PD CEN/TR 16364:2012

BSI Standards Publication

Influence of materials on water intended for human consumption — Influence due to migration — Prediction of migration from organic materials using mathematical modelling

...making excellence a habit.™

National foreword

This Published Document is the UK implementation of CEN/TR 16364:2012.

The UK participation in its preparation was entrusted to Technical Committee EH/6, Effects of materials on water quality.

A list of organizations represented on this committee can be obtained on request to its secretary.

ISBN 978 0 580 76777 7

ICS 13.060.20

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 31 July 2012.

Amendments issued since publication

Date	Text affected

TECHNICAL REPORT
RAPPORT TECHNIQUE
TECHNISCHER BERICHT

CEN/TR 16364

June 2012

ICS 13.060.20

English Version

Influence of materials on water intended for human consumption - Influence due to migration - Prediction of migration from organic materials using mathematical modelling

Influence des matériaux sur l'eau destinée à la consommation humaine - Influence de la migration - Utilisation de modèles mathématiques pour prévoir la migration depuis des matériaux organiques

Einfluss von Materialien auf Wasser für den menschlichen Gebrauch - Einfluss infolge der Migration - Abschätzung der Migration aus organischen Materialien mittels mathematischer Modellierung

This Technical Report was approved by CEN on 9 April 2012. It has been drawn up by the Technical Committee CEN/TC 164.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. CEN/TR 16364:2012: E

Contents

Foreword

This document (CEN/TR 16364:2012) has been prepared by Technical Committee CEN/TC 164 “Water supply”, the secretariat of which is held by AFNOR.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

Introduction

During the last two decades, several scientific investigations have demonstrated that migration from organic materials into liquid simulants is a physical process that can be modelled successfully. Mass transfer from an organic material into a liquid simulant is predictable because in many cases it follows Fick´s law of diffusion, i.e. the diffusion process is the rate determining step. To predict migration from organic materials into contacting media a corresponding diffusion model was established.

This Technical Report describes the application of predictive diffusion modelling to the estimation of the migration of a substance from a product intended for contact with water intended for human consumption – for convenience, and where appropriate, referred to as drinking water in this report. The application applies to organic materials, such as polymers, used to make such products.

The purpose of the report is to stimulate the use of such techniques in member states such that sufficient experience is generated to enable the value of such modelling to be assessed in relation to complementing or substituting the conventional approach.

Normally in member states the estimation of such migration is performed by standardised procedures based on laboratory testing and analysis, i.e. an experimental approach. Migration modelling is an alternative to this type of experimental testing. The experimental determination of the specific migration of substances into test water (simulated drinking water) often requires a considerable amount of time and it can be costly. This conventional approach has worked well and, of course, it generates data on the actual concentration of a substance in test water. However, in some cases the analysis is difficult or even impossible due to problems caused, for example, by chemical degradation, volatilisation of the substance. In addition, the substance may not be amenable to, or the target concentration of interest may be too low for, available analytical techniques Therefore, the application of a mathematical model could have considerable benefits for industry and regulators, as experience has shown in the control of migration from plastic materials in contact with foodstuffs.

Thus, the modelling approach is attractive because, in principle, it is quicker and more flexible than the conventional testing approach, in that different exposure conditions can be readily investigated - and it should be cheaper.

Modelling of migration has been used for several years in the United States as an additional tool in support of regulatory decisions. Also, the European Union has introduced such diffusion modelling by means of EU Directive 2001/62/EC (the 6th amendment of Directive 90/128/EEC), consolidated in Directive 2002/72/EC as a compliance and quality assurance tool for plastic materials intended to come in contact with foodstuff [3].

The European project SMT-CT98-7513, *Evaluation of Migration Models in Support of Directive 90/128/EEC*, successfully demonstrated the practical value of such diffusion models. The main objectives of this project were to demonstrate:

- the validity of migration models for compliance purposes;
- that a relationship between the specific migration limit (SML) and the concentration of a substance in the finished product can be established.

A report of this project has been finalised and the project results were published in a scientific journal [4]. As indicated above, a major advantage of migration modelling is that it enables calculation of migration values independent of the limitations that affect the experimental/analytical approach. For example, at low cost one can quickly investigate, for compliance or research purposes, a wide range of conditions of contact between material with test water.

The diffusion modelling approach described was originally developed for, and accepted by, the European Commission in the area of plastic materials in contact with foodstuffs. It has been successfully used to simulate the conventional experimental/analytical approach to compliance testing of plastics in contact with foodstuffs. In this latter approach different liquid food simulants, including aqueous simulants, are used.

In principle, the approach is applicable to many organic materials. However, today it has been applied mainly to different types of polyethene, polypropene, polystyrene and polyvinyl chloride.

Like the experimental approach, the mathematical approach has its limitations. An accurate prediction of the migration of a substance from an organic material to water requires detailed knowledge of the diffusion behaviour of the materials and substances under investigation. The level of information may well require extensive experimental studies – more than the experimental, analytical approach would require. An important feature of the mathematical approach is the possibility of generalisation. Based on known average diffusion behaviour of polymers and substances, a maximum or 'upper-limit' migration can be calculated. This so-called 'worst-case' result may then be used for compliance purposes.

1 Scope

This Technical Report describes a procedure, based on a diffusion model, to be applied to the estimation of specific migration of substances into drinking water from organic materials intended to come into contact with drinking water.

The modelling approach is readily applicable to certain organic materials, as explained in this report. In principle, the diffusion modelling approach is applicable to other organic materials but practical difficulties, in relation to obtaining data to feed into the diffusion model, may restrict or prevent its application. Accordingly, in addition to the diffusion model, scientific estimation procedures for the required data inputs need to be considered.

The approach is normally applicable to organic substances that are soluble in the material matrix. Substances applied externally to a product made of an organic material, e.g. antistatic agents, lubricants, etc. are excluded from the diffusion modelling approach, as are electrolytes, salts, oxides and metals. Only organic substances with well-defined molecular weight or mixtures with well-defined ranges of molecular weights are amenable to the diffusion modelling approach.

The diffusion modelling approach is readily applicable to amenable organic materials in the form of a pipe or a sheet, where data such as material thickness is readily calculable. More complicated product shapes, such as fittings, require assumptions to be made.

It may not be possible to model the effects of test waters that are chemically active, for example test waters to which chlorine has been added to simulate chlorinated drinking water. This is because substances that migrate from a material into water containing chlorine can be converted by chemical reaction into substances with different properties.

2 Normative references

Not applicable.

3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

3.1
diffusion model
Fick's Second Law of diffusion that simulates the diffusion of substances from a material into drinking water

3.2
experimental test
technical operation that consists of the determination of one or more characteristics of a given product

3.3
experimental testing procedure
set of instructions for determining by experiment the migration of a substance from a material into water

3.4
software tool
set of instructions for a computer (e.g. a computer program)

Note1 to entry: In this document it refers to instructions designed to model migration of substances from a material into water.

3.5
product
manufactured item intended for contact with drinking water

3.6
monolayer
product this is or contains a material that consists of one layer

3.7
multilayer
product this is or contains a material that consists of more than one layer

3.8
migration
movement of a substance or substances from one compartment (a material) into a second compartment (water)

3.9
migration period
period of time in which the migration is carried out under specified conditions

3.10
migration rate
mass of a measured substance or substances migrating from the surface of a test piece into the test water in one day

3.11
substance
chemical that is a constituent of a material used in contact with drinking water with the potential to migrate into drinking water

3.12
contact area
surface area of a material in contact with a specific volume of water

3.13
volume to area ratio
ratio of the volume of water in contact with a specific area of material

3.14
test water
water used for migration testing

3.15
diffusion equation
partial differential equation known as Fick's Second Law that describes the variation of the concentration of a substance in a system (e.g. a polymer in contact with water) depending on time and location

3.16
diffusion coefficient
factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time (e.g. from polymer to water)

3.17
molecular weight
mass of one mole of molecules calculated using standard atomic weights, expressed as g/mol

3.18
partition coefficient
ratio of the concentrations, at equilibrium, of a substance in the two phases of a mixture of two immiscible solvents

Note1 to entry: Examples are polymer and water or in the case of the Octanol-Water Partition Coefficient, 1-octanol and water.

4 Principle

Current predictive mathematical models for the estimation of migration of a substance from an organic material into another medium, such as a food simulant or drinking water, are based on diffusion theory and partitioning effects. Various parameters and information are needed to make the diffusion model work, in terms of calculating the concentration of a substance in test water or a migration rate.

Various assumptions need to be valid for the model to work satisfactorily.

If the described data inputs are available, or can be estimated, and the various assumptions valid, then the model can be used to estimate reliably the concentration of a substance in water after a specific time of contact between an organic material and water - and at a specific temperature. If required this concentration can be used to calculate a migration rate.

Depending on how the various data inputs are obtained, or used, the diffusion model can be used to estimate a worst-case value of migration, i.e. to produce a value that is likely to be higher than a value estimated by means of the conventional experimental/analytical approach.

The diffusion model can be used in a manner that simulates the conditions applied in the conventional analytical approach used in member states.

Annex A provides detail on the principles on which the diffusion modelling approach is based.

5 Apparatus

In order to predict migration a personal computer set-up capable of running an appropriate validated software tool is required. See Annex C for information on validation of the numerical algorithm and the software. Currently suitable software to run the diffusion model is available.

6 Assumptions that need to be valid

The diffusion model is based on the following assumptions being valid:

1) the migration process of the substance within organic materials shall obey the law of diffusion (Fick’s Second Law);

2) the migrant is an uncharged, organic substance;

3) the mass of the substance in the system is conserved, i.e. no substance is consumed or built up;

4) the initial concentration of the substance in the material shall be homogeneous, i.e. it does not vary significantly and is constant, i.e. is non-degradable by chemical reaction; this applies to each layer in the case of multilayer products;

5) the material thickness shall be uniform (i.e. it does not vary significantly);

6) the volume of the organic material and the water is finite;

7) there shall be no boundary resistance for the transfer of the substance between the organic material and water;

8) the uptake of the substance by the water shall be fast, i.e. the water is a high diffusivity medium or well-mixed liquid;

9) the interaction between the organic material and water shall be negligible such that no swelling of organic material by uptake of water occurs during the migration process.

7 Required data inputs

7.1 General

The data inputs required to use the diffusion model are described in 7.2 to 7.10.

7.2 Diffusion coefficient of the substance (D_P)

The diffusion coefficient is a parameter dependant on the properties of the substance and of the organic material. It relates to the mobility of the substance in the organic material. It may be obtained in several ways:

a) from tables;

b) determined by experiment [5];

c) estimated by a validated scientific estimation procedure:

    1) Arrhenius equation [6];

    2) estimation procedure developed by Piringer validated in the EU Project SMT-CT98-7513 [4]; the diffusion coefficients for various organic materials can be estimated from their polymer-specific parameter, A_P [7];

d) assumed to be a worst-case value.

A detailed explanation on how to obtain and use diffusion coefficients, see A.4.

7.3 Partition coefficient of the substance ($K_{P,W}$).

The partition coefficient $K_{P,W}$ is a parameter dependant on the relative solubility of the substance in relation to the organic material and the water. It relates to what extent the substance moves from the organic material into water at thermodynamic equilibrium. It may be obtained in several ways:

a) from tables;

b) determined by experiment;

c) estimated by a validated scientific estimation procedure;

    1) estimation from the solubility of the substance in water, i.e. the concentration in the water will not exceed its water solubility (worst-case assumption) [8];

    2) estimated from the octanol/water partition coefficient of the substance [9,10];

d) assumed to be a worst-case value.

A detailed explanation on how to obtain and use partition coefficients, see A.5.

7.4 Temperature of the system (T)

In many cases the temperature of the system (material and test water) to be modelled will be specified in the relevant regulations or standard. For example, in EN 12873-1, the temperature for ‘cold’ water simulation is 23 °C.

7.5 Geometry of the material

The surface area of the material (S) and the amount of test water (V_{DW}) in contact with the material shall be known. In the case of organic materials in the form of sheets or piping (cylinders) these values are readily calculable. More complex product forms may require assumptions and approximations to be made. These should be noted in the report (see Clause 10).

7.6 Material thickness, (d_P)

Evidence is needed, or an assumption shall be made, that the thickness does not vary significantly.

7.7 Initial concentration of the substance in the material ($c_{P,0}$)

This is important because it has a prime influence on the magnitude of the predicted level of migration. It may be obtained by:

- determination (analysis of the substances in the organic material – the feasibility of this will depend on the specific substance/material combination);
- based on the amount added during the production of the material; this applies readily to additives but not, of course, monomers and other reactive starting substances.

7.8 Chemical identity of the substance and its relative molecular weight

The exact chemical identity (not commercial names) of the substance and its relative molecular weight (M_r) in g/mol are required.

7.9 Specific gravity of the material (ρ_P)

The specific gravity of the material is required.

7.10 Simulation of contact of organic material with test water

The diffusion modelling process simulates the conditions of contact of the organic material with test water. The contact may relate to:

- duration of the contact of the sample of organic material with water during pre-washing and conditioning (t_s) in s;
- duration of the contact of the sample of organic material with test water during migration test (t_n) in s;
- number of migration test cycles, the successive periods of contact of the sample of organic material with test water (N).

8 Procedure

The exact procedure will depend on the software used and its ‘user-friendliness’.

In principle, migration models can be used to complement or substitute conventional experimental testing in member state approval schemes for products intended for contact with drinking water. At present member states use different approval schemes. However, it is possible at some point in future many, or all, member states will adopt EN 12873-1 and -2.

It can be applied assuming conditions of contact between material and test water that constitutes a worst-case situation (i.e. unlikely in practice) that would lead to enhanced migration. Additionally, worst-case values for diffusion and partition coefficients could be used. This would provide safety factors in that, if a satisfactory (in relation to not exceeding a corresponding limit value) migration value were obtained, then one could be satisfied that conventional testing would show the organic material to be satisfactory.

Annex B gives examples of the application of the diffusion modelling approach to assessments as described above.

9 Expression of results

The result of a prediction based on the migration models can be expressed in several ways. This depends on the software tool used and the objective of the calculation. The result is a value representing mass transfer from the organic material to water. A migration rate can be calculated following the provisions in EN 12873-1 or -2. Below is a list of examples:

- migration rate, m_t/S (µg/dm^2 × day);
- concentration of the substance in test water, $c_{w,t}$ (µg/l);
- residual concentration of the substance in the material, $c_{p,t}$ (mg/kg);
- amount of substance that has migrated into the test water, $m_{w,t}$ (µg);
- residual amount of substance remaining in the material, $m_{p,t}$ (µg).

10 Report

The report should include if relevant a full description of:

- the organic material under test;
- the modelling software used;
- the report shall provide the values of all the inputs and their source or derivation;
- concentration of the substance in the material;
- the specific gravity of the material;
- thickness of the material;
- chemical identity (not commercial trade names) of the substances;
- molecular weight of the substance;
- diffusion coefficient of the substances in the organic material (if applicable the estimation procedure and relevant parameters used);

- partition coefficient of the substances between the organic material and water (if applicable the estimation procedure and relevant parameters used);
- the report shall provide full details of the simulated migration test;
- the temperature of the migration test;
- duration and number of migration periods;
- the ratio of the surface area of the material to the volume of test water.

Any deviation from the procedures described in this report shall be reported.

Annex A
(informative)

Principles of the modelling approach

A.1 Migration modelling

Currently, existing predictive mathematical models for migration estimation are essentially based on diffusion theory and consideration of partitioning effects. The mass transfer of organic substances from organic materials to contact media (e.g. drinking water) is simplified down to the diffusion process being in most cases the rate determining step, i.e. a diffusion model (accounting for different number of layers and geometries) based on the law of diffusion (Fick's Second Law) results. Processes like chemical reactions, swelling of the organic material, boundary resistance, etc. are excluded because of the limitations given in Clause 6. The underlying key parameters are the diffusion coefficient of the substance in the organic material, D_P, as well as the partition coefficient of the substance between the organic material and the contacting medium, e.g. drinking water, $K_{P,W}$. Although these models are still under further scientific discussion, refinement and development they have been shown to be able to provide an estimation of worst-case migration for homogeneous materials. One of these upper-limit migration models has been validated within the EU project SMT-CT98-7513 [4] It is based on a series of initial and boundary conditions and is designed such that migration estimation with a sufficient safety margin results.

A.2 Initial and boundary conditions

The migration modelling approach is based on a diffusion model that reliably maps the experimental procedure of interest. The experimental procedure represents the most widely-applied approach applicable for organic materials. The diffusion model is applicable to homogeneous (mono- and multilayer) organic materials used to make products intended for use in contact with drinking water, provided that it fulfils the following initial and boundary conditions:

1) the migration process of the substance within the material follows the law of diffusion - also known as Fick’s Second Law;

$$\frac{\partial c}{\partial t} = D_P \frac{\partial^2 c}{\partial x^2} \tag{A.1}$$

where

c is the concentration of substance in the organic material at time t at distance x from the origin of the x-axis and D_P is the constant diffusion coefficient in organic material;

2) a homogeneous material, regarded as a polymer film/sheet/mould of finite and constant thickness (d_P) is in contact with water, of finite volume (V_{DW});

3) the substance, with relative molecular weight M_r, is distributed homogeneously (at T = 0) in the organic material;

4) the migrant is an uncharged, organic substance;

5) there is no boundary resistance for the transfer of the substance between the organic material and water; the uptake of the substance in the water is fast, i.e. the water is a high diffusivity well mixed liquid;

6) it is assumed that the interaction between the organic material and water is negligible such that no swelling of the organic material by uptake of water occurs during the migration process;

7) the substance is homogeneously distributed in drinking water, i.e. the uptake of the substance by the water shall be fast, i.e. the water is a high diffusivity medium or well-mixed liquid;

8) the total amount of the substance in the organic material and water is constant during the migration process.

A.3 Solution of the diffusion equation

The migration estimation is based on the solution of the diffusion equation with respect to time / temperature, which might be the same conditions employed for experimental testing. At the beginning of the first contact period ($t = 0$) a step-wise concentration profile is considered, i.e. the substance is distributed homogenously in the organic material with the initial concentration $c_{P,0}$ and the concentration of the substance in the water is zero. Because of the nature of the experimental migration testing approach, i.e. application of one stagnation period and several consecutive migration test cycles, the concentration profile in the organic material from the previous contact period shall be available. This requirement requires solution of the diffusion equation (partial differential equation) numerically for which Finite Differences or Finite Elements methods may be employed.

Finite Differences or Finite Elements methods have been used for many years to solve partial differential equations (PDEs). These methods were used for example in chemical engineering science where mathematical models are used to describe chemical processes. The equations in chemical engineering models are often more complicated than the diffusion equation. Nevertheless with Finite Differences or Finite Elements methods these equations can be solved and are helpful tools in the design of chemical production plants.

Finite Element Analysis (FEA) is the application of the Finite Element Method. In FEA the object or system is represented by a geometrically similar model consisting of multiple, linked, simplified representations of discrete regions, i.e. finite elements. The analysis is, therefore, done by modelling an object into thousands of small pieces. The finite approximations are used for solving PDEs approximately. Solutions are approximated by rendering the PDE into an equivalent ordinary differential equation, which is then solved using the techniques of linear algebra. For the calculation of the migration in monolayer or multilayer organic materials, the diffusion equation, derived from applicable physical considerations, is applied to each element which enables the construction of a system of simultaneous equations. FEA uses a complex system of points called nodes which make a grid called a mesh. This mesh is programmed to contain the organic material properties which define how the migration will occur. Nodes are assigned at a certain density throughout the organic material depending on the anticipated diffusion rates of a particular area (i.e. layer). Regions that will present higher diffusion rates and high concentration gradients usually have a higher node density than those which experience little or no diffusion. Points of interest may consist of interface between two different layers and high concentration areas. As the number of nodes is increased (higher node density) a more accurate solution is obtained at each point in the diffusion model. However, accuracy of the numerical analysis cannot for practical reasons be improved indefinitely. There is an upper limit after which the accuracy of a number of nodes stays practically the same, while computing time increases drastically [11].

A.4 Obtaining and using diffusion coefficients

A.4.1 Diffusion coefficients from literature

Diffusion coefficients can be found in scientific literature for various specific situations, i.e. for a given substance in a given organic material at given temperature. Unfortunately, the use of these diffusion coefficients is limited to the specific situation and in many cases does not fit to the situation to be modelled. A collection of diffusion coefficients for various substances in different organic materials can be found in the Annex to *Plastic Packaging*… Piringer, Otto G., Baner, A. L. (Ed.) [12]. This is based on a collection of diffusion coefficients from literature contracted by the EU Commission - DG SANCO [13].

A.4.2 Diffusion coefficients from experiment

The Modelling Task Force of the EU Commission - DG SANCO hosted by the Joint Research Centre (JRC), Ispra has worked out a technical guidance document to determine diffusion coefficients of migrants to update the A_P value of a food contact plastic (i.e. organic material) for migration evaluation by mathematical modelling [14].

A.4.3 Estimation of diffusion coefficients

Diffusion coefficients may be estimated by various procedures. The basis for many of these estimation procedures is the Arrhenius Equation [6]. A selection of estimation procedures can be found in Clause 5 of *Plastic Packaging…*, Piringer, Otto G., Baner, A. L. (Ed.) [12].

If the diffusion coefficient D_P of a substance in an organic material at a given temperature is not available, D_P can be estimated with a reliable procedure. One of the estimation procedures based on the Arrhenius Equation is the procedure developed by Piringer [15].

Arrhenius Equation:

$$D = D_0 \cdot e^{\frac{-E}{R \cdot T}}$$

where

D is diffusion coefficient in cm²/s;

D_0 is pre-exponential factor cm²/s;

E_A is activation energy in J/mol;

T is temperature in K;

R is gas constant 8,314 J/mol × K.

From phenomenological derivation and statistical evaluation of experimental diffusion and migration data with respect to diffusion of substances in organic material materials [16], a realistic diffusion coefficient, D_P can be estimated by the following an Arrhenius-type relationship [12].

$$D_P = 10^4 \exp\left[A_P^{'} - 0{,}1351 \cdot M_r^{2/3} + 0{,}003 \cdot M_r - \frac{(\tau + 10\,454) \cdot R}{R \cdot T} \right] \qquad \text{(A.2)}$$

where

D_P is realistic diffusion coefficient of substance in cm²/s;

M_r is relative molecular mass of substance in g/mol;

T is temperature in K;

A_P' is polymer-specific parameter (e.g. mean value);

τ is polymer-specific 'activation energy' parameter;

R is gas constant 8,314 J/mol × K.

For convenience the two parameters A_P' and τ are concentrated in one polymer-specific parameter, the A_P-value, i.e. $A_P = A_P' - \tau/T$ (see Equation (A.4)).

The A_P-value describes the real diffusion properties of a given organic material. The experimental data may produce a range of A_P-values are available for one organic material. The mean value of the set may be considered best to describe the real (average) diffusion behaviour of the organic material (see also A.4.5).

A.4.4 Upper-limit diffusion coefficient

If the diffusion coefficient D_P of a substance in an organic material at a given temperature is not available, D_P may be replaced with an upper-limit diffusion coefficient, D_P^*. Using such a diffusion coefficient the migration estimation leads to worst-case migration values.

The diffusion coefficient of a substance in a given organic material is related to the temperature independent polymer-specific parameter, the A_P'-value, its relative molecular weight, M_r, and the activation energy E_A associated with the diffusion process.

The activation energy is the sum of two terms ($E_A = E_{A,ref} + \Delta E_A$) where:

1) the reference activation energy $E_{A,ref} = 10\ 454 \times R = 87$ kJ/mol, i.e. mean value characteristic for low density polyethylene, LDPE showing the highest diffusivity of common organic materials; and

2) the polymer-specific deviation from the reference activation energy $\Delta E_A = \tau \times R$, where τ is the corresponding polymer-specific activation energy parameter.

From phenomenological derivation and statistical evaluation of experimental diffusion and migration data with respect to diffusion of substances in organic material materials, an upper-limit diffusion coefficient, D_P^* can be estimated by the following Arrhenius-type relationship [12].

$$D_P^* = 10^4 \exp\left[A_P'^* - 0{,}1351 \cdot M_r^{2/3} + 0{,}003 \cdot M_r - \frac{(\tau + 10\ 454) \cdot R}{R \cdot T}\right] \tag{A.3}$$

where

D_P^* is upper-limit diffusion coefficient of substance in cm²/s;

M_r is relative molecular mass of substance in g/mol ;

T is temperature in K;

$A_P'^*$ is upper-limit polymer-specific parameter;

τ is polymer-specific 'activation energy' parameter;

R is gas constant 8,314 J/mol × K.

For convenience the two parameters $A_P'^*$ and τ are concentrated in one polymer-specific parameter, the A_P^*-value.

$$A_P^* = A_P'^* - \frac{\tau}{T} \tag{A.4}$$

The A_P^*-value describes the upper-limit diffusion properties of a given organic material. It is the 95 %-percentile value from a set of A_P-values available for a given organic material (see A.4.5).

A.4.5 Validated AP', AP'* and τ values

For a number of polymers the actual values of A_p' and τ were calculated from available diffusion coefficients in the literature with Equation (A.2) using a database consisting of well-defined diffusion experiments reported in the literature over the last four decades A.4.1. For given organic materials various diffusion coefficients were available, with respect to several substances and temperatures investigated resulting in a set of A_P'-values for a given organic material. Calculation of the 95 %-percentile value (high number N > 20 of values in the data set) or the 95 % confidence interval (low number of values N < 20 in the data set) of that data set gives the upper-limit A_P'*-value.

Using these values for A_P'* and τ in (Equation (A.3)) results in upper-limit diffusion coefficients, D_P^*, which overestimate in 95 % of all cases the migration in contact media (in most cases simulants) determined in various experimental projects [17, 18, 19, 20, 21].

Table A.1 — Known A_P', $A_P'^*$ and τ values [7]

Polymer	A_P'	$A_P'^*$	τ
(linear) low density polyethylene ((L)LDPE)	10,0	11,5	0
high density polyethylene (HDPE)	10,0	14,5	1 577
polypropylene (PP), homo and random	9,40	13,1	1 577
polypropylene (PP) rubber		11,5	0
polystyrene (PS)	-2,80	0,0	0
high impact polystyrene (HIPS)	-2,70	1,0	0
polyethylene terephthalate (PET)	2,20	6,0	1 577
polyethylene naphthalate (PEN)	-0,34	5,0	1 577
polyamide 6,6 (PA 6,6)	-1,54	2,0	0

NOTE PEN = polymer of ethylene glycol and naphthalene dicarboxilic acid, PA 6,6 = polymer of hexanediamine and hexanediacid.

A.4.6 Diffusion coefficients for other materials

After the EU-project SMT-CT98-7513 [4] finished in 2003 some further materials were investigated in industry projects from which the parameters listed in Table A.2.

Table A.2 — More recent AP', AP'* and τ values

Polymer	A_P'	$A_P'^*$	τ
polyvinylchloride (PVC) [5]	-4,0	-1,0	0
cross-linked polyethylene (PE-X) [22]		14,5	1 577
epoxy based coatings [23]		7,0	0

Besides the polymers described above other organic materials can be found on the market. In addition new material developments may happen in the future.

In principal, migration modelling is also applicable to other organic materials.

It shall be demonstrated that the migration of substances from the organic material into contact media, e.g. drinking water follows the generally accepted law of diffusion as described in more detail in A.4.2 and the cited Technical Guidance Document, TGD [14].

From the experimental diffusion data gained in accordance with the TGD the basic diffusivity of the new organic material expressed as individual A_P' values data set is calculated by Equation (A.2) and the corresponding upper-limit polymer-specific constant ($A_P'^*$-value) established through statistical evaluation of the data set.

In the case of diffusion coefficient of new materials for modelling purposes under national approval schemes, it may be necessary for the relevant national regulatory/technical committee to agree on the new diffusion coefficients.

A.4.7 Worst-case diffusion coefficients

Using a worst-case upper-limit $A_P'^*$-value of $A_P'^* = 20$ and $\tau = 0$ gives worst-case diffusion coefficients D_P^* appropriate for organic liquids.

Using a worst-case lower limit $A_P'^*$-value of $A_P'^* = -20$ and $\tau = 0$ gives a worst-case diffusion coefficient D_P^* corresponding to a 'barrier material' like aluminium foil.

A.5 Obtaining and using partition coefficients

A.5.1 General

A partition coefficient between adjacent layers in a multilayer organic material with a number of n layers is defined as:

$$K_{P_{n-1},P_n} = \frac{c_{P_{n-1},\infty}}{c_{P_n,\infty}} \tag{A.5}$$

where

$c_{\mathrm{Pn-1},\infty}$ is concentration of substance in layer n-1 of the organic material at equilibrium in mg/l;

$c_{\mathrm{Pn},\infty}$ is concentration of substance in layer n of the organic material at equilibrium in mg/l.

A partition coefficient between the last layer of the organic material and water is defined as:

$$K_{P,DW} = \frac{c_{P_n,\infty}}{c_{DW,\infty}} \tag{A.6}$$

where

$c_{\mathrm{Pn},\infty}$ is concentration of substance in the last layer of the organic material at equilibrium in mg/l;

$c_{\mathrm{W},\infty}$ is concentration of substance in water at equilibrium in mg/l.

A.5.2 Partition coefficients from literature and from experiment

In the literature only a very limited number of partition coefficients between organic materials and contact media is available. A selection of literature references can be found in Clause 4 of *Plastic Packaging…*, Piringer, Otto G., Baner, A. L. (Ed.) [12].

A.5.3 Partition coefficients from experiment

Partition coefficients between organic materials and contact media can be easily determined by bringing into contact a film of the organic material and a contact medium at a well-defined temperature. After establishment of the equilibrium the concentration of the substance in the organic material and in the contact medium is determined by an appropriate analytical method. The ratio of the two concentration gives the required partition coefficient [10].

A.5.4 Estimation of partition coefficients

A.5.4.1 Based on substance solubility in water

If the partition coefficient between the contact layer of the organic material and water is not available for a substance used in a given application, a worst-case partition coefficient, $K_{Pn,DW}$* can be estimated under the general assumption that the concentration of the substance in the water cannot exceed its water solubility. Water solubilities for substances can be obtained by use of the EPI Suite [8].

Due to the mass balance, which is fulfilled according to the boundary conditions in Clause 5, an upper-limit partition coefficient can be estimated from the known initial concentration of the substance in the organic material and the known water solubility of the substance. For a monolayer organic material the following relationship can be established based on the mass balance in the system:

$$K_{P,DW}{}^{*} = \frac{c_{P,0} \cdot \rho_P}{S_W} - \frac{V_{DW}}{V_P} \tag{A.7}$$

where

$c_{P,0}$ is initial concentration of the substance in the material;

ρ_P is specific gravity of the material;

S_W is solubility of the substance in water;

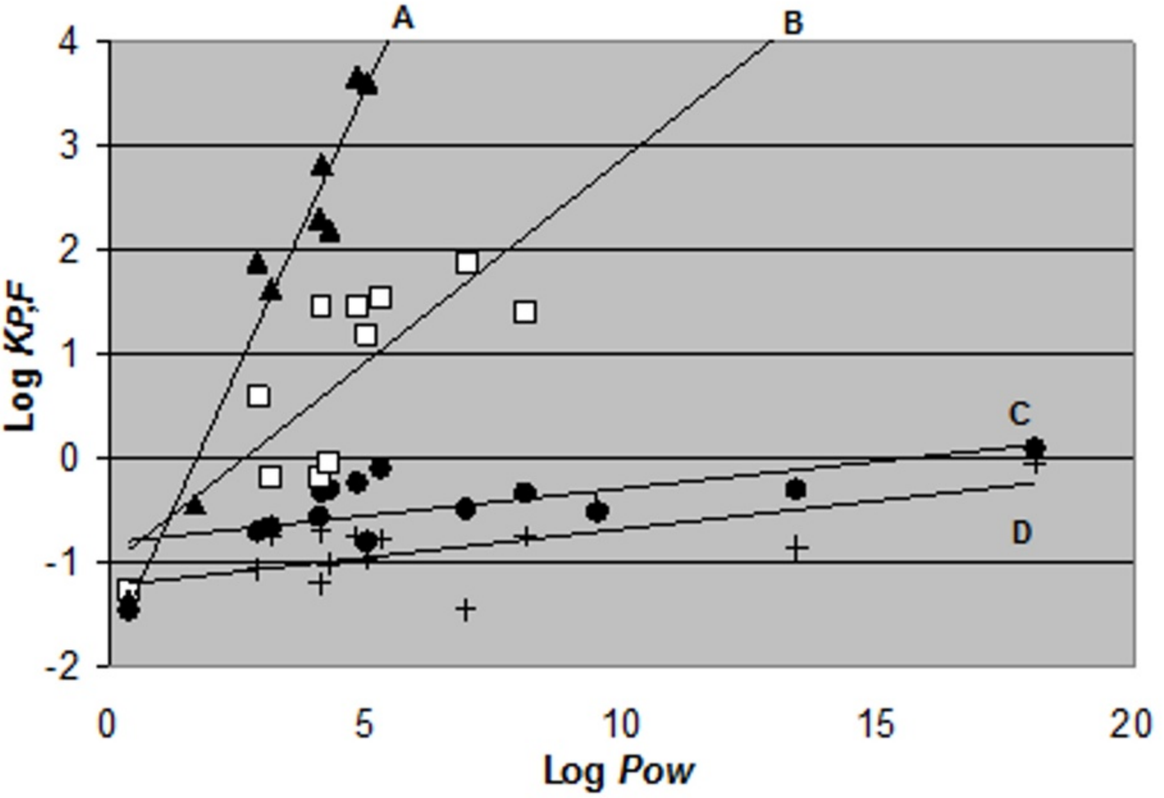
V_W is volume of the water in contact with the material;

V_P is volume of the contact layer of the organic material.

A more complex mathematical expression exists for multilayer organic materials.

A.5.4.2 From the octanol/water partition coefficient of the substance [9,10]

In recent work the partition coefficients $K_{P,F}$ of 15 substances between LDPE and several food simulants were determined. Moreover, the relationship between $K_{P,F}$ and the migrant's octanol-water partition coefficient log P_{OW} was examined as shown in Figure A.1.



Key

A (▲)	ethanol 10 %
B (□)	ethanol 50 %
C (●)	ethanol 95 %
D (+)	olive oil;
Log $K_{P,F}$	logarithm of the partition coefficient between polymer and food simulant
Log P_{OW}	logarithm of the octanol-water partition coefficient

Figure A.1 — Correlation between partition coefficients log $K_{P,F}$ of the substances between organic material (LDPE) and simulants and octanol-water partition coefficients log P_{OW} of the substance

The linear relationship for 10 % ethanol can be used to estimate the partition coefficient between polyolefines and drinking water based on the octanol-water partition coefficient of the substance due to the increased solubility of the substance in 10 % ethanol compared to drinking water. Due to the same polarity of all polyolefines (LDPE, LLDEP, HDPE and PP) the approach can be extrapolated from LDPE to all polyolefines.

A.5.5 Worst-case partition coefficients

If the water solubility of the substance is not known and provided typical volume-to-surface-area ratios encountered in practice are used, a worst-case partition coefficient of $K_{P,W}{}^* = 1$ is used. This selection assumes good solubility of the substance in drinking water and leads to the highest migration values, i.e. 99 % transfer of the substance from the organic material into water at equilibrium, For substances with low water solubility a worst-case partition coefficient of $K_{P,W}{}^* = 1\,000$ may be used, i.e. 50 % transfer of the substance from the organic material into water at equilibrium results.

Annex B
(informative)

Examples of the application of modelling to migration of substances from a material into drinking water

B.1 Introduction

The following examples illustrate the application of migration modelling in the field of assessment of effects of materials on drinking water quality.

B.2 Contact conditions

The water contact conditions are derived from EN 12873-1. However, for simplicity, the flushing and prewashing stages have been omitted.

B.3 Example calculations

B.3.1 General

In this paragraph two examples are given of the estimation of the migration of an additive under the requirements of Directive 2002/72/EC and the comparison with experimental data with assumptions for drinking water materials.

The examples involve a polyethylene pipe with the following characteristics:

- density = 0,95 g/cm³;
- material thickness = 5 mm;
- inner diameter of the pipe = 40 mm.

The used additive is a typical stabiliser PM-REF-No. 59120 with:

- molecular weight M = 637;
- SML-value = 45 mg/l (for food contact);
- $c_{P,0}$ = 100 ppm.

Other parameters are:

a) Contact medium: drinking water, with density = 1,0 g/cm³;

b) Condition of migration:

   1) 24 hours stagnation at T = 23 °C (pre-conditioning step);

   2) 72 hours stagnation at T = 23 °C (first test period);

3) 72 hours stagnation at T = 23 °C (second test period);

4) 72 hours stagnation at T = 23 °C (third test period).

B.3.2 Example 1, cold water test with the material constant in accordance to [7]

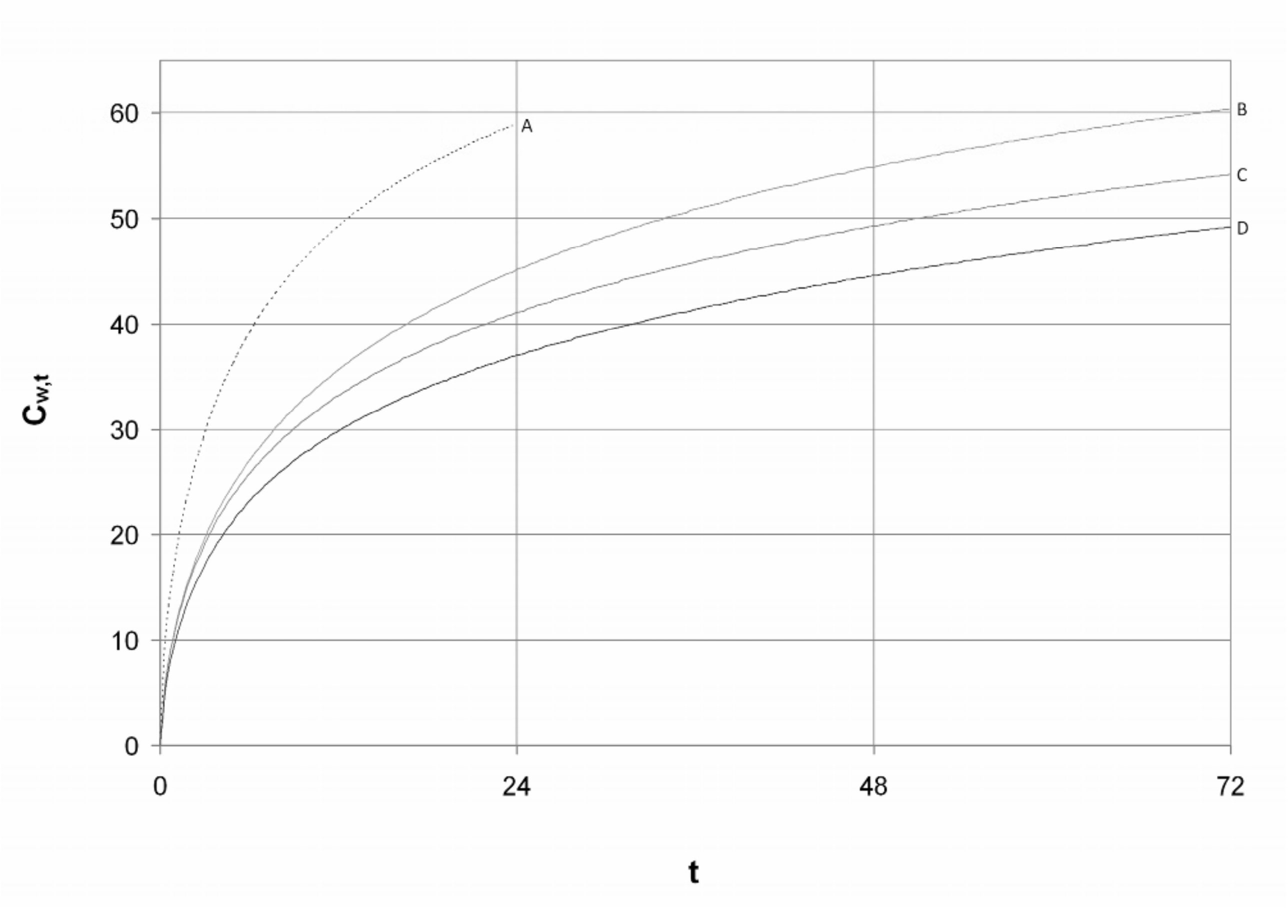
Diffusion coefficient:

$D_{polymer}$ ~ 1,8 × 10^{-11} cm²/s, (A'_p = 14,5 and τ = 1 577)

D_{water} ~ 1 × 10^{-4} cm²/s

Partition coefficient: $K_{p,w}$ = 1 000 (insoluble)

At the end of the third migration test period 99,8 % of the migrant remains in the polymer, see Figure B.1.



Key

A pre-conditioning step
B first test cycle
C second test cycle
D third test cycle
$c_{w,t}$ concentration of the substance in test water, $c_{w,t}$ (µg/l)
t time (hour)

Figure B.1 — Time dependent migration during pre-conditioning and three test cycles; $K_{P,W}$ = 1 000

B.3.3 Example 2 Cold water test with “realistic” material constants (experimentally measured)

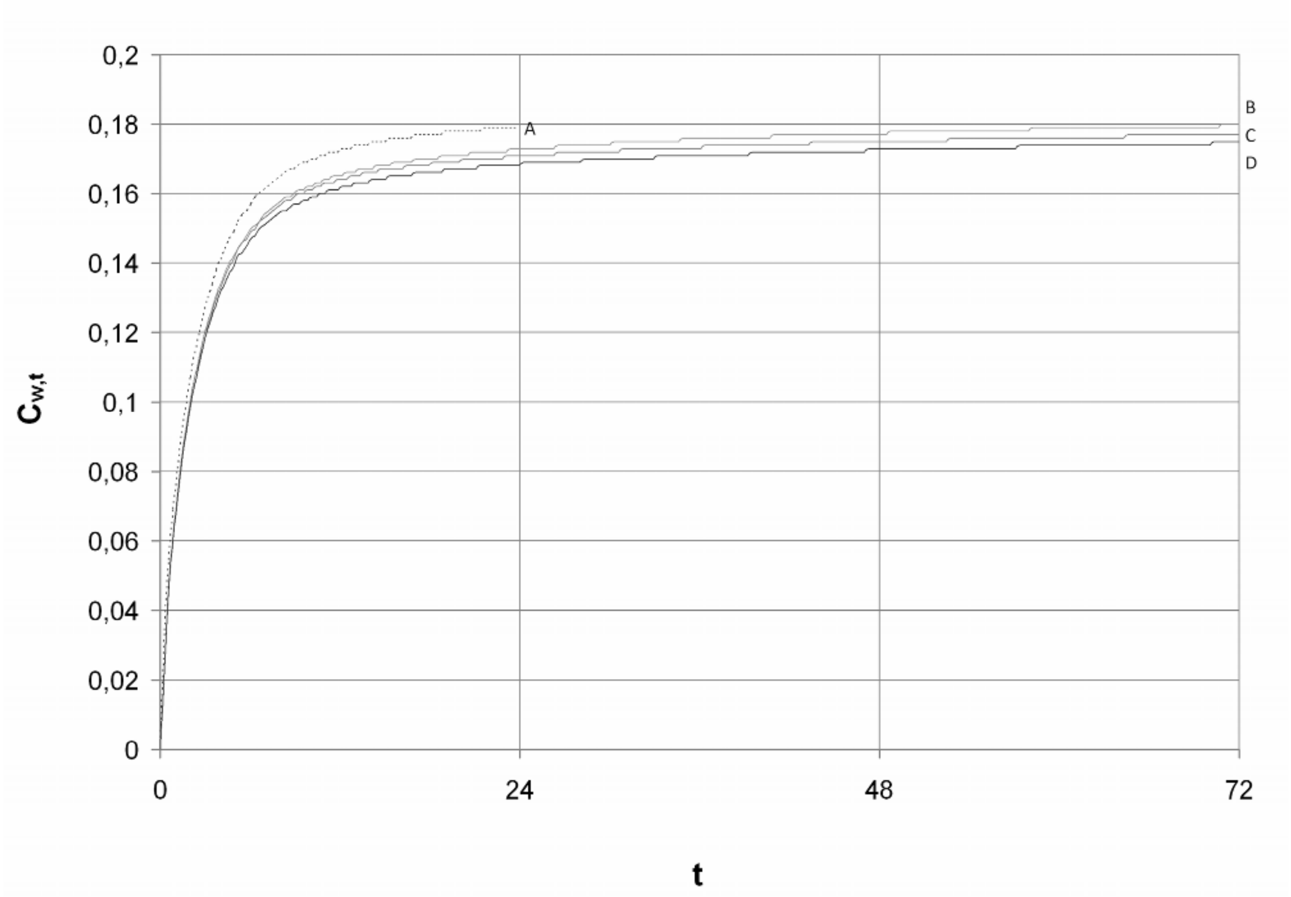
Diffusion coefficient:

$D_{polymer}$ ~ 5,6 × 10^{-15} cm²/s, (A'_p = 6,5 and τ = 1 600, estimated from experimental results)

D_{water} ~ 1 × 10^{-4} cm²/s

Partition coefficient: $K_{p,w}$ = 500 000 (not soluble, experimentally measured)

At the end of the third test period 99,998 % of the migrant remains in the polymer, see Figure B.2.



Key

A pre-conditioning step
B first test cycle
C second test cycle
D third test cycle
$c_{w,t}$ concentration of the substance in test water, $c_{w,t}$ (µg/l)
t time (hour)

Figure B.2 — Time dependent migration during pre-conditioning and three test cycles; $K_{P,W}$ = 1 000

Examples 1 and 2 were estimated with the software MIGRAPIPE © FABES 2008, which is based on a Finite Difference Elements (FDE) technique, to solve Equation (A.1) in cylindrical coordinates. Technical data of software: 500 discretisation mesh points, Crank-Nicolson factor 0,55 and each estimation step uses the migrant concentration profiles in the sample from the previous step.

Examples 1 and 2 demonstrate the strong influence of the $K_{P,W}$-value. $K_{P,F}$ = 1 000 for substances not soluble in water. This leads to a large over-estimation in Example 1. The value of $K_{P,W}$ = 500 000 (Example 2) is based on experimental data and, therefore, provides realistic time-dependent migration curves.

NOTE Realistic estimates of the input parameters (diffusion coefficient D_P and partition coefficient $K_{P,W}$) give results close to the real migration behaviour in the system (organic material in contact with drinking water). Realistic estimates of the input parameters bear the risk of underestimation compared to the worst-case values. On the other hand too high overestimates of the input parameters may overestimate the migration in the first test cycle and cause underestimation in later test cycles. If the migration into drinking water in the first test cycle exceeds 10 % of the initial amount of substance in the organic material a risk of underestimation in the last regarded cycle exists. In this case, for compliance evaluation with a drinking water migration limit, only the migration value modelled in the first test cycle can be used.

Worst-case values for input parameters D_P and $K_{P,W}$ according to Directive 2002/72/EC (food contact), i.e. D_P from A_P^*-value and $K_{P,F}$ = 1 for substances, soluble in water and $K_{P,W}$ = 1 000 for substances, not soluble in water work well in food contact applications but result in a dramatic overestimation of migration values, which may lead to non-compliance results when compared to the given drinking water migration limit. In drinking water applications this may cause limited applicability because many drinking water migration limits are in the ppb range.

Accordingly the overestimation regarding the $K_{P,W}$-value should be reduced. A more realistic estimation of the $K_{P,W}$-value is possible if the solubility of the substance in water and/or its octanol-water partition coefficient is known, either from the literature or from the producer of the substance. From a known water solubility and known concentration of the substance in the organic material, but still overestimated, a more realistic $K_{P,W}$-value can be estimated (see A.5.4).

Annex C
(informative)

Validation of the numerical algorithm and software tools

C.1 General

This annex deals with the criteria for assessing the correctness of calculation of migration by software tools.

The calculation of the migration from plane or cylindrical structures of monolayer- and multilayer organic materials in a contacting medium (e.g. drinking water) with a restricted volume can be carried with an analytical solution of the diffusion equation [24] (monolayer, only one test cycle) as well as with a numerical algorithm (mono- and multilayer, several test cycles).

Such methods take into account both the diffusion of the migrant into organic material as well as the partition coefficient at the interface with the water.

The calculation of the migration from plane or cylindrical structures of multilayer organic materials into contact media (drinking water) with a restricted volume can carried out only with numerical algorithm.

Such methods take into account both the diffusion coefficients of the migrant in each layer of the system and the partition coefficient at all interfaces i.e. between the layers of the organic materials and between the contact layer and the water.

The correctness of the migration calculation with numerical methods for plane or cylindrical test samples (articles or products) can be tested in accordance with the following criteria:

1) If the migration from a plane or cylindrical monolayer organic materials into drinking water is calculated with the analytical algorithm and with the numerical algorithm the relative maximal deviation between the numerical and the analytical results shall be less then 0,5 % or 1,00 % (if minimum 5 % of the initial amount of the migrant migrates from the organic material to water and if the discretisation is minimum 200 points/layer);

2) The mass balance in the system after calculations with the analytical and the numerical algorithm should not exceed a relative maximal deviation of 0,5 % or 1,00 %;

3) If assumed that in a plane or cylindrical multilayer organic material at the interface between the layers no distribution takes place (i.e. partition coefficient between all layers K = 1) the calculations with numerical algorithm may have a relative maximal deviation in the continuity of the concentration at the interfaces less then 0,5 % or 1,0 %;

4) If it is assumed that in a plane or cylindrical multilayer organic material at the interface between the layers distribution takes place then the calculations with numerical algorithm may have a relative maximal deviation in the continuity of the concentration at the interfaces less then 0,5 % or 1,0 % (if minimum 10 % of the total migration time is passed);

5) For the numerical algorithm the calculation of the mass balance during migration from plane or cylindrical test samples shall be possible every time in all layers of an organic material/drinking water system; the obtained results might deviate a maximal 0,5 % or 1,0 % of the starting value (if minimum 5 % of the total migration time is passed).

If the above mentioned criteria are fulfilled, it is ensured that a numerical method for the estimation of the migration from plane or cylindrical mono- or multilayer organic materials in contact with drinking water is correct.

The relative and absolute impreciseness of this kind of algorithm is, at a minimum, one order of magnitude lower than the impreciseness of the analytical methods that would be employed for the experimental determination of the migration.

C.2 Example A

A comparison of calculations with the analytical formula $C_{w,t}$(A) with calculation with the numerical methods $C_{w,t}$(N) in accordance with the first criteria for the migration from plane monolayer into a liquid medium was calculated with MIGRATEST$^{©}$Lite (analytic) and MIGRATEST$^{©}$EXP (numeric) and the results are shown in Figure C.1.

The small oscillations at short times are ascribed to the analytical solution because it is also no exact solution of the diffusion equation, it is from an expansion in series which contain transcendent equations. In view to the low percentage fluctuations this plays no role in practice.

- $C_{w,t}$(A) = time dependent concentration in water calculated with the analytical solution of the diffusion equation, i.e. software MIGRATEST$^{©}$Lite.

- $C_{w,t}$(N) = time dependent concentration in water calculated with the numerical solution of the diffusion equation, i.e. software MIGRATEST$^{©}$EXP.

The following parameters are used in the calculations:

- organic material: polymer with a thickness of the layer of 500 µm, a density of 1,0 g/cm³ and a surface of 6 dm² ;

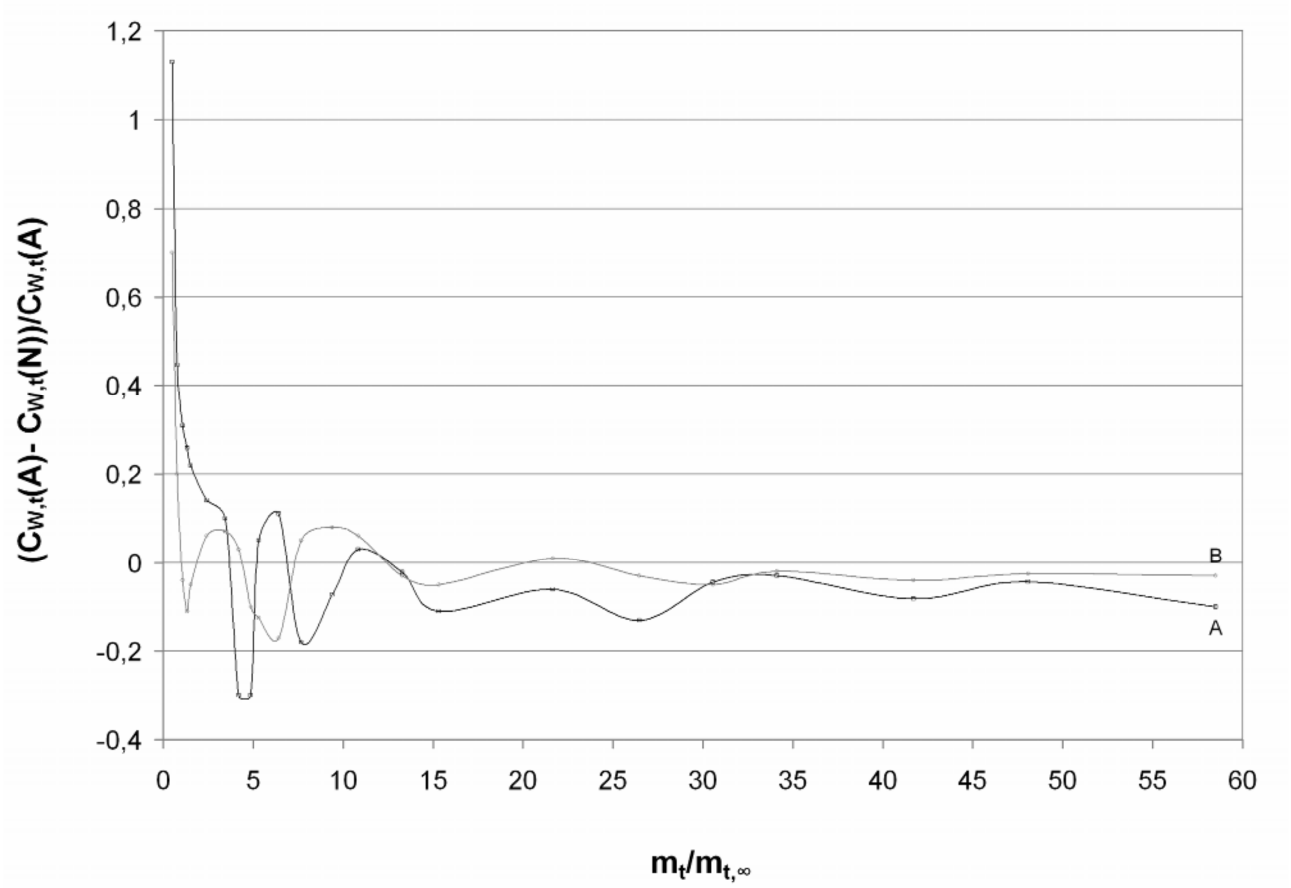
- drinking water: density = 1,0 g/cm³, volume = 1 000 cm³;

- migrant: organic substance with M_w = 300 g/mol, $c_{p,o}$ = 1 000 mg/kg;

- diffusion coefficient: $D_p = 5 \times 10^{-12}$ cm²/t, $D_W > 1 \times 10^{-4}$ cm²/s;

- partition coefficient: $K_{P,W}$ = 1, $K_{P,W}$ = 1 000;

- maximum migration time: t = 1 500 days.



Key

A $K_{P,W}$ = 1
B $K_{P,W}$ = 1 000
$m_t/m_{t,\infty}$ migration ratio (%)
$(C_{W,t}(A)- C_{W,t}(N))/C_{W,t}(A)$ relative difference (%)

Figure C.1 — Relative difference between the analytical (A) and numerical (N) estimation of migration from a plane sample. Software: MIGRATEST$^{©}$Lite for (A) and MIGRATEST$^{©}$EXP for (N)

C.3 Example B

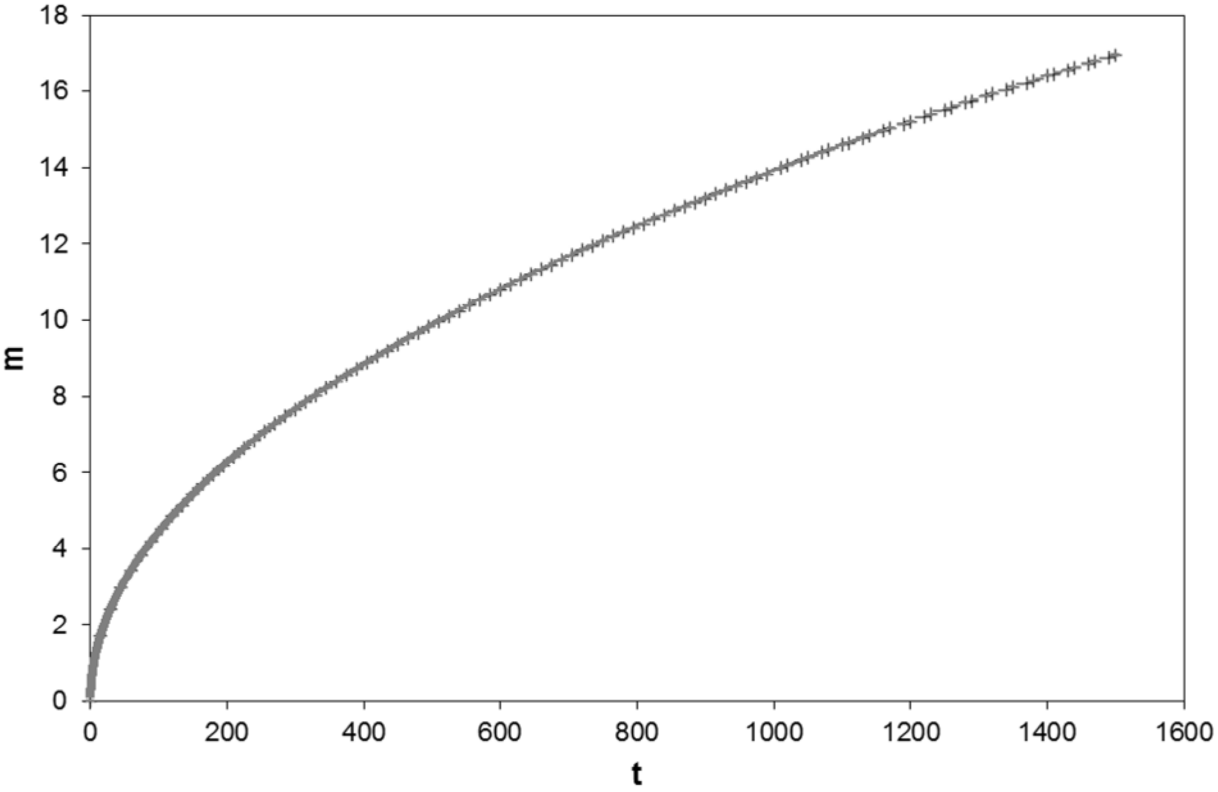
A comparison of calculations of concentrations with analytical formula $C_{w,t}(A)$ and with the numerical methods $C_{w,t}(N)$ in accordance to the first criteria for the migration from plane monolayer into a liquid medium was calculated with the Software SML 2.0 (analytic) and SML 4.3 (numeric) and the results are shown in figures.

The small oscillations are ascribed to the analytical solution because the version of the Software 2.0 (analytic) calculates only with a preciseness of two decimal places and therefore interpolation between was needed. In view to the low percentage fluctuations plays this plays practice no role.

The following parameters are used in the calculations:

- organic material: polymer with a thickness of the layer of 500 µm, a density of 1,0 g/cm³ and a surface of 6 dm² ;
- drinking water: density = 1,0 g/cm³, volume = 1 000 cm³;

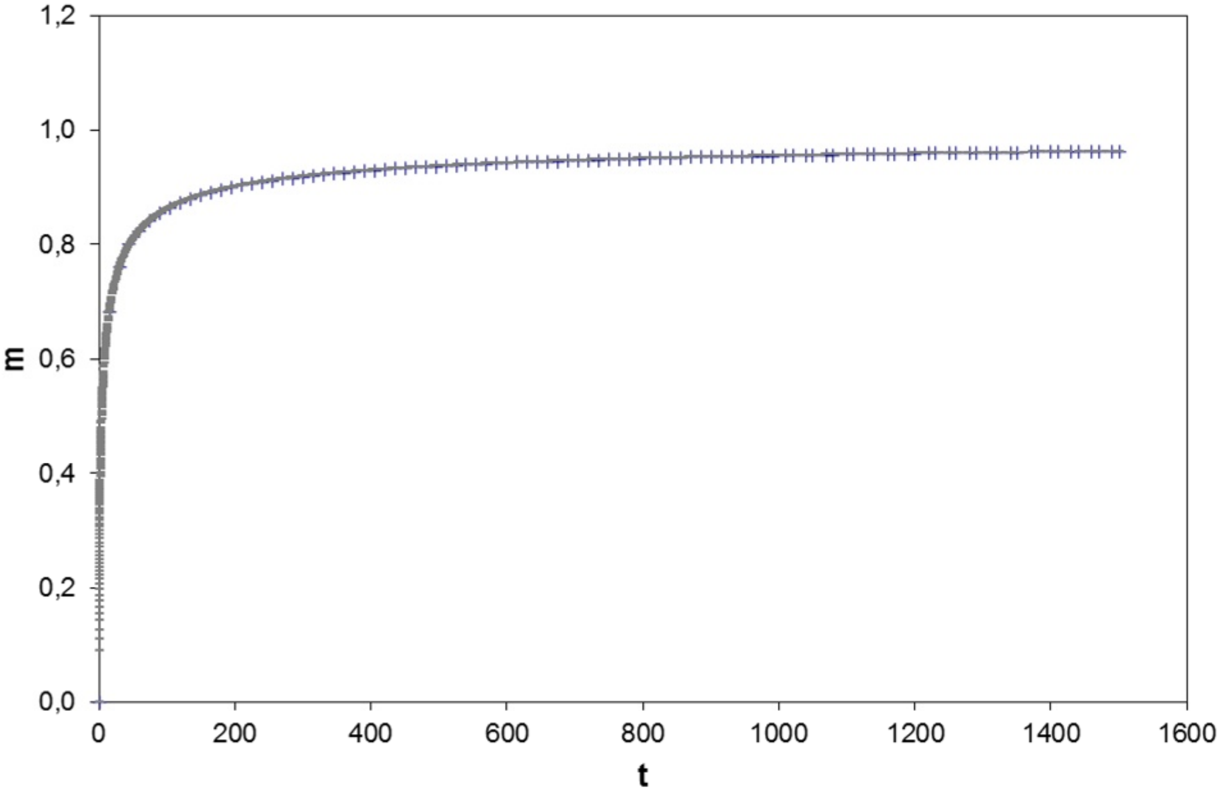
- migrant: organic substance with M_w = 300 g/mol, $c_{p,o}$ = 1 000 mg/kg;
- diffusion coefficient: $D_p = 5 \times 10^{-12}$ cm²/t, $D_W > 1 \times 10^{-4}$ cm²/s;
- partition coefficient: $K_{P,W}$ = 1, $K_{P,W}$ = 1 000;
- maximum migration time: t = 1 500 days



Key

+	analytical solution with software SML 2.0
-	nummerical solution with software SML 4.3
m	migration of the substance in test water (mg/kg)
t	time (days)

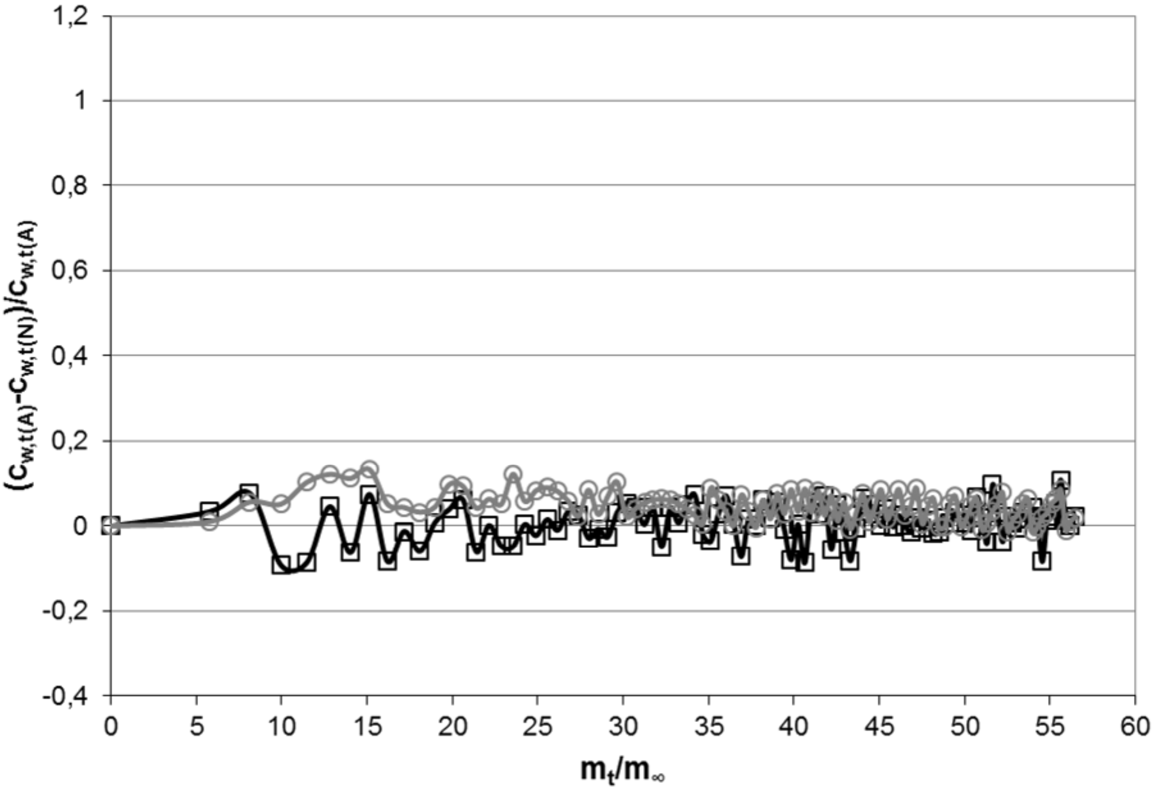
Figure C.2 — Time dependent migration during one test cycle; $K_{P,W}$ = 1; comparison between analytical and numerical solution of the diffusion equation



Key

+ analytical solution with software SML 2.0
- nummerical solution with software SML 4.3
m migration of the substance in test water (mg/kg)
t time (days)

Figure C.3 — Time dependent migration during one test cycle; $K_{P,W}$ = 1 000; comparison between analytical and numerical solution of the diffusion equation



Key

□ partition coefficient $K_{P,F}$ = 1
○ partition coefficient $K_{P,F}$ = 1 000
$m_t/m_{t,\infty}$ migration ratio (%)
$(C_{W,t(A)}- C_{W,t(N)})/C_{W,t(A)}$ relative difference (%)

Figure C.4 — Relative Differences: Comparison between time dependent migration calculations performed with the analytical solution [($c_{w,t}$(A)] - SML 2.0 and the numerical solution [($c_{w,t}$(N)] - SML 4.3 of the diffusion equation during one test cycle; $K_{P,W}$ = 1 and $K_{P,W}$ = 1 000

Bibliography

[1] EN 12873-1*, Influence of materials on water intended for human consumption — Influence due to migration — Part 1: Test method for non-metallic and non-cementitious factory made products*

[2] EN 12873-2, *Influence of materials on water intended for human consumption — Influence due to migration — Part 2: Test method for non-metallic and non-cementitious site-applied materials*

[3] COMMISSION DIRECTIVE 2002/72/EC of 6 August 2002 relating to plastic materials and articles intended to come into contact with foodstuffs

[4] T. Begley, L. Castle, A. Feigenbaum, R. Franz, K. Hinrichs, T. Lickley, P. Mercea, M. Milana, A. O'Brien, S. Rebre, R. Rijk, O. Piringer; Evaluation of migration models that might be used in support of regulations for food-contact plastics; *Food Additives and Contaminants*, January 2005; 22(1): 73-90

[5] JRC Scientific and technical Reports, 2008, "*Technical guidance document to determine diffusion coefficients of migrants to update the A_P value of a food contact plastic for migration evaluation by mathematical modelling*"

[6] Atkins, Peter W. / de Paula, Julio, "*Physical Chemistry*", 4th edition, 2006, Wiley-VCH, Weinheim

[7] Repealed from the EU-Commission: Practical Guide of the EU Commission in Annex 1, Mathematical Models,http://crl-fcm.jrc.it/resource_centre/legislative_documents.htm
In the future: C. Simoneau, ed., "*Estimation of specific migration by generally recognised diffusion models in support of EU Directive 2002/72/EC*", JRC Scientific and Technical Reports, 2008

[8] EPI Suite v3.20, U.S. Environmental Protection Agency

[9] Asako Ozaki1, Anita Gruner, Angela Störmer, Rainer Brandsch, Roland Franz, "*Correlation of partition coefficients KPolymer/Food and KOctanol/Water for potential migrants in food contact polymers*.", Poster at the ILSI Europe Conference, Prague, 2008, to be published

[10] Asako Ozaki, Anita Gruner, Angela Störmer, Rainer Brandsch, Roland Franz, "*Correlation between Partition Coefficient Factor and Log P_{OW} of 15 Migrants in LDPE*", to be published

[11] B. Roduit, C.H. Borgeat, S. Cavin, C. Fragniere, & V. Dudler, Application of Finite Element Analysis (FEA) for the simulation of release of additives from multilayer polymeric packaging structures, *Food Additives and Contaminants, October 2005*; 22(10): 945–955

[12] Piringer, Otto G. / Baner, A. L. (Ed.), *Plastic Packaging - Interactions with Food and Pharmaceuticals*, second edition, 2008, Wiley-VCH, Weinheim

[13] Mercea P. and Piringer O. Data bank to validate a mathematical model to estimate the migration of additives and monomers from polyolefins into foodstuffs and food simulants, EU-contract No. ETD/97/501370 (DG3), 1998

[14] EU Commission "*Technical guidance document to determine diffusion coefficients of substances to update the AP value of a food contact plastic for migration evaluation by mathematical modelling*", prepared by the JRC Task Force on migration modelling, (2005)

[15] Brandsch, J., Mercea, P., Rüter, M., Tosa, V., Piringer, O., Migration modelling as a tool for quality assurance of food packaging, Second International Symposium on Food Packaging, 8-10 November 2000, Vienna. *Food Additives and Contaminants, 19 (supplement), 29-41 (2002).*

[16] T. Begley, L. Castle, A. Feigenbaum, R. Franz, K. Hinrichs, T. Lickley, P. Mercea, M. Milana, A. O'Brien, S. Rebre, R. Rijk, O. Piringer; "Evaluation of migration models that might be used in support

of regulations for food-contact plastics."; *Food Additives and Contaminants, January 2005*; 22(1): 73-90

[17] EU-project G6RD-CT-2000-00411, "*Certified Reference Materials for the specific migration testing of plastics for food packaging needed by industry and enforcement laboratories. (Support to the development of)*", 2004

[18] N. H. Stoffers, A. Stormer, E. L. Bradley, R. Brandsch, I. Cooper, J. P. H. Linssenk and R. Franz, "Feasibility study for the development of certified reference materials for specific migration testing. part 1: initial migrant concentration and specific migration", *food Additives and Contaminants, Vol. 21, No. 12 (December 2004),* pp. 1203–1216

[19] N. H. Stoffers1, R. Brandsch, E. L. Bradley, I. Cooper4, M. Dekker, A. Stormer, & R. Franz, "*Feasibility study for the development of certified reference materials for specific migration testing. Part 2: Estimation of diffusion parameters and comparison of experimental and predicted data.*", Food Additives and Contaminants, February 2005; 22(2): 173–184

[20] O´Brien A., Goodson A., Cooper J., *Polymer additive migration to foods – a direct comparison of experimental data and values calculated from migration models for high density polyethylene (HDPE)*, Food Additives and Contaminants 16, 367-380 (1999)

[21] O´Brien A., Cooper J., Practical experience of the use of mathematical models to predict migration of additives, Second International Symposium on Food Packaging, 8-10 November 2000, Vienna. Food *Additives and Contaminants, 19 (supplement)*, 63-72 (2002)

[22] Industry project sponsored by TEPFFA, 2007

[23] German Environmental Protection Agenca, *Leitlinie zur mathematischen Abschätzung der Migration von Einzelstoffen aus organischen Materialien in das Trinkwasser (Modellierungsleitlinie)*, Umweltbundesamt" - UBA, 2008

[24] Crank, J., *Mathematics of Diffusion*, 2nd Edition, 1975, Clarendon Press, Oxford University Press

This page deliberately left blank

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

bsi.

...making excellence a habit.™