EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

Certification of a refillable PET bottle material with respect to chemical inertness behaviour according to a pr-CEN standard method

BCR-712

R. Franz, G. Palzer, B.M. Gawlik, A. Bernreuther,
A. Lamberty, D. Bennink

Report EUR 21075

The mission of IRMM is to promote a common European measurement system in support of EU policies.

European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

Tel.: +32 (0)14 571 211
Fax: +32 (0)14 590 406

http://www.irmm.jrc.be
http://www.jrc.cec.eu.int

EUR Report 21075
Luxembourg: Office for Official Publications of the European Communities

ISBN 92-894-7220-0

Printed in Belgium

European Commission

BCR information
REFERENCE MATERIALS

Certification of a refillable PET bottle material with respect to chemical inertness behaviour according to a pr-CEN standard method

BCR-712

R. Franz, G. Palzer

Fraunhofer Institute for Process Engineering and Packaging (Fraunhofer IVV)
Department of Product Safety and Analysis
D-85354 FREISING (Germany)

B.M. Gawlik, A. Bernreuther, A. Lamberty

European Commission DG Joint Research Centre
Institute for Reference Materials and Measurements
B-2440 GEEL (Belgium)

D. Bennink

European Commission, DG RTD
Standards, Measurements and Testing, CEC
B-1049 BRUSSELS (Belgium)

Report EUR 21075 EN

Institute for Reference Materials and Measurements

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

ABSTRACT

A standardised and easy-to-apply method for general chemical inertness testing of refillable PET bottles was developed. It is applicable not only for the industry but also suitable for enforcement laboratories having for the first time a systematic control possibility to check the food safety of refilled PET bottles taken from the market. This chemical inertness test covers the sum of possible mechanical stress influences on the inertness behaviour of a PET material and, in case of complaint, allows 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.

In addition, a food grade reference PET material was prepared which fulfils the principle requirement of article 2 of the Framework Directive 89/109/EEC (1). This reference material was certified with respect to its interactivity values as shown below. Certified values were accompanied by an expanded uncertainty according to the requirements laid down in the Guide for the Expression of Uncertainty in Measurement (GUM) (2).

Certified values of BCR-712. Chemical inertness⁽¹⁾ expressed in mg/dm^2

Analyte	*Mean⁽²⁾*	*Uncertainty⁽³⁾*
Toluene	7.3	0.6
Phenol	4.1	0.5
Limonene	3.9	0.5
Menthol	1.78	0.18
Phenylcyclohexane	3.5	0.4
Benzophenone	5.6	0.6

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

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

(3) Expanded uncertainty with a coverage factor of k=2 according to the GUM (2).

LIST OF ABBREVIATIONS AND SYMBOLS

ae	after extraction
A_{eff}	effective area
ANOVA	Analysis of variance
BCR	Community bureau of reference
CRM	Certified reference material
CV	Coefficient of variation
CV %	Coefficient of variation in per cent
ES	Extraction solvent
FDA	US Food and Drug Administration
FID	Flame Ionisation Detector
GC	Gas chromatography
H.W.	half-width
ILSI	International Life Sciences Institute
k	coverage factor
L	Laboratory
mc	model compound
m_{ce}	mass with cut edges
m_S	mass after sorption
n	number of replicates
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
RM	reference material
RT	room temperature (+20 °C)
SD	Standard deviation
S_w	Standard deviation within units
S_b	Standard deviation between units
TB	Test batch
u_{bb}	uncertainty contribution for the inhomogeneity included in U_{CRM}
u_{char}	uncertainty contribution for the batch characterisation included in U_{CRM}
u_{sts}	uncertainty contribution for the short-term stability of the material (transportation, not included in U_{CRM})
u_{lts}	uncertainty contribution for the long-term stability of the material (storage) included in U_{CRM}
U_{CRM}	expanded uncertainty of the certified value
v/v	volume per volume
$\bar{x}$	mean

TABLE OF CONTENTS

1. INTRODUCTION

1.1 Background and need for BCR-712

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. Therefore the increasing demand for bottles of PET inevitably led to the optimisation of existing production processes.

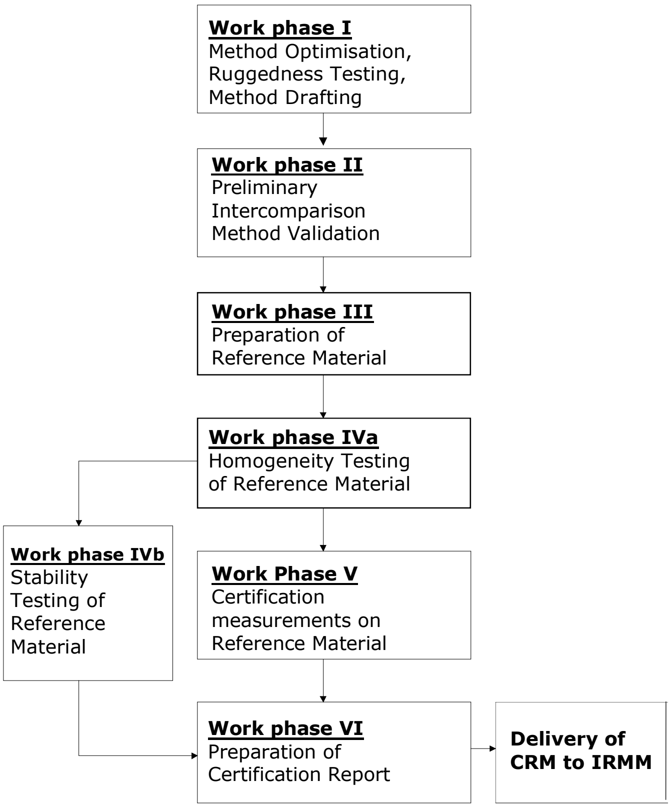
Due to the stability of the material the multi-use system of PET bottles is common in many countries. The robustness of PET material is one reason that beverage bottles can achieve high circulation rates between the bottler and the consumer. The use of a rugged material, however, cannot rule out the 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 re-migrate 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 was 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 project (3) 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 systematic control possibility to check the food safety of refilled PET bottles taken from the market. This report describes the development and application of a chemical inertness test procedure, to be implemented as CEN-Standard (4) as well as the production of a Certified Reference Material (BCR-712) 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.

1.2 Choice of the material for BCR-712

The material should be a food grade reference PET material which already fulfils the principal requirement of article 2 of the Framework Directive 89/109/EEC (1) and certifiable as a reference with respect to its interactivity values. The most common form of PET bottles on the market is the refillable 1.5 litre bottle. For the production of a certified 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). The shape of the bottle was chosen in such a manner that the brand of the BCR-712 PET couldn't be detected after the production and preparation of the CRM.

1.3 Design of the project and the certification procedure

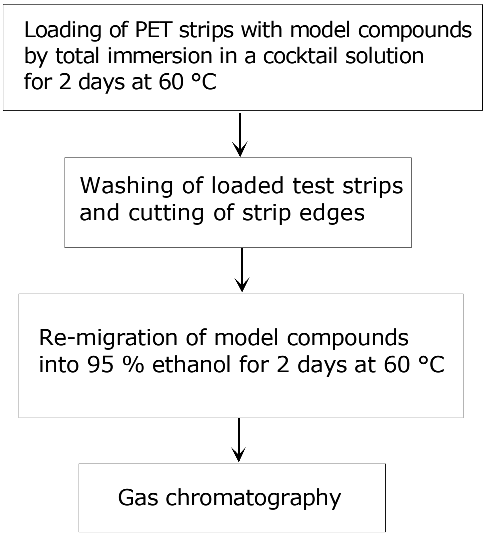
The following Scheme 1-1 shows the design and structure of the certification procedure applied.



Scheme 1-1 - Flow chart of the work phase sequence of the certification procedure

The main activities in work phase I were the modification, optimisation and simplification of the chemical inertness test method already developed in a previous EU project (5) and therefore to establish a practical and easy-to-apply test procedure for refillable PET bottles with respect to the chemical inertness interactivity. On the basis of the drafted method a first ruggedness testing was carried out. Producing a first test batch of reference PET bottles and carrying out a preliminary intercomparison between six laboratories a feasibility study was performed in work phase II. According to test results obtained within work phase II the chemical inertness test procedure was further optimised and validated. Scheme 1-2 describes the process of the finalised chemical inertness test procedure.

The PET inertness test simulates the misuse of a plastic bottle by loading the PET material with 6 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 principal idea of a chemical inertness test was to simulate the possible real life interaction of refillable PET bottles with chemical compounds by using one "cocktail" solution of model compounds with different chemical and physical properties. Interactivity processes between the PET material and the chemical model compounds can be achieved by contacting PET bottle wall strips with a mixture of model compounds under defined standard conditions, thus "loading" PET test material. After a defined sorption phase of 2 days at 60 °C a re-migration phase with immersion of loaded PET strips into a food simulant was carried out. The concentrations of the model compounds are finally determined by gas chromatography.



Scheme 1-2 - Chemical inertness test

In the following work phase III the certified reference material batch was produced. During work phase IV a homogeneity as well as a stability study was carried out with the reference material batch to be certified. After performing the homogeneity study in work phase IVa a certification exercise within 10 laboratories was carried out. Based on the test results obtained in work phase IV and V a statistical evaluation led to certified values of the BCR-712 in work phase VI.

1.4 Expression of results

The chemical inertness test results for all six model compounds of the test procedure are expressed in (mg/dm^2) as specified in the chemical inertness method as shown in Appendix I.

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 final interactivity values for the model compounds in mg/dm^2 are calculated from:

$$Interactivity_{mc} = \frac{x_{mc} \cdot m_{ae}^{ES}}{A_{eff}}$$

where

$Interactivity_{mc}$ [mg/dm^2]	extracted amount of model compound in mg per square decimetre of a PET test strip taking both sides into account;
x_{mc} [mg/g]	mass fraction of model compound (mc) in mg/g in 95 % Ethanol (extraction solvent) evaluated by GC analysis;
A_{eff} [dm^2]	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} [g]	mass of extraction solvent (ES) 95 % Ethanol in g after the extraction phase of PET strips after extraction (ae).

2. PARTICIPANTS

2.1 Preparation of the reference material

- Fraunhofer Institute for Process Engineering and Packaging, Freising DE
- Schmalbach Lubeca PET Container Deutschland GmbH, Mendig DE

2.2 Homogeneity and stability studies

- Fraunhofer Institute for Process Engineering and Packaging, Freising DE
- University of Ioannina, Department of Chemistry, Section of Industrial and Food Chemistry, Ioannina GR

2.3 Analyses within the preliminary interlaboratory studies

- Fraunhofer Institute for Process Engineering and Packaging, Freising DE
- Ministry of Agriculture, Fisheries and Food, Central Science Laboratory Food Science Laboratory, Norwich UK
- Pira International, Leatherhead, UK
- Swedish Institute for Food Research - SIK, Gothenburg SE
- The Netherlands Organisation of Nutrition and Food Research, TNO, Zeist NL
- University of Ioannina, Department of Chemistry, Section of Industrial and Food Chemistry, Ioannina GR

2.4 Analyses within the certification exercise

- Fraunhofer Institute for Process Engineering and Packaging, Freising DE
- Swedish Institute for Food Research - SIK, Gothenburg SE
- University of Ioannina, Department of Chemistry, Section of Industrial and Food Chemistry, Ioannina GR
- The Netherlands Organisation of Nutrition and Food Research, TNO, Zeist NL
- FABES, Munich DE
- Pira International, Leatherhead UK
- Istituto Superiore di Sanità, Laboratorio di Tossicologia Applicata Reparto Materiali di Interesse Sanitario, Rome IT
- VTT Biotechnology and Food Research, Espoo FI
- Danish Veterinary and Food Administration, Institute of Food Research and Nutrition, Division of Chemical Contaminants, Søborg DK
- Wageningen Agricultural University, Department of Food Technology & Nutritional Sciences, Wageningen NL

2.5 Statistical analysis

- Fraunhofer Institute for Process Engineering and Packaging, Freising DE
- European Commission, DG RTD, SM&T Programme (SMT), Brussels BE
- European Commission, DG JRC, IRMM, Geel BE

3. FEASIBILITY STUDY OF CHEMICAL INERTNESS TESTING

3.1 Preliminary stability tests

In the beginning, two test batches of PET bottles were produced to establish the stability of the PET bottle material as well as to study the feasibility of producing a PET bottle material as reference material itself. For the better understanding of test results as well as distinguishing of preliminary exercises before the stability testing of the BCR-712 the following Table 3-1 summarises the codes of different test batches of PET bottles produced within the project.

Table 3–1 - PET batches produced within the Project

Code of test batch (TB)	
TB [1]	Test batch of approx. 150 PET bottles produced in January 1998
TB [2]	Test batch of approx. 100 middle parts of PET bottles produced and cut out in June 1998
BCR-712	Reference material batch of 2300 PET bottles produced on 13th of July 1999 for certification.

The chemical inertness test procedure is carried out with six model compounds by exposing the material to a mixed cocktail solution (toluene, phenol, limonene, menthol, phenylcyclohexane and benzophenone) and measuring of the re-migration into a food simulant. The CAS numbers as well as the purity of model compounds used within the chemical inertness test procedure are listed in Table 3-2.

Table 3–2 - Model compounds used within the chemical inertness test

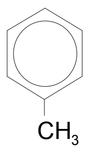
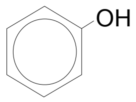
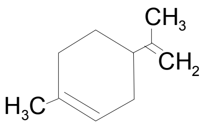
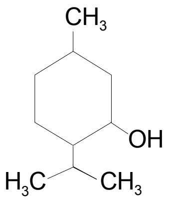
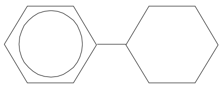
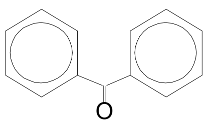
Model compound	*CAS No.*	*Purity*
Toluene	108-88-3	> 99.5 %
Phenol	108-95-2	> 99 %
Limonene	5989-27-5	98 %
Menthol	89-78-1	99 %
Phenylcyclohexane	827-52-1	98 %
Benzophenone	119-61-9	> 99 %

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.

Table 3–3 - Chemical properties of model compounds

Model compound	*Molecular mass*	*Properties*
Toluene 	92	hydrocarbon, volatile, non-polar, aromatic Toluene is widely used in adhesives and dyes and is also a constituent of automotive products and motor oils
Phenol 	94	alcohol, volatile, polar, aromatic Phenol is used as constituent of disinfectants and is highly aggressive towards the PET polymer structure
Limonene 	136	hydrocarbon, non-polar 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.
Menthol 	156	alcohol, polar Menthol is widely used as constituent of numerous hygiene products due to its antiseptic properties.
Phenyl cyclohexane 	160	hydrocarbon, non-volatile, non-polar, aromatic Substance proposed by ILSI-Europe for application as a model compound in Challenge tests
Benzophenone 	182	ketone, non-volatile, non-polar, aromatic Substance proposed by the FDA and ILSI for application as a model compound in Challenge tests

The inertness of a PET material depends on material properties like e.g. molecular mass distribution or crystallinity. 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.

3.1.1 Parameters affecting chemical inertness test results of stability studies

The first test batch TB [1] of approximately 150 bottles was produced in January 1998 while the second test batch TB [2] of approximately 100 cut out middle parts of PET bottles was produced half a year later in 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 PET inertness tests were carried out with both test batch materials to compare the chemical inertness behaviour of the PET bottles. The results of the investigation are shown in Figure 3-1.

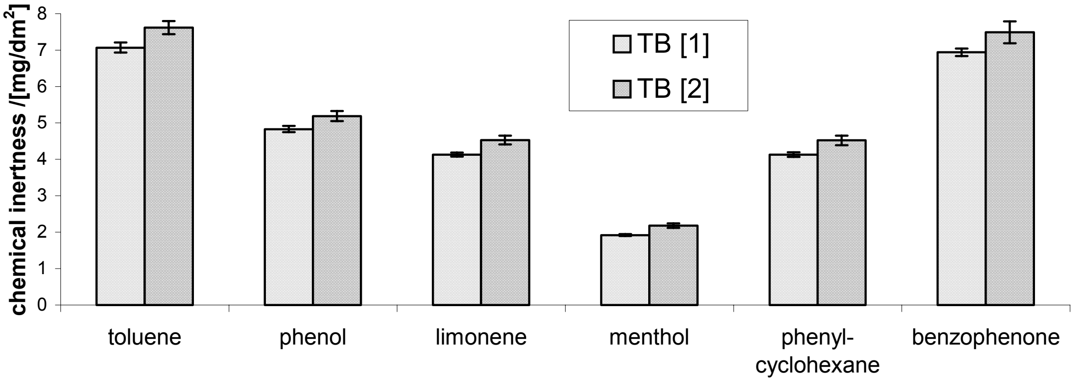


Figure 3–1 - Comparison of chemical inertness test results of TB [1] and TB [2]

The investigation of the chemical inertness behaviour of bottles out of test batch TB [1] and TB [2] showed that bottles out of test batch TB [2] 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

- differences between one phase (direct from granulate to bottle) or two phase (first preform, than bottle) production of bottles;
- differences in the temperature profiling and programme during the moulding process of a bottle and therefore;
- differences in the crystallinity as well as amount of amorphous areas;
- the polymer properties;
- the residual amount of monomers as well as additives.

The difference of test batch TB [1] and TB [2] 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 TB [2] 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 TB [2] and TB [1] 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 newly produced 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 could be shown that the PET material of test batch TB [2] reached a steady state concerning the chemical inertness behaviour after a storage of at least two 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).

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 of test batch TB [2] reached constancy as clearly shown in Figures 3-2 to 3-7. The results presented are normalised to chemical inertness test results obtained for freshly produced bottles of TB [2] without storage at 60 °C. The continued line at 1.0 represents by definition the initial interactivity, the dotted line shows the mean value after equilibration.

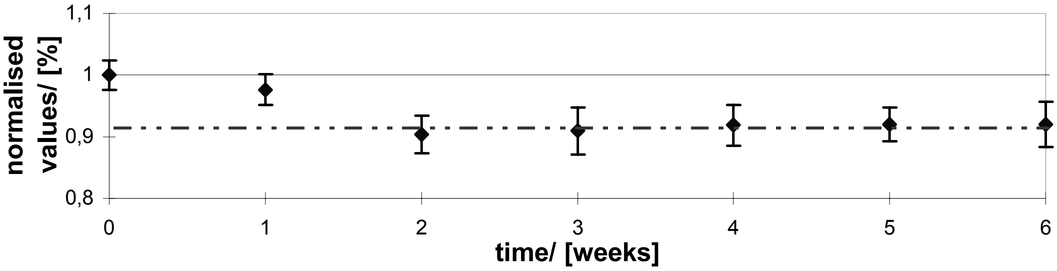


Figure 3–2 - Evaluation of the temperature stability of PET bottles at 60 °C with respect to chemical inertness interactivity of toluene normalised to the initial value at time zero (n = 6)

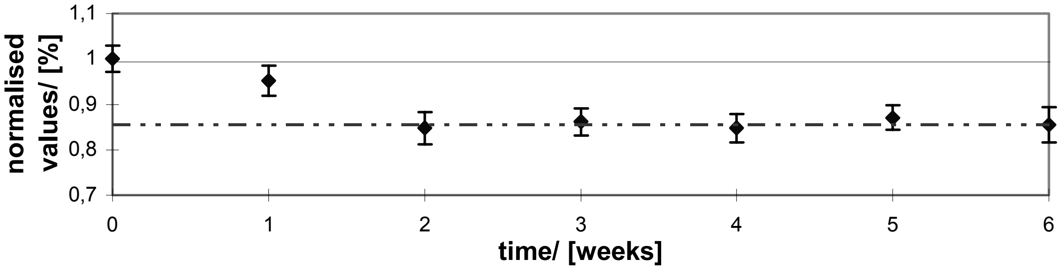


Figure 3–3 - Evaluation of the temperature stability of PET bottles at 60 °C with respect to chemical inertness interactivity of phenol normalised to the initial value at time zero (n = 6).

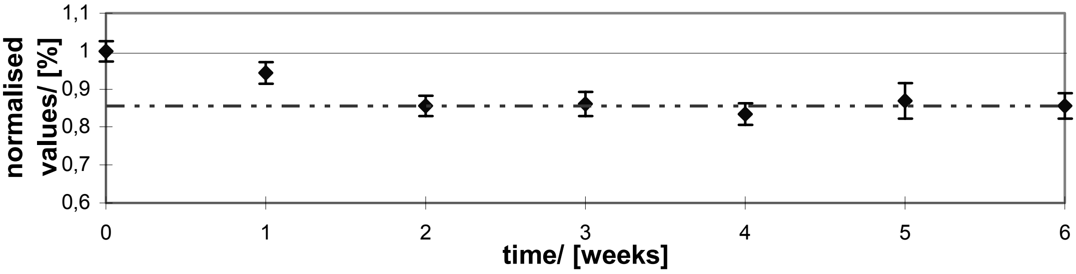


Figure 3–4 - Evaluation of the temperature stability of PET bottles at 60 °C with respect to chemical inertness interactivity of limonene normalised to the initial value at time zero (n = 6).

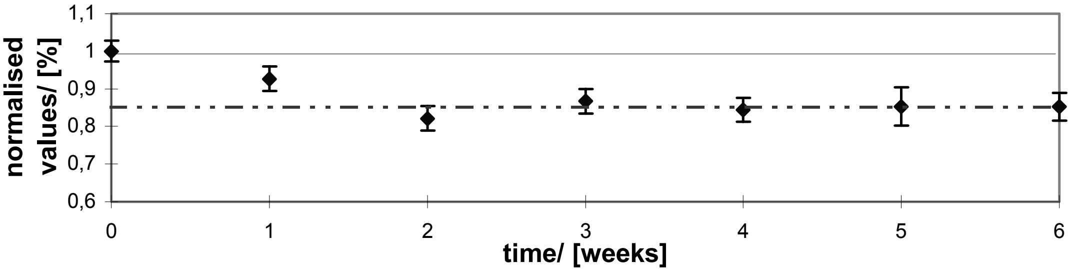


Figure 3–5 - Evaluation of the temperature stability of PET bottles at 60 °C with respect to chemical inertness interactivity of menthol normalised to the initial value at time zero (n.= 6)

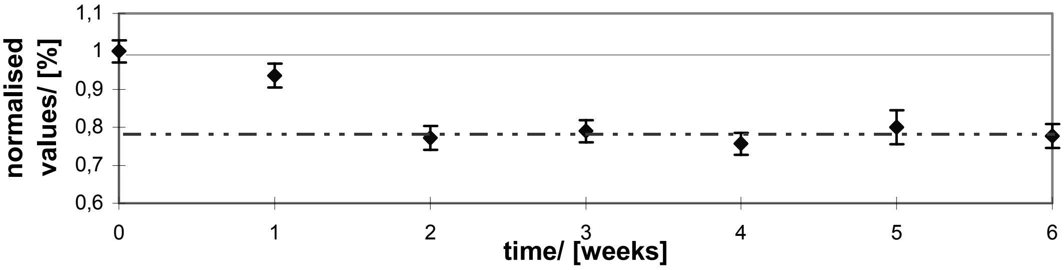


Figure 3–6 - Evaluation of the temperature stability of PET bottles at 60 °C with respect to chemical inertness interactivity of phenyl cyclohexane normalised to the initial value at time zero (n = 6)

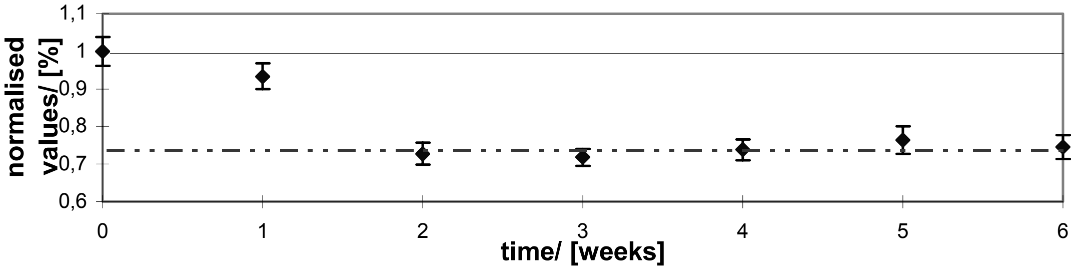


Figure 3–7 - Evaluation of the temperature stability of PET bottles at 60 °C with respect to chemical inertness interactivity of benzophenone normalised to the initial value at time zero (n = 6)

The consequence for the production of a reference material batch was that the PET bottles had to be conditioned for two weeks at 60 °C to make sure that *relaxation processes* were accelerated and therefore the chemical inertness behaviour of the material reached a steady state.

The stability testing of test batches TB [1] was furthermore carried out in a way that bottles out of TB [1] 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 then an additional storage at 60 °C would not influence the chemical inertness behaviour at all.

The following Table 3-4 summarises the storage conditions of PET bottles out of test batch TB [1]

Table 3–4 - Structure of the stability testing of PET bottles out of test batch TB [1] carried out in the course of investigations of work phase II

	No.	*Date of analysis*	*storage condition*
TB [1]	1	Sept. 1998	room temperature
	2	January 1999	room temperature + 7d/60 °C
	3	January 1999	room temperature + 7d/60 °C
	4	January 1999	room temperature + 14d/60 °C
	5	January 1999	room temperature + 14d/60 °C
	6	January 1999	room temperature + 21d/60 °C
	7	January 1999	room temperature + 21d/60 °C
	8	January 1999	room temperature + 28d/60 °C
	9	January 1999	room temperature + 28d/60 °C
	10	March 1999	room temperature
	11	February 1999	room temperature + 7d/60 °C
	12	March 1999	room temperature + 14d/60 °C
	13	March 1999	room temperature + 21d/60 °C
	14	March 1999	room temperature + 28d/60 °C
	15	March 1999	room temperature + 35d/60 °C
	16	March 1999	room temperature + 42d/60 °C
	17	April 1999	42d/60 °C + 28d at room temperature
	18	April 1999	42d/60 °C + 56d at room temperature

The following Figures 3-8 to 3-11 show the chemical inertness test results of PET bottles out of TB [1] after different storage conditions and times normalised to test results obtained from bottles of TB [1] in September 1998. TB [1] was produced in January 1998 so that the PET bottles were already nine months old.

It should be noted here that at analysis numbers 12, 17 and 18 slight technical deviations from the described procedure were made which explain the outlying values for the substance menthol. Test results of the preliminary stability testing were accepted when test results achieved comparable results to those of the preliminary intercomparison with a maximum reproducibility range (on a 95 % probability level) of 20 to 25 %.

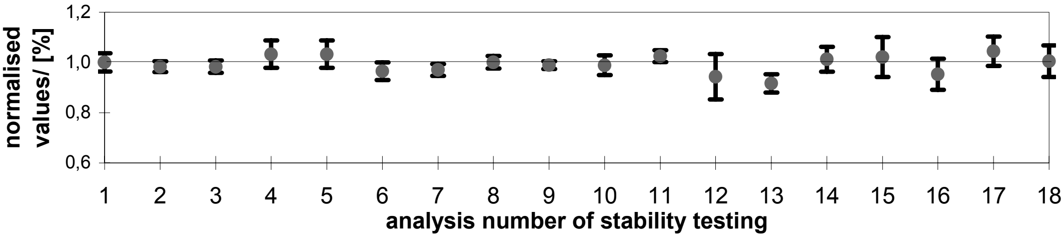


Figure 3–8 - Results of toluene obtained during the preliminary stability study of the PET bottle material normalised to values of PET bottle no. 1.

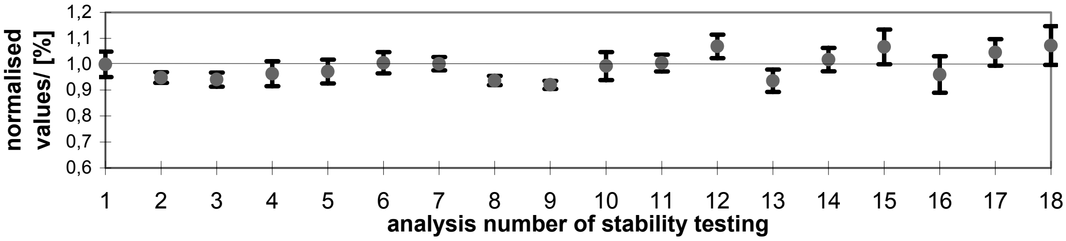


Figure 3–9 - Results of phenol obtained during the preliminary stability study of the PET bottle material normalised to values of PET bottle no. 1.

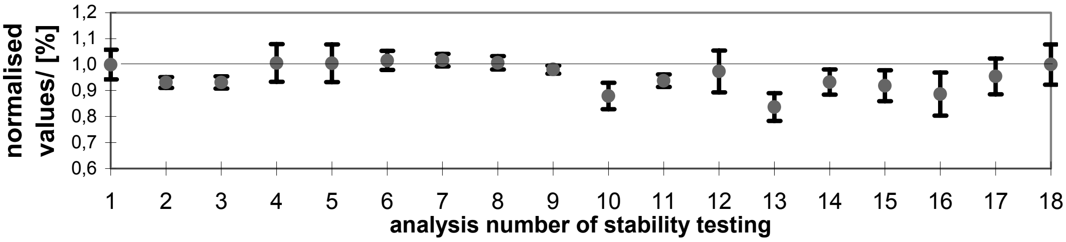


Figure 3–10 - Results of limonene obtained during the preliminary stability study of the PET bottle material normalised to values of PET bottle no. 1.

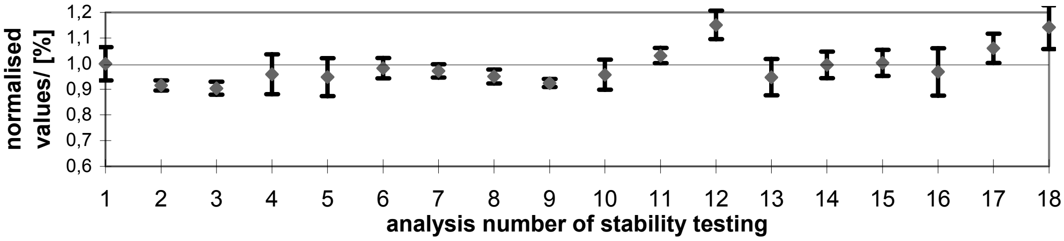


Figure 3–11 - Results of menthol obtained during the preliminary stability study of the PET bottle material normalised to values of PET bottle no. 1.

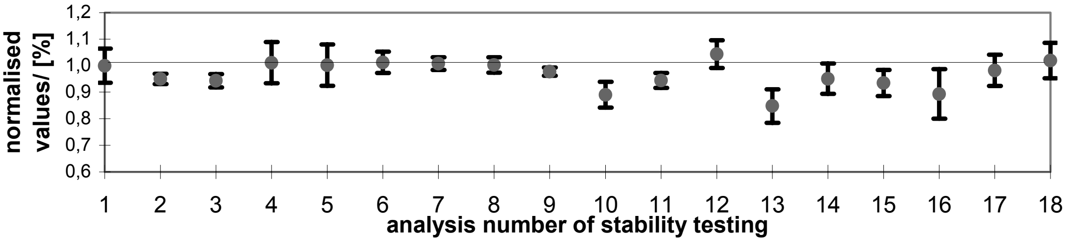


Figure 3-12: Results of phenyl cyclohexane obtained during the preliminary stability study of the PET bottle material normalised to values of PET bottle no. 1.

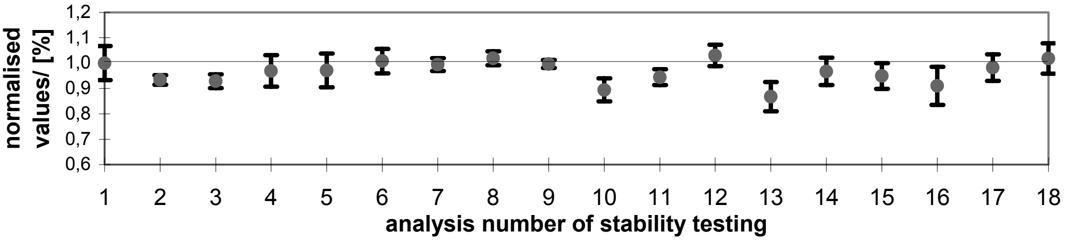


Figure 3–12 - Results of benzophenone obtained during the preliminary stability study of the PET bottle material normalised to values of PET bottle no. 1.

According to test results of preliminary interlaboratory testing the following CVs of the chemical inertness method could be established for each of the six model compounds:

Table 3–5 - Coefficients of variation for model compounds of the chemical inertness test method according to results of preliminary stability testing

Model compound	*CV [%]*
Toluene	3.01
Phenol	4.94
Limonene	5.22
Menthol	6.46
Phenylcyclohexane	6.36
Benzophenone	6.74

3.1.2 Conclusions

According to the production process of 1.5 L multi-use PET bottles the homogeneity as well as stability of the PET material can be expected. Test results of bottles out of TB [1] and TB [2] showed that 1.5 L refillable PET bottles out of different batches produced in the same way show comparable test results ($t_{0.95}$ - test) after a conditioning phase of newly produced PET bottles for 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 TB [1] and TB [2] it can be assumed that the reference material to be certified also reaches a homogenous as well as stable state after conditioning of the material.

3.2 Preliminary interlaboratory testing

The objective of the preliminary intercomparison which included six laboratories (L1 – L6) was to achieve a further method validation and also to obtain acceptance criteria which could be applied in the certification exercise. Prior to the preliminary intercomparison study the drafted method and reporting sheets were made available to each of the participants L1 to L6.

For this exercise, PET bottles were chosen at random out of test batch TB [1]. From the chosen PET bottles top and bottom parts were cut off to obtain the cylindric middle parts which then were cut vertically into two half-cylinders. The two half-cylinders from one bottle were stacked into one another and packed into aluminium foil. Each of the six participating project partners L1 to L6 obtained four of these sample packages. Each sample was labelled identifying test batch and sample number.

Each project partner had to carry out the inertness test in the order of increasing bottle numbers examining the samples in two separate test runs each on a pair of samples. Start of both test runs was in time separated by several days. It was required to follow precisely the instructions of the drafted chemical inertness method. For the reporting of test results test protocol sheets were designed.

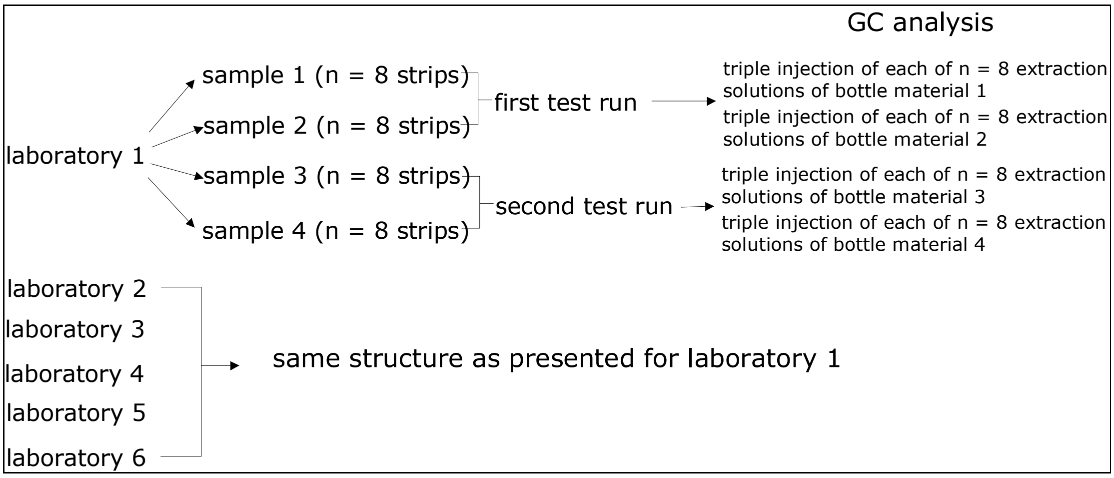


Figure 3–13 - Overview of test protocol

Before starting the intercomparison exercise, the analytical competence of the participating laboratories was checked by the analysis of an unknown solution prepared by the project co-ordinator. The value obtained for the concentration was a single reported value.

Table 3-6 shows that five laboratories were able to determine the nominal amount of model compounds in the unknown solution. Laboratory L3 did not analyse the extract because of too much labour in the laboratory at the time when the spiked solution was sent to the participants.

Table 3–6 - Results of the analysis of an unknown solution of model compounds before the preliminary interlaboratory testing

Extract mass fraction/ [µg/g]	*nominal*	*L1*	*L2*	*L6*	*L4*	*L5*
Toluene	239	235	244	240	236	239
Phenol	139	142	142	146	149	147
Limonene	144	143	147	146	147	147
Menthol	134	136	140	133	143	140
Phenylcyclohexane	90	87	88	92	89	90
Benzophenone	183	180	182	189	189	189

3.2.1 Test results of the preliminary interlaboratory testing

The following Figures 3-14 to 3-19 present normalised means of 10 data sets consisting each of 8 individual test results (8 strips from one bottle) with their standard deviation. The results are normalised to the statistically evaluated overall mean of the 10 data sets.

Within the project [2] it was defined that the participants should achieve comparable results with a maximum reproducibility (between laboratories) range of 20 to 25 % on a 95 % probability level as well as a maximum repeatability (within laboratory) range of 15 % to 20 %. This precondition was achieved for each of the six model compounds.

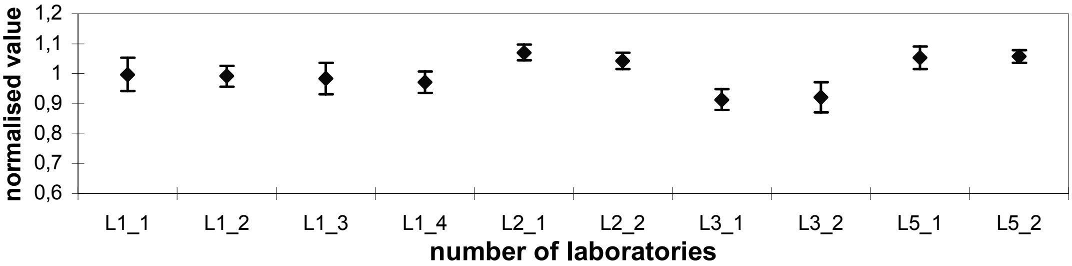


Figure 3–14 - Results of preliminary interlaboratory testing for the model compound toluene normalised to the statistically evaluated overall mean of the 10 data sets (Lab x_sample y).

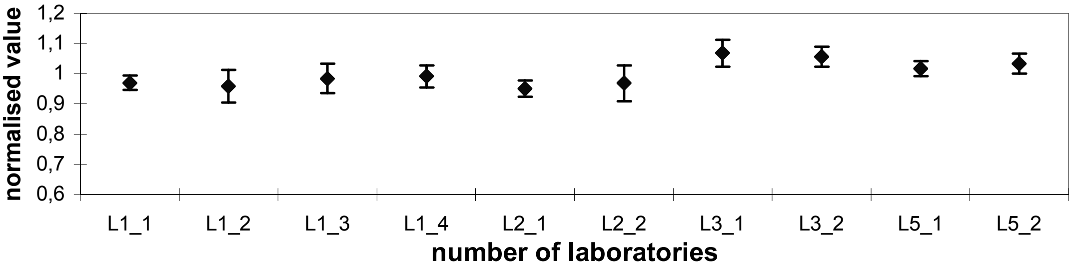


Figure 3–15 - Results of preliminary interlaboratory testing for the model compound phenol normalised to the statistically evaluated overall mean of the 10 data sets (Lab x_sample y).

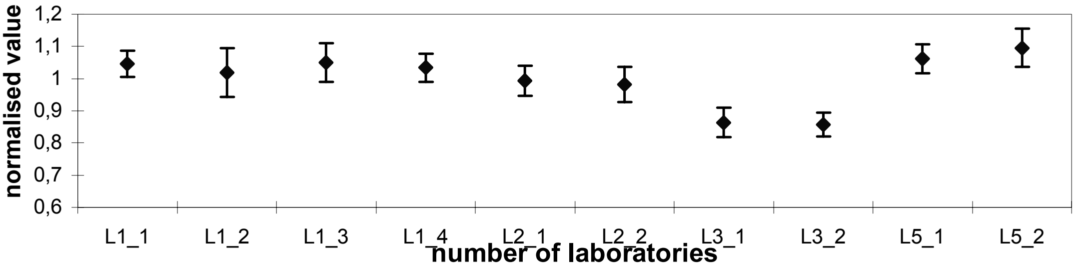


Figure 3-16: Results of preliminary interlaboratory testing for the model compound limonene normalised to the statistically evaluated overall mean of the 10 data sets (Lab x_sample y).

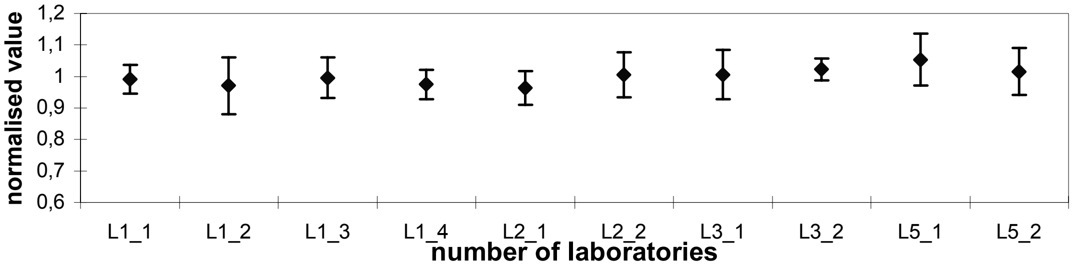


Figure 3–16 - Results of preliminary interlaboratory testing for the model compound menthol normalised to the statistically evaluated overall mean of the 10 data sets (Lab x_sample y).

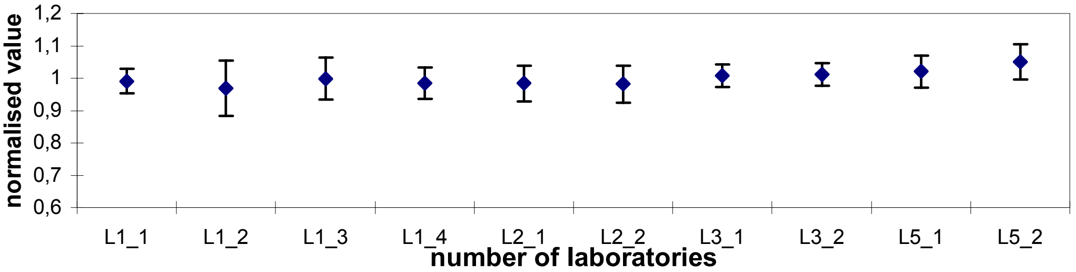


Figure 3-18: Results of preliminary interlaboratory testing for the model compound phenyl cyclohexane normalised to the statistically evaluated overall mean of the 10 data sets (Lab x_sample y).

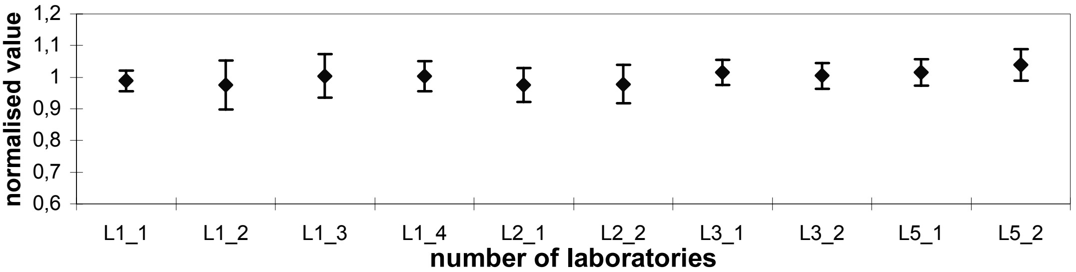


Figure 3–17 - Results of preliminary interlaboratory testing for the model compound benzophenone normalised to the statistically evaluated overall mean of the 10 data sets (Lab x_sample y).

Results from laboratories with deviations from the prescribed procedure were discarded for technical reasons not on statistical considerations.

For the statistical evaluation 10 acceptable data sets were available with 79 replicates altogether for each model compound. For all six model compounds both variances and mean values did not show any outliers. Variances of all model compounds were homogeneous and test results normal distributed.

3.2.2 Conclusions

According to test results of the preliminary interlaboratory testing the method was fit for purpose and could be further validated.

4. PREPARATION OF THE MATERIAL

The Polyethylene terephthalate (PET) 1.5 L multi-use bottles from which the reference material was obtained were manufactured under the supervision of the project co-ordinator 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 as well as approximately 300 additional bottles for homogeneity, stability and certification measurements it was necessary to produce three pallets à 1008 PET bottles due to fixed machinery adjustments.

The 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 (see Figure 4-1). At the end of the sampling 10 control batches of 16 bottles each were available.

At the end of the production line the bottles were stored on pallets and numbered in the order of their production. In that way 3 pallets of 7 stages of 144 bottles were produced. The pallets were numbered according to their production number of the day with 48, 49 and 50. Respectively, the stages on the pallets 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 pallet number xx with zzz from 001 to 144, y from 1 to 7 and xx from 48 to 50.

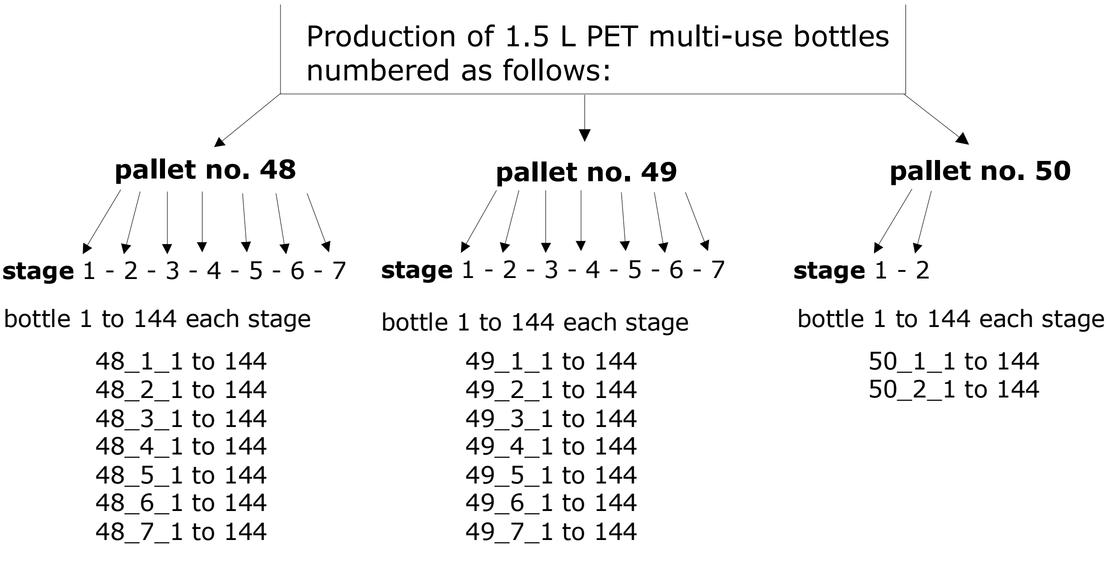


Figure 4–1 - Overview of BCR-712 batch production

The bottles were stored until end of July 1999 at ambient temperatures (from 16 °C to 25 °C) and then conditioned (the whole pallet 48, 49 as well as stages 50_1 and 50_2) in a horizontal position in a climate chamber for two weeks at 60 °C to accelerate *relaxation processes* of the PET material as described in detail under chapter 6 Stability testing. During the conditioning phase of the PET bottles at 60 °C the temperature was measured every hour and recorded. After conditioning the PET bottles were stored again at ambient temperature (19 °C to 25 °C).

In September 1999, the project co-ordinator developed a cutting implement with which the middle part cylinder of the 1.5 L PET bottle was cut out mechanically in order to make the bottle design and brand anonymous as well as to save space.

The bottle wall cylinders as the final shape of the reference material were canned into tin cans of 800 ml volume under nitrogen flow in September/ October 1999. The reference material samples as well as the cans were labelled with the production number of the PET bottle. Afterwards the cans with the reference material were stored at ambient temperatures (15 °C to 25 °C).

The PET bottles of stages 50_3 to 50_7, which were not needed, were kept on stock in case that something went wrong during the production of the reference material until packaging and were later on discarded. The essential stages in the preparation of the BCR-712 are detailed and summarised in Table 4-1.

Table 4–1 - The essential stages in the preparation of BCR-712

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 [I]	After control 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.
Preparation of cyclindric of bottle middle parts	In order to preserve the anonymity of the bottle design and brand the cylindric middle parts of the PET bottles walls were cut out mechanically using a suitable cutting implement.
Packing	Each PET bottle wall cyclinders was packed into a can under a nitrogen flow. A quantity of about 2000 units are available for sale.
Homogeneity testing [II]	The homogeneity testing of control batch no. 4 which consists of materials from 16 bottles was established after packaging.
Storage	The packaged material was stored at ambient temperatures. (15 °C to 25 °C)

5. HOMOGENEITY TESTING

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 control sampling was carried out for the homogeneity testing. Before the start of the control sampling someone was posted at the end of the production line. When the first twelve PET bottles were put on the first stage of pallet number 48 a sign was given. At this time the control 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 in their production order while the other reference PET bottles produced were packed on three following pallets at the end of the assembly line. At the end of the sampling 10 control batches of 16 bottles each were available. Figure 5-1 shows the scheduled structure of the control sampling for the homogeneity study I.

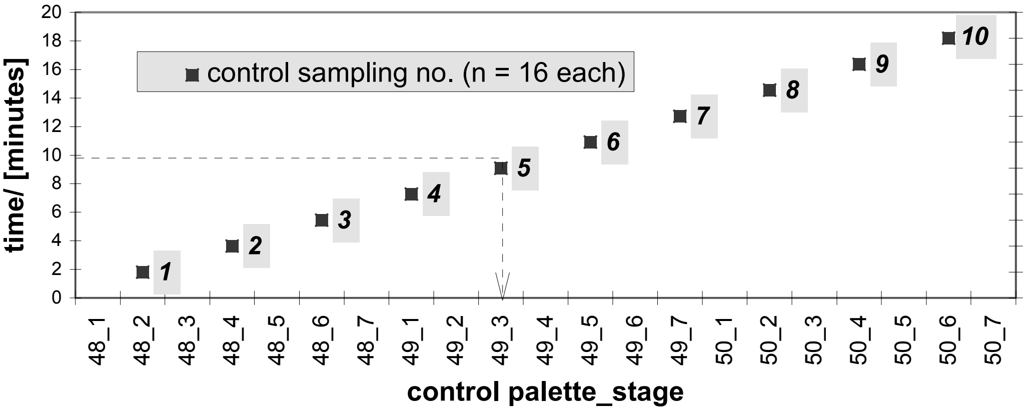


Figure 5–1 - Structure of control sampling for homogeneity testing during the production of reference material bottles (the dotted line for example indicates that after 10 minutes pallet stage 49_3 was produced from which the control sampling batch no. 5 consisting of 16 bottles was taken).

On the day of production the bottle masses of the control batch samples no.s 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 control sampling no. 4 was carried out to check the between- and within-unit homogeneity regarding the chemical inertness behaviour of the material.

5.1 Homogeneity testing [I] of control batch samples 1 to 10 during the production

The homogeneity of BCR-712 was studied 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.

5.1.1 Measurement of homogeneity concerning the mass of a PET bottle

Table 5-1 presents individual test results of the mass of PET bottles out of sample batches no.s 1 to 7 which were relevant for the produced reference PET bottles of pallets 48_1 to 50_2 of the production. The above presented Figure 5-1 describes the sampling structure of sampling 1 to 7 each consisting of 16 PET bottles. Samples were analysed in the order of sample 1 to sample 7. Within a given sample batch the mass of individual bottles was determined in the order of bottle 1 to bottle 16.

Table 5–1 - Mass [g] of control sampling 1 to 7 during the production of BCR-712 (n = 16)

	Sampling batch						
	1	2	3	4	5	6	7
Mean	105.56	105.59	105.55	105.55	105.50	105.58	105.57
± SD.	0.10	0.08	0.09	0.09	0.09	0.09	0.10
CV %	0.097	0.076	0.088	0.088	0.082	0.085	0.099

Table 5-1 confirms that PET bottles from control sampling 1 to 7 were homogenous concerning the material mass of the PET bottles. The resolution of the balance was ± 0.01 g.

5.1.2 Measurement of homogeneity concerning material thicknesses

Measurements were carried out directly after the production to determine the bottle wall thickness of each of the 160 PET bottles at different heights. Table 5-2 shows the bottle wall thickness of a multi-use 1.5 L PET bottle at different heights as the average of 160 individual PET bottle results.

Table 5–2 - PET bottle wall thickness at different heights of a 1.5 L multi-use PET bottle (n = 160)

height in mm	*material thickness in mm*	*± sd*	*CV %*
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 the 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 5-3 shows statistically evaluated test results for the bottle wall thickness at height 110 mm for control sampling no. 1 to 7 out of the production of reference PET bottles.

Table 5–3 - Material thickness at height 110 mm of 1.5 L multi-use PET bottles (n = 16)

control sample batch no.	*mean in mm*	*± sd*	*CV %*
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

5.1.3 Conclusions

No significant difference (F-Test) at the 95 % confidence level was found between mass as well as material thickness results at height 70 mm to height 165 mm. Therefore the BCR-712 PET shows no significant ($F_{0.95}$ - test) material inhomogeneity between units.

The raw data of the homogeneity study, which are compiled in Annex III were used to derive at an estimate of the uncertainty source "material homogeneity". This estimate was included in the expanded uncertainty of the certified values. For the statistical background of this operation refer to Chapter 8.

6. STABILITY TESTING

Plastic reference materials normally are used as calibrants or reference matrices for the analysis and determination of contained additives, monomers or other chemical substances. For these plastic RMs it is necessary to establish the stability of already included substances and not only to determine the stability of the plastic material itself.

In the present case, unlike other plastic RMs, not the value of an already contained substance was certified but the property of the PET material to show a certified value of model compounds *after* applying the chemical inertness test procedure. In other words not the stability of a characteristic additive of a plastic material had to be tested but the constant and stable inertness behaviour of the BCR-712 PET material itself towards the sorption and re-migration of six model compounds.

6.1 Design of the stability study

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. - 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 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 BCR-712 was therefore carried out for twelve months at 3 different temperatures, i.e. 10 °C, 23 °C and 60 °C.

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.

In the stability testing on packaged BCR-712 units, 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 each time point, one unit was removed per temperature from the storage and tested with six replicates using the chemical inertness test procedure described in Appendix I.

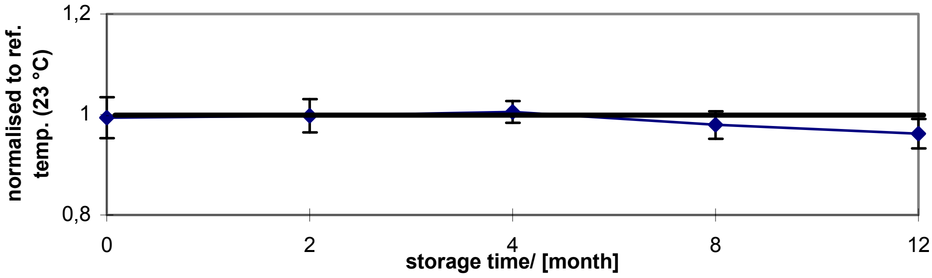
6.2 Results of the stability study

The results obtained in the stability study are based on the chemical inertness values for the six model compounds according to the procedure described in Appendix I. Six replicate measurements were obtained for each unit of PET material at each time point and for each storage temperature. The individual stability data are presented in Appendix II.

It should be noted that the values at time zero were obtained by measuring three different units, again with 6 replicates each, at three different days. Each of the three time zero data sets was then used as the starting point result for one of the three different temperatures.

The results of the stability studies are presented below in Figures 6-1 to 6-6 such that the results for the borderline storage temperatures 10 °C and 60 °C are given for each model compound as data normalised to stability results obtained at 23 °C (reference temperature) at the respective time point.

10 °C



60 °C

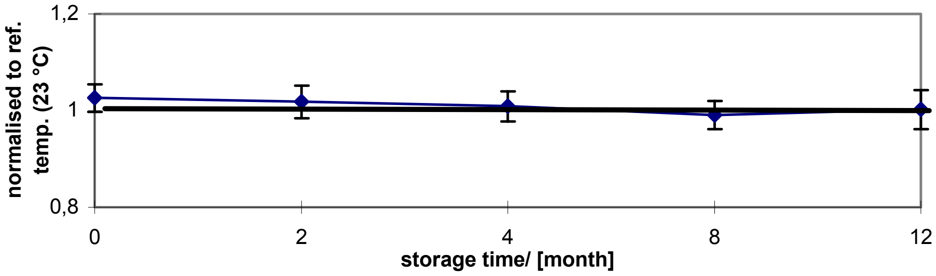
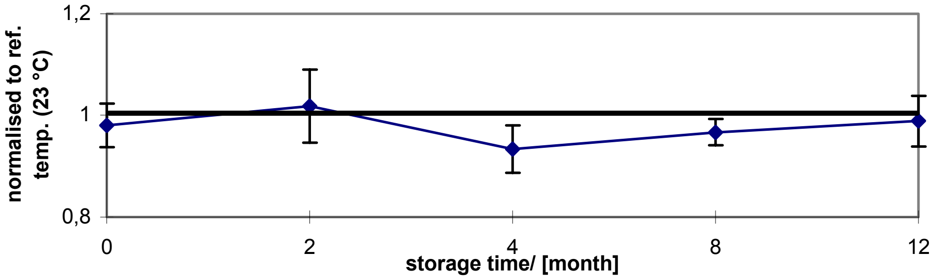


Figure 6–1 - Normalised (to 23 °C) chemical inertness test results obtained for toluene during storage at 10 °C and 60 °C for stability testing (n= 6).

10 °C



60 °C

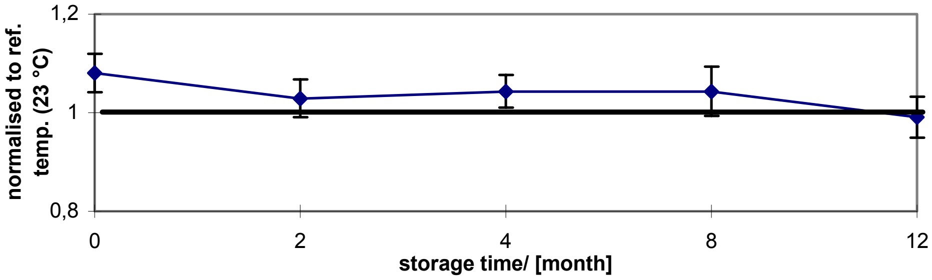
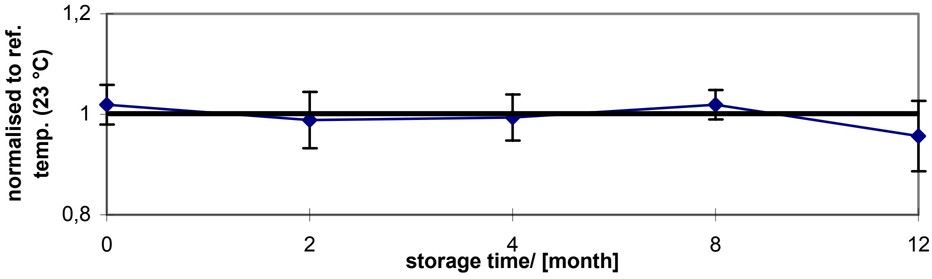


Figure 6–2 - Normalised (to 23 °C) chemical inertness test results obtained for phenol during storage at 10 °C and 60 °C for stability testing (n= 6).

10 °C



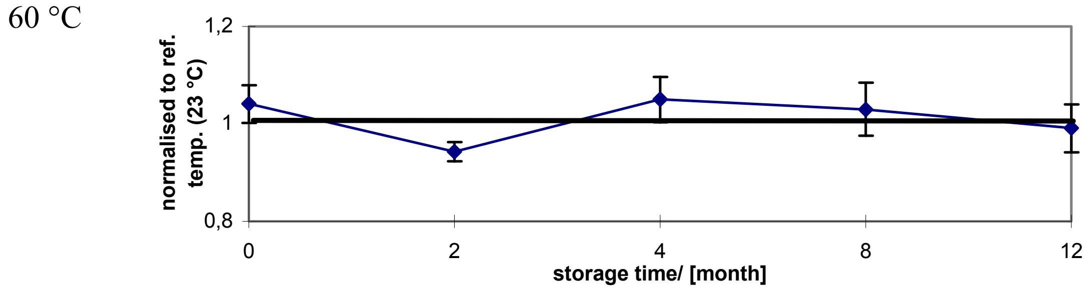


Figure 6–3 - Normalised (to 23 °C) chemical inertness test results obtained for limonene during storage at 10 °C and 60 °C for stability testing (n= 6).

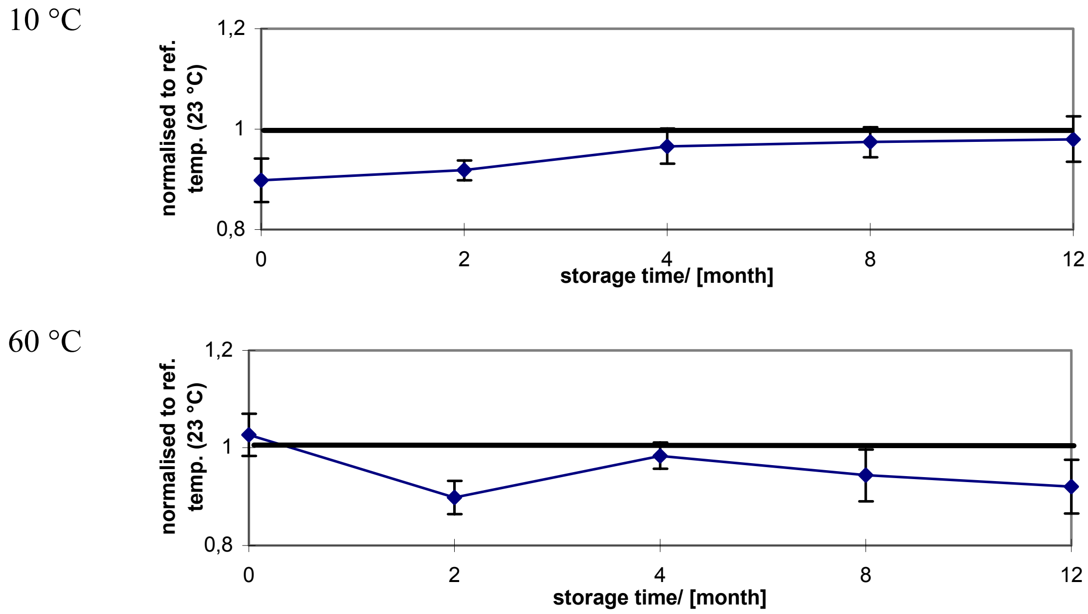


Figure 6–4 - Normalised (to 23 °C) chemical inertness test results obtained for menthol during storage at 10 °C and 60 °C for stability testing (n= 6).

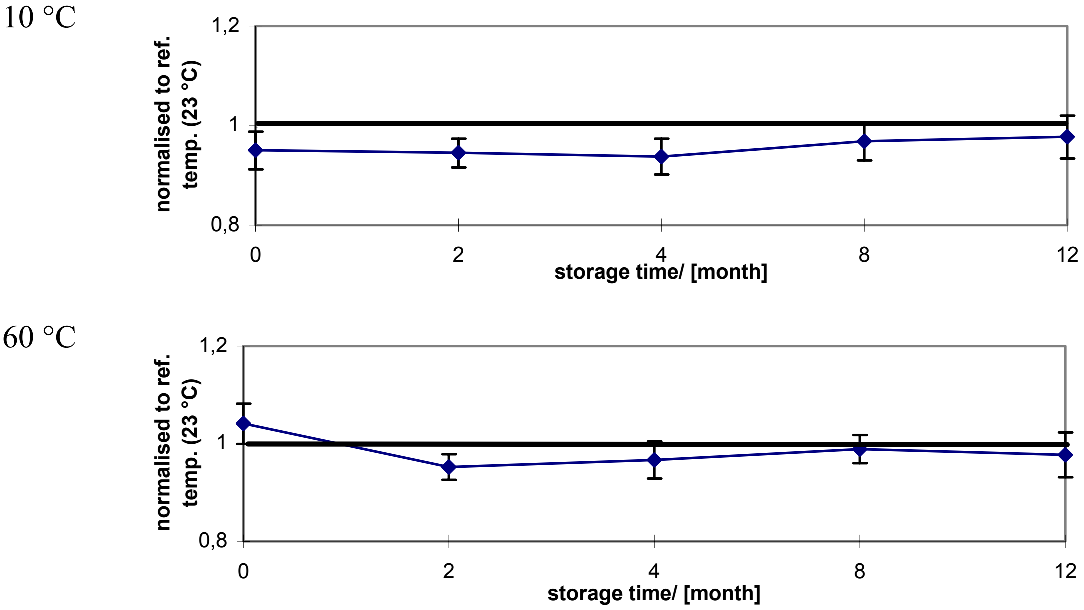


Figure 6–5 - Normalised (to 23 °C) chemical inertness test results obtained for phenyl cyclohexane during storage at 10 °C and 60 °C for stability testing (n= 6).

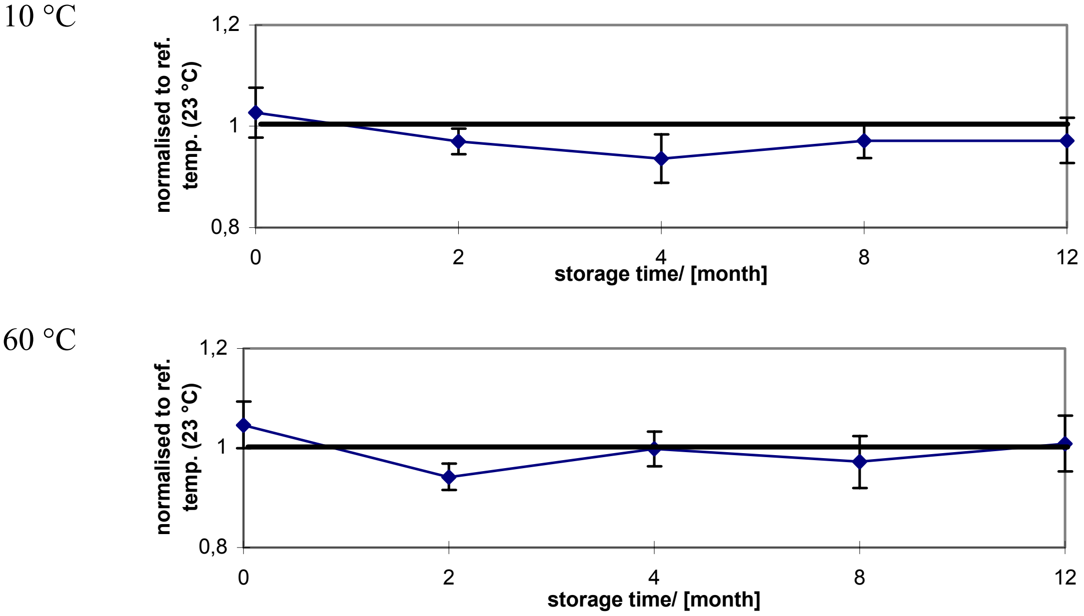


Figure 6–6 - Normalised (to 23 °C) chemical inertness test results obtained for benzophenone during storage at 10 °C and 60 °C for stability testing (n= 6).

6.3 Conclusion

For the evaluation of the stability of the BCR-712 test results of each model compound, obtained after storage at different temperatures, were correlated to corresponding storage times of the BCR-712 (see Figures 6-1 to 6-6). 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.

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 did not significantly change during the time of storage at 10 °C, 23 °C as well as at 60 °C. However, it should be noted that 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 observed for the significance level of 0.95 only. Since these two singular observations cannot be reasonably explained from a physico-chemical point of view and even appear to be physically impossible it can be justifyingly assumed that no real effects have been detected in these two case by the applied statistical means.

Therefore, in addition 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 were carried out and indeed 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 BCR-712 stored at different temperatures up to 12 months showed that chemical inertness test results did not 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 BCR-712 concerning the chemical inertness behaviour were kept stable at storing temperatures of 10 °C, 23 °C and 60 °C. Therefore the uncertainty for long-term stability has not been detected.

As a practical conclusion no special precautions concerning long-term storage and shipment of BCR-712 will be necessary. The raw data of the stability study, which are compiled in Annex II were used to derive at an estimate of the uncertainty source “material long-term satbility”. This estimate was included in the expanded uncertainty of the certified values. For the statistical background of this operation refer to Chapter 8.

7. THE CERTIFICATION EXERCISE

7.1 Design of the certification exercise

At the end of February 2000 the project co-ordinator sent 9 packaged BCR-712 units to each of the participants. The certification exercise started in March/April 2000. The acceptance criteria for data applied for the certification exercise were as following:

- certification exercise instructions were fully complied with
- no deviations were made from the described chemical inertness test procedure.

The certification exercise design was as follows:

Each laboratory obtained 9 units of BCR-712 which were to be subdivided into 3 series (I to III) of measurements in separate weeks on 3 units each time. In this way from each unit at least 8 replicate chemical inertness values for each model compound should be obtained where the extraction solution for each replicate was to be GC analysed for all six model compounds by triplicate injections.

Table 7–1 - Overview test protocol for a given laboratory:

Series	*Units*	*strips*[*)]	*Extraction solutions* [**)]	*GC injections* [**)]
I	3	24 (8 per unit)	24 (1 per strip)	72 (3 per extraction solution)
II	3	24 (8 per unit)	24 (1 per strip)	72 (3 per extraction solution)
III	3	24 (8 per unit)	24 (1 per strip)	72 (3 per extraction solution)
Total	9	72	72	216

[*)] Two strips per unit used as blanks are not included

[**)] For each replicate (extraction solution from a given strip) triplicate GC injections were made and averaged to end up with the values for the 6 compounds for the given replicate.

Protocol and reporting sheets including the method description were provided.

7.1.1 Materials provided

The following materials were provided by the co-ordinator for the certification exercise:

- 9 units of BCR-712 in the final packaging;
- Method description of the chemical inertness test procedure;
- Check-list of sources of uncertainties/ deviations which had to be considered and checked;
- Reporting/ evaluation sheets as hardcopy as well as in form of files on a disk;
- Instructions for completing the reporting sheets.

7.1.2 Design of PET BCR-712 units measured within the certification exercise

The laboratory numbers were encoded in order to make participants anonymous. The unit numbers were chosen in such a way that carrying out the chemical inertness test within one laboratory would allow to detect any possible trends. The unit numbers were chosen and examined under the following aspects:

- Nine following numbers of one stage of one palette in increasing order
- Nine following numbers of one stage of one palette in decreasing order
- Nine units of the same number of 9 different stages of the palettes
- Every 16th bottle of one stage of a palette in increasing order
- Every 16th bottle of one stage of a palette in decreasing order.
- Nine unit numbers were chosen by chance.

7.1.3 Analytical method used

The analytical method used in the certification exercise was the chemical inertness test method described in Appendix I. This method is in alignment with the respective Draft CEN-Technical Specification on Chemical Inertness Testing (4).

7.2 Evaluation of test results

Laboratories L1, L2, L3, L5, L6, L7, L8, L9, L10 and L11 took part in the certification exercise. L4 withdraw and did not take part due to an internal work overload.

All the participants were invited to attend a meeting to evaluate the outcome of the certification exercise. This meeting was held in Brussels on 4th of December 2000. All the data were carefully evaluated. The participants at the meeting examined the reliability of the individual sets of data from each laboratory. No data were rejected on statistical grounds, only on technical grounds. The set of acceptance criteria of section 7.1 above was employed. If the results were not acceptable according to these criteria then results were not accepted for certification.

As a result of this evaluation meeting, the data of L2, L6 and L9 were agreeably rejected because of technical reasons or not following the protocol. Also, for the other laboratories some results could either not be provided or were rejected.

- Laboratory 1: All data of the 3 series of the chemical inertness procedure were accepted (9 units).
- Laboratory 3: Data of series I and III were accepted. Data of series II were rejected due to deviations from the chemical inertness method (the extraction of test specimens was not carried out immediately after the sorption phase).
- Laboratory 5: For organisational reasons in the lab L5 carried out only 2 series of chemical inertness tests. Series I was discarded due to deviations of given technical requirements of the method as well as due to missing reported basic data.
- Laboratory 7: Data of series I and II were accepted. Data of series III were rejected due to deviations from the chemical inertness method (the extraction of test specimens was not carried out immediately after the sorption phase).
- Laboratory 8: All data were accepted (9 units). Although L8 was detected as an outlier no technical reasons could be found so that all test results are included in the statistical evaluation of the certified chemical inertness values.

- Laboratory 10: All data were accepted (9 units).
- Laboratory 11: All data except one unit were accepted (8 units). The reason was that in the rejected case the mass increase of the test specimens was significantly higher due to another position in the oven than of the other two units analysed at the same time.

7.3 Statistical evaluation of results

Statistical analysis was carried out on the results, which passed the technical discussion and the acceptance criteria, using the software provided by the Standards, Measurements and Testing Programme (6). No data was rejected on statistical grounds alone.

The following statistical tests were carried out with accepted certification data. The statistical test are described in a brief summary as written in the statistic programme SoftCRM (6). The number of accepted data sets (7) corresponds to the number of labs finally accepted in the certification exercise. The number of individual data (50) corresponds to the number of BCR-712 sample units analysed by all labs. In case of replicate measurements on a sample only the mean of these measurements is taken into account. The following Table 7-2 presents the certified properties of the six model compounds used within the certification exercise. Figures 7-1 to 7-6 show the corresponding bar-graphs of the certified values of model compounds. Outliers were included in the statistical evaluation in case no technical reasons could be found.

Table 7–2 - Summary of statistical Data for BCR-712 for the six model compounds of the chemical inertness test

Certified Property		*Re-migration value* [mg/dm^2]					
		Toluene	Phenol	Limonene	Menthol	Phenyl cyclohexane	Benzo-phenone
Number of data sets		7	7	7	7	7	7
Number of individual data		50	50	50	50	50	50
All data sets compatible two by two (Scheffe's multiple t-test)		no	no	no	no	no	no
Outlying data sets	Dixon's test	no	no	no	no	no	no
	Nalimov t-test	L8 at 0.05	no	L8	L11	no	no
	Grubbs test	no	no	L8 at 0.05	no	no	no
Outlying variances (Cochran's test)		L8	L7	L10	L10	L10	L10
Mean of data set means		7.284	4.146	3.872	1.775	3.487	5.575
Within data sets SD		1.330	0.589	0.546	0.152	0.493	1.080
Between-data sets SD		0.339	0.390	0.275	0.319	0.286	0.452
Between-data sets SD significant different (Snedecor F-test)		yes	yes	yes	yes	yes	yes
Variances homogeneous (Bartlett-test)		yes	no	yes	no	yes	yes
SD of data set means		0.470	0.209	0.186	0.067	0.187	0.388
Data set means normally distributed (Kolmogorov-Smirnov-Lilliefors-test)		yes	yes	yes	not normal	yes	yes
Half width of the 95 % confidence interval of the mean of means		0.435	0.194	0.172	0.062	0.173	0.359
Half width of the 95 % tolerance interval of the data set means		1.884	0.839	0.747	0.268	0.751	1.556

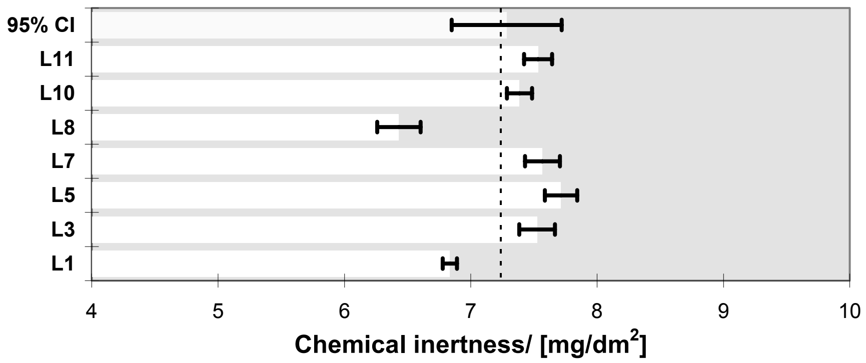


Figure 7–1 - Bar-graph for the toluene value for accepted laboratory means and 95 % confidence interval for BCR-712

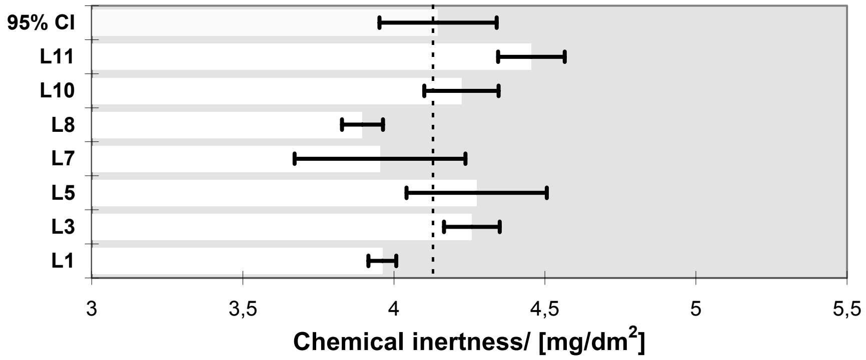


Figure 7–2 - Bar-graph for the phenol value for accepted laboratory means and 95 % confidence interval for BCR-712

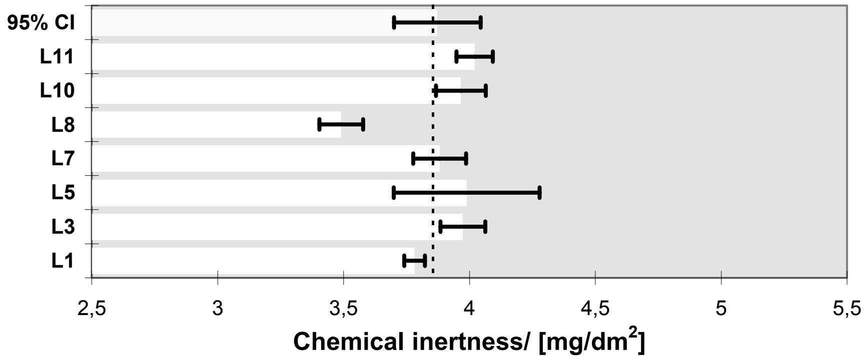


Figure 7–3 - Bar-graph for the limonene value for accepted laboratory means and 95 % confidence interval for BCR-712

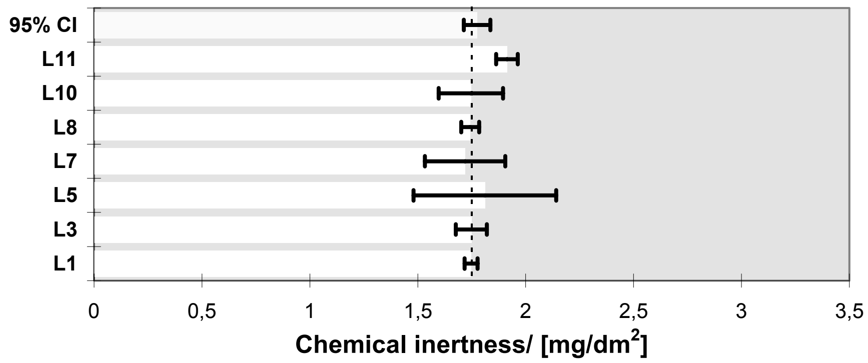


Figure 7–4 - Bar-graph for the menthol value for accepted laboratory means and 95 % confidence interval for BCR-712

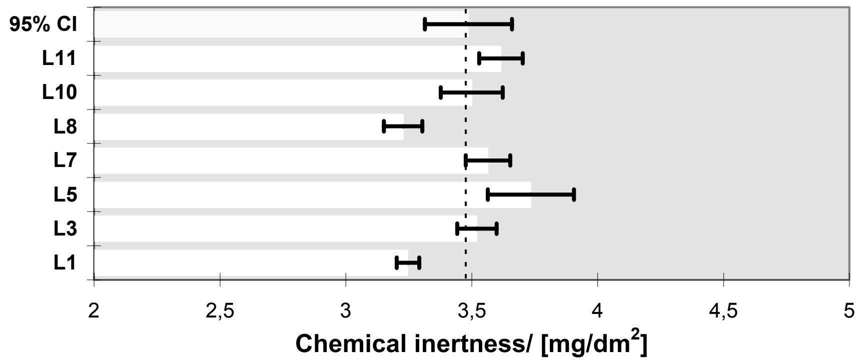


Figure 7–5 - Bar-graph for the phenyl cyclohexane value for accepted laboratory means and 95 % confidence interval for BCR-712

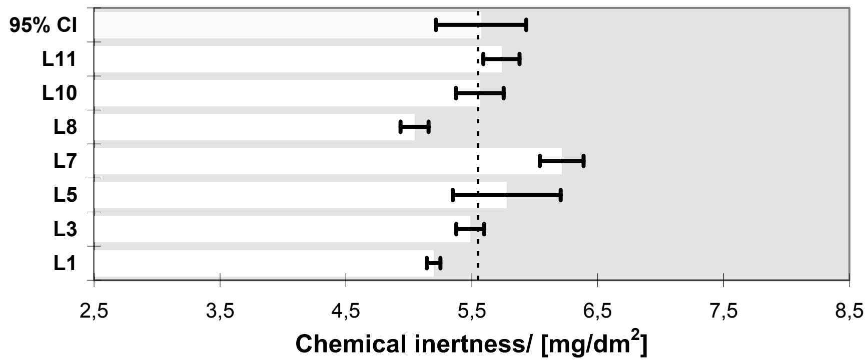


Figure 7–6- Bar-graph for the benzophenone value for accepted laboratory means and 95 % confidence interval for BCR-712

8. CERTIFIED VALUES AND THEIR UNCERTAINTIES

The uncertainty evaluation described hereafter is based on a concept described by Pauwels *et al.* (7 and literature cited) and uses available data discussed in the previous chapters.

8.1.1 Uncertainty evaluation

Based on the data obtained in the stability and homogeneity studies as well as the scattering of results in the batch characterisation estimates for u_{bb} (homogeneity), u_{lts} (long-term-stability) and u_{char} (batch characterisation) were obtained and combined according the following equation:

$$U_{CRM} = 2 \cdot \sqrt{u_{bb}^2 + u_{lts}^2 + u_{char}^2}$$

Due to the transport conditions selected for dispatch, the uncertainty constituent for short-term stability (u_{sts}) is negligible and consequently not included in the overall uncertainty. The estimation of the other uncertainty sources is described below.

8.1.2 Uncertainty source "homogeneity"

The homogeneity study is exhaustively described in chapter 5. From these data (Annex III), an estimation of u_{bb} was derived from the homogeneity study as described by Linsinger *et al.* (8). An one-way ANOVA was performed on the data of Annex III.

According to this approach, s_{bb} (being the standard deviation between units) or u^*_{bb} (being the upper limit of inhomogeneity that can be hidden by the method repeatability) are used as estimates of u_{bb}. Values for s_{bb} and u^*_{bb} were calculated accordingly:

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}}$$

and

$$u_{bb}^* = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt[4]{\frac{2}{\nu_{MSwithin}}} ,$$

where *n* is the number of replicates per unit, MS_{within} and $MSbetween$ the respective mean-of-squares from the ANOVA (Chapter 5) and $\nu_{MSwithin}$ the degrees of freedom of MS_{within}. If the value of s_{bb} is below the minimum value as determined by the repeatability of the method and the number of replicates performed, u^*_{bb} is used to estimate u_{bb}.

8.1.3 Uncertainty source "stability"

Similarly, a quantitative estimate of the uncertainty related to stability, u_{lts}, was obtained plotting the shelf-life as described elsewhere (8). The uncertainty was estimated for a shelf-life of 36 months. Although the study was no isochronous experiment and despite the fact

23 °C originally foreseen as reference temperature, the shelf-life plots referred to the data obtained at 10 °C as reference temperature. In order to compensate for the lack of repeatability conditions, only the data series after 8 or 12 months of storage at 10 °C, which were closest to the mean value of data sets observed at 23 °C, were included in the shelf-life plot. This somewhat arbitrary choice decreases the influence of fluctuations of the analytical method. However, appropriate isochronous stability studies have been started while this report is being printed. These studies will allow a confirmation of the forecasted shelf-life life.

The estimated uncertainty contribution, u_{lts}, which is included in the combined and expanded uncertainties of the certified values, will be used to establish an expiry date of the certificate. Please refer to the certificate for further details.

8.1.4 Uncertainty source "batch characterisation"

An estimate for u_{char} was derived from the standard error obtained on the mean of laboratories means.

8.1.5 Uncertainty budget

Based on these uncertainty contributions the following uncertainty budget is established:

Table 8–1 – Uncertainty budget for BCR-712

Inertness Parameter	*Toluene*	*Phenol*	*Limonene*	*Menthol*	*Phenyl Cyclohexane*	*Benzophenone*
Mean value	7.284	4.146	3.872	1.775	3.487	5.575
u_{char} (%)	2.44	1.91	1.82	1.43	2.03	2.63
s_{bb} (%), n=28	0.10	0.10	0.10	0.10	0.10	0.10
u^*_{bb} (%), df=84	0.21	0.21	0.21	0.21	0.21	0.21
u_{lts} (%), 36 months	3.26	5.33	5.11	4.8	3.89	4.2
U_{CRM} (%)	8.15	11.33	10.85	10.02	8.78	9.92
U_{CRM}	0.59	0.47	0.42	0.18	0.31	0.55

8.2 Certified values

The certified values and their associated uncertainties are given in the tables below. Expanded uncertainties (coverage factor k=2) were expressed according to the Guide for the Expression of Uncertainties in Measurement (GUM) (2).

Table 8–2 – Certified values and Uncertainties. All parameters are expressed in mg/dm^2. Rounding was done according to the requirements of ISO-Standard 31-0 (9).

Inertness Parameter	*Toluene*	*Phenol*	*Limonene*	*Menthol*	*Phenyl Cyclohexane*	*Benzophenone*
Certified value (mg/dm^2)	7.3 ± 0.6	4.1 ± 0.5	3.9 ± 0.5	1.78 ± 0.18	3.5 ± 0.4	5.6 ± 0.6

9. INSTRUCTIONS FOR USE

9.1 Storage, handling and transportation

The PET BCR material should be stored at room temperature. As long as originally packed, no special precautions concerning long-term storage and shipment are required. The chemical inertness test procedure must be strictly followed without deviation. Strict adherence to all parts of the test procedure is absolutely essential.

It should be noted that variations in the temperature of the sorption as well as extraction phase may lead to chemical inertness values which differ significantly from the certified values. As a performance check of the sorption phase the mass increase of a PET CRM test specimen can be used which lies normally within the range of 2.0 to 4.0 mg.

9.2 Use of the certified values

The certified values are specific to the described chemical inertness test procedure (Appendix I). If the CRM is used for the verification of the performance , the user can refer to results of the certification exercise. The user may assess the laboratory bias from the difference between the mean value of the replicate laboratory measurements (X) and the certified value (μ): $X - \mu$.

The criterion for acceptance is given in ISO Guide 33 (10) as follows:

$$-a_2 - 2\,\sigma_L < X-\mu < a_1 + 2\,\sigma_L$$

in which a1 and a2 are the adjusted values, chosen by the user according to economic or technical limitations or stipulations and σ_L is the long-term within-laboratory standard deviation.

10. REFERENCES

[1] European Council (1988). Council Directive 89/109/EEC of 21 December 1988 on the approximation of the laws of the Member States relating to materials and articles intended to come into contact with foodstuffs. Official Journal **L 040 (**11/02/1989), 38 – 44.

[2] ISO-IEC-BIPM-IFCC-IUPAC-IUPAP-OIML. Guide to the Expression of Uncertainties in Measurement (GUM), Geneva, Switzerland (ISBN 92-67-10188-9).

[3] European 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. Project duration January 1997 – December 2000.

[4] CEN (2002). Draft CEN Technical Specification: "Method of Test for refillable PET bottles with respect to their chemical inertness behaviour", as of October 2002, CEN Doc. No. CEN TC194/SC1/WG1 N234.

[5] European Project AIR2-CT93-1014: Programm to establish criteria to ensure the quality and safety in use of recycled and re-used plastics for food packaging. Project duration January 1994 – December 1997. Working Group Refillables, Final Report. September 1997.

[6] Soft CRM: a new software for the development of certified reference materials. www.weblab.gr/softcrm/softcrm.htm.

[7] A.M.H. Van der Veen, T.P.J. Linsinger, H. Schimmel, A. Lamberty, J. Pauwels (2001). Uncertainty calculations in the certification of reference materials. 4. Characterisation and certification. Accred. Qual. Assur. **6**, 290-294.

[8] T.P.J Linsinger, J. Pauwels, A.M.H. van der Veen, H. Schimmel, A. Lamberty (2001). Homogeneity and stability of reference materials. Accred. Qual. Assur. **6**, 20-25.

[9] ISO-Standard 31 (1992). Quantities – part 0: General principles. International Organization for Standardization, Geneva, Switzerland.

[10] ISO Guide 33 (1989). Uses of certified reference materials. International Organization for Standardization, Geneva, Switzerland.

[11] P. G. Demertzis, F. Johansson, C. Lievens and R. Franz (1997). Studies on the development of a quick inertness test procedure for multi-use PET containers. Packaging Technology and Science **10**, 45 - 58.

[12] P. G. Demertzis and R. Franz (1998). Studies on the development of a quick test for predicting the sorption properties of refillable polycarbonate bottles. Presented at the 9th International Flavor Conference 'Gerorge Charalambous Memorial Symposium, July 1-4, 1997, Island of Limnos, Greece. Published in: Contis E.T. et al. (editors.): Developments in Food Science 40: Food Flavors: Formation, analysis and packaging influences. Elsevier Science B.V., Amsterdam 1998, pp 719 – 733.

[13] G. Palzer and R. Franz (1998). Chemical Inertness of Multi-trip PET Beverage Bottles – Test method for determining the inertness and therefore the functionality of PET bottle material. Kunststoffe plast europe **88** (6), 20 - 21.

[14] R. Franz (200): 'Migration of plastic constituents'. Chapter 10, pp. 287 – 357. In: Piringer, O.-G. and Baner, A.L. (editors): Plastic Packaging Materials for Food - Barrier Function, Mass Transport, Quality Assurance and Legislation. Wiley-VCH Verlag GmbH Weinheim, 2000.

11. ANNEX I - DESCRIPTION OF THE PET INERTNESS TEST METHOD

The method description was prepared by Fraunhofer Institut für Verfahrenstechnik und Verpackung (IVV) within the EU Project SMT4 - CT96 – 2129.

Contents

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 has developed a certified reference PET material which will become available from EC-JRC-IRMM identified as BCR 712 (5).

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 extent of sorption of model chemicals by the PET material and given quantitatively in mass [mg] absorbed per surface area [dm^2]. 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 material for returnable packaging applications when compared directly to the certified PET bottle material *[BCR 712]* and provided that the certified interactivity values for each model compound are met according to ISO guide 33 (1989) 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 toeconomic or technical limitations or stipulations

and σ_L is the long-term within-lab standard deviation.

2 Principle

The principal 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.

NOTES: 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 then the users must satisfy themselves that this condition holds - 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 ($C_{13}H_{10}O$), purity ≥ 99 % (GC); alternative name: diphenyl ketone; CAS No. 119-61-9; BRN 1238185; EG No. 2043376

3.1.2 (R)-(+)-Limonene ($C_{10}H_{16}$), purity 98 %; alternative name: (R)-(+)-4-isopropenyl-1-methyl-cyclohexene CAS No. 5989-27-5

3.1.3 Menthol ($C_{10}H_{20}O$), purity 99 %; alternative name: 2-isopropyl-5-methyl-cyclohexanol, CAS No. 89-78-1

3.1.4 Phenol (C_6H_6O), purity ≥ 99 %; alternative names: hydroxybenzene, carbolic acid, CAS No. 108-95-2; BRN 969616; EG No. 2036327

C*aution: Phenol is a toxic substance !*

3.1.5 Phenyl cyclohexane ($C_{12}H_{16}$), purity 98 %; alternative name: cyclohexyl benzene, CAS No. 827-52-1

3.1.6 Toluene (C_7H_8), 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 (C_8H_{10}), purity > 99,0 %.; alternative name: 1,4-dimethyl-benzene; CAS No. 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 (1.13 kg/L) middle-mol-mass: 380-420

3.3 Solutions

3.3.1 95 % aqueous ethanol

Place 50 mL of distilled water into a 1 L 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 (100 mL 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 10 mL of the stock solution (3.3.2) and note down the mass of stock solution in g for each dilution. For the volume 0.1 mL 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 μg 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. 20 mL 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 (50 mL 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 ±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 ±1 % of each model compound. The resulting total volume of the cocktail solution amounts then to approximately 260 mL. 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 0.5 mg

4.2 Magnetic stirrer

4.3 Tightly closeable 20 mL glass vials with crimp closures, lined with septa (diameter 20 mm; height 75 mm; neck size 13 mm)

4.4 Volumetric flasks of volumes 100 mL, 50 mL and 20 mL, complying with the minimum requirements of ISO 4787

4.5 Tightly closeable glass tubes of volume 50 mL and 100 mL, 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 0.2 mL and complying with the minimum requirements of ISO 685

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 60 mm

4.14 Blunt-nosed tweezers, stainless steel,

4.15 Thermostatically controlled oven capable of maintaining a temperature of (60 ± 1) °C

4.16 Gas chromatograph (GC), with flame ionisation detector (FID) equipped with an appropriate column and with an automated 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.

NOTE: This relatively high initial number of test strips is necessary to ensure finally at least 5 valid results in case that samples may need to be discarded from technical reasons as described in 6.2. However, it should be aimed to carry all of the 8 test strips through the whole procedure and build the test result on the maximum 8 data sets.

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 ±1) mm . With the aid of a rule shorten the strips to the final length of exactly (60 ±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 test specimen 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 $2x\ (6 \times 1.1)\ cm^2 = 13.2\ cm^2$.

Strips which are not needed for the test may be stored in closed glassware at ambient temperature (20 ± 5) °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 ± 1) °C and leave the vials in the oven for a time period of (48 ± 0.5) 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 <u>m</u>ass after <u>s</u>orption, 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).

<u>Specimens with homogenous thickness distributions:</u>

After cutting, re-weigh each strip and note the mass as the <u>m</u>ass with <u>c</u>ut <u>e</u>dges, 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 <u>eff</u>ective surface <u>a</u>rea, A_{eff} in dm^2, of the cut-edge strips is calculated as follows:

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

<u>Specimens with inhomogenous thickness distributions:</u> 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 (~ 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}.

NOTE: *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 (~ 5 mL) 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 ± 1) °C. Leave the glass vials for a time period of (48 ± 0.5) 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 °C.*

Calculate the loss of extraction solution as follows:

$ES\_m_{ae}^{*} = ES\_m_{be} - (m_{be} - m_{ae})$ in g

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

$[(m_{be} - m_{ae}) / ES\_m_{be}] \times 100\ \%$ = 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 start 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 4 g (≅ 5 mL) of each of the diluted standard solutions (3.3.3) as well as 0.5 mL internal standard solution (3.3.4) into a 10 mL glass vial. Close and mix thoroughly. Transfer from each of the obtained 5.5 mL volume calibration solutions 1 mL portions into 3 glass vials of e.g. 2 mL volume (4.8) for GC auto samplers.

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. 2 mL glass vials for GC auto samplers.

In this way a set of test sample solutions (8 x 3) and blank sample solutions (2 x 3) 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: 30 M LENGTH X 0.32 MM INTERNAL DIAMETER FUSED SILICA CAPILLARY E.G. DB-1 WITH A FILM THICKNESS OF 5 µM

Detector temperature:	280 °C	
Injector temperature:	250 °C	
Injection volume:	2 µL	
Carrier gas:	H_2	
Column pressure:	66 kPa	
Injection mode:	split flow 20 mL/min	
Oven programme:	initial temperature	80 °C
	initial time	2 min
	heating rate	15 °C/min
	final temperature	280 °C
	final time	0 min

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

Under these conditions a full separation of the model compounds was achieved with the following retention times (in minutes):

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 must be rectilinear with a correlation coefficient of at least 0.996.

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.

NOTE: In case that the gas chromatogram obtained from blank samples shows an interference at the retention time of a model compound then following should be considered:

A correction for the blank value should be made in case that the interference does not exceed 10 % of the area of the analyte peak and remains constant within +/- 20 % in absolute size in the triplicate injections.

In case that the interference exceeds the above requirement then the particular model compound should be taken out of the evaluation and the result be based on the remaining interference-free model substances.

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} [PR] = a_{mc} * x_{mc} [mg/g] + b_{mc}

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

C_{mc} [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 contact area (in dm^2) of test specimen taking both sides of the PET strip into account:

Calculation of the final interactivity values for the model compounds in mg/dm^2 is achieved as follows:

$$Interactivity_{mc}\left[{}^{mg}\!/\!_{dm^2}\right] = \frac{C_{mc}\left[{}^{mg}\!/\!_{g}\right] \cdot ES\_m_{ae}\ [g]}{A_{eff}\left[dm^2\right]}$$

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

8 Precision

The method was evaluated in a collaborative trial with 7 laboratories where to each laboratory 9 samples were made available. Statistical evaluation (ISO 5725) at the 95 % probability level of 50 valid data sets (out of 63) yielded the following repeatability (**r**) and reproducibility (**R**) values at the certified interactivity values obtained for the individual model compounds

Model compound	Certified interactivity value [mg/dm^2]	r [mg/dm^2]	R [mg/dm^2]
Toluene	7.28	0.35	1.32
Phenol	4.15	0.36	0.59
Limonene	3.87	0.27	0.52
Menthol	1.78	0.29	0.19
Phenyl cyclohexane	3.49	0.26	0.52
Benzophenone	5.58	0.43	1.09

9 Test report

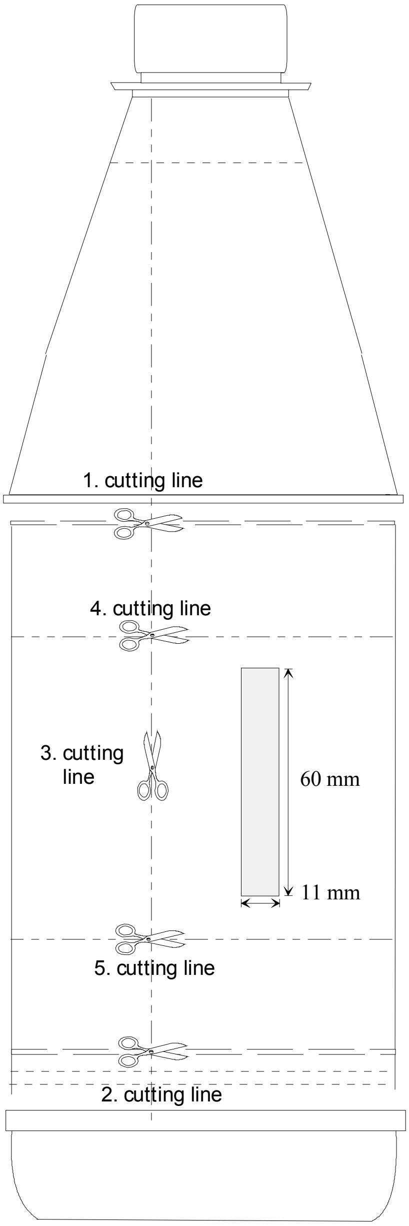
The test report shall include the following:

- reference to this method [standard];
- all information necessary for complete identification of the sample;
- departures from the specified procedure, and reasons for these;
- individual test results for each sample and model compound (mc), and the mean of these,

expressed as interactivity$_{mc}$ in milligrams of model compound per square decimetre of sample;

- relevant comments on the test results.

Annex A: Figure: Cutting diagram for a refillable PET bottle



Annex B: Bibliography

[1] Feron, V., Jetten, J., De Kruijf, N. and van den Burg, F., 1994, Polyethylene terephthalate returnable bottles (PRBs): a health and safety assessment. . Food Additives and Contaminants Vol. 11, 571-594.

[2] EU Project AIR2-CT93-1014: Working Group Refillables, Final Report, September 1997.

[3] Demertzis, P.G., Johansson, F. and Franz, R., 1997, Studies on the Development of a Quick Inertness Test Procedure for Multi-use PET Containers - Sorption Behaviour of Bottle Wall Strips. Packaging Technology and Science Vol 10, 45-58.

[4] Nielsen, T., Damant, A.P. and Castle L., 1997, Validation studies of a quick inertness test for predicting the sorption and washing properties of refillable plastic bottles. Food Additives and Contaminants Vol. 14, 685-693.

12. ANNEX II – STABILITY DATA

The significance deviating from zero of the slopes was calculated by SOFTCRM. The software did not provide a readout of the slope values but only indicated a 'no' or 'yes' and indicated a SE slope value (probably standard error of slope) these SE slope values were only given by SOFTCRM for the 95 % probability level. These SE slope values are given in the following tables below in brackets.

12.1 Output for toluene

Measurements are expressed in mg/dm^2

Table 12–1 - Data for T= 23 °C (Reference temperature). Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	6,904	7,143	6,79	7,012	7,204
2	7,022	6,868	7,017	7,353	7,189
3	6,88	6,873	7,078	6,864	7,174
4	6,713	6,895	6,856	6,945	6,802
5	6,713	6,799	7,08	7,054	6,984
6	6,812	6,679	6,821	7,088	6,95
Mean	6,841	6,876	6,940	7,053	7,051
STDev	0,120	0,153	0,133	0,168	0,164
CV(%)	1,753	2,220	1,915	2,375	2,324

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : Yes (SE 0.004)

Table 12–2 - Data for T= 10 °C Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	6,927	6,989	7,03	6,795	6,831
2	6,626	7,101	7,005	6,878	6,591
3	7,061	6,81	6,972	7,013	6,837
4	6,468	6,848	7,05	6,997	6,855
5	6,65	6,733	6,846	6,805	6,648
6	7,06	6,649	6,931	6,95	6,916
Mean	6,799	6,855	6,972	6,906	6,780
STDev	0,251	0,166	0,075	0,095	0,129
CV(%)	3,691	2,422	1,075	1,373	1,902

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.007)

Table 12–3 - Data for T= 60 °C Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	6,996	6,944	7,025	7,068	6,739
2	7,142	7,171	6,961	7,121	7,082
3	7,154	6,815	7,306	7,09	7,331
4	7,131	6,943	6,986	6,847	6,853
5	6,858	7,252	6,821	6,877	7,317
6	6,823	6,892	6,918	6,927	7,067
Mean	7,017	7,003	7,003	6,988	7,065
STDev	0,149	0,170	0,164	0,119	0,239
CV(%)	2,121	2,432	2,344	1,698	3,384

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.005)

12.2 Output for phenol

Measurements are expressed in mg/dm^2

Table 12–4 - Data for T= 23 °C (Reference temperature). Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	3,813	3,974	3,88	3,828	4,172
2	3,845	3,876	4,109	4,069	4,215
3	3,942	3,838	4,043	3,97	4,335
4	3,941	3,928	4,005	4,077	3,933
5	3,945	3,997	4,149	3,953	4,068
6	4,053	3,725	4,054	4,063	4,089
Mean	3,923	3,890	4,040	3,993	4,135
STDev	0,085	0,100	0,093	0,097	0,138
CV(%)	2,170	2,573	2,313	2,430	3,336

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.008)

Table 12–5 - Data for T= 10 °C Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	3,939	4,053	3,81	3,898	3,969
2	3,842	4,312	4,013	3,822	4,043
3	3,942	3,544	3,776	3,906	3,943
4	3,562	4,09	3,875	3,823	4,057
5	3,938	3,933	3,558	3,816	4,159
6	3,836	3,83	3,6	3,898	4,371
Mean	3,843	3,960	3,772	3,861	4,090
STDev	0,146	0,261	0,171	0,044	0,157
CV(%)	3,807	6,586	4,523	1,144	3,839

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.014)

Table 12–6 - Data for T= 60 °C. Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	4,047	3,915	4,36	4,161	4,079
2	4,223	4,06	4,2	4,038	4,074
3	4,372	4,153	4,183	4,172	4,083
4	4,177	4,072	4,101	4,007	4,186
5	4,347	3,927	4,16	4,129	3,931
6	4,28	3,895	4,274	4,494	4,246
Mean	4,241	4,004	4,213	4,167	4,100
STDev	0,120	0,106	0,091	0,174	0,108
CV(%)	2,829	2,636	2,169	4,166	2,642

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.010)

12.3 Output for limonene

Measurements are expressed in mg/dm^2

Table 12–7 - Data for T= 23 °C (Reference temperature). Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	4,09	3,978	3,618	3,726	3,97
2	3,956	4,029	3,813	3,934	3,666
3	3,906	4,098	3,88	3,752	4,131
4	3,881	4,112	3,87	3,921	3,842
5	3,89	4,063	4,008	3,956	3,953
6	3,921	4,006	3,671	3,814	3,963
Mean	3,941	4,048	3,810	3,851	3,921
STDev	0,078	0,053	0,144	0,100	0,155
CV(%)	1,974	1,300	3,783	2,587	3,960

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.011)

Table 12–8 Data for T= 10 . Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	4,015	4,139	3,837	3,882	3,865
2	3,941	4,274	3,865	3,902	3,285
3	4,123	3,636	3,816	3,958	3,836
4	3,788	4,062	3,89	3,916	3,891
5	4,12	3,962	3,65	3,871	3,855
6	4,114	3,917	3,672	4,003	3,791
Mean	4,017	3,998	3,788	3,922	3,754
STDev	0,134	0,219	0,102	0,050	0,232
CV(%)	3,330	5,469	2,692	1,275	6,183

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.010)

Table 12–9 - Data for T= 60 °C Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	3,913	3,821	4,108	3,933	3,82
2	4,094	3,859	3,975	3,777	3,896
3	4,222	3,867	4,004	4,012	3,874
4	3,988	3,889	3,851	3,826	3,983
5	4,222	3,742	3,974	3,968	3,71
6	4,174	3,733	4,096	4,289	4,041
Mean	4,102	3,819	4,001	3,968	3,887
STDev	0,129	0,067	0,094	0,180	0,117
CV(%)	3,136	1,742	2,355	4,549	3,022

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.010)

12.4 Output for menthol

Measurements are expressed in mg/dm^2

Table 12–10 - Data for T= 23 °C (Reference temperature). Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	2,015	1,949	1,806	1,83	1,934
2	1,959	1,976	1,905	1,904	1,968
3	1,902	1,996	1,854	1,871	2,005
4	1,863	2,006	1,855	1,933	1,837
5	1,866	1,985	1,916	1,863	1,898
6	1,917	1,946	1,846	1,902	1,877
Mean	1,920	1,976	1,864	1,884	1,920
STDev	0,058	0,025	0,041	0,036	0,062
CV(%)	3,040	1,241	2,180	1,936	3,206

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.006)

Table 12–11 - Data for T= 10 °C Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	1,772	1,79	1,754	1,873	1,858
2	1,704	1,848	1,796	1,786	1,85
3	1,757	1,758	1,826	1,857	1,812
4	1,602	1,824	1,726	1,773	1,878
5	1,75	1,831	1,851	1,857	1,899
6	1,756	1,83	1,848	1,865	1,993
Mean	1,724	1,814	1,800	1,835	1,882
STDev	0,064	0,033	0,051	0,044	0,062
CV(%)	3,704	1,831	2,853	2,382	3,287

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : Yes (SE 0.004)

Table 12–12- Data for T= 60 °C. Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	1,879	1,704	1,85	1,863	1,857
2	1,98	1,781	1,886	1,778	1,819
3	2,033	1,814	1,797	1,769	1,827
4	1,926	1,692	1,823	1,898	1,642
5	2,007	1,853	1,822	1,729	1,67
6	2,003	1,806	1,827	1,634	1,797
Mean	1,971	1,775	1,834	1,779	1,769
STDev	0,058	0,064	0,030	0,095	0,090
CV(%)	2,935	3,610	1,661	5,325	5,077

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.004)

12.5 Output for phenyl cyclohexane

Measurements are expressed in mg/dm^2

Table 12–13 - Data for T= 23 °C (Reference temperature). Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	3,572	3,626	3,388	3,39	3,597
2	3,572	3,616	3,555	3,557	3,638
3	3,627	3,584	3,475	3,475	3,715
4	3,442	3,445	3,452	3,569	3,394
5	3,389	3,58	3,596	3,481	3,499
6	3,588	3,544	3,473	3,557	3,495
Mean	3,532	3,566	3,490	3,505	3,556
STDev	0,094	0,066	0,075	0,070	0,116
CV(%)	2,653	1,849	2,138	1,985	3,253

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.004)

Table 12–14 - Data for T= 10 °C. Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	3,381	3,412	3,309	3,408	3,418
2	3,421	3,391	3,202	3,243	3,435
3	3,256	3,379	3,236	3,325	3,372
4	3,213	3,312	3,116	3,571	3,457
5	3,406	3,472	3,376	3,468	3,494
6	3,462	3,242	3,384	3,333	3,667
Mean	3,357	3,368	3,271	3,391	3,474
STDev	0,099	0,081	0,105	0,117	0,103
CV(%)	2,950	2,391	3,214	3,445	2,964

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.012)

Table 12–15 - Data for T= 60 °C. Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	3,506	3,376	3,295	3,566	3,41
2	3,67	3,433	3,389	3,398	3,511
3	3,781	3,44	3,481	3,481	3,498
4	3,596	3,478	3,48	3,434	3,583
5	3,769	3,351	3,192	3,535	3,308
6	3,742	3,299	3,4	3,382	3,631
Mean	3,677	3,396	3,373	3,466	3,490
STDev	0,109	0,066	0,112	0,074	0,117
CV(%)	2,963	1,947	3,327	2,147	3,355

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.007)

12.6 Output for benzophenone

Table 12–16 - Data for T= 23 °C (Reference temperature). Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	5,614	5,41	5,597	5,597	5,508
2	5,515	5,599	5,48	5,857	5,558
3	5,193	5,563	5,743	5,693	5,717
4	5,196	5,684	5,471	5,516	5,176
5	5,259	5,51	5,754	5,483	5,371
6	5,417	5,677	5,408	5,824	5,382
Mean	5,366	5,574	5,576	5,662	5,452
STDev	0,177	0,104	0,147	0,157	0,186
CV(%)	3,298	1,872	2,642	2,768	3,404

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.008)

Table 12–17 - Data for T= 10 °C. Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	5,541	5,381	5,283	5,52	5,229
2	5,516	5,23	5,57	5,507	5,241
3	5,66	5,452	5,194	5,634	5,116
4	5,155	5,424	5,319	5,419	5,26
5	5,664	5,488	4,942	5,325	5,366
6	5,532	5,473	4,992	5,579	5,592
Mean	5,511	5,408	5,217	5,497	5,301
STDev	0,186	0,095	0,231	0,111	0,163
CV(%)	3,382	1,759	4,423	2,022	3,084

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.016)

Table 12–18 - Data for T= 60 °C. Storage Time in Months

Replicate no.	*0*	*2*	*4*	*8*	*12*
1	5,344	5,201	5,745	5,473	5,473
2	5,577	5,3	5,554	5,291	5,291
3	5,803	5,319	5,505	5,541	5,541
4	5,496	5,408	5,375	5,301	5,301
5	5,734	5,177	5,521	5,442	5,442
6	5,726	5,114	5,67	5,954	5,954
Mean	5,613	5,253	5,562	5,500	5,500
STDev	0,174	0,108	0,130	0,243	0,243
CV(%)	3,094	2,057	2,346	4,417	4,417

Slope of the linear regression significantly <> 0 (99 %) : No

Slope of the linear regression significantly <> 0 (95 %) : No (SE 0.015)

12.7 Ratio-of-Means Tables for model compounds

Table 12–19 - Ratio of Means Table for model compound Toluene (R(T)=XT/Xref ± Uncertainty(T)). Slope of the Linear Regression significantly <> 0 ? Measurement unit : mg/dm^2

	0	*2*	*4*	*8*	*12*
R(10) ± U(10)	0,994 ± 0,041	0,997 ± 0,033	1,005 ± 0,022	0,979 ± 0,027	0,962 ± 0,029
R(60) ± U(60)	1,026 ± 0,028	1,018 ± 0,034	1,009 ± 0,031	0,991 ± 0,029	1,002 ± 0,041

	a = 99 %	a = 95 %
R(10)	No	(SE Slope 0.001) No
R(60)	No	(SE 0.001) No

Table 12–20 - Ratio of Means Table for model compound Phenol (R(T)=XT/Xref ± Uncertainty(T)). Slope of the Linear Regression significantly <> 0 ? Measurement unit : mg/dm^2

	0	*2*	*4*	*8*	*12*
R(10) ± U(10)	0,980 ± 0,043	1,018 ± 0,072	0,934 ± 0,047	0,967 ± 0,026	0,989 ± 0,050
R(60) ± U(60)	1,081 ± 0,039	1,029 ± 0,038	1,043 ± 0,033	1,043 ± 0,050	0,991 ± 0,042

	a = 99 %	a = 95 %
R(10)	No	(SE 0.004) No
R(60)	No	(SE 0.003) No

Table 12–21 - Ratio of Means Table for model compound Limonene ((R(T)=XT/Xref ± Uncertainty(T)), Slope of the Linear Regression significantly <> 0 ? Measurement unit : mg/dm^2

	0	*2*	*4*	*8*	*12*
R(10) ± U(10)	1,019 ± 0,039	0,988 ± 0,056	0,994 ± 0,046	1,019 ± 0,029	0,957 ± 0,070
R(60) ± U(60)	1,041 ± 0,039	0,943 ± 0,020	1,050 ± 0,047	1,030 ± 0,054	0,991 ± 0,049

	a = 99 %	a = 95 %
R(10)	No	(SE 0.002) No
R(60)	No	(SE 0.005) No

Table 12–22 - Ratio of Means Table for model compound Menthol (R(T)=XT/Xref ± Uncertainty(T)). Slope of the Linear Regression significantly <> 0 ? Measurement unit : mg/dm^2

	0	*2*	*4*	*8*	*12*
R(10) ± U(10)	0,898 ± 0,043	0,918 ± 0,020	0,966 ± 0,035	0,974 ± 0,030	0,980 ± 0,045
R(60) ± U(60)	1,027 ± 0,043	0,898 ± 0,034	0,984 ± 0,027	0,944 ± 0,053	0,921 ± 0,055

	a = 99 %	a = 95 %
R(10)	No	(SE 0.004) Yes
R(60)	No	(SE 0.005) No

Table 12–23 - Ratio of Means Table for model compound Phenyl cyclohexane. (R(T)=XT/Xref ± Uncertainty(T)). Slope of the Linear Regression significantly <> 0 ? Measurement unit : mg/dm^2

	0	*2*	*4*	*8*	*12*
R(10) ± U(10)	0,950 ± 0,038	0,945 ± 0,029	0,937 ± 0,036	0,968 ± 0,038	0,977 ± 0,043
R(60) ± U(60)	1,041 ± 0,041	0,952 ± 0,026	0,966 ± 0,038	0,989 ± 0,029	0,981 ± 0,046

	a = 99 %	a = 95 %
R(10)	No	(SE 0.003) No
R(60)	No	(SE 0.002) No

Table 12–24 - Ratio of Means Table for model compound Benzophenone (R(T)=XT/Xref ± Uncertainty(T)), Slope of the Linear Regression significantly <> 0 ? Measurement unit : mg/dm^2

	0	*2*	*4*	*8*	*12*
R(10) ± U(10)	1,027 ± 0,049	0,970 ± 0,025	0,936 ± 0,048	0,971 ± 0,033	0,972 ± 0,045
R(60) ± U(60)	1,046 ± 0,047	0,942 ± 0,026	0,998 ± 0,035	0,972 ± 0,051	1,009 ± 0,056

	a = 99 %	a = 95 %
R(10)	No	(SE 0.003) No
R(60)	No	(SE 0.003) No

13. ANNEX III – HOMOGENEITY DATA

Table 13–1 - Individual test results of bottle material thickness at height 110 mm

Sampling batch	*Individual test results*			
1	0.624	0.626	0.618	0.614
	0.621	0.627	0.612	0.621
	0.626	0.607	0.623	0.610
	0.621	0.619	0.617	0.614
2	0.616	0.617	0.624	0.622
	0.616	0.620	0.622	0.614
	0.623	0.626	0.614	0.608
	0.621	0.619	0.615	0.615
3	0.623	0.622	0.622	0.616
	0.617	0.623	0.602	0.611
	0.618	0.615	0.620	0.623
	0.619	0.623	0.608	0.614
4	0.621	0.616	0.622	0.628
	0.607	0.615	0.604	0.607
	0.622	0.609	0.616	0.616
	0.618	0.605	0.615	0.625
5	0.623	0.613	0.616	0.621
	0.609	0.617	0.623	0.611
	0.626	0.613	0.600	0.605
	0.612	0.605	0.611	0.624
6	0.614	0.634	0.620	0.619
	0.621	0.621	0.602	0.612
	0.624	0.610	0.614	0.618
	0.622	0.615	0.613	0.620
7	0.626	0.621	0.608	0.625
	0.618	0.622	0.627	0.618
	0.613	0.621	0.612	0.620
	0.624	0.628	0.609	0.623

European Commission

EUR 21075 – DG Joint Research Centre, Institute for Reference Materials and Measurements –
Certification of a refillable PET bottle material with respect to chemical inertness behaviour according to a pr-CEN standard method, BCR-712
Authors: R. Franz, G. Palzer, B.M. Gawlik, A. Bernreuther, A. Lamberty, D. Bennink
Luxembourg: Office for Official Publications of the European Communities
2004 – 62 pp. –21.0 x 29.7 cm
Scientific and Technical Research series
ISBN 92-894-7220-0

Abstract

A standardised and easy-to-apply method for general chemical inertness testing of refillable PET bottles was developed. It is applicable not only for the industry but also suitable for enforcement laboratories having for the first time a systematic control possibility to check the food safety of refilled PET bottles taken from the market. This chemical inertness test covers the sum of possible mechanical stress influences on the inertness behaviour of a PET material and, in case of complaint, allows 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.
In addition, a food grade reference PET material was prepared which fulfils the principle requirement of article 2 of the Framework Directive 89/109/EEC (1). This reference material was certified with respect to its interactivity values as shown below. Certified values were accompanied by an expanded uncertainty according to the requirements laid down in the Guide for the Expression of Uncertainty in Measurement (GUM) (2).

The mission of the Joint Research Centre is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of European Union policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Community. Close to the policy-making process, it serves the common interest of the Member States, while being independent of commercial and national interests.

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

15 LA-NA-21075-EN-C

ISBN 92-894-7220-0
9 789289 472203

Publications Office
Publications.eu.int