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Establishment of a standard test procedure for PET bottle materials with respect to chemical inertness behaviour including the preparation of a certified PET reference material

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eines

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genehmigten Dissertation.

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Prüfer der Dissertation: 1. Univ.-Prof. Dr. G. Cerny
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Die Dissertation wurde am 19.11.2001 bei der Technischen Universität München eingereicht und durch die Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt am 18.12.2001 angenommen.

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ABBREVIATIONS

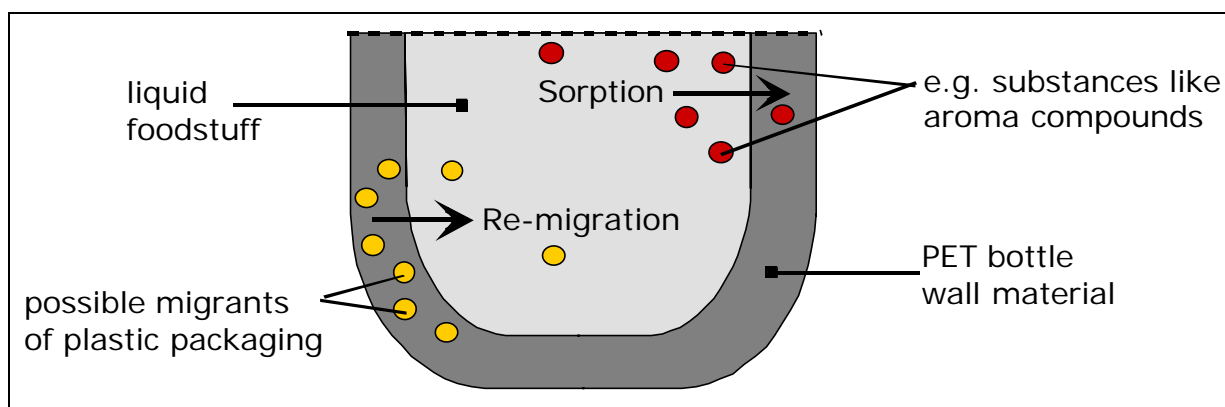
ANOVA	Analysis of variance
APET	Amorphous Polyethylene terephthalate
BESTPET	Barrier enhanced silica treated Polyethylene terephthalate
BgVV	Bundesinstitut for gesundheitlichen Verbraucherschutz und Veterinärmedizin
CPET	Crystalline Polyethylene terephthalate
CRM	Certified Reference Material
CSD	Carbonated soft drink
CV	Coefficient of Variation
d	day
DEG	Diethylene glycol
DGT	Diethylene glycol terephthalate
DLC	Diamond like carbon
DMT	Dimethyl terephthalate
EC	European Community
EG	Ethylene glycol
EPA	Environmental Protection Agency
EU	European Union
EVOH	Ethylene vinyl alcohol
FDA	Food and Drug Administration
FhG-IVV	Fraunhofer Institute for process engineering and packaging
GC/ FID	Gas chromatography/ Flame Ionisation Detector
GRAS	Generally recognised as safe
HFIP	Hexafluoro-isopropanol
ILSI	International Life Science Institute
IV	Intrinsic viscosity
LCP	Liquid crystal polymers
MCS	Model compound solution
min	minutes
OPET	Oriented Polyethylene terephthalate
PEG	Polyethylene glycol
PEN	Polyethylene naphthalate
PET	Polyethylene terephthalate
PETG	Glycol modified Polyethylene terephthalate
PVDC	Polyvinylidene chloride
RM	Reference material
RPET	Recycled Polyethylene terephthalate
SCF	Scientific Committee of Food
SML	Specific migration limit
SMT	Standard, Measurement and Testing
TPA	Terephthalic acid
(W/V)	weight to volume

1 INTRODUCTION

The world food markets are nowadays glutted by a high variety of plastic packaging materials for just as many varied sorts of food products. Only to name a few - Polyethylene, Polypropylene, Polystyrene and Polycarbonate are commonly used in form of foils, bags, boxes and containers. With the introduction of a 2 litre bottle in 1976 Polyethylene terephthalate (PET) steadily conquered the market and emerged as a material of choice for beverage bottles. The characteristic properties of PET like stability, transparency and lower weight have led to the fact that glass bottles are more and more replaced. Due to the stability of the material the multi-use system of PET bottles is common in many countries. The strength and ruggedness of the nearly indestructible PET material is one reason that beverage bottles can achieve high circulation rates between the bottler and the consumer. The use of a rugged material, however, cannot rule out the fact that material changes may occur during the life time of a bottle. On the account of a direct contact between the PET bottle and the beverage interactions e.g. migration processes can occur during the often long storage time. Plastics have for example the ability to absorb organic compounds easily. For this reason the aspect that a number of refillable PET bottles may be misused by the consumer is very important for the quality assurance and safety-in-use of refillable bottles. Consumer may "misuse" the bottles for example by filling them with beverages with strong flavour, household chemicals or even pesticides. Compounds absorbed in this way will not be fully removed during the washing and cleaning procedure of a refillable bottle. Therefore these substances may be able to remigrate into a refilled foodstuff or beverage which in turn can result in an off-flavour. Due to the intrinsic interactivity of a refillable plastic bottle with contacting chemicals the question of testing compliance with food regulations arises. To this day there is neither any specific national or EU regulation nor a standard test available which could be applied by industry and enforcement laboratories to cover this problem. One of the main purposes of the EU project SMT4-CT96-2129 was to establish a standardised and easy-to-apply method for general chemical inertness testing in conjunction with the production of a certified reference material of PET applicable not only for the industry but also suitable for enforcement laboratories and therefore having a systematical control possibility to check the food safety of refilled PET bottles taken from the market. The following work describes the development and application of a chemical inertness test procedure as well as the production of a Reference Material PET within the framework of the European project SMT4-CT96-2129 with which the inertness of a PET material can be established.

2 GENERAL BASICS - PET AS PACKAGING MATERIAL FOR FOODSTUFFS

The thermoplastic Polyethylene terephthalate belongs to packaging materials for foodstuffs with relative high chemical inertness compared to other plastic packaging materials. The chemical inertness of a plastic packaging material is measured as the amount of chemical substances absorbed as well as re-migrated into a re-filled foodstuff during the direct contact with the plastic material as shown in Scheme 2-1. The higher the chemical inertness of a plastic material the lower are the absorbed as well as returned (re-migrated) concentrations of chemical substances. The chemical inertness of a plastic material depends on parameters like e.g. resin quality as well as mechanical and physical properties of the polymer which also can be influenced to a certain degree by the manufacturing technique of the package itself. Therefore the following paragraphs describe the principles of manufacturing polyethylene terephthalate as a *food-grade* packaging material as well as the implication on (re-)migration and chemical inertness considerations respectively.



Scheme 2-1: Sectional drawing of the lower part of a PET bottle illustrating sorption as well as re-migration processes.

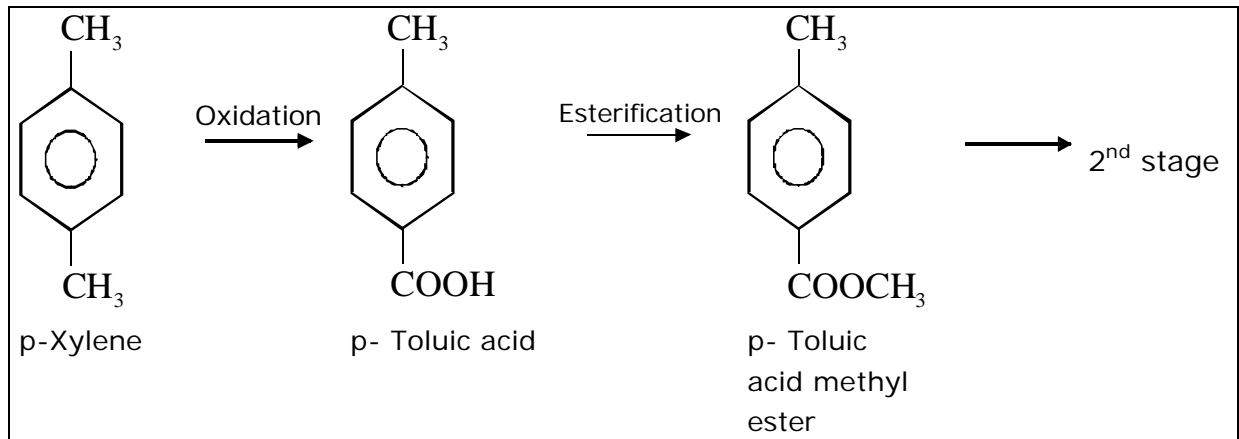
In 1941 the *British Company Calico Printers* developed Polyethylene terephthalate (PET) for the use in synthetic fibres. In the textile industry the use of polyester fibres has since been increased considerably. The second principal application of PET was in form of films. In 1966, PET also became available for manufacturing of injection-moulded and extruded parts. The breakthrough and amazing growth of PET as a packaging material for beverages started with the development of biaxially oriented PET bottles and the launching of the first 2-L PET beverage bottle in the USA in 1976 (Brody; Kenneth, 1997).

2.1 RAW MATERIALS FOR THE MANUFACTURING PROCESS OF DIETHYLENE GLYCOL TEREPHTHALATE (DGT) - MONOMER OF PET

Polyethylene terephthalate as a thermoplastic polyester belongs to the group of polymers which are manufactured by polycondensation. The raw materials, Dimethyl terephthalate or Terephthalic acid and Ethylene glycol, are derived from crude oil. While Dimethyl terephthalate and Terephthalic acid respectively are manufactured from p-Xylene out of the naphtha fraction, Ethylene glycol is produced by oxidation and hydrolysis of Ethylene out of the gas fraction of the crude oil (Brody; Kenneth, 1997).

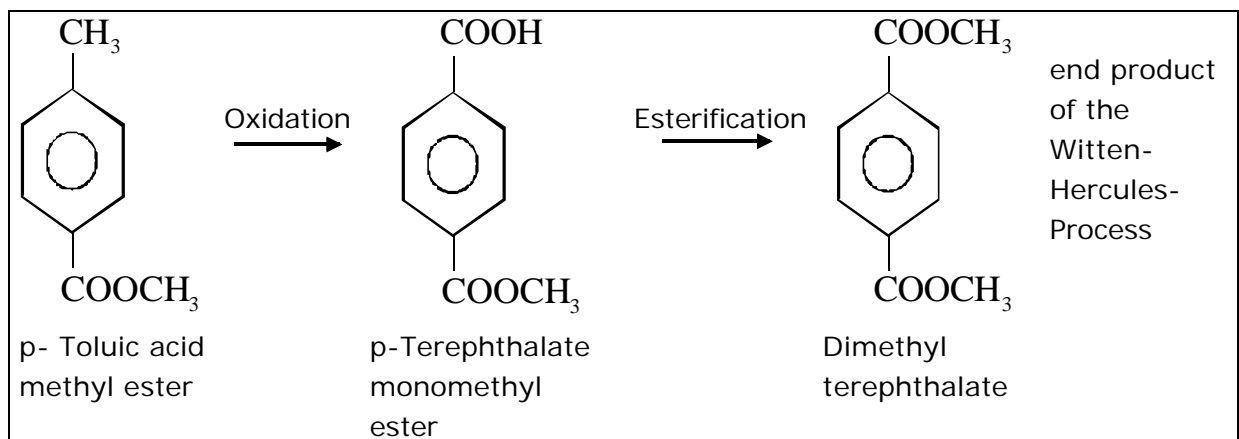
2.1.1 Dimethyl terephthalate (DMT)

The most important process for the production of Dimethyl terephthalate is the two-stage Witten-Hercules process. The following Schemes describe the first and second stage of this process.



Scheme 2-2: First stage of the production process of Dimethyl terephthalate

The oxidation of p-Xylene with air is carried out under the presence of cobalt-manganese salts at 150 to 170 °C and a pressure between 4 and 8 bar. The developing p-Toluic acid as an intermediate product of the first stage is esterified with Methanol to p-Toluic acid methyl ester at 240 °C and a pressure of 30 to 40 bar.

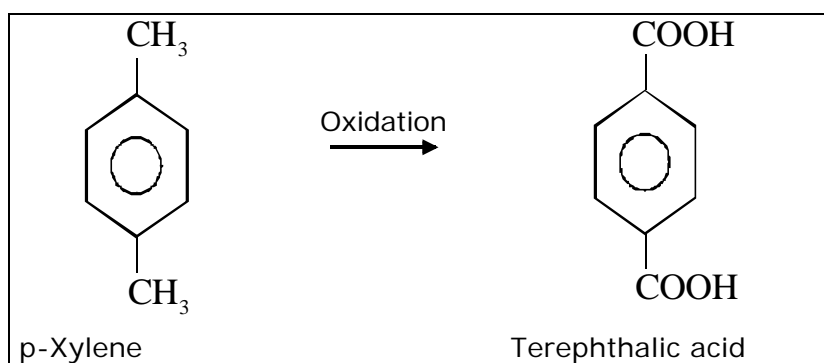


Scheme 2-3: Second stage of the manufacturing process of Dimethyl terephthalate

In the second stage p-Toluic acid methyl ester is further oxidised to p-Terephthalate monomethyl ester and finally esterified to Dimethyl terephthalate. Within the technical process both stages of the oxidation as well as the esterification are performed in the same reactors. Dimethyl terephthalate as end product of the Witten-Hercules-Process achieves a purity of higher than 99,99 % due to following re-crystallisation and distillation procedures (Bottenbruch, 1992).

2.1.2 Terephthalic acid (TPA)

The Amoco-Process is widely used for the technical production of Terephthalic acid. During the technical process the one-stage oxidation of p-Xylene with air is continually carried out in acetic acid under the presence of cobalt-manganese salts as oxidation catalysts and bromine substances as additional activators. The chemical reactions are carried out at temperatures between 215 and 235 °C under a pressure of 25 to 35 bar. Crude Terephthalic acid is mainly polluted with 4-Carboxybenzaldehyde. Therefore the crude Terephthalic acid has to be purified applying hydrogenation and re-crystallisation processes after which a purity of 99.99 % can be achieved (Bottenbruch, 1992).



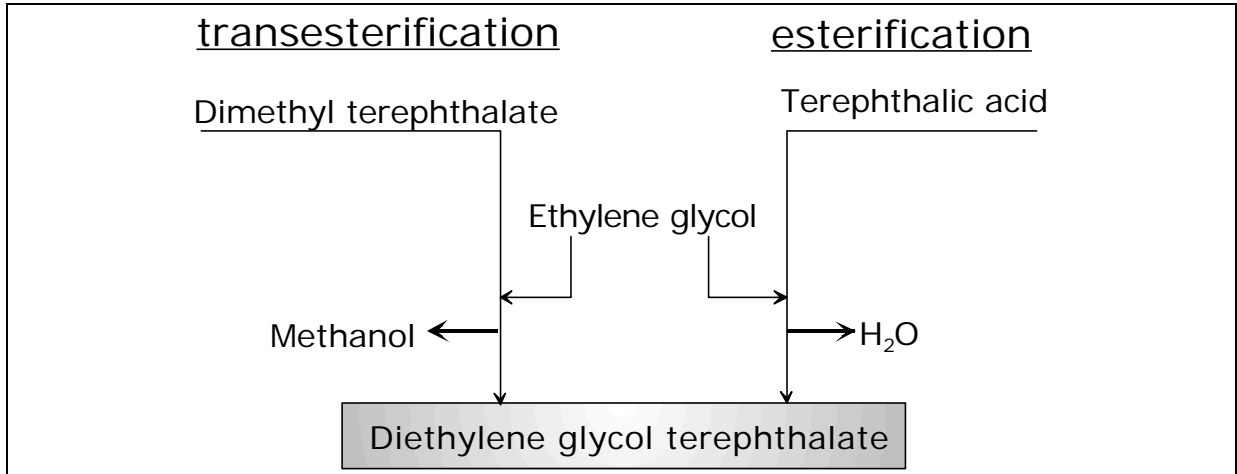
Scheme 2-4: Oxidation of p-Xylene to Terephthalic acid

2.1.3 Ethylene glycol (EG)

The technical process of manufacturing Ethylene glycol [HO-(CH₂)₂-OH] is exclusively based on the transformation of Ethylene oxide with a surplus of water. Applying a high surplus of water as well as avoiding a re-mixing in the reactor the development of Diethylene glycol and oligomeric glycols can be kept on a low level. A mass relation of 30:4:1 between Ethylene glycol, Diethylene glycol and Triethylene glycol can be assumed as a typical ratio for the end products. A separation of different glycols is achieved by the following rectification in vacuum-distillation-columns (Bottenbruch, 1992)

2.2 PRODUCTION PROCESS OF THE MONOMER DIETHYLENE GLYCOL TEREPHTHALATE (DGT)

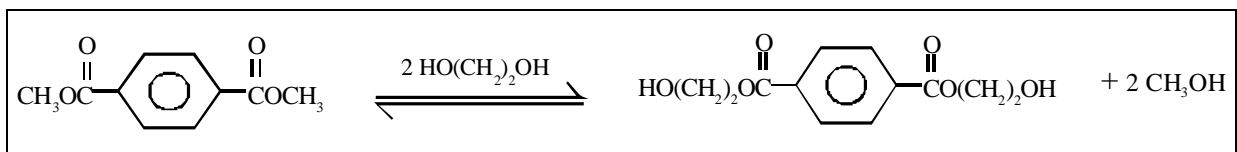
Nowadays there exist two processing routes to manufacture the monomer DGT: one by way of Dimethyl terephthalate (DMT) and the other by way of Terephthalic acid (TPA). Both are dibasic acids (Brody; Kenneth, 1997).



Scheme 2-5: Synthesis of DGT monomers for the manufacturing process of PET.

2.2.1 Transesterification of Dimethyl terephthalate (DMT)

Within the ester interchanger the methyl end-groups of DMT are continuously replaced by ethyl end-groups of Ethylene glycol (EG) to form Diethylene glycol terephthalate (DGT). In this chemical process EG is consumed while Methanol is evaporated and re-collected to be returned to the DMT plant. The ester transformation is accelerated by catalysts using the acetates of calcium, manganese, cobalt, cadmium, lead or zinc. Scheme 2-6 describes the chemical reaction of DMT and EG to DGT. (Bottenbruch, 1992).



Scheme 2-6: Ester transformation of DMT to DGT, the monomeric unit of PET

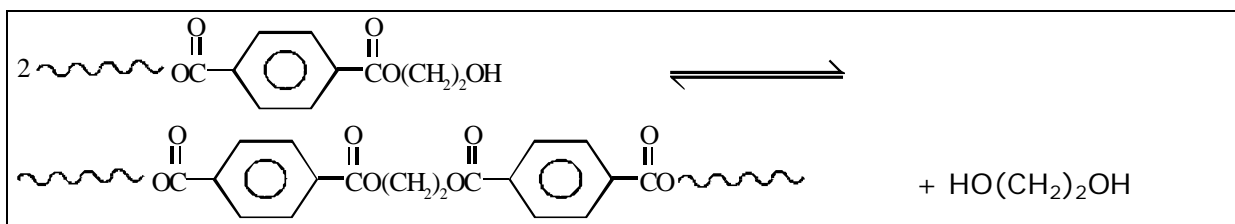
2.2.2 Esterification of Terephthalic acid

The second manufacturing process consists of the esterification of Terephthalic acid with Ethylene glycol to Diethylene glycol terephthalate. During the process water is continuously removed as a by-product. Contrary to the transesterification of DMT, a molar surplus of 10 % of Ethylene glycol is sufficient to obtain the esterification product (Bottenbruch, 1992).

2.3 MANUFACTURING PROCESS OF THE POLYMER POLYETHYLENE TEREPHTHALATE (PET)

2.3.1 Melt polycondensation

The final product of the transesterification as well as the esterification process already contains oligomers. Prior to the polycondensation process excessive Ethylene glycol has to be removed under vacuum applying higher temperatures. The catalysts of the previous ester transformation process also have to be inactivated (e.g. by using phosphoric acid) because of favouring the formation of Diethylene glycol as well as the thermal destruction of polyester chains. The actual polycondensation process, a catalytically accelerated polyester interchange reaction, leads to the formation of Polyethylene terephthalate (PET) chains, under elimination of Ethylene glycol. Evaporating Ethylene glycol as a by-product of the polyester condensation process by intensive mixing under vacuum and maximising of the melt surface shifts the equilibrium of the chemical reaction towards long polymer chains.



Scheme 2-7: Equilibrium reaction of the polyester interchange process

Not only the evaporation of Ethylene glycol but also

1. the melt temperature (normally between 270 and 285 °C)
2. the concentration of reaction partners
3. the material thickness of the melt
4. the concentration of end groups and last but not least
5. the use of catalysts

have an influence on the kinetics of the reaction and therefore on the molar mass of the polymer PET.

For the polycondensation process of Polyethylene terephthalate special catalysts are used on the basis of Antimony, Germanium, Titan or lead substances. The final end product of the melt-polycondensation is an amorphous PET resin obtained after extrusion of the melt as strands or ribbon, quenched in water and cut to the desired chip size. Applying usual technological parameters for the melt polycondensation process molar masses between 15 000 and 25 000 can be achieved.

2.3.2 Solid state polycondensation

The quality of amorphous PET produced by melt polycondensation is not suitable for the injection moulding of food containers. Higher molecular polyesters with a molar mass of more than 30 000 and enhanced mechanical as well as thermal properties with higher qualities are therefore produced in an additional solid-state polycondensation process. The reaction time of the solid-state polycondensation essentially depends on the diffusion of Ethylene glycol onto the surface of polyester particles as well as on the polycondensation temperature. The solid-state polycondensation is therefore carried out either under vacuum or under a flow of inert gas. During the solid-state polycondensation not only polyester interchanges but also polyesterification as competing reaction are taking place. (Bottenbruch, 1992).

2.4 REACTION BY-PRODUCTS IN THE MANUFACTURING PROCESS OF POLYETHYLENE TEREPHTHALATE (PET)

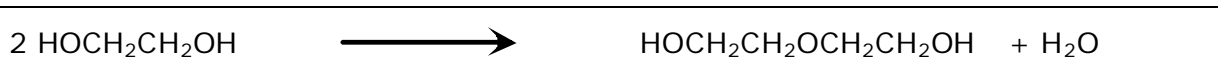
For the manufacturing of a food-grade PET polymer there exist nowadays stringent industrial product quality specifications. PET resins offering material properties like high strength, stiffness, stability as well as chemical and heat resistance must meet requirements of e.g. high intrinsic viscosity that means a high molecular weight of polymer chains. Therefore the development of undesirable side products which have an influence on the properties of PET polymers has to be kept within limits that would not affect quality requirements (Besnoin; Choi, 1989). The most important side products which influence and change material properties of PET are :

- Diethylene glycol
- Carboxyl end groups
- Vinyl end groups - resulting in
- Acetaldehyde
- Water

2.4.1 Diethylene glycol (DEG)

DEG is one of the most important side products of the polycondensation process. PET which is directly produced by esterification of Terephthalic acid usually contains more DEG than PET produced by transesterification of DMT (Chen, 1998 a). Most of the DEG is formed during the preheating of the melt- polycondensation by intermolecular dehydration of Ethylene glycol. The dehydration of Ethylene glycol is catalysed by acids and therefore promoted by a high concentration of carboxyl end-groups.

In the course of polycondensation DEG is also co-polymerised in the polyester chain causing a decrease in melting temperature of PET. In general, the melting point of PET decreases by about 5 °C for each percent increase in DEG concentration.

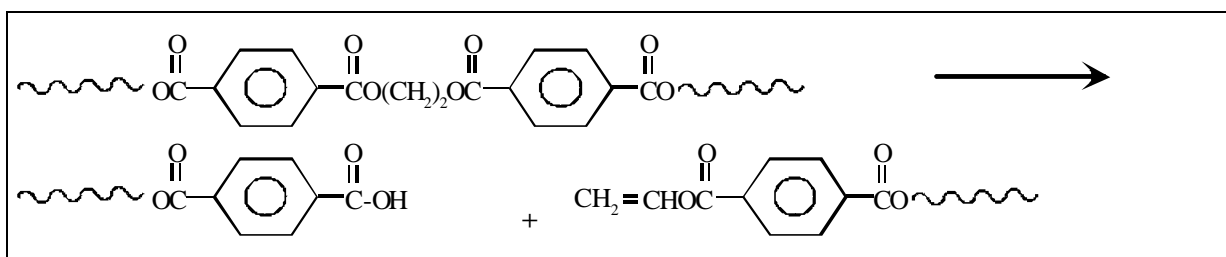


Scheme 2-8: Formation of DEG

The incorporation of DEG in the polymer PET also deteriorates mechanical properties, the hydrolytic and light stability as well as the thermal and oxidative degradation behaviour of the material (Bottenbruch, 1992). Besnoin and Choi (1989) also discussed other possibilities for the formation of DEG during the polycondensation and manufacturing process of PET.

2.4.2 Carboxyl and Vinyl end groups

Another important side reaction during the production of the polyester PET is the degradation of polymer chains by random thermal cleavage of ester links forming carboxyl end groups and vinyl end groups respectively.



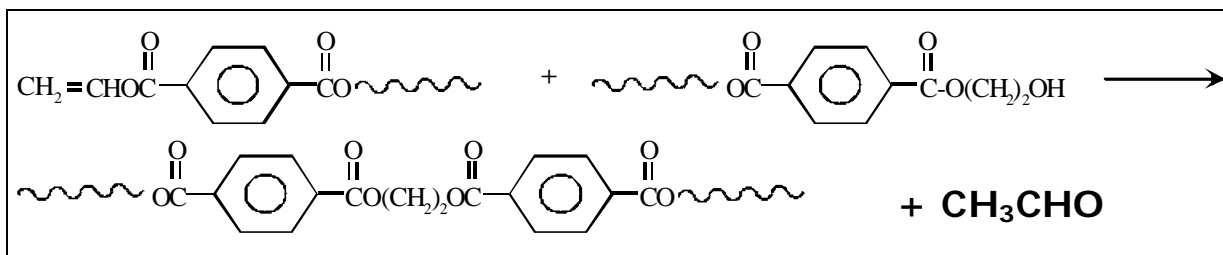
Scheme 2-9: Formation of carboxyl as well as vinyl end groups by random thermal cleavage of ester links (Bottenbruch, 1992)

The amount of carboxyl end groups is an important factor due to the susceptibility to hydrolysis of the polymer since these end-groups have a catalytic effect in the process as already mentioned above.

Vinyl end-groups may also polymerise to polyvinyl esters which are responsible for the coloration of PET (Besnoin; Choi, 1989).

2.4.3 Acetaldehyde

The vinylester end group of PET can be transesterified under the formation of Acetaldehyde as shown in Scheme 2-10. The Acetaldehyde concentration of PET granules is of great importance when manufacturing PET bottles for soft drinks especially when used for carbonated mineral water. Migrating to the beverage, retained Acetaldehyde can cause an intensive off-flavour.



Scheme 2-10: Formation of Acetaldehyde as a by-product of the polycondensation process of PET (Bottenbruch, 1992)

Acetaldehyde is not only formed during the polycondensation process but also occurs during blow moulding of PET bottles from PET resin (Besnoin; Choi, 1989)


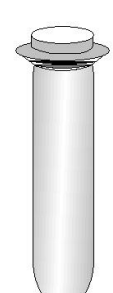

2.4.4 Water

The amount of water is of great importance concerning the hydrolysis, leading to a decrease in the degree of polymerisation and intrinsic viscosity respectively. The intrinsic viscosity is a measure of the molecular weight of the PET resin. Moreover, water also has an influence on rheological as well as physical properties of the PET material (Jabarin; Lofgren, 1984).

2.5 INJECTION AND STRETCH BLOW MOULDING OF PET BEVERAGE CONTAINERS

The production process of PET beverage containers can be divided into two parts which can be performed either in one or in two different process stages. The first part consists of the injection moulding of PET preforms while the second part performs the final production of the PET beverage container (Table 2-1).

Table 2-1: Production phases of PET beverage containers

	Part I	Part II
<i>Product</i>	PET preforms	PET containers
<i>Process</i>	injection moulding	stretch blow moulding
one stage	→	
two stage	→	reheat-blow-moulding step →
 PET resin	 PET preform	 PET bottle

2.5.1 Injection moulding of PET preforms

Generally there exist three problem areas within the injection moulding process of preforms which are specific for PET correlating with the quality of PET resin properties. The problem areas are the intrinsic viscosity drop, the generation of Acetaldehyde as well as the lack of clarity (Schaul, 1981).

The injection moulding of PET preforms consists of five process steps.

- I. Before melting the PET resin the crystallised PET pellets have to be dried to a moisture content of 20 to 30 ppm H₂O. Otherwise, higher water contents of the pellets will cause a hydrolytic degradation of the polyester chain leading to a drop of intrinsic viscosity (IV) of the material. In the melt state water molecules attack ester linkages quantitatively. The percentage by which any starting IV will be decreased can be related to the moisture content. The decrease of IV from the granulate to the preform means a reduction in molecular size due to the moulding process causing undesirable consequences like faster crystallisation as well as decreased toughness in non-oriented parts of the finished bottle (Schaul, 1981).
- II. In the second process step the plastication of the PET resin to a melt is carried out. The melt environment once again has an enormous influence on the thermal as well as oxidative degradation of PET. The decrease of intrinsic viscosity as variable for thermal degradation of the PET melt depends on parameters like melt temperature, melt environment as well as melt residence time. Melting under vacuum and nitrogen flow turned out to be the most appropriate melting conditions for PET concerning the decrease of IV (Jabarin; Lofgren, 1984). Moreover, PET produces Acetaldehyde in melt processing when manufactured or moulded. The generation of Acetaldehyde is directly correlated to the heat history of the melt increasing with melt temperature and residence time (Schaul, 1981).
- III. The third process step consist of the injection of the accumulated melt into the mould cavities of the moulding machine. In 1996 approximately 100.000 cavities were in operation producing different sorts of PET preforms. Nowadays, an injection moulding system normally exists of 16 to 96 cavities (Schramm, 1996).
- IV. After injection of the PET melt a rapid cooling is carried out using chilled cavities and core rod surfaces producing a PET preform to a clear amorphous glass. The quality of a PET preform is additionally measured in form of its clarity.
- V. The final process step consists of the opening and ejection of the preform.

2.5.2 Stretch blow moulding of Polyethylene terephthalate containers

For the manufacturing of PET containers there exist two processing routes as already mentioned: The one and two stage manufacturing process respectively. The one stage process is characterised by carrying out the whole production process of PET containers from the PET resin to the final product in one moulding system at the same time whereas the production of PET preforms and containers is carried out separately as well as independently in the two stage process. The advantage of the one stage process is therefore that the preforms don't have to be re-heated during the manufacturing process thus saving energy and costs especially for small units of specially designed containers. The two stage process is commonly used for the mass production of standardised PET containers on the market. Bottlers often dispose of stretch blow moulding systems only thus buying the PET preforms from the world market (Lerche, 1996). The following paragraphs describe the stretch blow moulding of PET bottles of a two stage process which can be divided in three main phases as follows:

- I. Phase Re-heating of PET preforms
- II. Phase „Balancing“ of temperatures
- III. Phase Final stretch blow moulding of PET containers

2.5.2.1 *Re-heating of PET preforms*

The cold PET preforms are introduced into a heating system consisting of different short-wave infrared radiators. Not only the temperature of the whole preform wall has to be risen but also a temperature profile in axial direction has to be build up. With the profiling of the preform temperature in axial direction the material distribution of the final PET bottle can be influenced. Comparing the emission spectrum of the radiators with the absorption as well as transmission spectrum of the PET material shows that a partial amount of radiation goes through the material whereas another considerable part is absorbed on the surface of the PET preform. Since the polymer PET is a bad heat conductor the absorbed energy cannot be distributed at once and therefore an overheating of the surface area, causing intense crystallisation, has to be prevented using air cooling in between (Lerche, 1996).

2.5.2.2 *„Balancing“ of temperatures*

The second phase of the stretch blow moulding process is called „balancing“. It describes the time period necessary for the homogenisation of the temperature of the preform material additionally taking into account that the axial temperature profile is generally maintained (Lerche, 1996).

2.5.2.3 Final stretch blow moulding of PET containers

The expression stretch blow moulding means that the tempered preform (between 80 °C and 125 °C) is first mechanically stretched by a stretch rod in axial direction and finally blow moulded using two following pressure levels. Applying 12 to 25 bar in the first compression stage already provides 90 % of the container form whereas the final contour of the PET container is obtained within the second compression applying up to 40 bar. The distribution of the PET material can be heavily influenced by the control of a delay time between the stretching and the blowing of the PET preform. With the mechanical stretching the PET material of the preform is axially orientated whereas the final blowing in radial direction lead to the well known biaxially orientation of the PET bottle material. With the second blowing stage the PET material is pressed against the moulding form and suddenly cooled by fixing the material structure of the PET bottle (Lerche, 1996).

2.5.3 Relaxation behaviour of stretch blow moulded PET containers

After the ejection of the blow moulded PET container the volume of the bottle is prescribed due to the form and design. Measuring the volume of a freshly produced PET container at regular intervals, however, shows that the measured value decreases to a certain degree. A PET bottle normally reaches the final volume 72 hours after the production. The shrinkage of the PET bottle can be explained by the degradation of material tensions, built up during the manufacturing process. The shrink behaviour of PET containers is called „relaxation“. The shrinking of a PET bottle can be accelerated using tempered moulding forms (Lerche, 1996). Moreover, the thermal relaxation of PET bottles during the moulding process is a well known process for the increase of thermal stability of a PET container.

2.6 PET CONTAINERS FOR THE BEVERAGE MARKET - AN OVERVIEW

Nowadays there exist a huge variety of PET containers available for just as varied sorts of beverages on the world food market. Trying to define and characterise different sorts of PET containers, parameters like polymer composition, production technique as well as general market requirements can be used.

Table 2-2: Possible characterisation of PET containers on the food market

polymer composition	production technique	market requirements
<ul style="list-style-type: none"> • homopolymer • co-/ block polymers • polymer blends 	<ul style="list-style-type: none"> • hotfill - heatset bottles • one-layer /multilayer bottles and therefore • bottles - with functional barrier 	<p>RECYCLABILITY</p> <ul style="list-style-type: none"> • one / two-way bottles • refillable PET bottles

2.6.1 Polymer composition of PET beverage containers

Carbonated soft drink (CSD) bottles consisting of PET as a homopolymer normally show a partially crystalline structure which have to be distinguished from amorphous (APET) as well as crystallised (CPET) PET containers. Oriented PET materials (OPET) show better barrier properties and thermal stability than standard PET. Nowadays there exist an enormous variety of beverages from unspectacular mineral water to adventurous „Scarab“ beer. The packaging requirements resulting from the protection function of PET bottles are therefore as varied as the beverages themselves. Co-polymerising PET with e.g. Isophthalic acid or Cyclohexane dimethanol glycol (PETG) or blending PET with Polyethylene naphthalate (PEN) are two of the countless possibilities of meeting requirements like heat resistance, enhanced barrier properties or hydrolytic stability. Especially the co-polymerising of PET with PEN in form of low-level (up to 15% PEN) or high level (more than 85% PEN) copolymers is increasing for beverages requiring higher barrier properties concerning oxygen and CO₂ permeation, respectively.

2.6.2 Manufacturing techniques of PET beverage containers

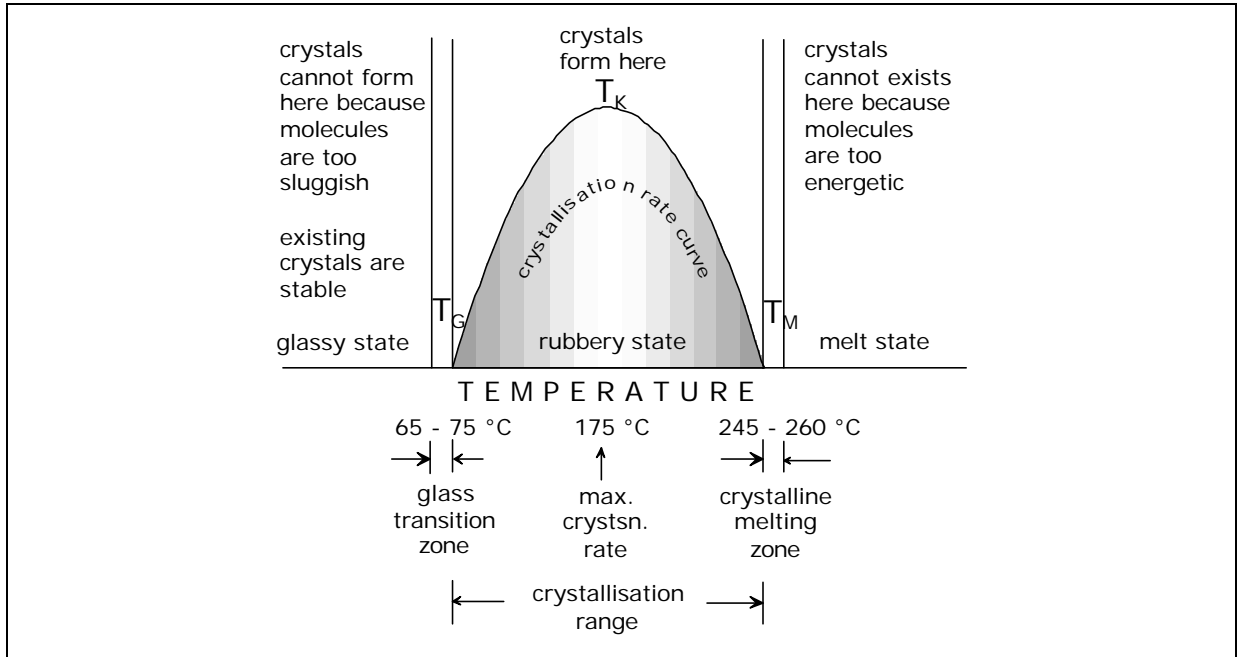
2.6.2.1 PET containers for hotfill and heatset applications

Beverages containing organic compounds have to be sterilised in order to avoid microbial spoilage. Sensible beverages like e.g. fruit juices have to be packaged under preserving packaging conditions like pasteurisation, aseptic filling or hot filling of PET containers. Sterilisation procedures are limited to packaging under e.g. Ethylene oxide atmosphere or irradiation due to the hydrolytic proneness of PET (Domininghaus, 1998). For the hotfilling of foodstuffs like teas, isotonic beverages as well as fruit and vegetable juices PET beverage bottles have to withstand temperatures from 82 °C to 95 °C for different periods of time depending on the composition of the beverage. Due to production technique and design hotfill bottles not only sustain thermal but also mechanical stresses arising during the hotfilling process. PET beverage bottles for hotfill applications can be either made of homo- or co-polymers. A significant parameter of a PET material designated for the production of hotfill containers is surely the intrinsic viscosity IV which normally lays between 0.70 to 0.85 dL/g. Moreover, the crystallisation behaviour of a PET material (graphically presented in Table 2-3) is of special interest for the manufacturing process of hotfill containers because of partially providing the necessary thermal stability of hotfill bottles. (Appel, 1997)

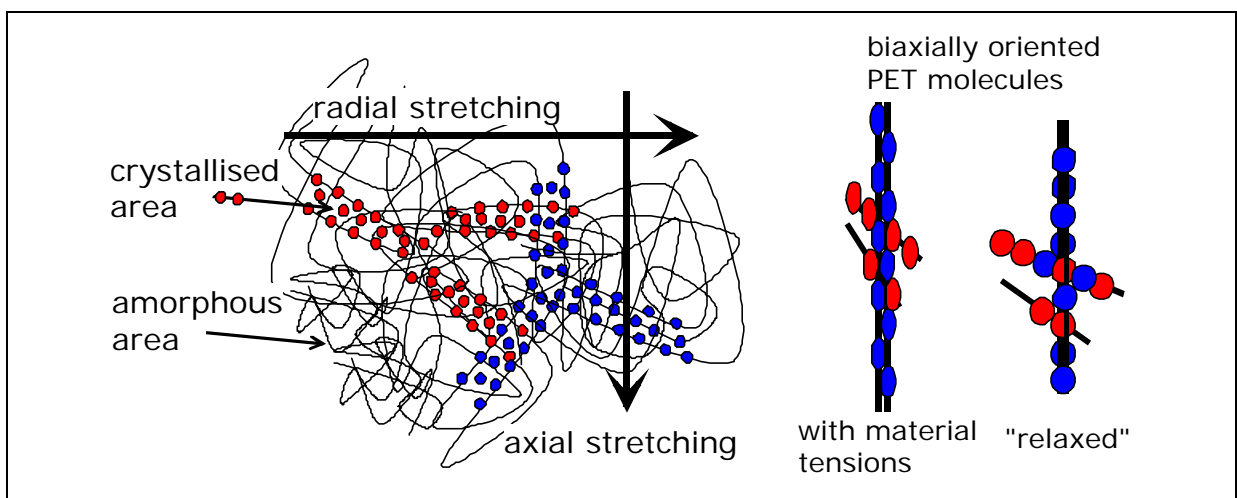
Describing the thermal behaviour of the polymer PET three characteristic temperatures and temperature ranges, respectively, are of special interest. The glass temperature T_G , the crystallisation temperature T_K as well as the melting temperature T_M . Below the glass temperature PET is stiff and tough.

Near the glass temperature T_G PET behaves caoutchouc like elastic, beginning to crystallise when reaching the crystallisation temperature range. The maximum crystallisation rate is reached at the crystallisation temperature T_K . A further increase of the temperature leads to a decrease in crystallisation until the melting state of the PET material is reached at T_M (Schaul, 1981).

Table 2-3: Crystallisation behaviour of Polyethylene terephthalate (according to Schaul, 1981)



The morphological structure of crystallised PET significantly depends on the orientation of the material. The rate of thermally as well as mechanically induced crystallinity as well as the morphological structure of crystallites significantly influence the thermal stability of a PET beverage bottle (Appel, 1996 b).



Scheme 2-11: Drawing of the morphological structure of semi-crystallised, oriented PET

The manufacturing process of hotfill or heatset PET bottles is based on processing procedures like thermal relaxation of oriented PET materials, thermal nucleation as well as thermal crystallisation (Appel, 1996 b).

Hotfill PET bottles not only have to withstand thermal but also mechanical material stresses while hotfilled and cooled afterwards. The advantage of PET in comparison to glass bottles is the unnecessary tempering of bottles before the filling process in order to prevent bursting of bottles. PET bottles can be hotfilled in a cold condition with temperatures up to 95 °C and directly be cooled without risking to burst the bottle. Cooling the beverage directly after hotfilling leads to a below atmospheric pressure in the bottle due to the change of density of the beverage. Equalising the change of pressure, PET hotfill bottles show specially designed „vacuum“ surface areas along the bottle wall which compensate the hypotension within the bottle (Koch; Jaszat, 1995). Table 2-4 summarises application fields and conditions for hotfill as well as heatset PET bottles.

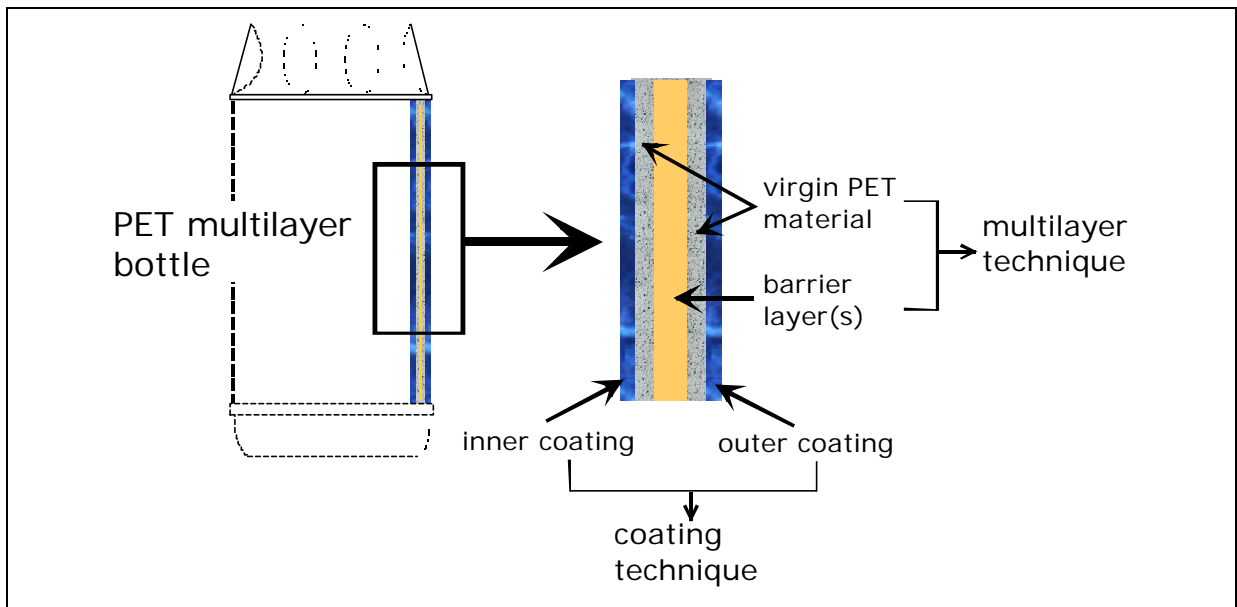
Table 2-4: Application conditions for hotfill and heatset PET containers (according to Appel, 1996 b)

BOTTLES	HOTFILL	HEATSET	
	hot filling of	refillable bottles for	hot filling of
Examples	<ul style="list-style-type: none"> isotonic beverages 	<ul style="list-style-type: none"> soft drinks carbonated mineral water 	<ul style="list-style-type: none"> fruit juices teas non-carbonated water
Filling conditions			
Filling temperature [°C]	28 - 88		85 - 95
Pasteurisation time [s]	10 - 30		90 - 360
Washing temperature [°C]		75 - 85	
Washing time [min]		20	

2.6.2.2 Multi-layer bottles and bottles with functional barrier properties

With the introduction of a 2 litre bottle for carbonated soft drinks in 1976 the emerging packaging material PET conquered more and more the shelves of supermarkets by displacing aluminium cans or glass bottles. The opportunities of lower weight, transparency, flexible design and breakproofing led to the development of innovative technologies providing PET containers for a wide range of other beverages. Since then, not only carbonated soft drinks but also more sensitive beverages like mineral water, fruit and vegetable juices, teas, isotonic beverages and recently even beer have been bottled in PET. Due to the fact that plastic materials are more or less permeable for gases, volatiles or water steam the question concerning barrier properties of PET linked with shelf life aspects of

packaged products arose. For the shelf life of oxygen sensitive beverages like fruit juices or beer the gas barrier properties of PET for oxygen as well as CO₂ are of great importance. As a general rule the shelf life of beer is defined as the time within the permeated oxygen concentration reaches 1 mg/ litre beer (Wirsig, 1998). However, depending on the sort of beer it is assumed that absorbed oxygen concentrations of 1 mg to 4 mg per litre cause beer to go bad. Furthermore, the permeation of oxygen may also lead to changes in beverage colour, emerging off-flavours, microbial spoilage and degradation of vitamins e.g. (Hertlein et al., 1997). The barrier properties of standard PET materials as used for carbonated soft drink bottles are not high enough for the requirements of oxygen sensitive beverages. Bottling of sensitive beverages meant in the past that PET materials with higher barrier properties had to be developed. Nowadays several technical solutions for PET materials with higher barrier properties are available. As already mentioned the orientation of PET leads to a higher density of the material and therefore to a higher barrier for gases. The co-polymerisation of PET with PEN is furthermore a possibility to enhance the gas barrier properties. With the development of a *multilayer* technique for PET beverage bottles new perspectives and fields of application were opened. The multilayer technique can be described as a „sandwiching“ of the PET bottle wall. Hereby, virgin PET surrounds possibly up to three inner layers consisting of another material as „functional“ barrier. The inner and outer coating respectively, is an additional technique of enhancing the barrier properties of PET bottles as schematically shown in Scheme 2-12.



Scheme 2-12: Schematic structure of a PET multilayer bottle

Following, customary materials used for the multilayer and coating processes are described:

Coatings

- **BESTPET™ - (Barrier Enhanced Silica Treated PET)**

BESTPET is a coating process for the **outer** surface of a PET bottle based on a physical vapour deposition (PVD) of Silicon oxide (SiO_x) applying high vacuum under plasma conditions. (N.N., 2000 a)

- **Glaskin-System**

Similar to the BESTPET process for the outer surface of a PET bottle, the Glaskin system put a thin layer of Silicon oxide on the **inner** layer of a PET container (N.N., 2000 a)

- **Polyvinylidene chloride (PVDC)**

New coatings in the stage of development:

- **Diamond Like Carbon (DLC)**

In Japan, a process was developed using diamond qualified carbon as an inner or outer layer for PET bottles. Apart from excellent barrier properties, DLC as an outer layer can also reduce the scuffing of PET bottles. The carbon layer cannot be removed from the surface of a PET bottle and therefore recycling may be restricted (Schaper, 2000 a)

- **ACTIS - process**

The inner surface of PET bottles is coated with amorphous carbon which provides acceptable barrier properties but is sensitive to mechanical stresses (Schaper, 2000 a).

- **Epoxy amine**

The great advantage of epoxy amine as barrier coating for PET bottles is the possibility to remove the coating using an activator during the washing process. At the moment it is the only coating process for PET which allows bottle-to-bottle recycling (Schaper, 2000 a).

Multilayer materials

- **Nylon/ MXD6 (Polyamid)**

The most common multilayer processing is the production of a three layer PET bottle consisting of PET / Nylon as barrier layer / PET. The advantage of Nylon is the high transparency and the low price (Schaper, 2000 a).

- **Ethylene vinyl alcohol (EVOH)**

EVOH has a better barrier property than Nylon, is transparent and also show acceptable mechanical properties. The disadvantage of EVOH is the absorption of humidity and therefore EVOH can only be used if the PET bottles at least are made of five layers, normally in form of PET/ Nylon/ PET/ EVOH/ PET (Schaper, 2000 a).

- **Liquid Crystal Polymers (LCP)**

Using LCP is a combined process of multilayer and blend technique. LCP is mixed with PET (15 % / 85 %, w/w) to a blend and used as an inner layer with a thickness of up to 30 % of the whole bottle thickness (Schaper, 2000 b). During the stretch blow moulding LCP are biaxially orientated forming a micro structure like flaky pastry. These structures have a labyrinth effect on the permeation of gases. Because LCP are not allowed for the direct contact with foodstuffs they are used as an inner layer of multilayer PET bottles. The disadvantage of LCP is that they aren't transparent (Wirsig, 1998).

Table 2-5 presents average permeation data for oxygen as well as carbon dioxide of different PET materials.

Table 2-5: Permeation data of different PET materials (Schaper, 2000 a)

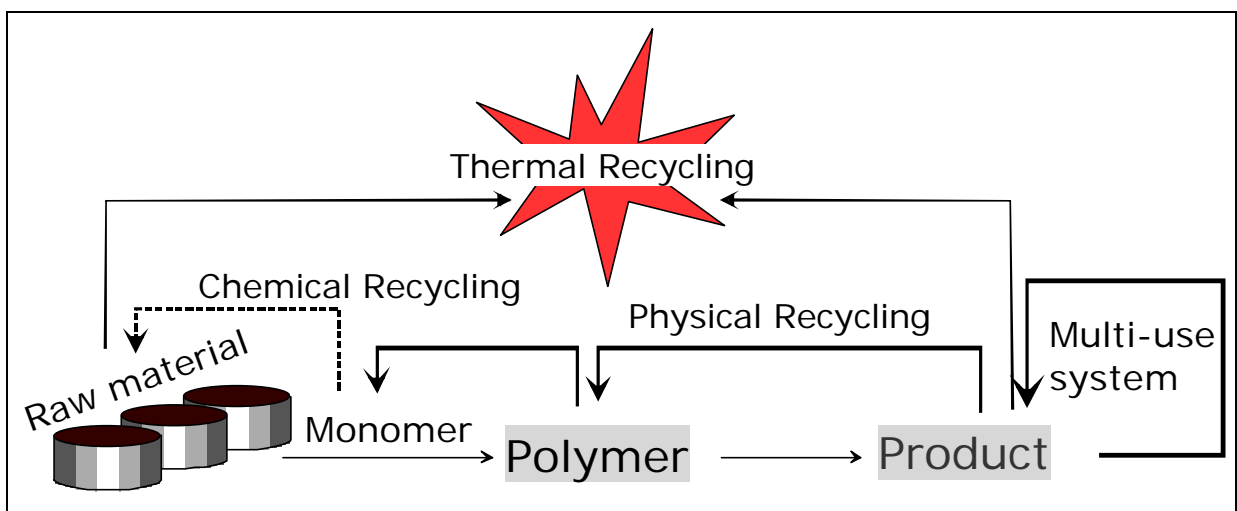
	CO₂ permeation [cm ³ · mm/(m ² · d· bar)]	O₂ permeation [cm ³ · mm/(m ² · d· bar)]
PET	16	4
OPET	8	2
PEN	2	0.5
PVDC coating	0.05	0.03
EVOH	0.05	0.01
SiO ₂	0.01	0.002

The multi-layer technique not only provides the possibility of enhancing barrier properties in form of special inner layers but also is suited for the use and processing of recycled PET (RPET). PET as a packaging material is not totally inert because of the permeable nature of plastic materials generally. Thus, recycled PET can contain contaminants which could remigrate inadmissibly from the package into the food in case of a direct contact. Using recycled PET as an inner layer means that surrounding virgin layers constitute a functional barrier against migration of potential contaminants. Repeatedly performed studies of Franz et al. (1996) showed that an intact virgin PET layer of approximately 25 µm represents an efficient functional barrier against migration from any possible contaminants encapsulated in a recycled PET material under normal conditions of use for soft drink bottles. Therefore at least 25 % of recycled PET material could be used as an inner layer which furthermore could be increased to any technically feasible percentage provided that the properties of the virgin PET as a functional barrier remains unchanged (Franz et al., 1996).

2.6.3 Market requirements - RECYCLABILITY

The imagination of billions of PET bottles on the market arises the question in what way the emerging packaging waste problem can be overcome with a minimum of environmental pollution. In the past, the question of recyclability of plastic materials came up more and more and is nowadays of prime importance even when plastic packaging materials are newly developed and launched.

Although plastic materials only contribute about 4% to 7% to the weight of the municipal solid waste (MSW) they are blamed as a major contributor to landfills due to their substantial fraction caused by an unfavourable mass to volume ratio (Miltz et al.; 1997). PET as a plastic packaging material does not create a direct hazard to the environment, but due to the high resistance against atmospheric and biological agents and due to its extensive volume it is seen as a noxious material. In 1993 the European Union drafted a Directive on Packaging and Packaging Waste to protect the environment. According to this Directive 94/62/EC at least 50% by weight of the packaging waste has to be recovered whereas at least 25% by weight of plastic materials have to be recycled with a minimum of 15% by weight for each packaging material (Crockett; Sumar, 1996 a). When managing the PET packaging waste, the prevention of arising packaging waste in form of reducing the PET packaging quantity has to be given preference. Additionally, the reuse of PET packaging materials, the recycling of the PET material as well as other forms of recovery represent further fundamental principles of waste management. According to the environmental impact, the reuse and recycling of PET should be considered preferably. The possibilities of recovering PET packaging waste is summarised in Scheme 2-13.



Scheme 2-13: Possibilities of recovering PET packaging materials (according to Fumio; Takeshi, 1997/98)

PET as a plastic packaging material has advantageous recycling characteristics in comparison to other plastic packaging materials provided that a maximum possible return of packaging waste is guaranteed by extensive collection systems. Switzerland for example is up to now the country with the highest recovery rate for PET packaging waste as presented in Table 2-6.

Table 2-6: Recovery of PET packaging waste in Switzerland (according to PET Recycling Schweiz (PRS), Naglerwiesenstr. 4, 8049 Zürich, Switzerland or under www.petrecycling.ch)

year	total consumption	collection results	collection quote
1991	4175 t	548 t	13 %
1992	6196 t	3300 t	53 %
1993	8473 t	6136 t	72 %
1994	13623 t	9454 t	70 %
1995	17023 t	12609 t	74 %
1996	18245 t	14448 t	79 %
1997	21471 t	17086 t	79.6 %
1998	24081 t	19100 t	79.1 %
1999	27600 t	22700 t	82 %

Because of the exploding quantities of PET packaging waste based on continuously increasing demands of PET as packaging material, the possibilities of recovering PET, also in view of the fact that recycled PET could be further used as a packaging material for foodstuffs, are described in detail in the following chapter 2.7.

2.7 RE-USE AND RECYCLING OF PET CONTAINERS

Recovering of packaging waste is one of the main targets of the EU Directive 94/62/EEC. However, recovery of PET packaging waste is only useful and profitable, respectively, as long as new end-use markets and applications are available. Fulfilling the enforced requirement of recovering at least 15 % of PET waste by weight puts pressure on finding market solutions for recycled PET materials especially in the case of recycling PET back into food contact materials.

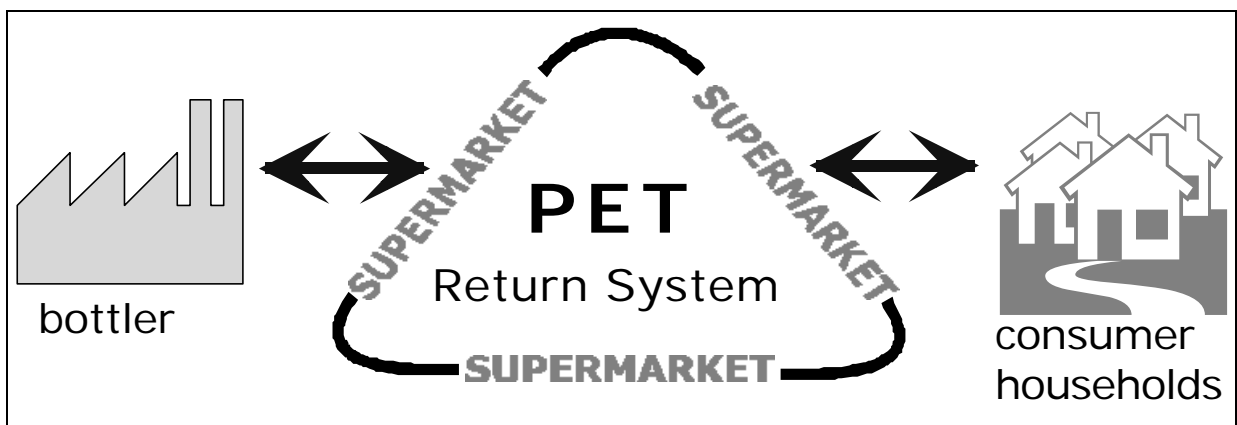
Recycled plastics for direct food contact have to meet all the requirements of the appropriate directives on chemical composition and migration in the same way as virgin materials (Huber; Franz, 1997). As already shown in Scheme 2-13 the recycling of PET packaging materials can be performed by three distinct approaches. The PET packaging may be reused directly, undergo physical reprocessing, or be subjected to chemical treatment whereby its components are isolated and reprocessed. According to notes published by the German „Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin“ (BgVV) a now widespread nomenclature and categorisation of returnable and recycling products have been established in order to provide guidance on application possibilities in the food area. Recovered PET packaging materials can be categorised as follows (BgVV, 1995):

- [A] **Re-use systems**
Refillable, returnable packaging articles
- [B] **Physical reprocessing**
 - [B.I.] **Primary recycling** material (pre-consumer character)
 - Class 1: Production scrap comparable in quality with virgin material
 - [B.II.] **Secondary recycling** material (post-consumer character)
 - Class 2: High purity material with almost primary quality due to control on the return system and complete knowledge of the prior application.
 - Class 3: Low purity material without any control on the return system and knowledge of the prior application.
- [C] **Chemical reprocessing**
Tertiary recycling material

The Environmental Protection Agency (EPA) of the United States considers „recycling“ to be the processing of PET waste to make new PET articles. Since bottles intended for reuse are not made to be discarded or to become waste, reuse is not considered recycling by the EPA. Reuse can simply be regarded as one form of source reduction. Although EPA does not consider reuse to be a recycling process, it could be considered „zeroth order“ recycling (FDA; 1992).

2.7.1 Reuse of PET containers as packaging for foodstuffs

Within a return system of PET bottles as shown in Scheme 2-14, consumers can purchase different sorts of beverages in PET containers which are returned, washed, sterilised and then refilled. The reuse of PET bottles which circulate between bottler and consumer is of special concern. Since plastic bottles are more likely to absorb contaminants than e.g. glass, absorbed substances could be released back into refilled foodstuffs (FDA; 1992)



Scheme 2-14: Return system for refillable PET bottles

Safety concerns of refillable PET bottles can be minimised in different ways. The most important way may be educating the consumer to avoid storing household chemicals in reusable PET containers e.g. by labelling the bottles „Food Use Only“. Requiring a deposit on the bottles not only presents a possibility of ensuring the return of refillable PET bottles but also might avoid misuse, hence consumers would be less likely to destroy a bottle that required an investment. Reusable PET bottles are directly returned to the store by the consumer or collected by the distributor, thereby adding a measure of control over the source of refillable PET containers (FDA; 1992).

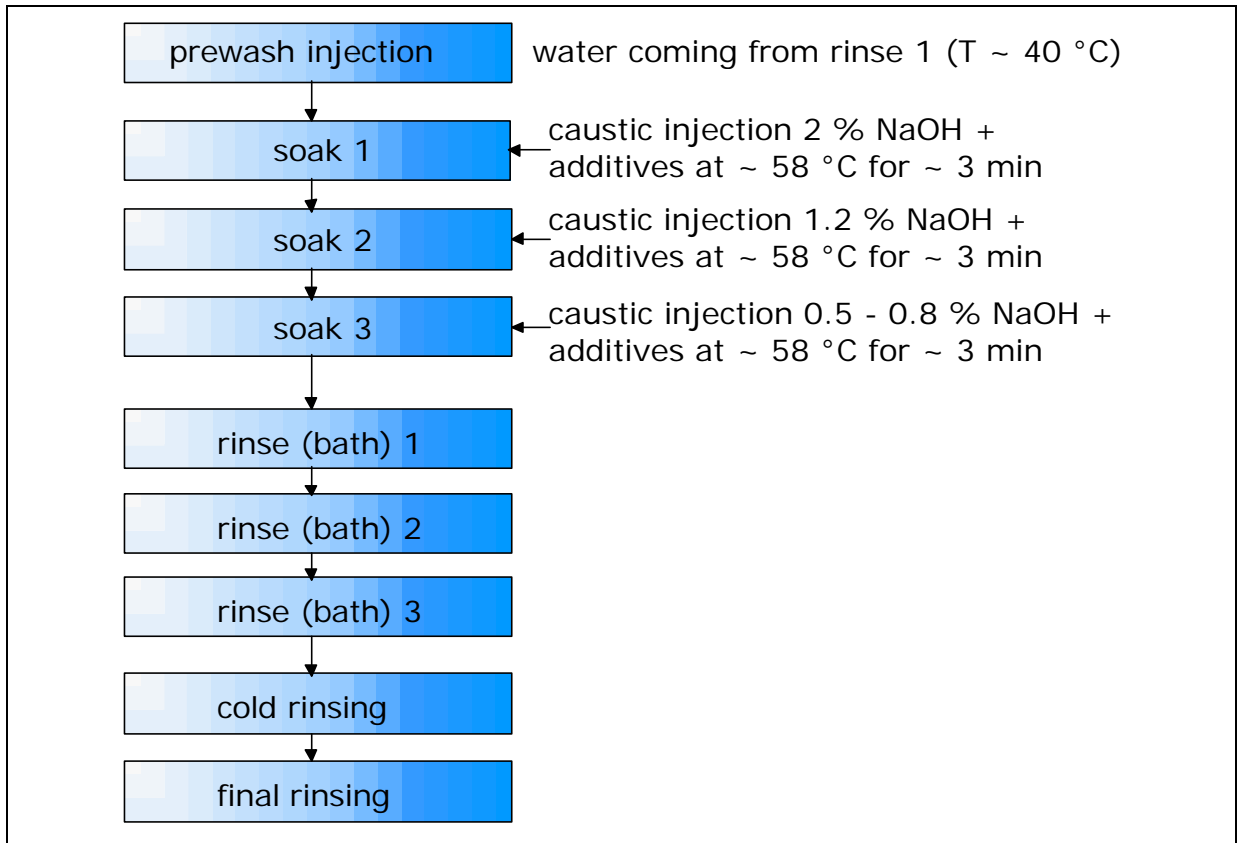
Standard industrial washing procedure for refillable PET bottles

Refillable PET bottles which circulate between bottler and consumer must be intensively cleansed by washing and sanitising in a way that possible contamination residue levels are low enough not to adulterate refilled foodstuffs. The pollution of returned PET bottles can be superficial, with adsorption of substances onto the plastic surface or it can be more extensive by absorption of substances into the polymer PET due to migration processes. The latter contamination of refillable PET bottles not only has to be understood as a result of consumer misuse e.g. by storing or diluting household chemicals. „Contamination“ of a PET bottle may also occur in form of absorbed flavour compounds of previous fillings or in form of absorbed chemicals arising from microbial deterioration. Therefore, contamination of refillable PET bottles not only presents a potential problem from a health point of view, but also if off-tastes and organoleptical changes of refilled foodstuffs occur due to re-migration of residual aroma compounds in the plastic material.

Before refilling, used PET containers are inspected twice, before and after the washing procedure. The screening and inspection of used PET containers is presently limited to visual inspection (manual or machine) for gross contamination or foreign bodies as well as „sniffer“ devices for the detection of volatile substances. These inspections work in-line in automated bottle cleaning and refilling lines (Hilche, Haux; 1995). An extensive and integral screening which is able to detect all possible contaminants from potential chemicals to micro-organisms is practically impossible and will not be changeable in the foreseeable future.

The resistance, strictly speaking the inertness of a PET material to the uptake of chemicals will therefore largely dictate the suitability for refilling applications. As it is statistically unlikely that a consumer will be exposed repeatedly over time to contaminated containers, the exposure to chronic toxins is not a concern. The main concern in re-use of containers is the exposure to acute toxins, a single exposure at an acute level. In case of refillable PET bottles, the risk of contamination of the new filling is greatly minimised by the high chemical resistance of the polymer PET.

However, reuse can adulterate plastic materials thus influencing absorption and desorption properties (Crockett; Sumar, 1996 b). For ensuring the ultimate quality and safety-in-use of reused articles, research was extensively carried out to establish the efficacy of commercial washing processes as well as the effect of repeated reuse on material properties. The following Scheme 2-15 shows a standard industrial cleaning procedure of used refillable PET bottles.



Scheme 2-15: Cleaning procedure of returned refillable PET containers (according to Jetten et al.; 1999).

The washing and sanitising process from the pre-wash injection to the final rinsing of returned PET bottles takes 17 minutes altogether. The efficiency of the cleaning procedure of returned PET bottles can be specifically influenced by parameters like temperature, time, mechanical forces as well as concentration of caustic solution and detergents. The ranges, within these parameters can be varied during the cleaning procedure, are limited due to material properties and characteristics of the polymer PET. Nielsen (1994) evaluated the sorption of two orange flavour components into PET as well as the effect of different washing procedures on the removal of sorbed compounds. Refillable 500 mL PET bottles were contaminated with Limonene e.g. and washed on a laboratory scale at 60 °C as well as 70 °C with sodium hydroxide solutions of 1.5 % (w/v) and 3 % (w/v) respectively. He found that less than a third (22 %) of the Limonene sorbed into the PET bottles was removed by washing at 60 °C at both sodium hydroxide concentrations. When the washing temperature was increased up to 70 °C, the Limonene content in the

plastic could be decreased to 69 % of the initial value. Nielsen (1994) stated, that the concentration of NaOH in the washing solution seemed to have no effect, but increased washing temperature had some influence on the washing efficiency regarding Limonene. Furthermore, he also determined that washing containers prior to filling seemed to diminish the future sorption of Limonene. PET bottles washed six times absorbed only 70 % as much as did untreated bottles. Experiments of Devlieghere et al. (1997 b) showed, that the desorption behaviour of several investigated contaminants was not influenced by the number of preceding washing trips of the bottles (up to 40 washing cycles). They additionally performed research concerning the optimisation of the cleaning process of contaminated refillables. Principally corresponding to Nielsen (1994), the results of the investigation showed that the additive concentration was not significantly influencing the cleaning efficiency towards the removal of d-Limonene. The caustic soda concentration (NaOH) and especially the temperature as already mentioned, seemed to be the major controlling parameters of the cleaning process. Unlike Nielsen (1994), Devlieghere et al. (1997 b) determined the „residual contamination“ of refillable PET bottles after the washing procedure not in the polymer material itself but as concentration of contaminants re-migrated into re-filled foodstuffs.

Analysing the concentration of re-migrating contaminants in re-filled foodstuffs after defined storage conditions provides more meaningful test results than measuring the residual amount of contaminants in the material itself. In practice, it can be excluded that contaminants presented in refillable PET bottles re-migrate exhaustively into a re-filled foodstuff. Devlieghere et al. (1997 b) found that the concentration of d-Limonene in refilled water was very low and amounted from 1 ± 0.2 ppm to 0.4 ± 0.1 ppm depending on previous washing conditions. Optimal washing conditions for refillable, hotwash PET bottles were reached at 70 °C and 2 - 2.8 % (w/v) sodium hydroxide. The lowest removal efficiency was obtained at washing conditions at 55 °C, 1 % (w/v) NaOH and 0.3 % (w/v) additive (commercially available chemicals for cleaning returnable bottles: P3 Stabilon flüssig, containing nonionogenic surface active compounds, phosphonates and phosphoric acid).

However, since the differences between worst and optimal washing conditions concerning the removal of d-Limonene were mostly not very pronounced, it is important not to come to false conclusions regarding „optimal“ washing conditions of refillable PET bottles. The fact that a higher temperature seems to correspond with a better cleaning efficiency can be explained by the higher solubility of contaminants in the washing solution. Cleaning at high temperatures (up to 80 °C) in combination with a high caustic concentration however, also can have a negative influence on removing contaminants from PET. High concentrated sodium hydroxide solutions in combination with high temperatures could be aggressive

towards the PET itself and thus enhancing migration due to changes in the morphology of the material (Safa; Bourelle, 1999 b). However, it can be concluded that there is no washing procedure available which is able to remove absorbed flavour compounds quantitatively. When strong flavours are brought into refillable PET bottles, flavour carryover into a refilled foodstuff is likely to occur. That means, that refillable PET bottles have to be distinguished whether they are used for soft drink markets or mineral water applications.

Removal of micro-organisms from PET bottles

Safety-in-use criteria of refillable PET containers not only comprise aspects of possible chemical contamination but also microbiological quality and safety concerns. Devlieghere and Huyghebaert. (1997 a) examined the microbial rinsability of refillable PET containers using *Staphylococcus aureus* as well as *Bacillus cereus* as model micro-organisms. Obtained results showed that the influence of temperature on the cleaning efficiency was small compared to the effect of the concentration of applied caustic and additive solution. Caustic cleaning did not inactivate the attached micro-organisms with the applied heat of 78 °C but removed them from the surface. Micro-organisms can show a high resistance e.g. by a protective barrier effect afforded by the polymeric matrix and therefore, withstand higher temperature/time combinations applied during the washing procedure. Such micro-organisms have to be removed physically from the bottle wall. From a microbiological point of view the use of additives is very important for the cleaning efficiency of refillable PET bottles. The effect of commercial additives containing nonionogenic surface active compounds, phosphonates and phosphoric acid can be explained by its capacity to decrease the surface tension of the caustic solution. Commercial additives contain chelating agents which lower the ionic strength of the liquid and therefore decrease possible electrostatic interactions between polymer substrates and the cells. Concerning the removal of micro-organisms the use of 2 % NaOH in combination with approximately 6 % additives has to be given preference. In standard industrial washing procedures comparable low concentrations of sodium hydroxide solutions are preferred to avoid foaming. (Devlieghere; Huyghebaert, 1997 a).

Hazing and stress cracking of refillable PET bottles

Washing procedures for refillable PET bottles not only have to be optimised concerning the cleaning efficiency. The influence of washing parameters on material properties like visual appearance of a PET bottle has also to be taken into account.

- *Hazing*

Polyethylene terephthalate is manufactured by esterification of dibasic alcohols with dibasic acids. During the washing procedure, the presence of hydroxide ions (OH^-) of the caustic solution give rise to the cleavage of ester links. The adulteration of the material leads to the development of pores and grooves on the surface of a PET bottle. By diffusive reflection of light the effect of material deterioration becomes visible as bottle hazing (Theyssen, 1999).

- *Stress-cracking*

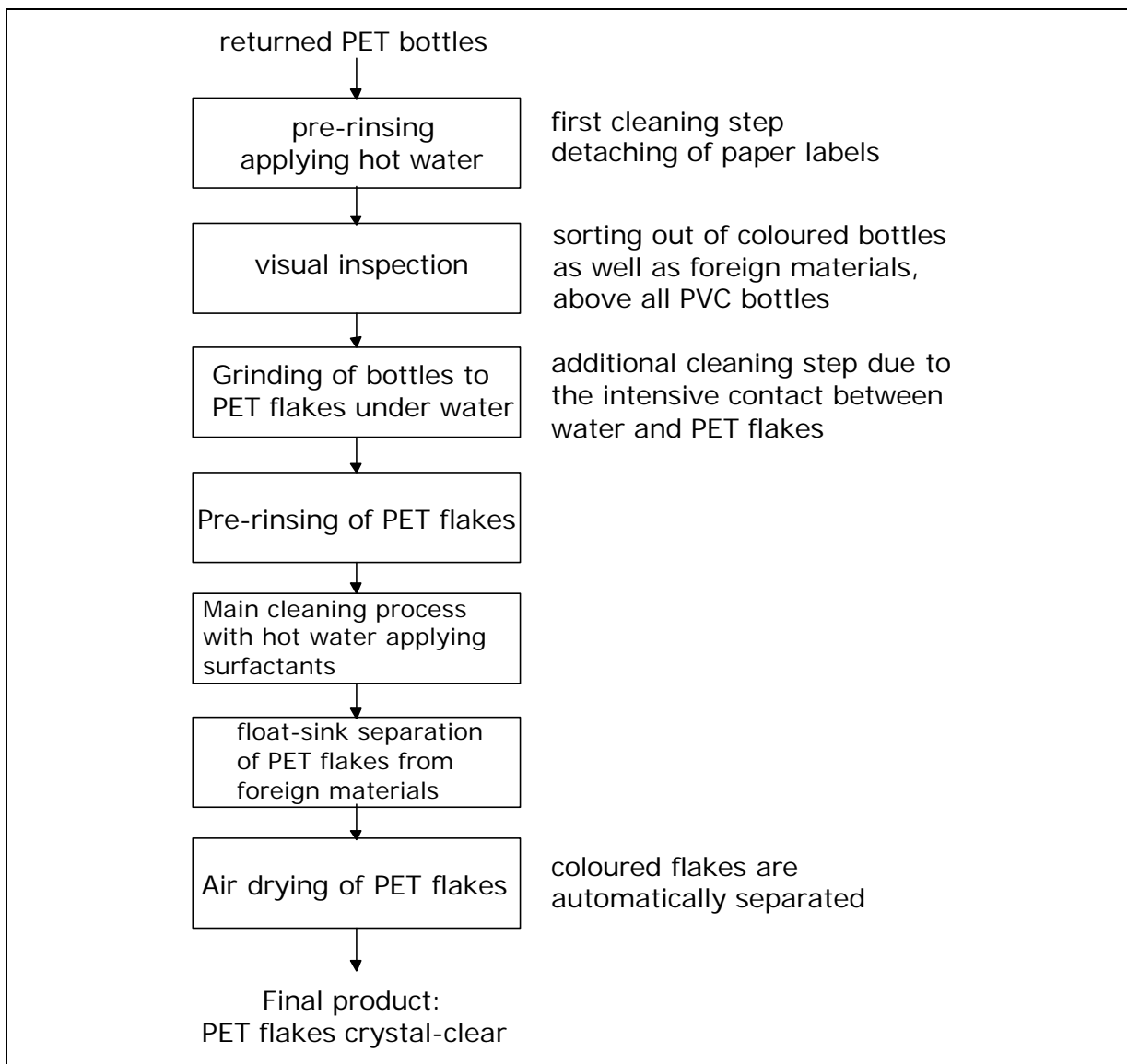
In contrary to hazing, stress-cracking is released by different sorts of chemicals such as adhesives and caustic additives. Migrating into the polymer structure, the chemicals give rise to material stiffening which leads to a stress-cracking of the material while applying pressure (Theyssen, 1999).

2.7.2 Physical reprocessing of PET packaging waste

Physical reprocessing of PET packaging waste can be divided into primary and secondary recycling depending on source and composition of PET packaging waste. While PET materials with pre-consumer character are used as source for primary recycling, secondary recycling is performed using post-consumer PET, returning from consumer households in different qualities.

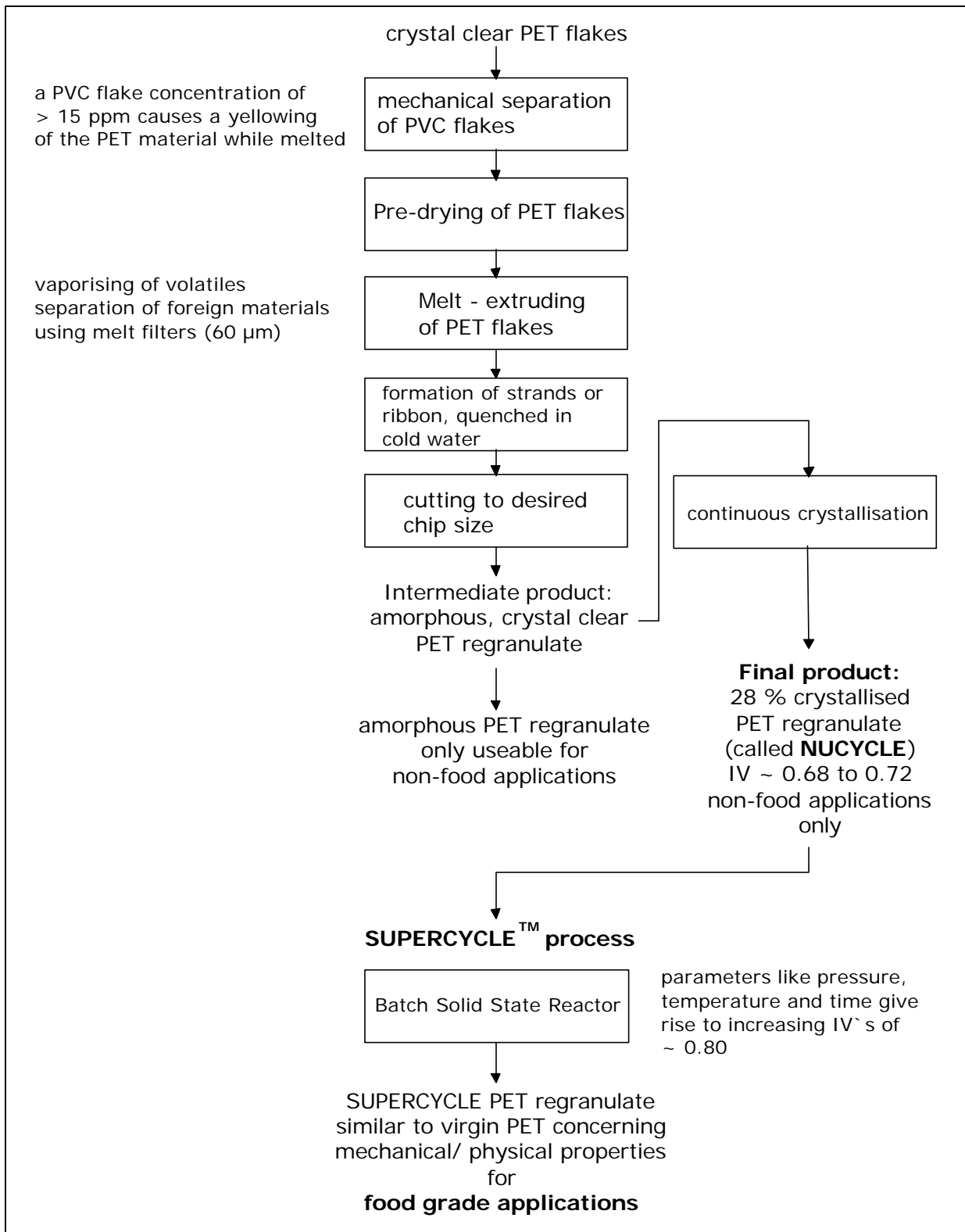
The quality of PET production scrap for primary recycling is comparable with virgin materials and increasingly used for chemical reprocessing of PET. The possibility of locating a chemical recycling plant in the polymer production line led to the fact, that large PET manufacturers are directly recovering monomers from waste PET arising within the production cycle (Paszun; Spsychaj, 1997).

Physical reprocessing of secondary recycling materials involves grinding, melting and reprocessing of PET packaging waste. The quality and safety of recycled post-consumer PET waste is heavily influenced by source control, effective dilution of possible contaminants as well as the amount of degradation products, built up during reprocessing. The source control of PET packaging waste is decisive for the use of mechanically recycled PET as packaging material for foodstuffs. Using mechanically recycled PET as packaging material for foodstuffs mainly requires that possible contaminants are effectively reduced to levels which are not able to endanger human health. High purity PET materials with almost primary quality and complete knowledge of the prior application can be obtained due to the control of return systems for one- and two-way PET bottles, respectively. Low purity PET materials without any control on the return system and knowledge of the prior application only can be used for non-food applications when physically recycled. In the following Scheme 2-16 and Scheme 2-17 principally describe the physical recycling process of post-consumer PET producing PET flakes in a first stage, before manufacturing amorphous as well as crystallised PET granules for food and non-food applications.



Scheme 2-16: First stage of physical reprocessing of PET post-consumer packaging waste to PET flakes (according to Jacobs, 1998)

The removal of paper, glue and impurities is a significant step in the recycling of PET bottles. After intensively washing, PET must be dried to less than 20 ppm water since residual moisture causes hydrolytic degradation during operations like extrusion or thermoforming. Mechanically reprocessed PET flakes can be used for the manufacture of staple fibres, textiles, carpets, thermoformed packaging trays for non-food applications and recently are also used in the automobile industry (Scheirs, 1998). Furthermore, high quality PET flakes can be mechanically recycled to crystallised PET granulates for non-food and in special cases for food applications as shown in Scheme 2-17.



Scheme 2-17: Physical reprocessing of PET flakes to PET granulate for food and non-food applications (according to Jacobs, 1998)

Since non-food applications for physically recycled PET are limited, technologists of Johnson Control USA strove to develop a physical recycling process called SUPERCYCLE™ providing food-grade PET regranulate in order to close the cycle for one-way PET beverage containers.

In 1994, the FDA gave a letter of „no-objection“ for supercycled PET regranulate for direct food contact applications. The Supercycle™ process applies a combination of high-temperature washing (250 °C), high pressure and long residence time under vacuum, since washing alone even with NaOH solution has not been effective enough in removing chemical contaminants from PET (Scheirs, 1998). However, recyclers must be able to demonstrate that contamination concentration in mechanically recycled PET is sufficiently reduced at the end of the recycling process to assure that resulting packaging would not adulterate food or endanger human health. Under the responsibility of the International Life Science Institute (ILSI) guidelines for recycling of plastics for food contact use were established in 1997. According to the guidelines, recycling operations are required to minimise adventitious contamination of articles returned for recycling. Thus, any recycling operation must demonstrate the capability to select and use only food-grade feedstock at a minimum effectiveness of 99 %. Furthermore, practical tests are required to show the efficiency of the recycling process in removing adventitious contamination (ILSI, 1998).

Challenge test for assessing the cleaning efficiency of PET recycling processes

So-called *challenge tests* have been developed which „challenge“ the recycling process by introducing surrogates together with uncontaminated feedstock at an appropriate point in the process. The simulated situation has the character of a worst case scenario for consumer misused PET containers e.g. by storing household or garden chemicals and returning them for recycling. Therefore, the surrogates used to simulate consumer misuse have to cover the full range of chemical/physical properties of potential pollutants such as polarity, volatility and compatibility with the polymer type. The quality control of PET recyclate for the sensitive application in direct food contact is based on the analytical quality assurance by analysing and reporting surrogate concentrations from the PET feedstock material to the final PET container. For challenging the recycling process, post-consumer PET flakes are artificially contaminated with the following surrogates (Franz; Welle, 1999):

Table 2-7: List of surrogates used for the challenge test (M_w : molecular weight)

Name	M_w	functional group	properties
Acetone	58.1	aliphatic ketone	volatile, polar, water soluble
Toluene	92.1	aromatic hydrocarbon	volatile, non-polar
Chlorobenzene	112.6	halogenated hydrocarbon	volatile, medium-polar, very aggressive to PET
Phenylcyclohexane	160.3	aromatic hydrocarbon	non-volatile, non-polar
Benzophenone	182.2	aromatic ketone	non-volatile, polar
Methyl stearate	298.5	aliphatic ester	non-volatile, polar

Real-life contaminants as suggested by the FDA also include solvents like chloroform and herbicides like Lindane and Diazinone. Since the latter are highly toxic substances, the handling according to the challenge test proposed by FDA involves a hazardous risk to the workers on the recycling plant. For this reason the Fraunhofer Institute for Process Engineering and Packaging (FhG-IVV) developed a modified as well as simplified challenge test (Welle; Franz, 1999). In favour of consumer safety the challenge testing (Scheirs, 1998) was designed to „play the

- ↪ contaminating 100 % of the plastic material subject to physical recycling and quality testing (in reality only approximately 1 of 10.000 bottles is considered to be contaminated)
- ↪ generally higher concentrated contamination solutions than chemicals used by consumers. Prior to recycling PET flakes are soaked with each of the contaminants to a level of 1000 ppm (0.1 %).
- ↪ determining the concentration of surrogates in the recycled PET and assuming that migration into a refilled foodstuff would be 100 % and if failing,
- ↪ modelling or analysing the maximum quantity re-migrating into foodstuffs under normal conditions of use assuming that the final article consists to 100 % of recycled PET material.

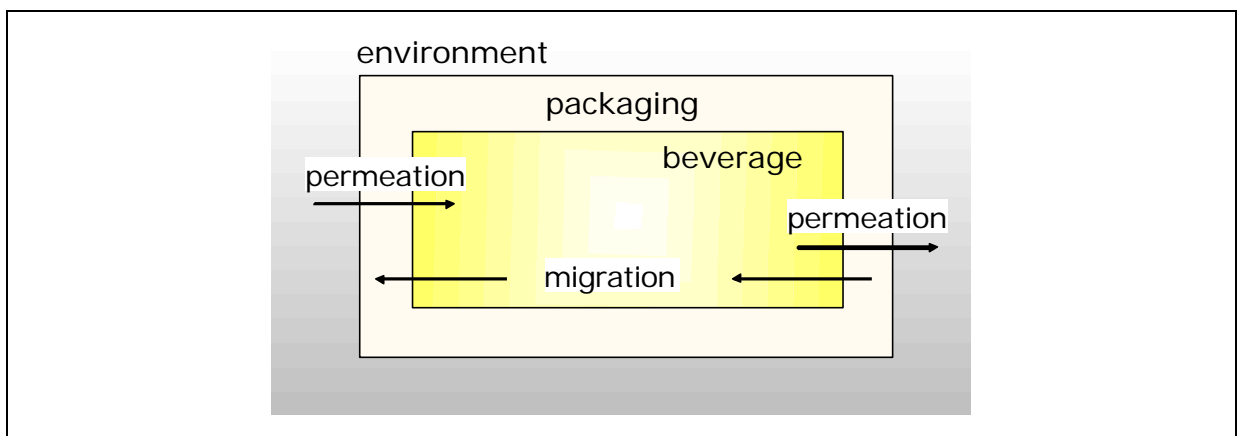
Establishing the quality and safety of reprocessed PET granulate not only of mechanically but also chemically recycled PET-regranulate can be examined applying the Challenge test. In the case of chemical recycling the depolymerisation reactor can be „spiked“ with 0.1 % of contaminant per weight unit of PET flakes (Scheirs, 1998).

2.7.3 Chemical reprocessing of post consumer PET

The great advantage of chemical (tertiary) recycling is the total or partial depolymerisation which allows that any contaminants bound to the polymer chain can be removed by purification of mono- and oligomers. The main chemolysis reactions used in PET recycling are glycolysis, methanolysis and hydrolysis using ethylene glycol, methanol as well as water as degrading chemical agents. After depolymerisation the monomers are purified and re-polymerised with ethylene glycol to give once again virgin PET. However, chemically recycled PET principally can be used in food-contact applications but only if economically incentive and not more expensive than virgin PET (Scheirs, 1998).

2.8 MIGRATION CONSIDERATIONS OF PET AS PACKAGING MATERIAL FOR FOODSTUFFS

In order to fulfil a series of functions, plastic packaging materials come in most cases in direct contact with foodstuffs. On account of this direct contact interactions between the plastic packaging and foodstuff can occur during the often long storage time. The term „interaction“ can be summarised as the mass transfer of substances from the packaging and environment into the packaged foodstuff as well as that in the opposite direction. Interactions which can occur in a packaging system are distinguished into permeation and migration processes as shown in Scheme 2-18. Permeation means transfer of substances through the packaging material. Migration on the other side indicates the transport of substances from the plastic packaging into the foodstuff as well as vice versa. Although PET has been reported to have a great resistance to absorption and desorption of „substances“ in comparison to other plastic packaging materials it is necessary to remark that the packaging is not totally inert.



Scheme 2-18: Interactions between packaging material and foodstuff.

2.8.1 Fundamentals

Mass transfer of mobile substances, particularly low molecular compounds from the plastic material to the packaged food is a consequence of diffusion processes in the polymer and can be described by Fick`s First and Second law.

In a first step mobile compounds can migrate into the foodstuff due to a boundary area diffusion. As a result of this mass transfer impoverished regions of low molecular substances arise on the surface of the plastic material. These surface areas with lower concentrated mobile compounds were equalised by thermal removing of substances from deeper layers of the plastic.

The food contact area of a plastic packaging material is therefore a permanent region of departure for migration of plastic compounds. The migration potential of a plastic material depends on several parameters. The initial concentration of mobile compounds in the plastic material is proportional to the amount migrating into the foodstuff. Therefore the physical and chemical properties of the polymer

material as well as the chemical characteristics of mobile components are of great importance. The migration potential can also be influenced by the production technique in form of morphological properties like crystallinity, surface porosity or wall thickness. The intensity of interaction between packaging and foodstuff also depends on the composition and textural structure of the packaged food. Finally, the influence of contact time and storage temperature in the system plastic packaging/ foodstuff have not to be left out of account.

The sorption (migration) mechanism for glassy polymers also involves ordinary „dissolution“ of substances and „hole“ filling. At low concentrations migrants are quasi-chemically bound or immobilised within a polymer matrix rather than physically entrapped. Total migration of substances from PET consist of three thermodynamically molecular populations defined as follows (Kim; Gilbert, 1988):

- „freely diffusible“ substances which are dissolved in the amorphous region of polymeric matrix
- „Sorbed“ or „bound“ substances localised at active sites or „holes“ within the glassy polymeric matrix
- „Completely bound“ or „immobilised“ substances which are non-diffusible within the matrix, i.e. where the bonding energy is considerably above activation energy required for diffusion.

Migration processes can be described mathematically under simplifying assumptions and worse case considerations. Predicting the migration potential it is assumed that the polymer and the food/solvent are infinitely thick, the diffusion coefficient is only a function of temperature and the migrant is uniformly distributed in the polymer and well soluble in the food/ solvent. Then the time dependent migration M_t can be described by the following relationship (Piringer, 2000):

$$M_t = \frac{m_t}{A} = 2 C_{P,0} * \sqrt{\frac{D_p * t}{\pi}} \quad (\text{equation 1})$$

m_t/A is the mass transfer of a substance in μg per contact area A in cm^2 at time t in seconds

$C_{P,0}$ is the initial concentration of the substance at time $t = 0$ in the polymer in $\mu\text{g}/\text{cm}^3$

D_p is the diffusion coefficient of the substance in the polymer in cm^2/s

t time in seconds

With known $C_{P,0}$ and D_p it is possible to undertake pre-considerations about the migration potential of a package with respect to the packaging design. However, D_p values are not always available and their determination is often very time

consuming. For this case the PIRINGER equation for the calculative estimation of D_p - values can be employed (Piringer, 2000):

$$D_p = 10^4 \exp\left(A_p - 0,01 * M_r - 10450 * \frac{1}{T}\right) \quad (\text{equation 2})$$

The equation reduces D_p to be dependent on the polymer type (A_p - value), the relative molecular weight M_r and the temperature T (Kelvin).

For PET A_p values have been established to lay between -3 and -5 (Franz, 1995).

2.8.2 Migration potential of PET

The safe use of PET as packaging material for foodstuffs is related to the degree to which the PET components are migrating into food as well as the toxicological properties of the material. Substances possibly migrating from virgin PET containers can be determined routinely since they are well defined and restricted manufacturing components of PET, summarised in a so-called positive list. Refillable PET bottles and PET containers consisting of recycled materials however, might contain uncountable, unknown contaminants due to consumer misuse.

Migration potential of virgin PET containers

For migration testing from virgin PET, containers are exposed to food-simulating liquids like water, 3 % acetic acid, 10 % ethanol as well as olive oil (or substitutes like isooctane and 95 % ethanol) to determine compliance with migration limits for various conditions of use. Table 2-8 shows specific migration limits for monomers commonly used for the manufacturing of PET.

Table 2-8: Monomers commonly used for PET and their specific migration limits

Monomer	Specific migration limit
Terephthalic acid	7.5 mg/kg
Dimethyl terephthalate	no SML
Isophthalic acid	no SML
Dimethyl isophthalate	no SML
Ethylene glycol (EG)	30 mg/kg (alone or with diethylene glycol)
1,4- Cyclohexanedimethanol	no SML

Not only monomers but also oligomers, polymerisation aids, colorants or degradation products, used for the manufacturing process of PET, could possibly migrate into foodstuffs. Based on material characteristics, PET is relatively free of additives and adventitious low molecular weight constituents and so has intrinsic low migration characteristics that have made PET desirable as a food contact

material. In the meantime PET bottles are extensively used for carbonated soft drinks and mineral waters but also for beers, wines, spirits and edible oil. PET is furthermore increasingly used in form of trays for conventional or microwave ovens. The conditions under which PET is nowadays used are extremely varied and must be considered when assessing the possible migration of components from PET into food. In the past, numerous research studies were carried out to determine potential migrants from commercial PET.

In 1987 Kim and Gilbert isolated and identified a total of seven potential migrants as residual monomers, dehydration and transesterification products by Soxhlet extraction of the PET polymer under worse case conditions as follows:

- Ethylene glycol 1.8 mg/kg
- Diethyl terephthalate 3.8 mg/kg
- Terephthalic acid 2.8 mg/kg
- Ethyl 2-hydroxyethyl terephthalate 2.3 mg/kg

They also identified fatty acids in form of palmitic acid, oleic acid and stearic acid which are commonly used as lubricants and considered as GRAS (generally recognised as safe) according to FDA.

Further migration studies of Ethylene glycol from PET bottles into the food simulant 3 % Acetic acid stored for 6 months showed levels of about 0.1 mg/kg (Kashtock; Breder, 1980) which are insignificant in relation to the maximum level of 30 mg/kg permitted in foods in the European Community. Terephthalic acid determined as residual monomer in PET showed concentrations of 1.5 mg/kg and 1.7 mg/kg for films and bottles, respectively, whereas the migration into food simulants was found to be <0.01 mg/kg for water, acetic acid and 10 % ethanol as well as 0.02 and 0.03 mg/kg for migration into 50 % ethanol and olive oil (Tice, 1988).

Ashby (1988) examined the migration from PET under all conditions of use. He found that specific migration results of constituents of PET - such as monomers, catalysts, residues and breakdown products - had very low levels of migration into all type of foods when tested under realistic conditions of use. The following table shows extracts of test results established by Ashby (1988) for PET bottles:

Table 2-9: Specific migration results from PET bottles (according to Ashby, 1988)

Migrant	Simulant	Exposure	Result
Acetaldehyde	water	10 d/ 40 °C	< 15 ppb
Antimony	water, 3 % acetic acid, 10 % ethanol, olive oil	10 d/ 40 °C	nd < 10 ppb
Cobalt	water, 3 % acetic acid, 10 % ethanol, olive oil	10 d/ 40 °C	nd < 3 ppb
Colorant	water, 3 % acetic acid, 50 % ethanol, n-heptane	21 d/ 49.5 °C	nd < 50 ppb
Overall migration	water, 3 % acetic acid, 10 % ethanol, 50 % ethanol olive oil	10 d/ 40°C	0.33 to 0.70 mg/dm ²

As trace amounts of Acetaldehyde can negatively influence the taste of beverages especially carbonated mineral water, levels have to be closely monitored. The human detection threshold of Acetaldehyde has been reported to range between 10 to 20 µg/L up to 40 µg/L for mineral water depending on contents of Carbon dioxide (Eberhartinger et al., 1990; Nijssen et al., 1996; Pepin and Communal, 1983).

PET oligomers form the largest mass fraction potentially migrating from the polymer into food during storage and handling (Dobias et al., 1996). The levels of extractable oligomers range from 0.06 to 1.0 % (w/w) depending on the type of PET. Oligomers mainly consist of cyclic compounds from dimer to pentamer among which the cyclic trimer forms about 81 % (Castle et al., 1989). Directives of the European Community (EC) specify an overall migration limit for plastic packaging materials of 10 mg/dm² of food-contact surface or 60 mg/kg of food for total migration from the packaging material. As shown in Table 2-9 the specific as well as overall migration results for constituents of PET are usually found far below the required migration limits.

Migration potential of recycled and reused PET containers

As already mentioned PET containers could absorb unknown contaminants due to consumer misuse which could be released back into food in case of a direct contact. Recycling processes have to meet high requirements concerning the quality and safety of recycled PET material if intended to be used as packaging material for foodstuffs. The Supercycle™ process provides secondary recycled PET which is of comparable quality as virgin PET due to optimised processing techniques. It is theoretically possible however, that contaminant residues e.g. traces of carcinogenic or toxic contaminants remain in the material/ package and could conceivably develop very low steady-state concentrations over long term recycling. The existing potential that consumers could be exposed to low concentrations of carcinogens over a long period of time led to the development of criteria

concerning acceptable residual levels that would not comprise the public health. The Centre for Food Safety and Applied Nutrition of the US FDA suggested that dietary exposures to contaminants from recycled food-contact articles in the order of 1 ppb or less are generally of negligible risk. The maximum residual level for a contaminant that would contribute no more than 1 ppb to the daily diet can therefore be calculated as follows (FDA, 1992):

$$CF * \langle M \rangle = CF * \sum_{i=1}^4 (M * f_T)_i = \text{dietary concentration} \quad (\text{equation 3})$$

		In case of PET
CF	consumption factor	0.05
f_T	food-type distribution factor	1.0 / 0.97 (aqueous)
$\langle M \rangle$	concentration of migrant into a food-simulating solvent i	
i	simulating food types: aqueous, acidic, alcoholic and fatty foods	

Assuming that a PET container has a density of 1.4 g/cm³ and a thickness of 50 µm a package will have a mass-to-surface ratio of 0.07 g/cm². Further it is assumed that 1.50 g of food contacts one square centimetre of container. The migration level from package to food is calculated as follows:

$$\begin{aligned} 1 \text{ ppb in the diet} &= 0.05 * (M) * 1.0 \\ \langle M \rangle &= (1 * 10^{-9} \text{ g contaminant/ g food}) / 0.05 \\ &= 2 * 10^{-8} \text{ g contaminant/ g food} \end{aligned}$$

Then,

$$(0.07 \text{ g packaging/cm}^2) / (1.50 \text{ g food/cm}^2) = 0.046 \text{ g packaging/g food}$$

therefore

$$(M) = 4.3 * 10^{-7} \text{ g contaminant / g packaging}$$

In other words, if 430 ppb of contaminant were present in the PET container and if 100 % migration of the contaminant into food were assumed, the concentration of the contaminant in the daily diet would be 1 ppb. Thus, individual chemical contaminants should not be present at e.g. greater than 430 ppb in PET containers (FDA, 1992). Residual contaminants migrating from recycled PET containers into food have to be considered as indirect additives and therefore have to comply with regulations of enforcement authorities. In Europe there are up to now neither for recycled PET containers nor for refillable PET bottles specific regulations available. The FDA established a so-called 'threshold of regulation' policy whereby those substances in food-contact articles that result in minimal migration into food would be exempted from regulation as „food additive“ (FDA,1995). As a general principle, the threshold of regulation is applicable to a wide range of safety assessments. Based on data of nearly 18 000 acute and chronic toxic compounds as well as over

400 carcinogenic chemicals, toxicologists have proposed a negligible or *de minimis* risk level of $< 1 \mu\text{g}/\text{kg}$. This would be low enough to prevent any toxicological risk. The final ruling of the 'threshold of regulation' in 1995 however, established a threshold concentration for indirect food additives of $0.5 \mu\text{g}/\text{kg}$ (0.5 ppb) (Bayer, 1997).

The sorts of household chemicals and pesticides possibly stored in PET containers can be delimited due to the restricted availability of hazardous chemicals to consumer households. Simulating misuse of e.g. refillables by contamination of virgin PET bottles, several chemicals can be excluded from safety studies. Household chemicals which are extremely aggressive to PET in form of hazing or partially destroying the clarity can be excluded straight away as they can easily be detected by visual inspection systems. Furthermore abused PET bottles which were filled with chemicals containing strong flavour compounds such as motor oils or fabric softeners are rejected when passing so-called „Sniffer“ devices. Several research studies have been carried out using common household chemicals and pesticides in order to simulate consumer misuse and migration potential of PET bottles under realistic conditions of use. Tawfik et al. (1997) used fungicide, insecticide as well as herbicide to determine the absorption as well as desorption potential of refillable PET bottles. It could be demonstrated that refillable PET bottles showed in general the lowest residual contamination in comparison to other plastic packaging materials like HDPE or PP. The chemical contamination level of water in refilled bottles showed to be low and none of the investigated chemicals were shown to migrate at concentration levels that would pose a public health concern (Tawfik et al., 1997).

TNO Nutrition and Food Research investigated the potential public health risks of the reuse of PET bottles following possible misuse. PET refillable bottles were exposed to 62 contaminants including pesticides, that a consumer could potentially store in PET bottles. The results indicated that chemicals can be absorbed into the bottle wall of PET, if misused. Measurements of contamination levels after washing showed that only relatively low fractions of totally available amounts of substances actually entered the bottle wall. When analysing the re-migration into beverages, 17 chemicals could not be detected at levels greater than the detection limit of the analytical method. It could be shown that several substances, once absorbed, had greater affinity for the bottle wall so that not all of the retained amount migrated back into the beverage. The solubility of a substance is therefore a limiting factor for the migration from the bottle wall into the beverage. Toxicological evaluation of the analytical results showed that even under exaggerated conditions there was no public health concern (Feron et al., 1994).

The likelihood that a misused bottle will be returned to the market place can be greatly minimised by effective quality assurances practices. In co-operation with 25 industrial companies the Netherlands Organisation for Applied Scientific Research

(TNO) carried out a large multi-client project in order to evaluate and draft an industrial code of practice (COP) for refillable PET and PC bottles including guidelines of Good Manufacturing Practices (de Kruijf, 1997). The second edition of the COP has been issued in 2000 and describes specifications, testing methods as well as procedures related to a proper handling of refillable bottles.

2.9 CURRENT REGULATIONS AND SAFETY ISSUES IN THE EUROPEAN UNION

Until now there exist neither for refillable PET bottles nor for recycled PET containers specific regulations. Refillable or recycled PET containers have principally to meet and fulfil same requirements and regulations as virgin PET containers. A number of directives have been introduced on a European level to protect the consumer by ensuring that chemical migration does not impair the quality nor the safety of food.

Framework directive 89/109/EEC on materials and articles intended to come into contact with foodstuffs is supplemented by specific directives.

- **89/109/EEC** Framework Directive governing materials and articles intended to come into contact with foodstuffs

As an essential requirement this directive addresses the inertness of food contact articles which is laid down in article 2:

„Materials and articles must be manufactured in compliance with good manufacturing practice , so that, under normal or foreseeable conditions of use, they do not transfer their constituents to foodstuffs in quantities which could endanger human health or bring about an unacceptable change in the composition of the foodstuffs or a deterioration in the organoleptic characteristics thereof.“

- **90/128/EEC** gives the positive list of permitted monomers (plus amendments)

The so-called plastic directive has been revised and completed by 4 following amendments. Essential elements are a list of compounds authorised for the manufacture of the food contact plastic, an overall migration limit of 10 mg/dm² or 60 mg/kg and specific restrictions for a number of compounds in form of specific migration limits (SML) or maximum quantities (QM) remaining in the finished food contact article.

- **82/711/EEC** (plus amendments) lays down the basic rules for testing migration
- **93/8/EEC**

Basic rules for migration testing e.g. comprise definition of time-temperature conditions and types of food simulants. The selection of test conditions depends on the intended actual conditions of use of a food contact article.

- **85/572/EEC** lays down the list of simulants to be used in testing for migration

- ***Threshold-of-regulation-concept***

The Scientific Committee of Food (SCF) of the European Commission discusses whether a concentration level of „no concern“ can be established similarly to the FDA threshold-of-regulation concept. This concept was established on the basis of a comprehensive scientific evaluation of toxicological data which tolerates a transfer of even unknown substances into food as long as a threshold concentration of 0.5 ppb ($\mu\text{g}/\text{kg}$ food) is not exceeded.

On national levels in Europe there exist different opinion and regulations concerning the use of recycled plastics for direct food contact applications. The regulations range from

- legal ban (e.g. Spain) to
- case-by-case decisions or single products by no-objection letters (e.g. UK, The Netherlands, Sweden, Switzerland) and ending up in
- setting recycled materials equal to virgin materials unless they fulfil the legal requirements in the same way.

According to a legal note of the German „Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin“ (BgVV) recycled plastics are not principally excluded from reuse but have to fulfil the same postulates as Article 2 of 89/109/EEC. The BgVV recommends the application of recycled plastics in food packaging only when the contamination of the food can be excluded. The BgVV additionally clearly states that investigations necessary for food contact approval are completely in the responsibility of the manufacturer.

3 METHOD DEVELOPMENT OF A CHEMICAL INERTNESS TEST PROCEDURE FOR PET BEVERAGE BOTTLES

The characteristic properties of PET like stability, transparency and lower weight have led to the fact that glass bottles are more and more replaced. Due to the stability of the material the multi-use system of PET bottles is common in many countries. The strength and ruggedness of the nearly indestructible PET material is one reason that PET beverage bottles can achieve high circulation rates (up to 15 cycles) between the bottler and the consumer. The use of a rugged material, however, cannot rule out the fact that material changes may occur during the life time of a bottle. The aspect that a number of refillable PET bottles may be misused by the consumer is additionally very important for the quality assurance and safety-in-use. Absorbed compounds will not be fully removed during the washing and cleaning procedure of a refillable bottle. Therefore these substances might be able to remigrate into a refilled foodstuff or beverage which in turn can result in an off-flavour.

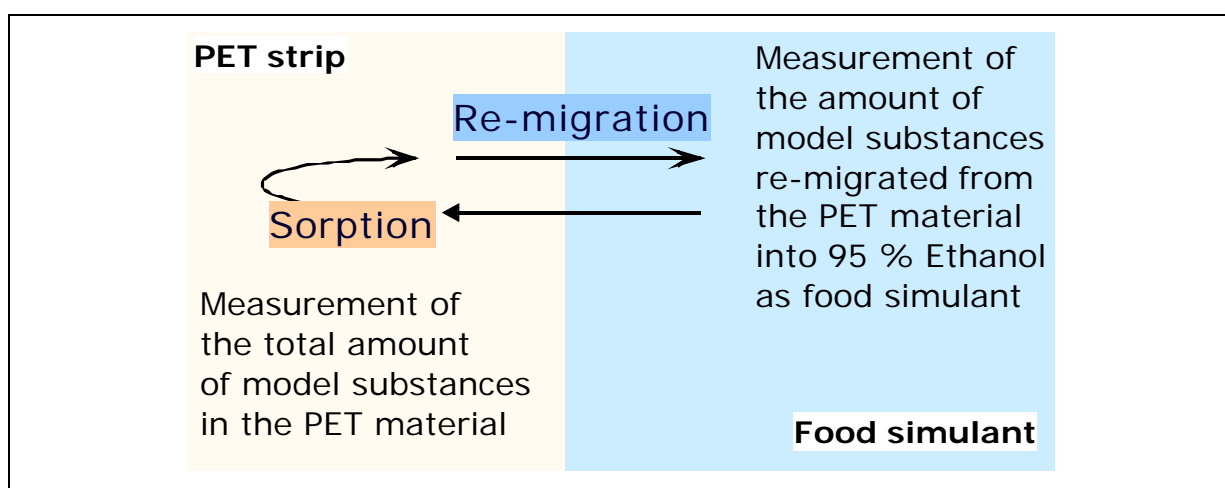
Due to the intrinsic interactivity of a refillable plastic bottle with contacting chemicals the question of testing compliance with food regulations arises. To this day there is neither any specific national or EU regulation nor a standard test available which could be applied by industry and enforcement laboratories to cover this problem. One of the main purposes of this research work SMT4-CT96-2129 was to establish a standardised and easy-to-apply method for general chemical inertness testing in conjunction with the production of a certified reference material of PET, applicable not only for the industry but also suitable for enforcement laboratories. With the chemical inertness test procedure a systematical control possibility will be available to check the food safety of refilled PET bottles taken from the market.

Following, the development and application of a chemical inertness test procedure as well as the production of a Certified Reference Material (CRM) PET is described with which the inertness of a PET material can be established. On the basis of this chemical inertness test method and the use of a CRM PET as a control of analysis performance, the quality of industrially developed new PET materials can be tested on the one hand, whereas foodstuffs-legislation compliance of refillable PET plastic packaging on the market may be warranted on the other hand. The main intention of the research work were the modification, optimisation and simplification of a chemical inertness test method previously developed within EU project AIR2-CT93-1014 as well as to establish a practical and easy-to-apply test procedure for refillable PET bottles with respect to the chemical inertness interactivity.

3.1 MODIFICATION AND OPTIMISATION OF A CHEMICAL INERTNESS TEST PROCEDURE PREVIOUSLY ESTABLISHED WITHIN PROJECT AIR2-CT93-1014

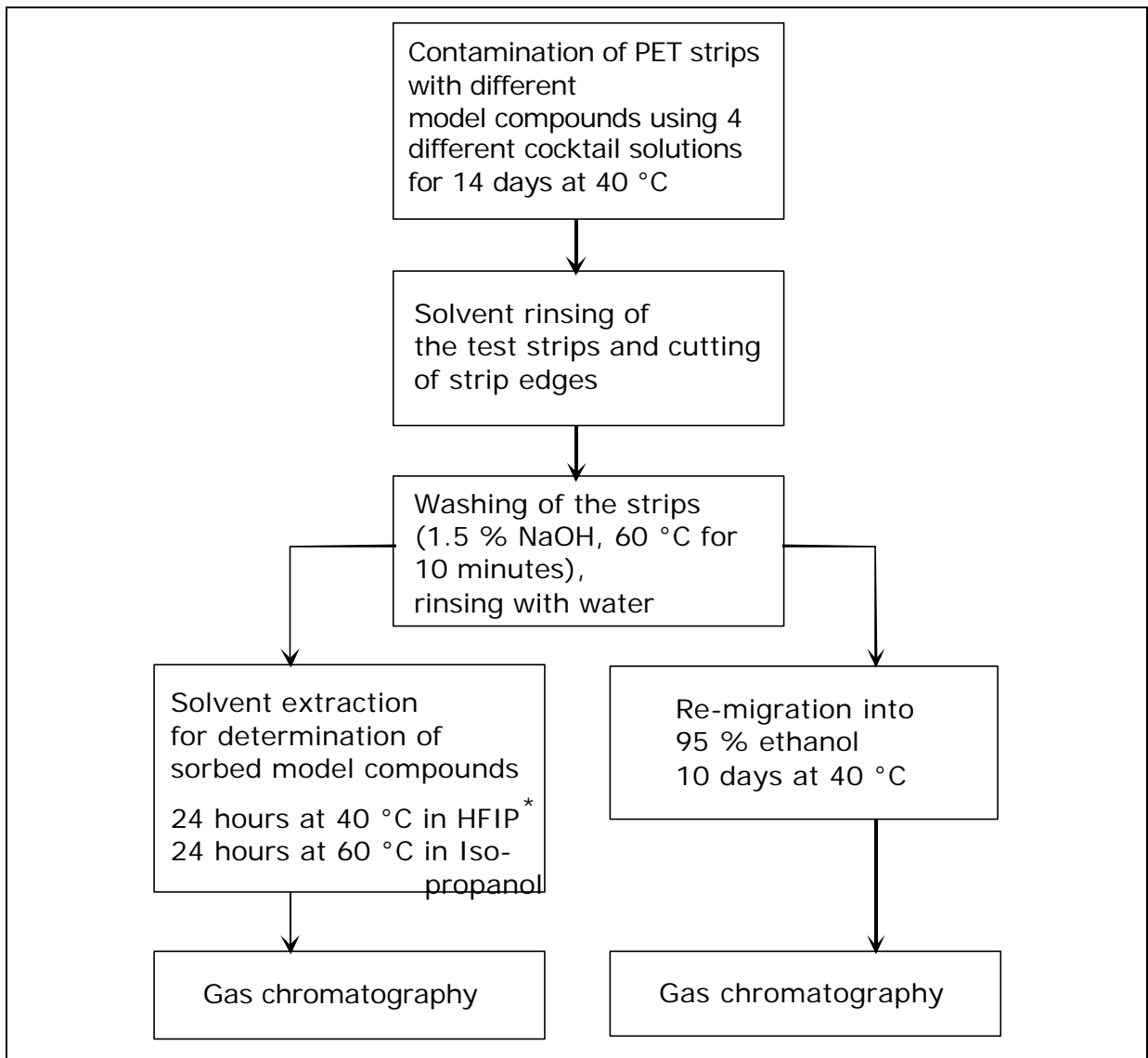
The PET inertness test simulates the misuse of a plastic bottle by loading the PET material with model substances. The amount of these re-migrating model substances into a food simulant correlates with the inertness and therefore the functionality of the PET bottle material. The start of a standardised chemical inertness test method was made in the previous EU project AIR2-CT93-1014. Recognising that investigations with a simple strip test would allow prediction of what happens with whole bottles, a chemical inertness test procedure was realised using only bottle wall strips instead of whole bottles. For the optimisation and simplification of the chemical inertness testing as well as the further ruggedness testing of the inertness method, multi-use PET bottles of 1.5 L volume supplied by Continental PET Europe (France) have been investigated.

The method developed in project AIR2-CT93-1014 was modified, optimised and simplified. For the evaluation of the chemical inertness of a PET material there principally exist two possibilities. On the one hand the chemical inertness can be evaluated by measuring the total amount of absorbed chemicals in the PET material itself, after direct contact with a cocktail solution at defined exposure conditions. On the other hand the chemical inertness can also be established as the amount of substances re-migrating from the PET material into a food simulant after defined storage conditions (Scheme 3-1). Within the first approach of establishing a chemical inertness test procedure, the uptake of model compounds from four different cocktails into PET bottle strips was measured after storage of 14 days at 40 °C. Furthermore the re-migration of these substances from PET strips into food simulants was additionally determined after storage for 10 days at 40 °C.



Scheme 3-1: Possible kinds of measurements for the evaluation of the chemical inertness of a PET material.

The principle idea of a chemical inertness test is to simulate the possible real life interaction of refillable PET bottles with chemical compounds by using one „cocktail“ solution of model chemicals with different chemical and physical properties. The interactivity between the PET material and the chemical model compounds is measured as the sorption of these substances by the PET material. Experimentally, this is achieved by contacting PET bottle wall strips with a mixture of model compounds under defined standard conditions, thus „contaminating“ or strictly speaking loading the PET test material. After a defined sorption phase a re-migration phase with immersion of contaminated PET strips into a food simulant can be carried out additionally. The concentrations of the model compounds are finally determined by gas chromatography. The following Scheme 3-2 principally describes the test procedures established within AIR2-CT93-1014 for evaluating the chemical inertness of a PET material.



Scheme 3-2: Test principles for the determination of the chemical inertness behaviour of PET beverage bottles (* Hexafluoro - isopropanol)

3.1.1 Reduction of model compounds to one cocktail solution

The first aim of this work was to reduce the amount of model compounds (20 altogether) applied in form of four different cocktail solutions to approximately 6 to 8 model compounds applicable in form of one cocktail solution. The composition of previous cocktails A to D is shown in Table 3-1.

Table 3-1: Previous cocktails of model compounds for the chemical inertness testing

Cocktail A alcohol-type compounds	Cocktail B ester/ketone- type compounds	Cocktail C hydrocarbon-type compounds	Cocktail D strongly interactive chlorinated compounds
<i>Propylene glycol</i>	Ethyl acetate	<i>Toluene</i>	Chlorbenzene
<i>Phenol</i>	Cyclohexanone	n-Heptane	1,1,1-Trichloroethane
n-Hexanol	Isoamyl acetate	<i>p-Xylene</i>	
2-Phenyl ethanol	<i>Benzophenone</i>	<i>Limonene</i>	
<i>Menthol</i>	Linalyl acetate	<i>Phenyl cyclohexane</i>	
1,2-Decandiol	Methyl stearate	Phenyl decane	

The model compounds applied as one cocktail solution in the final chemical inertness test method were selected under the following aspects:

- variation of chemical structures and polarities
- variation of molecular weights
- comparison of aromatic versus non-aromatic structures
- comparison of strongly interactive compounds
- consideration of surrogates proposed by the FDA
- availability of chemicals to consumer households
- environmental and safety considerations
- simple handling and gas chromatographic analysis (GC/FID) of all model compounds using only one cocktail and method of analysis.

In the first instance of reducing four cocktail solutions of 20 model compounds to only one cocktail solution, 8 model compound were selected. At the beginning of the method optimisation the cocktail solution consisted of

- | | | |
|---------------------|---------------------|----------------------|
| • Propylene glycol | • Benzophenone | • Toluene |
| • Phenol | | • p-Xylene |
| • Menthol | | • Limonene |
| | | • Phenyl cyclohexane |
| (out of Cocktail A) | (out of Cocktail B) | (out of Cocktail C) |

Chlorinated substances out of cocktail D were not taken into account because of environmental and safety aspects. The selected model compounds could be ideally separated by gas chromatographic (GC) analysis exemplarily shown in Figure 3-1. The GC unit used was a Hewlett Packard 5890 Gas Chromatograph equipped with an auto injector as well as a flame ionisation detector (FID). The separation column was a 30 m x 0.32 mm internal diameter fused silica capillary DB-1 with a film thickness of 5 µm. As carrier gas served Hydrogen with a split flow of 20 mL/min. The following temperature programme was applied: 80 °C were hold for 2 min increasing the temperature with 10 °C per minute afterwards up to 280 °C which were further hold for 10 minutes.

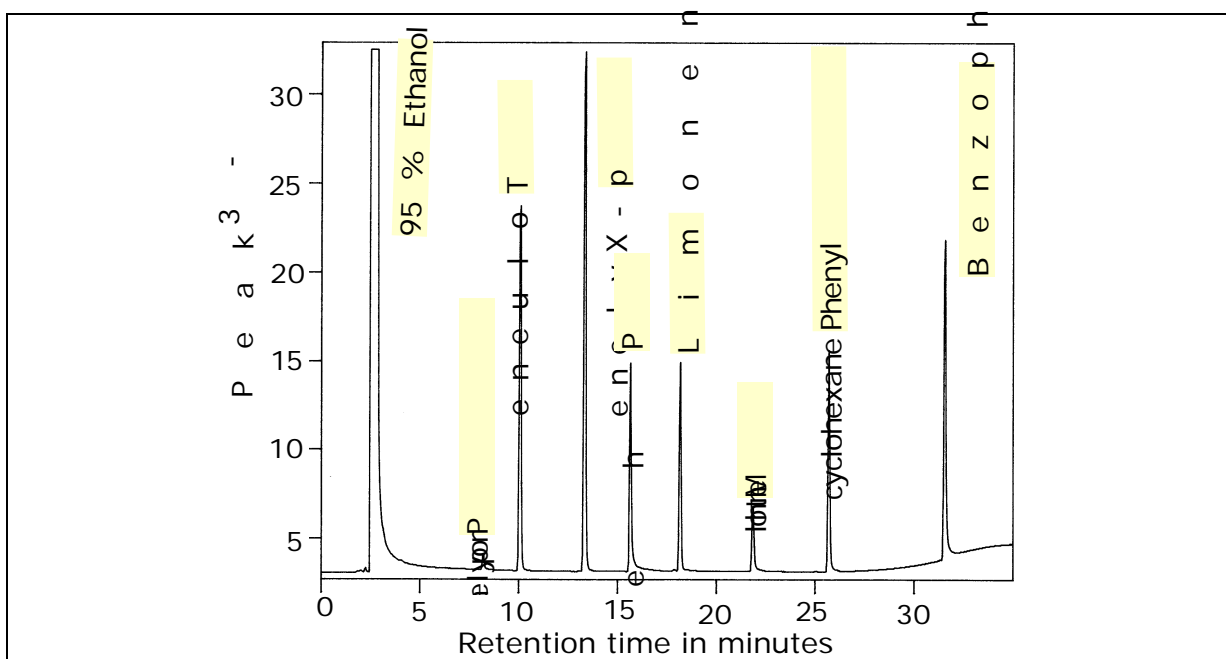


Figure 3-1: Gas chromatographic analysis of selected model compounds

The cocktail solution of 8 model compounds was prepared by dissolving solid model compounds like Phenol, Menthol and Benzophenone in the liquid ones. To prepare the cocktail solution equal mass parts of each model compound were mixed. The concentration of individual model compounds in the resulting solution was therefore 1:8 or 12.5 mass %. Without further dilution the PET swelling effect of the 1:8 concentrated solution was measured under different storage conditions on the basis of gravimetric analysis of PET strips. Results of the gravimetric measurements are shown in Table 3-2.

Table 3-2: Swelling effect of the 1:8 concentrated cocktail solution on PET strips

sorption condition	swelling effect [mg / strip]	swelling effect [%]
14 d / 40 °C	16.62	2.90
7 d / 50 °C	28.21	4.50
2 d / 60 °C	25.78	4.43

In spite of the high swelling values after direct contact with the cocktail solution the surface of the PET strips was not visually changed. However, the most favourable concentration of the model compound cocktail must be understood to be such that only such a degree of swelling of the PET strips takes place which allows significant sorption of model compounds but does not lead to an optical as well as physical change of the PET strips. The model compound solution was therefore diluted with Polyethylene glycol 400. The swelling effect of diluted solutions with concentrations of model compounds of 1:10 and 1:15 respectively are shown in Table 3-3 and Table 3-4.

Table 3-3: Swelling effect of the 1:10 dilution of model compounds on PET strips

sorption condition	swelling effect [mg / strip]	swelling effect [%]
14 d / 40 °C	4.94	0.85
7 d / 50 °C	9.36	1.57
2 d / 60 °C	9.10	1.57

Table 3-4: Swelling effect of the 1:15 dilution of model compounds on PET strips

sorption condition	swelling effect [mg / strip]	swelling effect [%]
14 d / 40 °C	1.63	0.28
7 d / 50 °C	3.60	0.58
2 d / 60 °C	3.00	0.50

The swelling effect of PET strips shows that the interaction of PET strips with the 1:15 diluted solution of model compounds causes less than a 1 % swelling. A still higher dilution, i.e. 1:20 will certainly give a much lower swelling effect but here the question arose if the sorption of model compounds into the PET strips and therefore the interaction between model compounds and PET strip is still high enough to produce satisfyingly significant ($t_{0.95}$ - Test) results.

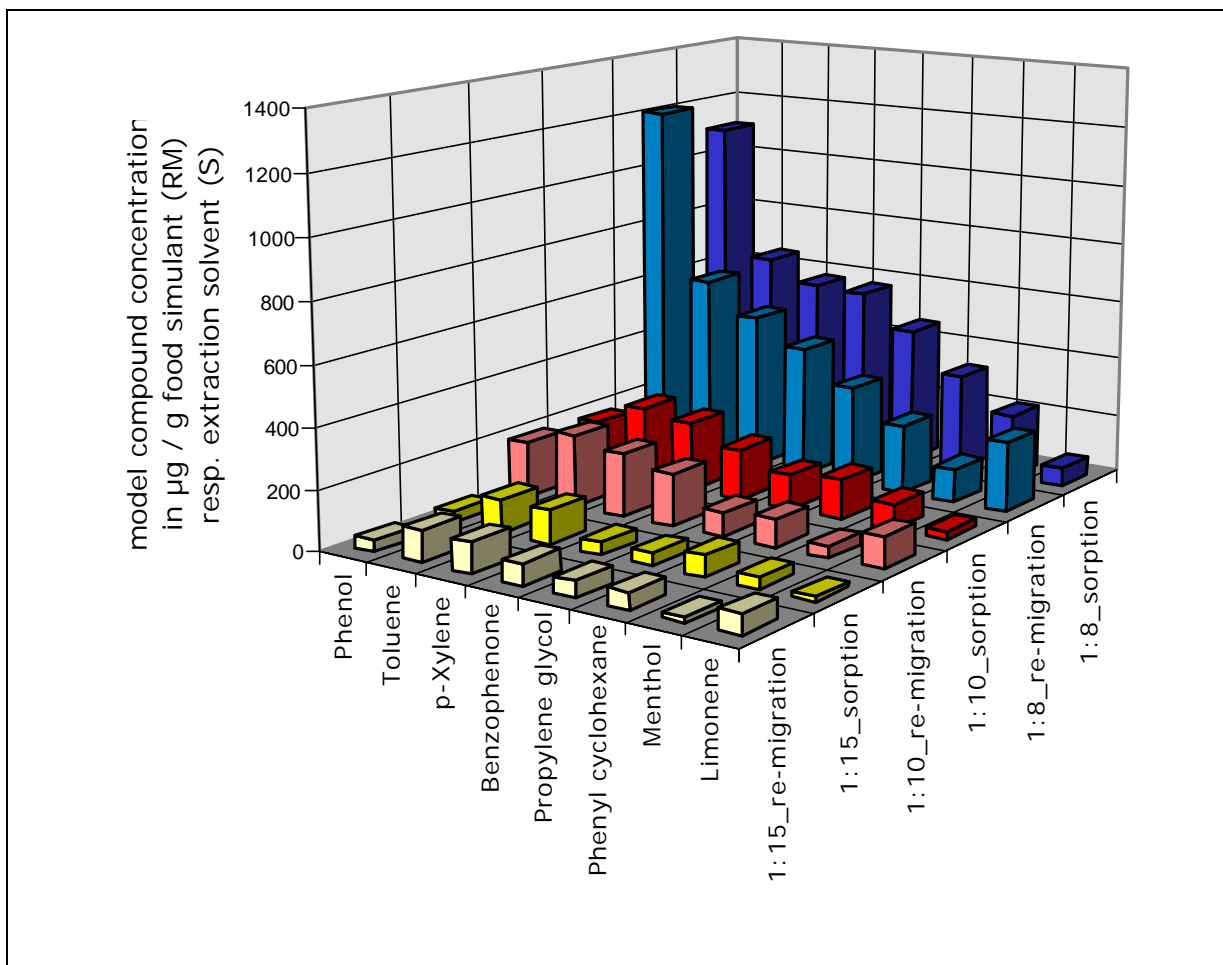


Figure 3-2: Concentrations of absorbed and re-migrated model compounds after exposure conditions of 14 days at 40 °C for different cocktail concentrations. (RM: re-migration; S: Sorption)

Figure 3-2 presents the amount of absorbed model compounds determined by destructive analysis of PET strips as well as the concentrations of re-migrated substances from PET strips into 95% Ethanol after 10 days at 40 °C.

The difference in test results between 1:10 and 1:15 diluted model compounds is proportionally very little compared to the relation of results for 1:8 and 1:10 diluted model compounds. Diluting the model compounds with a ratio of 1:8 results in very high amounts of sorbed model compounds due to the aggressiveness of the cocktail. Especially the model compound Phenol is very aggressive to PET so that higher concentrations lead to the destruction of the polymer PET. Since misuse of PET bottles has to be simulated according to realistic conditions of use lower concentrations such as 1:10 and 1:15 has to be given preference. A model compound dilution of 1:15 yield to the lowest and nearly negligible swelling of PET strips. However, looking at test results obtained for 1:15 diluted model compounds makes obvious that sorbed amounts of model compounds are extremely low, strictly speaking in some cases near the detection limit.

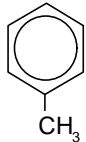
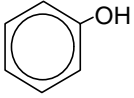
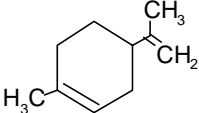
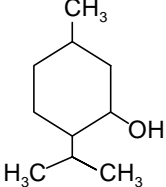
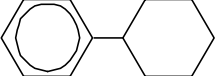
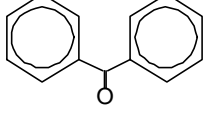
The purpose of a chemical inertness test is not only to provide data concerning the chemical inertness of a PET material but also to enable industry and enforcement laboratories to compare different material qualities of PET concerning the inertness behaviour. For this reason concentrations of model compounds near the detection limit are not suitable to evaluate significant differences between PET beverage materials.

Therefore, the most appropriate dilution concentration of the cocktail was found to be 1:10 (6 equal parts of model substances diluted with 4 equal parts of PEG 400) where the swelling effect of the model compound solution didn't exceed a 2% mass increase of PET strips under all conditions of use.

At the beginning, the model cocktail solution contained Propylene glycol as well as p-Xylene. After carrying out the PET inertness test with the newly established model cocktail the question addressed the usefulness of having Toluene and p-Xylene together in one set. The conclusion was that p-Xylene did not give any new information in addition to the Toluene value concerning the inertness of a PET material since it behaves very similar. For this reason p-Xylene was removed from the cocktail but was furthermore used as an internal standard of the gas chromatographic (GC) analysis. In the course of further research work Propylene glycol turned out to be not stable and was therefore removed from the cocktail.

Table 3-5 shows the final composition of model compounds and their chemical properties.

Table 3-5: Final set of model compounds of the chemical inertness test procedure

Model compound	Molecular mass	Properties
<p>Toluene</p> 	92	<p>hydrocarbon, volatile, non-polar</p> <p>Toluene is widely used in adhesives and dyes and is also a constituent of automotive products and motor oils</p>
<p>Phenol</p> 	94	<p>alcohol, volatile, polar</p> <p>Phenol is used as constituent of disinfectants and is highly aggressive towards the PET polymer structure</p>
<p>Limonene</p> 	136	<p>hydrocarbon, aromatic, non-polar</p> <p>Limonene is known to be a main compound of citrus oil based flavours which are commonly used in many soft drinks. It is additionally an indicator compound for recycled materials.</p>
<p>Menthol</p> 	156	<p>alcohol, aromatic, polar</p> <p>Menthol is widely used as constituent of numerous hygiene products due to its antiseptic properties.</p>
<p>Phenyl cyclohexane</p> 	160	<p>hydrocarbon, non-volatile, non-polar</p> <p>Substance proposed by ILSI-Europe for application as a model compound in Challenge tests</p>
<p>Benzophenone</p> 	182	<p>ketone, non-volatile, non-polar</p> <p>Substance proposed by the FDA and ILSI for application as a model compound in Challenge tests</p>

In order to establish optimised exposure conditions the influence of different time and temperature conditions on the swelling effect and the amount of sorbed substances was additionally measured with cocktail concentrations of 1:8, 1:10 and 1:15. Corresponding test results are graphically shown in chapter 3.1.2 Optimisation of exposure conditions time and temperature.

3.1.2 Optimisation of exposure conditions time and temperature

As already mentioned there exist two possibilities to measure and evaluate the chemical inertness of a PET material. On the one hand the total uptake of model compounds in the material itself can be directly measured after a defined sorption phase by destructive analysis (extraction) of PET strips. On the other hand, following a defined sorption phase, the measurement of the re-migration of absorbed model compounds from the PET strip into a food simulant under defined test conditions gives information of the real inertness behaviour of a material in contact with foodstuffs. In this case PET strips or materials are not destroyed giving the possibility of further measurements of material properties if needed or of special interest. In the previous project AIR2-CT93-1014 the method applied standard loading and re-migration conditions of the material of 14 days at 40 °C (sorption) and 10 days at 40 °C (additional re-migration). The intention was to shorten the time period at somewhat higher temperatures but also to gain approximately same loading / re-migration levels of the PET material in a shorter and so more practically applicable time. For this reason the amount of absorbed model compounds of the optimised cocktail solution was investigated for 2, 5, 7, 9 and 14 days at 40 °C, 50 °C and 60 °C, respectively, by destructive analysis of PET strips. The results are shown in Figure 3-3 to Figure 3-9. The bold line represents the sorption value obtained after 14 days at 40 °C.

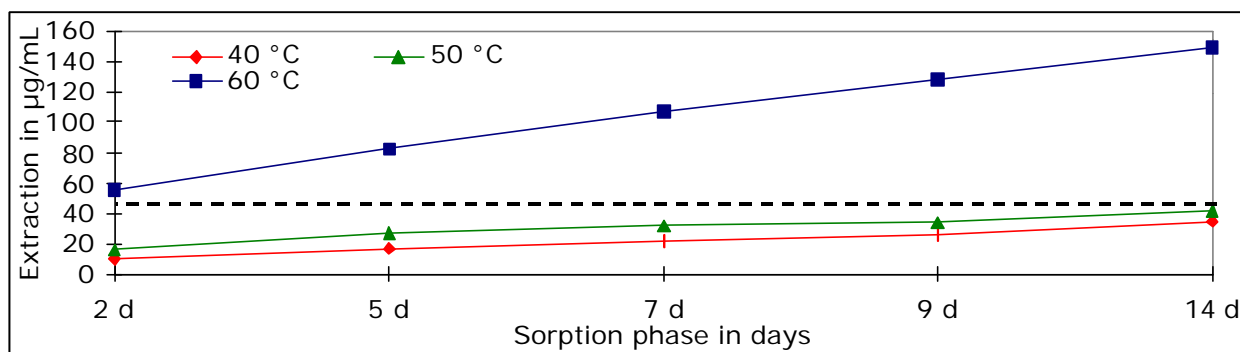


Figure 3-3: Amount of absorbed Propylene glycol after different exposure conditions

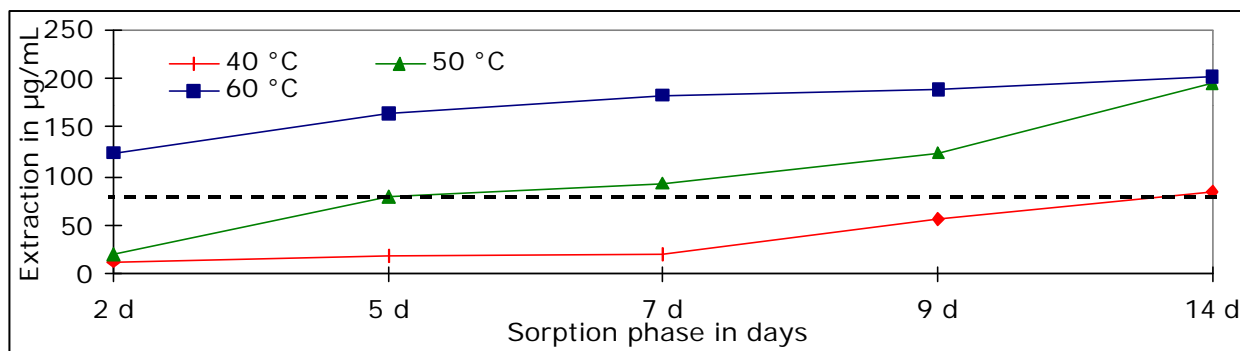


Figure 3-4: Amount of absorbed Toluene after different exposure conditions

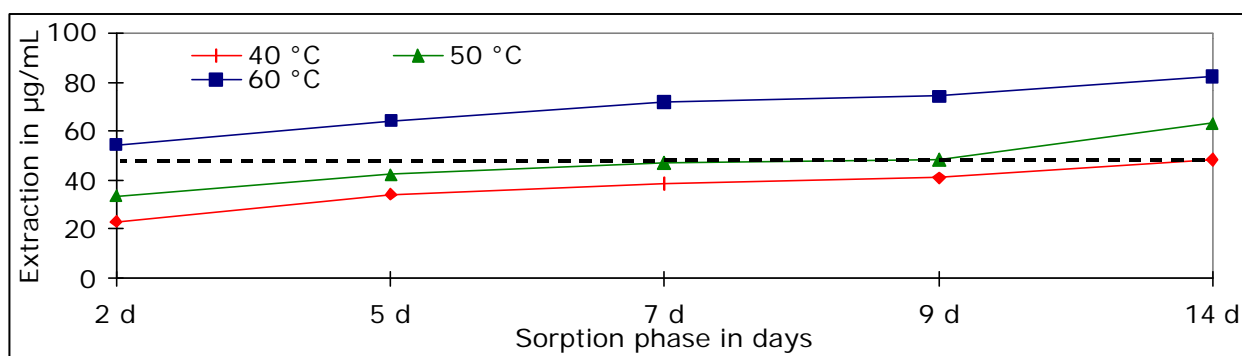


Figure 3-5: Amount of absorbed Phenol after different exposure conditions

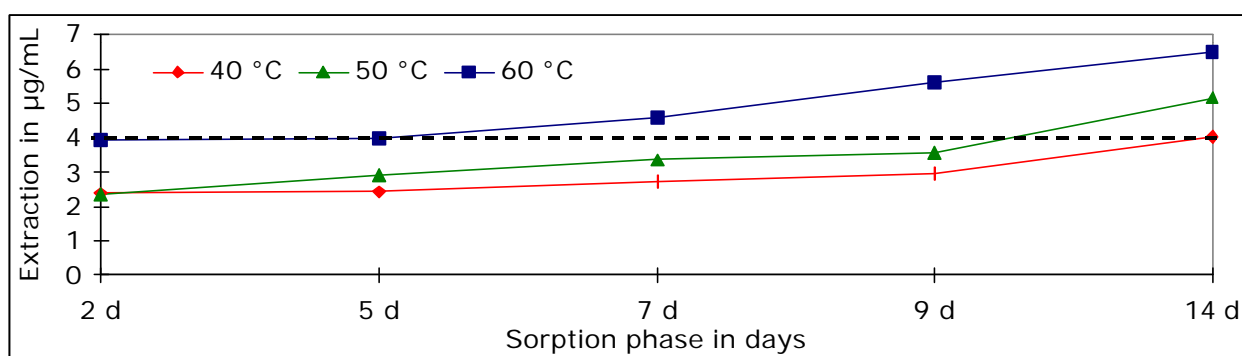


Figure 3-6: Amount of absorbed Limonene after different exposure conditions

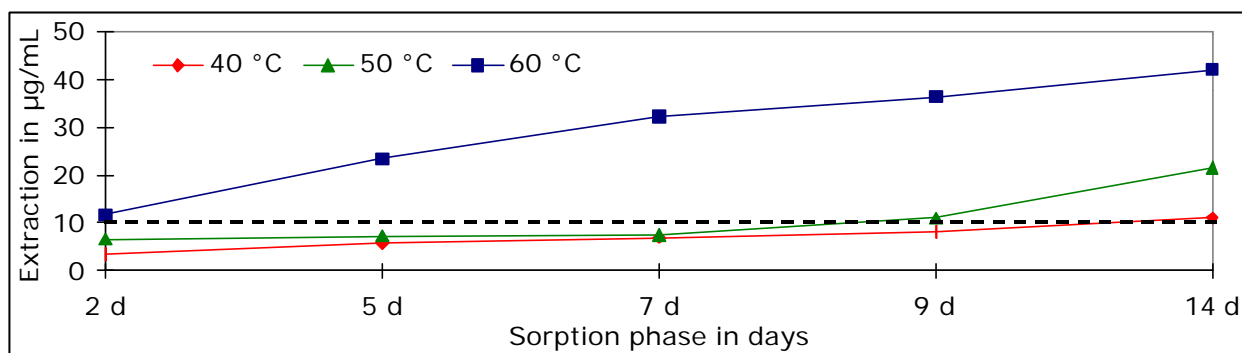


Figure 3-7: Amount of absorbed Menthol after different exposure conditions

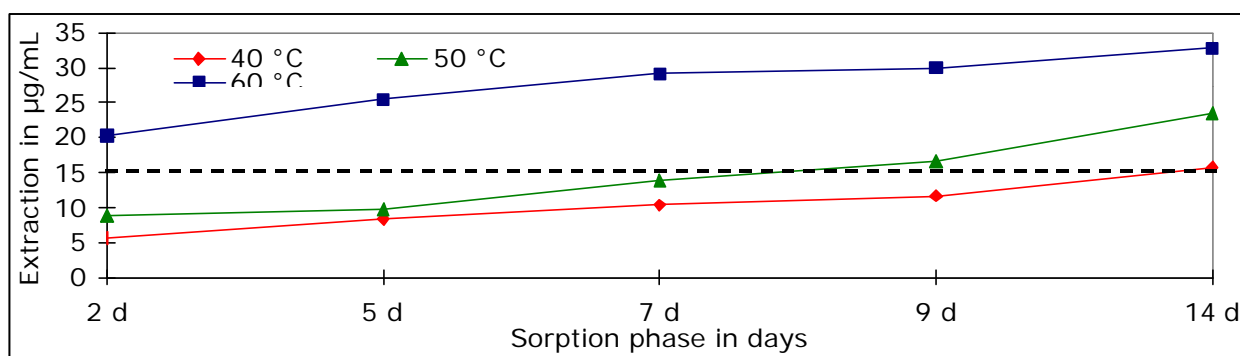


Figure 3-8: Amount of absorbed Phenyl cyclohexane after different exposure conditions

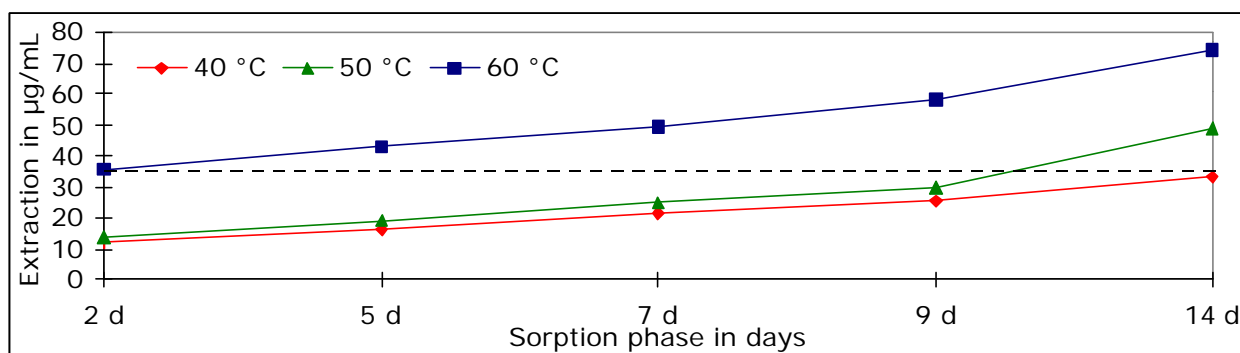


Figure 3-9: Amount of absorbed Benzophenone after different exposure conditions

For the evaluation of optimised exposure conditions the model compound p-Xylene was already removed from the cocktail solution. Therefore, the cocktail (further called model compound solution, MCS) consisted of equal parts of Propylene glycol, Toluene, Phenol, Limonene, Menthol, Phenyl cyclohexane and Benzophenone, diluted with 3 equal parts of Polyethylene glycol 400 to obtain a concentration of 1:10 by mass. For this reason test results as presented in Figure 3-3 to Figure 3-9 show somewhat lower concentrations of absorbed model compounds than shown in Figure 3-2. Looking at test results obtained for different exposure conditions it can be concluded that results obtained after 14 days at 40 °C satisfyingly correspond to results obtained after 2 days at 60 °C for most of the model compounds investigated. Only in case of Toluene and Phenyl cyclohexane somewhat higher but comparable test results were obtained. For exposure conditions of 7 days at 50 °C several model compounds additionally showed test results comparable with the exposure for 14 days at 40 °C.

Therefore the following exposure conditions were investigated using different MCSs with concentrations of 1:8, 1:10 and 1:15 by mass:

Table 3-6: Exposure conditions examined in the course of optimisation

Sorption phase	and following	Re-migration in 95 % Ethanol
14 d at 40 °C		10 d at 40 °C
7 d at 50 °C		7 d at 50 °C
2 d at 60 °C		2 d at 60 °C

Figure 3-10 shows the comparison of test results obtained after different sorption phases as absorbed amounts of model substances of the PET strip material in mg/dm². The test results demonstrate that a sorption phase of 2 days at 60 °C as well as a sorption phase of 7 days at 50 °C deliver higher sorption values of the PET material than the former sorption phase of 14 days at 40 °C. The difference between earlier presented sorption data obtained at exposure conditions of 14 days / 40 °C and 2 days / 60 °C (Figure 3-3 to Figure 3-9) which stated that test results are comparable can be explained by different conditions of solvent extraction. The obviously higher test results of model compounds stored at 50 °C and 60 °C in comparison to 40 °C are based on the fact that exaggerated test conditions were applied during the solvent extraction resulting in exhaustive extraction of model compounds. The destructive analysis of PET strips by solvent extraction with Hexafluoro-isopropanol (HFIP) and following Isopropanol was carried out at conditions of 2 days at 60 °C each time instead of 1 day at 40 °C and a following day at 60 °C.

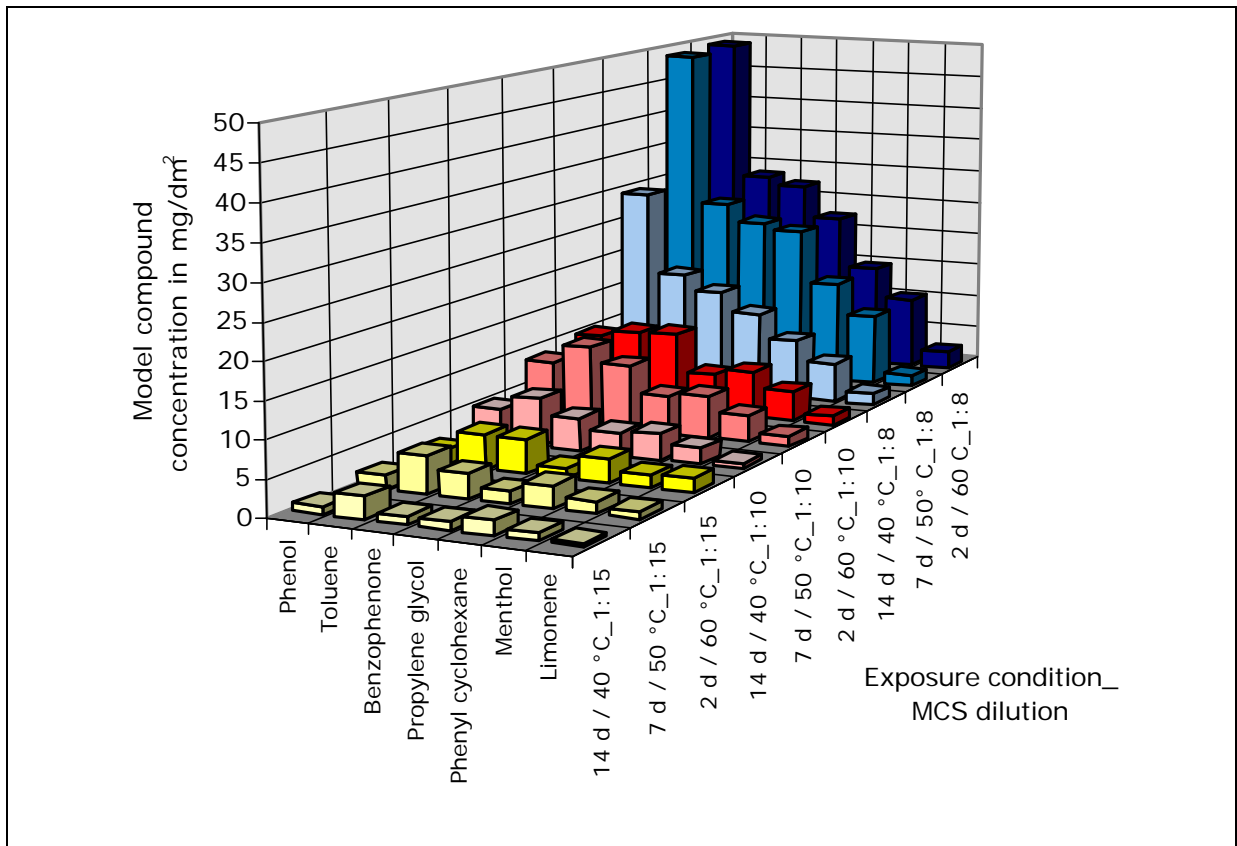


Figure 3-10: Concentration of absorbed model compounds obtained for different dilutions of the MCS after different exposure conditions

Looking at test results presented in Figure 3-10 it is remarkable that the concentration of absorbed Limonene kept nearly steady regardless which exposure conditions were applied. The comparable low concentrations can be lead back to chemical reactions of Limonene with the extraction solvent HFIP especially under exaggerated extraction conditions. The chemical reaction of model compounds with extraction solvent HFIP is a great disadvantage of the sorption test procedure. In the course of sorption measurements test results obtained for Propylene glycol also turned out to be not repeatable due to the instability of the substance at higher temperatures. As already mentioned Propylene glycol was therefore removed from the model compound solution and replaced by one further part of Polyethylene glycol 400.

Not only the exposure conditions of the sorption test procedure but also the test conditions for evaluating the re-migration potential of model compounds from PET strips into a food simulant were optimised. In order to facilitate the comparison of sorption and re-migration test results, PET strips were „loaded“ with model compounds at the exposure conditions listed in Table 3-6.

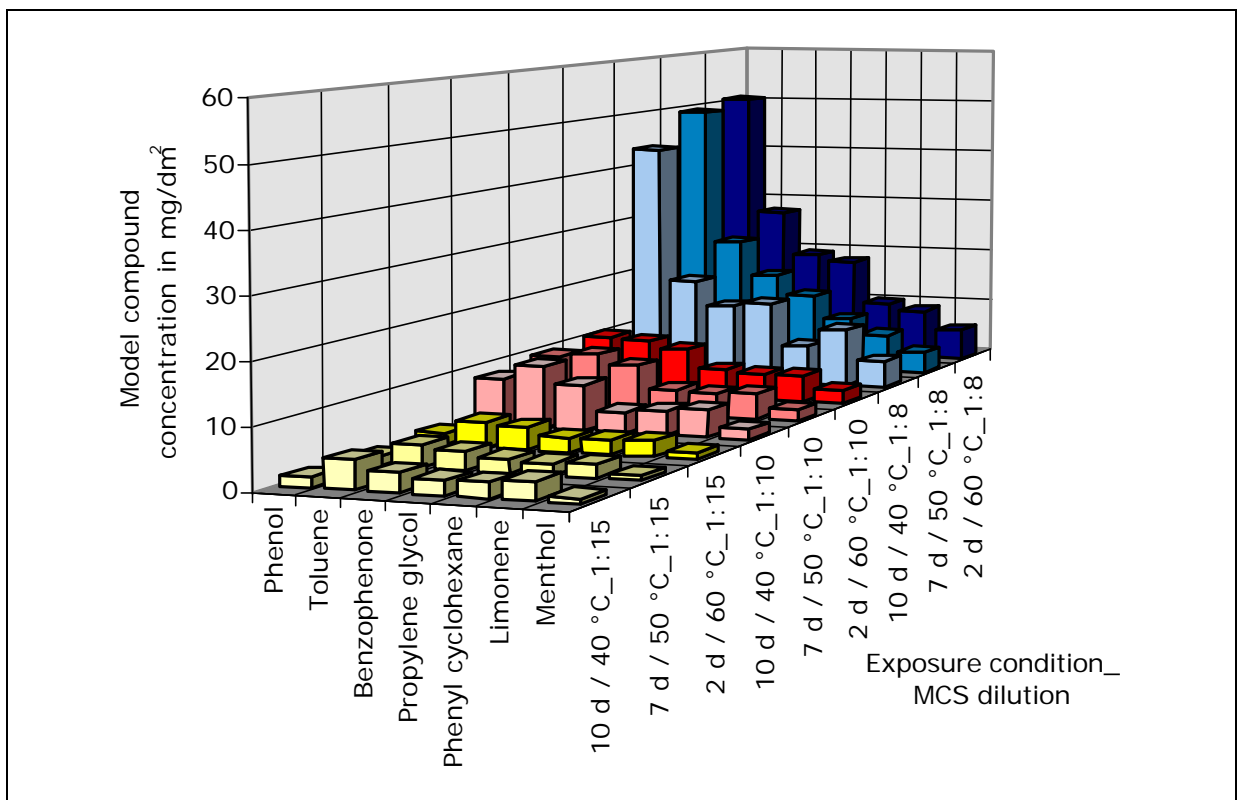


Figure 3-11: Concentration of re-migrated model compounds obtained for different dilutions of the MCS after different exposure conditions

Figure 3-11 shows that concentrations of re-migrated model compounds obtained after exposure conditions of 7 days at 50 °C and 2 days at 60 °C are comparable to those obtained after 10 days at 40 °C for 1:15 and 1:10 diluted MCS. Only in case of 1:8 diluted model compounds the amount of re-migrating substances is

increasing with increasing temperatures. According to test results presented in Figure 3-11 the evaluation of an optimal model compound concentration at a dilution of 1:10 by mass could be further confirmed.

The comparison of sorption and re-migration values in Figure 3-12 shows that on the one side test results after different re-migration phases are similar whereas on the other side the sorption values after sorption conditions of 2 / 5 days at 60 / 50 °C are definitely higher than those after 14 days at 40 °C.

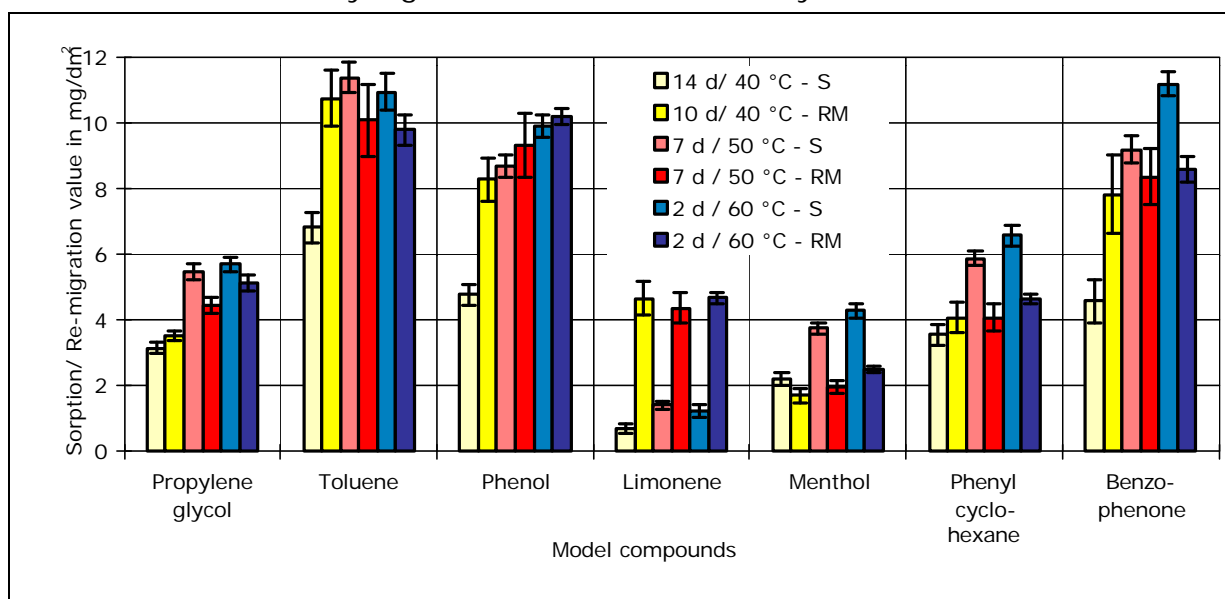


Figure 3-12: Comparison of sorption and re-migration values obtained after different exposure conditions using a 1:10 diluted MCS (S: Sorption, RM: Re-migration)

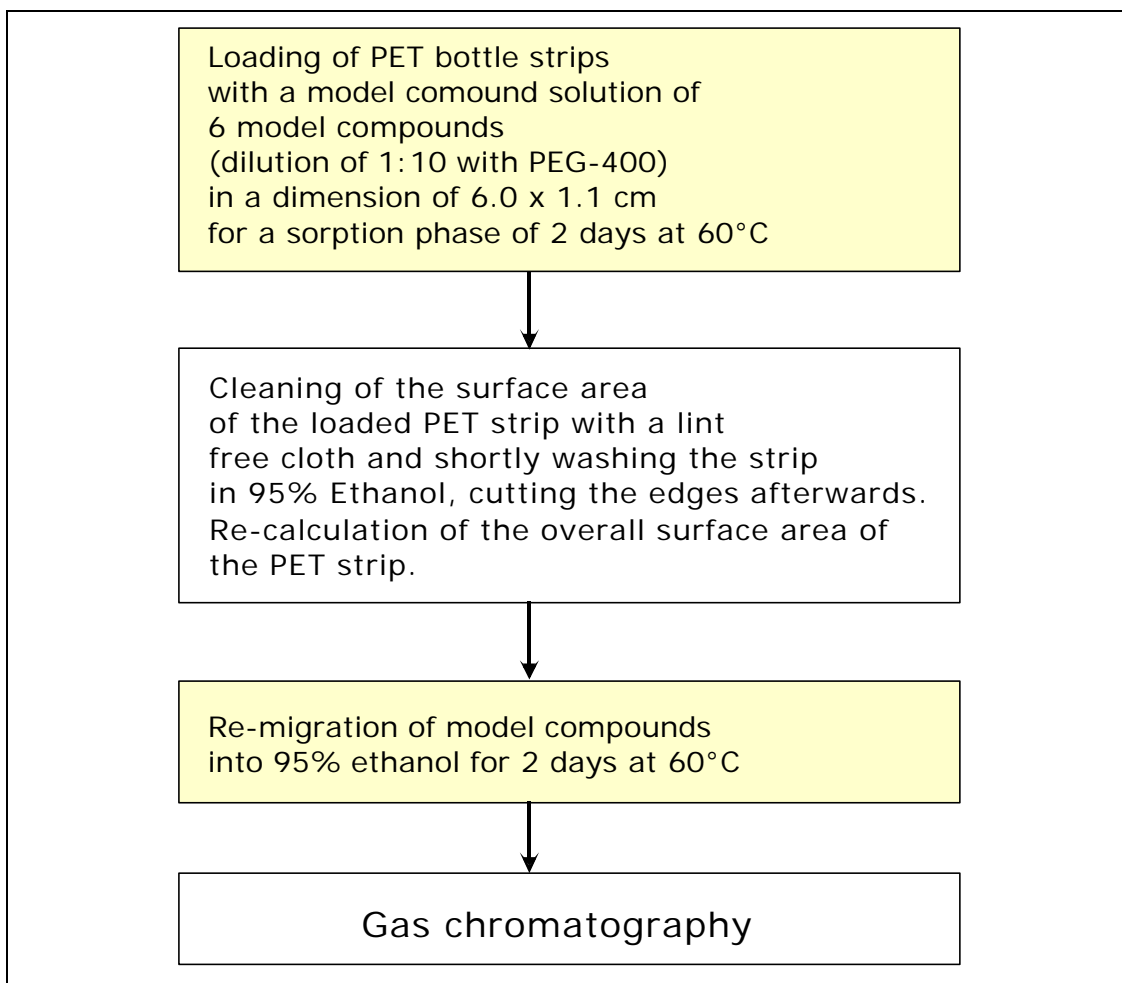
It is also remarkable that the determination of absorbed amounts of model compounds analysed after a sorption phase of 14 days at 40 °C result in lower model compound values than after a further re-migration phase in 95 % Ethanol for 10 days at 40 °C. Especially in the case of Limonene the sorbed amounts in the PET strip material are significantly lower than the amounts determined after a re-migration phase in 95 % Ethanol. As already mentioned these differences could be led back to chemical reactions of several model compounds with the extraction solvent Hexafluoro-isopropanol (HFIP) and therefore the sorbed amounts of model compounds are expected to be higher in reality.

Summarising the test results presented in Figure 3-3 to Figure 3-12 the following optimisation of exposure conditions could be established:

- On the basis of similar test results in 95 % Ethanol at different exposure conditions, the analysis of model compounds after a re-migration phase with the use of 95 % Ethanol as food simulant has to be given preference. The use of 95 % Ethanol also excludes chemical reaction with model compounds as observed with HFIP and therefore provides valid test results.

- According to similar test results obtained at exposure conditions of 14 days at 40 °C/ 10 days at 40 °C and exposure conditions of 2 days at 60 °C/ 2 days at 60 °C the chemical inertness test of PET strips could be shortened to an overall time period of one week.

Scheme 3-3 gives a brief summarising and description of finally optimised and simplified standard test conditions:



Scheme 3-3: Principle of the optimised and simplified chemical inertness test procedure within the EU project SMT4-CT96-2129

3.1.3 Modification and final drafting of the chemical inertness test procedure

Before the validation of the chemical inertness method it was necessary to determine possible sources of error as well as uncertainties of the test procedure.

In the chemical analysis it is well known that each individual step might contain possible sources of systematic errors as well as deviations and therefore can lead to method uncertainty. For the evaluation of possible sources of error the chemical inertness test procedure was divided in four sections.

1. the PET strip preparation
2. the sorption phase
3. the extraction phase and finally
4. the GC analysis and evaluation of test results

As an illustration the following Scheme 3-4 once again describes the procedure of the chemical inertness method in detail.

Chemical inertness test procedure	
preparation of strips	determination of the surface area of the PET strip (length-width)
weighing of strips	determination of the initial strip mass m_i
addition of model compound solution	
sorption phase of 2 days at 60 °C	influence of time and temperature parameters
cleaning of strip surfaces from model compounds after the sorption phase	
weighing of strips	determination of the sorption mass m_s of the strips after sorption
cutting of strip edges	
re-weighing of strips	determination of cut-edged strip mass m_{ce}
calculation of the effective strip area A_{eff}	
addition of extraction solvent	determination of the mass of 95 % Ethanol $ES_{m_{be}}$ and the mass of the whole extraction system m_{be} respectively
extraction phase of 2 days at 60 °C	influence of time and temperature parameters
weighing of the extraction system after the extraction phase	determination of the mass of the extraction system m_{ae} after the extraction calculation of the remaining mass of extraction solvent $ES_{m_{ae}}$
removing of strip	
addition of internal standard	measurement of the added mass of internal standard solution m_{is}
GC analysis	check of the GC performance check of appropriate GC conditions

Scheme 3-4: Detailed description of the chemical inertness test procedure

3.1.3.1 PET strip preparation

According to chemical inertness test results obtained by different laboratories the question arose if strips from different areas of the bottle wall and herewith the different initial masses have an influence on the test results of the different model compounds. Individual test results of the measurements of six laboratories were therefore correlated with the initial mass of PET strips and the correlation coefficient was evaluated. Contemplating the correlation results it is necessary to take into account that all individual test results of chemical inertness measurements were used for the evaluation, including possible outliers. Therefore it is necessary to reflect on that slight trends may be overestimated. The correlation coefficient of each model compound is shown in Table 3-7.

Table 3-7: Correlation coefficient of initial mass and model compound concentration

correlation coefficient	Toluene	Phenol	Limonene	Menthol	Phenyl cyclohexane	Benzo-phenone
R	0.245	0.141	0.226	0.289	0.403	0.336

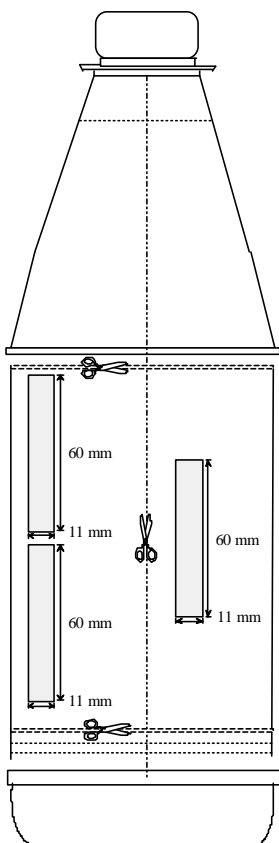


Figure 3-13:

Cutting scheme for the preparation of test strips out of a 1.5 L PET bottle

The correlation coefficients shown in Table 3-7 demonstrate that the extraction results of model compounds are not influenced by the initial mass of a PET strip and therefore are independent from the sampling of strips from the area of a bottle wall that means whether the PET strips were cut out at the top or the bottom of the bottle wall. However, Table 3-7 also show that the correlation coefficients of Phenyl cyclohexane and Benzophenone are twice as high as the correlation coefficients of the other substances although the trends can be neglected. Migration processes only occur in layer dimensions of μm of the surface area and therefore bottle wall thickness as a possible reason can be left out of account. The fact that only higher molecular substances lead to slightly trends between initial mass and extraction result contains a reference to the influence of cristallinity of the material. Moreover, the distribution of initial masses of strips from 0.534 g to 0.735 g also demonstrated that laboratories preferred to cut out the strips at the top of the bottle wall. Preventing the trend of preferably using strips out of the top of a bottle wall as well as decreasing the effect of cristallinity the area where the strips have to

be cut out was restricted and newly defined in the chemical inertness method.

3.1.3.2 Evaluation of possible uncertainties within the sorption phase

Evaluating the sources of uncertainty and errors of the method a correlation between the absolute mass increase of PET strips and the amount of migrated model compounds into the extraction solvent 95 % Ethanol was carried out. Figure 3-14 to Figure 3-19 show the correlation of the absolute mass increase of a strip and the chemical inertness test result of the six model compounds.

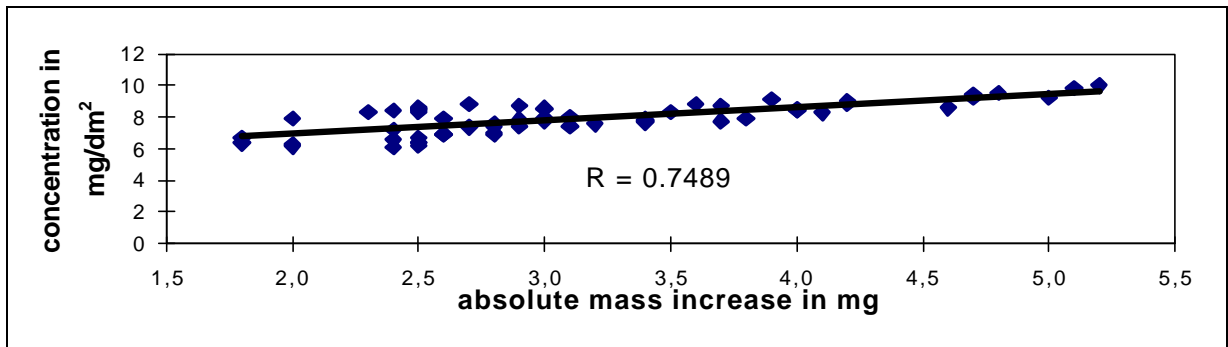


Figure 3-14: Correlation of the absolute mass increase of a PET strip after the sorption phase with the chemical inertness test result of **Toluene**

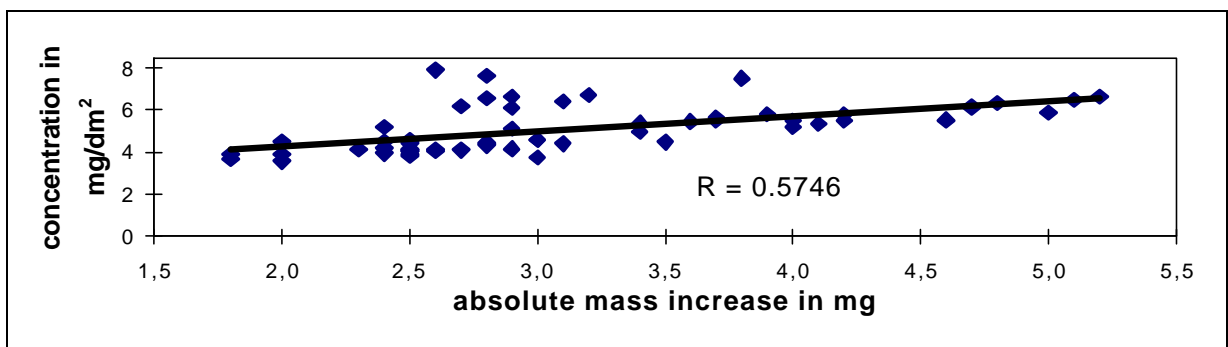


Figure 3-15: Correlation of the absolute mass increase of a PET strip after the sorption phase with the chemical inertness test result of **Phenol**

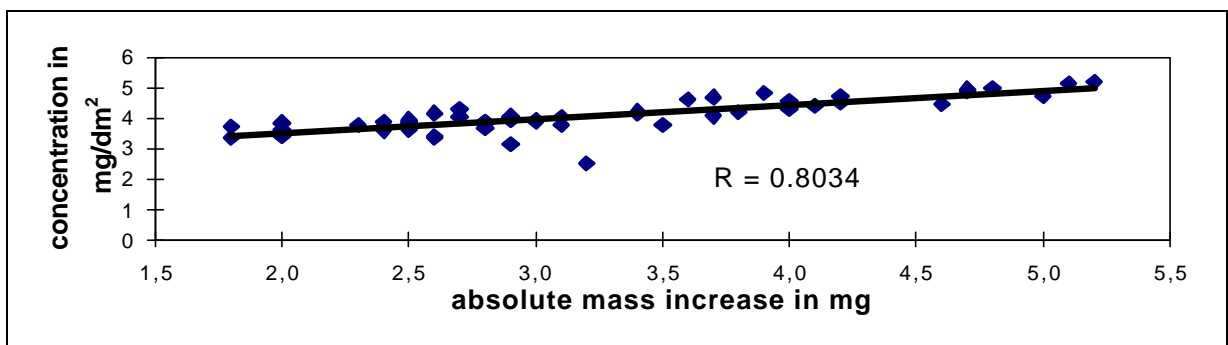


Figure 3-16: Correlation of the absolute mass increase of a PET strip after the sorption phase with the chemical inertness test result of **Limonene**

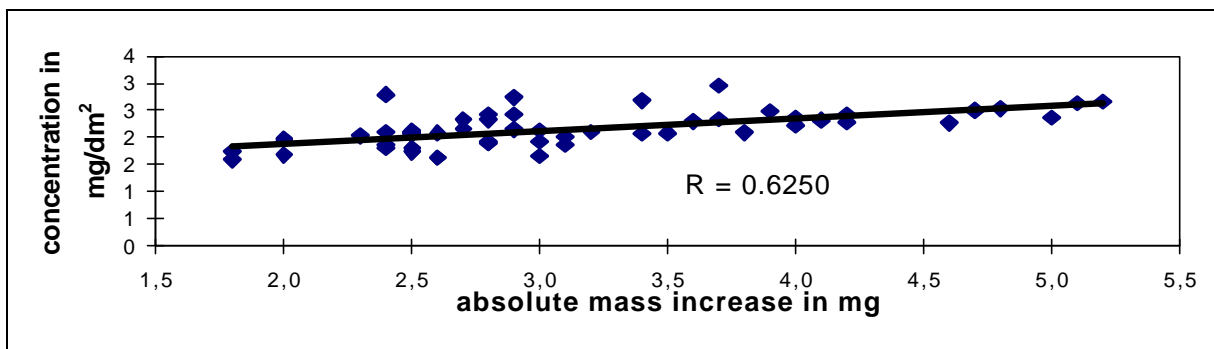


Figure 3-17: Correlation of the absolute mass increase of a PET strip after the sorption phase with the chemical inertness test result of **Menthol**

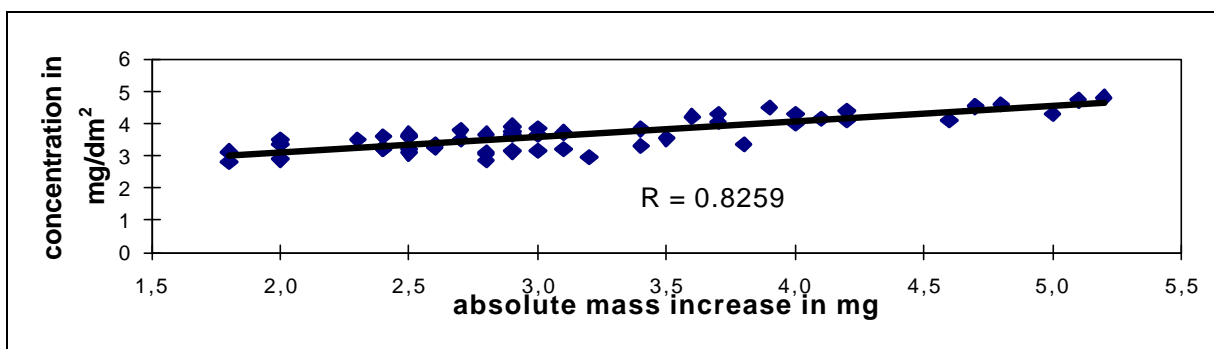


Figure 3-18: Correlation of the absolute mass increase of a PET strip after the sorption phase with the chemical inertness test result of **Phenyl cyclohexane**

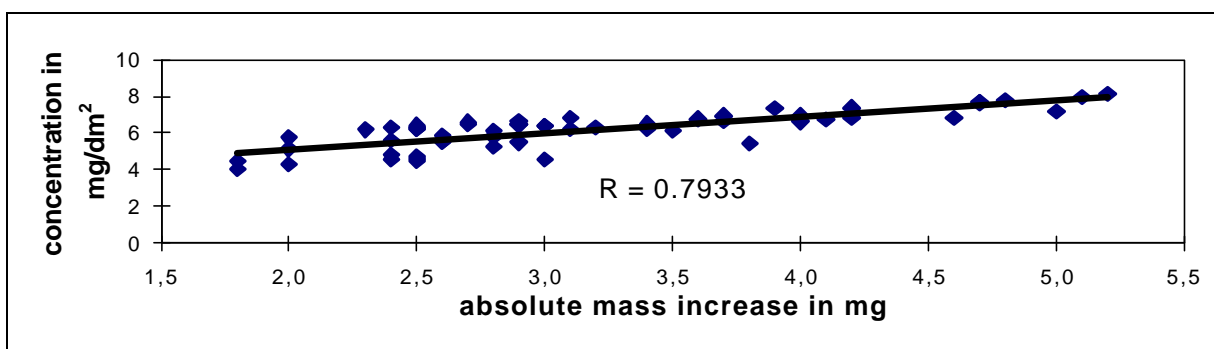


Figure 3-19: Correlation of the absolute mass increase of a PET strip after the sorption phase with the chemical inertness test result of **Benzophenone**

Because of the correlation of the absolute mass increase of a PET strip and test results of model compounds it was necessary to establish and introduce a tolerance interval of the absolute mass increase of PET strips after the sorption phase. 1.5 L PET bottles out of test batch TBJ0198 produced in January 1998 were further used for the preparation of PET strips within the validation exercise of the method. After the sorption phase e.g. the mass increase of the PET reference material can indicate possible deviations of temperature parameters during the storage of the PET material as well as during the sorption phase of the chemical analysis. If the PET material itself is stored at temperature conditions of less than 0 °C e.g. the chemical inertness of this material will lead to higher model compound values already indicated by higher mass increases of the test strips after the sorption

phase. If the absolute mass increase of a PET strip was higher or lower than the defined tolerance interval the following reasons were possible:

1. The temperature of the thermostatically controlled oven was higher or lower than $60\text{ °C} \pm 1\text{ °C}$.
2. The storage time was longer or shorter than $48\text{ h} \pm 0.5\text{ h}$
3. The PET strip wasn't totally immersed during the whole storage time
4. The mass of individual substances in the model compound solution differed to much.

3.1.3.3 Evaluation of possible uncertainties within the extraction phase

STRIP PREPARATION - Cleaning of PET strips

After a sorption phase of 2 days at 60 °C the strips have to be prepared for the extraction phase. Taking the strips out of the model compound solution they have to be cleaned superficially with a lint free cloth to remove sticking model compound solution. Furthermore they have to be gently washed in 95 % Ethanol to make sure that residual model compounds were completely removed from the surface area. The following Table 3-8 shows test results of the analysis of three following „washing“ reservoirs of 50 mL 95 % Ethanol after washing of 8 PET strips.

Table 3-8: Concentration of model compounds in three following „washing“ solutions of 50 mL ethanol after „washing“ of 8 PET strips. (n.d. not detectable)

model compound in $\mu\text{g/mL}$ solution	95 % ethanol reservoir 1	95 % ethanol reservoir 2	95 % ethanol reservoir 3
Toluene	271.40	4.41	1.99
Phenol	464.16	6.92	0.13
Limonene	418.51	4.35	n.d.
Menthol	465.74	6.72	0.42
Phenylcyclohexane	435.87	3.32	n.d.
Benzophenone	420.54	3.12	n.d.

The results clearly show that at least 3 x 50 mL of 95 % Ethanol has to be used to fully remove the model compound solution from the surface area of a maximum of 8 PET strips. Therefore, after carrying out the washing procedure with 8 strips the washing reservoirs have to be renewed. Using the washing solvents for more than 8 strips would mean that test results especially for Toluene can be falsified due to residual amounts on the surface area of the PET strip.

STRIP PREPARATION - Cutting of strip edges

After cleaning and weighing, the edges of the PET strips have to be cut off because of edge sorption effects which negatively influence the chemical inertness test results. To eliminate the edge sorption effects the edges of a strip were cut off approximately 1 mm around. Figure 3-20 to Figure 3-25 show the correlation of the cut off mass of a PET strip with chemical inertness test results.

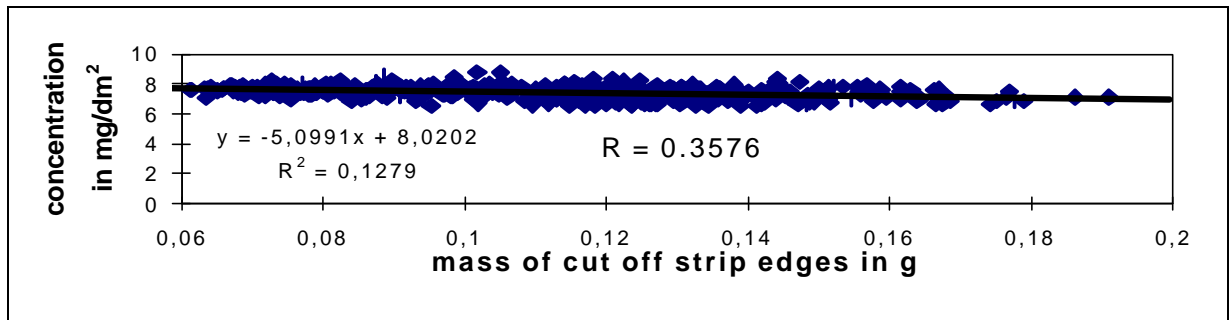


Figure 3-20: Correlation of the mass of cut off strip edges with the chemical inertness test result for **Toluene**

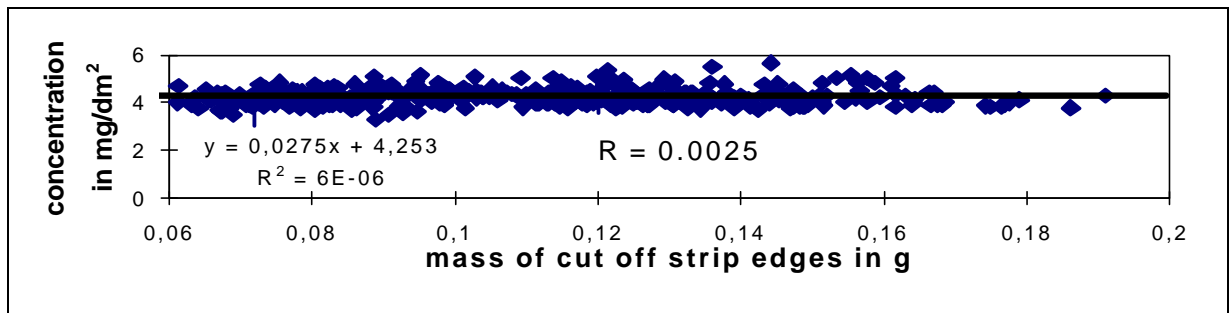


Figure 3-21: Correlation of the mass of cut off strip edges with the chemical inertness test result for **Phenol**

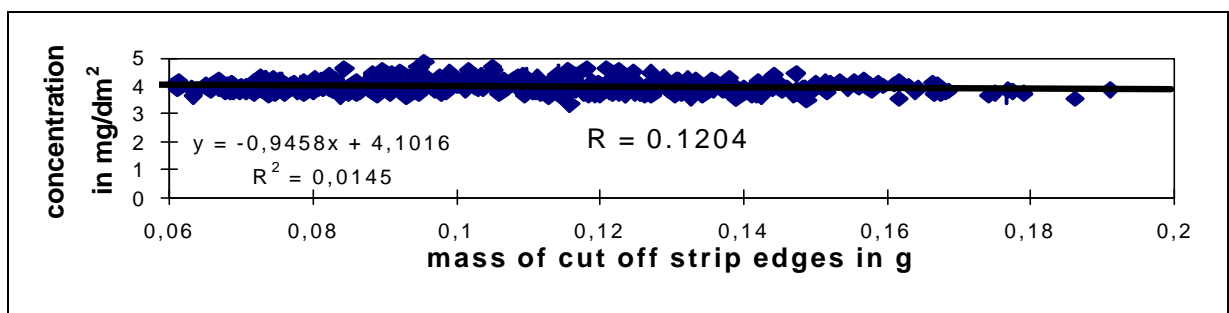


Figure 3-22: Correlation of the mass of cut off strip edges with the chemical inertness test result for **Limonene**

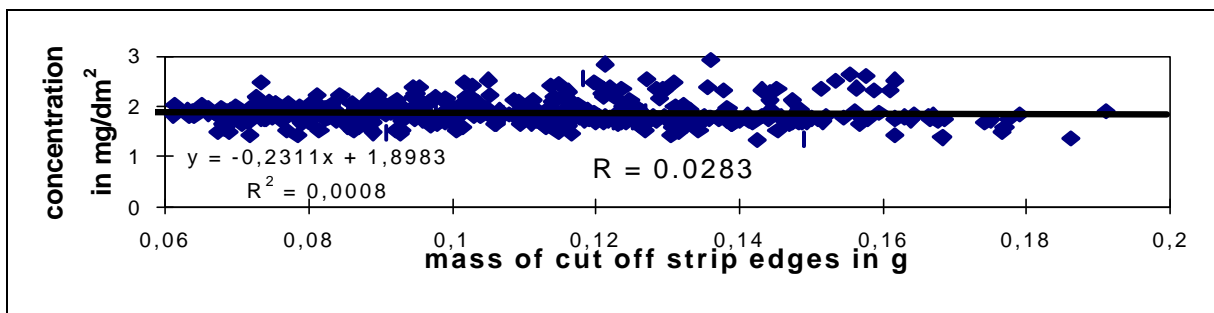


Figure 3-23: Correlation of the mass of cut off strip edges with the chemical inertness test result for **Menthol**

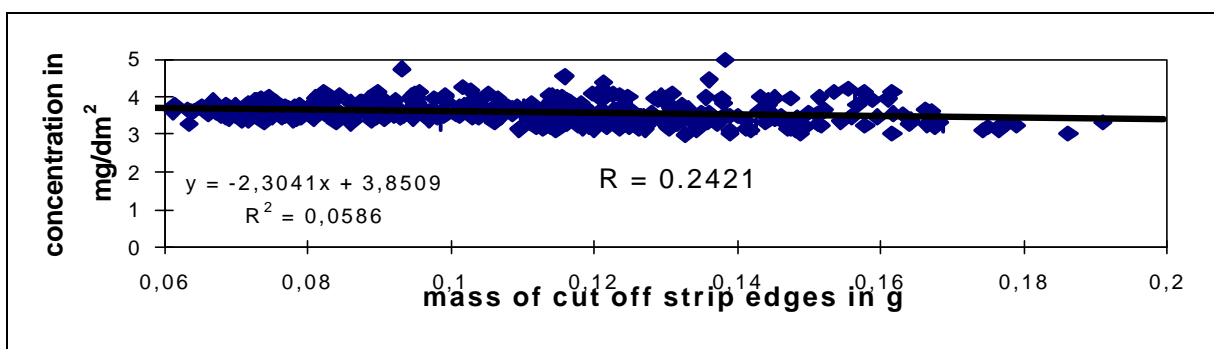


Figure 3-24: Correlation of the mass of cut off strip edges with the chemical inertness test result for **Phenyl cyclohexane**

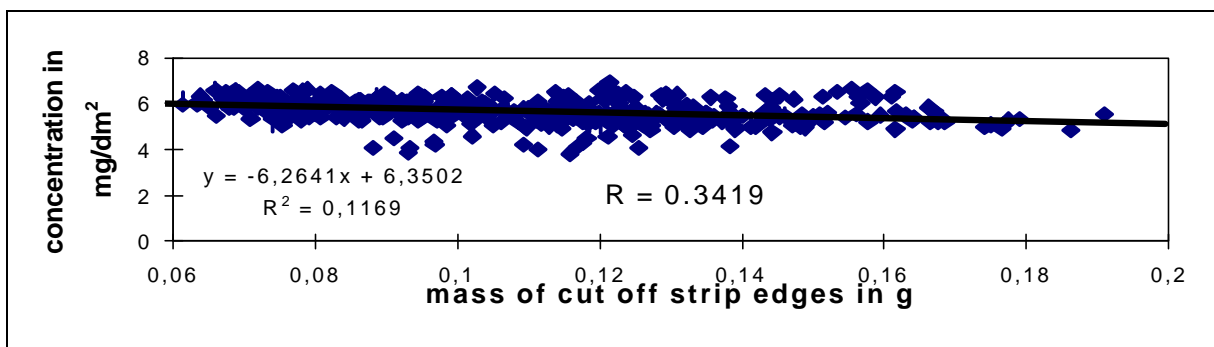


Figure 3-25: Correlation of the mass of cut off strip edges with the chemical inertness test result for **Benzophenone**

The sorption of model compounds through the edges into the PET strip doesn't correspond to real migration conditions. Cutting the strip edges too economically therefore means that sorption effects can't be totally excluded. Figure 3-20 to Figure 3-25 show that there exists a slight correlation of chemical inertness test results with the mass of cut off strip edges for the model compounds Toluene and Benzophenone whereas the correlation of the model compounds Phenol, Limonene, Menthol and Phenyl cyclohexane with the amount of cut off strip edges can be neglected. However, cutting the edges more generously prevents the negative influence of edge sorption effects.

PREPARATION OF THE EXTRACTION PHASE

As already mentioned migration processes only occur in layer dimensions of μm of the surface area of a PET strip. For this reason it turned out to be very important for the chemical inertness test procedure that there is no lack of time between the sorption and the extraction phase of the PET strips due to a loss of model compounds on the basis of desorption processes during the storage. Figure 3-26 presents the analysis of the desorption of model compounds from the surface of PET strips stored at room temperature after a sorption phase of two days at $60\text{ }^\circ\text{C}$.

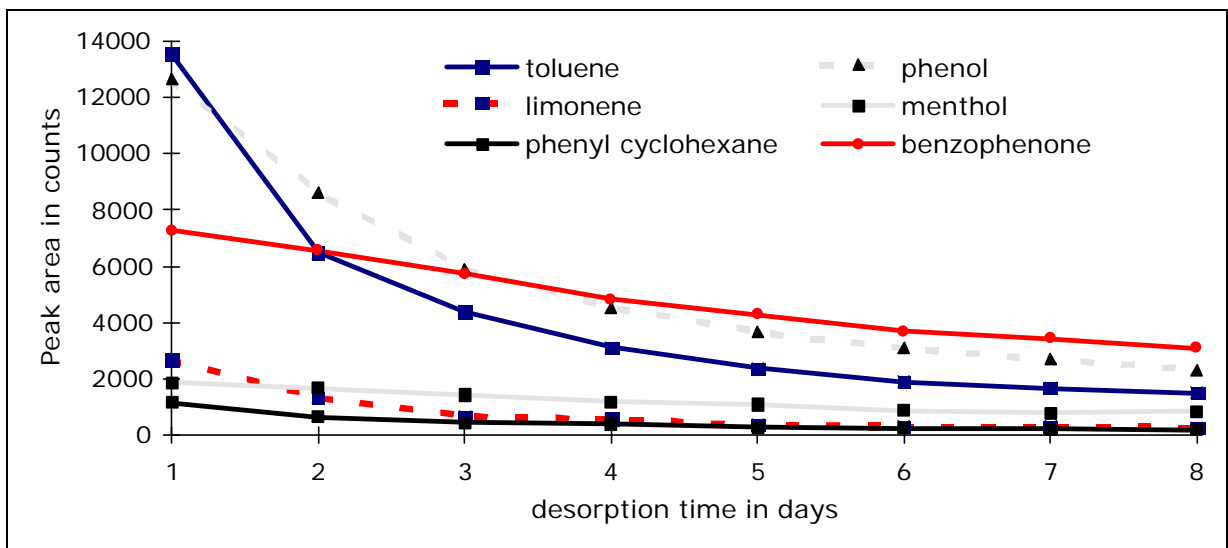


Figure 3-26: Desorption of model compounds from the surface of PET strips stored at room temperature after the sorption phase

After one week the residual amount of model compounds of the PET strips were furthermore analysed proceeding with the extraction phase of the chemical inertness test procedure.

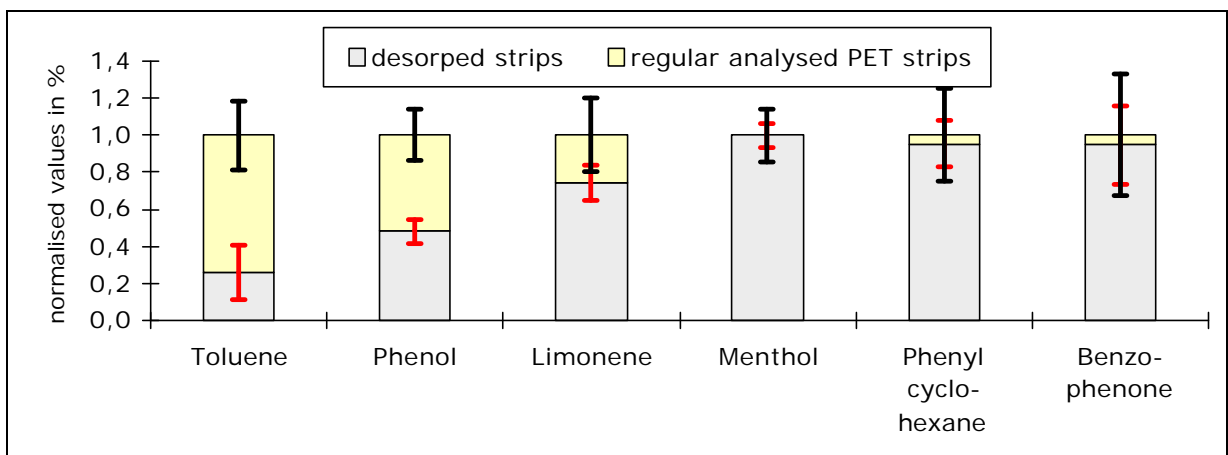


Figure 3-27: Comparison of residual amounts of model compounds after desorption of 7 days at room temperature with normally analysed PET strips

While the concentration of sorbed volatile model compounds already decreased after a storage time of one day the residual amount of non-volatile model

compounds didn't significantly change in comparison to test results of regular analysed PET strips. According to the desorption of volatile model compounds during the storage of PET strips even at lower temperatures the extraction phase has to be performed immediately after the sorption phase.

3.1.3.4 Gas chromatographic analysis of extracts - evaluation of test results

The uncontrolled loss of the 95 % Ethanol solvent during the extraction phase could also result in falsified re-migration results of model compounds. For determining the loss of 95 % Ethanol a weighing step prior to and after the exposure of the whole sample was included in the chemical inertness method. Based on test results of different laboratories it was concluded that a loss of extraction solvent higher than 5 % could not be accepted. Thus the strip solutions with a loss of Ethanol higher than 5 % have to be repeated. For preventing the case that a strip solution has to be rejected, 8 PET strips have to be prepared as samples at the beginning of the inertness test. The chemical inertness procedure will further work with 6 specimens by choosing the 6 best specimens concerning the quantity of loss of 95 % Ethanol in the case that the loss of Ethanol is lower than 5 %. At least 5 specimens with a loss of lower than 5 % have to be available for the further analysis. Otherwise the whole PET inertness testing has to be repeated from the beginning of the procedure. Performing the chemical inertness test procedure within the preliminary intercomparison testing of six laboratories it turned out to be technical feasible to restrict the loss of 95 % Ethanol to a maximum of 2 % of the absolute amount of extraction solvent. In fact a loss of 5 % of the extraction solvent may also be tolerable but if technically feasible a loss of 95 % Ethanol of less than 2 % has to be given preference. The following Table 3-9 summarises the durability of extracts and solutions used within the chemical inertness test procedure.

Table 3-9: Durability of solutions used within the chemical inertness test procedure.

solution	durability
model compound solution	2 months at 4 °C
calibration stock solution	2 months at 4 °C
internal standard solution	2 months at 4 °C
calibration diluted standard solution	1 week at 4 °C
extracts of the PET strips	1 week at 4 °C

For the gas chromatographic analysis of model compounds it is essential that appropriate GC conditions are used e.g. all model compounds have to be clearly separated.

For the evaluation of model compound concentrations calibration curves are established for each model compound.

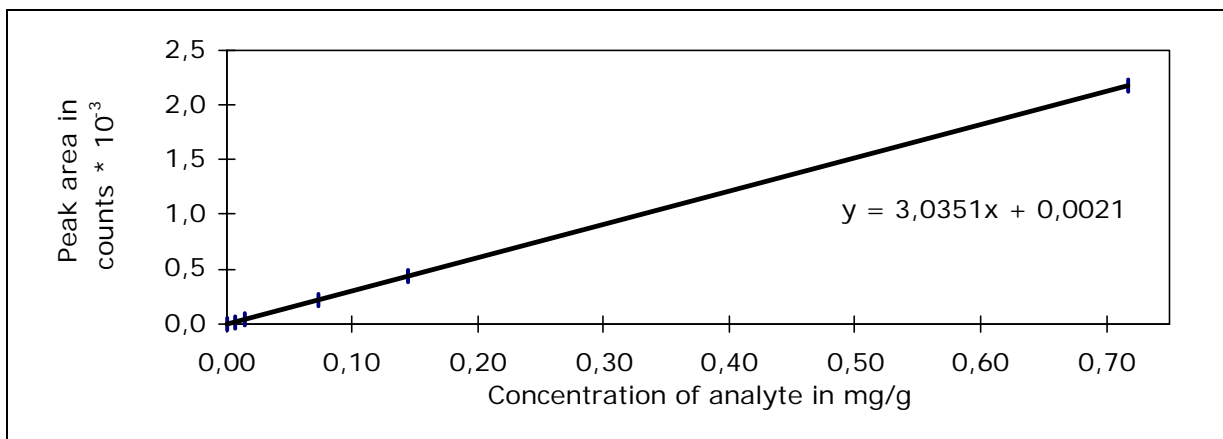


Figure 3-28: Exemplary calibration curve for model compound toluene

The peak area values obtained by gas chromatographic analysis applying an internal standard method are calculated for each model compound of a test sample. The model compound concentration of the test samples is read from the individual calibration graph of each model compound as shown in Figure 3-28. The calibration curve is obtained by analysing defined concentrations of model compounds in 95 % Ethanol. The resulting peak area values of the GC analysis of model compounds are correlated with corresponding concentrations of each model compound. The further calculation of model compound concentrations of test samples from the regression parameters is performed as follows:

If the regression equation of each model compound (mc) is

$$y_{mc} [\text{counts}] = a_{mc} \cdot x_{mc} [\text{mg / g}] + b_{mc} \quad (\text{equation 4.1})$$

y_{mc} value of the peak area of a model compound in counts * 10⁻³

a_{mc} slope of the calibration curve of a model compound

x_{mc} concentration of model compound in mg/g in 95 % Ethanol

b_{mc} intercept of the calibration curve of a model compound (blank value)

then the concentration of each model compound in 95 % Ethanol is

$$x_{mc} [\text{mg / g}] = \frac{y_{mc} - b_{mc}}{a_{mc}} \quad (\text{equation 4.2})$$

For each model compound the interactivity value is expressed as extracted amount (in mg) per square decimetre of test specimen taking both sides of the PET strip into account. The calculation of the final interactivity values for the model compounds in mg/dm² is achieved as follows:

$$\text{Interactivity}_{\text{mc}} \left[\frac{\text{mg}}{\text{dm}^2} \right] = \frac{x_{\text{mc}} \left[\frac{\text{mg}}{\text{g}} \right] \cdot m_{\text{ae}}^{\text{ES}} [\text{g}]}{A_{\text{eff}} [\text{dm}^2]} \quad (\text{equation 5})$$

$\text{Interactivity}_{\text{mc}}$	extracted amount of model compound in mg per square decimetre of a PET test strip taking both sides into account
x_{mc}	concentration of model compound in mg/g in 95 % Ethanol (extraction solvent)
A_{eff}	effective area of a PET strip after cutting the edges (taking both sides of the test specimen into account) in dm^2
$m_{\text{ae}}^{\text{ES}}$	mass of extraction solvent 95 % Ethanol in g after the extraction phase of PET strips

3.2 RUGGEDNESS TESTING OF THE OPTIMISED AND SIMPLIFIED CHEMICAL INERTNESS TEST METHOD

After optimising the chemical inertness method a first ruggedness testing was carried out between three laboratories. The ruggedness testing was performed in a way that one laboratory prepared PET strips out of the middle part of a PET bottle as well as one model compound solution for each laboratory. Moreover, each laboratory also prepared PET strips of another PET bottle as well as a model compound solution (MCS) themselves. The PET inertness test was then carried out on four following weeks with different PET test specimens. Table 3-10 describes the structure of the ruggedness testing.

Table 3-10: Structure of measurements performed within the ruggedness testing

Bottle no	Laboratory_1		Laboratory_2		Laboratory_3	
	strips	MCS	strips	MCS	strips	MCS
19_x (1,2,3)	L1	L1	L1	L1	L1	L1
20_x (1,2,3)	L1	L1	L1	L2	L1	L3
21_1	L1	L1				
21_2	L1	L1				
22_1			L2	L1		
22_2			L2	L2		
23_1					L3	L1
23_2					L3	L3

Figure 3-29 to Figure 3-34 show the average of 6 PET strip test results of the test specimens 19 to 23 for each model compound. The test results of the chemical inertness testing are normalised to test results obtained for the test specimen 19_1. Test results for the model compound Propylene glycol (which was still

included in the set at that time) aren't listed because of the instability of this compound.

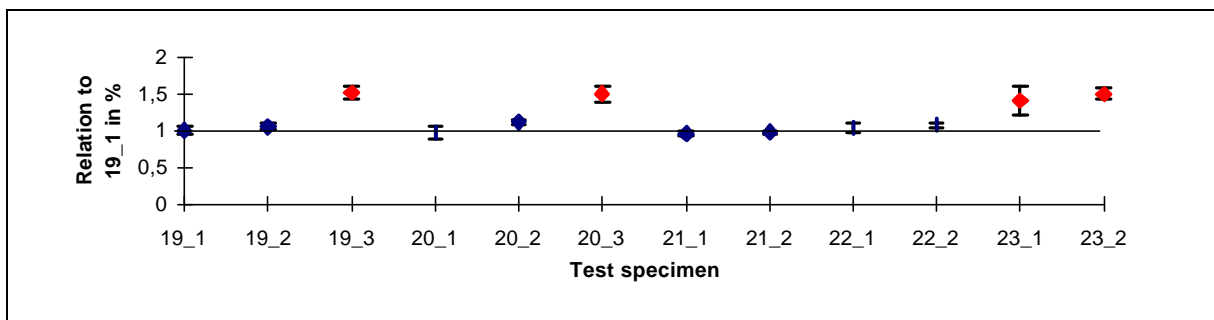


Figure 3-29: Test results of the ruggedness testing for the model compound **Toluene**

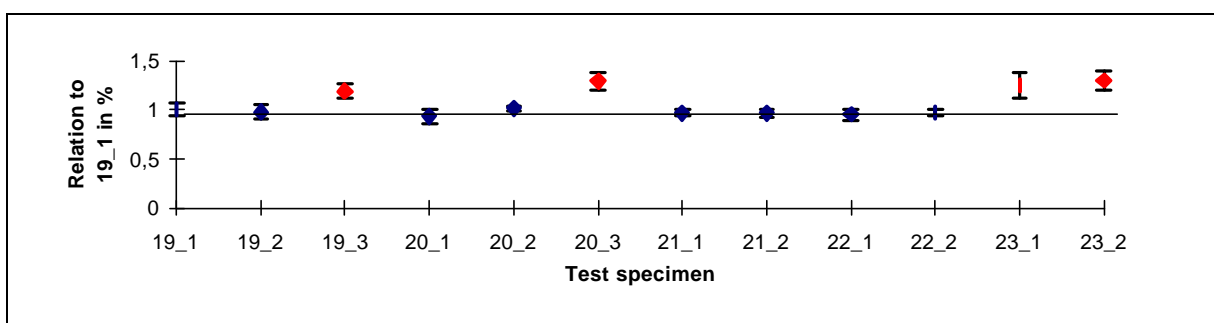


Figure 3-30 Test results of the ruggedness testing for the model compound **Phenol**

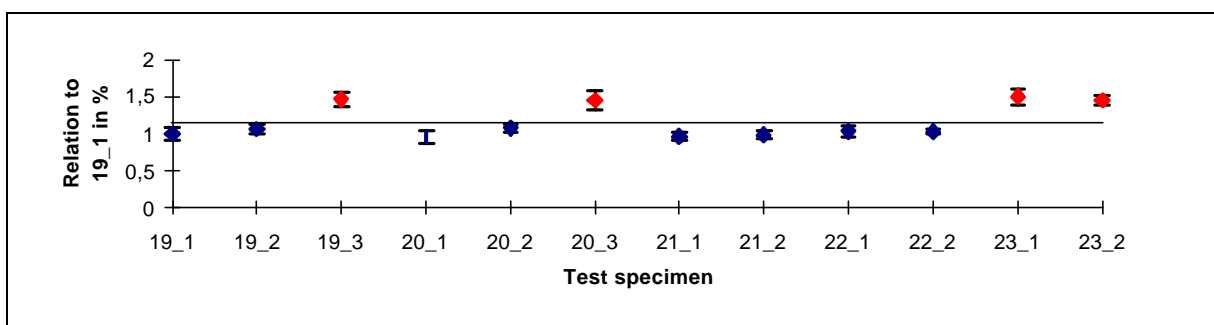


Figure 3-31: Test results of the ruggedness testing for the model compound **Limonene**

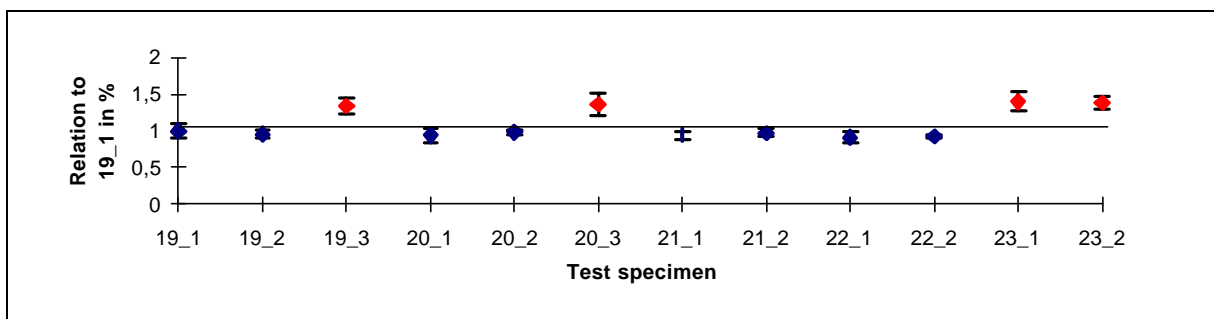


Figure 3-32: Test results of the ruggedness testing for the model compound **Menthol**

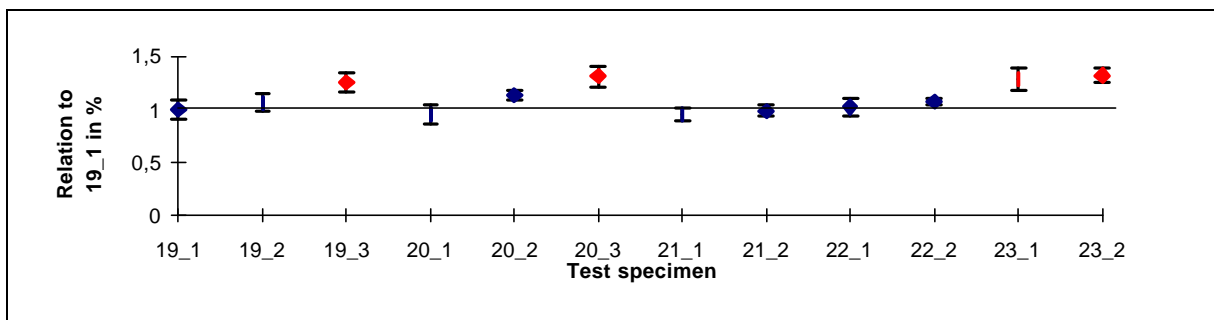


Figure 3-33: Test results of the ruggedness testing for the model compound **Phenyl cyclohexane**

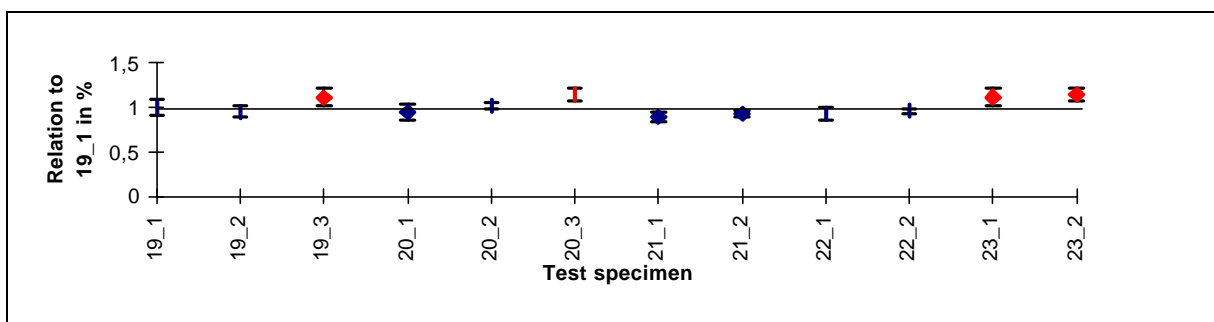


Figure 3-34: Test results of the ruggedness testing for the model compound **Benzophenone**

Comparing the PET inertness test results between laboratory L1, L2 and L3 it is obvious that L3 obtained higher test results than L1 and L2. However, test results of L1 and L2 are significantly corresponding. For the higher extraction values of L3 several technical reasons could be identified. Due to an inefficient washing of PET strips which were only rinsed with Ethanol, there were residual model compounds on the surface area of the PET strips. Reasons for the deviation of test results were also due to uncontrolled temperature parameters during the sorption (loading) phase of the PET strips. The divergence from the exposure condition of temperature led to higher sorption amounts respectively to a higher mass increase of the PET strips and therefore higher PET inertness results for the model compounds. It turned out to be very important that the control of precise test conditions during the test procedure has to be guaranteed.

Figure 3-29 to Figure 3-34 show clearly that the different PET inertness tests carried out within the laboratories L1, L2 provide satisfying significant results which were independent from

- * the preparation of initial PET strips out of the middle part of a PET bottle
- * the preparation of the model compound solution
- * the source of used chemicals

The following Table 3-11 shows the statistical evaluation of test results of laboratory 1 and laboratory 2.

The statistical evaluation of the individual test results with the statistic programme HOSTAN provided by the European Commission¹ showed that test results of all six model compounds were normal distributed as well as homogenous on a level of significance of 0.05.

Model compound	\bar{x}	S_1	S_2	S_w	S_b
Toluene	10.461	0.733	0.583	0.524	0.542
Phenol	6.548	0.374	0.176	0.364	0.094
Limonene	5.383	0.405	0.244	0.361	0.194
Menthol	2.158	0.155	0.067	0.153	0.025
Phenylcyclohexane	4.688	0.408	0.294	0.324	0.262
Benzophenone	7.544	0.555	0.325	0.502	0.252

Table 3-11: Statistical evaluation of test results of the ruggedness testing between laboratory 1 and 2

\bar{x} Overall mean

S_1 Standard deviation of distribution of individual values

S_2 Standard deviation of distribution of means

S_w Within-labs standard deviation

S_b Between-labs standard deviation

3.3 PRELIMINARY INTERCOMPARISON AND METHOD VALIDATION

Based on the practical experience obtained in the first ruggedness testing between laboratory L1 to L3 the preliminary intercomparison testing was carried out after a more detailed description of the test procedure of the drafted test method. The chemical inertness test method was changed to the effect that wherever possible measurements were traced back to the SI units (e.g. solvents are measured by mass and not by volume).

The objective of the preliminary intercomparison was to expose the pre-validated method to ring testing including six laboratories in order to achieve a further validation. For the preliminary intercomparison testing a second test batch of PET bottles was produced. For a better distinguishing of the PET bottle materials as well as test results the first test batch was called TBJ0198 as already mentioned, while bottles out of the second test were called PI040698. Visual examining of the PET bottle material PI040698 intended to be used within the preliminary intercomparison testing showed, that the material might not have been produced on the same day under the same production conditions due to e.g. differing wall thicknesses and different flexibility of the material. Assuming that the wall

¹ European Commission - DG XII - SMT Programme, Building MO-75, B-1049 Brussels, Belgium.

thickness of PET bottles does not influence the chemical inertness test results this PET bottle material was further used for additional investigations, but however, due to the visual inhomogeneity, it was decided to use rather TBJ0198 and not PI040698 as a test material for the preliminary intercomparison experiment. The preliminary intercomparison exercise was carried out by sending four middle parts of PET bottles chosen by chance out of test batch TBJ0198 to each of the six participating laboratories L1 to L6. Each laboratory had to carry out the inertness test in the order of increasing bottle numbers examining two bottles in one test run at two following days or weeks by precisely following the instructions of the drafted chemical inertness method.

The following Figure 3-35 to Figure 3-40 present test results for each model compound with their 95 % confidence interval of the preliminary intercomparison of laboratory L1 to L6. For the validation of the chemical inertness method it was fixed that the laboratories should achieve comparable results with a maximum reproducibility range of 20 to 25 % on a 95 % probability level as well as a maximum repeatability range of 15 to 20 %. This precondition could be achieved for each of the six model compounds.

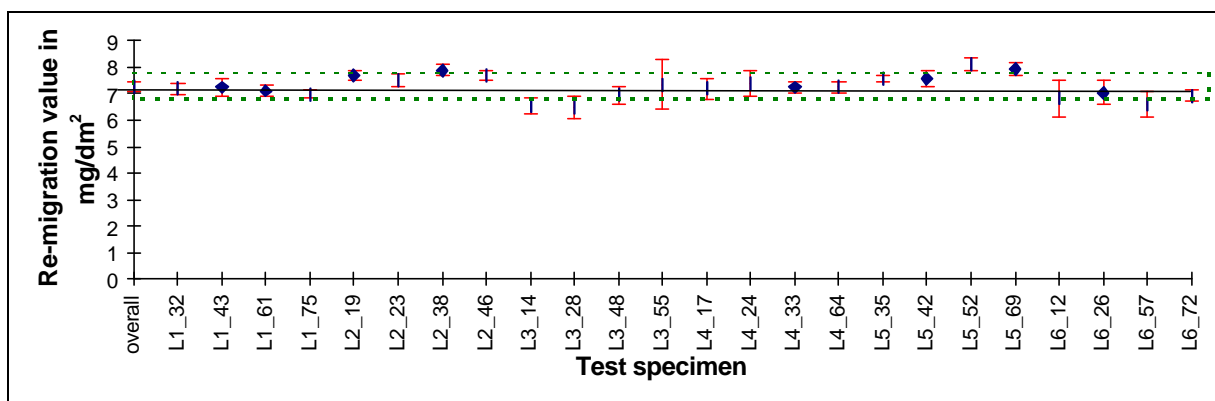


Figure 3-35: Preliminary Intercomparison test results of six laboratories for the model compound **Toluene**

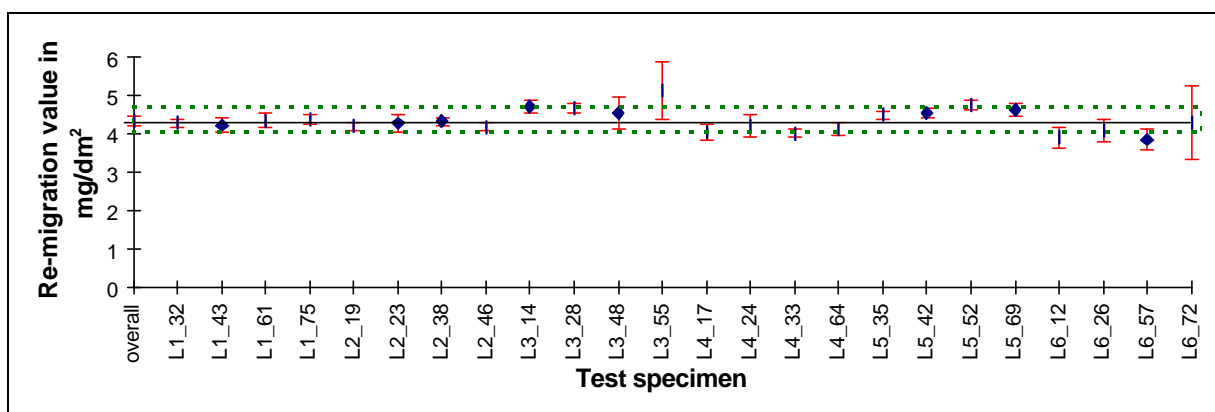


Figure 3-36: Preliminary Intercomparison test results of six laboratories for the model compound **Phenol**

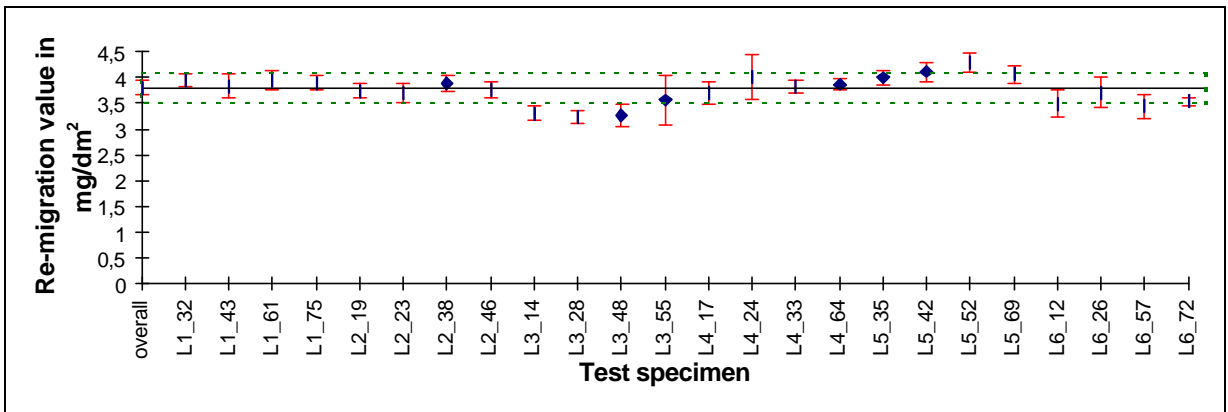


Figure 3-37: Preliminary Intercomparison test results of six laboratories for the model compound **Limonene**

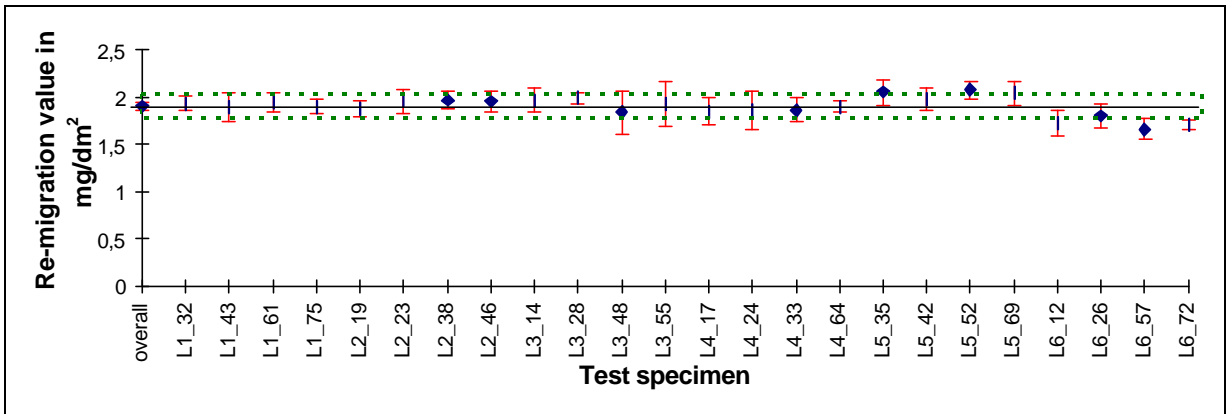


Figure 3-38: Preliminary Intercomparison test results of six laboratories for the model compound **Menthol**

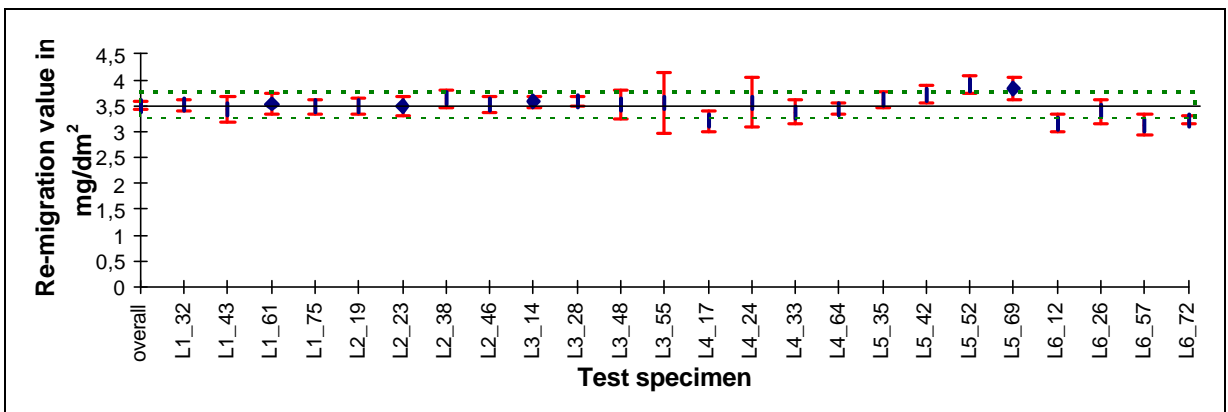


Figure 3-39: Preliminary Intercomparison test results of six laboratories for the model compound **Phenyl cyclohexan**

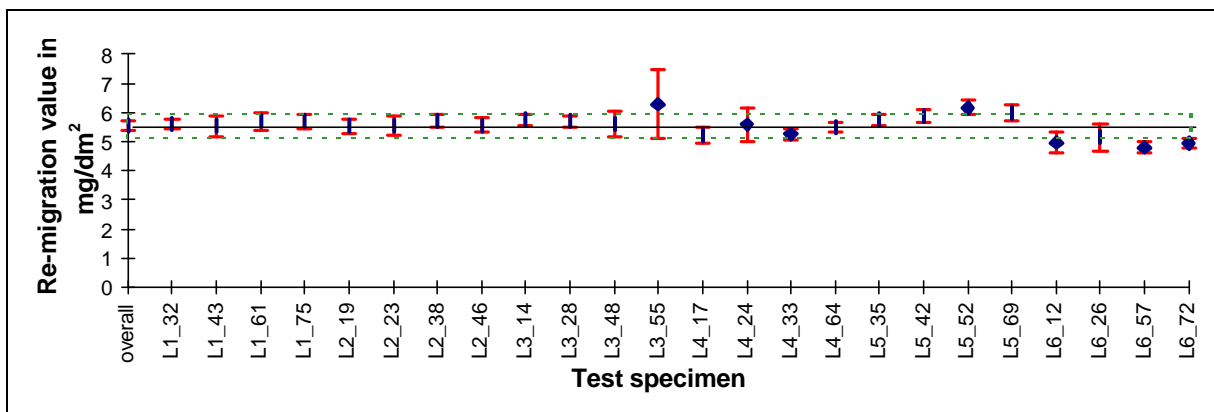


Figure 3-40: Preliminary Intercomparison test results of six laboratories for the model compound **Benzophenone**

Regarding Figure 3-35 to Figure 3-40 several laboratories attract attention because of outlying measurements or higher standard deviations and 0.95 % confidence intervals, respectively. The following technical reasons could be detected for the individual laboratories:

Laboratory L1

Laboratory L1 strictly followed the drafted method and hadn't outlying measurements or remarkable standard deviations. However during the GC analysis of the extract solutions a lack of carrier gas occurred at the weekend so that the samples of BOT 61/75 were stored at room temperature for 2 days before the analysis could be rerun.

Laboratory L2

Laboratory L2 also strictly followed the drafted method but carried out the analysis of all four test bottles in one test run. The analysis of all test strips (40 strips) of the four bottle specimens in one GC run took more than one week. Performing the calibration only at the beginning of the GC run means that the GC performance might have changed when analysing strips of the specimens 38/46 three days later. For this reason the test results of bottle 38 and 46 were not included in the final statistical evaluation of the preliminary intercomparison testing.

Laboratory L3

Regarding test results of laboratory L3 it is remarkable that the standard deviations became larger from measurement to measurement. One reason for the increasing standard deviations of test results with increasing bottle number of laboratory L3 e.g. could be found in differing parameters of GC analysis. The extraction solutions of bottle 48 and 55 were 20 and 16 days old before they were analysed. Higher test results and standard deviations of model compounds result e.g. in the evaporation of 95 % ethanol during the long storage time. The different duration of GC analysis due to manual injection could also lead to deviations in the GC analysis.

However, a storage duration of longer than 14 days for extraction solutions can not be accepted due to possible chemical changes of the solutions. Therefore the test results of bottle 48 and 55 were discarded.

Laboratory L4

Laboratory 4 had problems in maintaining the loss of 95 % ethanol below 5 %. For the bottle numbers 24 and 64 only four extraction solutions remained with a loss of 95 % ethanol of lower than 5 %. Laboratory 4 carried out the PET inertness test with bottle 17/24 and 33/64 on two following days but analysed the extraction solutions in one GC run. Due to a short GC programme of 8 minutes in total the toluene was not efficiently separated from the ethanol peak. During the GC analysis it also turned out that the column had a too thin film thickness so that the Menthol peak broadened and interfered with the Phenyl cyclohexane peak. The peak areas for these two model substances were later on manually adjusted and integrated. Due to the loss of 95 % ethanol as well as inappropriate GC conditions the test results of laboratory L4 were not included in the final statistical evaluation of the preliminary intercomparison testing.

Laboratory L5

Laboratory L5 analysed the PET bottle materials in descending order of the bottle numbers. (69, 52, 42, 35). The GC analysis of all extraction solutions was performed in one test run so that the extraction solutions of the first chemical inertness testing were already three weeks old. Test results of bottle 69 and 52 were therefore discarded.

Laboratory L6

Due to a lot of work in the period of the preliminary intercomparison testing laboratory L6 froze the PET material before carrying out the PET inertness tests approximately half a year later. Freezing a plastic like PET means destroying the material by changing physical as well as mechanical properties of the material. Moreover, laboratory L6 used polyethylene glycol 300 instead of polyethylene glycol 400 for the preparation of the model compound solution so that the vapour pressure of the model compounds in the cocktail solution was changed. Therefore test results of laboratory L6 were discarded.

The following Table 3-12 to Table 3-18 summarise results of the statistical evaluation carried out with the statistic programme HOSTAN provided by the European Commission for each of the six model compounds. All statistically evaluated test results of the preliminary intercomparison are given in mg/ dm².

Table 3-12: Statistical results of the preliminary intercomparison valid for each of the six model compounds if not stated otherwise

Statistical evaluation based on	laboratory means	individual values
Number of accepted sets of results	10	10
Number of accepted replicates	79	79
Outlying variance	no	no
Homogeneity of variances	homogeneous	homogeneous
Normality of distribution	normal	normal
Outlying mean values	none	none

Table 3-13: Statistically evaluated test results of **Toluene** of the preliminary intercomparison between laboratory L1 to L6

Statistical evaluation based on	laboratory means	individual values
Mean of	7.182	7.178
Standard deviation of distribution of	0.400	0.463
Within-labs standard deviation	0.278	0.278
Between-labs standard deviation	0.388	0.388
0.95 confidence interval	7.182+/-0.286	7.178+/-0.104

Table 3-14: Statistically evaluated test results of **Phenol** of the preliminary intercomparison between laboratory L1 to L6

Statistical evaluation based on	laboratory means	individual values
Mean of	4.422	4.423
Standard deviation of distribution of	0.184	0.242
Within-labs standard deviation	0.176	0.176
Between-labs standard deviation	0.174	0.174
0.95 confidence interval	4.422+/-0.132	4.423+/-0.054

Table 3-15: Statistically evaluated test results of **Limonene** of the preliminary intercomparison between laboratory L1 to L6

Statistical evaluation based on	laboratory means	individual values
Normality of distribution	normal	not normal
Mean of	3.771	3.772
Standard deviation of distribution of	0.303	0.345
Within-labs standard deviation	0.196	0.196
Between-labs standard deviation	0.297	0.297
0.95 confidence interval	3.771+/-0.217	3.772+/-0.077

Table 3-16: Statistically evaluated test results of **Menthol** of the preliminary intercomparison between laboratory L1 to L6

Statistical evaluation based on	laboratory means	individual values
Normality of distribution	normal	about normal
Mean of	1.954	1.954
Standard deviation of distribution of	0.053	0.132
Within-labs standard deviation	0.130	0.130
Between-labs standard deviation	0.026	0.026
0.95 confidence interval	1.954+/-0.038	1.954+/-0.026

Table 3-17: Statistically evaluated test results of **Phenyl cyclohexane** of the preliminary intercomparison between laboratory L1 to L6

Statistical evaluation based on	laboratory means	individual values
Mean of	3.544	3.545
Standard deviation of distribution of	0.085	0.198
Within-labs standard deviation	0.192	0.192
Between-labs standard deviation	0.050	0.050
0.95 confidence interval	3.544+/-0.061	3.545+/-0.044

Table 3-18: Statistically evaluated test results of **Benzophenone** of the preliminary intercomparison between laboratory L1 to L6

Statistical evaluation based on	laboratory means	individual values
Mean of	5.669	5.670
Standard deviation of distribution of	0.116	0.302
Within-labs standard deviation	0.299	0.299
Between-labs standard deviation	0.047	0.047
0.95 confidence interval	5.669+/-0.083	5.670+/-0.068

Table 3-19: Statistically evaluated repeatability and reproducibility values of the six model compounds for the chemical inertness test procedure.

model compound	standard deviation S	repeatability	reproducibility
toluene	0.463	0.278	0.478
phenol	0.242	0.176	0.247
limonene	0.345	0.196	0.356
menthol	0.132	0.130	0.132
phenylcyclohexane	0.198	0.192	0.199
benzophenone	0.302	0.299	0.303

According to test results of the preliminary intercomparison the chemical inertness method was fit for purpose and could be validated on the basis of a level of significance of 0.05.

4 CHARACTERISATION OF PET MATERIALS FOR REFERENCE TESTING

Up to now there are neither any specific regulations nor standard tests available with which the food safety and quality of e.g. refillable PET bottles can be tested. The chemical inertness test method is dedicated to provide a systematical control possibility to check the inertness behaviour and therefore safety of PET bottles during their life cycle. However, the chemical inertness of a PET bottle only can be judged if reference values are available. The additional intention of the presented research work was therefore to prepare a food grade reference PET material which already fulfils the principal requirement of Article 2 of the Framework Directive 89/109/EEC and to establish this material as a reference material with respect to its interactivity values.

The most common form of PET bottles on the market is the refillable 1.5 litre PET bottle. For the development of the chemical inertness test procedure as well as the establishment of a reference PET material a commonly used 1.5 litre refillable bottle for soft drinks was chosen which has been generally accepted from a health risk point of view (i.e. which has already been investigated in misuse studies and which was found to be safe provided that the usual precautions like electronic and visual inspections of returned bottles were applied).



Figure 4-1: 1.5L refillable PET bottle

The shape of the bottle was chosen in such a manner that the brand of the reference material (RM) PET couldn't be detected after the production and preparation. The research work of developing a chemical inertness test procedure in conjunction with the establishment of a reference PET bottle was carried out using following test batches of 1.5 litre PET bottles:

Table 4-1: Test batches of PET bottles used within the chemical inertness project

Test batch	Application
TBJ0198 PIO40698	PET bottles used as test material for the optimisation, modification and simplification of the chemical inertness test procedure
CE130799	Reference material

The 1.5 litre PET bottles of the three test batches were produced as monolayer bottles consisting of virgin homopolymer PET which was manufactured by polymerisation of Dimethyl terephthalate. The manufacture of all three test batches was carried out applying same manufacturing conditions and parameters. The determination of the chemical inertness interactivity of PET beverage bottles in conjunction with the evaluation and establishment of food safety aspects of PET bottles presuppose that

1. bottles coming from the same material feedstock and production line show significantly comparable interactivity results. In other words, bottles from the same manufacturing batch have to be homogenous concerning the chemical inertness behaviour. Otherwise it would not be possible let alone useful to predict and generally compare the chemical inertness behaviour of PET bottles manufactured under defined conditions.
2. virgin PET bottles show constant and stable interactivity values if stored under conditions which exclude environmental stresses on the material over a period of time. If the chemical inertness of virgin PET bottles changes gradually it is absolutely useless to manufacture and establish a PET bottle as reference material.

The inertness of a PET material depends on material properties like e.g. molecular mass distribution or cristallinity. Producing PET bottles under the same production conditions from raw materials to blow- moulding parameters like temperature profiles, pressures etc. means that PET bottles have the same material properties and therefore also have to show the same chemical inertness behaviour against model compounds. For this reason the stability and the homogeneity of PET multi-use bottles in the future used as reference material were investigated concerning the chemical inertness behaviour.

4.1 STABILITY TESTING OF TEST BATCHES TBJ0198 AND PI040698

The first test batch TBJ0198 of approximately 150 bottles was produced in January 1998 while the second test batch PI040698 of approximately 100 cut out middle parts of PET bottles was produced half a year later on June 1998. Both test batch materials were produced on the same production line under same production parameters with the same source of PET preform material. Both test batches were about the same design of 1.5 L multi-use PET bottles which already were on the market. On the basis of same production conditions it was therefore presumed that the PET bottles of the two different test batches also must show the same chemical inertness behaviour. For this reason the chemical inertness of both test batch materials was established in order to compare the inertness behaviour of the PET bottles.

The results of the investigation are shown in Figure 4-2 and Table 4-2.

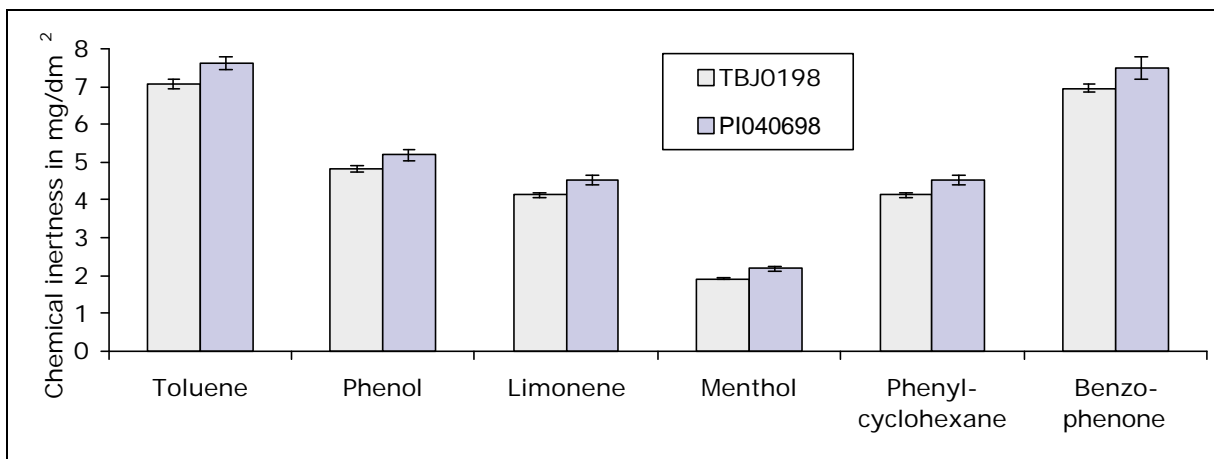


Figure 4-2: Comparison of chemical inertness test results of TBJ0198 and PI040698.

Table 4-2: Comparison of chemical inertness test results of TBJ0198 and PI040698.

Model compounds	TBJ0198			PI040698		
	mean in mg/dm ²	stdv in %	CV in %	mean in mg/dm ²	stdv in %	CV in %
Toluene	7.07	± 0.14	1.98	7.48	± 0.15	2.01
Phenol	4.83	± 0.09	1.86	5.18	± 0.12	2.32
Limonene	4.13	± 0.06	1.45	4.54	± 0.10	2.20
Menthol	1.92	± 0.03	1.56	2.18	± 0.05	2.29
Phenyl cyclohexane	4.13	± 0.06	1.45	4.53	± 0.11	2.43
Benzophenone	6.94	± 0.10	1.45	7.52	± 0.26	3.46

The investigation of the chemical inertness behaviour of bottles out of test batch TBJ0198 and PI040698 showed that bottles out of test batch PI040698 obtained significantly ($t_{0.95}$ - test) higher test results for the six model compounds. Varying test results concerning the inertness behaviour of *different* PET materials may depend e.g. on

1. differences between one phase (direct from granulate to bottle) or two phase (first preform, than bottle) production of bottles
2. differences in the temperature profiling and programme during the moulding process of a bottle and therefore
3. differences in the cristallinity as well as the amount of amorphous areas
4. the polymer properties - quality of PET resin
5. the residual amount of monomers as well as additives

The difference of test batch TBJ0198 and PI040698 only consisted of different production times and therefore different ages of the PET bottles at the time of investigation. The fact that bottles out of test batch PI040698 showed significantly higher test results for all six model compounds can be explained as follows:

After the moulding process a PET bottle changes its volume due to relaxation processes. Material tensions which were built up during the thermal processing „relax“ after cooling and storing of the bottle. In average the main „relaxation process“ is completed within the following 72 hours after the production of a bottle. Further investigations with test batch PI040698 and TBJ0198 showed that the age of a virgin PET bottle correlates to a certain degree with the chemical inertness of the PET material until a steady state is reached. Decreasing material tensions in form of relaxation processes means increasing the chemical inertness of a PET material until a steady state. The steady state of a PET bottle concerning relaxation appears either after a long-term storage at ambient temperature or, to accelerate the process, applying higher storage temperatures after the production of the PET bottles. Determining the influence of higher temperatures on the stability of a PET material it also could be shown that the PET material of test batch PI040698 reached a steady state concerning the chemical inertness behaviour after a storage of more than one week at 60 °C.

Table 4-2 to Figure 4-8 show test results of PET bottles stored at 60 °C up to 5 weeks.

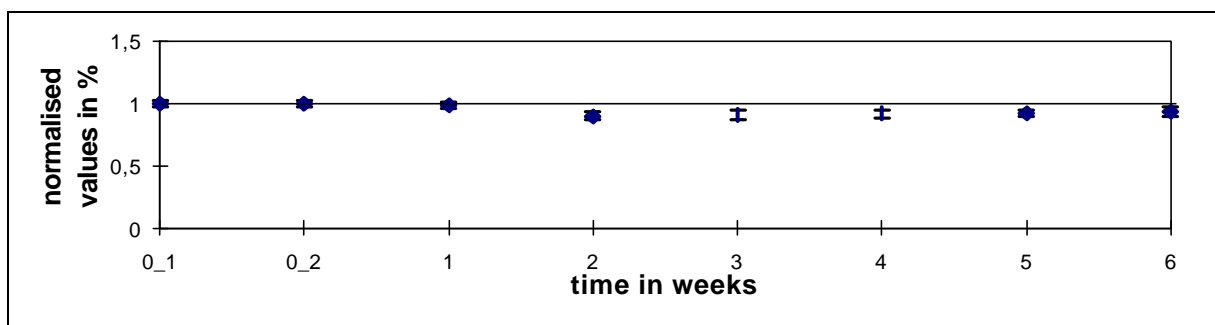


Figure 4-3: Chemical inertness results of **Toluene** for PET bottles stored at 60 °C normalised to the value of PET bottles stored at ambient temperature.

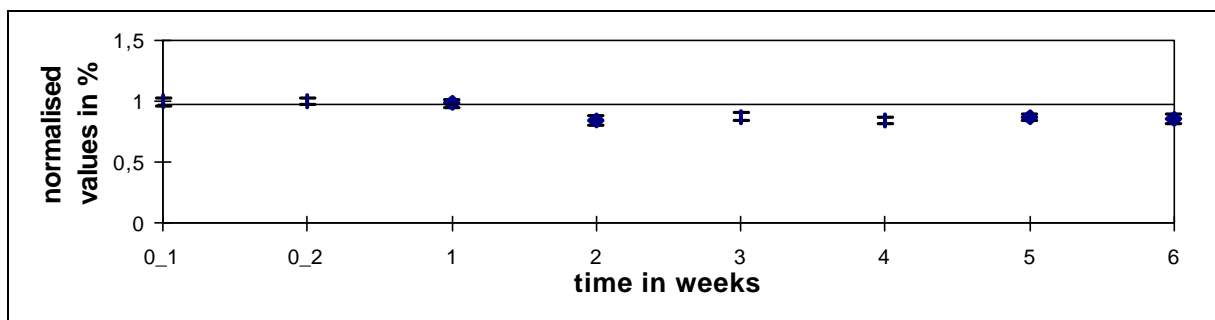


Figure 4-4: Chemical inertness results of **Phenol** for PET bottles stored at 60 °C normalised to the value of PET bottles stored at ambient temperature.

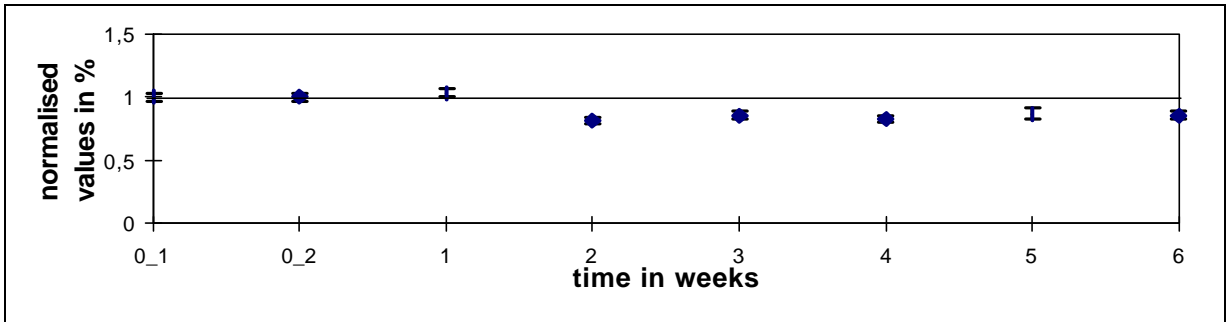


Figure 4-5: Chemical inertness results of **Limonene** for PET bottles stored at 60 °C normalised to the value of PET bottles stored at ambient temperature.

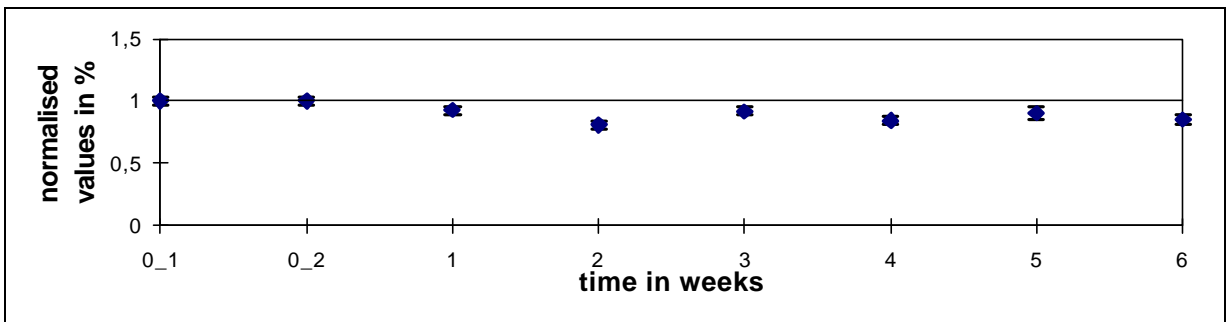


Figure 4-6: Chemical inertness results of **Menthol** for PET bottles stored at 60 °C normalised to the value of PET bottles stored at ambient temperature.

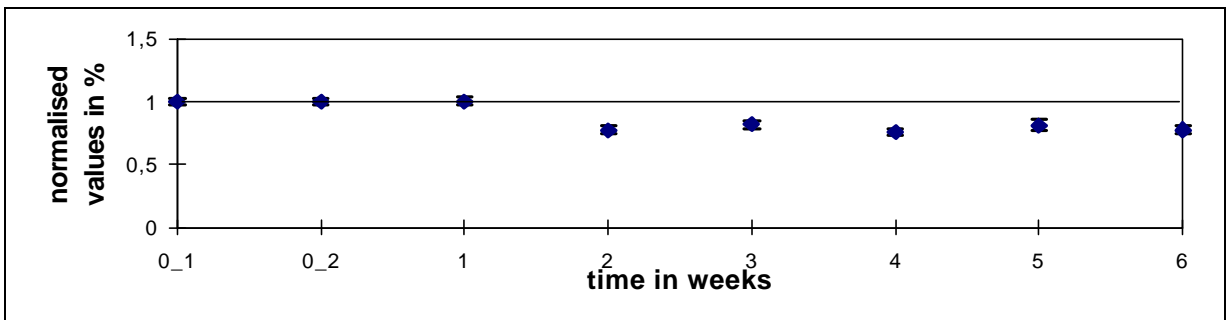


Figure 4-7: Chemical inertness results of **Phenyl cyclohexane** for PET bottles stored at 60 °C normalised to the value of PET bottles stored at ambient temperature.

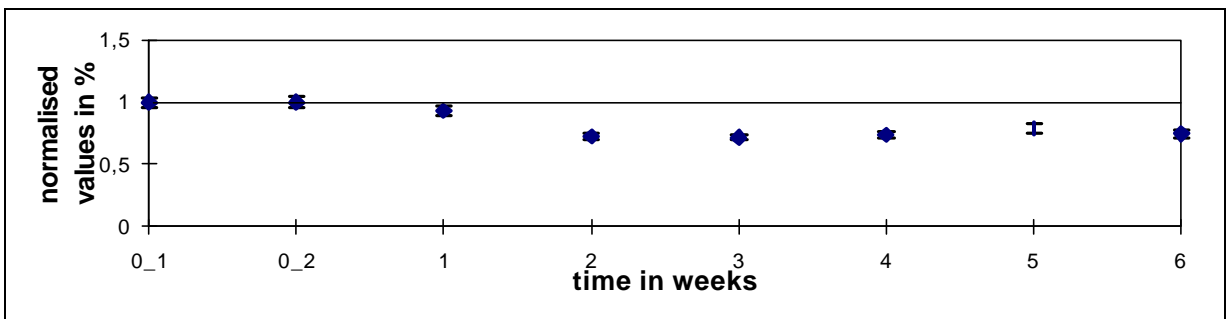


Figure 4-8: Chemical inertness results of **Benzophenone** for PET bottles stored at 60 °C normalised to the value of PET bottles stored at ambient temperature.

PET bottles out of test batch PI040698 were stored up to six weeks at 60 °C. In practice PET bottles are only exposed to this temperature conditions during the washing procedures for an essentially shorter time (for minutes only).

Table 4-2 to Figure 4-8 show definitely that the chemical test results obtained for the six model compounds went down more or less slightly during the storage at worse case conditions of 60 °C depending on the molecular mass of substances. Test results for Benzophenone as a substance with relatively high molecular mass fell down more sharply than e.g. Toluene with a lower molecular mass. The decrease of migration results can be determined after a storage time between one and two weeks at 60 °C.

In the course of the investigation test results became steadily for all of the six model compounds after a storage period of two weeks at 60 °C. The reason for the decrease of chemical test results can be found in the consequences of the technical moulding process of a PET bottle as already mentioned. In the industry the „relaxation“ of a PET bottle after moulding is a well known process. After the moulding process a PET bottle changes its volume due to relaxation processes. Material tensions which were built up during the thermal processing „relax“ after cooling and storing of the bottle. The changes of chemical test results after storage at 60 °C can therefore be understood on the basis of further „relaxation processes“ as well as morphological changes of the PET material accelerated at higher temperatures. After a storage of two weeks at 60 °C these effects were completed so that chemical test results reached constancy.

As described above test results of model compounds can be influenced by storing the material at higher temperatures (60 °C). Comparing test results of TBJ0198 obtained in May 1998 with test results obtained in September 1998 makes clear that test results can also be influenced in the same way by a long-term storage at room temperature. Especially the test results of Phenyl cyclohexane and Benzophenone in September 1998 were significantly different from test results obtained in May 1998. Changes in material properties like re-cristallinisation can also be responsible for the fact that the sorption and the extraction of substances with higher molecular mass were getting lower during a period of time.

Storing a freshly produced and virgin PET bottle for two weeks at 60 °C means therefore accelerating the process of relaxation and reaching the steady state in a faster way than long-term storage at room temperature would come to. On the other hand if bottles of TBJ0198 reached the steady state in September 1998 after a storage of nearly half a year at room temperature as shown in Figure 4-9 the conclusion would be that a further storage at 60 °C of these bottles might not effect the chemical inertness behaviour at all.

However, on the basis of test results presented in Figure 4-9 it could be demonstrated that PET bottles which were produced under same production conditions also show the same chemical inertness behaviour after reaching a steady state.

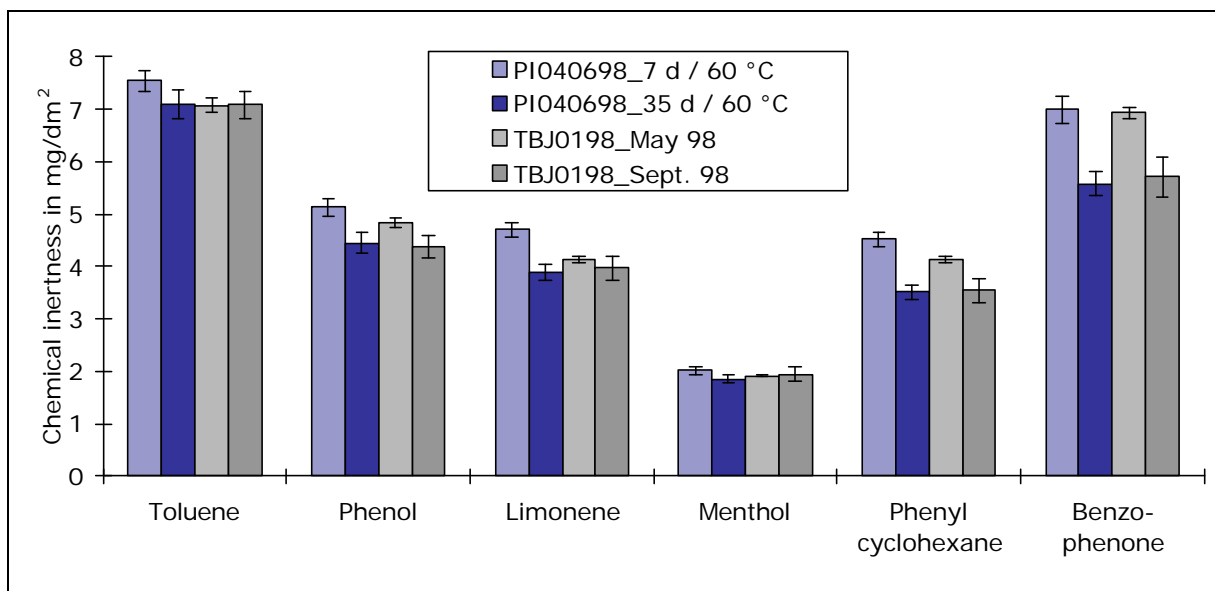


Figure 4-9: Comparison of chemical inertness test results of test batch PI040698 and TBJ098 concerning the behaviour after temperature/ long-term storage.

The consequence for the production of a reference material batch is therefore, that the PET bottles have to be conditioned for two weeks at 60 °C to make sure that relaxation processes are accelerated and therefore the chemical inertness behaviour of the material reaches a steady state.

The stability testing of test batches TBJ0198 as well as PI040698 was carried out in a way that bottles out of TBJ0198 which were already stored at room temperature (23 °C) for nearly one year were additionally stored at 60 °C for several weeks. The consideration was if PET bottles really reached constancy after a long-term storage of one year at room temperature than an additional storage at 60 °C would not influence the chemical inertness behaviour at all. The following Table 4-3 summarises the storage conditions of PET bottles out of test batch TBJ0198 and PI040698.

Table 4-3: Structure of the stability testing of PET bottles out of test batch TBJ0198 and PI040698.

	No.	Date of analysis	storage condition
TBJ0198 produced in January 1998	1	May 1998	room temperature
	2	Sept. 1998	room temperature
	3	January 1999	room temperature + 7 d / 60 °C
	4	January 1999	room temperature + 7d / 60 °C
	5	January 1999	room temperature + 14 d / 60 °C
	6	January 1999	room temperature + 14 d / 60 °C
	7	January 1999	room temperature + 21 d / 60 °C
	8	January 1999	room temperature + 21 d / 60 °C
	9	January 1999	room temperature + 28 d / 60 °C
	10	January 1999	room temperature + 28 d / 60 °C
PI040698 produced on 4 th of June 1998	11	July 1998	14 d / 60 °C
	12	July 1998	21 d / 60 °C
	13	July 1998	28 d / 60 °C
	14	August 1998	35 d / 60 °C
	15	August 1998	42 d / 60 °C
TBJ0198 produced in January 1998	16	March 1999	room temperature
	17	February 1999	room temperature + 7 d / 60 °C
	18	March 1999	room temperature + 14 d / 60 °C
	19	March 1999	room temperature + 21 d / 60 °C
	20	March 1999	room temperature + 28 d / 60 °C
	21	March 1999	room temperature + 35 d / 60 °C
	22	March 1999	room temperature + 42 d / 60 °C
	23	April 1999	42 d / 60 °C + 28 d at room temperature
	24	April 1999	42 d / 60 °C + 56 d at room temperature

The following Figure 4-10 to Figure 4-15 show the chemical inertness test results for PET bottles out of TBJ0198 as well as PI040698 after different storage conditions and times normalised to test results obtained from bottles of TBJ0198 in September 1998. TBJ0198 was produced in January 1998 whereas PI040698 was produced on 4th of June 1998.

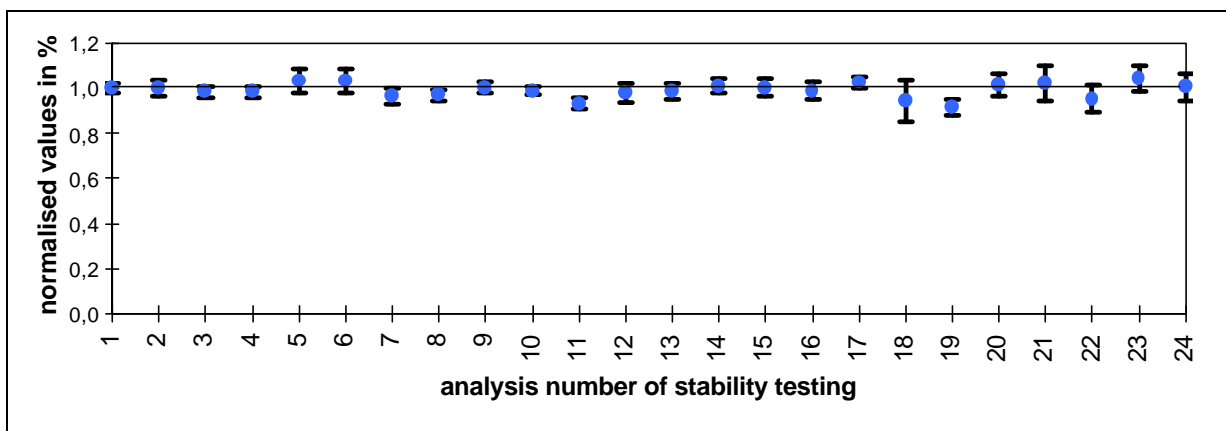


Figure 4-10: Normalised values of **Toluene** obtained during the preliminary stability study of the PET bottle material.

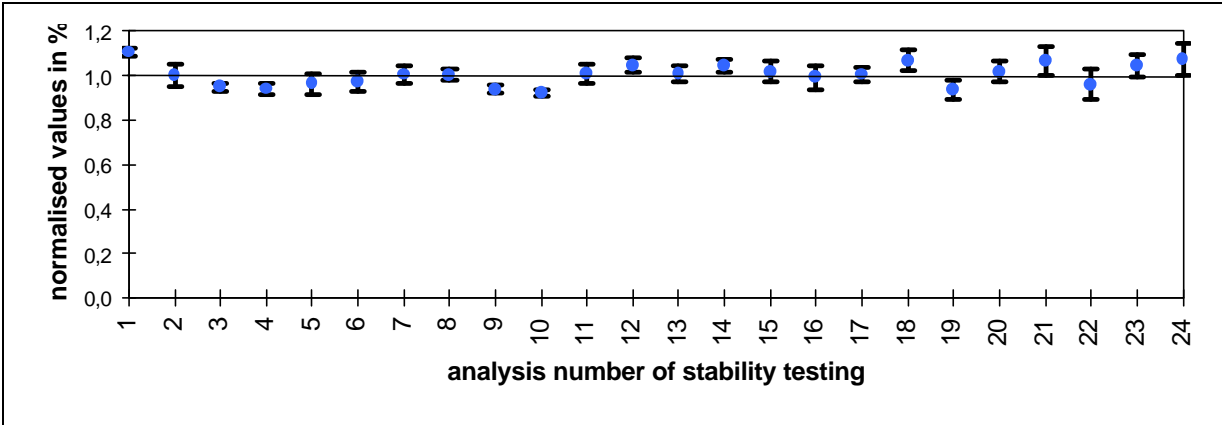


Figure 4-11: Normalised values of **Phenol** obtained during the preliminary stability study of the PET bottle material

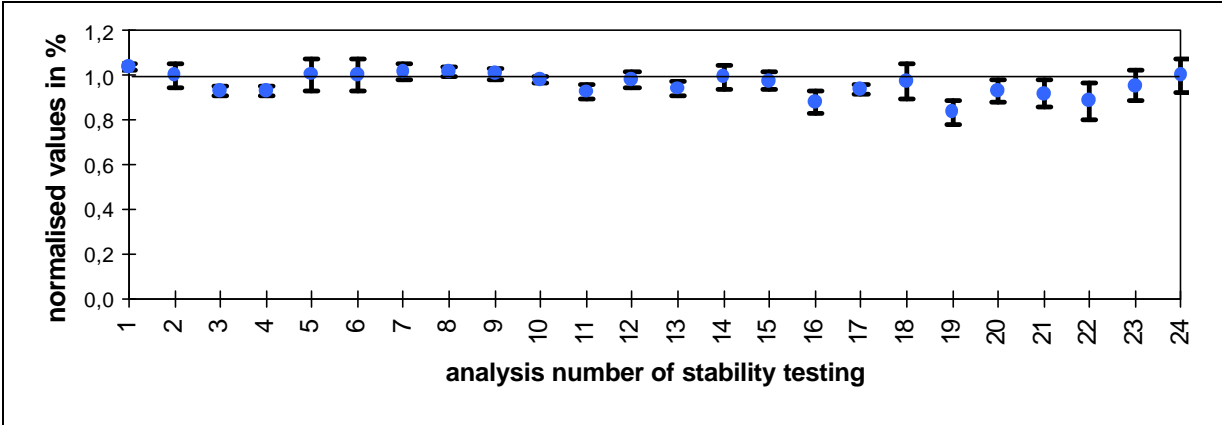


Figure 4-12: Normalised values of **Limonene** obtained during the preliminary stability study of the PET bottle material

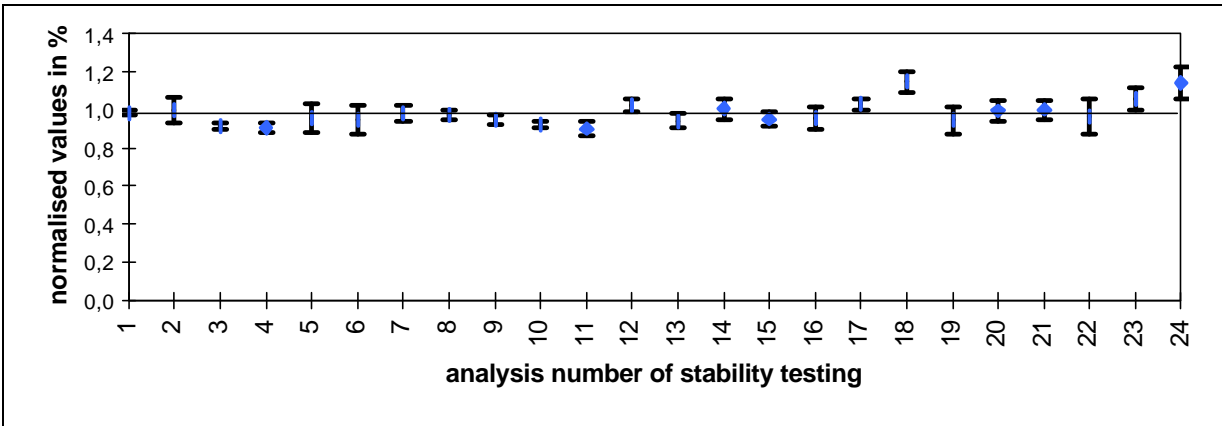


Figure 4-13: Normalised values of **Menthol** obtained during the preliminary stability study of the PET bottle material

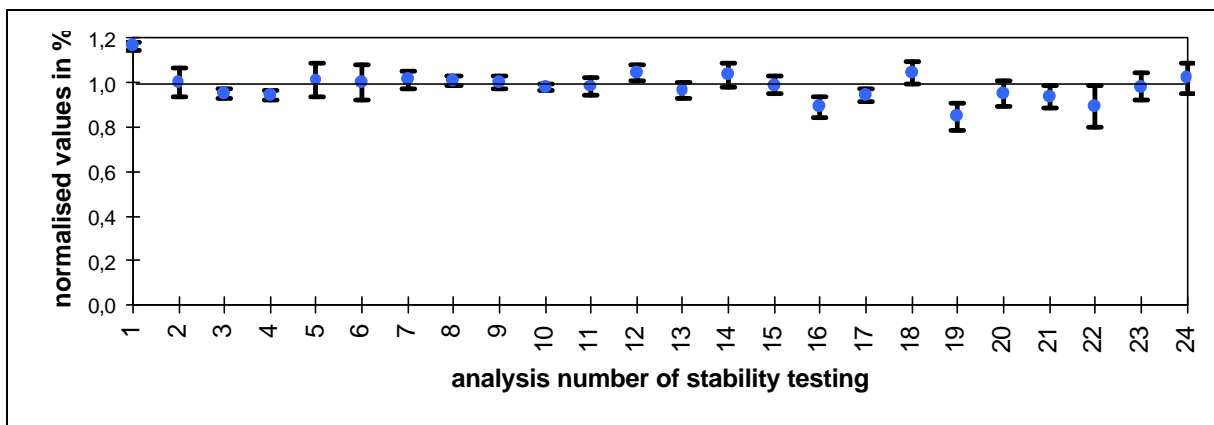


Figure 4-14: Normalised values of **Phenyl cyclohexane** obtained during the preliminary stability study of the PET bottle material

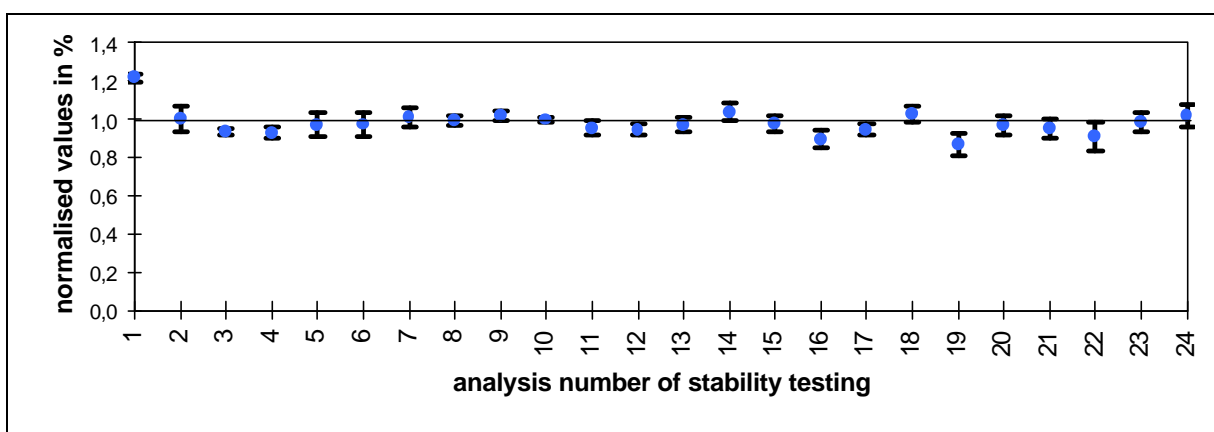


Figure 4-15: Normalised values of **Benzophenone** obtained during the preliminary stability study of the PET bottle material

For the sake of completeness it has to be mentioned that the test results of number 18, 23 and 24 are outliers especially for the substance Menthol due to technical deviations of the method and normally have to be discarded.

Test results shown in Figure 4-10 to Figure 4-15 demonstrate that 1.5 L refillable PET bottles out of different batches produced in the same way show significantly comparable test results ($t_{0.95}$ - test) after a conditioning phase of 2 weeks at 60 °C. The conditioning effect on chemical inertness test results can also be determined after a long-term storage at room temperature (23 °C). The additional treatment of PET bottles at 60 °C for several weeks after a previous storage time of at least half a year at room temperature showed that refillable PET bottles reach a stable state either after a specific period of time at room temperature or after conditioning of newly produced bottles at 60 °C for at least two weeks. Due to the same production technique of refillable PET bottles out of TBJ0198 and PI040698 it can be assumed that the reference material CE130799 also reached a homogenous as well as stable state after conditioning of the material.

4.2 PRODUCTION OF PET REFERENCE BOTTLES - TEST BATCH 130799

4.2.1 Production of test batch CE130799 as reference material

The Polyethylene terephthalate (PET) 1.5 L multi-use bottles from which the reference material was obtained were manufactured on 13th of July 1999 at Schmalbach Lubeca PET Container GmbH, Germany. For the production of the 1.5 L PET multi-use bottles the blow moulding machine No. 6 with 128 cavities was used producing 8500 bottles per hour. The PET resin for the production of the PET preforms was made of Dimethyl terephthalate (DMT) as basic product of the polymerisation process. The production of the PET bottles used as reference material was carried out within the usual day production of 1.5 L PET multi-use bottles for the beverage market. With a machine capacity of 8500 bottles per hour the 2300 PET bottles as reference material were produced within less than 20 minutes. For the provision of 2000 reference bottles it was necessary to produce three palettes à 1008 PET bottles due to fixed machinery adjustments.

The random sampling for the homogeneity as well as stability testing was carried out in a way that every 2 minutes 16 PET bottles were taken from the production line. At the end of the sampling 10 random batches of 16 bottles were available.

At the end of the production line the bottles were stored on palettes and numbered in the order of their production. In that way 3 palettes of 7 stages à 144 bottles were produced. The palettes were numbered according to their production number of the day with 48, 49 and 50. Respectively, the stages on the palettes were numbered from 1 to 7 and the bottles on each stage from 1 to 144. In that way each bottle was coded as follows xx_y_zzz where zzz is the number of the bottle on the stage y of the palette number xx with zzz from 001 to 144, y from 1 to 7 and xx from 48 to 50.

After storing the bottles at ambient temperatures (from 16 °C to 25 °C) the PET bottles were transported to the PTS - Papiertechnische Stiftung, Munich, Germany at the end of July 1999. In July/ August 1999 the PET bottles (the whole palette 48, 49 as well as stages 50_1 and 50_2) were conditioned in a horizontal position in a climate chamber for two weeks at 60 °C to accelerate relaxation processes of the PET material. The essential stages in the preparation of the PET reference material (RM) are detailed and summarised in Table 4-4.

Table 4-4: The essential stages in the preparation of PET RM

Process	Description
Production of RM bottles	Approximately 2500 PET multi-use bottles (1.5 L) were produced within the regular production of PET bottles for the beverage market
Homogeneity testing	After random sampling of 16 bottles every 2 minutes a homogeneity testing was carried out in form of measuring the mass as well as the material thickness on different heights of the 1.5 L PET bottle.
Conditioning	To accelerate relaxation processes of the PET material the bottles were stored at 60 °C for two weeks.
Cutting of middle parts	In order to preserve the anonymity of the bottle design and brand the middle parts of the PET bottles were cut out mechanically using a suitable cutting implement.
Packing	The PET material was packed into cans under a nitrogen flow. A quantity of about 2000 units is planned to be sold as CRM under the number BCR 712 at IRMM ¹ .
Homogeneity testing	The homogeneity testing of random batch no. 4 which consists of 16 bottles was established after packaging.
Storage	The packaged material was stored at ambient temperatures. (15 °C to 25 °C)

4.2.2 Homogeneity testing of the reference material CE130799

The homogeneity studies were carried out at different stages of the production of the reference material. During the production of the 1.5 L multi-use PET bottles a random sampling was carried out for the homogeneity testing. Before the start of the random sampling a person was posted at the end of the production line. When the first twelve PET bottles were put on the first stage of palette number 48 a sign was given. At this time the random sampling started by taking 16 following PET bottles almost directly coming out of the blow-moulding machine. In that way every 2 minutes 16 PET bottles were taken from the production line and numbered according to their production order while the other produced reference PET bottles were packed on three following palettes at the end of the assembly line. At the end of the sampling 10 random batches of 16 bottles were available. Figure 4-16 shows the scheduled structure of the random sampling for the homogeneity study.

¹ IRMM, Retieseweg, B - 2440 Geel, Belgium

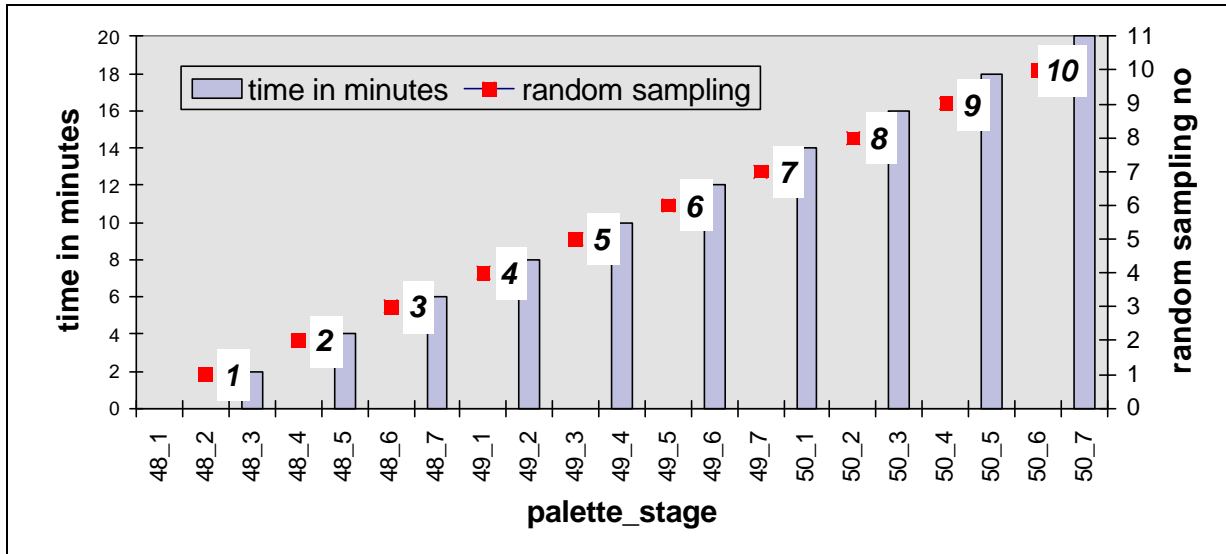


Figure 4-16: Structure of random sampling for homogeneity testing during the production of reference material bottles.

A machine capacity of 8500 bottles per hour produces approximately 142 bottles per minute. For the production of reference PET bottles the machine capacity meant that every minute one stage of a palette was completed at the end of the production line.

On the day of production the bottle masses of the random sampling 1 to 7 were determined as parameter for homogeneity.

The material thickness on different heights of the PET bottles was also measured as an indicator for material homogeneity directly after the production.

The homogeneity testing of the conditioned and packed random sampling no. 4 was carried out to check the between- and within-unit homogeneity regarding to chemical inertness behaviour of the material.

The homogeneity of the RM was studied by using material quality parameters like bottle mass as well as bottle wall thicknesses along the height of a PET bottle which stand for the regularity of the production. The advantage of measuring the mass as well as the material thickness of a PET bottle was that a huge quantity of specimens could be easily measured by one person on the same day of production delivering commonly used quality parameters of PET bottles.

Nowadays, machines producing 8500 PET bottles per hour are more usual than a challenge. The demand of a constant quality of multi-use PET bottles on the market led to the development of blow-moulding machines which were capable to keep exactly set production parameters.

Producing 142 bottles per minute (2.4 bottles per second) meant that it was very unlikely to happen that production parameters like temperature profiles or pressures changed during the production of the reference PET material. Table 4-5 present individual test results of the mass of PET bottles out of random sampling 1 to 7.

Table 4-5: Individual test results of the measurement of mass [g] of random sampling 1 to 7 during the production of RM.

bottle no. of	Random sampling in g						
	1	2	3	4	5	6	7
1	105.72	105.65	105.46	105.47	105.69	105.68	105.53
2	105.53	105.65	105.51	105.67	105.52	105.72	105.55
3	105.56	105.42	105.60	105.68	105.47	105.49	105.47
4	105.55	105.73	105.67	105.68	105.59	105.55	105.78
5	105.72	105.56	105.55	105.52	105.51	105.55	105.46
6	105.39	105.50	105.57	105.47	105.50	105.44	105.46
7	105.47	105.60	105.46	105.35	105.54	105.50	105.71
8	105.68	105.57	105.40	105.44	105.47	105.60	105.61
9	105.46	105.63	105.55	105.58	105.51	105.65	105.54
10	105.53	105.53	105.60	105.48	105.50	105.69	105.59
11	105.64	105.70	105.57	105.56	105.43	105.58	105.44
12	105.48	105.53	105.77	105.56	105.36	105.58	105.47
13	105.70	105.54	105.45	105.58	105.42	105.46	105.61
14	105.55	105.59	105.64	105.58	105.49	105.50	105.52
15	105.47	105.66	105.51	105.57	105.34	105.71	105.60
16	105.54	105.54	105.55	105.63	105.58	105.58	105.74
X in g	105.56	105.59	105.55	105.55	105.50	105.58	105.57
± s in g	0.102	0.080	0.093	0.093	0.086	0.090	0.104
CV in %	0.097	0.076	0.088	0.088	0.082	0.085	0.099

Table 4-5 clearly demonstrate that the PET bottles out of random sampling 1 to 7 were homogenous concerning the material mass of the PET bottles.

The bottle wall thickness of each of the 160 PET bottles at different heights was additionally determined to demonstrate homogeneity. Table 4-6 shows the bottle wall thicknesses of a multi-use 1.5 L PET bottle at different heights as the average of 160 individual PET bottle results.

Table 4-6: PET bottle wall thicknesses at different heights of a 1.5 L multi-use PET bottle

height in mm	material thickness in mm	± s in mm	CV in %
280	0,8533	0,0436	5.1
240	0,5837	0,0185	3.2
215	0,5425	0,0089	1.6
200	0,5505	0,0124	2.3
165	0,5852	0,0081	1.4
150	0,5623	0,0083	1.5
110	0,6178	0,0097	1.6
90	0,6682	0,0128	1.9
70	0,7457	0,0189	2.5
40	0,6901	0,0295	4.3

Cutting out PET strips of the middle part of a bottle wall means that only the heights from approximately 70 to 165 mm have to be taken into account. Therefore test results at the height of 110 mm were statistically evaluated. The following Table 4-7 shows statistical test results for the bottle wall thickness at height 110 mm for the random sampling no. 1 to 7 of the production of reference PET bottles.

Table 4-7: Material thickness at height 110mm of 1.5 L multi-use PET bottles.

random sample	mean in mm*	± s in mm.	CV in %
1	0.61875	0.00602	0.97
2	0.61825	0.00468	0.76
3	0.61725	0.00613	0.99
4	0.61538	0.00729	1.18
5	0.61431	0.00763	1.24
6	0.61744	0.00708	1.15
7	0.61969	0.00627	1.01

Homogeneity assessment concerning chemical inertness test results was carried out by examining random sampling number 4 which was chosen by chance. The chemical inertness behaviour was tested using three replicates of strips out of each of the 16 middle parts of PET bottles in one procedure by one analyst. The test procedure of the chemical inertness method is given in detail in Appendix 1. An analysis of variance (ANOVA) was carried out on the data presented in the tables, using the statistical analysis software SoftCRM² developed and provided by the European Commission. Graphs of the individual test results of the six model compounds used to determine the chemical inertness of a PET material are shown below.

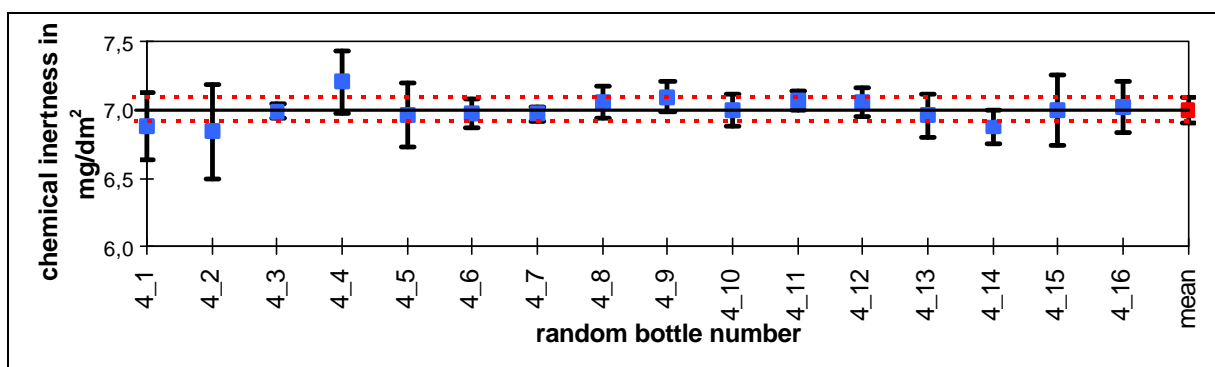


Figure 4-17: Chemical inertness test results of **Toluene** of the homogeneity exercise of random sample 4 after packaging.

² The software can be downloaded under www.weblab.gr/softCRM/softCRM.htm

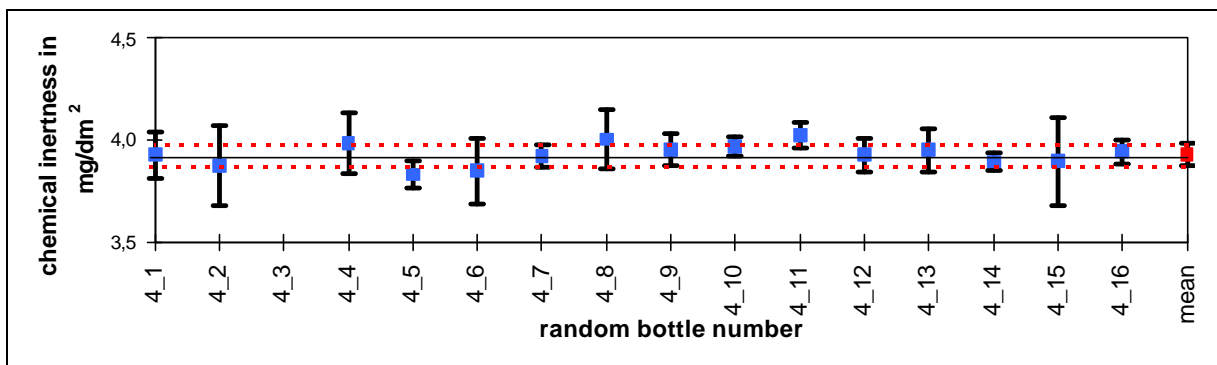


Figure 4-18: Chemical inertness test results of **Phenol** of the homogeneity exercise of random sample 4 after packaging.

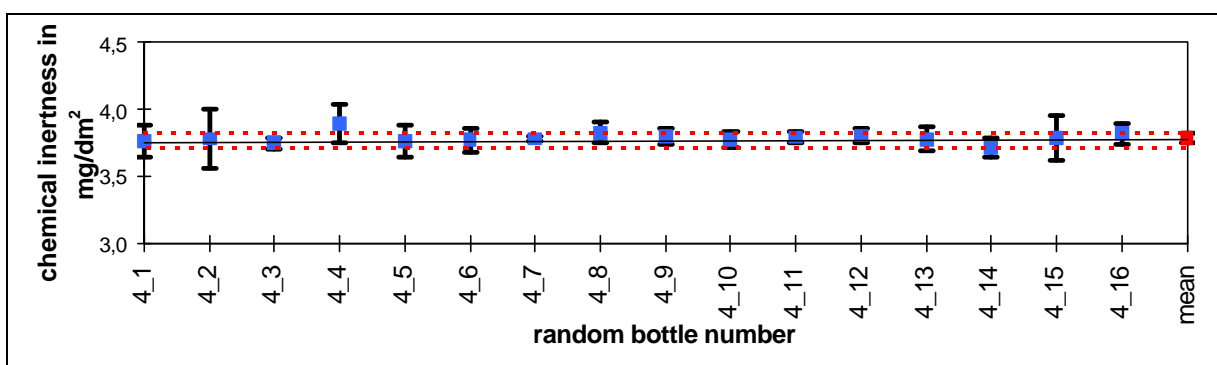


Figure 4-19: Chemical inertness test results of **Limonene** of the homogeneity exercise of random sample 4 after packaging.

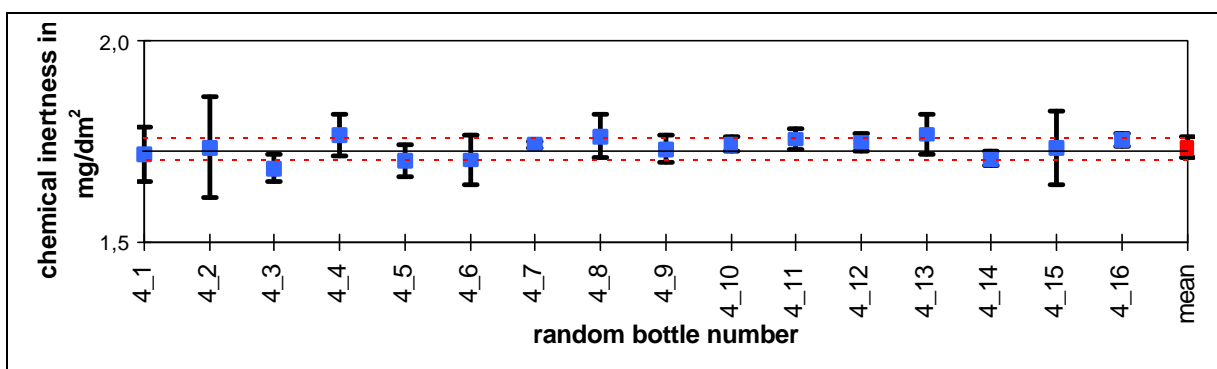


Figure 4-20: Chemical inertness test results of **Menthol** of the homogeneity exercise of random sample 4 after packaging.

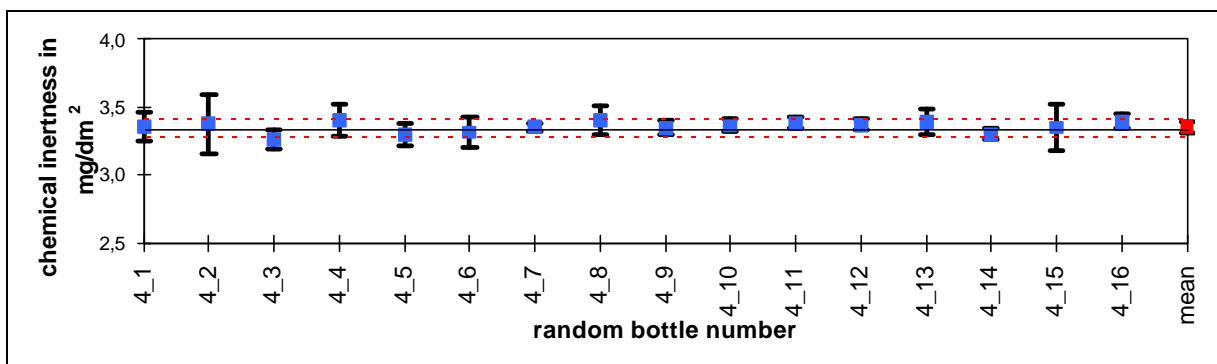


Figure 4-21: Chemical inertness test results of **Phenyl cyclohexane** of the homogeneity exercise of random sample 4 after packaging.

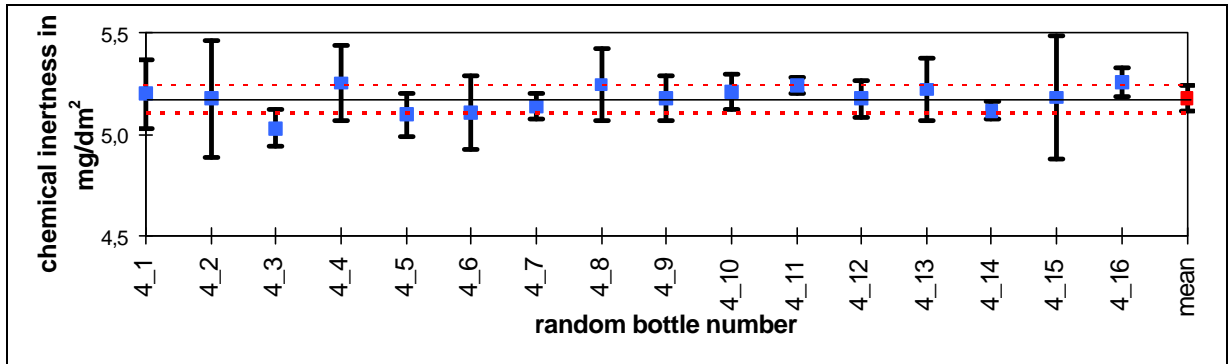


Figure 4-22: Chemical inertness test results of **Benzophenone** of the homogeneity exercise of random sample 4 after packaging.

The analysis of variance (ANOVA) showed that no significant difference at the 95 % confidence level was found between as well as within the chemical inertness test results along the bottle numbers 1 to 16 of random sampling number 4 of all six model compounds. Therefore no significant ($F_{0.95}$ - test) inhomogeneity between-units could be found concerning the chemical inertness behaviour of the reference PET material.

Conclusion of the homogeneity testing

No significant difference (F-Test) at the 95 % confidence interval was found between mass as well as material thickness results at height 70 mm to height 165 mm. Therefore the PET RM shows no significant ($F_{0.95}$ - test) material inhomogeneity between-units.

4.2.3 Stability testing of the reference material CE130799

According to physical properties of the blow-moulded PET material, the 1.5 L multi-use bottles are not suitable for storing at temperatures of less than 0 °C. At freezing temperatures of e.g. minus 18 °C physical/ chemical material properties are changed as well as mechanical polymer characteristics are destroyed. For this reason the stability testing of the PET reference material was not performed under freezing conditions. In reality a PET bottle material is only exposed to refrigerator or ambient temperatures concerning long-term storage as well as periodically to washing temperatures of 60 °C for several minutes. The stability study of a PET RM was therefore carried out for twelve months at temperatures of 10 °C, 23 °C and 60 °C respectively.

Storing a PET bottle at 60 °C which presents the glass temperature of a PET material for up to twelve months definitely simulates worst case storage conditions. Table 4-8 illustrates the design of the long-term stability study.

Table 4-8: Design of the long-term stability study of RM 712
6: replicates from one unit of PET bottle material

	Months				
Storage temperature	0	2	4	8	12
10 °C	6	6	6	6	6
23 °C	6	6	6	6	6
60 °C	6	6	6	6	6

Stability testing was carried out by determining the chemical inertness of the material in form of re-migrating model substances after exposure of the stored RM at the storage temperatures by total immersion of PET strips to a cocktail solution for 2 days at 60 °C.

The units were selected from the production of the reference material. The selected units were stored at 10 °C, 23 °C and 60 °C for periods of 0, 2, 4, 8 and 12 months. At appropriate times one unit of the reference material was removed from the storage and tested with six replicates.

The results obtained in the stability study are based on the chemical inertness values of six model compounds of different structure obtained after total immersion of PET strips in a cocktail solution for 2 days at 60 °C. Six replicate measurements were obtained for each unit of PET material at each storage temperature. The chemical inertness value of time zero was obtained by measuring three different PET specimens at three following days.

The results of the stability studies are listed for each temperature for each model compound.

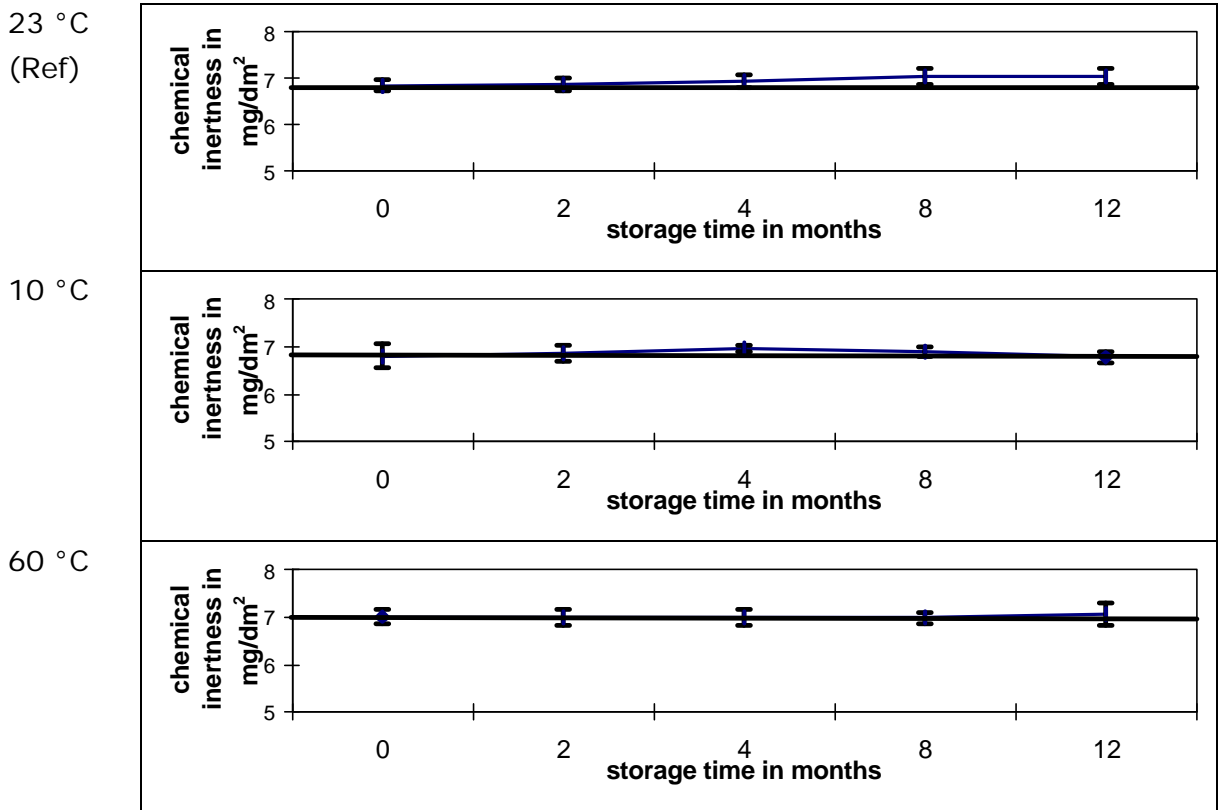


Figure 4-23: Chemical inertness test results of **Toluene** after long-term storage at different temperatures.

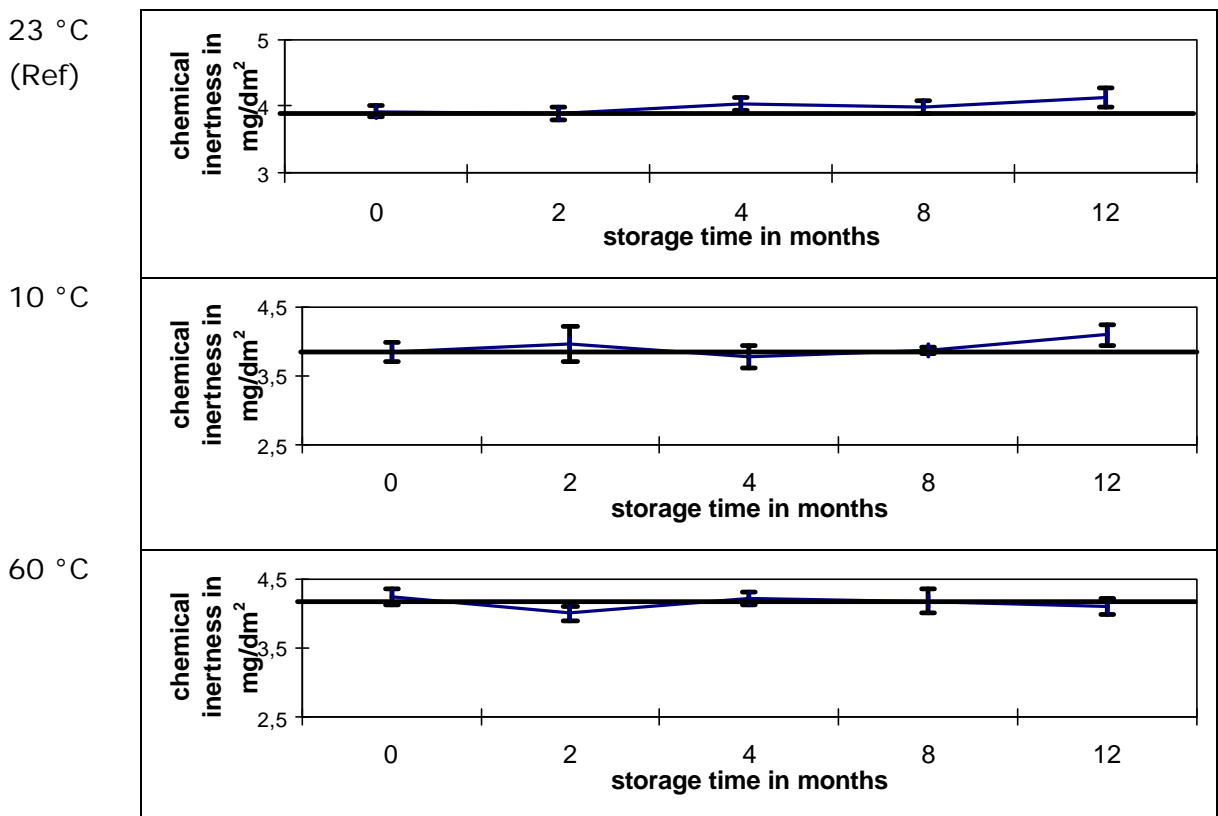


Figure 4-24: Chemical inertness test results of **Phenol** after long-term storage at different temperatures.

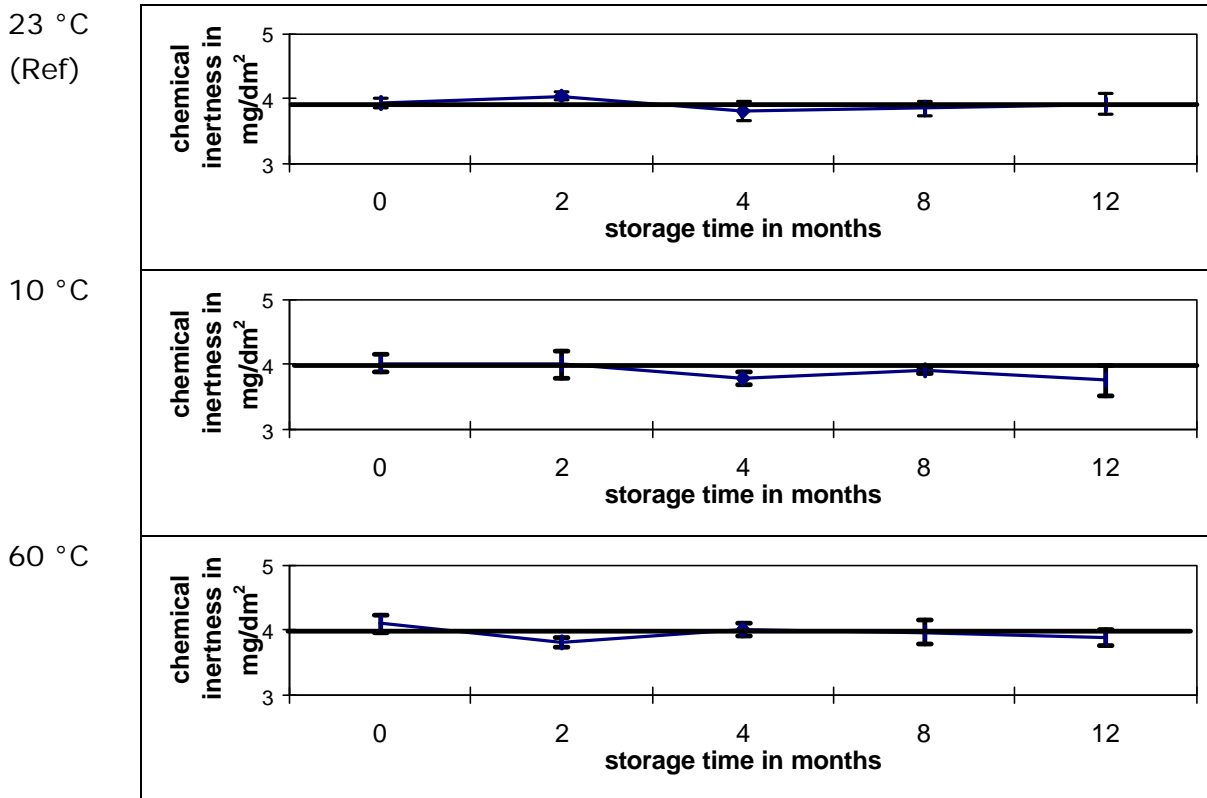


Figure 4-25: Chemical inertness test results of **Limonene** after long-term storage at different temperatures.

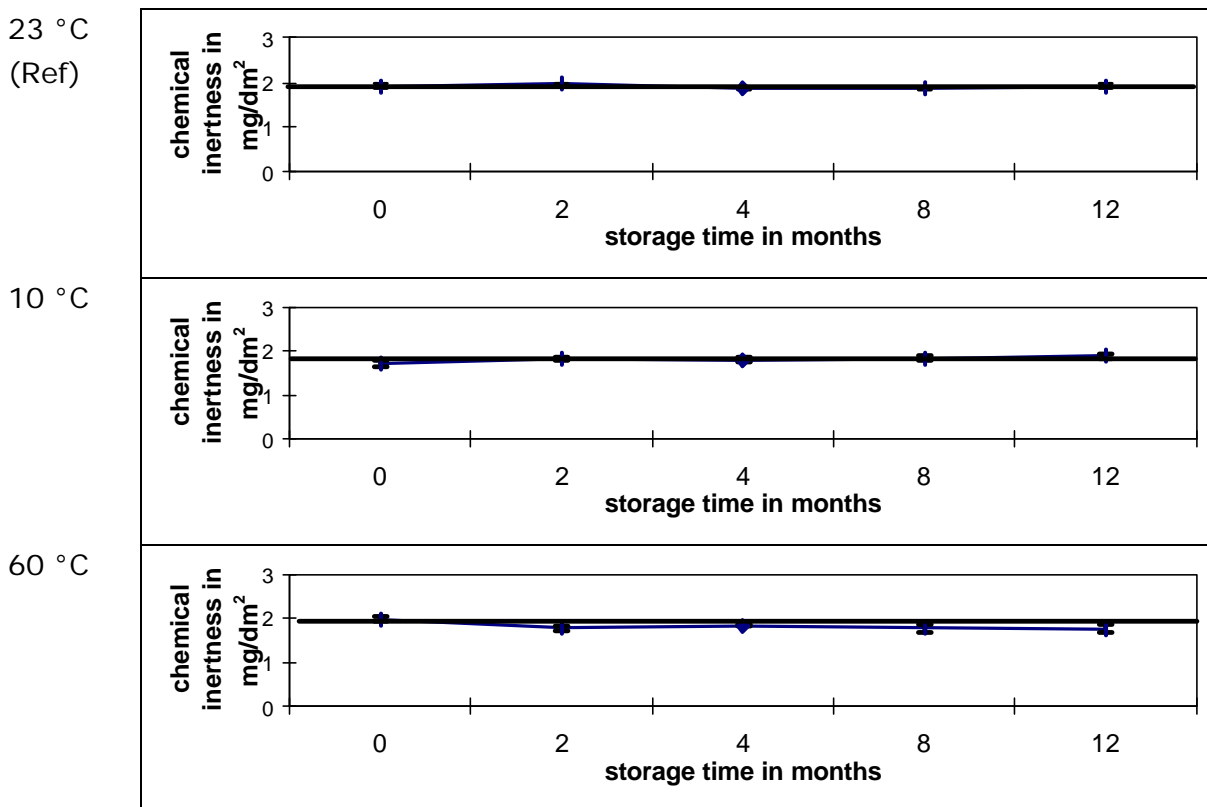


Figure 4-26: Chemical inertness test results of **Menthol** after long-term storage at different temperatures.

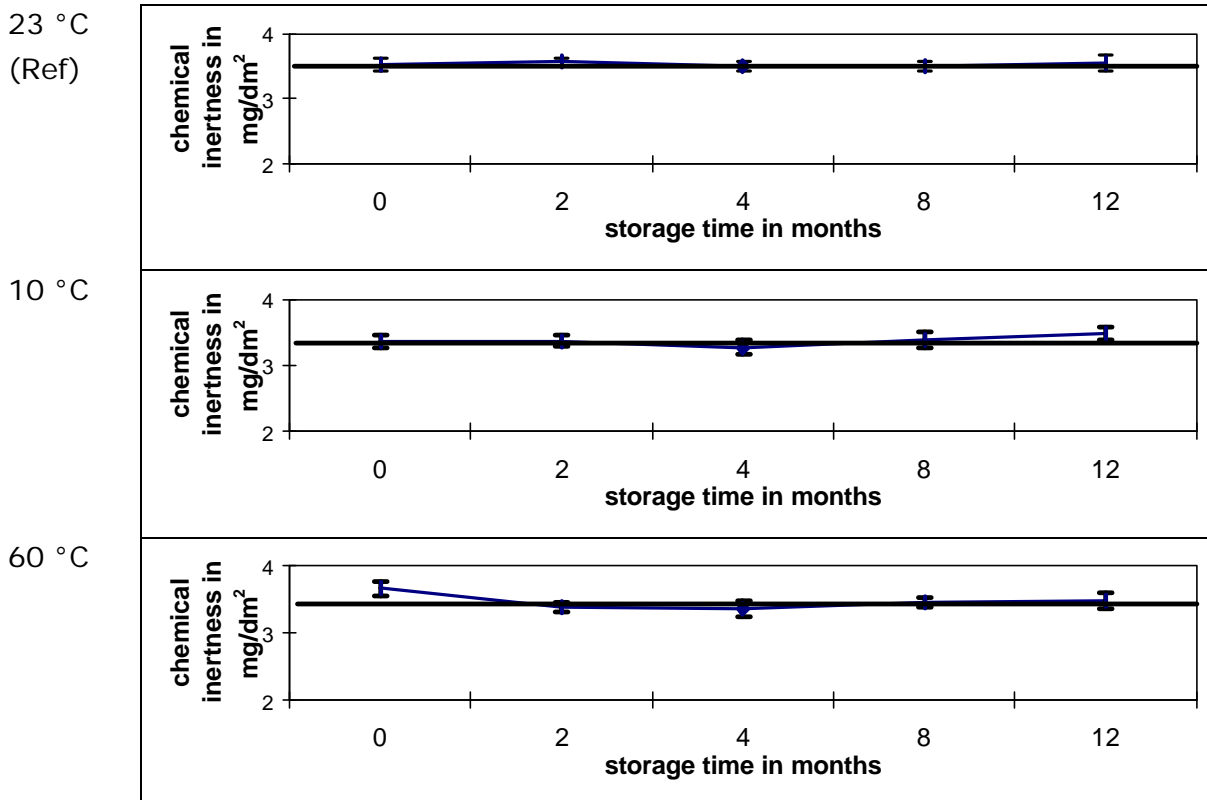


Figure 4-27: Chemical inertness test results of **Phenyl cyclohexane** after long-term storage at different temperatures.

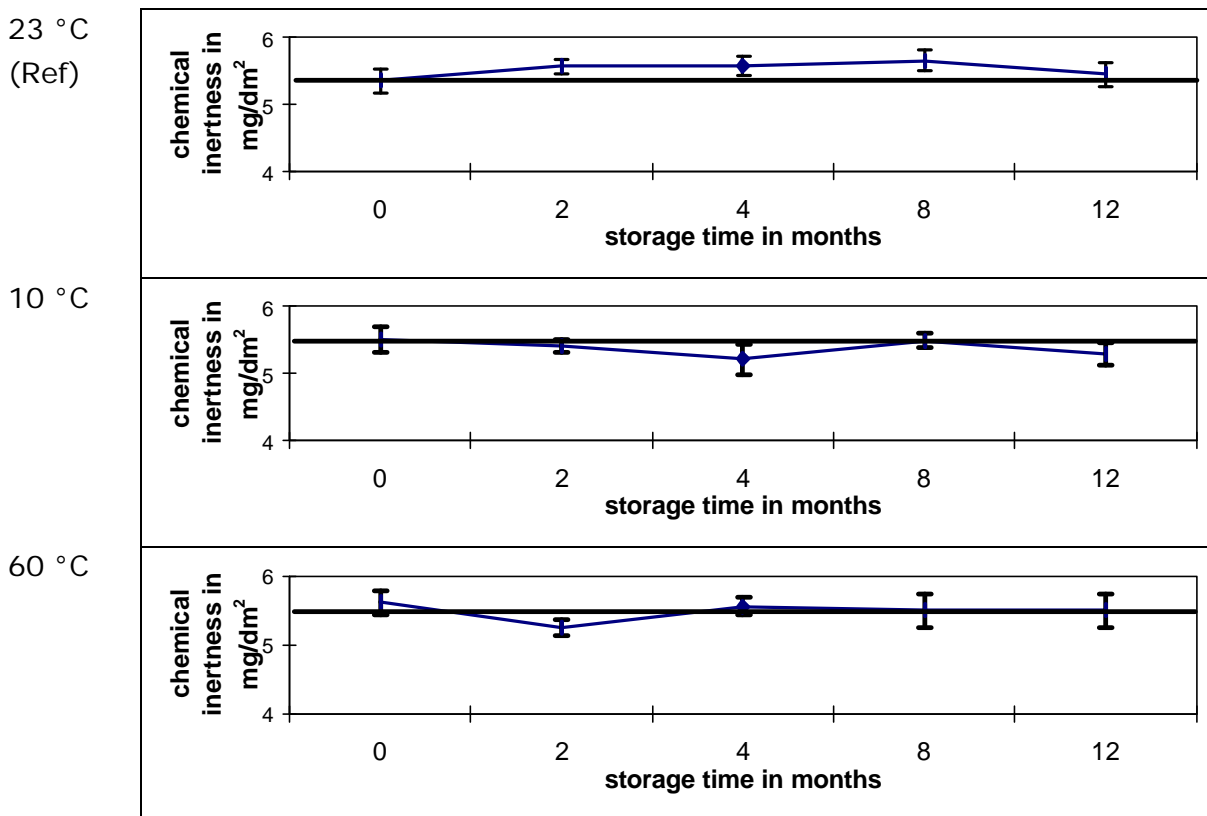


Figure 4-28: Chemical inertness test results of **Benzophenone** after long-term storage at different temperatures.

Conclusion of the stability study

For the evaluation of the stability of the PET RM test results of each model compound, obtained after storage at different temperatures, were correlated to corresponding storage times of the PET RM (see Figure 4-23 to Figure 4-28).

It was statistically evaluated whether the slope of the linear regression of test results and storage time was significantly different from zero at significance levels of 0.95 as well as 0.99. Table 4-9 summarises the results of the statistical evaluation of each model compound after storage at temperatures of 10 °C, 23 °C and 60 °C.

Table 4-9: Statistical evaluation of the significant difference from zero of the slope of the linear regression of model compound test results / storage time of PET RM at different temperatures.

Model compound	Storage temperature					
	23 °C		10 °C		60 °C	
<i>significance level</i>	0.99	0.95	0.99	0.95	0.99	0.95
Toluene	no	yes	no	no	no	no
Phenol	no	no	no	no	no	no
Limonene	no	no	no	no	no	no
Menthol	no	no	no	yes	no	no
Phenyl cyclohexane	no	no	no	no	no	no
Benzophenone	no	no	no	no	no	no

The statistical evaluation of possible relations between test results and corresponding storage times showed that there was no correlation detectable in other words that test results for all model compounds didn't significantly change during the time of storage at 10 °C, 23 °C as well as at 60 °C. Only in case of Toluene at 23 °C and Menthol at 10 °C a significant difference of the slope of the linear regression from zero could be detected for the significance level of 0.95.

The statistical evaluation of ratios of test results obtained at 10 °C and 60 °C respectively with test results obtained at 23 °C as a reference temperature showed that there was no significant difference of test results detectable at significance levels of 0.95 and 0.99 respectively.

The stability study of the PET RM stored at different temperatures up to 12 months showed that chemical inertness test results didn't significantly change at least at a level of significance of 0.99 as well as 0.95 or that is rather to say the material properties of the PET RM concerning the chemical inertness behaviour were kept stable at storing temperatures of 10 °C, 23 °C and 60 °C.

4.2.4 Summary of chemical inertness values of reference bottles

A „certification exercise“ was carried out with 10 participating laboratories to evaluate the reference model compound concentrations for the PET RM of test batch CE130799.

Table 4-10 gives a summary of reference values and their uncertainties

Table 4-10: Reference values of model compound concentrations of test batch CE130799

PET CRM 712	
<i>Method</i>	<i>Drafted chemical inertness method^(a)</i>
Model compounds	Chemical inertness values mean \pm stdev. in mg/dm ²
Toluene	7.28 ^(b) \pm 0.44 ^(c)
Phenol	4.15 ^(b) \pm 0.19 ^(c)
Limonene	3.87 ^(b) \pm 0.17 ^(c)
Menthol	1.78 ^(b) \pm 0.06 ^(c)
Phenylcyclohexane	3.49 ^(b) \pm 0.17 ^(c)
Benzophenone	5.58 ^(b) \pm 0.36 ^(c)

(a)The results are specific to the drafted chemical inertness test method.

(b)This values are the unweighted mean of accepted means obtained independently by seven different laboratories

(c)This uncertainty is taken as the half width of the 95 % confidence interval of the mean defined in (b)

5 EXPLOITATION OF THE PRACTICAL POTENTIAL OF THE CHEMICAL INERTNESS METHOD

As a result of intercomparison testing the chemical inertness test procedure could be validated on a level of significance of 0.05. Applying the final validated inertness method, interactivity values of model compounds of a reference PET material were established which will be certified in the near future.

After validating the chemical inertness method the question arose whether the procedure is sensitive enough to show differences between virgin and reused PET bottles as well as between different PET materials in general. Vice versa, whether the differences of PET containers introduced to the market are high enough concerning their inertness behaviour to be detected by the established method.

In the course of investigations not only the influence of multi-use systems but also the influence of environmental stresses on the chemical inertness behaviour of PET bottles were tested.

Furthermore, tests with bottles made of Polyethylene naphthalate (PEN) should demonstrate whether the inertness test could be performed with other plastic materials intended to be used in direct contact with foodstuffs.

5.1 INERTNESS TESTING APPLIED TO PET BOTTLES DRAWN FROM THE BEVERAGE MARKET

Refillable PET bottles of different brands of mineral water were purchased in order to establish the chemical inertness behaviour. The following Figure 5-1 shows chemical inertness test results of a 1.5 L PET bottle of ~105 g (PET bottle type 1) and a 1.0 L PET bottle of ~ 80 g (PET bottle type 2) for carbonated mineral water. Bottles with low and visually comparable scuffing were chosen.

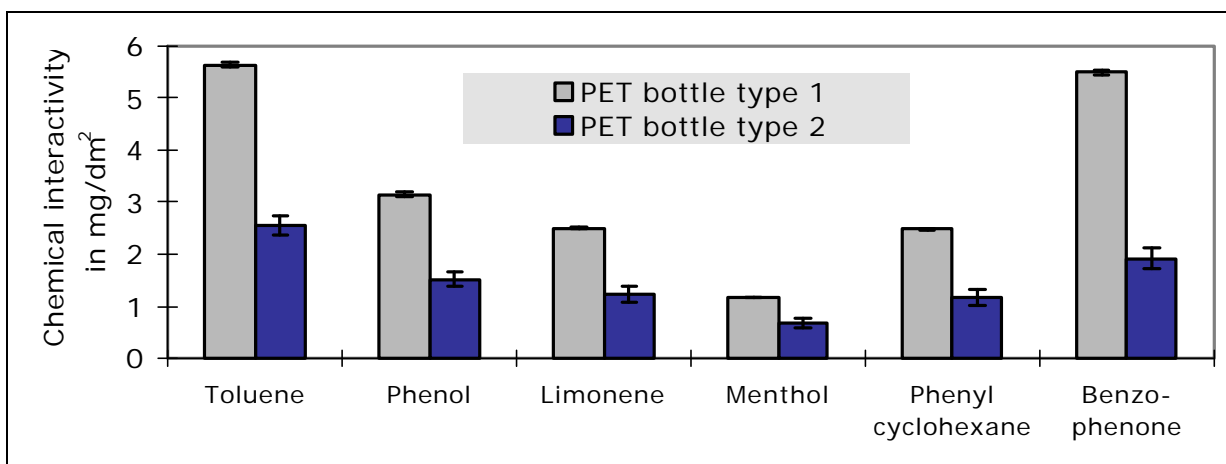


Figure 5-1: Comparison of different PET multi-use bottles concerning the chemical inertness behaviour

As shown in Figure 5-1 differences of PET multi-use bottles concerning the chemical interactivity could significantly be established by applying the chemical inertness test procedure. PET multi-use bottles introduced to the beverage market actually show different interactivity values for model compounds of the chemical inertness method.

Regarding Figure 5-1 the question might arise whether the clearly recognisable difference of test results is based on different masses or possibly different wall thicknesses of PET bottles. Since the migration of substances only occur within μm thin layers of a PET material the influence of bottle wall thickness as well as mass of a bottle definitely can be excluded. Figure 5-2 present chemical inertness test results of a 1.0 L multi-use bottle (PET bottle type 2) weighing approximately 80 g in comparison to a 1.5 L one-way PET bottle (PET bottle type 3) weighing approximately 40 g. As already expected, the chemical interactivity of the multi-use bottle was significantly lower than results of the one-way bottle although having a higher bottle mass and bottle wall thickness.

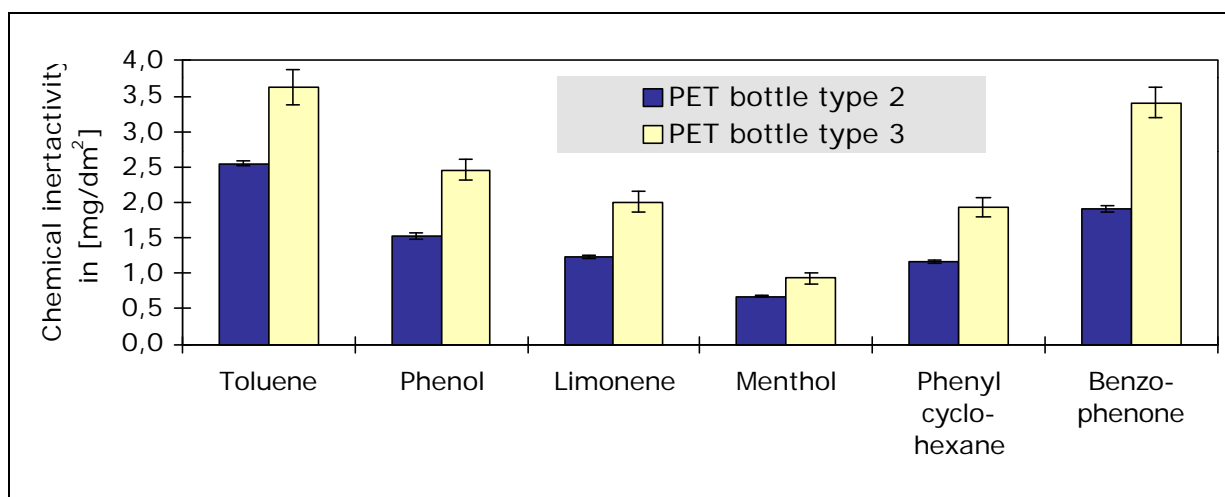


Figure 5-2: Chemical inertness test results of a 1.0 L multi-use bottle (PET bottle type 2) in comparison to a 1.5 L one-way PET bottle (PET bottle type 3)

Multi-use bottles have to show higher material qualities since they have to last up to 15 filling cycles ideally. Material properties like intrinsic viscosity and cristallinity e.g. have a greater influence on the chemical inertness than the bottle mass itself.

5.2 INFLUENCE OF MULTI-USE SYSTEMS ON THE CHEMICAL INTERACTIVITY OF REFILLABLE PET BOTTLES

Another objection to test results shown in Figure 5-1 might be the unknown cycle number of investigated PET bottles. Higher test results of the 1.5 L PET bottle presented in Figure 5-1 might be caused by or related to a higher number of washing cycles. In order to establish whether the chemical inertness procedure is able to detect differences in the chemical inertness behaviour of PET bottles

independent from influences of multi-use systems on the beverage market, virgin multi-use bottles for mineral water were tested.

The influence of different washing cycles on the inertness behaviour of PET was excluded by investigating virgin 1.0 L PET bottles for mineral water with approximately the same mass (~80 g) and bottle shape but different production parameters. Excluding the possible influence of washing cycles by examining visually comparable multi-use bottles, Figure 5-3 demonstrate, that except for model compound Limonene, significantly different chemical interactivity values could be established.

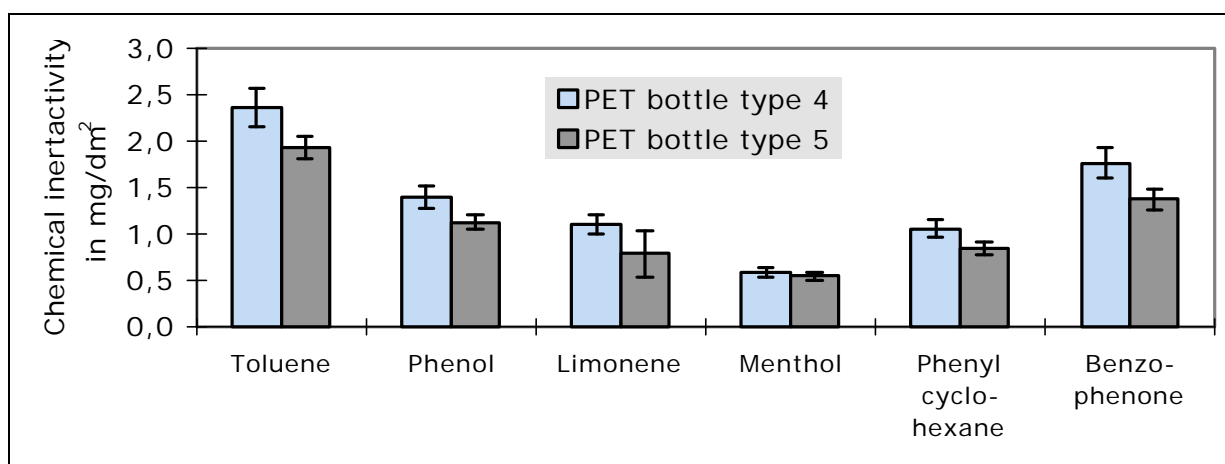


Figure 5-3: Chemical inertness of multi-use PET bottles of different colour

Differences between PET bottles of type No. 4 and PET bottles of type No. 5 were significant but not as high as the difference of test results presented in Figure 5-1. Comparing chemical inertness results of Figure 5-1 and Figure 5-3 gave rise to the consideration to which degree different washing cycles contribute to changes of chemical interactivity of refillable PET bottles and whether these changes could be significantly determined by the chemical inertness method.

The influence of numbers of washing cycles on the chemical inertness behaviour of PET bottles was investigated by washing and re-filling virgin PET bottles for a defined number of cycles.

Multi-use PET bottles intended to be filled with soft drinks were commercially treated in order to simulate 1, 5 and 10 bottle cycles, each cycle consisting of a washing and refilling step. Afterwards the chemical inertness values were determined and compared to test results of virgin PET bottles.

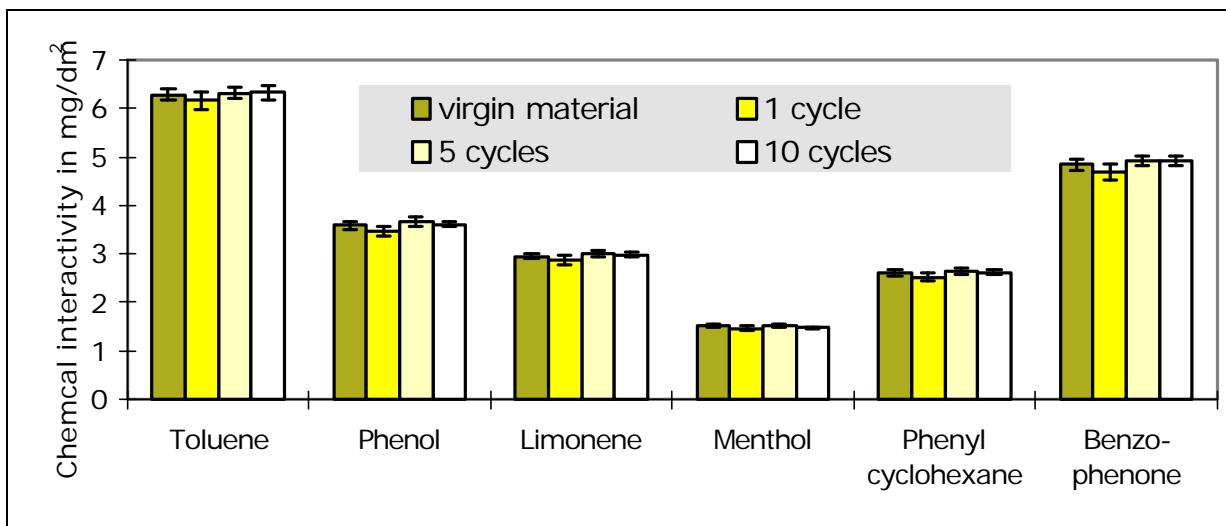


Figure 5-4: Chemical interactivity results of refillable PET bottles for soft drinks after different washing/re-filling cycles.

The chemical inertness of the investigated 1.0 L PET bottles for soft drinks did not significantly change after 10 washing and re-filling cycles.

Material qualities of PET beverage bottles vary depending on the sort of beverage to be filled in. In the case of soft drink bottles e.g. the Acetaldehyde content plays a secondary role since the caused off-flavour is masked by strong soft drink flavours. Mineral water on the other side has to be filled in PET bottles of highest quality since possibly occurring off-flavours even at low concentrations could immediately be detected. Following, the influence of washing/ re-filling cycles on the chemical inertness behaviour of PET bottles intended to be filled with mineral water was investigated additionally.

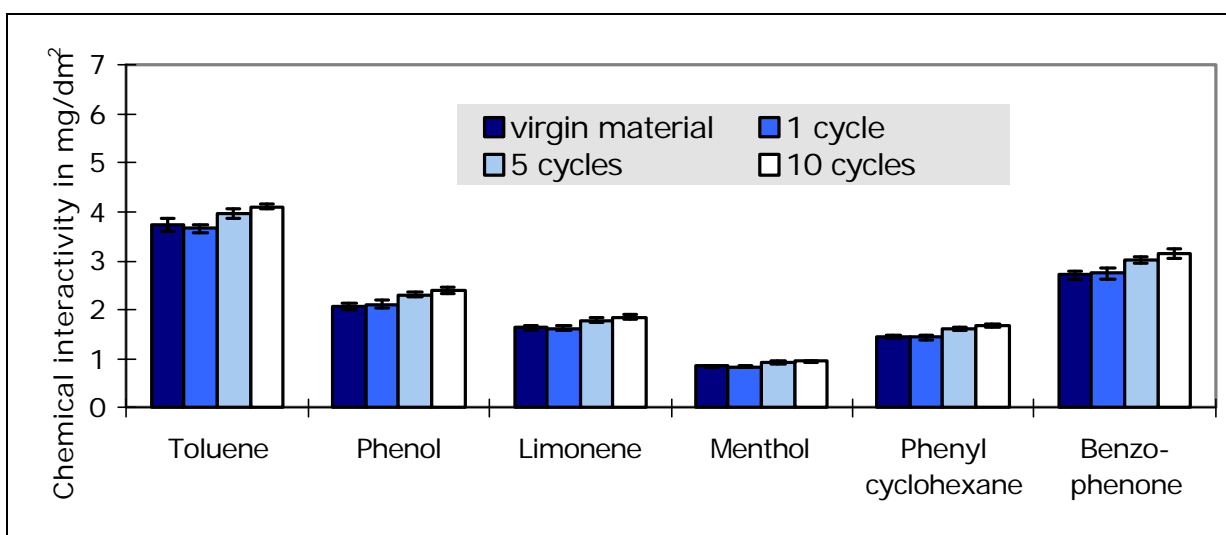


Figure 5-5: Chemical interactivity results of refillable PET bottles for mineral water after different washing/re-filling cycles.

Unlike the chemical inertness of PET bottles for soft drinks, the chemical inertness of PET bottles for mineral waters decreased with increasing number of bottling

cycles. The chemical inertness behaviour of PET bottles depend as already mentioned on quality parameters like thermal stability, cristallinity, degree of residual monomers, oligomers and by-products. Quality criteria of PET materials extremely depend on demands of beverages to be filled in PET bottles. PET bottles for soft drinks or fruit juices e.g. have to withstand higher temperatures due to higher filling temperatures in order to avoid microbial spoilage. While the amount of Acetaldehyde is secondary for soft drink bottles, it is of highest importance for carbonated mineral waters because of causing an intensive off-flavour. Chemical inertness test results presented in Figure 5-5 give the impression that the chemical inertness of the PET material becomes worse with increasing number of bottling cycles. However, having a closer look on results presented in Figure 5-4 and Figure 5-5 makes obvious that the chemical inertness results of PET bottles for mineral water after 10 washing/ re-filling cycles are still lower than those of PET bottles for soft drinks (Figure 5-6).

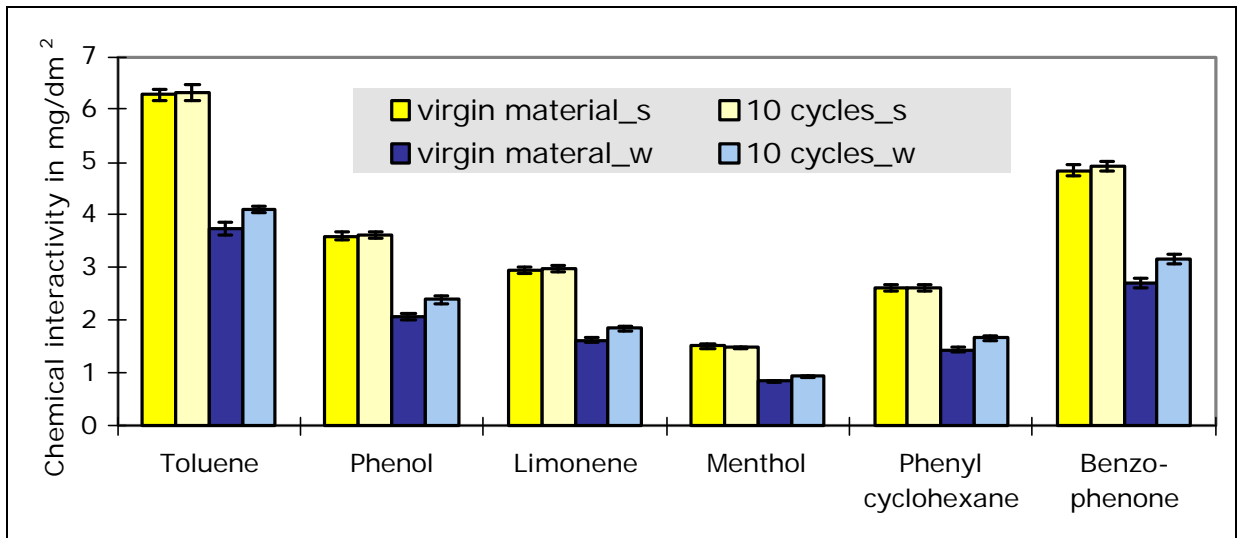


Figure 5-6: Comparison of chemical inertness values of different PET bottles after different bottling cycles.(w: water; s: soft drinks)

Therefore, the conclusion can be drawn that investigated PET bottles for mineral water „negatively“ changed their chemical inertness behaviour with increasing number of washing cycles, but in comparison to PET soft drink bottles the interactivity was still low enough to be acceptable provided that the sensorial quality of refilled mineral water remains unchanged.

5.3 INFLUENCE OF PET FEEDSTOCK MATERIALS ON THE CHEMICAL INERTNESS BEHAVIOUR

Differences in used PET material qualities not only can be found for bottles of varying sorts of beverages. For mineral water e.g. there exist different qualities of PET materials concerning the residual amount of Acetaldehyde. PET bottles for mineral water with high content of carbon dioxide have to show lower Acetaldehyde contents, since carbon dioxide support the Acetaldehyde off-flavour.

Assuming that the quality of a PET material relates to the amount of Acetaldehyde, the chemical inertness of different types of PET bottles for mineral water was analysed.

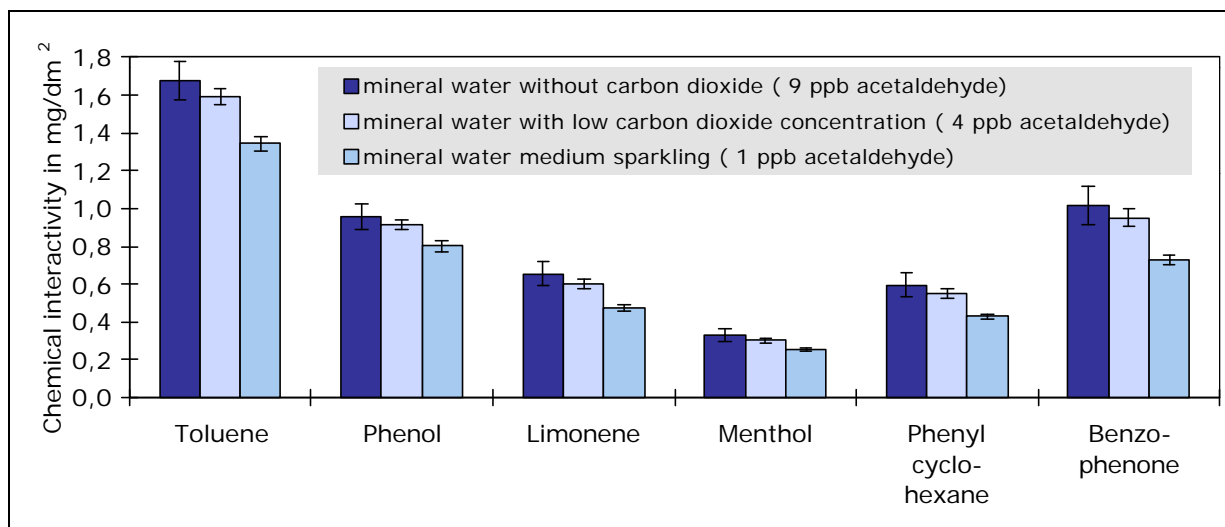


Figure 5-7: Chemical inertness of PET bottles with different concentrations of Acetaldehyde.

Results of Figure 5-7 illustrate that the chemical inertness of a PET bottle increases with increasing material quality of the polymer PET. The PET material with the lowest Acetaldehyde concentration and therefore highest PET quality also showed the highest chemical inertness against model compounds of the chemical inertness test method. As the concentration of Acetaldehyde is an important quality criteria of PET bottles for mineral water, material developments were carried out to reduce the concentration of Acetaldehyde. For the manufacturing of PET bottles so-called Acetaldehyde blockers were used in order to prevent the formation of Acetaldehyde during the manufacturing process. Figure 5-8 shows the influence of such Acetaldehyde blockers on the chemical inertness of a PET material.

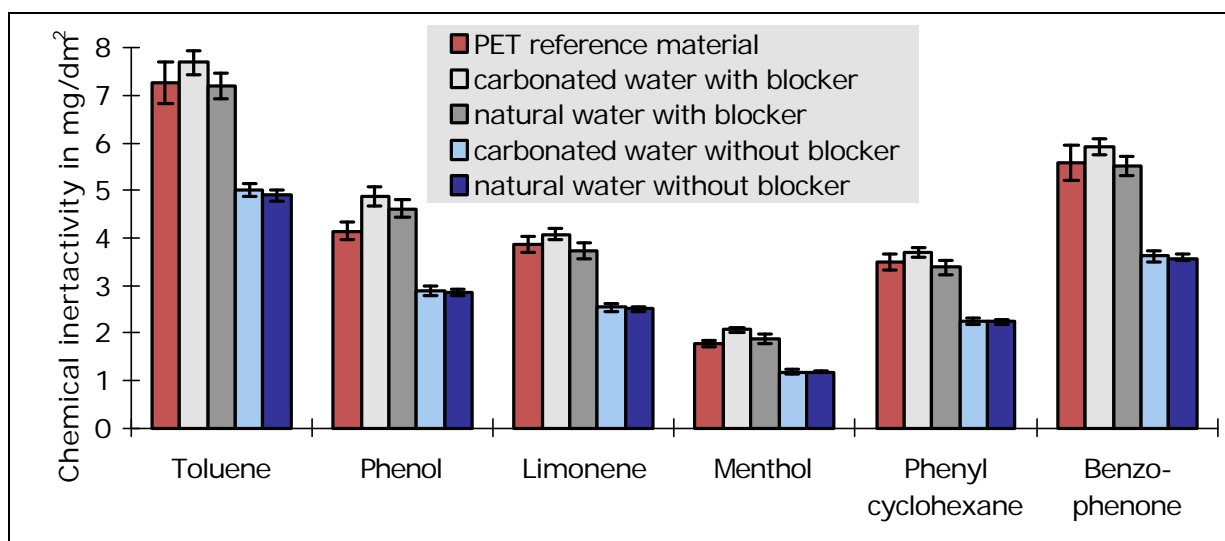


Figure 5-8: Comparison of chemical inertness test results of PET materials for mineral water manufactured without and with the use of Acetaldehyde blockers

As shown in Figure 5-8 the chemical inertness behaviour was heavily influenced by the use of Acetaldehyde blockers during the manufacturing process of PET. It can be assumed that using Acetaldehyde blockers changed the polymer structure in such a way that model compounds could more easily be absorbed. Furthermore, comparing the chemical inertness of Acetaldehyde modified PET with results of the PET reference material makes clear, that the chemical inertness became worse compared to technical feasible values of an already widespread used refillable PET bottle complying with EU regulations. According to test results shown in Figure 5-8 beverage bottles made of PET with chemically reduced Acetaldehyde content are less resistant to chemical interaction and therefore not suitable or recommendable for multi-use systems.

5.4 INFLUENCE OF TEMPERATURE ON THE CHEMICAL INERTNESS OF PET BEVERAGE BOTTLES

The chemical inertness method can not only be used to evaluate the chemical inertness behaviour of PET materials in general regarding food safety assessment but also can be applied to predict the influence of environmental stresses on chemical inertness properties. For this reason the influence of washing temperatures of 60 °C as well as freezing temperatures were investigated.

5.4.1 Influence of high temperatures on the chemical inertness behaviour

During the washing process multi-use PET bottles have to withstand temperatures of at least 60 °C for several minutes. For this reason the influence of higher temperatures on the chemical inertness of PET bottles was investigated by storing PET bottles at 60 °C up to five weeks. Test results of Toluene as volatile and Benzophenone as non-volatile model compound are exemplary presented in Figure 5-9 and Figure 5-10.

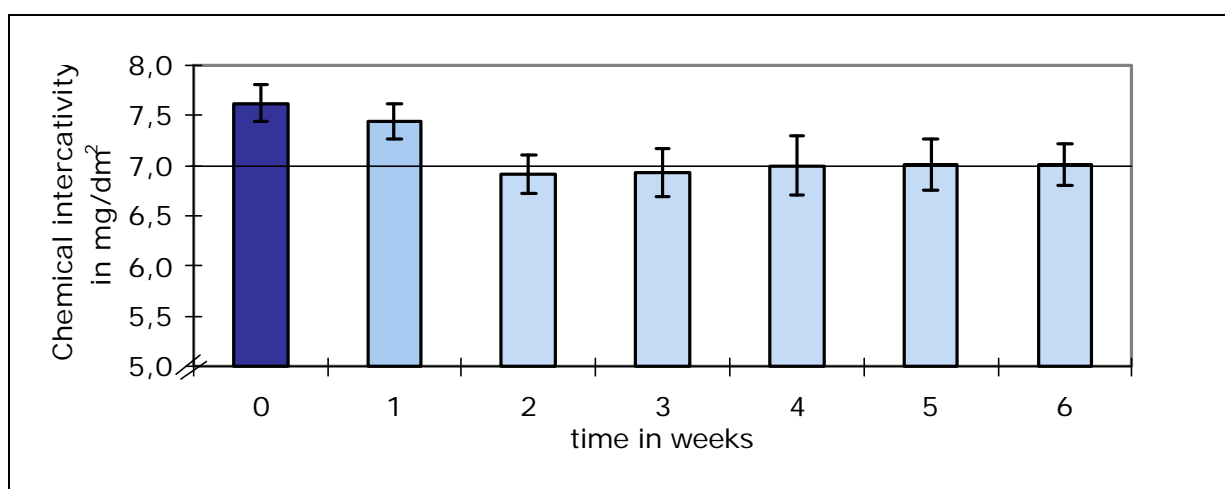


Figure 5-9: Chemical inertness test results of reference PET bottles stored at 60 °C for several weeks for model compound **Toluene**

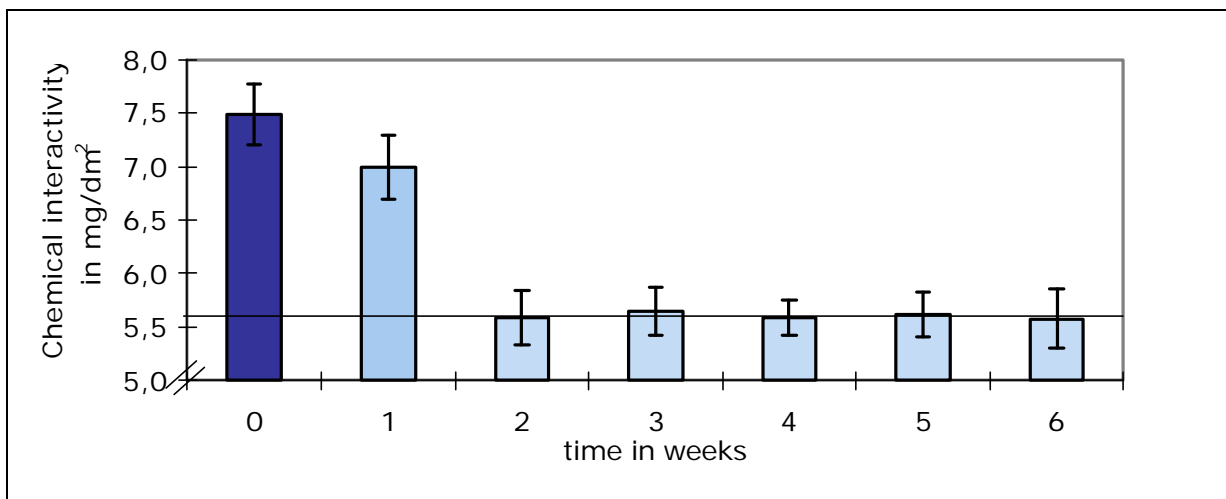


Figure 5-10: Chemical inertness test results of reference PET bottles stored at 60 °C for several weeks for model compound **Benzophenone**

It could be shown that test results of investigated reference bottles decreased after a storage of two weeks at 60 °C and also reached a stable state concerning the inertness behaviour after this time. Decreasing model compound concentrations after storage at 60 °C were due to relaxation processes of material tensions of PET bottles at temperatures near the glass transition. Volatile model compounds with low molecular mass decreased more slightly than non-volatile model compounds with higher molecular mass. Furthermore it could be shown that freshly produced virgin PET bottles showed higher model compound concentrations compared to PET bottles which were already stored for a longer period of time at room temperature. The consequence is, that whenever PET inertness values are compared, the age of a bottle has to be taken into account. The chemical inertness of a PET bottle changes until a steady state is reached, in other words, relaxation processes are completed. The steady state of chemical inertness behaviour of a PET bottle will be reached either after a defined period of time at room temperature or after accelerated processes at 60 °C for at least two weeks.

Refillable PET bottles normally have to withstand washing conditions of approximately 60 °C. If freshly produced PET bottles are stored at 60 °C for e.g. two weeks the established chemical interactivity values of model compounds will give an idea of how PET bottles will chemically behave or react within a multi-use system. Figure 5-11 shows test results of PET materials produced by different PET manufacturers which were stretch blow moulded at the same time under approximately same manufacturing conditions.

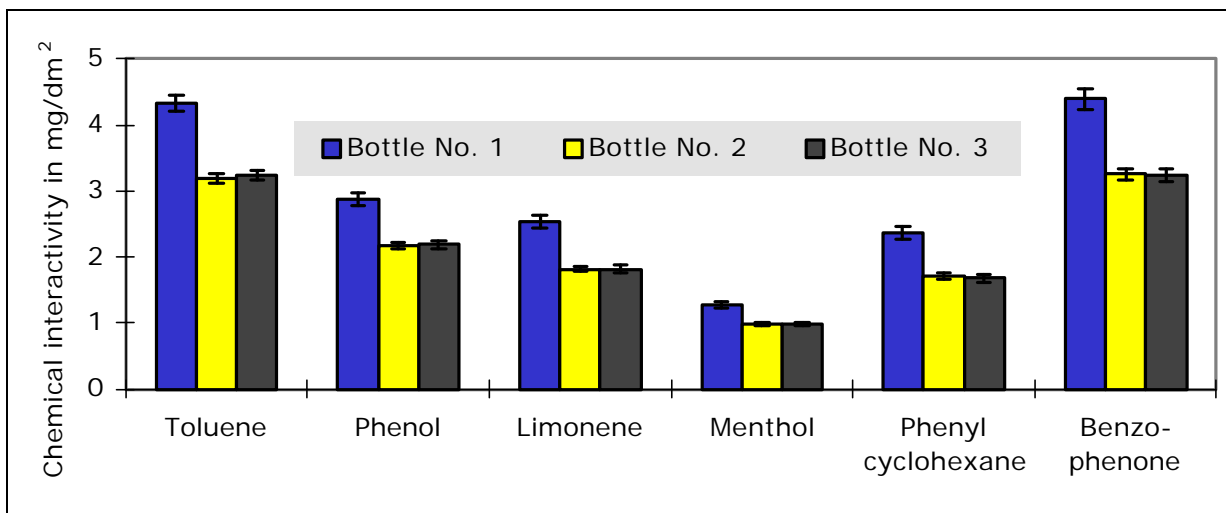


Figure 5-11: Chemical inertness test results of three different PET materials coming from different suppliers which were manufactured under the same conditions.

In comparison to bottle No.2 and No. 3, bottle No.1 showed the most unfavourable chemical inertness behaviour whereas bottle No. 2 and No.3 could be significantly compared. Test results shown in Figure 5-11 were obtained for freshly produced PET bottles. If a PET bottle manufacturer had to choose between material 1, 2 or 3 in case of one-way bottles, materials 2 or 3 would be favourable concerning the chemical inertness interactivity. The question of how PET bottles from material 1 to 3 would behave in a multi-use system was investigated by storing PET bottles of each material at 60 °C for two weeks. Obtained test results after a storage of two weeks at 60 °C are shown in Figure 5-12 in comparison to results of freshly produced PET bottles.

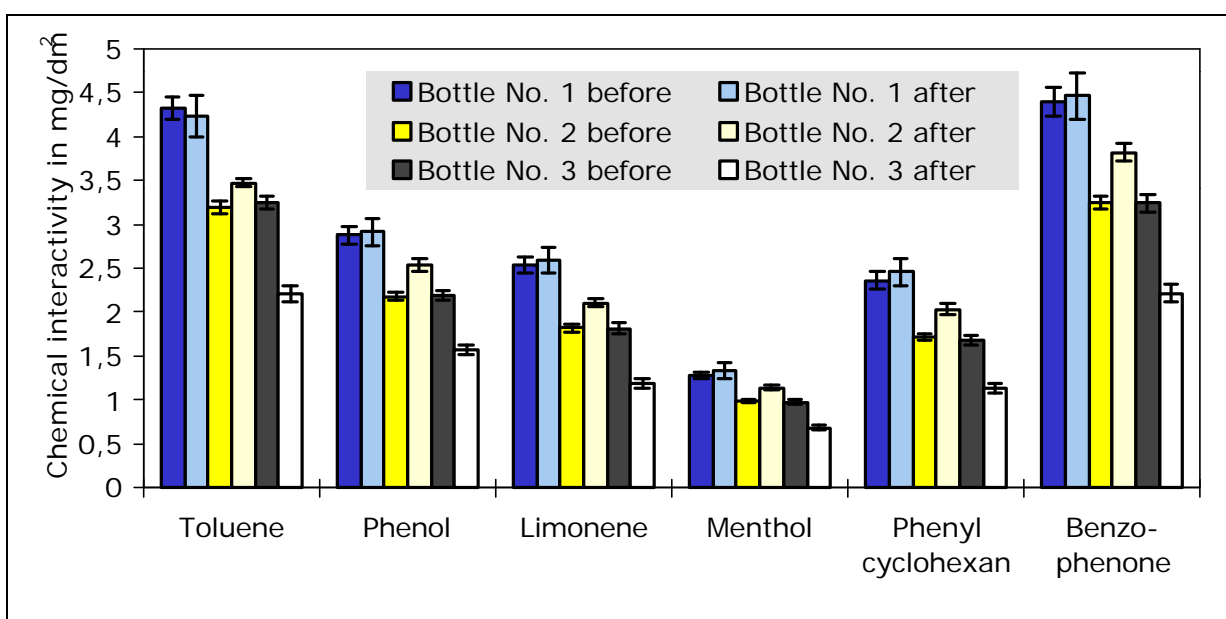


Figure 5-12: Comparison of chemical inertness results of different PET materials before and after storage at 60 °C for two weeks

Chemical inertness test results of bottle No. 1 did not significantly change after a storage of two weeks at 60 °C. It can be concluded that PET bottles of material No. 1 were manufactured under temperature conditions which minimised the development of material tensions which means that relaxation processes were already completed shortly after manufacturing. For bottle material No. 2 it could be shown that the chemical inertness was negatively changed after the storage at 60 °C. Increasing chemical inertness values might be drawn back to thermal and hydrolytic degradation processes of the PET material. Concerning the chemical inertness behaviour PET material No. 3 would be the most favourable for the use as refillable PET bottles in a multi-use system since the chemical interactivity considerably decreased after storage at 60 °C.

5.4.2 Influence of low temperatures on the chemical inertness behaviour

The advantage of PET in comparison to glass bottles is the unnecessary tempering of bottles before the filling of hot beverages in order to prevent bursting of bottles. On the other side beverages can also be frozen in PET bottles in hot summers in order to provide freshly cooled drinks without risking to burst the bottle. The influence of material stresses caused by freezing and thawing of PET on the chemical inertness behaviour was investigated. Empty as well as filled PET bottles were stored for one day at -18 °C followed by thawing at room temperature. The chemical inertness of the materials was evaluated and compared to results of PET bottles stored at room temperature.

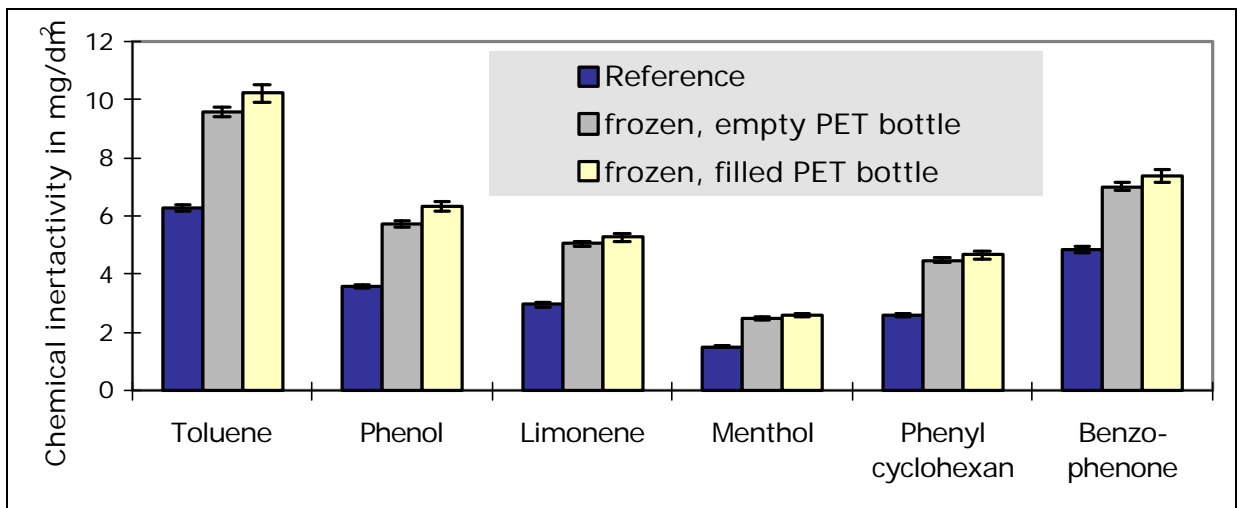


Figure 5-13: Influence of freezing conditions on the chemical inertness behaviour of PET bottles

According to test results of Figure 5-13 it could be shown that investigated 1.5 L multi-use beverage bottles were not suitable to be stored at freezing conditions. The „mis-use“ by storing these PET bottles at freezing temperatures destroyed the PET material structure and led to higher chemical inertness values.

5.5 INFLUENCE OF CAUSTIC AND ACID SOLUTIONS ON THE CHEMICAL INERTNESS BEHAVIOUR

Influence of caustic solution on the chemical inertness of PET bottles

During the washing procedure PET multi-use bottles come intensively in contact with sodium hydroxide/ caustic solutions at high temperatures. The possible influence of different concentrations of sodium hydroxide solution on the chemical inertness behaviour of a refillable 1.5 L PET bottle was tested by filling and storing PET bottles for 24 hours at 60 °C (Figure 5-14).

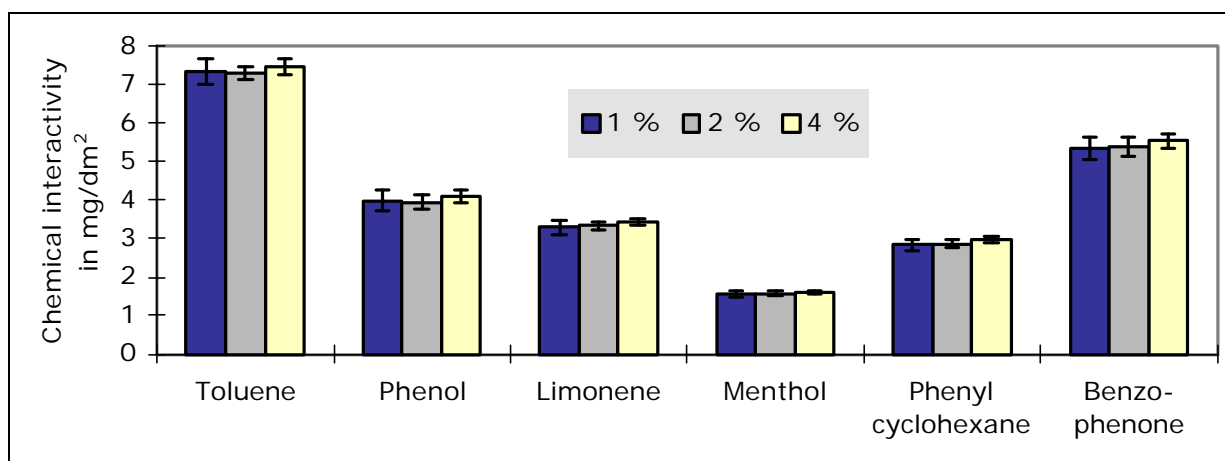


Figure 5-14: Influence of sodium hydroxide solutions on the chemical inertness behaviour of PET bottles

Refillable 1.5 L PET bottles were filled with 1 %, 2 % and 4 % sodium hydroxide solutions and stored for 24 hours at 60 °C. In reality PET bottles come into direct contact with caustic solutions only for minutes during the washing procedure. Therefore the direct contact of PET bottles with caustic solution for 24 hours at 60 °C simulated worst case conditions. Test results shown in Figure 5-14 demonstrate that the chemical inertness test was not able to detect a considerably change of chemical inertness values for PET bottles investigated. Therefore it could be assumed that the different concentrations of caustic solution did not affect the PET material at all.

Influence of acid solutions on the chemical inertness of PET bottles

The influence of 3 % acetic acid on the chemical inertness behaviour of one-way and 1.5 L multi-use PET bottles of the same shape and produced by the same manufacturer was tested by filling with acetic acid and storing the PET bottles for three months at room temperature. Test results of filled PET bottles were tested in comparison to empty PET bottles stored at room temperature.

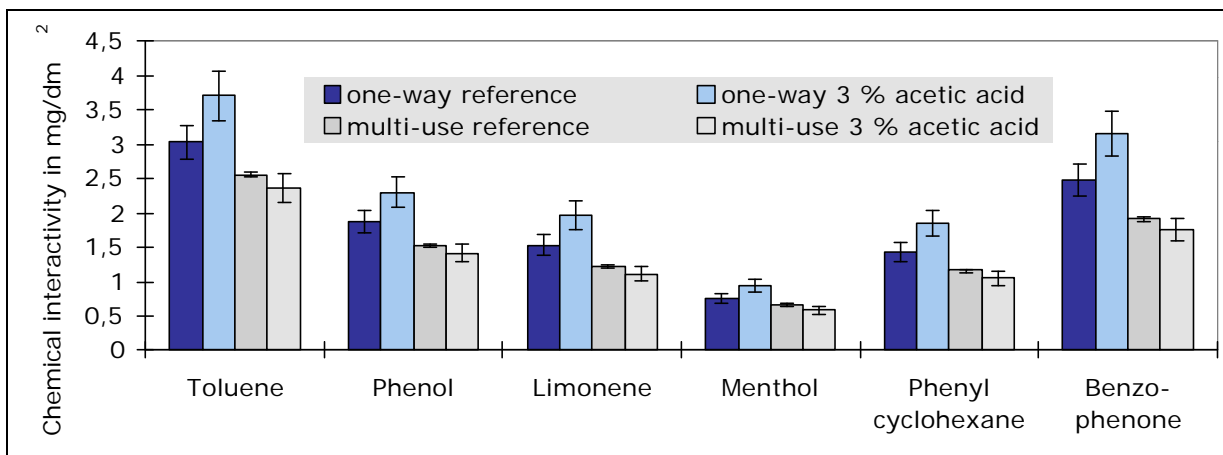


Figure 5-15: Influence of 3 % acetic acid on the chemical inertness behaviour of one-way as well as multi-use PET bottles

In general, the investigated one-way PET bottles showed significantly higher model compound values than multi-use PET bottles due to a higher feedstock quality of the PET material. While chemical test results of PET multi-use bottles were not significantly influenced by 3 % acetic acid, the one-way bottles were negatively affected. The PET material of the investigated one-way bottle showed significantly higher test results than the corresponding reference bottles after the storage in direct contact with 3 % acetic acid. Therefore it can be assumed that the influence of acid solutions on the chemical inertness behaviour of PET depends therefore on the quality of feedstock material PET.

5.6 INFLUENCE OF STERILISATION PROCEDURES ON THE CHEMICAL INERTNESS BEHAVIOUR OF PET

PET multi-use bottles not only can be cleaned by intensive washing procedures but also can be sterilised using e.g. H₂O₂ or plasma sterilisation. Following, it was established whether the chemical inertness procedure was able to detect changes in the chemical inertness behaviour caused by different sterilisation procedures of PET multi-use bottles.

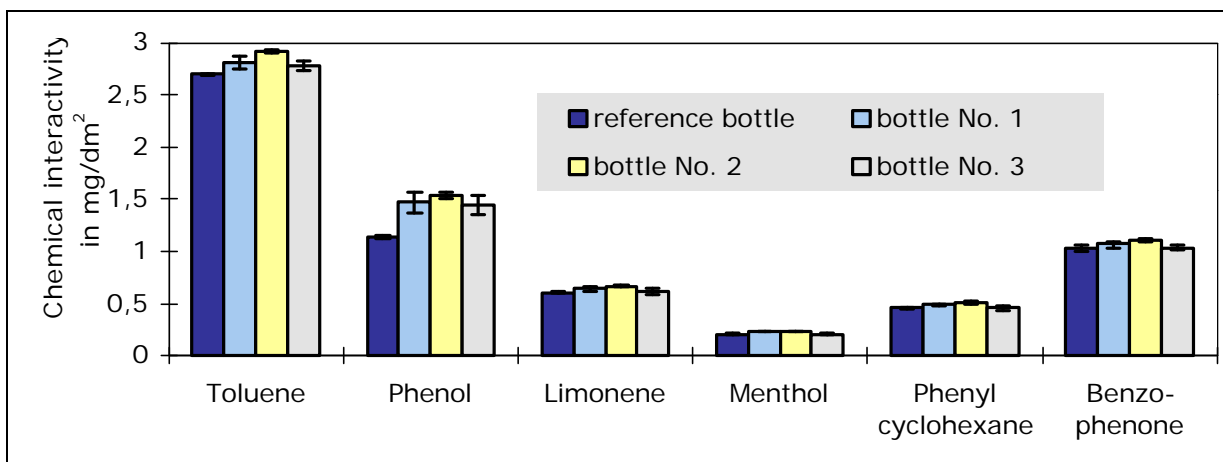


Figure 5-16: Influence of plasma sterilisation on the chemical inertness of PET bottles

The plasma sterilisation was carried out using oxidising (bottle No. 1) as well as reducing sterilisation conditions (bottle No. 3). PET bottle No. 2 was first sterilised under oxidising conditions and followed by reducing sterilisation conditions. In case of Toluene and Phenol (volatile substances) a lower chemical inertness could be detected after sterilisation resulting in significantly higher model compound concentrations. Furthermore, as shown in Figure 5-17 the influence of H₂O₂ sterilisation was tested with 1.5 L one-way PET bottles. In this case an significant influence of the sterilisation procedure on the chemical inertness behaviour could not be detected.

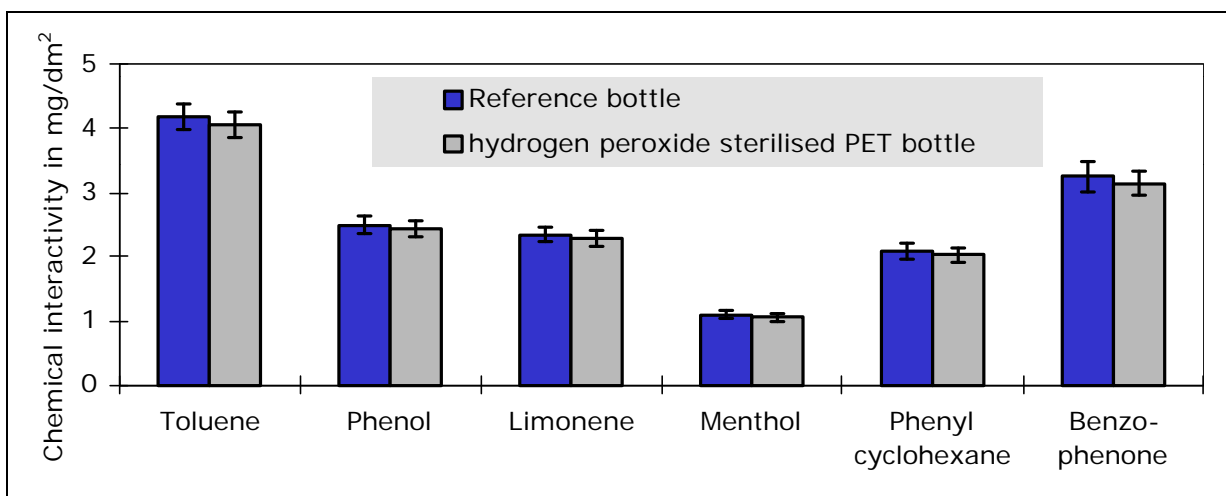


Figure 5-17: Chemical inertness test results of H₂O₂ sterilised PET bottles

5.7 CHEMICAL INERTNESS BEHAVIOUR OF RECYCLED PET BOTTLES

PET as packaging material for beverages is increasingly used all over the world. Due to the emerging packaging waste the pressure of developing recycling techniques for PET materials which become once again applicable as packaging for foodstuff arose. Figure 5-18 show chemical inertness test results of PET bottles containing up to 50 % recycled PET material.

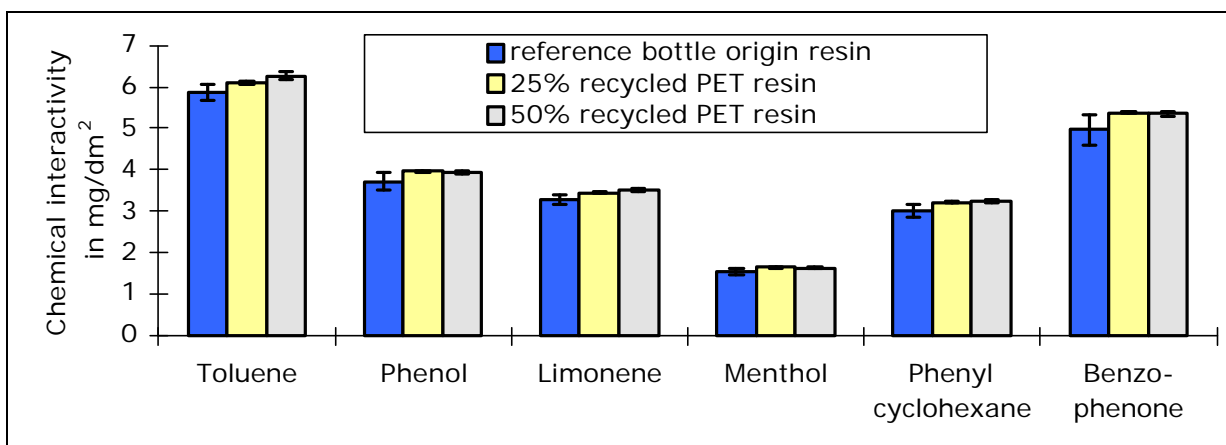


Figure 5-18: Chemical inertness test results of PET bottles containing recycled PET material

It could be shown that PET bottles which contained 25 % and 50 % recycled PET material only changed slightly the chemical inertness behaviour. Moreover, regarding the chemical inertness behaviour it did not play a role whether 25 % or 50 % of recycled PET material was used for the production of monolayer PET bottles.

5.8 CHEMICAL INERTNESS OF BEVERAGE BOTTLES MADE FROM POLYETHYLENE NAPHTHALATE (PEN)

The chemical inertness test procedure was also developed in view of the fact that the inertness of other plastic packaging materials principally could be tested in the same way. Due to a higher temperature stability and enhanced barrier properties Polyethylene naphthalate (PEN) might be the material of choice for sensitive beverages in the future. Therefore it was established whether the chemical inertness test could also be carried out with bottles made from PET/PEN copolymers or even 100 % PEN.

Investigation of low level (85 / 15 %) PET/PEN bottles

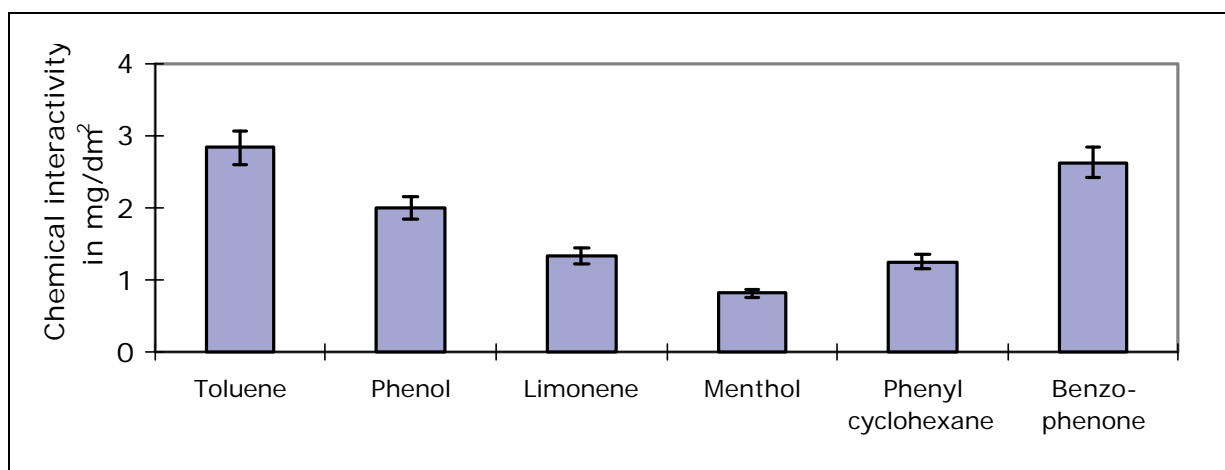


Figure 5-19: Chemical inertness test results of a PET bottle made of low level PET

There arose no difficulties in performing the chemical inertness test with PET bottles made from low level PET/PEN.

Considering the test results presented in Figure 5-19 it can be mentioned that the model compound concentrations are comparable with concentrations obtained by 100 % PET bottles. The disadvantage of carrying out the chemical inertness test with copolymers or multi-layer bottles is the fact that only an „overall“ chemical inertness can be established. There is no possibility to evaluate to which degree PEN or PET contribute to the chemical inertness of a beverage bottle.

Investigation of PEN bottles

The chemical inertness test was carried out with 0.5 L beverage bottles made from 100 % Polyethylene naphthalate.

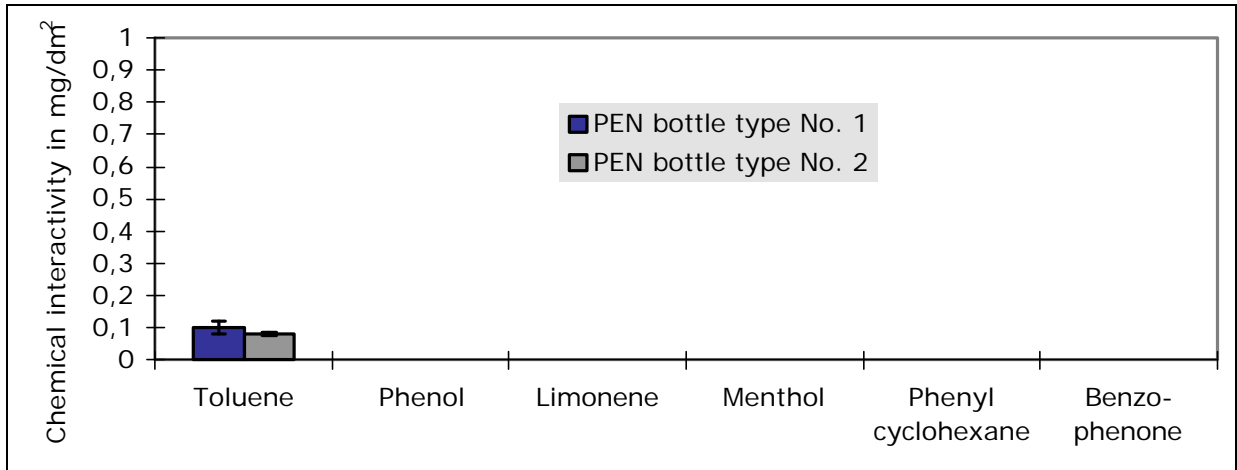


Figure 5-20: Chemical inertness test results of PEN bottles

After performing the chemical inertness test with the polymer Polyethylene naphthalate only the model compound Toluene could be detected at extremely low concentrations. It can be concluded that the chemical inertness of PEN bottles is tremendously higher than those of PET bottles if same model compound cocktails are used. Moreover, if the chemical inertness test should be applied to show differences in the chemical inertness of PEN bottles another model compound cocktail has to be used with possibly higher concentrations or other types of model compounds.

In case of the chemical inertness it could be shown that PEN is superior to PET for filling beverages, but has not substituted PET bottles considerably so far due to the higher costs of PEN.

6 DISCUSSION

Nowadays there exist a high variety of plastic packaging materials for foodstuffs. Depending on characteristic properties of foodstuffs and their quality requirements, plastic packages can be designed specifically. At the moment the favourite plastic packaging material for liquid foodstuffs is certainly Polyethylene terephthalate. In the past characteristic properties of PET like lower weight have led to the fact that glass bottles were more and more replaced - not only from a packaging point of view but also under environmental aspects. In 1993 the European Union drafted a Directive on Packaging and Packaging Waste to protect the environment. According to the environmental impact of PET due to its extensive volume and high resistance against atmospheric and biological agents PET is seen as a noxious material. For this reason the PET packaging waste is nowadays preferably managed in form of re-use systems or recycling facilities especially in the field of PET containers for beverages.

In a re-use system the strength and ruggedness of PET is one reason that PET beverage bottles can achieve high circulation rates of up to 15 cycles between bottler and consumer. However, the use of a rugged material like PET cannot rule out the fact that material changes might occur during the life time of a PET bottle.

Furthermore, on the account of a direct contact between beverages and PET bottles migration processes might occur during the often long storage time. Hereby, the aspect that the treatment of PET beverage bottles by consumers remains a „black box“ of the history of returning PET bottles is of great importance. Consumers might misuse PET bottles e.g. by filling them with household chemicals. These substances might be able to re-migrate in refilled foodstuffs in case that the washing procedure is not able to fully remove them.

According to Article 2 of the Framework Directive 89/109/EEC of the European Commission the use of plastic packaging materials for foodstuffs generally requires that *„under normal or foreseeable conditions of use plastic packaging materials do not transfer constituents to foodstuffs in quantities which could endanger human health or bring about unacceptable change in the composition of the foodstuffs or a deterioration in the organoleptic characteristics“*.

Due to the intrinsic interactivity of refillable plastic bottles with contacting chemicals as well as due to the fact that consumers might misuse PET bottles the „contamination“ of multi-use bottles is not foreseeable and therefore the question of testing compliance of refillable PET bottles with food regulations arose.

To this day there are neither any specific national nor EU regulations available concerning the quality assurance and safety-in-use of refillable PET bottles. On the other side are regulations only useful in case of available standard procedures for testing and proofing compliance of refillable PET bottle.

For this reason a standardised and easy-to-apply method was established and validated. It should serve in general for chemical inertness testing of refillable PET bottles applicable not only for the industry but also suitable for enforcement laboratories, thus having for the first time a systematical control possibility to check the food safety of refilled PET bottles taken from the market.

The start of a standardised method was made in a previous EU project AIR2-CT93-1014. The principal idea of a general chemical inertness method was the specific contamination of PET beverage bottles with several defined chemicals as surrogates for household chemicals. The determination of the absorbed amount of these substances in the plastic material as well as the re-migration of these chemicals into food simulants should proof how inert PET bottles were against „consumer misuse“.

In the beginning of the development of a chemical inertness method refillable 1.5 L PET bottles were filled with four different „cocktail“ solutions consisting of 20 surrogates in total. Although the volume of the 1.5 L PET bottles was minimised by using glass balls as additional filler 350 mL of each cocktail solution had to be prepared in order to fully contaminate one PET bottle. This meant that after triplicate measurements over 1 L of chemicals had to be used for each cocktail solution. The chemical waste of over 4 L cocktail solution for one chemical inertness test gave rise to the consideration whether the use and investigation of simple PET strips cut out of the middle part of a PET bottle would also allow prediction of what happens to whole bottles. Recognising that PET strip tests would allow prediction of what happens with whole bottles the handling of the chemical inertness test procedure could be simplified.

Within the presented research work the chemical inertness test procedure could furthermore be extremely optimised and simplified providing an easy-to-apply test procedure which will further be applicable for industry as well as enforcement laboratories not expecting that laboratories have to be specially equipped.

The first intention of the research work was the considerable simplification of the chemical handling of the method. Therefore, the 4 cocktail solutions with 20 constituents altogether had to be reduced to only one cocktail solution with a minimised number of surrogates but still giving evidence concerning the chemical inertness of a PET material. The 20 surrogates of the 4 cocktail solutions were reduced to one set according to considerations like e.g. consumer availability, chemical structures or safety aspects. The optimised cocktail solution finally contained Toluene, Phenol, Limonene, Menthol, Phenyl cyclohexane and

Benzophenone as model compounds for the contamination of PET strips. Herewith, the use of only one cocktail solution not only saves chemicals but also labour time and costs.

The chemical inertness of a PET material was previously established on the one hand by measuring the amount of absorbed chemicals in the PET material itself on the other hand by measuring re-migrating substances from contaminated PET bottles into re-filled food simulants. The principle idea of a chemical inertness method was to simulate the possible real life interactions of refillable PET bottles with chemical compounds. It could be shown that the absorbed amount within the PET bottle material correlated to a certain degree with re-migrating model compounds. The performance of both test procedures addressed therefore the usefulness of carrying out sorption as well as re-migration measurements at the same time. Since both test procedures resulted in comparable model compound concentrations the analysis of re-migrating model compound was given preference due to more realistic migration conditions of refilled PET beverage containers.

Migration regulations of the European Commission for plastic packaging materials often provide that migration measurements are carried out at test conditions of 10 days at 40 °C. Using such test conditions for the contamination (sorption) as well as the re-migration phase of PET strips would mean that the chemical inertness test would take at least 4 weeks until test results would be available. Since time is money and important decisions often have to be made shortly the presented research work strove to find alternative test conditions. It could be shown that conditions of 2 days at 60 °C led to comparable test results like obtained at test conditions of 10 days at 40 °C. Reducing the analysis time from at least 4 weeks to one week extremely optimised the test procedures since laboratories are enabled to deliver results as a basis of further decisions in a short time.

Finally, the optimised as well as simplified inertness method was satisfyingly validated by carrying out several intercomparison testing trials including the attendance of 11 laboratories altogether. With the final chemical inertness method a standardised test procedure is available which is dedicated to provide a systematical control possibility to check the inertness behaviour and therefore safety of PET bottles during their life cycle.

The chemical inertness method can be applied for the comparison and determination of interactivity values of every thinkable sort of PET bottle and PET bottle material on the market. Nevertheless it has to be mentioned that chemical interactivity values of PET materials slightly depend on the age of a PET bottle due to relaxation processes. If different PET bottles should be compared concerning their chemical inertness the age of a PET bottle has to be taken into account.

Chemical inertness values of PET bottles can be assessed if the test procedure is carried out with different materials at the same time in order to be able to

compare interactivity values. For the beverage industry e.g. this will mean that decisions between different suppliers of PET bottle might be made on the basis of chemical inertness values. In other words PET bottles most suitable for reuse systems might be chosen according to their chemical inertness interactivity and quality. Furthermore, the influence of material stresses, environmental influences on the material quality etc. can be established comparing differently treated PET materials.

The chemical inertness test procedure only can provide „overall“ interactivity values. In case of multi-layer bottles or bottles made from co-polymers it is not possible to state to what degree the different materials contributed to the chemical inertness of a PET bottle.

However, the chemical inertness value of a special PET bottle only can be judged if reference values are available. In the future the establishment of acceptable migration limits for model compounds of the chemical inertness procedure has to be discussed. On the basis of a market research of chemical interactivity values of PET bottles which are already launched on the beverage market might be compared as well as specific migration limits established. The availability of an easy-to-apply method enables enforcement laboratories to assess chemical inertness values of PET bottles on the market and therefore to judge whether newly developed materials might be launched or not. If newly developed materials show higher chemical inertness values than technical feasible enforcement laboratories would for the first time be able to protect the consumer in form of restrictions.

At the moment only few plastic reference materials are available to check the performance and reliability of methods or laboratories. Thus, the additional intention of the presented research work was to prepare a food grade reference PET material which already fulfils the principal legal requirements. As a reference material a common 1.5 L refillable PET bottle was chosen which already has been generally accepted from a health risk point of view. Within the research work this PET material was established as reference material on the basis of its interactivity values which were determined and certified. The certified values of the PET material are specific to the drafted chemical inertness test procedure (listed in Appendix 1). As already mentioned the certified PET reference material will be available for sale in the near future at IRMM, Geel, Belgium.

Summarising it could be said that the chemical inertness test covers the sum of all possible mechanical stress influences on the inertness behaviour of a PET material and, in case of complaint, allow the conclusion to the enforcement authority that something in the bottle manufacture process or in the washing/ refilling system went wrong or the recycle number might be too high. A standardised and easy-to-

apply method for general chemical inertness testing of refillable PET bottles in connection with a certified reference material is applicable not only for the industry but also suitable for enforcement laboratories having then for the first time a systematical control possibility to check the food safety of currently used refillable PET bottles on the beverage market.

7 SUMMARY

Due to the underlying principle of a plastic bottle refill system, i.e. circulation between the bottler and the consumer, and due to the intrinsic interactivity of plastics with contacting chemicals, a special and possibly even unique situation arises concerning the question of testing compliance with food regulations.

Currently, there is neither any specific national or EU regulation nor a standard test available which could be applied by industry or enforcement laboratories to cover this problem. As a consequence, the food safety quality control of washed and refilled PET bottles before they go out again to the consumer is completely in the hands of the bottle fillers.

Before the presented research work authorities and enforcement laboratories did not have any access to compliance testing on a refilled PET bottle drawn from the market place by an own, independent test method.

For this reason the European Commission supported and financed the research activities concerning the establishment of a chemical inertness test method for refillable PET containers within the EU project SMT4-CT96-2129.

The development of a chemical inertness test method was based on the intention of having a systematical control possibility to check the food safety of refilled PET bottles taken from the market.

Within the presented research work a standardised and easy-to-apply method for general chemical inertness testing of refillable PET bottles was developed. This test is based on dipping PET strips into a mixture of distinct solutes under defined conditions in the following re-migration of these compounds into a food simulant (95 % alcohol and detection by GC). It is applicable not only for the industry but also suitable for enforcement laboratories.

With the establishment of a chemical inertness test procedure, for the first time at all, a systematical control possibility to check the food safety of refilled PET bottles taken from the market. The chemical inertness behaviour of PET beverage containers concerning misuse, material stresses can predicted and PET material qualities be judged.

In the course of investigation the chemical inertness test method could be optimised and simplified taking only one week in total for the chemical analysis of the inertness of PET materials. So it is an easy-to-apply test method which could be used by industry as well as enforcement laboratories to predict the chemical inertness and therefore food safety of PET beverage containers.

This chemical inertness test covers the sum of all possible mechanical stress influences on the inertness behaviour of a PET material and, in case of complaint, allow the conclusion to the enforcement authority that something in the bottle manufacture process or in the wash/refill system went wrong or the recycle number might be too high.

The chemical inertness method was developed in order to establish the interactivity of PET materials intended to be used in form of refillable containers. In the course of investigation it could be shown that the chemical inertness method could also be used to compare chemical inertness values of

- PET materials with different feedstock qualities
- PET materials produced under varying manufacturing conditions and parameters
- Influence of environmental material stresses

In addition, the intention was to prepare a food grade reference PET material which fulfils the principle requirement of article 2 of the Framework Directive 89/109/EEC and to certify this reference material with respect to its interactivity values.

Moreover, the production of a defined reference PET material with certified chemical inertness values will further provide a good possibility for the verification of laboratory performance.

Since the reference PET material consists of a food grade PET material which already fulfils the principal requirement of article 2 of the Framework Directive 89/109/EEC, the chemical inertness values could additionally be used as „comparative values“ in order to assess PET materials concerning their chemical interactivity. However, the chemical inertness values of the reference PET material not have to be understood as „interactivity limits“ which have not to be exceeded but as a reference of technical feasible chemical inertness values.

For the first time the chemical inertness test procedure offers a possibility to minimise the potential public health risks of the reuse of PET bottles following possible misuse by applying the chemical inertness method for refillable PET bottle as quality and safety criteria of refillable PET containers.

EQUATIONS

Equation 1:

$$M_t = \frac{m_t}{A} = 2 C_{P,0} * \sqrt{\frac{D_p * t}{\pi}}$$

m_t/A is the mass transfer of a substance in μg per contact area A in cm^2 at time t in seconds

$C_{P,0}$ is the initial concentration of the substance at time $t = 0$ in the polymer in $\mu\text{g}/\text{cm}^3$

D_p is the diffusion coefficient of the substance in the polymer in cm^2/s

Equation 2:

$$D_p = 10^4 \exp\left(A_p - 0,01 * M_r - 10450 * \frac{1}{T}\right)$$

D_p is the diffusion coefficient of the substance in the polymer in cm^2/s

A_p polymer dependent value, for PET established to lay between -3 and -5

M_r relative molecular weight

T temperature in Kelvin

Equation 3

$$CF * \langle M \rangle = CF * \sum_{i=1}^4 (M * f_T)_i = \text{dietary concentration}$$

CF consumption factor

f_T food-type distribution factor

$\langle M \rangle$ concentration of migrant into a food-simulating solvent i

i simulating food types: aqueous, acidic, alcoholic and fatty foods

Equation 4.1

$$y_{mc}[\text{counts}] = a_{mc} \cdot x_{mc} [\text{mg / g}] + b_{mc}$$

Equation 4.2

$$x_{mc}[\text{mg / g}] = \frac{y_{mc} - b_{mc}}{a_{mc}}$$

- y_{mc} value of the peak area of a model compound in counts * 10^{-3}
- a_{mc} slope of the calibration curve of a model compound
- x_{mc} concentration of model compound in mg/g in 95 % Ethanol
- b_{mc} intercept of the calibration curve of a model compound (blank value)

Equation 5

$$\text{Interactivity}_{mc} \left[\frac{\text{mg}}{\text{dm}^2} \right] = \frac{x_{mc} \left[\frac{\text{mg}}{\text{g}} \right] \cdot m_{ae}^{ES} [\text{g}]}{A_{eff} [\text{dm}^2]}$$

- $\text{Interactivity}_{mc}$ extracted amount of model compound in mg per square decimetre of a PET test strip taking both sides into account
- x_{mc} concentration of model compound in mg/g in 95 % Ethanol (extraction solvent)
- A_{eff} effective area of a PET strip after cutting the edges (taking both sides of the test specimen into account) in dm^2
- m_{ae}^{ES} mass of extraction solvent 95 % Ethanol in g after the extraction phase of PET strips

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APPENDIX 1

DRAFT METHOD

METHOD OF TEST FOR REFILLABLE PET BOTTLES
WITH RESPECT TO THEIR
CHEMICAL INERTNESS BEHAVIOUR

Prepared by

Fraunhofer Institut für Verfahrenstechnik und Verpackung (IVV)

within the EU Project

SMT4 - CT96 - 2129

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Foreword

This analytical test method has been established within the EU project SMT4-CT96-2129 "Establishment of a standard test procedure for refillable PET bottles with respect to chemical inertness behaviour as well as sensory interactivity including preparation of a certified reference PET material" co-ordinated by Fraunhofer Institute of Process Engineering and Packaging, Freising, Germany, in co-operation with Schmalbach Lubeca PET Containers and further 10 European laboratories.

In addition, the project will develop a certified reference PET material which will become available from BC-JRC-IRMM under the CRM number 712.

0 Introduction

Plastic materials can interact with chemicals by absorptive uptake of substances. Due to the underlying principle of circulation of a refillable PET bottle between the bottler and the consumer and due to the intrinsic interactivity of plastics with contacting chemicals a special situation arises concerning the question of chemical inertness of refillable PET bottle materials. Food constituents or chemical substances which may have been absorbed by the bottle material may time-dependently re-migrate into the refilled foodstuff. Although statistical evaluation of considerable R&D work in this field has scientifically proven that refillable PET bottles can be re-used safely under certain circumstances, an appropriate, generally accepted test method is required to define the bottles interactivity thus ensuring its quality and compliance with food regulations.

1 Scope

This method describes a test procedure for the determination of the interactivity of a PET bottle material with a set of 6 chemical model compounds under given sorption conditions. The measured interactivity is understood as the extend of sorption of model chemicals by the PET material and given quantitatively in mass [mg] absorbed per surface area [dm²]. The method is proposed to be used as a comparative method, i.e. comparing two or more different PET materials with respect to their interactivity. In this way the method is capable to test the chemical inertness behaviour of different PET formulations or batches or to investigate the influence of stress parameters such as number of wash cycles or other, applied to a given PET material. The method can also be used to demonstrate food regulatory compliance of a PET test material when compared directly to the certified PET bottle material [CRM number 712] and provided that the certified interactivity values are met according to ISO guide 33 (1988) as follows:

$$-a_2 - 2\sigma_L < (x - \mu) < a_1 + 2\sigma_L$$

where x : mean value of replicate measurements
 μ : certified value
 $a_1; a_2$: adjusted values chosen by the user according to economic or technical limitations or stipulations
and σ_L is the long-term within-lab standard deviation.

2 Principle

The principle idea of this interactivity test is to simulate the possible real life interaction of refillable PET bottles with chemical compounds by using a „cocktail“ of 6 selected model chemicals with different chemical and physical properties. The interactivity between the PET material and the chemical model substances is measured as the sorption of substance by the PET material. Experimentally, this is achieved by contacting PET bottle wall strips with a mixture of the model compounds under standard conditions (2 days/60°C) thus loading the PET test material. This sorption

phase is followed by an exhaustive re-migration phase with immersion of the loaded PET strips into 95% ethanol for 2 days at 60°C thus extracting the absorbed amounts of model compounds into the ethanol solution. Finally, the concentrations of the model compounds in the ethanolic solution are determined by gas chromatography.

NOTE: The sorption conditions, i.e. concentration of model compounds and time/temperature have been chosen such that the PET material shows only a slight swelling effect which cannot be recognised visually. This situation is believed to be the most critical one with refillable PET bottles since electronic and visual inspection systems may fail in these cases. The time-temperature conditions for the sorption phase (2 days/60°C) have been found to correlate with the generally applied contamination conditions of 14 days at 40°C as applied so far in testing of returnable PET bottles. Exhaustive extraction under the applied re-migration conditions was confirmed by comparison with results obtained from complete extractions using hexafluoroisopropanol as an aggressive swelling and dissolution solvent.

Further experiments and measurements in the SMT project SMT4-CT96-2129 have shown that interactivity results obtained from whole bottles do compare to the strip test interactivity. From these findings, strip test results may be used to estimate the whole bottle behaviour.

If differences in morphology could be expected than the users must satisfy themselves that this condition hold - e.g. by testing specimens from different locations of the bottle.

3 Reagents

All reagents and solvents shall be of analytical quality, unless otherwise specified.

3.1 Chemicals

3.1.1 Benzophenone (C₁₃H₁₀O), purity ≥ 99% (GC);
alternative name: diphenyl ketone;
CAS No. 119-61-9; BRN 1238185; EG No. 2043376

3.1.2 (R)-(+)-Limonene (C₁₀H₁₆), purity 98%;
alternative name: (R)-(+)-4-isopropenyl-1-methyl-cyclohexene
CAS No. 5989-27-5

3.1.3 Menthol (C₁₀H₂₀O), purity 99%;
alternative name: 2-isopropyl-5-methyl-cyclohexanol,
CAS No. 89-78-1

3.1.4 Phenol (C₆H₆O), purity ≥ 99%;
alternative names: hydroxybenzene, carboic acid,
CAS No. 108-95-2; BRN 969616; EG No. 2036327
Precaution: Phenol is a toxic substance !

-
- 3.1.5 Phenyl cyclohexane (C₁₂H₁₆), purity 98%;
alternative name: cyclohexyl benzene,
CAS No. 827-52-1
- 3.1.6 Toluene (C₇H₈), purity > 99,5%;
alternative name: methyl benzene,
CAS No. 108-88-3; BRN 635760; EG No. 601-021-00-3; EINECS No.
2036259
- 3.1.7 p-Xylene (C₈H₁₀), purity > 99,0%.;
alternative name: 1,4-dimethyl-benzene;
CASNo. 106-42-3; BRN 1901563; EG No. 2033965
- 3.2 Solvents
- 3.2.1 Ethanol (ethyl alcohol); purity > 99,8%
- 3.2.2 Polyethyleneglycol 400 for synthesis; OH-number 267-295;
WGK 1; EG-number: 2034733 (1.13kg/L) middle-mol-mass: 380-420
- 3.3 Solutions
- 3.3.1 95% aqueous ethanol
- Place 50 mL of distilled water into a 1L flask and fill up to the mark with ethanol (3.2.1).
- 3.3.2 Stock solution of model compounds in 95% ethanol at a defined concentration of approx. 1.25 mg/g.
- Sequentially, weigh with a balance accuracy of ± 0.5 mg to the nearest approximately 100 mg of each of the model compounds
- benzophenone (3.1.1)
 - limonene (3.1.2)
 - menthol (3.1.3)
 - phenol (3.1.4)
 - phenyl cyclohexane (3.1.5)
 - toluene (3.1.6),
- starting with 3.1.1 and ending with 3.1.6, into one 100 mL volumetric flask. Dissolve the six analytes by adding 50 mL 95% ethanol (3.3.1) and shaking. Make sure that solids are totally dissolved. Then fill up to the mark with 95% ethanol (3.3.1), note down the mass of totally filled-up 95% ethanol and mix thoroughly.
- Calculate the nominal concentration of each model compound in the stock solution in mg/g.
- NOTE: This stock solution must be stored in tightly closeable glassware (100mL volume vials). The stock solution of model compounds may be stored for a maximum period of 2 months in a refrigerator at approximately +4°C.*

3.3.3 Diluted standard solutions of model compounds in 95% ethanol

Pipette into a series of 20 mL volumetric flasks 0, 0.1, 0.2, 1, 2, and 10mL of the stock solution (3.3.2) and note down the mass of stock solution in g for each dilution. For the volume 0.1mL and 0.2mL please use a glass syringe. It is important not to use plastic but glass pipettes. Fill the volumetric flasks up to the mark with analyte-free 95% ethanol (3.3.1), note down the mass of filled-up 95% ethanol in g and mix thoroughly.

*NOTE: The obtained diluted standard solutions of model compounds contain approx. 0, 5, 10, 50, 100 and 500 **ng** of model compound per mL 95% ethanol.*

Calculate the nominal concentration of each model compound in the diluted standard solution in mg/g.

NOTE: The diluted standard solutions may be stored far up to one week at + 4°C in tightly closed glassware.

3.3.4 Internal standard solution in 95% ethanol at a defined concentration of approx. 2.5 mg/g

Weigh with a balance accuracy of ± 0.5 mg to the nearest approximately 100 mg of the internal standard p-xylene (3.1.7) into a 50 mL volumetric flask. Dissolve the p-xylene in approx. 20mL 95% ethanol (3.3.1). Then fill up to the mark with 95% ethanol, note down the mass of totally filled-up 95% ethanol and mix thoroughly.

NOTE: The internal standard solution must be stored in tightly closeable glassware (50mL volume vials). This solution may be stored for a maximum period of 2 months in a refrigerator at approximately +4°C.

3.3.5 Preparation of the model compound 'cocktail' for the sorption phase

NOTE: The 'cocktail' of model compounds is used for the contact with the PET strips in order to load the plastic with the substances. Dilution with polyethylene glycol 400 (PEG 400) is necessary in order to diminish the aggressiveness of the cocktail and to achieve just such an interaction with the PET which does not lead to too exaggerated swelling effects (see also NOTE in 2. Principle).

Weigh equal parts with an accuracy of $\pm 1\%$ (same mass unit) of the model compounds (3.1.1 to 3.1.6) into a glass bottle with screw cap (of max. 300 ml volume). Dilute the obtained mixture of model compounds in the bottle by addition of four further equal parts (four times the mass unit used for one model compound) of polyethylene glycol (PEG) 400 (3.2.2). Close the

bottle and mix the cocktail solution for at least 45 minutes using a magnetic stirrer to ensure that all solid particles of model compounds are dissolved.

The so prepared cocktail solution should be colourless and clear and has relative model compound concentrations of 1:10 (by mass).

NOTES: It is useful to produce not too large cocktail quantities because of possible chemical decomposition after a long storage time. The suggestion is to take as a maximum mass unit not more than 25g \pm 1% of each model compound. The resulting total volume of the cocktail solution amounts then to approximately 260mL. With this volume, 7 inertness tests can be carried out.

The solid model compounds, benzophenone (3.1.1), menthol (3.1.3) and phenol (3.1.4) are soluble in the other liquid compounds which serve as a solvent mixture.

The cocktail solution may be stored tightly closed for a maximum period of 2 months in a refrigerator at approximately + 4°C in the dark.

4 Apparatus

- 4.1 Analytical balance capable of determining a change in mass of 0.1 mg
- 4.2 Magnetic stirrer
- 4.3 Tightly closeable 20ml glass vials with crimp closures, lined with septa (diameter 20 mm; height 75mm; neck size 13 mm)
- 4.4 Volumetric flasks of volumes 100 mL, 50 mL and 20 mL, complying with the minimum requirements of ISO 4788
- 4.5 Tightly closeable glass tubes of volume 50 mL and 100mL, with crimp closures, lined with Butyl/PTFE septa
- 4.6 Closeable glass bottles of volume approx. 300 mL
- 4.7 Pipettes of volumes 1 mL, 2 mL, 4 mL, 5 mL, 10 mL, 20 mL and 50 mL as well as glass syringes for 0.1 and 0.2mL and complying with the minimum requirements of ISO 648
- 4.8 Sealable glass vials for GC autosampler, e.g. 2 mL
- 4.9 Glass petri dishes
- 4.10 Gloves, lint free cloth, paper wipes
- 4.11 Cutting slab: clean smooth glass, metal or plastic slab of suitable area to prepare test specimens
- 4.12 Cutting implement: scalpel, scissors or sharp knife or other suitable device

-
- 4.13 Rule, graduated in millimetres; metal templates for preparing test specimens, 11 mm x 60mm
- 4.14 Blunt-nosed tweezers, stainless steel,
- 4.15 Thermostatically controlled oven capable of maintaining a temperature of $60^{\circ}\text{C} \pm 1^{\circ}\text{C}$
- 4.16 Gas chromatograph (GC), with flame ionisation detector (FID) equipped with an appropriate column and with an automatic injection sampler

NOTES: Depending on the type of gas chromatograph and separation column used for the determination, establish the appropriate GC parameters.

The GC column must be capable to separate fully the model compounds and from the internal standard as well as from solvent peaks.

5 Test specimens

5.1 General

It is essential that test specimens are clean and free from surface contamination (plastics can attract dust due to static charges). Any surface contamination should be removed from the test specimens by gently wiping with a lint free cloth, or by brushing with a soft brush. Under no circumstances should test specimens be washed using a solvent. Minimise handling of the test specimens and wear cotton gloves during test specimen preparation.

5.2 Number of test specimens

The whole inertness test of one bottle involves 10 PET strips. 8 strips are required for the contact with model compounds and 2 strips are needed for the blank test. *[It may be, depending on ring trial results, that the number is to be changed in the future].*

5.3 Preparation of PET strips from PET bottles

NOTES: The test strips with dimensions 60 mm length and 11 mm width must be cut in a vertical direction of the bottle wall from the middle part as indicated in the figure of Annex A.

PET bottles on the market will have either plain bottle wall shapes or an uneven structure with a wavy shape or contain a profile. Plain walled bottles as depicted in the figure of Annex A should here be treated as described after. The test specimen obtained here will have a homogenous or almost homogenous thickness distribution which allows to correlate the strip weight with its area. In the case of unevenly walled bottles, test specimens must be carefully selected with respect to their thickness distribution to fulfill the above mentioned correlation between mass and area. If

this is not feasible, then the strips must be defined by determination of the area only.

First of all, cut off the top and bottom of the bottle applying the 1st and 2nd cutting lines as depicted in figure of Annex A to obtain in this way the middle part of the bottle. Then apply cutting line 3, preferably along the visible moulding seams, to obtain two equal sectors of the middle part. Each of these two sectors is further shortened by cutting along line 4 and 5. The distance between cutting line 1 and 4 must be approximately the same as the distance between cutting line 2 and 5. In this way two equal area compartments are obtained from the middle of the bottle wall.

The PET test strips are prepared from these two compartments in the following way:

Lay one of the compartments on a cutting slab and reduce the width to approx. 65 mm by cutting parallel to cutting line 5. From this width-reduced compartment cut off subsequently the test strips each with a width of 11 mm using a template or a rule. The resulting PET strips have a length of approx. 65 mm and an exact width of 11 mm ± 1 mm. With the aid of a rule shorten the strips to the final length of exactly 60 mm ± 1 mm. Finally, use the rule to determine the exact dimensions of the prepared test strips and weigh each test strip. Select from each of the four compartments the most suitable strips and note both the initial area, A_i in cm^2 , taking both sides into account, as well as the initial mass, m_i , in grams of each of the 10 test strips. Place the test strips into a series of 10 glass vials (4.3).

NOTES: *It is important to achieve representativeness for the bottle wall area with the test strip preparation. This can be satisfyingly ensured by the above described procedure of taking 10 samples from the different bottle wall compartments. [Since in this way up to 30 strips can be isolated there are numerous strips left over. These strips may be used to increase the number of test samples if large variations in the results are obtained.]*

Normally, following these cutting instructions, the area A_i will be $6 \times 1.1 \times 2 = 13.2 \text{ cm}^2$.

Strips which are not needed for the test may be stored in closed glassware at ambient temperature ($20^\circ\text{C} \pm 5^\circ\text{C}$).

6 PROCEDURES

6.1 Sorption phase

6.1.1 Exposure of test specimens to the cocktail

Take eight of the glass vials (4.3) containing each a weighed PET strip as prepared in 5.3 and mark the vials to allow clear identification of the respective test specimen. Pipette 4 mL of the model compound cocktail solution (3.3.5) into each of the eight vials and close the vials tightly. Store the glass vials in a horizontal position in a thermostatically controlled oven at a temperature of $60^\circ\text{C} \pm 1^\circ\text{C}$ and leave the vials in the oven for a time period of $48\text{h} \pm 0.5\text{h}$.

NOTE: It is important that the strips are totally in contact with the cocktail solution (3.3.5) during the whole storage time. Therefore, and in order to economise the cocktail solution a horizontal storage position is essential.

6.1.2 Preparation of loaded test specimens for the extraction phase

NOTE: Prepare 3 glass petri-dishes each containing approx. 50 mL 95% ethanol for the washing procedure of the loaded PET strips after the exposure conditions

Take the glass vials (6.1.1) out of the oven and let them cool down for 5 min. to achieve approx. ambient temperature. Pull out the loaded strips from the vials and remove the remaining cocktail solution from the surface of each strip with a lint free cloth. Immerse each strip using tweezers under gentle agitation of 10 seconds and sequentially into each of the 3 petri-dishes containing 95% ethanol in the same order to remove completely any residual cocktail solution from the surface. Afterwards wipe the strips clean and dry, using paper wipes. The 95% ethanol for cleaning should be replaced after each PET inertness test.

Re-weigh the test specimens and note the mass after sorption, m_s .

NOTE: It was found that when extracting the loaded PET strips just after this washing procedure, edge sorption effects do negatively influence the results. Therefore, to eliminate edge sorption effects it is necessary to cut off the edges as described below.

Cut off the edges of the cleaned and re-weighed strips applying approx. 1 mm around the whole strip using a suitable cutting implement (4.12).

Specimens with homogenous thickness distributions:

After cutting, re-weigh each strip and note the mass as the mass with cut edges, m_{ce} .

NOTE: A correlation between mass and effective area, A_{eff} , to be considered for the area-related sorption can be made (see NOTES in 5.3):

The effective surface area, A_{eff} in dm^2 , of the cut-edge strips is calculated as follows:

$$A_{eff} = [A_i \times (m_{ce}/m_s)] / 100 \quad [dm^2]$$

Specimens with inhomogenous thickness distributions: After cutting, measure the reduced length and width dimensions using a rule and calculate the effective surface area, A_{eff} , in cm^2 .

NOTE: It is essential that the strips prepared in this way for the extraction phase are immediately treated as described below in 6.2.

6.1.3 Treatment of blank strips

Take 2 of the glass vials (4.3) containing each a weighed PET strip as prepared in 5.3 and mark the vials to allow clear identification of the respective test specimen. Proceed with these two strips in the same way as described under 6.1.1 and 6.1.2, but omit the addition of cocktail solution (strips are stored in air during the sorption phase).

NOTE: Wash the blank strips in the three ethanol baths before washing the loaded strips, to avoid carry-over.

6.2 Exposure to 95% ethanol (extraction phase)

Place the eight loaded PET strips (prepared in 6.1.2) and two blank strips (prepared in 6.1.3) each into a separate 20 mL glass vial (4.3) and mark the vials to allow clear identification of the respective test specimen. Pipette 4g (\cong 5mL) 95% ethanol (3.3.1) in each of the eight glass vials and note down the mass of the extraction solvent 95% ethanol ($ES_{m_{be}}$) before the extraction phase. Close the vials tightly using crimp closures. Weigh the closed vials again to the nearest ± 1 mg and record the mass as the total mass of the vial before exposure m_{be} .

NOTES: It has been observed occasionally that there may be loss of liquid from the vials due to vaporisation or leakage through the closures. Therefore, before starting the exposure conditions, the level of liquid in the vial in the upright position should be marked and compared with the level obtained after the exposure to make sure that significant losses of solvent will be recognised. A significant loss can and must be determined by weighing the capsuled vial containing the strip and 4g (\cong 5mL) 95% ethanol before exposure to 60°C and after the exposure.

It is essential that the strips are totally in contact with the 95% ethanol during the whole storage time. Therefore, store the glass vial in a horizontal position in a thermostatically controlled oven set at the exposure temperature of $60^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Leave the glass vials for a time period of $48\text{h} \pm 0.5\text{h}$ in the oven.

After exposure, re-weigh the capsuled vial in total and note the mass as the mass after exposure, m_{ae} . Remove the strips from the glass vials and close the vial again to obtain with the remaining liquid in the vial the extraction solution in which the model compounds will be quantified by gas chromatography as described below.

Note: If the analysis of the obtained extraction solution is not carried out immediately, then the glass vials may be stored well closed and in the dark for a maximum period of one week in a refrigerator at approx. $+4^{\circ}\text{C}$.

Calculate the loss of extraction solution as follows:

$$ES_{m_{ae}}^* = ES_{m_{be}} - (m_{be} - m_{ae}) \text{ in g}$$

* mass of extraction solvent 95% ethanol after the extraction phase

$$[(m_{be} - m_{ae}) \text{ in g} / ES_{m_{be}} \text{ in g}] \times 100 = \text{Loss of extraction solution in \%}$$

NOTE: A significant loss must be considered in case of a solvent loss higher than 2% of initial volume (80 mg). If the solvent loss exceeds 2% then that test specimen must be discarded for the further evaluation. As a minimum sample number for evaluation 5 test specimen without significant loss must be finally available. If this requirement is not fulfilled then one must starting again the sorption phase (6.1.2) with a new complete set of test specimen.

6.3 Gas chromatograph determination of model compounds

6.3.1 Preparation of samples for GC injection

6.3.1.1 Calibration samples

Pipette 4g (\cong 5mL) of each of the diluted standard solutions (3.3.3) as well as 0.5 mL internal standard solution (3.3.4) into a 10mL glass vial. Close and mix thoroughly. Transfer from each of the obtained 5.5 mL volume calibration solutions 1 mL portions into 3 e.g. 2mL glass vials (4.8) for GC autosamplers.

In this way a set of calibration solutions is obtained which allows triplicate determination per calibration concentration.

6.3.1.2 Test and blank samples

Pipette 0.5 mL internal standard solution (3.3.4) to each of the extraction solutions (6.2) and note down the mass IS. Close the vials and mix thoroughly. Transfer from each of the so obtained 5.5 mL volume extraction solutions 1 mL portions into 3 e.g. 2mL glass vials for GC autosamplers.

In this way a set of test sample (8 x 3) and blank sample (2 x 3) solutions is obtained which allows triplicate determination per extraction solution.

6.3.2 Gas chromatographic analysis

The test samples, blanks as well as calibration samples prepared in 6.3.1.1 and 6.3.1.2 are analysed as they are without any further treatment.

Three 1 mL replicates are analysed for each of the samples and blanks. Each of these three replicates is GC analysed (injected) once.

NOTE: When starting measurements, baseline stability and response linearity of the detector should be examined.

Gas chromatographic parameters:

For guidance, the parameters established for the selected column are given below:

Column:

30m length x 0.32mm internal diameter fused silica capillary e.g. DB-1 with a film thickness of 5µm

Detector temperature:	280°C
Injector temperature:	250°C
Injection volume:	2µL
Carrier gas:	H ₂
Column pressure:	66 kPa
Injection mode:	split flow 20mL/ minute

Oven programme:	initial temperature	80°C
	initial time	2 minute
	heating rate	15°C/ minutes
	final temperature	280°C
	final time	10 minutes

NOTE: The same GC conditions should be maintained throughout the measurements of all sample and calibration solutions.

Under these conditions, the retention time (in minutes) of the model substances were as follows:

Toluene	9.6
Phenol	14.1
Limonene	16.2
Menthol	18.9
Phenyl cyclohexane	21.9
Benzophenone	26.6
p-Xylene (int.stand.)	12.3

6.3.3 Calibration

Inject each of the three replicates of calibration samples as prepared in clause 6.3.1.1 one time into the GC column (one injection per vial). Measure the peak area of each model compound and the internal standard p-xylene. Divide the peak area of each model compound by the peak area of p-xylene. Calculate for each model substance the average of peak area ratio obtained from the three replicates of one calibration concentration as calculated in 3.3.3 and graphically plot peak ratios (PR) against the concentration of model compounds in the calibration samples in mg/g.

In this way six calibration curves, one for each model compound are obtained.

NOTE: The calibration curves should be rectilinear and the correlation coefficient should be 0.996 or better.[Minimum requirements will be defined later]

6.3.4 Evaluation of data

NOTE: The following calculations assume that for all measurements exactly in the same volumes of 95 % ethanol solutions have been used for sample preparation.

6.3.4.1 GC interferences

Following the method described, no interferences have been detected.

6.3.4.2 Calculation of model compound concentration in the test sample solutions (6.2)

NOTE: The following calculations do not take account of the dilution of the test samples achieved by the addition of 0.5 ml internal standard solution as prepared in 6.3.1.2. The calculated concentrations refer directly to the extraction solution obtained in 6.2.

Graphical determination

Calculate the average of peak area ratio (PR) values obtained from the test sample replicates according to 6.3.1.2 and read the model compound concentration of the test samples from the individual calibration graph of each model compound as obtained from 6.3.3.

Calculation from the regression parameters

If the regression equation of each model compound (mc) is

$$y_{mc} [\text{PR}] = a_{mc} * x_{mc} [\text{mg/g}] + b_{mc}$$

then the concentration of each model compound in 95% ethanol is

$$C_{mc} [\text{mg/g}] = (y_{mc} - b_{mc}) / a_{mc}$$

7 Expression of results

Express for each model compound the interactivity value as extracted amount (in mg) per square decimetre of test specimen taking both sides of the PET strip into account:

Calculation of the final interactivity values for the model compounds in mg/dm² is achieved as follows:

$$\text{Interactivity}_{mc} \left[\frac{\text{mg}}{\text{dm}^2} \right] = \frac{C_{mc} \left[\frac{\text{mg}}{\text{g}} \right] \cdot ES_{-m_{ae}} [g]}{A_{eff} [dm^2]}$$

NOTE: The effective surface area, A_{eff} , is normally around 0.11dm^2 (compare NOTES under 5.3).

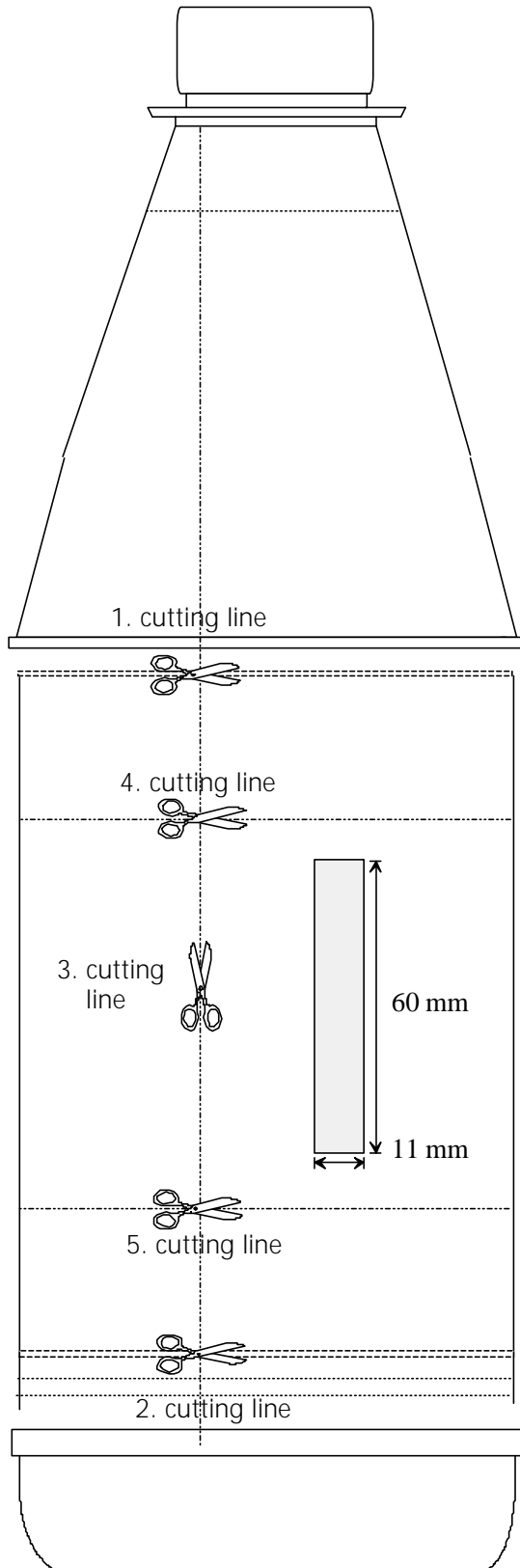
8 Test report

The test report shall include the following:

- a) reference to this method [standard];
- b) all information necessary for complete identification of the sample;
- c) departures from the specified procedure, and reasons for these;
- d) individual test results for each sample and model compound (mc), and the mean of these, expressed as $\text{interactivity}_{\text{mc}}$ in milligrams of model compound per square decimetre of sample;
- e) relevant comments on the test results.

Annex A:

Figure: Cutting diagram for a refillable PET bottle



Annex B: Bibliography

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Acknowledgements

Whenever you start to work scientifically you have to rely on the professional as well as moral support of colleagues, professors, family and friends.

Therefore I would like to thank heartily all my colleagues at the Fraunhofer Institute for Process Engineering and Packaging for always supporting and encouraging me during the time of my work at the FhGIVV.

I especially like to thank Dr. R. Franz for the provision of the subject and the varied scientific support of my PhD thesis.

I also like to thank M. von Bergmann for never stop asking „When will you eventually finish your PhD thesis?“.

I would further like to thank Prof. G. Cerny and Prof. H. Weisser for scientifically accompanying the PhD thesis at the Technical University of Munich and the conscientious proof-reading of the work.

Within my family I really have to be grateful for the endless baby-sitting hours of my mother and the great humour and staying power of my husband Stefan.

Furthermore, I would like to acknowledge the financial support of this work by the European Commission within the framework of project SMT4-CT96-2129.

