consequently, it seems that overall migration is not a limiting factor in the case of ovenable boards. Compounds originating from the sizing agents were the main migrants from ovenable boards.

Experiments on the diffusion of volatile model compounds through laboratory kraft pulp sheets confirmed the practical relevance of the simulation model created for diffusion. For all compounds the effective diffusion constants obtained from the experiments and simulations were of the same order of magnitude. Experimental methods and devices developed for the modeling study are suitable for many applications designed to study the diffusion and barrier properties of materials.

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APPENDIX I

Examples of conventional conditions for migration tests with food simulants according to the Commission Directive 97/48/EC

CONDITIONS OF CONTACT IN WORST FORESEEABLE USE	TEST CONDITIONS
Contact time	**Test time**
5 min < t ≤0.5 hours	0.5 hours
0.5 h < t ≤ 1 hour	1 hour
1.0 h < t ≤ 2 hours	2 hours
2 h < t ≤ 4 hours	4 hours
4 hours < t ≤ 24 hours	24 hours
t > 24 hours	10 days
Contact temperature	**Test temperature**
T ≤ 5 ºC	5 ºC
5 ºC < T ≤ 20 ºC	20 ºC
20 ºC < T ≤ 40 ºC	40 ºC
40 ºC < T ≤ 70 ºC	70 ºC
70 ºC < T ≤ 100 ºC	100 ºC or reflux temperature
100 ºC < T ≤ 121 ºC	121 ºC*
121 ºC < T ≤ 130 ºC	130 ºC*
130 ºC < T ≤ 150 ºC	150 ºC*
T > 150 ºC	175 ºC

* This temperature shall be used only for simulant D. For simulants A, B or C the test may be replaced by a test at 100 ºC or at reflux temperature for a duration of four times the time selected according to the general rules of paragraph 1.

Simulant A = Distilled water or water of equivalent quality
Simulant B = Acetic acid 3% (w/v)
Simulant C = Ethanol 10% (w/v)
Simulant D = Rectified olive oil or other fatty food simulants