SLOVENSKI STANDARD
SIST ENV 1186-12:1997

01-januar-1997

Materiali in predmeti v stiku z živili - Plastične mase - 12. del: Preskusne metode za celotno migracijo pri nizkih temperaturah

Materials and articles in contact with foodstuffs - Plastics - Part 12: Test methods for overall migration at low temperatures

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Kunststoffe - Teil 12: Prüfverfahren für die Gesamtmigration bei tiefen Temperaturen

Matériaux et objets en contact avec les denrées alimentaires - Matiere plastique - Partie 12: Méthodes d'essai pour la migration globale a basses températures

Ta slovenski standard je istoveten z: **ENV 1186-12:1995**

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English version

Materials and articles in contact with foodstuffs - Plastics - Part 12: Test methods for overall migration at low temperatures

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CEN members are required to announce the existance of this ENV in the same way as for an EN and to make the ENV available promptly at national level in an appropriate form. It is permissible to keep conflicting national standards in force (in parallel to the ENV) until the final decision about the possible conversion of the ENV into an EN is reached.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Contents

Foreword

This European Prestandard has been prepared by the Technical Committee CEN/TC 194 "Utensils in contact with food", the secretariat of which is held by BSI.

Further Parts of this prestandard have been prepared, and others are in preparation, concerned with the determination of overall migration from plastics materials into food simulants.

Their titles are as follows:

ENV 1186-1 Guide to the selection of conditions and test methods for overall migration

ENV 1186-2 Test methods for overall migration into olive oil by total immersion

ENV 1186-3 Test methods for overall migration into aqueous food simulants by total immersion

ENV 1186-4 Test methods for overall migration into olive oil by cell

ENV 1186-5 Test methods for overall migration into aqueous food simulants by cell

ENV 1186-6 Test methods for overall migration into olive oil using a pouch

ENV 1186-7 Test methods for overall migration into aqueous food simulants using a pouch

ENV 1186-8 Test methods for overall migration into olive oil by article filling

ENV 1186-9 Test methods for overall migration into aqueous simulants by article filling

ENV 1186-10 Test methods for overall migration into olive oil (modified method for use in cases where incomplete extraction of olive oil occurs)

ENV 1186-11 Test methods for overall migration into mixtures of ^{14}C-labelled synthetic triglyceride

Further Parts in preparation are as follows:

ENV 1186-13 Test methods for overall migration at high temperatures

Annex A to this prestandard is normative where applicable.

ENV 1186-12 should be read in conjunction with ENV 1186-1. Since Part 1 of this prestandard was agreed by Subcommittee (SC1) of TC194 'Utensils in

According to the CEN/CENELEC Internal Regulations, the following countries are bound to implement this European Prestandard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

contact with food' Council Directive 82/711/EEC has been amended, thus table A.1 of ENV 1186-1:1994 has been superseded by table A.1 of this Part of 1186.

1 Scope

This Part of this European Prestandard describes test methods for the determination of the overall migration from plastics intended to come into contact with foodstuffs at low temperatures, i.e. for 0,5 h, 1 h, 2 h, 24 h and 10 days at 5 °C or at 20 °C.

These test methods are suitable for plastics samples in a wide variety of forms.

The fatty food simulant used in these methods is dewaxed sunflower oil since, unlike olive oil, it remains liquid at the lower test temperatures.

NOTE: The test methods described are applicable to most types of plastics, although there are some plastics for which the methods for overall migration into dewaxed sunflower oil are known not to be applicable, for example, owing to incomplete extraction of dewaxed sunflower oil; these are listed in Part 1 of this prestandard.

2 Normative references

This European Prestandard incorporates by dated and undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to and revisions of any of these publications apply to this European Prestandard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ISO 648:1977 Laboratory glassware - One mark pipettes

ISO 4788:1980 Laboratory glassware - Graduated measuring cylinders

ISO 8442:1988 Stainless steel and silver plated table cutlery [1)]

ENV 1186-1 Guide to the selection of conditions and test methods for overall migration

ENV 1186-2 Test methods for overall migration into olive oil by total immersion

ENV 1186-4 Test methods for overall migration into olive oil by cell

ENV 1186-6 Test methods for overall migration into olive oil using a pouch

ENV 1186-8 Test methods for overall migration into olive oil by article filling

1) A European Standard for stainless steel and silver plated cutlery is in the course of preparation.

ENV 1186-3 Test methods for overall migration into aqueous food simulants by total immersion

ENV 1186-5 Test methods for overall migration into aqueous food simulants by cell

ENV 1186-7 Test methods for overall migration into aqueous food simulants using a pouch

ENV 1186-9 Test methods for overall migration into aqueous simulants by article filling

prEN 10088 Stainless steels [2)]

2) In preparation.

3 Overall migration into dewaxed sunflower oil

3.1 Total immersion method

3.1.1 Principle

The overall migration from a sample of the plastics is determined as the loss in mass per unit of surface area intended to come into contact with foodstuffs.

The selection of the conditions of test will be determined by the conditions of use, see clause 3 of ENV 1186-1:1994.

Test specimens of known mass are immersed in dewaxed sunflower oil for 0,5 h, 1 h, 2 h, 24 h or 10 days at 5 °C or 20 °C then taken from the dewaxed sunflower oil, blotted to remove oil adhering to the surface and reweighed.

The specimens will usually retain absorbed dewaxed sunflower oil which is extracted and determined quantitatively by means of gas chromatography after conversion to methyl esters. Methylation is carried out by reacting a boron trifluoride/methanol complex with fatty acids formed by hydrolysing the oil with potassium hydroxide. An internal standard, triheptadecanoin, is added prior to the extraction of the absorbed dewaxed sunflower oil from the test specimens. This ensures that any active or extractable components of the plastics react with the internal standard, as well as with the extracted dewaxed sunflower oil. The internal standard is also subjected to the hydrolysis and methylation reactions, providing compensation for any inefficiencies in the hydrolysis and methylation processes.

Migration into the dewaxed sunflower oil is calculated by subtracting the mass of dewaxed sunflower oil retained by the test specimen from the mass of the test specimen after removal from the dewaxed sunflower oil, and then subtracting this mass from the initial mass of the specimen.

The total loss in mass is expressed in milligrams per square decimetre of surface area of the specimen and the overall migration is reported as the mean of a minimum of three determinations on separate test specimens.

To allow for inaccuracies which may arise during the procedure and which may be difficult to detect, due for example to contamination or loss of oil during the sample handling stages, quadruplicate determinations are carried out on the sample allowing for the result from one specimen to be discarded.

This method includes variations which are applicable to certain plastics and to experienced laboratories.

3.1.2 Reagents

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

3.1.2.1 Dewaxed sunflower, Simulant D as specified in 4.2. of ENV 1186-1:1994.

3.1.2.2 Extraction solvent (see 7.1 of ENV 1186-1:1994).

3.1.2.2.1 Pentane 98 % (mixed isomers) boiling point 36 °C.

NOTE 1: Pentane is a very volatile and highly flammable solvent. Care should therefore be taken when handling this solvent to prevent contact with sources of ignition. It is not recommended that extractions with this solvent be left unattended, particularly overnight.

NOTE 2: Due to the low boiling point of this solvent, cooled condenser water may be required to prevent undue loss of the solvent from the condenser.

or

3.1.2.2.2 Other suitable solvent.

NOTE 1: In previous methods for determining overall migration into dewaxed sunflower oil the extraction solvent used has been 1,1,2 trichloro trifluoroethane. For environmental reasons the use of this solvent should be avoided where possible, see 7.1 of ENV 1186-1:1994. Experience has shown that this solvent although effective for most plastics requires longer periods of extraction.

NOTE 2: Some solvents may contain non-volatile substances which, after hydrolysis and methylation processes, produce gas chromatography peaks with retention times similar to the retention times of dewaxed sunflower oil methyl esters and methyl heptadecanoate from the internal standard. Solvents found to contain such substances should be redistilled before use.

3.1.2.3 Internal standard, triheptadecanoin (glyceryl trimargarate) CAS No. 2438-40-6 *) of a quality such that the products from hydrolysis and methylation processes do not contain substances giving detectable gas chromatography peaks (see 7.3 of ENV 1186-1:1994) with similar retention times to the dewaxed sunflower oil methyl ester peaks Prepared as a solution containing 2,0 mg/ml in n-heptane.

3.1.2.4 Potassium hydroxide solution, 11,0 g/l in methanol.

3.1.2.5 Boron trifluoride, methanol complex, approximately 150 g/l BF_3.

3.1.2.6 n-Heptane.

3.1.2.7 Sodium sulphate.

3.1.2.8 Sodium sulphate, anhydrous, Na_2SO_4

3.1.2.9 Sodium sulphate, saturated solution.

3.1.3 Apparatus

3.1.3.1 Cutting slab, clean smooth glass, metal or plastics slab of sufficient area to prepare test specimens, 250 mm x 250 mm is suitable.

*) The source of this is the Chemical Abstracts published by the American Chemical Society

3.1.3.2 Tweezers, stainless steel, blunt nosed.

3.1.3.3 Cutting implement, scalpel, scissors, sharp knife or other suitable device.

3.1.3.4 Metal templates 100 mm ± 0,2 mm x 100 mm ± 0,2 mm (square).

3.1.3.5 Rule, 25 mm ± 1 mm wide.

3.1.3.6 Rule, graduated in mm, and with an accuracy of 0,1 mm.

3.1.3.7 Analytical balance capable of determining a change in mass of 0,1 mg.

3.1.3.8 Specimen supports, constructed of stainless steel with cross arms attached by welding or silver soldering. Stainless steel X4 CrNi 18 10 according to prEN 10 088 or of composition, chromium 17 %, nickel 9 %, carbon 0,04 %, is suitable. Before initial use thoroughly clean the steel supports. The use of a degreasing solvent and then dilute nitric acid has been found to be suitable.

NOTE: The method has been written for the supports shown in figure B1 of ENV 1186-1:1994 which have been found to be suitable for holding thin film and sheet test pieces. However other supports may be used providing they are capable of holding and keeping the test pieces apart and at the same time ensuring complete contact with the simulant. For rigid samples, supports with a single cross arm may be used.

3.1.3.9 Gauze, pieces of fine stainless steel gauze, with a mesh size of 1 mm have been found to be suitable, approximately 25 mm x 100 mm for insertion between the test pieces on the supports. Before initial use thoroughly clean the gauze, first with a degreasing solvent and then with dilute nitric acid.

3.1.3.10 Conditioning containers, for conditioning test specimens at 50 % ± 5 % relative humidity and 80 % ± 5 % relative humidity at 20 °C ± 3 °C.

NOTE: For 50 % relative humidity, 43 % w/v sulphuric acid solution in water is suitable and for 80 % relative humidity, 27 % w/v sulphuric acid solution is suitable. The solutions should be freshly prepared by adding a weighed amount of acid to a suitable volume of water, cooling to room temperature and making up to the required volume.

3.1.3.11 Glass tubes, ground neck and stoppers, for retaining the dewaxed sunflower oil and test specimens. Tubes with an internal diameter of approximately 35 mm and length in the range of 100 mm to 200 mm, excluding the ground neck (see 5.2 of ENV 1186-1:1994) have been found to be satisfactory.

3.1.3.12 Thermostatically controlled incubator or refrigerator capable of maintaining a temperature of 5 °C ± 1 °C and 20 °C ± 2 °C.

3.1.3.13 Filter paper, lint-free.

3.1 3.14 Anti-bumping beads.

3.1.3.15 Soxhlet type extractors, capable of holding test specimens on the supports, with 250 ml or 500 ml round bottom flasks to fit.

NOTE: Alternative extractors capable of satisfactorily extracting absorbed dewaxed sunflower oil from the test specimens may be used.

3.1.3.16 Water bath, capable of holding the flasks of soxhlet type extractors (3.1.3.15).

3.1.3.17 Rotary evaporator or distillation apparatus, for evaporation and collection of the extraction solvent.

NOTE: Artificially cooled water may be necessary for efficient condensation of a low boiling point solvent.

3.1.3.18 Steam bath or hot plate.

3.1.3.19 Flasks, 50 ml, long neck with condensers to fit, for methyl ester preparations.

3.1.3.20 Measuring cylinders, complying with the minimum requirements of ISO 4788, 500 ml, 250 ml, 100 ml, 25 ml, and 10 ml. A 10 ml graduated syringe may be used in place of the 10 ml measuring cylinder.

3.1.3.21 Pipettes, complying with the minimum requirements of ISO 648, 5 ml and 10 ml.

3.1.3.22 Glass beads, 2 mm to 3 mm in diameter or glass rods, 2 mm to 3 mm in diameter and approximately 100 mm long (see 5.2 of ENV 1186-1:1994).

3.1.3.23 Gas chromatograph, with flame ionisation detector equipped with an appropriate column capable of giving baseline resolution of the C_{17} methyl ester internal standard (methyl heptadecenoate) from C_{18} methyl 9-octadecenoate (methyl oleate) and the C_{16} methyl hexadecenoate (methyl palmitate) components derived from dewaxed sunflower oil.

NOTE: The following arrangements have been found to be suitable:

- Column 1, WCOT fused silica column, length 50 m, internal diameter 0,25 mm, coated with a 0,21 micrometre film of cyanopropyl silicone;

- Column 2, fused silica capillary column, length 12 m, internal diameter 0,32 mm, liquid phase dimethyl siloxane;

- Column 3, stainless steel column 2 mm to 3 mm internal diameter and 2 m to 3 m length with a packing of 10 % to 20 % by weight of polyestersuccinate on a stationary phase of diatomaceous earth 80 mesh to 100 mesh.

3.1.3.24 Glass tubes with ground glass necks and stoppers, of a volume of approximately 10 ml, for storing the heptane layer if necessary.

3.1.3.25 Vacuum oven or vacuum desiccator

3.1.3.26 Desiccator containing self indicating silica gel or anhydrous calcium chloride

3.1.4 Preparation of test specimens

Prepare the test specimens in accordance with ENV 1186-2.

3.1.5 Procedure

3.1.5.1 Initial weighing of test specimens

Perform the initial weighing in accordance with ENV 1186-2.

3.1.5.2 Exposure to food simulant

Take five of the glass tubes, mark them for identification purposes. Measure 100 ml ± 5 ml of dewaxed sunflower oil into each tube by measuring cylinder and stopper the tube. Alternatively mark the tubes for a volume of 100 ml and fill with dewaxed sunflower oil to the mark.

Place into four of the tubes containing dewaxed sunflower oil, weighed test specimens prepared as in 3.1.5 and conditioned if necessary. Stopper the tubes. Ensure that the test specimens are totally immersed in dewaxed dewaxed sunflower oil; if they are not, then add either glass beads or glass rods to raise the level of the dewaxed sunflower oil until total immersion is achieved.

NOTE 1: The dewaxed sunflower oil in the fifth tube is used as a reference standard in constructing the calibration graph.

Place the remaining two test specimens into the empty tubes and stopper.

NOTE 2: These two test specimens are used to check whether the sample loses mass from the evaporation of volatiles, such as solvents, during the test period.

Place the five tubes, and two empty tubes, in the thermostatically controlled incubator or refrigerator, set at the required test temperature, and leave until the test temperature has been attained.

Place all seven tubes in the thermostatically controlled incubator or refrigerator with the thermostat set to the required test temperature.

Observe the temperature of the thermostatically controlled incubator or refrigerator and leave the tubes for a period of $30\ ^{+1}_{0}$ min, $60\ ^{+2}_{0}$ min, $120\ ^{+5}_{0}$ min, $24\ ^{+0,5}_{0}$ h or $240\ ^{+5}_{0}$ h, after the air bath of the thermostatically controlled incubator or refrigerator has reached a temperature within the permitted tolerance for the test temperature.

Take the tubes from the incubator or refrigerator and immediately remove the

test specimens from the tubes. For those specimens which have been in sunflower oil, allow the oil to drain. Remove any adhering dewaxed sunflower oil by gently pressing between filter papers. Repeat the pressing procedure until the filter paper shows no spots of dewaxed sunflower oil. For test specimens on supports, remove the individual test pieces from the supports to carry out this operation. Clean the supports of oil by washing with the extraction solvent and replace the test pieces on them.

3.1.5.3 Final weighing of test specimens

Perform the final weighing of the test specimens in accordance with ENV 1186-2.

3.1.5.4 Extraction of absorbed dewaxed sunflower oil

Extract the absorbed sunflower oil in accordance with ENV 1186-2.

3.1.5.5 Determination of extracted dewaxed sunflower oil

Determine the extracted dewaxed sunflower oil in accordance with ENV 1186-2.

3.1.6 Expression of results

3.1.6.1 Method of calculation

Calculate the results in accordance with ENV 1186-2.

3.1.6.2 Precision

NOTE: The repeatability (r) and the reproducibility (R) values are being determined from collaborative trials results.

3.1.7 Test report

Where the plastics is intended for use in contact with fatty foods for which reduction factors are permitted then these factors shall be taken into account when reporting the results (see 9.2 of ENV 1186-1:1994).

The test report shall include the following:

a) reference to this European Prestandard and to the Part used for the test procedure;

b) all information necessary for complete identification of the sample such as chemical type, supplier, trade mark, grade, batch number(s), thickness;

c) conditions of time and temperature of exposure to simulants;

d) departures from the specified procedure and reasons for these;

e) individual test results and the mean of these expressed as

milligrams lost per square decimetre of sample;

f) any adjustment made for loss of volatile substances from the test specimens;

g) relevant comments on the test results.