SLOVENSKI STANDARD
SIST ENV 1186-11:1997

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Materiali in predmeti v stiku z živili - Plastične mase - 11. del: Preskusne metode za celotno migracijo v zmes sintetičnih trigliceridov, označenih s 14C

Materials and articles in contact with foodstuffs - Plastics - Part 11: Test methods for overall migration into mixtures of 14C-labelled synthetic triglycerides

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Kunststoffe - Teil 11: Prüfverfahren für die Gesamtmigration in Mischungen aus 14C-markierten synthetischen Triglyceriden

Matériaux et objets en contact avec les denrées alimentaires - Matiere plastique - Partie 11: Méthodes d'essai pour la migration globale dans des mélanges de triglycérides synthétiques marqués au C14

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Materials and articles in contact with foodstuffs - Plastics - Part 11: Test methods for overall migration into mixtures of ^{14}C-labelled synthetic triglycerides

Matériaux et objets en contact avec les denrées alimentaires - Matière plastique - Partie 11: Méthodes d'essai pour la migration globale dans des mélanges de triglycérides synthétiques marqués au C^{14}

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Kunststoffe - Teil 11: Prüfverfahren der Gesamtmigration in Olivenöl durch völliges Eintauchen

This European Prestandard (ENV) was approved by CEN on 1993-09-23 as a prospective standard for provisional application. The period of validity of this ENV is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the ENV can be converted into an European Standard (EN).

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 1186-12 Test methods for overall migration at low temperatures

Further Parts in preparation are as follows:

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

Annexes A and B to this prestandard are normative where applicable.

ENV 1186-11 should be read in conjunction with ENV 1186-1.

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.

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 a fatty foodstuff, by total immersion in a ^{14}C-labelled mixture of synthetic triglycerides for 10 days, 24 h or 2 h at 40 °C or for 2 h at 70 °C.

The test methods described are applicable to all plastics.

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

prEN 10088 Stainless steels [2)]

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

2) In preparation.

3 Method 11A Total immersion

WARNING: The use and disposal of ^{14}C labelled substances are subject to regulations which vary from country to country. Laboratories should ensure that they comply with local legislation requirements.

NOTE: This method is most suitable for plastics in the form of films and sheets, but can be applied to a wide range of articles or containers from which test pieces of a suitable size can be cut.

3.1 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 a ^{14}C-labelled mixture of synthetic triglycerides for 10 days, 24 h or 2 h at 40 °C or for 2 h at 70 °C then taken from the ^{14}C-labelled mixture of synthetic triglycerides, blotted to remove triglycerides adhering to the surface and reweighed.

The specimens will usually retain absorbed ^{14}C-labelled mixture of synthetic triglycerides which is extracted and determined quantitatively by means of liquid scintillation counting.

For some plastics the soxhlet extraction process does not achieve complete recovery of the absorbed ^{14}C-labelled mixture of synthetic triglycerides. In this method the ^{14}C-labelled mixture of synthetic triglycerides that remains after soxhlet extraction is released by dissolution or combustion. The combustion method is suitable for all plastics, the dissolution method is only suitable for polymers that are soluble in a suitable solvent, e.g. tetrahydrofuran.

Migration into the ^{14}C-labelled mixture of synthetic triglycerides is calculated by subtracting the mass of ^{14}C-labelled mixture of synthetic triglycerides retained by the test specimen from the mass of the test specimen after removal from the ^{14}C-labelled mixture of synthetic triglycerides, 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 ^{14}C-labelled mixture of synthetic triglycerides 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.

3.2 Reagents

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

3.2.1 ^{14}C-labelled mixture of synthetic triglycerides, simulant D as specified in 4.2 of ENV 1186-1:1994.

NOTE: Details of suppliers may be obtained from CEN.

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

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

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

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

or

3.2.2.2 Other suitable solvent.

NOTE: In previous methods for determining overall migration in ^{14}C-labelled mixture of synthetic triglycerides 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.

3.2.3 Liquid scintillation cocktail, suitable for scintillation counting of ^{14}C-labelled mixture of synthetic triglycerides and in which the fat simulant is soluble.

3.3 Apparatus

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

3.3.2 Tweezers, stainless steel, blunt nosed.

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

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

3.3.5 Rule, 25 mm ± 1 mm wide.

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

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

3.3.8 Specimen supports, constructed of stainless steel with cross arms attached by welding or silver soldering. Stainless steel X4 CrNi 18 10 according to prENV 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: For rigid samples, supports with a single cross arm may be used.

3.3.9 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.

3.3.10 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 are suitable. The solutions should be freshly prepared by adding the weighed amount of acid to a suitable volume of water, cooling to room temperature and making up to the required volume.

3.3.11 Glass tubes, ground neck and stoppers, for retaining the ^{14}C-labelled mixture of synthetic triglycerides and test specimens. Tubes with an internal diameter of approximately 35 mm and length in the range of 120 mm to 200 mm, with a volume of not less than 120 ml, excluding the ground neck (see 5.2 of ENV 1186-1:1994), have been found to be satisfactory.

3.3.12 Thermostatically controlled oven or incubator capable of maintaining a temperature of 40 °C ± 1 °C and 70 °C ± 2 °C.

3.3.13 Filter paper, lint-free.

3.3.14 Anti-bumping beads.

3.3.15 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 ^{14}C-labelled mixture of synthetic triglycerides from the test specimens may be used.

3.3.16 Water bath capable of holding the flasks of soxhlet type extractors (3.3.15).

3.3.17 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.

3.3.18 Steam bath or hot plate

3.3.19 Measuring cylinders complying with the minimum requirement of ISO 4788, 500 ml, 250 ml and 100 ml

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

3.3.21 Liquid scintillation counter with integrated quench correction

3.3.22 Liquid scintillation vials to fit into the liquid scintillation counter (3.3.21)

3.3.23 Vacuum oven or vacuum desiccator

3.3.24 Desiccator containing self indicating silica gel or anhydrous calcium chloride

3.3.25 Device for combustion of ^{14}C-labelled materials for subsequent determination of radioactivity, e.g. Schöninger flask or automatic sample oxidizer.

3.4 Preparation of test specimens

3.4.1 General

It is essential that test specimens are clean and free from surface contamination (many plastics can readily attract dust due to static charges). Before preparing test specimens, remove any surface contamination from the sample by gently wiping it with a lint-free cloth, or by brushing with a soft brush. Under no circumstances wash the sample with water or solvent. If it is specified in the instructions for use of the article that it should be washed or cleaned before use see 6.1 of ENV 1186-1:1994. Minimize handling of the samples and, where necessary, wear cotton gloves.

To ensure that test pieces are well separated and that their surfaces are freely exposed to the ^{14}C-labelled mixture of synthetic triglycerides during the period of the test, for thin films insert a piece of fine stainless steel gauze (3.3.9) between the test pieces or for thick samples not placed on the supports, insert glass rods between the test pieces after immersion in the ^{14}C-labelled mixture of synthetic triglycerides. Where specimen supports are used, label the supports with a tag bearing the test specimen identification.

3.4.2 Number of test specimens

Six test specimens are required for samples, in the form of thin films, sheet, containers or similar articles. Eight test specimens, similar

dimensionally one to another, are required for samples of articles of irregular shape.

These test specimens are utilized as follows:

a) four test specimens for the migration test;

b) two test specimens to check for possible loss of volatiles;

c) two test specimens for determination of the surface area, in the case of samples of irregular shape (see 3.4.5).

The number of test specimens can be reduced if it is known that the loss of volatiles from test specimens during the test is less than 2 mg per test specimen.

A minimum of three valid test results is required to calculate the mean. Testing in triplicate is allowed but in this case if one test result is invalid the entire procedure has to be repeated.

3.4.3 Thin films and sheet materials

Lay the sample on the cutting slab (3.3.1) and cut the test specimens each 1 dm^2 (see 6.3 of ENV 1186-1:1994), using the 100 mm x 100 mm template (3.3.4). Check, using the rule (3.3.5), that the dimensions of the test specimen are within the specified deviation (± 1 mm).

Cut each test specimen into four test pieces 25 mm x 100 mm using the rule (3.3.5). Assemble one test specimen onto the support by piercing suitable holes in the test pieces and placing two test pieces on each side of the cross arms of the support. Repeat this procedure for all remaining test specimens.

3.4.4 Containers and other articles

Cut sections from the walls of the container or article to give test specimens each of area approximately 1 dm^2. For articles with individual areas less than 1 dm^2, use a number of articles to provide each test specimen. Measure the dimensions of each test specimen to the nearest 1 mm, using the rule. Measure only the surface area of the sample which is intended to come into contact with foodstuffs, i.e. cut edges and any surfaces not intended to come into contact with foodstuffs are ignored (see 6.3 of ENV 1186-1:1994). Calculate the area of each test specimen to the nearest 0,01 dm^2 and record. If necessary, cut each test specimen into smaller pieces to enable them to fit into the glass tubes (3.3.11). The test specimens or pieces are placed on the specimen supports if these are appropriate or, if the test specimens or pieces are sufficiently rigid, they can be tested unsupported.

3.4.5 Articles of irregular shape

Select representative portions of the article, or multiples of the article for small articles, to give nine dimensionally similar test specimens each with a surface area of approximately 2 dm^2. Measure the surface area of two

of these test specimens to the nearest 0,05 dm^2 using the Schlegel Method (see Annex B of ISO 8442:1988), or any other suitable method. Measure only the surface area of the sample which is intended to come into contact with foodstuffs, i.e. cut edges and any surfaces not intended to come into contact with foodstuffs are ignored, (see 6.3 of ENV 1186-1:1994). Record the surface area of each test specimen.

3.5 Procedure

3.5.1 General

Before weighing, discharge any build up of static electricity with an antistatic gun or other suitable means.

3.5.2 Initial weighing of test specimens

3.5.2.1 Determine the need for conditioning of the test specimens by carrying out the procedure described in annex A. If prior tests have established that sample conditioning is not required then annex A may be omitted. If prior tests have established that the conditioning procedure described in annex B is applicable to the sample then annex A may be omitted.

3.5.2.2 If the tests described in annex A show that conditioning is not necessary, determine and record the mass of each test specimen.

3.5.2.3 If the tests described in annex A show that conditioning is necessary, replace the test specimens in the container maintained at 50 % relative humidity weigh at intervals of about 24 h, until the change in mass between consecutive weighings of each test specimen is less than 2 mg and record the eventual mass of each test specimen.

3.5.2.4 If the tests described in annex A show that conditioning is necessary, but constant weight cannot be achieved within 5 days then carry out the conditioning procedure described in B.2.1.

NOTE 1: Long conditioning periods are not suitable as oxidation of the ^{14}C-labelled mixture of synthetic triglycerides may occur upon prolonged conditioning.

NOTE 2: The conditioning procedure described in annex B may be used if it has been established that the polymer type under test gives rise to conditioning difficulties when using the procedure described in annex A.

3.5.3 Exposure to food simulant

Take four of the glass tubes (3.3.11), mark them for identification purposes. Measure 100 ml ± 5 ml of ^{14}C-labelled mixture of synthetic triglycerides into each tube by measuring cylinder and stopper the tube. Alternatively mark the tubes for a volume of 100 ml and fill with ^{14}C-labelled mixture of synthetic triglycerides to the mark. Place the four tubes, and two empty tubes, in the thermostatically controlled oven or incubator (3.3.12) set at the test temperature (40 °C or 70 °C) and leave until the test temperature has been

attained. Place into the four tubes containing ^{14}C-labelled mixture of synthetic triglycerides, weighed test specimens prepared as in 6 and conditioned if necessary. Stopper the tubes. Ensure that the test specimens are totally immersed in ^{14}C-labelled mixture of synthetic triglycerides; if they are not, then add either glass beads or glass rods (3.3.20) to raise the level of the ^{14}C-labelled mixture of synthetic triglycerides until total immersion is achieved.

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

NOTE 1: 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.

NOTE 2: Experience has shown that it is not necessary to check the contribution of extracts from the test specimens not exposed to the fat simulant to the level of radioactivity in liquid scintillation counting.

Replace all six tubes in the thermostatically controlled oven or incubator set at the test temperature. This part of the operation should be carried out in the minimum time to prevent undue heat loss. Observe the temperature of the thermostatically controlled oven or incubator and leave the tubes for a test period of 240^{+5}_{0} h, or $24^{+0,5}_{0}$ h or 120^{+5}_{0} min, after the airbath of the thermostatically controlled oven or incubator has reached a temperature within 1 °C of the set temperature.

Take the tubes from the oven or incubator and immediately remove the test specimens from the tubes. For those specimens which have been in ^{14}C-labelled mixture of synthetic triglycerides, allow the ^{14}C-labelled mixture of synthetic triglycerides to drain. Remove any adhering ^{14}C-labelled mixture of synthetic triglycerides by gently pressing between filter papers (3.3.13). Repeat the pressing procedure until the filter paper shows no spots of ^{14}C-labelled mixture of synthetic triglycerides. For test specimens on supports, remove the individual test pieces from the supports to carry out this operation. Clean the supports of ^{14}C-labelled mixture of synthetic triglycerides by washing with the extraction solvent and replace the test pieces on them.

3.5.4 Final weighing of test specimens

3.5.4.1 For those specimens which did not require conditioning to obtain their initial masses (see 3.5.2.2), weigh all six test specimens i.e. the four that have been in ^{14}C-labelled mixture of synthetic triglycerides and the two that were in the empty tubes and record the mass of each test specimen.

3.5.4.2 If conditioning of the test specimens was carried out before the initial weighing (see 3.5.2.3), place all six test specimens in the container maintained at 80 % relative humidity for 24 h ± 4 h. Transfer all six test specimens to the container maintained at 50 % relative humidity, and weigh at intervals of not less than 20 h until the change in mass between consecutive

weighings of each test specimen is less than 2 mg and record the final mass of each test specimen.

3.5.4.3 If conditioning was carried out before the initial weighing using the procedure described in annex B (see 3.5.2.4) then carry out the procedure described in B.2.2.

3.5.4.4 If the final mass of each of the test specimens which have been in empty tubes is less than their initial mass by more than 2,0 mg, then volatile substances have been lost and adjustment may be made (refer to 7.5 of ENV 1186-1:1994) to the final mass for each test specimen such that the values obtained are a measure of the migration of non-volatile substances only.

3.5.5 Extraction of absorbed ^{14}C-labelled mixture of synthetic triglycerides

Take four round bottom flasks, 250 ml or 500 ml as appropriate to the size of the soxhlet to be used for the extraction, add sufficient extraction solvent to allow cycling of the soxhlet type extractor (approximately 200 ml or 400 ml, according to the size of the flask) with anti-bumping beads (3.3.14) to control boiling.

Place the four test specimens which have been in contact with ^{14}C-labelled mixture of synthetic triglycerides into soxhlet type extractors (3.3.15). Couple each soxhlet to a flask containing the extraction solvent. Using either a water bath or steam bath (3.3.18), extract for a period of $7\,0^{+1}$ h with a minimum of 6 cycles per hour, ensuring that the test pieces are totally submerged in the solvent during each soxhlet cycle, and that they remain separated from each other.

Remove the flasks from the soxhlet type extractors and evaporate the solvent almost to dryness using a rotary evaporator, or simple distillation apparatus (3.3.17). Transfer the remaining solvent from each of the flasks together with the residues containing the extracted ^{14}C-labelled mixture of synthetic triglycerides, to separate liquid scintillation vials (3.3.22), washing out with 3 portions of liquid scintillation cocktail.

Repeat the extractions for an additional $7\,0^{+1}$ h with further quantities of solvent. If previous testing has established that all of the ^{14}C-labelled mixture of synthetic triglycerides will be extracted from the test specimens during the first 7 h extraction then the second 7 h extraction may be omitted.

Isolate the residues in scintillation vials, using the procedure described above.

Determine the extracted ^{14}C-labelled mixture of synthetic triglycerides in both the first 7 h and the second 7 h extractions by the procedure described in 3.5.6 but retain the test specimens in the soxhlet type extractors until the extracted ^{14}C-labelled mixture of synthetic triglycerides has been determined for the second 7 h extractions. If more than 2,0 mg per test specimen is found in the second extract, then determine the retained

^{14}C-labelled mixture of synthetic triglycerides via liquid scintillation counting after combustion or dissolution of the test specimens.

3.5.6 Determination of extracted ^{14}C-labelled mixture of synthetic triglycerides

3.5.6.1 Standard and background samples

Take five scintillation vials and add ^{14}C-labelled mixture of synthetic triglycerides from the same batch as used for the migration test, the amounts being from 50 mg to 250 mg. Weigh to the nearest 0,1 mg and add liquid scintillation cocktail in the required amount. Take three scintillation vials and fill with cocktail only.

3.5.6.2 Liquid scintillation counting

Transfer the samples prepared according to 3.5.5 and 3.5.6.1 into the liquid scintillation counter (3.3.21) and determine the radioactivity in the sample. Make sure that the instrument has been set to the correct parameters for determination of carbon-14, including the correct quench curve.

3.5.6.3 Calculation of extracted ^{14}C-labelled mixture of synthetic triglycerides

Calculate the specific radioactivity, sA, of the ^{14}C-labelled mixture of synthetic triglycerides with consideration of the background value as follows:

$$sA = \frac{R_s - R_o}{w} \qquad (1)$$

where:

sA is the specific radioactivity, in disintegrations per minute per milligram;

R_s is the measuring rate, in disintegrations per minute, of the standard sample (see 3.5.6.1);

R_o is the measuring rate, in disintegrations per minute, of the background sample (see 3.5.6.1);

w is the weight of the standard sample, in milligrams.

Calculate the amount of extracted ^{14}C-labelled mixture of synthetic triglycerides as follows:

$$mc = \frac{R_M - R_o}{sA \times 1000} \qquad (2)$$