Ministry of Environment and Food of Denmark
Environmental Protection Agency

Determination of Migration Rates for Certain Phthalates

Survey of chemical substances in consumer products No. 149, 2016

Title:

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Authors:

Nils H. Nilsson
Jeanette Schjøth-Eskesen
Bjørn Malmgren-Hansen
Eva Jacobsen

Published by:

The Danish Environmental Protection Agency
Strandgade 29
DK-1401 Copenhagen K
www.mst.dk

Year:

2016

ISBN no.

978-87-93529-01-4

Contents

Preface

This report discusses the migration rates of the following five phthalates:

- Di(2-ethylhexyl) phthalate (DEHP)
- Diisononyl phthalate (DINP)
- Butyl benzyl phthalate (BBP)
- Di-n-butyl phthalate (DBP)
- Diisobutyl phthalate (DIBP)

The objective of this report is to identify and discuss the factors, which contribute to the uncertainties of migration rates published in the available literature, and to discuss why there seems to be no correlation between the migration rates and the concentration of phthalates in soft PVC articles, as would be predicted by Fick´s law for diffusion.

The project was carried out by Danish Technological Institute (DTI).

The following employees have contributed to the project:

Nils H. Nilsson (project leader), DTI
Jeanette Schjøth-Eskesen, DTI
Bjørn Malmgren-Hansen, DTI
Eva Jacobsen, DTI

This project was financed by the Danish Environmental Protection Agency (EPA), and the contact persons at Danish EPA were Shima Dobel and Toke Winther.

Summary and conclusion

The literature search covered essential literature from 1998 to 2015, with focus on literature from Denmark. In addition to studies from Denmark, a few other studies from the Netherlands, Austria, Sweden, Germany, Great Britain, Turkey, Canada, Japan and the United States were included. Besides the studies on migration rates, a search was also carried out on literature that discusses the results of the different migration studies.

It can be assumed that DEHP will have migration rates that are rather close to DINP because their molecular weights and physical/chemical properties are close to each other and the water solubility of both are extremely low (DINP < 1 µg/l and DEHP 3µg/l).

For DBP and DIBP, migration rates are expected to be much higher than for DEHP and DINP at the same concentration level due to their lower molecular weight and higher solubility in aqueous media (water, artificial sweat and saliva). However, in most cases the amount of these two phthalates will be rather low (a few percent and probably less than 10 % w/w) as they according to literature (Wilson, 1995) only are used as speciality plasticisers for facilitating the dispersion of the main primary plasticisers such as DEHP and DINP. A rather high content has been found in some consumer products (e.g. plastic sandals with 21.2 %w/w DIBP in Danish EPA no. 107 and training ball with 35.4 %w/w DIBP in Danish EPA no. 109). In these cases, DBP and DIBP are cheap primary plasticisers and the manufacturers have not tried to reduce the migration of phthalates.

BBP is mainly used for flooring and wallpaper and no migration rates have been found in the literature search. BBP probably has migration rates in between DINP/DEHP and DBP/DIBP at the same concentration level based on the solubility parameter, chemical structure and water solubility. It should be remembered that wear and tear is an important parameter for flooring and exposure from BBP can take place by dust generated in daily use.

It is not possible to determine one realistic migration rate for each of the five phthalates which will always be valid, since the migration rate of phthalates in soft PVC seems to be depending on many different factors such as the solubility of the given phthalate, the phthalate content in the specific product and other chemical and physical parameters.

The purpose of this report is to suggest migration rates for each of the five selected phthalates in soft PVC, which can be used for risk assessment purpose, in cases where the specific migration rate has not been measured. The suggested migration rates are based on numerous migration studies from the accessible literature.

One of the major factors on the migration rate is the way the migration analysis is carried out. Therefore, very different results were obtained depending on how vigorous the applied dynamic forces were. Due to that major factor, it has been necessary to divide the proposed migration rates according to the experimental set-up used.

Denmark, Austria and the United States use mild static or dynamic methods. The Netherlands have another dynamic method compared to Denmark, Austria and the United States that give higher migration rates but the migration rates are still below *in vivo* tests in adults. In contrast, Japan use very harsh dynamic tests in an attempt to obtain results in line with the *in vivo* test results obtained in voluntary adults to simulate children's mouthing and chewing on soft PVC products. This approach can be questioned, as it is not obvious that the adult *in vivo* measurements are the realistic values for migration for simulating children's exposure by sucking and chewing.

To our knowledge it is on a scientific base not possible to compare the conditions (chewing) of adults with the chewing/mouthing of children, as the oral cavity (e.g. musculature) of a child's mouth is not fully developed. Therefore, the chewing force of children is expected to be weaker than for adults. In addition, the stimulation of the saliva production by chewing might be different for children compared with adults. It can be questioned if the results from the *in vivo* adult studies are the true value for phthalate migration rates[1].

The analytical methods to determine the migration of phthalates are therefore divided into three categories: mild, medium and harsh conditions as seen in table 1. The mild conditions result generally in lower migration rates compared with the *in vivo* adult migration rates for the simulation of children's sucking and chewing on soft PVC products. The head over heels method (HOH) is judged as the most documented method of all, mostly for the migration rates for DINP to artificial saliva, but also a few for DEHP. The HOH method seems to be the most realistic method, since the given product is rotated once per second, which resembles how a child will chew on a toy. In addition, the test conditions such as temperature resemble the human body temperature at 37°C. For this reason and because the other methods are very different in their approach, the HOH method is recommended as the reference method for the determination of migration rates for phthalates well knowing that realistic migration rates are difficult to determine in *in vitro* or adult *in vivo* studies.

Compared with the mild methods based on static tests or dynamic tests using mild shaking or magnetic stirring the migration rates for the HOH method will be higher. Static tests will most likely give too low results, since products e.g. sandals and pacifiers will be in movement while being used.

When the migration rates are used for risk assessment purposes, a high migration rate will result in a more conservative risk assessment. The harsh method used by the Japanese studies seem far from reality by using dynamic test at 300 rpm and is judged to give too high migration rates.

As the HOH method first of all has been most documented for DINP the migration rates for the other phthalates have been determined by using a correction factor based on the mild migration studies or/and taking the chemical/physical properties of the phthalates in consideration (molecular weight, solubility in water, log K_{ow}, vapour pressure and δ_D (solubility parameter)).

TABLE 1
ANALYSIS METHODS DIVIDED INTO DIFFERENT CONDITIONS

	Analysis method
Mild	Static or dynamic conditions at 37±3°C (DK, A, TR, U.S.A.)
Medium	Head over heels method (NL) at 60 rpm
Harsh	Horizontal shaking at 300 rpm (J)

No migrations rates were found for BBP in the reviewed migration studies from the literature search. BBP was analysed for and detected in some products (e.g., sandals in the Danish EPA report no. 107, 2010 - Phthalates in plastic sandals), but the content of BBP was below the detection limit in most quantitative characterisations and in all the migration studies. This is as expected, as the

[1] Conferred with Professor Dorte Haubek, Aarhus School of Dentistry, Aarhus the 7th December 2015.

most common use is for flooring and wallpaper. It is expected that the migration rate of BBP would be similar or a little lower than DBP and DIBP due to the similar solubility parameter (δ_D) and partition coefficient (K_{ow}). Wormuth et al. 2006 and Wormuth 2006b listed migration rates for BBP (average migration rate was 0.002 µg/cm²/min and 0.02 µg/cm²/min respectively), but it was not possible to find the original reference with product information and analysis method.

Figure 1-4 give an overview of the results from the literature survey with the migration rates of the other four phthalates as a function of phthalate content.

FIGURE 1
MIGRATION RATE AS A FUNCTION OF DEHP CONTENT (%W/W) FOR THE MILD CONDITIONS (LEFT GRAPH) AND MEDIUM AND HARSH CONDITIONS (RIGHT GRAPH)

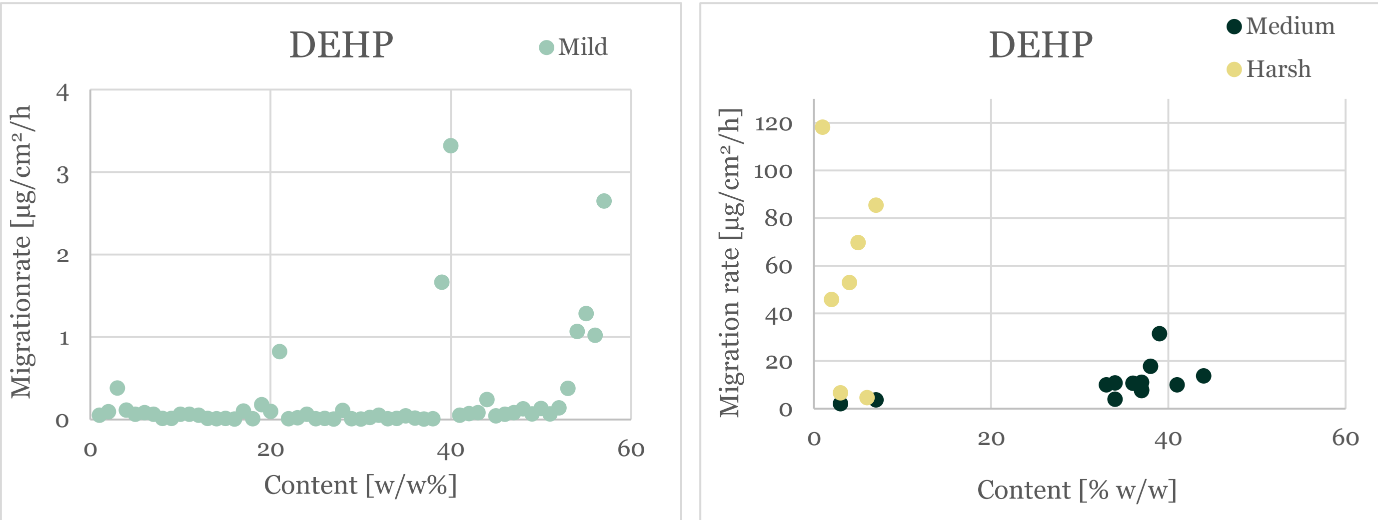


FIGURE 2
MIGRATION RATE AS A FUNCTION OF DINP CONTENT (%W/W) WITH MILD CONDITIONS (LEFT GRAPH) AND MEDIUM AND HARSH CONDITIONS (RIGHT GRAPH)

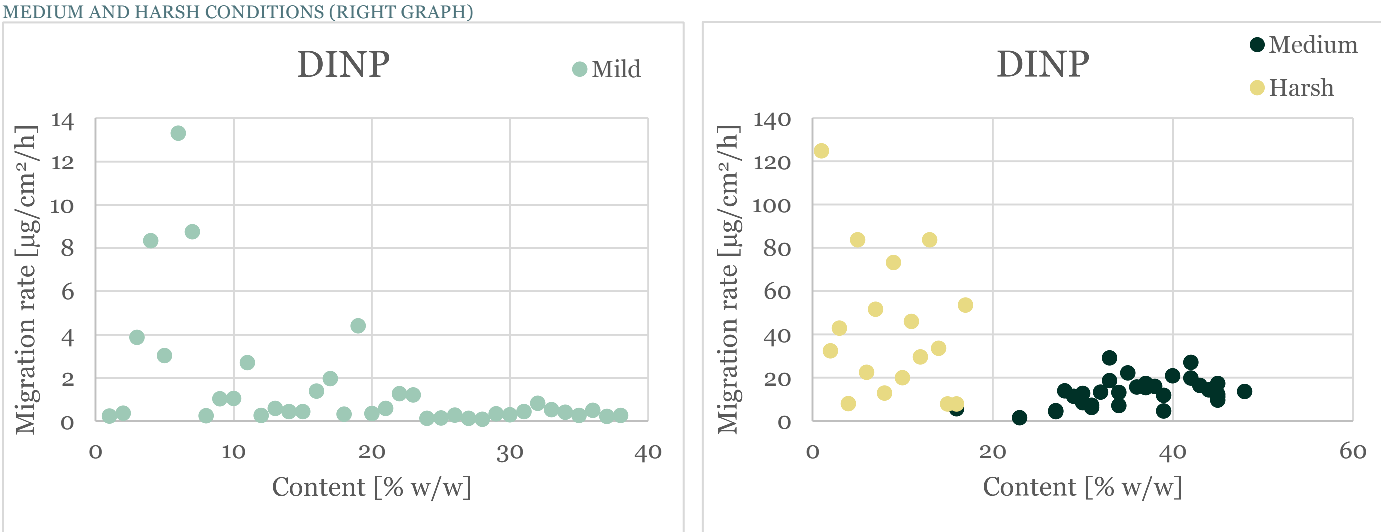


FIGURE 3

MIGRATION RATE AS A FUNCTION OF DBP CONTENT (%W/W) WITH MILD CONTIDIONS (LEFT GRAPH) AND HARSH CONDITIONS (RIGHT GRAPH)

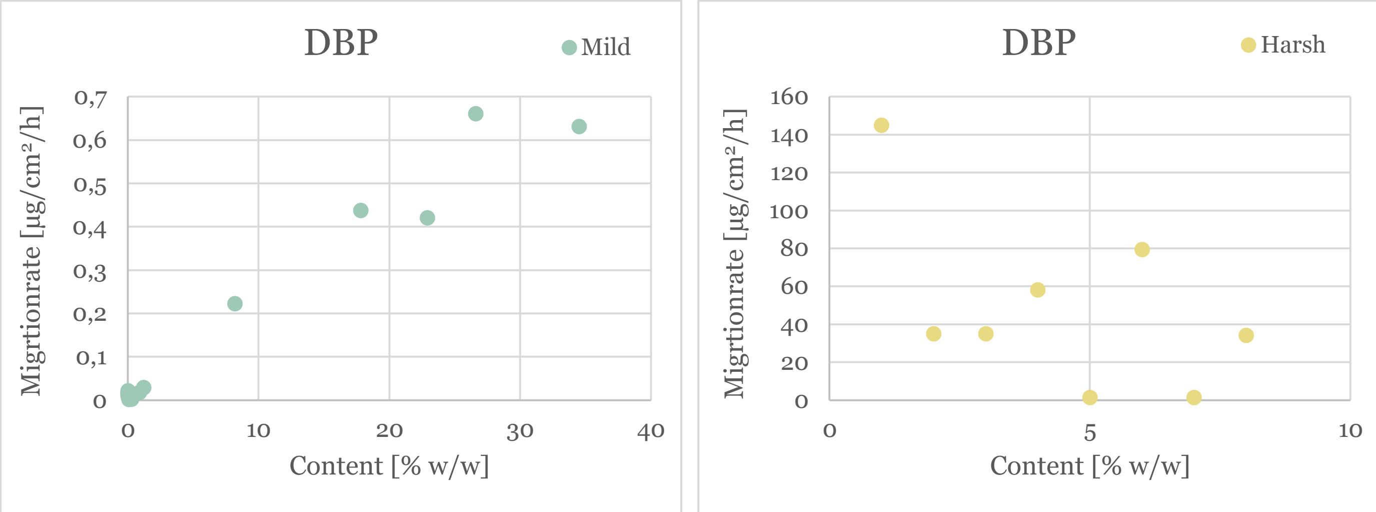
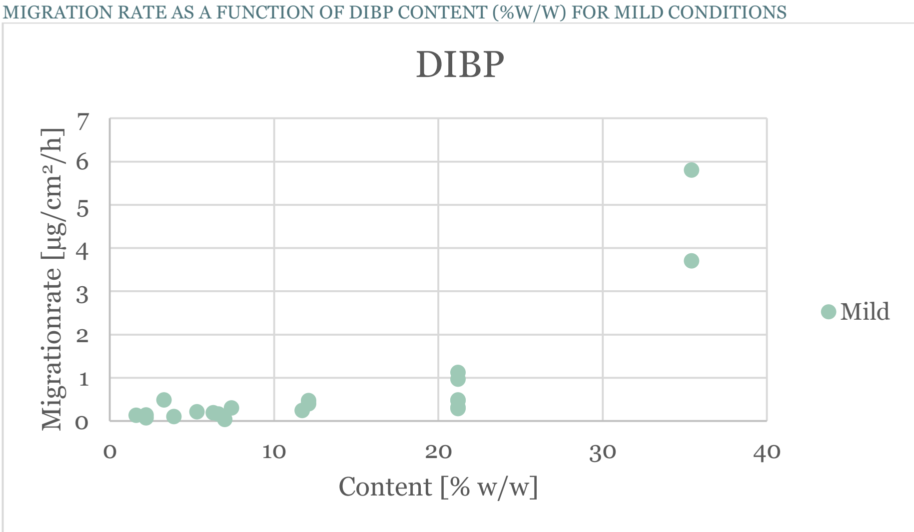


FIGURE 4
MIGRATION RATE AS A FUNCTION OF DIBP CONTENT (%W/W) FOR MILD CONDITIONS



The migration rates illustrated in the figures above have no clear correlations to the content of phthalates. The average migration rates are divided into the mild, medium and harsh analytical method conditions. The results have then been subdivided in minimum, mean and maximum values similar to Wormuth et al., 2006. The mean is obtained by taking all the mean values from the studies in the three conditions. The results are in the unit µg/cm²/h.

TABLE 2
MIGRATION RATES FOR THE MILD ANALYTICAL METHOD CONDITIONS

Migration Rate from PVC (µg/cm²/h)			
Phthalate	**Minimum**	**Mean**	**Maximum**
DEHP	0.002	0.27±0.62	3.31
DINP	0.09	1.61±2.80	13.3
DBP	0.001	0.17±0.24	0.66
DIBP	0.04	0.77±1.39	5.80

TABLE 3
MIGRATION RATES FOR THE MEDIUM ANALYTICAL METHOD CONDITIONS

	Migration Rate from PVC (µg/cm²/h)		
Phthalate	**Minimum**	**Mean**	**Maximum**
DEHP	0.04	10.7±7.99	31.3
DINP	1.5	13.3±6.44	29.1
DBP	-	-	-
DIBP	-	-	-

TABLE 4
MIGRATION RATES FOR THE HARSH ANALYTICAL METHOD CONDITIONS

	Migration Rate from PVC (µg/cm²/h)		
Phthalate	**Minimum**	**Mean**	**Maximum**
DEHP	4.4	54.6±41.0	118
DINP	7.8	44.8±33.4	124.8
DBP	1.17	48.5±46.9	144.8
DIBP	-	-	-

Calculations have been made in order to estimate migration rates for the five phthalates. The basis is the HOH method, since this method seems to give the most realistic migration rates, as the product is rotated once per second, resembling the use of a product. The HOH method is also the most documented for DINP to artificial saliva and the other methods make use of very diverse experimental conditions which make comparison difficult. The migration rates for the remaining four phthalates are based on the results from the mild migration studies by using a correction factor and/or taking the chemical-physical properties of the individual phthalates in consideration (molecular weight, solubility in water, log K_{ow}, vapour pressure and δ_D (solubility parameter)). For statistical reasons the HOH results were only based on DINP, since migration rates for DEHP were only measured a few times by HOH and migration rates for the three other phthalates were not measured by HOH.

At present as far as the many studies for migration of phthalates have been carried out in very different ways it shall be recommended to use the following migration rates for calculation of risk of exposure to the phthalates until further evidence is available:

TABLE 5
ESTIMATED MIGRATION RATES FOR THE FIVE PHTALATES

	DEHP	DINP	DIBP	DBP	BBP
Migration rate (µg/cm²/h)	10	13	13	13	12

The estimated migration rates are quite close to each other. The migration rates for DIBP and DBP should in theory be higher than the migration rates for DINP and DEHP if the content of the phthalates in the products are similar. The reason for the similar migration rates estimated is that the concentrations of DIBP and DBP in most cases are lower than the concentration of DEHP and DINP in the products. Even though results indicate that there is no correlation between the content and migration, very low contents of phthalates are expected to give relatively lower migration rates. This could also explain why the results are not compatible with Wormuth et al., 2006, because there are low concentrations of the phthalates in the products and these are most likely added as a processing aid before adding DEHP or DINP, but still have a softening effect. In Wormuth et al., 2006 it is also stated that only samples with low DIBP content are considered. According to Fick's law the migration rate will depend on the concentration level, therefore without knowing the phthalate content, it is difficult to compare the listed migration rates in table 5 with the results found from Wormuth et al., 2006.

A more in-depth discussion in ECHA, 2013 of the data for migration rates of DINP to artificial saliva has led to the conclusion that the migration rate from mouthing of toys will be an *in vitro* migration rate of 45 $\mu g/cm^2/h$, measured for a plate with a content of 40.7% w/w DINP and a typical *in vivo* estimate will be 14 $\mu g/cm^2/h$. The latter value of the migration rate is based on taking the mean of all the means from the *in vivo* studies. It is not evident why the *in vivo* results are lower than the *in vitro* result, but it is very interesting that our proposal for *in vitro* migration rates are comparable with the *in vivo* results from ECHA, 2013.

The above calculated migration rates do not consider the possible of using cosmetic products such as sun oil and other skin care products or fatty emulsions from e.g. milk and vegetable fat present in when making risk assessments. This would increase the migration rates as seen in the Danish EPA no. 107, 2010.

The method described in DS/EN 71-10 by using pure water as the simulant for both sweat and saliva should be considered to use in a standardized migration method. Carrying out the migration step at 20 °C for 1 hour is recommended for practical reasons in the standard instead of 37° C, as this does not seem to have a significant effect on the migration rate compared to other alterations, but still having in mind that migration rates will increase with temperature.

The correlation between *in vivo* and *in vitro* migration rates is not obvious. In one study the migration rate for DINP to artificial saliva was much higher *in vitro* than *in vivo* (Niino, 2003), but in another study the *in vivo* migration rate was a factor (in mean) 39.5 higher than the *in vitro* migration rate (Babich, 1998). In both studies, many factors influencing the migration rates have been discussed and it can be questioned as discussed above how valid "real" migration rates (determined *in vivo*) are to the true migration rate for children who chew and suck on soft PVC toys. It has to be mentioned that saliva might contain fatty emulsions from ingestion of food, e.g., milk and vegetable fat, and from contact with suntan lotion and fat/oil-containing cosmetics and the migration can increase several orders from 5 – 1000 times.

Abbreviations and acronyms

A	Austria
ACN	Acetonitrile
BBP	Butyl Benzyl Phthalate
BfR	Bundesinstitut für Risikobewertung
BnBzO	Benzoic acid Benzyl ester
Bs	British Standard
CSTEE	Scientific Committee on Toxicity, Ecotoxicity and the Environment
DBP	Dibutyl phthalate
DCM	Dichloro Methane
DEHP	Di(2-ethylhexyl) Phthalate
DINP	Diisononyl Phthalate
DK	Denmark
DOP	Di(2-ethylhexyl) Phthalate
DS	Danish Standard Organization
ECHA	The European Chemicals Agency
EN	European Norm
EPA	Environmental Protection Agency
GC/MS	Gas Chromatography with Mass Spectroscopy detection
HOH	Head Over Heels
HPLC	High Pressure Liquid Chromatography
HPTLC	High Performance Thin Layer Chromatography
ISO	International Standardization Organisation
J	Japan
JRC	Joint Research Centre
Log P_{ow}	The logarithm to the partition coefficient between octanol and water. Also known as Log K_{ow}.
LOUS	Danish List of Undesirable Substances
NL	Netherland
PVC	Polyvinyl Chloride
SOP	Standard Operating Procedure
t_g	Glass Transition Temperature
THF	Tetrahydrofuran
TPE	Thermo Plastic Elastomer
TR	Turkey
U.S.A.	United States of America
δ_D	Solubility Parameter
% w/w	Weight Percentage

1. Introduction

1.1 Background

Over the years, the Danish Environmental Protection Agency (EPA) has completed a number of projects involving studies on the migration rate of phthalates, in many cases from "worst-case" scenarios. The "worst-case" scenarios are set up based on the use of the products and the direct contact with the products either via skin contact or mouthing. These studies have involved a number of different consumer products with these five phthalates in focus, where the content in the products and the migration have been quantified. Surprisingly there does not seem to be a readily correlation between the concentration of phthalates in the products and the migration rates of the phthalates.

For international studies, the situation is the same. It is not possible to make a correlation between the content of phthalates and the migration rates.

The purpose of this report is to suggest migration rates for specific phthalates in soft PVC. The suggested migration rates will be based on numerous migration studies from the accessible literature. The background to the varying migration rates will be investigated, discussed and evaluated. Based on the evaluation suggested migration rates will be established without having to conduct actual migration analyses.

The focus in this report will only be on the migration of the following phthalates: di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), butyl benzyl phthalate (BBP), di-n-butyl phthalate (DBP) and diisobutyl phthalate (DIBP) from soft PVC that are in contact with artificial sweat or saliva simulants. Comparison with *in vivo* studies will be included when they exist.

These five phthalates are studied, because DEHP, BBP, DBP and DIBP are part of ECHA's authorisation scheme and that DINP is one of the most used phthalates in soft PVC.

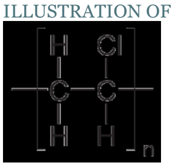
This report will highlight the factors and parameters that will influence the analytical determination of the migration rates for the five phthalates to artificial saliva and artificial sweat and the uncertainties they may contribute with in the calculations of the migration rates.

1.2 Soft PVC

1.2.1 Properties of PVC raw material

Soft polyvinyl chloride (PVC – Illustrated in Figure 1) - also called plasticised or flexible PVC - covers a very broad and manifold variety of formularies (recipes) that have different physical and mechanical properties. Soft PVC can be processed by nearly all methods used for thermoplastics.

FIGURE 5
ILLUSTRATION OF THE REPEATING UNIT OF PVC



The raw material of PVC is rigid and brittle with a glass transition temperature t_g = 80 °C to 107 °C (Wypych, 2015). Below t_g, the amorphous regions of a polymer are in the glassy state and the polymeric PVC molecules are nearly motionless which means that the polymer below t_g generally is hard, brittle and rigid. It is produced by chlorination of ethylene and the raw material is most commonly sold as a powder. The PVC raw polymer has a weight average molecular weight of between 70,000 and 500,000+ g/mol. The low molecular weight PVC resins aid the melting process and they can be used for high filler compositions, e.g., calcium carbonate.

In literature, PVC is described as an amorphous plastic material, but in fact there are small regions in well-arranged order within the polymeric structure, and the "crystallinity" of PVC is in the range of 0.5% to 10% and has a melting point of 285 °C (Wypych, 2015).

1.2.2 Plastification of PVC

The raw material of PVC becomes soft by adding plasticisers to the PVC in amounts of up to 50% w/w or even more. The typical range for soft PVC is 30 – 50% w/w (Baur et al., 2007). The most common plasticisers are phthalates of orthophthalic acid with linear or branched alcohols on the carbon chain (often on the seventh carbon (C7) to the thirteenth carbon (C13)). For many years, DEHP has been the most used plasticiser for PVC accounting for 65 – 70% of the world market (Baur et al., 2007). After the classification of DEHP as toxic for reproduction, DEHP was substituted for many uses and the use of DINP raise. DEHP, DBP and BBP have been restricted in toys and childcare articles in EU since 2007 and DINP has been restricted in toys and childcare articles that can be put in the mouth since 2007 (REACH Annex XVII, Entry 51 and 52). In addition, DIBP is restricted in toys (Toy Safety Directive 2009/48/EC) in concentrations above the classification limit.

The t_g of soft PVC depends on the amount of plasticiser. The higher the amount of plasticiser, the lower the t_g. For example, PVC with a content of 30%w/w DEHP has a t_g = 0 °C depending on the additives used in the PVC (Wypych, 2015). The hardness of soft PVC, measured as Shore A, is often used to characterize the soft PVC with regard to brittleness. In the range 60 – 70 Shore A, which also is typical for rubber, the soft PVC becomes brittle in the temperature interval -30°C to -50 °C (Baur et al., 2007)

The amorphous part of PVC accepts the plasticisers, while the ordered structure ("crystallites") preserves the structure. In order to fuse the main plasticiser (e.g., DEHP and DINP with rigid PVC) it is common practice to add phthalates like DBP and DIBP in the mixing process. DBP and DIBP will make the PVC swell as they have a solubility parameter closer to PVC than the main plasticisers do. This will lower the viscosity and make processing faster. It has not been possible to find information on how much DBP and DIBP is added to the formularies for soft PVC, but it is estimated to be low due to the higher tendency to migrate compared to DEHP and DINP because the molecules are smaller (around 5 – 15 % w/w). To maintain the physical properties of PVC it is important that the plasticisers do not destroy the crystalline part of the PVC, but solely enter the amorphous phase (Wilkes et al., 2005). However the literature studies surprisingly reveal that in some consumer products rather high amounts (10 – 35 % w/w) of DBP and DIBP is used e.g. sandals and balls.

1.2.3 Comparison of soft PVC and rubber/TPE

In many ways, soft PVC behaves like rubber. A comparison to TPEs (thermoplastic elastomers) is fair, as TPEs also behave like rubber due to the crystalline regions in the polymer molecular structure that imitates the chemical crosslinks in rubber. Soft PVC and TPEs can be melted again at temperatures above the melting point of the crystallites. That is not possible with rubber, due to the chemical bonds between the rubber polymer chains.

1.2.4 Other additives in soft PVC

Besides the plasticisers, the soft PVC formularies can contain a number of other additives such as stabilisers, lubricants, fillers, colorants, blowing agents and viscosity regulators, but in smaller amounts than the plasticisers. The filler content often ranges from 30 – 40% w/w in soft PVC.

Thermal stabilisers are the most important additives used in soft PVC besides the plasticisers and the fillers and are always part of the formularies. They are typically added in concentrations from 0.05 – 5% w/w. The thermal stabilisers are a group of different chemical substances. Important types are barium/calcium/zinc carboxylates, butyltin-based substances, epoxidised soybean oil and different organic phosphites. Synergy exists between these different substances and their function is to protect the PVC during processing by preventing oxidation and liberation of hydrogen chloride.

1.2.5 Processing of soft PVC and formularies

Soft PVC can be processed either through a melting process or as plastisols. The former most common melting processes are extrusion, calendaring and injection moulding. The latter are dispersions of the solid particulate components (mainly PVC emulsion resins) of a formulation in the mixed liquid component (mainly plasticisers). The main application of melted PVC is for construction, rigid pipes and wire and cable insulation. The main large-scale applications of plastisols comprise wallpaper, cushion vinyl flooring, upholstery, carpet backing and unsupported PVC for car interior trims. The plastisols are stable until 35 °C, but when heated to 150 – 220 °C they obtain the typical properties of soft PVC (Baur et al., 2007).

Table 6 shows an example of a formulary for toys from 1997, where DEHP was not yet banned for use in toys. Today non-orthophthalate ester plastisicers are often used instead, for example di(2-ethylhexyl) adipate and acetyl tributyl citrate (Report to the U.S. Consumer Product Safety Commission, 2014).

TABLE 6
EXAMPLE OF A FORMULARY FOR TOYS FROM 1997 (WYPYCH, G. 2015)

Raw material	Concentration, parts
PVC dispersion resin	50
PVC blending resin	50
DEHP	81
2,2,4-Trimethyl-1,3-pentanediol diisobutyrat	9
Epoxidised soybean oil	5
Stabiliser	3

In the PVC formulary (Wypych, 2015), around 600 formularies for soft PVC for different applications are recorded. However, it is estimated that several thousand formularies exist and they are most frequently used for technical articles and not for toys.

1.3 Rules for migration

The migration rate depends on a number of parameters such as size, molecular weight, chemical bonds, solubility and initial concentration in the plastic polymer. It can be complicated to determine the migration rate of phthalates from soft PVC, since they are not covalently bonded to the polymer chain. Therefore, the migration rate depends both on the properties of the plastic as well as on the properties of the specific phthalate.

The migration rate of organic chemical substances depends to a large degree on the size. The boiling points for a phthalate increase as the number of carbons increase in the ester groups. Small molecules, typically monomers and residual solvents, will migrate fast as they often have a low boiling point and a small molecular size, which makes it easier to travel through the amorphous phase of the plastic polymer because they need less space to find pathways in the polymeric plastic structure. For the five phthalates studied, the higher molecular weight chemical substances are bigger molecules. This means that they demand more space in the amorphous plastic structure since the molecule is larger. For this reason, the migration rate will slow down for chemical substances with similar chemical structures.

The molecular weight of substances used as additives in plastic are estimated to be in the range of 200 – 2000 g/mol. The five phthalates in this study have a molecular weight in the range of 278 to 404 g/mol and will migrate faster than high molecular weight components.

Another requirement for the additives is that the solubility of the additive in the plastic should be high, but low in a liquid in contact with the plastic. That can be judged by log P_{ow} (log K_{ow}) or the solubility data (solubility parameters δ). As originally defined, δ is directly related to the cohesive energy density, and different materials are mutually compatible when they have similar values of δ. The solubility of the five phthalates in water especially for DEHP and DINP are very low, and therefore the tendency to migrate to a water based simulant like artificial saliva or sweat will be low. This means that the migration rates for the discussed phthalates will be low or even undetectable in static *in vitro* experiments if the migration alone is based on the water solubility of the phthalates. However, migration is not only governed by the water solubility but also by the volatility depending on their chemical structure and boiling point.

The initial concentration of the chemical substance in the plastic, the thickness of the plastic item, the crystallinity of the plastic and the surface structure of the plastic item will influence the migration rate in a rather complex way, but the main route to migration is via the amorphous regions in the plastics. PVC is considered amorphous, but as mentioned earlier it has regions of some ordered structure (crystallites), which plays a major role for the properties of soft PVC.

The flux J of substances (additives) from plastics (in this case migration of plasticisers from soft PVC) obeys Fick's law:

$$J = -D \cdot \frac{dC}{dx}$$

where D is the diffusion coefficient of the substance, J is the flux (mole of substance per time unit) and dC/dx is the concentration difference of the substance over the diffusion distance.

The flux J will decrease over time when the concentration in the product decreases and the diffusion coefficient D will depend on the temperature according to an Arrhenius relation

$$D = K \cdot e^{-\frac{E}{RT}}$$

The flux can be integrated over time to a total migration M.

For a given time and temperature the total migration can be modelled according to:

$$M = C_0 \cdot t^{0.5} \cdot K \cdot e^{-\frac{E}{RT}}$$

Where M: Migration
C_0: Concentration of the migrant in the polymer
t: Time

K: Constant
T: Temperature
E: Activation energy
R: Gas constant

The constant K is a material constant. In this context, the constant depends on the formulary of soft PVC. The same is the case for the activation energy.

In practice, the migration of substances from plastics is measured in contact experiments under estimated worst-case scenarios, because this will give a higher safety factor in health exposure calculations. Some methods for food contact materials and for pharmaceuticals are standardised which makes comparison of results much more transparent. Other migration studies where standardised methods are not used have to be set up according to the use of the plastic. This is the case for most migration studies for consumer products.

Attempts have also been made to standardise experiments for determination of migration rates from soft PVC from consumer products to artificial saliva and sweat, but the success is limited and the correlation between the amount of phthalates in the products, the migration rates and *in vivo* adult studies simulating children sucking and chewing on soft PVC products is not obvious.

2. Factors affecting migration rates

2.1 Physical and chemical properties of the five phthalates

For each of the five phthalates an overview of some of their chemical and physical properties is given, e.g., structure, molecular weight and solubility parameter, as these are parameters that could influence the migration.

TABLE 7

OVERVIEW OF RELEVANT CHEMICAL AND PHYSICAL PROPERTIES OF DEHP

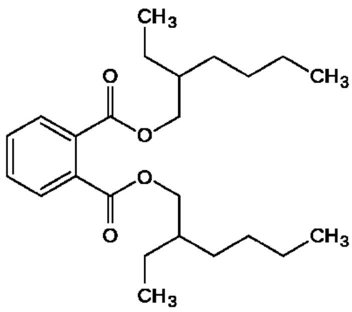
Substance	Bis (2-ethylhexyl) phthalate (DEHP)
Structure	
Molecular weight	390.56 g/mol
CAS No.	117-81-7
Migration properties	Boiling point: 385 °C at 1013 hPa, vapour pressure: 0.000034 Pa at 20 °C, partition coefficient (log value) log P_{ow}= 7.5 (Hansen & Nilsson, 2014). δ_d=16.6 $MPa^{0.5}$ (Wypych, 2015). Water solubility 3 µg/liter at 25 °C (Staples et al., 1997)

TABLE 8
OVERVIEW OF RELEVANT CHEMICAL AND PHYSICAL PROPERTIES OF DINP

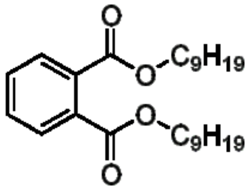
Substance	Diisononyl phthalate (DINP)
Structure	
Molecular weight	418.61 g/mol
CAS No.	68515-48-0/28553-12-0
Migration properties	DINP is not a pure substance, but a complex mixture containing mainly C_9 – branched alcohol isomers. Boiling point 244 to 252 °C at 7 hPa, vapour pressure: $9 \cdot 10^{-7}$ hPa at 25 °C, partition coefficient (log value) log Pow= 6.9 at 25 °C (Hansen & Nilsson, 2014). δ_d=16.2 $MPa^{0.5}$(Wypych, 2015), water solubility < 1 µg/liter at 25 °C (Staples, 1997)

TABLE 9
OVERVIEW OF RELEVANT CHEMICAL AND PHYSICAL PROPERTIES OF BBP

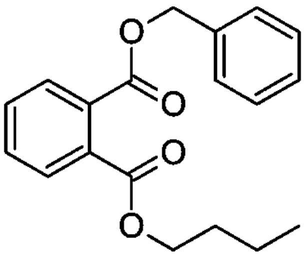
Substance	Benzyl butyl phthalate (BBP)
Structure	
Molecular weight	312.37 g/mol
CAS No.	85-68-7
Migration properties	Boiling point: 370°C at 10.10 hPa, vapour pressure: 0.00112 Pa at 20°C, partition coefficient (log value) log P_{ow}= 4.84 (Hansen & Nilsson, 2014). δ_d=19.1 $MPa^{0.5}$ (Wypych, 2015), water solubility 2700 µg /liter at 25 °C (Staples, 1997)

TABLE 10
OVERVIEW OF RELEVANT CHEMICAL AND PHYSICAL PROPERTIES OF DBP

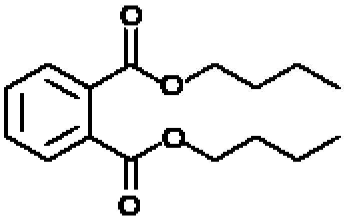
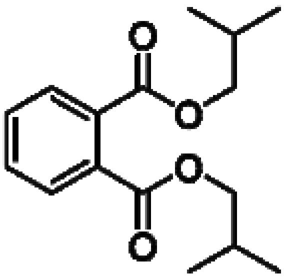
Substance	Dibutyl phthalate (DBP)
Structure	
Molecular weight	278.35 g/mol
CAS No.	84-74-2
Migration properties	Boiling point: 340°C at 10.013 hPa, vapour pressure: 9.7±3.3·10-5 Pa at 25 °C, partition coefficient (log value) log P_{ow}: 4.57 at 20°C (Hansen & Nilsson, 2014). δ_d=17.8 $MPa^{0.5}$ (Wypych, 2015), water solubility 11200µg/liter at 25 °C (Staples et al., 1997)

TABLE 11
OVERVIEW OF RELEVANT CHEMICAL AND PHYSICAL PROPERTIES OF DIBP

Substance	Diisobutyl phthalate (DIBP)
Structure	
Molecular weight	278.35 g/mol
CAS No.	84-69-5
Migration properties	Boiling point: 320 °C, vapour pressure: 0.01 Pa at 20 °C, partition coefficient (log value) log P_{ow}: 4.11 (Hansen & Nilsson, 2014). The solubility parameter (δd) is unknown, but the value is estimated to be similar to DBP, water solubility: 20000 µg/liter at 25 °C (Staples et al., 1997).

From the physical/chemical properties such as the solubility parameter and water solubility, the migration rate will be different for the five phthalates. At the same concentration levels, the migration rates for DBP and DIBP are expected to be the highest of the five phthalates. BBP is expected to have migration rates between DBP and DIBP, and DEHP and DINP, which latter is expected to have the lowest migration rates to artificial sweat and saliva.

2.2 Knowledge on formulary

In nearly all studies, the formulary of soft PVC is unknown. As the chemical substances in the formulary can influence the migration rates of the phthalates significantly, e.g., by using plasticisers in different concentrations and different chemical structure and mixtures, high filler content and extender oils, there is no fixed migration rate for phthalates in soft PVC. If the material is foamed, the number of closed and open cell structures will influence the migration because the cells will contain air or blowing gases. In addition, the molecular weight distribution of the PVC raw material and the amount of crystallites can influence the migration rates, as migration depends on the free volume between the polymer PVC chains. The influence of the filler depends on amount and particle size. Nanoparticular fillers can reduce the migration rates of plasticisers (Lirova, 2008).

The free volume is a measure of the internal space between the polymer chains. The higher the free volume is, the better the polymer chains can move between each other. The addition of plasticisers to rigid PVC lowers the glass transition temperature. In this way, they make the PVC more soft and rubber-like by increasing the free volume between the PVC polymer chains. This is because they force the chains from each other and in that way lowers the attraction between the PVC polymer chains (the so-called Van der Waals forces).

2.3 History of samples

In most cases, the samples for determination of content of phthalates and for migration measurements have been bought in supermarkets, toy shops etc. However, the history of the samples is unknown regarding manufacture and shipment to the shops (temperature and humidity during storage, packaging conditions) and storing before the customers purchase the product. All these factors can affect the migration of the phthalates in an unpredictable way. Shashoua, 2001, discusses factors affecting the migration and degradation of products made of soft PVC and stored in museums for long time.

Generally phthalates can migrate to the surface of soft PVC during storage and transport, phthalates that already have migrated to the surface of the products will contribute to the migration rates determined in the migration tests, but that will not significantly change the content in the article (Amberg Müller et al., 2010). In fact, the migration rate of the phthalates during exposure under static conditions will be lower according to Fick´s law compared to dynamic conditions, because the driving force is the difference in concentration between the outer part of the product and the concentration in the borderline in contact with the simulant. For dynamic test, the simulant at the surface will be exchanged with fresh simulant during the study, which will not be the case in the static tests. However, the phthalates that already have migrated to the surface will contribute to the concentration measured after exposure to the simulant, and therefore the determined migration rate is expected to be higher - especially in dynamic migration studies as explained above.

2.4 Sample preparation

The preparation of the sample before analysis can have a major influence on the results for the migration step of the analysis. In some studies, the sample is washed/dipped in fresh simulant before testing. Rinsing the surface with a detergent in water and rinsing with demineralised water will make it possible to remove already migrated phthalate from the surface of the soft PVC product before the migration test, and that will eliminate the problems with unknown prehistory mentioned above. Cutting the PVC products for the migration test might result in new surfaces with a surface structure that differs from the finished product.

2.5 Methods for migration analysis

Compared to the quantitative analysis of the specific phthalates in soft PVC, it is a challenge to make consistent migration analysis for phthalates to artificial saliva and sweat. This is reflected in the migration rates referenced in the open literature. The migration rates will be rather low in comparison with the very short exposure time used in the analysis. This means that the result in many cases will be that the concentration of phthalate is lower than the detection limit of the method.

Major factors influencing the migration rate are:

- Formulary of the soft PVC
- The history of the article
- Homogeneity of the article
- Surface structure and volume of the article
- Sample preparation
- Temperature during contact with artificial saliva or sweat
- Static or dynamic test conditions
- Migration time
- Differences between the artificial saliva and human saliva
- Differences between artificial sweat and human sweat

A few parameters regarding the technical aspect of the extraction procedure also have to be considered:

- Contamination of reagent solvents, utensils, glassware etc.
- Extraction yield in the concentration of phthalates by solvent extraction
- Selectivity of the chromatographic method of analysis and detection limit

2.5.1 Formulary, history and homogeneity of the article

As mentioned in chapter 2.2, the formulary of the soft PVC is usually unknown and so is the prehistory and homogeneity. The parameters are only known in cases where reference materials of soft PVC have been made.

2.5.2 Surface/volume/density of the article

The surface structure of the article might influence the migration rate as well as the volume/density. If the article is foamed, the number of closed and open cells will influence the migration. For foamed articles, the density will be low unless a filler has been added, like e.g., calcium carbonate.

2.5.3 Contamination of reagents, solvents, utensils, glassware etc.

It is common to specify that all laboratory equipment used for the analysis must be clean and phthalate free. However, in laboratories the possibility still exists for contamination with phthalates at low level because phthalates are also used for PVC hoses, in glue, etc. This is not problematic for the quantitative analysis, as the concentrations used for plasticising purpose are much higher than the levels of contamination from laboratory equipment. It can though be a problem when measuring the migration, as the concentration of phthalates in the migration liquid is rather low.

2.5.4 Static and dynamic tests

It must be expected that the static tests give lower migration rates because the dynamic experiments will remove already migrated phthalate from the sample surface.

In addition to the principle of dynamic testing, the shaking and stirring speed will influence the migration rate in a complex way. The preparation of the sample for analysis will also influence the migration. In most cases, a spherical or quadratic sample is removed from the article in various ways, e.g., by using a hobby knife, by scissoring or by using a punching press or cork borer.

Loose particles of soft PVC that are liberated during the dynamic test can have a major influence on the migration rate determined, as those particles will be extracted in the next step of the analysis (solvent extraction) and result in significantly higher migration rates. For this reason the JRC method describes the importance of avoiding loose particles in the sample preparation step.

2.5.5 Artificial saliva and sweat

Human saliva is a complex fluid, secreted by the major and minor saliva glands. A comparison between natural saliva and very complex formulary is discussed including surface tension studies (Preetha et al., 2005; Harvey et al., 2010; Callewaert et al., 2014).

As most studies for migration rates found in the literature have been carried out with artificial saliva or sweat as simulants, examples of standardised formularies for these are given below.

TABLE 12
FORMULARY FOR ARTIFICIAL SALIVA ACCORDING TO SIMONEAU ET AL., 2001A

Compound	mg/L
Magnesium chloride	166.7
Calcium chloride	147.0
Dipotassium hydrogen phosphate	753.1
Potassium carbonate	525.2
Sodium chloride	327.3
Potassium chloride	745.5

* The pH is adjusted to pH 6.8 by adding diluted hydrochloric acid.

TABLE 13
FORMULARY FOR ARTIFICIAL SALIVA ACCORDING TO BS 6684 (NOW WITHDRAWN)

Compound	g/L
Sodium chloride	4.5
Potassium chloride	0.3
Sodium sulphate	0.3
Ammonium chloride	0.4
Urea	0.2
Lactic acid	3.0

* The pH is adjusted to 4.5 – 5.0 with 5 M sodium hydroxide in water.

TABLE 14
FORMULARY FOR ARTIFICIAL SWEAT ACCORDING TO DS/EN 1811:2011, 4TH EDITION, AND DS/EN ISO 105-E04:2013

Compound	% w/w
Sodium chloride	0.5
Lactic acid	0.1
Carbamide	0.1

* The pH is adjusted to 6.50 by adding 1 and 0.1 M sodium hydroxide solution (in older formularies 0.1% ammonia solutions have been used instead).

TABLE 15
FORMULARY FOR ARTIFICIAL SWEAT ACCORDING TO EN-ISO 105-E04:2013

Chemical	g/L
1-histidine-monohydrochloride-1-hydrate	0.5
Sodium chloride	5
Sodium dihydrogen ortho phosphate dihydrate	2.2

* The pH is adjusted to 5.5 with 0.1 M sodium hydroxide solution.

The simulants do not approach the properties of human saliva and human sweat. From the composition, it is judged that they have been developed with the aim to study migration rates for heavy metals like nickel, lead, cadmium and mercury. Complexity of human saliva, is discussed in (Preetha, 2005) and human sweat it is discussed in (Harvey et al.,2010).

2.5.6 Extraction method and yield

When the sample has been exposed to artificial saliva or sweat, either statically or dynamically at the test temperature and the chosen surface/volume ratio, the contact simulant is extracted by an organic solvent. Examples are cyclohexane or dichloromethane (DCM) using a separatory funnel and ensuring that phthalates adsorbed to the bottle used in the test also are transferred to the funnel. The extraction step can be repeated to assure that the extraction yield is high.

The two phases are separated and the contact simulant (artificial saliva or sweat) is discarded. At this stage, an internal standard is added to a known volume of the solvent phase for the calculation of concentration in the chromatographic analysis.

The amount of phthalate to be analysed is very small and the solubility in water is very low, and therefore the extraction step can be critical, as external contamination of phthalates from other sources is possible, and as the phthalates might adhere to the surface of the glassware.

Solid phase micro extraction (SPME) was also used to concentrate the phthalates from the migrate simulant after exposure.

2.5.7 Chromatographic analysis of contact simulant extracts

To quantify the specific phthalates it is estimated that the only reliable method of analysis is GC/MS using a capillary column. The HPLC method, described in detail in the standard operating procedure (SOP), in Simoneau et. al, 2001b, does not have sufficient selectivity (use of UV detector at 225 nm) or resolving power (number of theoretical plates) to analyse migration extracts from soft PVC articles with unknown formulary. The same SOP uses BBP as internal standard. BBP is part of this study and cannot be used as internal standard for this reason alone. The risk of false positive is expected to be larger in the HPLC method because the chosen UV detection wavelength is rather unspecific. Only if the formulary is known, the HPLC method will be estimated to be valid. Determination of the migrated phthalates by HPTLC (High Performance Thin layer Chromatography) at least has the same drawback as HPLC because they are based on the same chromatographic rules.

By using GC/MS analysis with capillary columns, a very efficient separation of the different phthalates and phthalate isomers can be made even when the molecular structure is nearly identical. By using MS detection after separation, it is possible to avoid false positive. This can take place by using the quantification ions in DS/CEN ISO /TS 16181:2011 and the column and chromatographic parameters listed in this standard. A brief description of the method is summarised below:
The extraction according to this method is carried out by using hexane/acetone 80%/20% for 1 h at 50 °C and transferring the extract to a volumetric flask after filtration or centrifugation. The chromatographic column is specified in detail and so are the other GC parameters.

The primary MS target quantification ions are 149 m/z for DBP, BBP, DIBP and DEHP. For DINP the target ion is 293 or 149 m/z, but supplementary quantification ions are suggested and used in practice.

3. Results of the literature search

3.1 Method used for the literature search

The literature search covered essential literature from 1998 to 2015, with focus on literature from Denmark. In addition to studies from Denmark, a few other studies were included from the Netherlands, Austria, Sweden, Germany, Great Britain, Turkey, Canada, Japan and the United States. Besides the studies on migration rates, literature that discusses the results of the different migration studies was also investigated.

The literature search focused on migration rates for the five phthalates (DEHP, DINP, DBP, DIBP and BBP) in soft PVC to artificial sweat and artificial saliva and for *in vivo* tests when such studies were available. The search took place in basic scientific journals as well as in reports from test and research institutes. The results for migration rates from the literature search are listed in the Appendix and tables are listed later in this chapter.

In the survey, standardised test methods for analysis of phthalates, sample preparation and extraction methods were identified as well as standards for formulating artificial sweat and saliva.

A search on Google was conducted using the following terms: migration rates for phthalates, migration rates for the individual five phthalates, analysis of phthalates, migration rates for phthalates in consumer products, toys and childcare articles. The search terms have also been used in the EU databases (ECHA, Rapex, Annex 15), the Danish EPA, The Federal Institute for Risk Assessment (BfR) and the LOUS reports.

A collection of basic properties of the five phthalates has been updated as part of the literature search. A list of the identified documents, reports, and scientific journals of relevance has been compiled in the reference list.

3.2 Migration rates of the five phthalates

Overviews of the proposed migration rates according to the method the migration analysis has been carried out appear in the tables below.

The analytical methods to determine the migration of phthalates are divided into three categories: mild, medium and harsh conditions as seen in table 16. The mild conditions result generally in lower migration rates compared with the *in vivo* adult migration rates for the simulation of children's sucking and chewing on soft PVC products.

TABLE 16
ANALYSIS METHODS DIVIDED INTO DIFFERENT CONDITIONS

	Analysis method
Mild	Static or dynamic conditions at 37±3°C (DK, A, TR, U.S.A.)
Medium	Head over heels method at 60 rpm (NL)
Harsh	Horizontal shaking at 300 rpm (J)

In Japan, and in the UK (Braybrook et al., 1998), a lot of effort has been used to get as high migration rates as possible. This was done by using very rough dynamic mechanical influence, e.g., using centrifugal forces and high temperatures (for example the UK use 65 °C in some experiments) in an attempt to obtain results in line with *in vivo* tests.

To our knowledge it is on a scientific base not possible to compare the conditions (chewing) of adults with the chewing/mouthing of children, as the oral cavity (e.g. musculature) of a child's mouth is not fully developed. Therefore, the chewing force of children is expected to be weaker than for adults. In addition, the stimulation of the saliva production by chewing might be different for children compared with adults. It can be questioned if the results from the *in vivo* adult studies are close to a realistic value for phthalate migration rates[2] for children mouthing or chewing on products.

Very different results for *in vitro* migration are obtained depending on how vigorous the applied dynamic forces were. Therefore, it has been necessary to divide the proposed migration rates according to the experimental set-up used in the countries that carried out the studies.

The results have been divided in minimum, mean and maximum values similar to Wormuth et al., 2006. The mean is obtained by taking all the mean values from the studies in the three conditions.

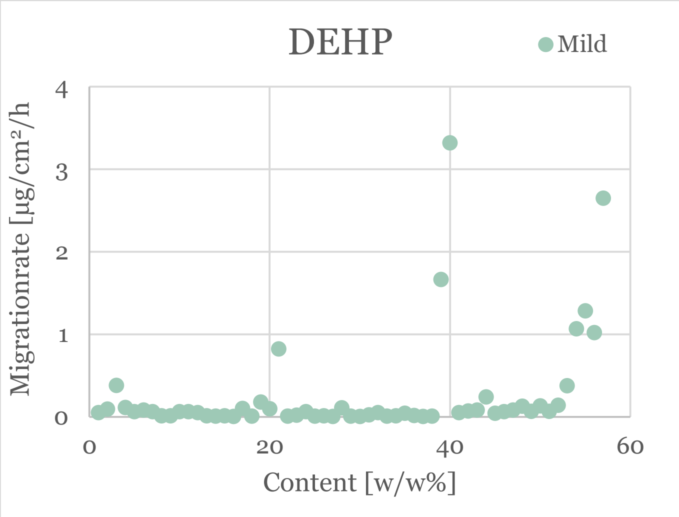
All results are recorded as µg/cm²/h. If another unit has been used in literature, it has been converted to this common unit by a calculation, which makes comparison between different literature results much easier. The recalculations used the listed masses, surface areas and exposure time from the references (if the experimental time was set to e.g. 16 hours, then the determined migration rate was divided with 16 to convert the migration rate into the desired unit).

No migrations rates were found for BBP in the reviewed migration studies from the literature search. BBP was analysed for and detected in some products (e.g., sandals in the Danish EPA report no. 107, 2010 - Phthalates in plastic sandals), but the content of BBP was below the detection limit in most quantitative characterisations and in all the migration studies. This is as expected, as their most common use is for flooring and wallpaper. It is expected that the migration rate of BBP would be similar or a little lower than DBP and DIBP due to the similar solubility parameter (δ_D) and partition coefficient (K_{ow}). Wormuth et al., 2006 and Wormuth, 2006b listed migration rates for BBP (Average migration rate was 0.002 µg/cm²/min and 0.02 µg/cm²/min respectively), but it was not possible to find the original reference with product information and analysis method.

The figures below show the migration rates of the remaining four phthalates as a function of phthalate content.

[2] Conferred with Professor Dorte Haubek, Aarhus School of Dentistry, Aarhus the 7th December 2015.

FIGURE 6
MIGRATION RATE AS A FUNCTION OF DEHP CONTENT (%W/W) FOR THE MILD CONDITIONS (LEFT GRAPH) AND MEDIUM AND HARSH CONDITIONS (RIGHT GRAPH)



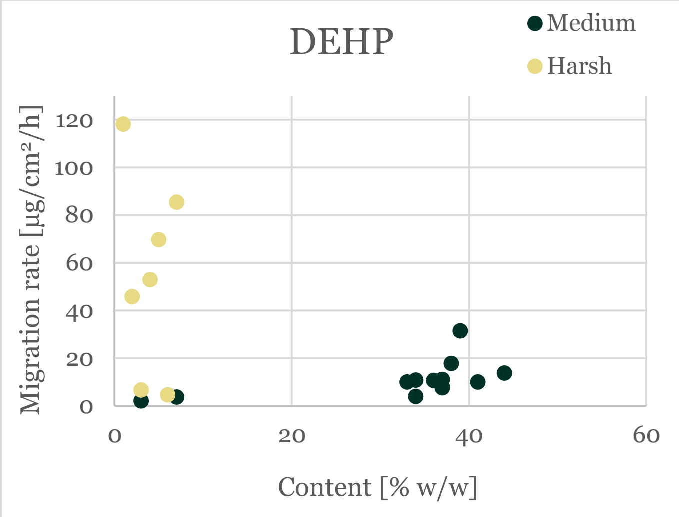
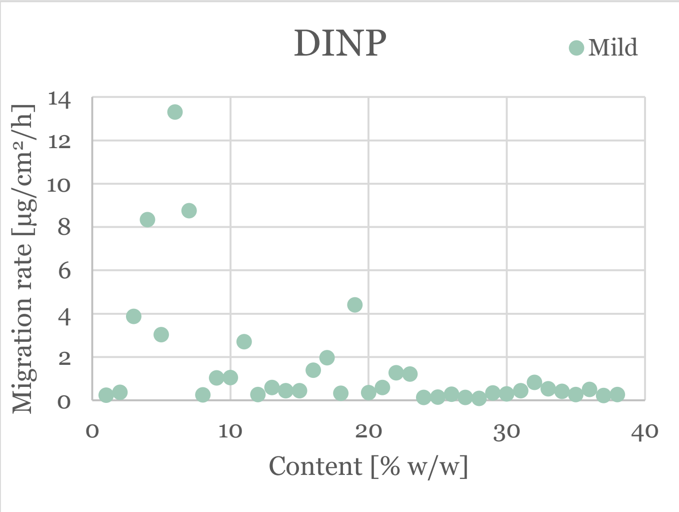


FIGURE 7
MIGRATION RATE AS A FUNCTION OF DINP CONTENT (%W/W) WITH MILD CONDITIONS (LEFT GRAPH) AND MEDIUM AND HARSH CONDITIONS (RIGHT GRAPH)



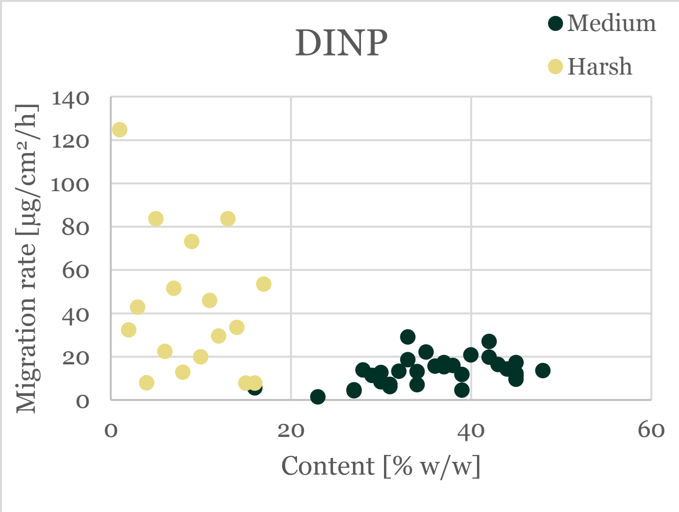
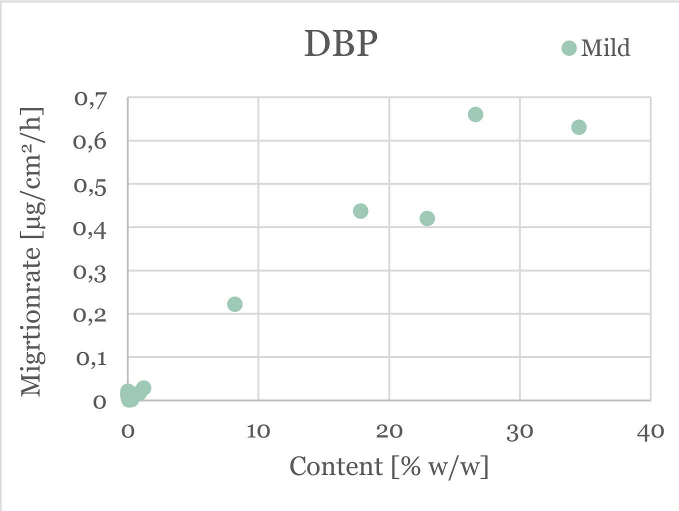


FIGURE 8
MIGRATION RATE AS A FUNCTION OF DBP CONTENT (%W/W) WITH MILD CONTIDIONS (LEFT GRAPH) AND HARSH CONDITIONS (RIGHT GRAPH)



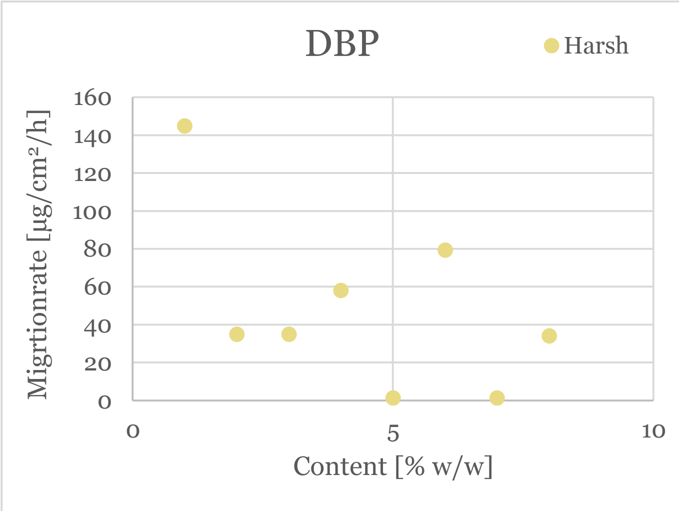
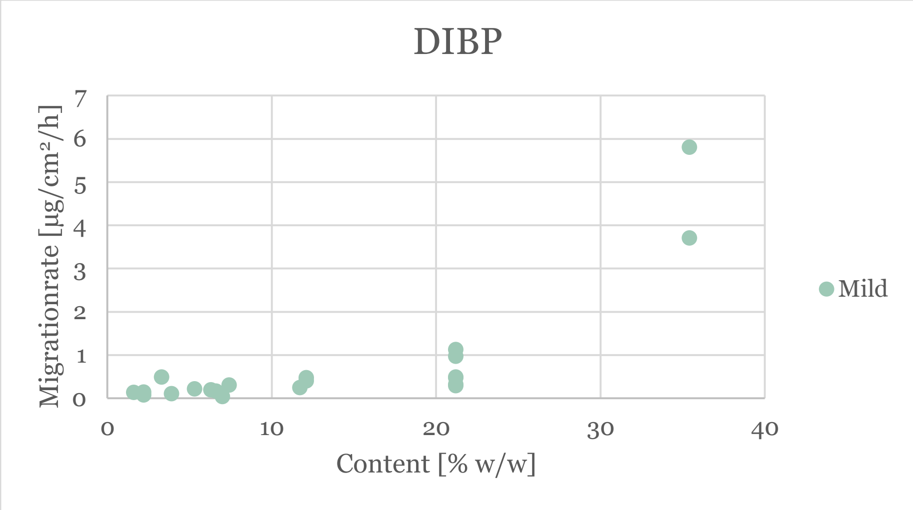


FIGURE 9
MIGRATION RATE AS A FUNCTION OF DIBP CONTENT (%W/W)



The migration rates illustrated in the figures above have been divided into the mild, medium and harsh analytical method conditions as explained above. In most cases it seems that very low concentrations of phthalates results in relatively low migration rates, but there does not seem to be a clear correlation between the migration rates and the content of the four phthalates. The results have then been subdivided in minimum, mean and maximum values similar to Wormuth et al., 2006. The mean is obtained by taking all the mean values from the studies in the three conditions.

TABLE 17
MIGRATION RATES FOR THE MILD ANALYTICAL METHOD CONDITIONS

	Migration Rate from PVC ($\mu g/cm^2/h$)		
Phthalate	**Minimum**	**Mean**	**Maximum**
DEHP	0.002	0.27±0.62	3.31
DINP	0.09	1.61±2.80	13.3
DBP	0.001	0.17±0.24	0.66
DIBP	0.04	0.77±1.39	5.80

TABLE 18
MIGRATION RATES FOR THE MEDIUM ANALYTICAL METHOD CONDITIONS

	Migration Rate from PVC ($\mu g/cm^2/h$)		
Phthalate	**Minimum**	**Mean**	**Maximum**
DEHP	0.04	10.7±7.99	31.3
DINP	1.5	13.3±6.44	29.1
DBP	-	-	-
DIBP	-	-	-

TABLE 19
MIGRATION RATES FOR THE HARSH ANALYTICAL METHOD CONDITIONS

Migration Rate from PVC (μg/cm²/h)			
Phthalate	**Minimum**	**Mean**	**Maximum**
DEHP	4.4	54.6±41.0	118
DINP	7.8	44.8±33.4	124.8
DBP	1.17	48.5±46.9	144.8
DIBP	-	-	-

3.3 The analysis methods from the literature survey

The studied analysis methods had very different conditions e.g. temperature, exposure time, static/dynamic test and different simulants.

Each subject is discussed further below, while looking into the differences in the method used for the determination of migration.

3.3.1 Temperature and migration time

The Danish EPA studies and some of the international studies of phthalate migration rates for consumer products were carried out at 37 °C or 40 °C as that is close to the human body temperature. The migration time differs depending on "worst-case" exposure scenarios for the products. This lead to migration times varying from 10 – 15 minutes up to 24 hours depending on the products. In many cases that means that the amount of migrating phthalate is below the detection limit of the analysis because the contact time is too low, for the phthalates to migrate e.g., 0.5 h to 4 h.

Analysis of the migrate might be carried out according to DS/EN 71-11 for toys but the analysis of phthalates is not part of the standard. The temperature of exposure is 20 °C according to DS/EN 71-10 and the JRC method. This is different from most other migration studies where the temperature is close to the body temperature (35 °C to 40 °C).

The reason for using 20 °C instead of 37 °C is judged to be for practical reasons, however some studies using the JRC method perform the method at 37 °C.

It must be expected that migration rates will increase with temperature according to the rules for migration.

3.3.2 The static and dynamic tests used in the analysis methods

In some of the migration studies, both static and dynamic test conditions were carried out. In general, the dynamic tests in Denmark, Turkey, Austria and the U.S. are very mild using gentle shaking or magnetic stirring, where static or dynamic test were conducted at 37 °C. The migration rates are quite low compared to the tests carried out in the Netherlands and Japan. The Netherlands use the Head over Heels method at 60 rpm, while Japan uses horizontal shaking at 300 rpm. In the UK, the experiments were carried out to obtain very high migration rates, e.g., by increasing the temperature to 65 °C (Braybrook et al., 1998).

The following principles for dynamic methods were identified:

- Head over heels
- Horizontal shaking
- Vertical shaking
- Magnetic stirring

- Ultrasound
- Pneumatic piston
- *In vivo* chewing/sucking

Babich 1998 (Chen, 1998) conducted phthalate migration studies by using either shaking or impaction for 6 h at 37 °C to compare *in vitro* and *in vivo* results. The impaction method used an air driven piston, with a force of 0.91 kg, 2.7 kg or 5.4 kg, a piston sizes of 1.27 cm, 1.59 cm or 2.54 cm. The piston was active for 2 seconds following a period of 2 seconds without pressure. The impaction method gave the best correlation with the *in vivo* measurements if the results were multiplied by a factor of 39.5.

Fiala et al., 2000 and Steiner et al., 1998 have compared different agitation methods for the release of DEHP and DINP into saliva simulant. The methods and their respective migration rates are shown in Figure 10 and Figure 11

.

FIGURE 10
MIGRATION RATES OF DEHP WITH DIFFERENT TEST CONDITIONS (FIALA ET AL., 2000)

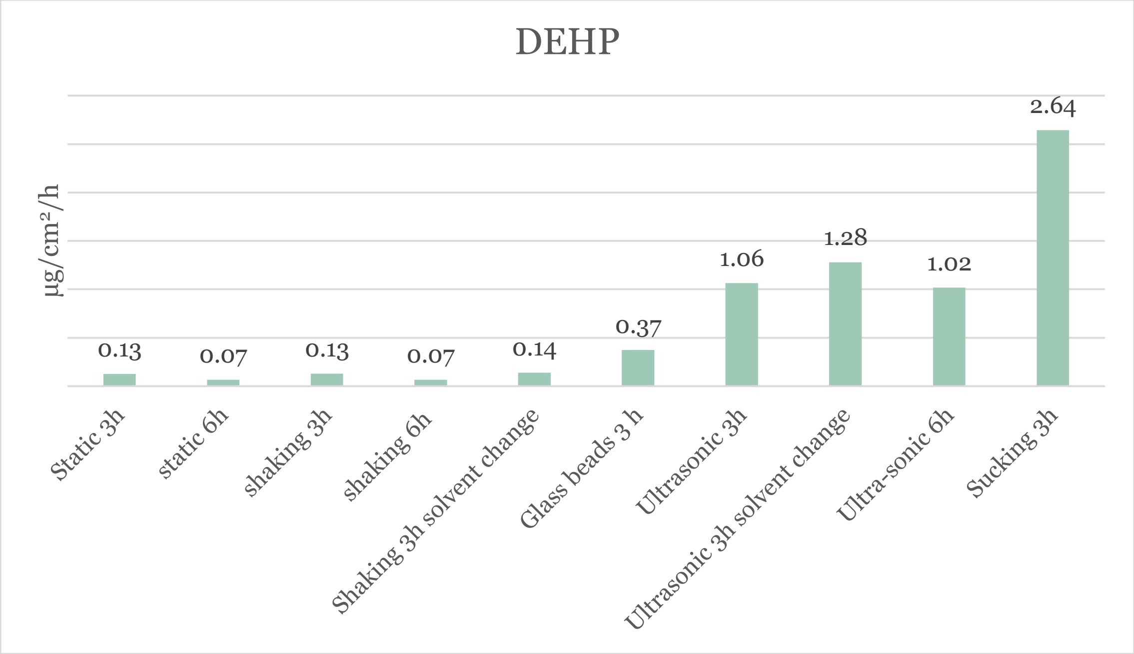
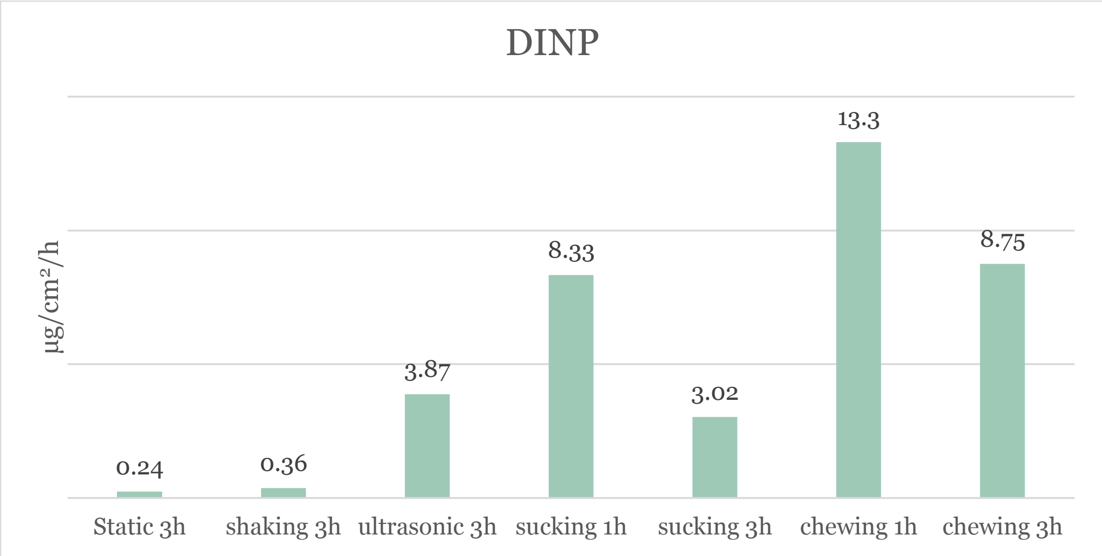


FIGURE 11
MIGRATION RATES OF DINP WITH DIFFERENT TEST CONDITIONS (FIALA ET AL., 2000)



Static conditions gave the lowest phthalate migration rate. Shaking did not significantly increase the migration rate; however, by using ultrasonic extraction the migration rate increased 10-fold. The average DEHP release using ultrasonic extraction was half the value compared to the average *in vivo* release migration rates. The release of DINP using ultrasound extraction was comparable with the *in vivo* release. Bouma et al., 2002, has compared the results from the studies of Fiala et al. 2000, and Steiner et al. 1998, with the head over heels method (HOH) method validated by Toegepast Natuurwetenschappelijk Onderzoek (TNO - the Dutch Organisation for Applied Scientific Research). The result was that the release of DINP was higher than in the *in vivo* release.

The Head over Heels (HOH) method is the preferred method for migration studies for toys in the EU because many studies have been carried out to standardise this dynamic way of exposure (Report to the U.S. Consumer Product Safety Commission, 2014). The method is described in Simoneau et al., 2001a and in Simoneau et al, 2001b. The method has been developed with the aim to be used for the determination of migration from toys. The standard EN 71-10 for toys also uses the HOH extraction dynamic test for migration studies.

The extraction bottles for both methods have a volume of 250 ml and the lid has a PTFE lined rubber septum. The HOH makes use of a bottle rotator capable of holding the extraction bottles in an end-over-end motion at a constant speed. The distance from the centre of the rotating axis to the centre of the flask will be approximately 150 mm. The rotator is rotated at 60+/-5 rpm for 60 +/-5 minutes. The preferred size of the sample is 10 cm² surface and the amount of simulant 100 ml. After exposure, the aqueous migrate solution in the bottle is filtered through a plug of glass wool.

3.3.3 Artificial saliva and sweat used in the literature

Human saliva is a complex fluid, secreted by the major and minor saliva glands. A comparison between natural saliva and very complex formulary is discussed including surface tension studies (Preetha et al., 2005; Harvey et al., 2010; Callewaert, 2014).

However, most migration studies for phthalate migration to artificial saliva and sweat simulants utilise simpler formulations, probably due to reasons related to chemical analysis as the artificial saliva is stable, and possible interference from substances found in human saliva is avoided.

The simulants do not approach the properties of human saliva and human sweat. From the composition it is judged that they have been developed with the aim to study migration rates for heavy metals like nickel, lead, cadmium and mercury. Complexity of human saliva, is discussed in (Preetha et al., 2005) and human sweat it is discussed in (Harvey et al., 2010).

3.4 ECHA´s opinion and conclusions based on available literature regarding DINP migration rates to artificial saliva

ECHA, 2013 has made an evaluation of new scientific evidence concerning DINP and DIDP including migration rates for DINP to artificial saliva and *in vivo* adult saliva. The migration rates for the other four phthalates were not evaluated in this report, with the exception of some comparison with DEHP.

Most migration studies have been carried out with DINP as DINP is the phthalate found in most toys and it has often been found in high concentrations (NICNAS, 2010).

The results discussed by ECHA are presented in the table below:

TABLE 20
MIGRATION RATES USED IN ASSESSMENT OF CHILDREN´S EXPOSURE TO DINP IN TOYS (ECHA, 2013)

Study/reference	Rate µg/cm²/h	Comments
RIVM, 1998; Meuling et al., 2000	10.8	Adult volunteer study: chew and spit, 10 cm² disc. Mean levels of leaching for 3 objects, 8.28, 14.64 and 9.78 µg/cm²/h respectively (overall mean 10.8 µg/cm²/h)
EC Risk Assessment (EC 2003 a)	53.4	Highest rate of leaching in the RIVM, 1998 study
Sugita et al., 2003	9.24 +/- 5.68	Study in adult volunteers asked to suck or lick specimens of PVC toys. Average rates for individual toys ranged from 1.32 to 24.04 µg/cm²/h
US CPSC, 2002	7.0	*In vitro* rates of 6.0 – 66.6 µg/cm²/h with mean of 24.6 µg/cm²/h determined for 41 children´s objects (head over heel method); calibrated against chew and spit *in vivo* measurements of adult volunteers (mean *in vivo*: *in vitro* ratio 0.28)
Chap 2001 (Chen 1998 as reported in Chap 2001)	60	95% upper confidence bound from US CPSC data.

As stated in ECHA, 2013: “that migration of phthalates depends on type of contact, time, temperature, plasticiser concentration difference, plasticiser level, molecular weight and molecular structure. In addition, another element that seems important when determining the migration rate is the process conditions for PVC manufacturing. *A relationship between the plasticiser’s content of PVC and the migration of plasticisers from PVC cannot be established based on experimental data*. The likely reason for this is the multitude of factors influencing the migration from PVC in combination with differences in experimental settings among the studies. Niino et al., 2003 a reported high effects of especially rotation speed (a migration rate of ca. 20 µg/cm²/h at 200 rpm versus ca. 150 µg/cm²/h at 400 rpm) and temperature (a migration rate of ca. 80 µg/cm²/h at 20 °C and ca. 170 µg/cm²/h at 40 °C)”.

Within the same experiment referred to above, higher percentages of DINP in general seemed to have resulted in higher migration rates, although it should be noted that data reported in Chen, 1998 did not indicate a clear relation between phthalate content and *in vitro* migration rates measured by means of impaction from 35 toys and childcare articles. Babich, 1998 has tabulated the results from Chen, 1998. In Chen, 1998 migration rates for the *in vivo* test were in average 39.5 times higher. This is in conflict with the results of Niino, 2003 where the *in vivo* migration rate was about four times lower than the *in vitro* results.

A more in-depth discussion in ECHA, 2013 from a report made by TNO (TNO, 2010) of the data for migration rates of DINP to artificial saliva has led to the conclusion that the migration rate from mouthing of toys will be an *in vitro* migration rate of 45 µg/cm²/h, measured for a plate with a content of 40.7% w/w DINP and a typical *in vivo* estimate will be 14 µg/cm²/h. The latter value of the migration rate is based on taking the mean of all the means from the *in vivo* studies. It is not evident why the *in vivo* results are lower than the *in vitro* result, but it is very interesting that the proposal for *in vitro* migration rates in this report are comparable with the *in vivo* results from ECHA, 2013.

However ECHA, 2013 concludes also that it is not straightforward to give preference to the *in vivo* data over the *in vitro* data as an estimate of the real-life migration during mouthing behaviour of children. This is fully in agreement with our opinion based on our discussion regarding the mouthing of children's compared with adults.

ECHA, 2013 finds that the lack of standardisation of the *in vivo* methods and the high variability in measurements is problematic. It is concluded that the *in vivo* data might not give a good representation of the population of toys on the European marked. On the other hand, it is mentioned that *in vitro* data might overestimate average real-life migration rates, and a lot of the available *in vitro* data has not been carried out by the current European standard (EN 71-10). It must be stressed that this standard is part of the three standards DS/EN 71-9, DS/EN 71-10 and DS/EN 71-11, which are valid for the study of migration of organic substances from toys. However, migration of phthalates is as already mentioned not covered by the standards.

ECHA, 2013 has also discussed the migration rates from sex toys, mainly based on Nilsson et al., 2006, VWA, 2009 and Janssen and Bremmer, 2010. Nilsson et al., 2006 found the worst-case migration rates for a vibrator with a content of 70.2% w/w DEHP run at maximum speed in contact with artificial sweat adjusted to pH 4.5 equal to the vaginal pH level for healthy women for 1 h at 40 °C. The migration rate was 0.06 µg/cm²/h. By simulating the use of a water-based lubricant and an oil-based lubricant, the migration rates increased to 0.4 µg/cm²/h and 54.8 µg/cm²/h. VWA 2009 found a rather high average migration rate of DINP (56.2 µg/cm²/h) from sex toys with a maximum rate 224.4 µg/cm²/h. VWA, 2009 used the head over heels method for the migration in sweat. Janssen and Bremmer, 2010 used maximum migration rates of 224 µg/cm²/h for DINP in sex toys for calculations of exposure. They used the HOH method on isolated parts of the article and a correction factor of 0.5 was used. ECHA, 2013 concludes that a typical value for the migration of DINP from sex toys is 65 µg/cm²/h based on the merged data from VWA, 2009 and worst-case will be 121 µg/cm²/h based on the 75th fractile from the same study.

In the reference US CPSC, 2002, the results of Chen, 1998 have been discussed. Chen, 1998 determined the migration rate into simulated saliva by using the HOH method from the Joint Research Centre (Simoneau et al., 2001) for DEHP and DINP with the following results (µg/cm²/min):

TABLE 21
MIGRATION RATES IN µG/CM²/MIN FOR TOYS MEASURED BY THE JRC DYNAMIC MIGRATION METHOD (HOH) (CHEN, 1998)

	DEHP	DINP
N*	3	25
Mean	0.13	0.42
S.D.	0.06	0.28
Max.	0.20	1.11

*N=Number of products

3.5 Methodology for proposal of migration rates

From the literature study, it appears that no specific scientifically based true migration rates exist for each of the five phthalates DEHP, DINP, BBP, DIBP and DBP and neither do true migration rates based on *in vivo* migration studies. Too many factors affect the migration rates especially with regard to the experimental set up both in the *in vitro* and the *in vivo* determination of migration rates. Most of the literature considers the migration of DINP in detail; especially for the *in vivo* migration studies DINP has been the "case story", probably because it was found that DINP was the most commonly used phthalate plasticiser in toys.

Due to lacking correlation between several migration studies for phthalates, it seems reasonable to consider the model used by Wormuth et al., 2006, where the migration rates are divided into minimum, mean and maximum migration rates based on the literature present at the time of publication. In Wormuth et al., 2006, migration rates from studies carried out later than 2006 and up to today were taken into consideration (see table 22). The listed migrations rates differ from Wormuth, 2006b with a significant factor for DEHP, BBP and DBP, but are in similar range for DINP.

TABLE 22
PHTHALATE MIGRATION RATES (WORMUTH ET AL., 2006)

Release Rate from PVC (µg/cm²/min)				
Phthalate	Minimum	Mean	Maximum	Remarks
DEHP	0.000	0.050	0.236	Mechanical agitation using artificial saliva; experiments with human volunteers
DINP	0.000	0.206	0.359	Mechanical agitation using artificial saliva; experiments with human volunteers
BBP	0.000	0.002	0.004	Mechanical agitation using artificial saliva; no maximum reported
DBP	0.000	0.001	0.002	Mechanical agitation using artificial saliva; only samples with low DBP content considered

It should be noted that the migration rates to sweat (skin contact) are expected to increase dramatically if the skin is treated with suntan lotion or other skincare products with oil/fat lubricants for DEHP or DINP (Danish EPA no. 77, 2006 and Danish EPA no. 107, 2010). Regarding oral contact, it is expected that the migration rates of DEHP and DINP will increase dramatically when babies lick products that contain phthalates after ingesting fat containing milk. For the more water soluble phthalates BBP, DIBP and DBP the effect of treatment as stated above is expected to be lower due to their more hydrophilic properties and that has been experimentally verified.

In some phthalate studies (LGC, 1999), the aim has been to obtain high migration rates that are comparable with the migration rates obtained in *in vivo* studies. In (LGC, 1999), CSTEE has requested a method capable of achieving a migration level for DINP to artificial saliva of 54.0 μg/cm²/h (based on a maximum migration value of 53.4 μg/cm²/h found in an *in vivo* study from an actual toy – RIVM, 1998). However, the mean migration rates in RIVM, 1998 are in the order of maximum 10 μg/cm²/h, which is close to the suggested migration rate in this report.

Higher migration rates can be obtained by increasing the dynamic force and/or temperature.

3.5.1 Dynamic force

When using high agitation speed, the migration increases due to a combination of the G-force $G - force\ =\ 1.12\ \cdot\ radius\ \cdot\ \left(\frac{RPM}{1000}\right)^2$) generated by the centrifugal rotation in the HOH method, which can drag the phthalates out of the PVC and a more efficient stirring will remove DEHP and the other phthalates from the surface.

A calculation of the G-force (which the PVC sample is exposed to in the HOH method) has been carried out based on 250 ml flasks, which have a distance of 150 mm from rotation axis to flask and where a rotation of 60 revolutions per minute is used. Based on that the acceleration can be calculated from the formula $a = \frac{4\pi^2 r}{t^2}$ where *r* is the radius (0.15 m) and *t* the time for one rotation (1 s) corresponding to 60 revolutions/min. From that formula, the acceleration is calculated to 5.9 m/s² or 0.6 G. It can be calculated that by going from 60 rev/min. to 400 rev/min. the G force will increase from 0.66 to 26.6, which is a very high force. That partly explains why very high migration rates were found in some studies by Niino et al., 2002, at high revolutions.

In LGC, 1999, a combination of temperature and dynamic force was used to simulate *in vivo* migration rates. The test was an exaggerated test at 65 °C with 10 stainless steel balls (12 mm Ø) and it was dynamically tested in a horizontal linear/transvers shaking bath (with an amplitude of movement of 38 mm). The agitation speed of 200 strokes/minute and the exposure time is 2 x 30 minutes exposure time for a disc with surface area of 10 cm² and artificial saliva is used. After the first 30 minutes, fresh saliva was added for the next 30-minute treatment, and the 2 x 50 ml artificial saliva was combined for extraction with, e.g., DCM for chromatographic analysis. The described *in vitro* method was used to achieve similar migration rates as found *in vivo* studies. Therefore, the tables in the appendix with suggested migration rates for the phthalates have been divided into three groups where the migration studies with extreme dynamic stress has been used, and migration studies where less harsh exposure experiments have been used. This approach has resulted in migration rates that depend on in which method the test was carried out from. No attempt was made to consider the *in vivo* results as the" true" migration rates for reasons discussed above.

3.5.2 Physical and chemical parameters

Besides the results from the literature regarding migration rates, the important physical and chemical parameters in the table below will be considered especially by determining the mutual migration rates for the five phthalates. The parameters stated earlier in Chapter 2.1 Physical and chemical properties of the five phthalates are compiled in Table 23.

TABLE 23
IMPORTANT PARAMETERS TO CONSIDER REGARDING MIGRATION RATES OF PHTHALATES

Phthalate	Mw, g/mol	Delta, $MPa^{0.5}$	Log (Pow)	Water solubility 25 °C., µg/l
DEHP	390.56	16.6	7.5	3
DINP	418.61	16.2	6.9	<1
BBP	312.37	19.1	4.84	2700
DBP	278.35	17.8	4.57	11200
DIBP	278.35	17.8	4.11	20000

Staples, 1997 has discussed different methods for the determination of the solubility of phthalates in water. Especially for the phthalates like DEHP and DINP with long alkyl chains, many experimental data appear confusing and result in too high values compared with the prediction of theoretical models. By using a HOH-like technique (shake flask/centrifugation method) will result in an increase in solubility for DEHP in water that is around 10-fold. By using the HOH-like method for measurement of water solubility, colloidal emulsions of undissolved phthalates might be formed and they are difficult to separate from the water phase.

As the water solubility of DEHP and DINP is very low (3 µg/l and < 1 µg/l at 25 °C), and as most migration studies use 100 ml of simulant, the amount of dissolved phthalate in the water phase will be 10 times less in mass because 100 ml is one tenth of 1 liter. Therefore, it seems reasonable to conclude that in the migration studies where high dynamic and mechanical stress is applied, a major part of the phthalates DEHP and DINP are present in the simulants as emulsions. By increasing the temperature to 37 °C or even 65 °C, more of the migrated phthalates might be soluble due to the higher temperature of exposure.

3.5.3 Temperature and simulants

As observed in studies by Niino et al., 2003, and Rose et al., 2012, the temperature can be used to increase migration.

In Rose et al., 2012 a study was performed on migration of DEHP from infusion sets made of PVC with DEHP. The study was performed at temperatures from 24°C, 32°C and 37°C and with migration to 0.9% saline solution and to 3 different lipid-based infusates using 6-hour migration periods. The study showed that a migration to saline solution could be detected only at 37 °C (425 µg) but not at lower temperatures.

When using lipid-based infusate, the migration increased with a factor of 1.7 to 6 when increasing the temperature from 24 °C to 37 °C depending on simulant type/test conditions. This illustrates that temperature and the extraction medium are important in order to obtain the realistic migration rate.

For this reason, tests should ideally be carried out at temperatures close to body temperature and it should be considered to develop other simulants than the presently used artificial saliva and sweat. Saliva may contain fatty emulsions from ingestion of food, e.g., milk and vegetable fat and at contact with suntan lotion and fat/oil-containing cosmetics the migration can increase several orders from 5 – 1000 times.

For practical reasons it will be much easier to use the EN 71-10 method described for toys and with water as simulant and then make further studies similar to the method used for infusion sets to get a measure of the level of migration using the much more easy EN 71-10 method at 20°C and 1 h exposure time and with pure water as simulant. Even though the body temperature is 37 °C, the small difference in temperature will not affect the migration rate significantly, because the exposure time is so short.

3.6 Migration rates proposed

Based on the literature search and the rules for migration it is obvious that one realistic migration rate for each of the five phthalates in focus in this report: DINP, DEHP, BBP, DBP and DIBP cannot be determined as the rates depend on the method used for the migration study.

As a lack of standard method makes a comparison between the different studies carried out it will be a great step ahead if a common agreement regarding the future method for carrying out migration studies can be made. The most convenient way to choose will be the method described in EN 71-10 by using pure water as the simulant for both sweat and saliva. The most optimal way will also be to carry out the migration step at 20 °C for 1 hour for practical reasons as recommended in the standard instead of 37° C having in mind that migration rates will increase with temperature.

The head over heels method (HOH) is judged as the most documented method of all, but only for the migration rates for DINP and DEHP to artificial saliva and is in our opinion the most realistic. For this reason, the HOH method is recommended as the reference method for the determination of migration rates for phthalates well knowing that realistic migration rates are difficult to determine in *in vitro* or adult *in vivo* studies.

Compared with the mild methods based on static tests or dynamic tests using mild shaking or magnetic stirring the migration rates for the HOH method will be higher.

When the suggested migration rates for the five phthalates are used for risk assessment purposes, a higher migration rate will result in more conservative risk assessment and in higher consumer protection against exposure to phthalates. The migration rates can therefore be used to indicate whether a product containing one of the five phthalates will pose a risk. The harsh method used by the Japanese seems far from reality by using dynamic test at 300 rpm and is judged to give too high migration rates.

As the HOH method first of all has been documented for DINP and DEHP the migration rates for the other phthalates have been determined by using a correction factor based on the mild migration studies or/and taking the chemical/physical properties of the phthalates in consideration (molecular weight, solubility in water, log K_{ow}, vapour pressure and δ_D (solubility parameter)).

It seems reasonable to use a one-hour exposure as migration will be higher in the beginning of the exposure and makes it possible to carry out more analysis than for longer exposure times.

By using pure water (e.g. MilliQ quality) it will be possible to use TOC (total organic carbon) analysis for the evaluation of the total migration of organic substances from the soft PVC.

This method is already used as an important parameter for the approval of plastic and rubber in contact with drinking water, it is very robust and have a low detection limit. It can be used directly on the water phase without using extraction and chromatography due to the principle of analysis (converting organic carbon to carbon dioxide and measuring the concentration of carbon dioxide by infrared dispersive detection).

At present as far as the many studies for migration of phthalates have been carried out in very different ways it shall be recommended to use the following migration rates for calculation of risk of exposure to the phthalates until further evidence is available:

- Use the means of all the migration rates calculated from the medium dynamic experiments carried out according to the HOH method at 60 rpm where results are available (DINP and DEHP), since this is the most documented method for migration rates studies.
- Not to distinguish between migration rates to artificial sweat and saliva
- To argue why the mild migration studies are not taken into account by multiplying with DIBP and DBP mild migration rates together with the ratio of the DEHP and DINP migration rates in the medium dynamic studies and the DEHP and DINP in the results from the HOH method (See calculations below).
- To use the same migration rate for DBP as for DIBP based on the multiplication proposed below.
- To use a migration rate for BBP as the mean between the migration rates for DEHP, DINP, DBP and DIBP calculated as proposed, due to the physical/chemical properties from the five phthalates.
- To consider the possible use of cosmetic products like sun oil and other skin care products or fats when making risk assessments.

The migration rates of DIBP and DBP are expected to be above both DEHP and DINP due to their solubility in water. Therefore, to estimate an average migration rate, the factors from the mild conditions are not used even though the migration rate for DIBP and DBP are then calculated as the same. From this condition and the above recommendations, DIBP and DBP will be estimated to have the following migration rates:

Migration rate for DIBP = $\frac{Average\ of\ the\ medium\ migration\ rates\ of\ DEHP\ and\ DINP}{Average\ of\ the\ mild\ migration\ rates\ of\ DEHP\ and\ DINP}$

$$= \frac{\frac{10.7\mu g/cm^2/h + 13.3\mu g/cm^2/h}{2}}{\frac{0.27\mu g/cm^2/h + 1.61\mu g/cm^2/h}{2}} = \frac{12\mu g/cm^2/h}{0.94\ \mu g/cm^2/h} = 12.77\mu g/cm^2/h$$

Migration rate for DBP = $\frac{Average\ of\ the\ medium\ migration\ rates\ of\ DEHP\ and\ DINP}{Average\ of\ the\ mild\ migration\ rates\ of\ DEHP\ and\ DINP} = 12.77\mu g/cm^2/h$

The migration rate of BBP, should be in between the four other phthalates and is calculated as the average of these values:

$$= \frac{Average\ of\ the\ medium\ migration\ rates\ of\ DEHP\ and\ DINP + Average\ of\ the\ medium\ migration\ rates\ of\ DIBP\ and\ DBP}{2}$$

$$= \frac{\frac{10.7\ \mu g/cm^2/h + 13.3\ \mu g/cm^2/h}{2} + 12.77\ \mu g/cm^2/h}{2} = 12.39\mu g/cm^2/h$$

Therefore, the migration rates for the five phthalates using the HOH method are estimated to:

TABLE 24
ESTIMATED MIGRATION RATES FOR THE FIVE PHTALATES

	DEHP	DINP	DIBP	DBP	BBP
Migration rate (µg/cm²/h)	10	13	13	13	12

The migration rates for the five phthalates are all in the same range. But the results from Wormuth et al. 2006 are rather different except for DINP. It would be expected from the chemical/physical properties that the migration rates for DBP and BBP should be higher than DINP and that DEHP should be at the same order as DINP and this is not the case. The true migration rates for DIBP and DBP would most likely be higher than DINP and DEHP, but because the concentrations in most cases are lower, the migration rates become similar. This could explain why the results are not compatible with Wormuth et al., 2006, because there are low concentrations of the phthalates in the products and these are most likely added as a processing aid before adding DEHP or DINP, but still have a softening effect. In Wormuth et al., 2006 it is also stated that only samples with low DIBP content are considered. According to Fick's law the migration rate will depend on the concentration level, therefore without knowing the phthalate content, it is difficult to compare the listed migration rates in table 24 with the results found from Wormuth et al., 2006.

4. References

Amberg Müller J.P. et al., Migration of phthalates from soft PVC packaging into shower and bath gels and assessment of consumer risk, Journal of Consumer Protection and Food Safety 5:429-442, 2010

Babich, M.A., The risk of Chronic Toxicity Associated with exposure to Diisononyl Phthalate (DINP) in Children´s Products, 1998

Baur et al., Saechtling Kunststoff Taschenbuch, Hanser verlag 30. Ausgabe, 2007

Bouma, K. & Schakel, D.J., "Migration of phthalates from PVC toys into saliva simulant by dynamic extraction", Food Additives and Contaminants, Vol. 19, No. 6, p.602-610, 2002

Braybrook, J. H., et al., "Laboratory-based Agitation Methods for the Determination of Phthalate Plasticise Migration from PVC Toys and Childcare Articles – 2 LGC Technical Report LGC/1998/DTI/009

Callewaert, C., Bysschaert, B., Vossen, E., Fievez, V., Van de Wiele, T., Boon, N., Artificial sweat composition to grow and sustain a mixed human axillary microbiome, Journal of Microbiological Methods 103 p. 6-8, 2014

Chap (2001) US Chronic Hazards Advisory Panel. Report to the U.S. Consumer Product Safety Commission by the Chronic Hazard Advisory Panel on Diisononyl Phthalate (DINP). U.S.

Chen, S.B. (2002), Screening of Toys for PVC and Phthalate Migration (from US CPSC (2002))

Danish EPA no. 77, 2006, Nilsson N.H. , Malmgren-Hansen B., Bernth N., Pedersen E. and Pommer K., Mapping and health assessment of chemical substances in sex toys, Survey of chemical Substances in Consumer Products no. 77, 2006, Danish Environmental Protection Agency

Danish EPA no. 103, 2009. Tønning K., Jacobsen E., Pedersen E., Strange M., Poulsen P.B. , Møller L. and Boyd H.B.
Exposure of two year old child for chemical substances, Survey of chemical Substances in Consumer Products no. 103, 2009, Danish Environmental Protection Agency

Danish EPA no. 107, 2010. Tønning K., Malmgren-Hansen, Pedersen E., Jacobsen E., Phthalates in plastic sandals, Survey of chemical Substances in Consumer Products no. 107, 2010, Danish Environmental Protection Agency

Danish EPA no. 109, 2010. Tønning K., Jacobsen E., Pedersen E. and Nilsson N.H., Phthalates in products that children are in direct contact with, Survey of chemical Substances in Consumer Products no. 109, 2010, Danish Environmental Protection Agency

Danish EPA no. 139, 2015. Strandesen M., Poulsen P. B., Hundebøll N., Bjarnov E., Blinkenberg-Thrane N. L., Survey and health assessment of phthalates in toys and other products for children, Survey of chemical Substances in Consumer Products no. 139, 2015, Danish Environmental Protection Agency

DS/CEN ISO/TS 16181, Footwear-Critical substances potentially present in footwear and footwear components- Determination of phthalates in footwear materials. 1st Edition 2011

DS/EN ISO 105-E04, 3.edition, 2013-04-16, textiles-Test for colour fastness – Part E04: Colour fastness to perspiration

DS/EN 1811 4. Edition 2011.04-27, Reference test method for release of nickel from all post assemblies, which are inserted into pierced parts of the human body and articles intended to come into direct and prolonged contact with the skin.

DS/EN 71-10, 2005, Safety of Toys- Part 10: Organic chemical compounds – Sample preparation and extraction

ECHA 2013, Evaluation of new scientific evidence concerning DINP and DIDP In relation to entry 52 of Annex XVII to REACH Regulation (EC) No 1907/2006, Final review report, Volume 36, Luxembourg: Office for Official Publications of the European Communities

EC 2003a, European Union Risk Assessment Report DINP, 2nd Priority List Vol. 35, 2003

Fiala F. et al., 2000, Migration of di-(2-ethylhexyl) phthalate (DEHP) and disiononyl phthalate (DINP) from PVC articles, Consumer Council, Austrian Standards Institute (2000)

Hansen & Nilsson 2014, Hazardous substances in plastics, Survey of chemical Substances in Consumer Products no. 132, 2014, Danish Environmental Protection Agency

Harvey C.J. et al., 2010, Formulation and stability of a novel artificial human sweat under conditions of storage and use, Toxicology *in vitro* 24, p. 1790-1796 (2010)

Janssen and Bremmer (2010). Risk assessment plasticizers from erotic objects. National Institute for Public Health and the Environment (RIVM), 29 September 2010. Available at: www.vwa.nl/txmpub/files/?p_file_id=2201039

LGC 1999, Consumer Safety research Report: Laboratory- Based Agitation Methods for the Determination af Phthalate Plasticicer Migration from PVC Toys and Childcare Articles-2. LGC Technical report no. LGC/1999/DTI/002, 1999

Lirova, B.I. et al, 2008, Influence of Filler on Migration from Plasticised Poly(vinyl chloride) composites, Russian Journal of Applied Chemistry, vol. 81 no.2, p 298-303 (2008)

Meuling WJA, Rijk MAH and Vink AA (2000). Study to investigate the phthalate release into saliva from plasticized PVC during sucking and biting by human volunteers. TNO report V98.680, Final Report, Project number 40393. TNO Voeding, 3700 AJ Zeist, The Netherlands. Sponsored by CEFOC/ECPI

NICNAS, 2010, Diethylhexyl phthalate, Priority Existing Chemical Assessment Report, Australian Government, Department of Health and Ageing, ISBN 978-0987221-3-0

Niino, T., Ishibashi, T., Itho, T., Sakai, S., Ishiwata, H., Yamada T. and Onoderad, S., Monoester Formation by Hydrolysis of Dialkyl Phthalate Migrating from Polyvinyl Chloride Products in Human Saliva, Journal of Health, Vol. 47, No.3, 2001

Niino, T., Asakura, T.Ishibashi, T.Itoh, Simple and Reproducible Testing Method for Dialkyl Phthalate Migration from Polyvinyl Chloride Products and Saliva Simulant", J.Food Hyg. Soc. Japan ,Vol.44, No.1, 2003

Preetha et al., Comparison of Artificial Saliva Substitutes, Trends Biomater. Artif. Organs, Vol 18 (2), January 2005

REACH Annex XVII, Entry 52. http://echa.europa.eu/da/addressing-chemicals-of-concern/restrictions/list-of-restrictions?p_p_id=viewsubstances_WAR_echarevsubstanceportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2&_viewsubstances_WAR_echarevsubstanceportlet_keywords=&_viewsubstances_WAR_echarevsubstanceportlet_advancedSearch=false&_viewsubstances_WAR_echarevsubstanceportlet_andOperator=true&_viewsubstances_WAR_echarevsubstanceportlet_orderByCol=synonymDynamicField_231&_viewsubstances_WAR_echarevsubstanceportlet_orderByType=asc&_viewsubstances_WAR_echarevsubstanceportlet_delta=200

REACH Regulation No. 1907, 2006, REACH Regulation No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No. 793/93 and Commission Regulation (EC) No. 1488/94 as well as Council Directive 76/769/EEC and Commission Directive 91/155/EEC, 93/67/EØF, 93/105/EEC and 2000/21/EC. http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1417522376864&uri=CELEX:02006R1907-20140822

Report to the U.S. Consumer Product Safety Commission by the Chronic Hazard Advisory Panel on Phthalates and Phthalates Alternatives, Appendix E2 "Children´s Oral Exposure to Phthalate Alternatives from Mouthing Soft Plastic Children´s Articles, July 2014

RIVM Report no. 613320 002, Phthalate release from soft PVC baby toys, ed. Könemann, W.H., 1998

Rose, R.J et al, The effect of temperature on di(2-ethylhexyl) phthalate leaching from PVC infusion sets exposed to lipid emulsions, Anasthesia, Vol. 67, p.514, 2012

Shashoua Y.R. Inhibiting the deterioration of plasticised poly(vinyl chloride) – a museum perspective, Ph. D. Thesis, 2001

Simoneau C., H. Geiss, Roncari, A., Zocchi, P., Hannaert, P. Validation of methodologies for the release of diisononylohthalate (DINP) in saliva simulant from toys, EUR 19826 EN, 2001a

Simoneau C. , Rijk R. Standard Operation procedure for the Determination of Release of Di-Isononylphthalate (DINP) in Saliva Simulant from Toys and Childcare Articles using a Head Over Heels Dynamic Agitation Device, JRC EUR 19899 EN, 2001b

Staples, C. A., Peterson, R. P., Parkerton, T. F. and Adams, W. J. The environmental fate of phthalate esters: A literature review, Chemosphere, Vol. 34, No. 4, 1997

Steiner, I., Scharf, L., Fiala, F. and Washüttl,J., Migration of di-(2-ethylhexyl) phthalate from PVC child articles into saliva and saliva simulant, Food Additives and Contaminants 7, 1998

Sugita T, Kawamura Y, Tanimura M, Matsuda R, Niino T, Ishibashi T, Hirabahashi N, Matsuki Y, Yamada T and Maitani T,Estimation of daily oral exposure to phthalates derived from soft polyvinyl chloride baby toys. Shokuhin Eiseigaku Zasshi. 44(2): 96-102. [Article in Japanese] Source National Institute of Health Sciences: 1-18-1, Kamiyoga, Setagaya-ku, Tokyo 158-8501, Japan. Reviewed by CPSC number V99.849 (as cited in US CPCS 2010), 2003.

TNO (2010). Analytical report prepared for ExxonMobil Petroleum & Chemicals, Machelen, Belgium.

Toy Safety Directive 2009/48/EC. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02009L0048-20140721

US CPSC (2002). Updated risk assessment of oral exposure to diisononyl phthalate (DINP) in children's products. US CPSC, Bethesda, MD 20814, June 2002. Available at: http://www.cpsc.gov/library/foia/foia02/brief/briefing.html

VWA (2009), Consumenten producten in de erotica branche. Fact sheet. Voedsel en Waren Autoriteit (VWA), Afdeling Signalering en Ontwikkeling, Regio Noord, Juni 2009.

Wilkes C.E. et al., PVC Handbook , Hanser, 2005

Wilson A., Plasticisers – Principles and Practice, the Institute of Materials, 1995

Wormuth M., Scheringer M., Vollenweider M. and Hungerbühler K., What Are the Sources of Exposure to Eight Frequently Used Phthalic Acid Esters in Europeans?, Risk Analysis, Vol. 26, No. 3, 2006a

Wormuth M., Consumer exposure to chemical substances with diverse applications - Contributions from retail products, building materials, and diffuse sources, 2006b

Wypych G., PVC Formulary 2nd edition, ChemTec Publishing, Toronto, 2015

Özer E. T. and Gücer S. Determination of di(2-ethylhexyl) phthalate migration from toys into artificial sweat by gas chromatography mass spectrometry after activated carbon enrichment, Polymer testing 31, p. 474-480, 2012

5. Appendix

The migration rates found in the literature appear in the tables below. The migration rates are listed according to each phthalate (in the order DEHP, DINP, DBP and DIBP) and with respect to the migration rates for sweat and saliva. All results are recorded as µg/cm²/h. If another unit was used in literature, it has been converted to this common unit by a calculation as that makes it much easier to compare the different literature results.

5.1 DEHP

5.1.1 Migration to artificial sweat

TABLE 25
OVERVIEW OF MIGRATION STUDIES FOR DEHP IN SWEAT – ALL SAMPLES WERE ANALYSED USING GC-MS

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Reference	Country
Oil cloth 1.6	25.3	0.05	Static condition for 10 min at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 109, 2010	DK
Oilcloth 1.8	13	0.09	Static condition for 1 hour at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 109, 2010	DK
Balance ball 1.14	44.2	0.38	Static condition for 1 hour at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 109, 2010	DK
Swimming pool 1.18	25.8	0.11	Static condition for 1 hour at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 109, 2010	DK
Shower curtain 1.31	25.1	0.06	Static condition for 1 hour at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 109, 2010	DK
Shower curtain 1.39	29.6	0.08	Static condition for 1 hour at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 109, 2010	DK
Toilet bag 1.65	17.6	0.06	Static condition for 1 hour at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 109, 2010	DK
Wrist watch U10	15	0.01	Static conditions for 24 hour at 37±3°C.	DS/EN ISO 105-E04	THF	Danish EPA no. 139, 2010	DK
Sex toys 2	0.07	0.01	Static conditions for 1 hour at	DS/ISO 12870:1997(	DCM	Danish EPA no. 77, 2006	DK

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Reference	Country
			40°C.	E). 1. edition			
Sex toys 8	70.2	0.06	Static conditions for 1 hour at 40°C.	DS/ISO 12870:1997(E). 1. edition	DCM	Danish EPA no. 77, 2006	DK
Sex toys 14	17.6	0.06	Static conditions for 1 hour at 40°C.	DS/ISO 12870:1997(E). 1. edition	DCM	Danish EPA no. 77, 2006	DK
Sex toys 15	20	0.05	Static conditions for 1 hour at 40°C.	DS/ISO 12870:1997(E). 1. edition	DCM	Danish EPA no. 77, 2006	DK
Plastic sandal 1.1*	2.2	0.01	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 5.2**	0.002	0.005	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 6.1*	30.2	0.011	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1a*	14.8	0.004	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1b*	14.8	0.098	Static condition for 16 hours at 37±3°C with new simulant after 8 hours.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1c*	14.8	0.006125	Static condition for 8 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1d*	14.8	0.1782	Dynamic condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1e*	14.8	0.0952	Static condition with sunscreen for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1f*	14.8	0.8214	Dynamic condition with sunscreen for 16	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Reference	Country
			hours at 37±3°C.				
Plastic sandal 8.2**	17.1	0.005	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 12.1*	46.1	0.019	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 13.2**	0.03	0.06	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 17.1*	24.5	0.006	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 18.1 – Middle of the sole	11.1	0.00940	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 18.2 – The outer part of the sole	21	0.00401	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 20.2**	1	0.1084	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 26.1*	34.5	0.00608	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 29.2 – The outer part of the sole	<LOD	0.00229	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 37.2**	20.9	0.02216	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 39.2**	25.8	0.04778	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 43.1*	32.8	0.00510	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal	46.2	0.01234	Static condition for 16 hours at	DS/EN ISO 105-E04	DCM	Danish EPA no. 107,	DK

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Reference	Country
44.1*			37±3°C.			2010	
Plastic sandal 46.1*	10.5	0.04102	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 46.2 – The outer part of the sole	15.4	0.01379	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 54.2**	0.37	0.003703	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 55.1*	0.013	0.006125	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Toy 1	33.9	1.659	Static conditions in 2 hours for 40°C.	DIN V 53160-2	BnBzO	Özer and Gücer 2012	TR
Toy 3	37.9	3.314	Static conditions in 2 hours for 40°C.	DIN V 53160-2	BnBzO	Özer and Gücer 2012	TR

* Sole of the sandal, ** Strap of the sandal, DCM = Dichloromethane, THF = tetrahydrofuran, BnBzO = Benzoic acid benzyl ester

5.1.2 Migration to artificial saliva

TABLE 26

OVERVIEW OF MIGRATION STUDIES FOR DEHP IN SALIVA

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction /dilution solvent	Analysis method	Reference	Country
Oilcloth 1.6	25.3	0.05	Static condition for 1 hour at 37±3°C	EU project (Simoneau et al., 2001, EUR 19826 EN)	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Oilcloth 1.8	13	0.07	Static condition for 1 hour at 37±3°C	EU project (Simoneau et al., 2001, EUR 19826 EN)	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Balance ball 1.14	44.2	0.24	Static condition for 1 hour at 37±3°C	EU project (Simoneau et al., 2001, EUR 19826 EN)	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Swimming pool 1.18	25.8	0.08	Static condition for 1 hour at 37±3°C	EU project (Simoneau et al., 2001, EUR 19826 EN)	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Shower curtain 1.31	25.1	0.04	Static condition for 1 hour at 37±3°C	EU project (Simoneau et al., 2001, EUR 19826 EN)	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Shower curtain 1.39	29.6	0.06	Static condition for 1 hour at 37±3°C	EU project (Simoneau et al., 2001, EUR 19826 EN)	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Toilet bag 1.65	17.6	0.08	Static condition for 1 hour at 37±3°C	EU project (Simoneau et al., 2001, EUR 19826 EN)	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Doll 3	3	1.86	Head over Heels method	EU project (Simoneau et al., 2001, EUR 19826 EN)	Isooctane	HPLC	Bouma et al., 2002	NL
Doll 8	38	17.64	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Doll 10	39	31.32	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Doll 15	44	13.56	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction /dilution solvent	Analysis method	Reference	Country
Inflatable furniture	37	7.38	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Inflatable furniture	41	9.84	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Swimming tool 2	33	9.84	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Swimming tool 3	36	10.50	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Swimming tool 4	37	7.86	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Swimming tool 5	37	10.86	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Apron	7	3.48	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Ball 1	34	10.62	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Can	34	3.78	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	HPLC	Bouma et al., 2002	NL
Plate B	47.7	118	Horizontal shaking at 300 rpm for 15 min at 35°C	BS 6684:1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Plate D	14.7	45.6	Horizontal shaking at 300 rpm for 15 min at 35°C	BS 6684:1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Plate F	13.2	6.4	Horizontal shaking at 300 rpm for 15 min at 35°C	BS 6684:1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Soft doll C	31.1	52.8	Horizontal shaking at 300 rpm for 15 min at 35°C	BS 6684:1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Ball A *in*	18.5	69.6	Horizontal	BS 6684:1987	ACN	HPLC	Niino et al.,	J

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction /dilution solvent	Analysis method	Reference	Country
vitro			shaking at 300 rpm for 15 min at 35°C	British Standard			2003	
Ball A *in vivo*	18.5	4.4	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	ACN	HPLC	Niino et al., 2003	J
Ball B	37.0	85.2	Horizontal shaking at 300 rpm for 15 min at 35°C	BS 6684:1987 British Standard	ACN	HPLC	Niino et al., 2003	J
PVC plate A	32	0.13	Static conditions at 37°C for 3 hours.	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate B	32	0.065	Static conditions at 37°C for 6 hours.	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate C	32	0.13	Shaking at 37°C for 3 hours	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate D	32	0.067	Shaking at 37°C for 6 hours	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate E	32	0.14	Shaking at 37°C for 3 hours with solvent change	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate F	32	0.37	Glass beads at 37°C for 3 hours.	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate G	32	1.06	Ultrasonic at 37°C for 3 hours	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate H	32	1.28	Ultrasonic at 37°C for 3 hours with solvent change	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate I	32	1.018	Ultrasonic at 37°C for 6 hours	BS 6684:1987 British Standard	DCM	HPTLC	Fiala et al. 2000	A
PVC plate	32	2.64	Sucking for 6	-	DCM	HPTLC	Fiala et al.	A

Sample name	Content of DEHP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction /dilution solvent	Analysis method	Reference	Country
J in vivo			hours				2000	

DCM = Dichloromethane, THF = Tetrahydrofuran, ACN = Acetonitrile

5.2 DINP

5.2.1 Migration to artificial sweat

TABLE 27
OVERVIEW OF MIGRATION STUDIES FOR DINP IN SWEAT – THE SAMPLE WAS EXTRACTED WITH DICHLOROMETHANE AND ANALYSED USING GC-MS

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Reference	Country
Sex toys 2	>50	<500	Static conditions for one hour at 40°C	Sweat: DS/ISO 12870:1997(E). 1. edition	Danish EPA no. 77, 2006	DK

5.2.2 Migration to artificial saliva

TABLE 28
OVERVIEW OF MIGRATION STUDIES FOR DINP IN SALIVA – NO SIMULANT WAS LISTED IN THE BABICH 1998

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Doll 1	29	11.28	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 2	30	12.66	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 3	32	13.32	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 4	33	18.54	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 5	37	17.28	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 6	37	16.92	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 7	37	15.36	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Doll 9	38	15.96	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 11	42	19.74	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 12	43	16.32	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 13	45	9.54	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 14	45	17.34	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Doll 15	48	13.56	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Animal figure 1	16	5.52	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Animal figure 2	27	4.2	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Animal figure 3	28	13.92	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Animal figure 4	34	13.08	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Bath toy 1	33	29.1	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Bath toy 2	36	15.6	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Bath toy 3	40	20.76	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Bath toy 4	42	27	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Teething	45	11.1	Head over	Simoneau et al.,	Isooctane	GC-MS	Bouma et al.	NL

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
ring			Heels method	2001, EUR 19899 EN			2002	
Inflatable Ball	30	8.34	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Inflatable cushion	34	7.08	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Inflatable cushion	31	7.2	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Swimming tool 1	31	6.12	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Key ring figure 2	39	4.5	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Key ring figure 3	44	14.28	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Key ring figure 4	45	12.18	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Ball 2	35	22.14	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Rucksack	23	1.5	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Rucksack	27	4.68	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Standard disk	39	11.82	Head over Heels method	Simoneau et al., 2001, EUR 19899 EN	Isooctane	GC-MS	Bouma et al. 2002	NL
Plate A *in vitro*	46.2	124.8	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Plate A *in vivo*	46.2	32.4	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	ACN	HPLC	Niino et al., 2003	J

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Plate D	14.4	42.8	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Plate E	14.1	8	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Rattle *in vitro*	38	83.6	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Rattle *in vivo*	38	22.4	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	ACN	HPLC	Niino et al., 2003	J
Teether *in vitro*	38.9	51.6	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Teether *in vivo*	38.9	12.8	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	ACN	HPLC	Niino et al., 2003	J
Pacifier *in vitro*	58.3	73.2	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Pacifier *in vivo*	58.3	20	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	ACN	HPLC	Niino et al., 2003	J
Toy food	31.1	46	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Soft doll A	16	29.6	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Soft doll B	29	83.6	Horizontal shaking at 300	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
			rpm for 15 min at 35°C					
Ball C *in vitro*	25.6	33.6	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	ACN	HPLC	Niino et al., 2003	J
Ball C *in vivo*	25.6	7.8	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	ACN	HPLC	Niino et al., 2003	J
Yellow teether I	36	0.24	Static conditions at 37°C for 3 hours.	BS6684:1987 British Standard	DCM	HPTLC	Fiala et al 2000	A
Yellow teether II	36	0.363	Shaking at 37°C for 3 hours	BS6684:1987 British Standard	DCM	HPTLC	Fiala et al 2000	A
Yellow teether III	36	3.87	Ultrasonic at 37°C for 3 hours	BS6684:1987 British Standard	DCM	HPTLC	Fiala et al 2000	A
Yellow teether IV	36	8.33	Sucking 1 hour	BS6684:1987 British Standard	DCM	HPTLC	Fiala et al 2000	A
Yellow teether V	36	3.02	Sucking 3 hours	BS6684:1987 British Standard	DCM	HPTLC	Fiala et al 2000	A
Yellow teether VI	36	13.3	Chewing 1 hour	BS6684:1987 British Standard	DCM	HPTLC	Fiala et al 2000	A
Yellow teether VII	36	8.75	Chewing 3 hours.	BS6684:1987 British Standard	DCM	HPTLC	Fiala et al 2000	A
Toy ball B *in vivo*	25.5	7.8	Rotary shaker at 300 rpm in an incubator at 35°C for 15 min.	-	ACN	HPLC	Niino et al 2002	J
Toy book 1-2	27.5	0.255	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 1-3	36.6	1.027	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Toy Tiger 1-5	48.1	1.045	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy Dolphin 1-6	43.7	2.700	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 1-7	30.0	0.264	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 1-8	43.3	0.582	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 1-9	33.5	0.436	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 1-10	54.4	0.445	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Corner Pads 1-11	44.0	1.382	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy Food 1-14	51.0	1.964	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy duck 2-1	40.8	0.327	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Toy duck 2-2	42.7	4.400	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 2-3	50.3	0.355	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy fish 2-4	37.0	0.591	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy treehouse 2-5	36.1	1.264	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Squeeze toy 2-7	32.6	1.209	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Soother 2-8	30.2	0.136	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 2-9	25.6	0.145	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Teether 2-10	19.3	0.273	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy book 2-11	17.5	0.127	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Bath toy 2-12	15.1	0.091	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy turtle 2-13	35.4	0.336	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy bear 2-14	19.9	0.300	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Spoon 2-15	35.2	0.436	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Spoons 2-16	34.3	0.827	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Ball 3-1	41.2	0.536	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy bear 3-2	41.2	0.409	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy 3-3	27.1	0.264	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Toy block 3-4	43.0	0.500	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.

Sample name	Content of DINP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Toy car 3-5	42.7	0.218	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.
Squeeze toy 3-6	52.5	0.264	Temperature = 37 °C. Impacted by a pneumatic piston.	Dulbecco's phosphate buffered saline with 0.16 % mucin	Not available	GC-MS	Babich, M 1998	U.S.A.

THF = Tetrahydrofuran, ACN = Acetonitrile, DCM = Dichloromethane

5.3 DBP

5.3.1 Migration to artificial sweat

TABLE 29
OVERVIEW OF MIGRATION STUDIES FOR DBP IN SWEAT – ALL SAMPLES WERE ANALYSED USING GC-MS

Sample name	Content of DBP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Reference	Country
Plastic sandal 1.1*	22.9	0.42	Static condition for 16 hours at 37±3°C	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 5.2**	26.6	0.66	Static condition for 16 hours at 37±3°C	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1b*	$1*10^{-4}$	0.009	Static condition for 16 hours at 37±3°C, with new simulant after 8 hours.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1c*	$1*10^{-4}$	0.015	Static condition for 8 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1d*	$1*10^{-4}$	0.021	Dynamic condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1e*	$1*10^{-4}$	0.0145	Static condition with sunscreen for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.1f*	$1*10^{-4}$	0.0164	Dynamic condition with sunscreen for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 8.2**	8	0.222	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 13.2**	34	0.630	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 17.1*	0.9	0.0168	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 18.1 – Middle of sole	0.2	0.00465	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic	0.08	0.00100	Static condition	DS/EN ISO	DCM	Danish EPA	DK

Sample name	Content of DBP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Reference	Country
sandal 18.2 – Outer part of sole			for 16 hours at 37±3°C.	105-E04		no. 107, 2010	
Plastic sandal 20.2**	17.8	0.4365	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 38.2**	1.2	0.02813	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK
Plastic sandal 46.1 – Middle part of sole	0.29	0.001563	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	Danish EPA no. 107, 2010	DK

* Sole of the sandal, ** Strap of the sandal, DCM = Dichloromethane

5.3.2 Migration to artificial saliva

TABLE 30
OVERVIEW OF MIGRATION STUDIES FOR DBP IN SALIVA – ALL SAMPLES WERE EXTRACTED WITH ACETONITRILE AND ANALYSED USING HPLC

Sample name	Content of DBP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Reference	Country
Plate C	47.1	144.8	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	Niino et al., 2003	J
Plate D	13.5	34.8	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	Niino et al., 2003	J
Plate G	12.9	34.8	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	Niino et al., 2003	J
Ball A *In vitro*	10	58	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	Niino et al., 2003	J
Ball A *in vivo*	10	1.2	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	Niino et al., 2003	J
Ball B	22	79.2	Horizontal shaking at 300 rpm for 15 min at 35°C	BS6684: 1987 British Standard	Niino et al., 2003	J
Toy ball A *in vitro*	10	3.39	Gently chewed for 15 min. Repeated four times with 5 min breaks.	BS6684: 1987 British Standard	Niino et al 2001	J
Toy ball A *in vivo*	10	1.17	Gently chewed for 15 min. Repeated four times with 5 min breaks.	-	Niino et al 2001	J

5.4 DIBP

5.4.1 Migration to artificial sweat

TABLE 31
OVERVIEW OF MIGRATION STUDIES FOR DIBP IN SWEAT

Sample name	Content of DiBP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Wrist watch U06	7	0.037	Static conditions under stirring for 24 hour at 37±3°C.	DS/EN ISO 105-E04	THF	GC/MS with SPME	Danish EPA no. 139, 2015	DK
Plastic sandals 1.1*	6.3	0.19	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 8.1a*	21.2	0.29	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 8.1b*	21.2	0.32	Static condition for 16 hours at 37±3°C, with new simulant after 8 hours.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 8.1c*	21.2	0.49	Static condition for 8 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 8.1d*	21.2	0.47	Dynamic condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 8.1e*	21 .2	0.97	Static condition with sunscreen for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 8.1f*	21.2	1.12	Dynamic condition with sunscreen for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 8.2**	7.4	0.30	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 17.1*	6.6	0.16	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 18.1 - Middle of sole	2.2	0.14	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK

Sample name	Content of DiBP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Plastic sandals - 18.2 The outer sole	11.7	0.24	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 20.2**	5.3	0.21	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 29.2**	1.6	0.13	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 37.2**	12.1	0.47	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 38.2**	12.1	0.40	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 46.1*	2.2	0.07	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals - 46.2 The outer sole	3.9	0.10	Static condition for 16 hours at 37±3°C.	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Plastic sandals 55.1*	3.3	0.49	Static condition for 16 hours at 37±3°C. pH 5.5	DS/EN ISO 105-E04	DCM	GC-MS	Danish EPA no. 107, 2010	DK
Training ball 1.24	35.4	5.80	Static condition for 1 hour at 37±3°C	Simoneau et al., 2001, EUR 19826 EN	DCM	GC-MS	Danish EPA no. 109, 2010	DK

* Sole of the sandal, ** Strap of the sandal, DCM = Dichloromethane

5.4.2 Migration to artificial saliva

TABLE 32
OVERVIEW OF MIGRATION STUDIES FOR DIBP IN SALIVA

Sample name	Content of DiBP (%w/w)	Migration rate (µg/cm²/h)	Migration conditions	Simulant	Extraction/ dilution solvent	Analysis method	Reference	Country
Training ball 1.24	34.5	3.70	Static condition for 1 hour at 37±3°C	Simoneau et al, 2001, EUR 19826 EN	DCM	GC-MS	Danish EPA no. 109, 2010	DK
Training ball	36.5	5.80	Static condition for 1 hour at 37±3°C	Simoneau et al, 2001, EUR 19826 EN	DCM	GC-MS	Danish EPA no. 109, 2010	DK

DCM = Dichloromethane

Determination of Migration Rates for Certain Phthalates

The purpose of the report is to suggest migration rates for the phthalates DEHP, DINP, BBP, DBP and DIBP in soft PVC. The suggested migration rates will be based on numerous migration studies from the accessible literature. The background to varying migration rates reported in the literature will be investigated, discussed and evaluated. One of the major factors on the migration rate is the way the migration analysis is carried out. Therefore, very different results were obtained depending on how vigorous the applied dynamic forces were. Due to that major factor, it has been necessary to divide the proposed migration rates according to the experimental set-up used. The analytical methods to determine the migration of phthalates are therefore divided into three categories: mild, medium and harsh conditions. The mild conditions result generally in lower migration rates compared with the in vivo adult migration rates for the simulation of children's sucking and chewing on soft PVC products. The head over heels method (HOH) is judged as the most documented method of all, mostly for the migration rates for DINP to artificial saliva, but also a few for DEHP. The HOH method seems to be the most realistic method, since the given product is rotated once per second, which resembles how a child will chew on a toy. For this reason and because the other methods are very different in their approach, the HOH method is recommended as the reference method for the determination of migration rates for phthalates well knowing that realistic migration rates are difficult to determine in in vitro or adult in vivo studies. Calculations have been made in order to estimate migration rates for the five phthalates. The basis is the HOH method, since this method seems to give the most realistic migration rates. The estimated migration rates are quite close to each other (between 10 and 13 µg/cm2/h). The migration rates for DIBP and DBP should in theory be higher than the migration rates for DINP and DEHP if the content of the phthalates in the products are similar. The reason for the similar migration rates

The Danish Environmental
Protection Agency
Strandgade 29
DK-1401 Copenhagen K

www.mst.dk