SLOVENSKI STANDARD
SIST ENV 13130-6:2000

01-april-2000

Materiali in predmeti v stiku z živili - Snovi v plastiļnih masah, katerih koncentracija je omejena - 6. del: Doloļevanje vinilidenklorida v plastiļnih masah

Materials and articles in contact with foddstuffs - Plastics substances subject to limitation - Part 6: Determination of vinylidene chloride in plastics

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Grenzwerten unterliegen - Teil 6: Bestimmung von Vinylidenchlorid in Kunststoffen

Matériaux et objets en contact avec les denrées alimentaires - Matieres plastiques soumises a des limitations - Partie 6: Détermination du chlorure de vinylidene dans les matieres plastiques

Ta slovenski standard je istoveten z: **ENV 13130-6:1999**

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67.250	Materiali in predmeti v stiku z živili	Materials and articles in contact with foodstuffs

SIST ENV 13130-6:2000 **en**

EUROPEAN PRESTANDARD
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English version

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 6: Determination of vinylidene chloride in plastics

Matériaux et objets en contact avec les denrées alimentaires - Matières plastiques soumises à des limitations - Partie 6: Détermination du chlorure de vinylidène dans les matières plastiques

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Grenzwerten unterliegen - Teil 6: Bestimmung von Vinylidenchlorid in Kunststoffen

This European Prestandard (ENV) was approved by CEN on 18 February 1999 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 a European Standard.

CEN members are required to announce the existence 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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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

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Contents

Foreword

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

This Part of this European Prestandard has been prepared by a Subcommittee (SC1) of TC194 'Utensils in contact with food' as one of a series of analytical test methods for plastics materials and articles in contact with foodstuffs.

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

Their titles are as follows:

ENV 13130-1	Guide to the test methods for the specific migration of substances from plastics into food and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants
ENV 13130-2	Determination of terephthalic acid in food simulants
ENV 13130-3	Determination of acrylonitrile in food and food simulants
ENV 13130-4	Determination of 1,3-butadiene in plastics
ENV 13130-5	Determination of vinylidene chloride in food simulants
ENV 13130-7	Determination of monoethylene glycol and diethylene glycol in food simulants
ENV 13130-8	Determination of isocyanates in plastics

Method development for other monomers subject to limitation is being coordinated by the Measurement and Testing Programme of DG XII (formerly BCR).

Annex A to this prestandard is normative where applicable.

This Part of this prestandard should be read in conjunction with Part 1 of this prestandard.

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

WARNING: Vinylidene chloride is a flammable, photosensitive, hazardous substance which is volatile at room temperature. The handling and preparation of solutions of vinylidene chloride should be carried out in a fume cupboard and skin and eye contact with vinylidene chloride solutions or the inhalation of vinylidene chloride vapour should be avoided. Vinylidene chloride should be protected from prolonged exposure to light and stored at 5 °C.

0 Introduction

Vinylidene chloride (1,1-dichloroethylene), $H_2C{=}CCl_2$, is a monomer used in the manufacture of certain plastics films and coatings intended to come into contact with foodstuffs. During the manufacture of vinylidene chloride polymers and copolymers, residual vinylidene chloride monomer can remain in the polymer and can migrate into food coming into contact with the polymer.

The method described in this European prestandard is to be used in conjunction with Part 1 of this prestandard, which describes the procedures required prior to the determination of vinylidene chloride.

1 Scope

This Part of this European Prestandard specifies a method for the determination of vinylidene chloride (VdC) in plastics materials and articles.

The method is applicable to poly(vinylidene chloride) (PVdC) films, PVdC coated films, and laminates and coextruded materials containing PVdC. The level of vinylidene chloride determined is expressed as milligrams of vinylidene chloride per kilogram of polymer. The method is appropriate for the quantitative determination of vinylidene chloride at a level of 5 mg/kg in plastics materials and articles.

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.

ENV 13130-1 Guide to the test methods for the specific migration of substances from plastics into food and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants

3 Principle

The level of vinylidene chloride in a polymer is determined by headspace gas chromatography with automated sample injection, using either electron capture detection (ECD) or flame ionization detection (FID). As it is not possible to obtain test material free of vinylidene chloride, the method of standard addition is employed. Quantification is achieved using 1-chloropropane (1-CP) as an internal standard.

Plastics samples are dissolved in N,N-dimethylacetamide (DMA) prior to headspace analysis. For samples not soluble in this solvent, e.g. laminates and co-extrusions, determination can be carried out by the 'hot jar' method in which the polymer alone is heated to release the vinylidene chloride.

If interferences are experienced with the internal standard then calibration is carried out by external standardization.

If automated headspace sampling cannot be performed then manual injection as described in annex A can be applied.

Confirmation of vinylidene chloride levels is carried out either by combined gas chromatography/mass spectrometry (GC/MS) or by re-analysis on a second GC column of different polarity.

4 Reagents

4.1 Vinylidene chloride, $H_2C=CCl_2$, of purity greater than 99 % (w/w).

4.2 1-Chloropropane, $CH_3(CH_2)_2Cl$, containing no impurity > 1 % by area which will elute at the same GC retention time as vinylidene chloride.

4.3 N,N-Dimethylacetamide $CH_3CON(CH_3)_2$ free of any interferences (< 1 % area) with the vinylidene chloride and 1-chloropropane peaks.

4.4 Standard solutions of vinylidene chloride in N,N-dimethylacetamide with defined concentrations in the range 25 mg/kg to 500 mg/kg, prepared as described in 4.4.1 and 4.4.2.

4.4.1 Prepare concentrated standard vinylidene chloride solutions at approximately 2,5 g/kg and 1,2 g/kg as follows:

a) To a 50 ml flask or vial tared with cap, add approximately 50 ml (46,5 g) N,N-dimethylacetamide (4.3), close and weigh to an accuracy of 0,1 mg. Add to the N,N-dimethylacetamide a quantity of approximately 0,1 ml (0,125 g) vinylidene chloride (4.1) and shake the closed flask. Determine the exact mass of vinylidene chloride added, in grams per kilogram, by re-weighing to an accuracy of 0,1 mg.

b) Repeat item a) using 0,05 ml (0,06 g) vinylidene chloride.

c) Repeat items a) and b) to provide a second set of concentrated standard solutions.

4.4.2 Prepare dilute standard vinylidene chloride solutions as follows;

a) To two 20 ml flasks or vials tared with cap, add 18 ml and 16 ml N,N-dimethylacetamide and weigh to an accuracy of 0,1 mg. Add 2 ml of the 2,5 g/kg concentrated standard solution to the first flask or vial and 4 ml to the second. Cap, re-weigh to an accuracy of 0,1 mg and shake thoroughly.

b) Repeat item a) using 19,6 ml and 18 ml dimethylacetamide and 0,4 ml and 2 ml of the 1,25 g/kg standard. The dilute standard solutions shall be stored in suitable glass septum-capped vials with minimal headspace volume.

c) Repeat items a) and b) using the second solutions prepared in 4.4.1 to provide a second set of four dilute standard vinylidene chloride solutions.

NOTE: The standard solutions with known vinylidene chloride concentrations of approximately 25 mg/kg, 125 mg/kg, 250 mg/kg and 500 mg/kg, respectively may be stored at - 20 °C for up to four weeks, protected from light.

4.5 Solution of 1-chloropropane (4.2) in N,N-dimethylacetamide at approximately 0,4 g/kg

4.5.1 Prepare a concentrated standard 1-chloropropane solution at approximately 2,0 g/kg as follows:

To a 50 ml flask or vial tared with cap, add 50 ml of dimethylacetamide. Close and weigh to an accuracy of 0,1 mg. Add to the dimethylacetamide, approximately 0,1 ml (0,090 g) of 1-chloropropane and shake the closed flask or vial. Determine the exact mass of 1-chloropropane added by re-weighing to an accuracy of 0,1 mg.

4.5.2 Prepare a dilute standard 1-chloropropane solution at approximately 0,4 g/kg as follows:

To a 20 ml flask or vial tared with cap, add 16 ml N,N-dimethylacetamide and weigh to an accuracy of 0,1 mg. Add 4 ml of 1-chloropropane solution, as prepared in 4.5.1. Close, re-weigh to an accuracy of 0,1 mg and shake thoroughly to mix.

5 Apparatus

NOTE: An instrument or item of apparatus is listed only where it is special, or made to a particular specification, usual laboratory equipment being assumed to be available.

5.1 Gas-chromatograph, equipped with either an electron capture detector or a flame ionization detector and fitted with an automated headspace sampler.

5.2 Gas-chromatographic column, capable of the separation of N,N-dimethylacetamide from vinylidene chloride and the internal standard such that the peaks of vinylidene chloride and the internal standard do not overlap by more than 1 % peak area with each other and with other compounds.

NOTE: The following are examples of GC columns found to be suitable for vinylidene chloride analysis:

a) 2 m x 2 mm internal diameter stainless steel column packed with n-octane chemicaly bonded to 100 mesh to 120 mesh uncoated silica beads;

b) 2,8 m x 2 mm internal diameter glass column packed with 80 mesh to 100 mesh cross linked porous polymer;

c) 50 m x 0,32 mm internal diameter fused silica capillary column with 1,2 um film thickness of 100 % dimethylsiloxane;

d) 50 m x 0,32 mm internal diameter fused silica capillary column with 1,2 um film thickness of 85 % dimethyl-, 7 % cyanopropyl- 7 % phenyl-, 1 % vinyl-siloxane;

e) 50 m x 0,53 mm internal diameter fused silica capillary column with 5,0 um film thickness of 100 % dimethylsiloxane.

5.3 Glass sample vials, of size suitable for the particular autosampler employed, with polytetrafluoroethylene faced silicone rubber septa and crimp-closures.

5.4 Microsyringe, of 50 µl capacity.

6 Samples

6.1 Sample storage

Keep the samples refrigerated at - 20 °C enclosed in several layers of non-lacquered aluminium foil.

6.2 Test sample preparation

The following precautions are advisable:

a) To avoid cross-contamination by volatilization, carry out preparation of the polymer samples in an area remote to that used for handling vinylidene chloride and the 1-chloropropane solutions;

b) To avoid loss of standard solutions to the septum when making additions, add solutions directly to the polymer dissolved in N,N-dimethylacetamide contained within the vial, rather than injecting them through the septum;

c) To reduce volatilization, add internal standard and vinylidene chloride to dissolved polymer samples as quickly as possible, injecting solutions into the solvent and sealing vials immediately after addition.

d) Polymer samples that dissolve in N,N-dimethylacetamide are treated as in section 6.2.1. Samples not soluble in this solvent are treated as in section 6.2.3.

6.2.1 Preparation of dissolved test sample solutions and standard addition solutions

Use a representative sample of the test material or article cut into small pieces. To ten vials (5.3) tared with caps, add 0,2 g ± 0,005 g of sample and weigh to an accuracy of 0,1 mg.

6.2.1.1 Prepare the test sample solutions as follows:

a) To one of the vials prepared in 6.2.1, add 4 ml of N,N-dimethylacetamide and weigh. Add 20 µl of dilute 1-chloropropane internal standard solution (4.5.2) and reweigh. Seal the vial.

b) Repeat item a) to provide a duplicate test sample solution.

6.2.1.2 Prepare the sample addition solutions as follows:

a) To one of the vials prepared in 6.2.1, add 4 ml of N,N-dimethylacetamide. Then, weighing after each addition, add 20 µl of dilute 1-chloropropane internal standard solution (4.5.2) and 20 µl of the 25 mg/kg (4.4.2) dilute standard vinylidene chloride solution. Seal the vial.

b) Repeat item a) to provide a duplicate sample.

c) Repeat item a) using the 125 mg/kg, 250 mg/kg and 500 mg/kg dilute vinylidene chloride standard solutions, preparing duplicate samples.

A second set of samples and standard additions shall be prepared using the second set of dilute vinylidene chloride standard solutions.

Calculate the concentration of vinylidene chloride and 1-chloropropane, in milligrams per kilogram of polymer sample. Place the vials in either an ultrasonic bath or on an orbital shaker for 2 h to dissolve the vinylidene chloride polymer.

WARNING: It is important that the weight of sample does not exceed the limit specified as this is a standard addition method. If sample weights are not kept constant errors will be introduced in the individual points of the standard addition graph.

6.2.2 Preparation of blank samples

6.2.2.1 To a vial (5.3) add 4 ml N,N-dimethylacetamide and 20 µl of dilute 1-chloropropane internal standard solution. Seal vial with cap and septum.

6.2.2.2 To a vial (5.3) add 0,2 mg of sample and 4 ml of N,N-dimethylacetamide. Seal vial with cap and septum. Place the vial in an ultrasonic bath or on an orbital shaker for 2 h to dissolve the vinylidene chloride polymer.

6.2.3 Preparation of 'hot jar' test samples

Prepare test samples, standard additions and blank samples as in 6.2.1 and 6.2.2 with the following alterations:

Cut samples in strips and arrange in the vial so as to expose the maximum surface area for equilibration. Omit the addition of 4 ml of N,N-dimethylacetamide to the test samples, the standard additions and the blank samples.