SLOVENSKI STANDARD
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Materiali in predmeti v stiku z ģivili - Snovi v polimernih materialih, katerih koncentracija je omejena - 5. del: Doloģ evanje vinilidenklorida v modelnih raztopinah za ģivila

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 5: Determination of vinylidene chloride in food simulants

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 5: Bestimmung von Vinylidenchlorid in Prüflebensmitteln

Matériaux et objets en contact avec des denrées alimentaires - Substances dans les matieres plastiques soumises a des limitations - Partie 5 : Détermination du chlorure de vinylidene dans les simulants d'aliments alimentaires

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Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 5: Determination of vinylidene chloride in food simulants

Matériaux et objets en contact avec des denrées alimentaires - Substances dans les matières plastiques soumises à des limitations - Partie 5 : Détermination du chlorure de vinylidène dans les simulants d'aliments alimentaires

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This European Standard was approved by CEN on 24 March 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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Foreword

This document (EN 13130-5:2004) has been prepared by Technical Committee CEN/TC 194 “Utensils in contact with food”, the secretariat of which is held by BSI.

This document was prepared by Subcommittee SC1 of TC 194 as one of a series of analytical test methods for plastics materials and articles in contact with foodstuffs.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2004, and conflicting national standards shall be withdrawn at the latest by November 2004.

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

This standard is intended to support Directives 2002/72/EC [1], 89/109/EEC [2], 82/711/EEC [3] and its amendments 93/8/EEC [4] and 97/48/EC [5], and 85/572/EEC [6].

At the time of preparation and publication of this part of EN 13130 the European Union legislation relating to plastics materials and articles intended to come into contact with foodstuffs is incomplete. Further Directives and amendments to existing Directives are expected which could change the legislative requirements which this standard supports. It is therefore strongly recommended that users of this standard refer to the latest relevant published Directive(s) before commencement of a test or tests described in this standard.

EN 13130-5 should be read in conjunction with EN 13130-1

Further parts of EN 13130, under the general title *Materials and articles in contact with foodstuffs - Plastics substances subject to limitation*, 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 specific monomers and additives in plastics. The other parts of EN 13130 are as follows.

Part 1: *Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants*

Part 2: *Determination of terephthalic acid in food simulants*

Part 3: *Determination of acrylonitrile in food and food simulants*

Part 4: *Determination of 1,3-butadiene in plastics*

Part 6: *Determination of vinylidene chloride in plastics*

Part 7: *Determination of monoethylene glycol and diethylene glycol in food simulants*

Part 8: *Determination of isocyanates in plastics*

Part 9: *Determination of acetic acid, vinyl ester in food simulants*

Part 10: *Determination of acrylamide in food simulants*

Part 11: *Determination of 11-aminoundecanoic acid in food simulants*

Part 12: *Determination of 1,3-benzenedimethanamine in food simulants*

Part 13: *Determination of 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A) in food simulants*

Part 14: *Determination of 3,3-bis(3-methyl-4-hydroxyphenyl)-2-indoline in food simulants*

Part 15: *Determination of 1,3-butadiene in food simulants*

Part 16: *Determination of caprolactam and caprolactam salt in food simulants*

Part 17: *Determination of carbonyl chloride in plastics*

Part 18: *Determination of 1,2-dihydroxybenzene, 1,3- dihydroxybenzene, 1,4- dihydroxybenzene, 4,4'-dihydroxybenzophenone and 4,4'dihydroxybiphenyl in food simulants*

Part 19: *Determination of dimethylaminoethanol in food simulants*

Part 20: *Determination of epichlorohydrin in plastics*

Part 21: *Determination of ethylenediamine and hexamethylenediamine in food simulants*

Part 22: *Determination of ethylene oxide and propylene oxide in plastics*

Part 23: *Determination of formaldehyde and hexamethylenetetramine in food simulants*

Part 24: *Determination of maleic acid and maleic anhydride in food simulants*

Part 25: *Determination of 4-methyl-pentene in food simulants*

Part 26: *Determination of 1-octene and tetrahydrofuran in food simulants*

Part 27: *Determination of 2,4,6-triamino-1,3,5-triazine in food simulants*

Part 28: *Determination of 1,1,1-trimethylopropane in food simulants*

Parts 1 to 8 are European Standards.

Parts 9 to 28 are Technical Specifications, prepared within the Standards, Measurement and Testing project, MAT1-CT92-0006, "*Development of Methods of Analysis for Monomers*".

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

Vinylidene chloride (VdC) (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 part of the standard should be used in conjunction with part 1 of this standard which describes the procedures required prior to the determination of vinylidene chloride.

1 Scope

This part of this European Standard specifies a method for the determination of vinylidene chloride monomer in food simulants. The method is applicable to aqueous food simulants, to the fatty food simulant olive oil and other fatty food simulants, simulants D, e.g. a mixture of synthetic triglycerides or sunflower oil or corn oil. The level of vinylidene chloride determined is expressed as milligrams of vinylidene chloride per kilogram of food simulant. The method is appropriate for the quantitative determination of vinylidene chloride at a level of 0,05 mg/kg.

NOTE This method was developed for the determination of vinylidene chloride in 15 % (v/v) aqueous ethanol, as required by the regulations in force at the time the development work was carried out. However, this method, developed for 15 (v/v) aqueous ethanol, should be applicable to the determination in 10 (v/v) aqueous ethanol.

2 Normative references

This European Standard incorporates by dated or 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 or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 13130-1:2004, *Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 1: Guide to test methods for the specific migration of substances from plastics to foods 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 food simulant is determined by headspace gas chromatography with automated sample injection and using either electron capture or flame ionization detection. Quantification is achieved using 1-chloropropane (1-CP) as internal standard with calibration against blank samples of simulant fortified with vinylidene chloride. If blank samples of simulant cannot be obtained then the method of standard addition described in annex A is employed.

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

If automated headspace sampling cannot be performed, manual injection as described in annex B shall 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

WARNING: All chemicals are hazardous to health to a greater or lesser extent. It is beyond the scope of this standard to give instructions for the safe handling of all chemicals, that meet, in full, the legal obligations in all countries in which this standard may be followed. Therefore, specific warnings are not given and users of this standard shall ensure that they meet all the necessary safety requirements in their own country.

4.1 Analyte and internal standard

4.1.1 Analyte

Vinylidene chloride (VdC), $H_2C{=}CCl_2$, of purity greater than 99 %.

4.1.2 Internal standard

1-Chloropropane (1-CP), $CH_3(CH_2)_2Cl$, of purity greater than 98 %.

4.2 Chemicals

N,N-dimethylacetamide (DMA), $CH_3CON(CH_3)_2$, of purity greater than 99 %.

4.3 Solutions of standards and internal standard

4.3.1 Preparation of stock solutions of vinylidene chloride

a) Stock solution of vinylidene chloride with a defined concentration of approximately 2,5 g/kg. To a 20 ml flask or vial with cap, add 20 ml N,N-dimethylacetamide (4.2), close and weigh to an accuracy of 0,1 mg. Add to the N,N-dimethylacetamide a quantity of approximately 40 µl (0,048g) vinylidene chloride (4.1.1) and shake the closed flask. Weigh to an accuracy of 0,1 mg. Determine the exact mass of vinylidene chloride added in grams per kilogram.

b) Repeat item a) to provide a second stock solution.

4.3.2 Intermediate solutions of vinylidene chloride

Intermediate solutions of vinylidene chloride in N,N-dimethylacetamide with defined concentrations in the range 5 mg/kg to 50 mg/kg are prepared as follows:

a) To five 10 ml flasks or vials tared with cap, add 10 ml of N,N-dimethylacetamide and weigh to an accuracy of 0,1 mg. Add respectively 20 µl, 50 µl, 100 µl, 150 µl and 200 µl of the 2,5 g/kg stock solution of vinylidene chloride (4.3.1a). Cap, re-weigh to an accuracy of 0,1 mg and shake thoroughly.

b) Repeat item a) using the second stock solution prepared in 4.3.1 b) to provide a second set of five intermediate solutions of vinylidene chloride.

NOTE The stock and intermediate solutions of vinylidene chloride, can be stored at - 20 °C for up to four weeks, protected from light. Solutions should be stored in suitable glass, septum-capped vials, with minimal headspace volume.

4.3.3 Internal standard stock solution

Prepare a stock solution of 1-chloropropane with a defined concentration of approximately 20 g/kg as follows:

To a 10 ml flask or vial tared with cap, add 10 ml N,N-dimethylacetamide. Close and weigh to an accuracy of 0,1 mg. Add to the N,N-dimethylacetamide, approximately 0,20 ml 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.

4.3.4 Intermediate internal standard solution

Prepare an intermediate solution of 1-chloropropane with a defined concentration of approximately 200 mg/kg as follows:

To a 10 ml flask or vial tared with cap, add 10 ml N,N-dimethylacetamide and weigh to an accuracy of 0,1 mg. Add 100 µl of 1-chloropropane stock solution (4.3.3). 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 an electron capture detector (ECD) or flame ionization detector (FID) and fitted with an automated headspace sampler.

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

NOTE 1 The following are examples of GC columns known to be suitable for vinylidene chloride analysis:

a) 50 m x 0,32 mm internal diameter 100 % dimethyl siloxane fused silica capillary column with 1,2 µm film thickness;

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

c) 50 m x 0,53 mm internal diameter polyethylene glycol capillary column with 2,0 µm film thickness.

NOTE 2 Depending on the type of gas chromatograph, automated headspace sampler and GC column, the appropriate operating conditions should be established. For guidance, the following range of parameters have been found suitable for column a):

Injector temperature:	120 °C
Oven programme:	70 °C (isothermal)
Detector (ECD):	280 °C
Carrier gas and flow rate:	helium, 1 ml/min
Injection mode:	split (ratio = 20:1).

Parameters found suitable for column c) are as follows:

Injector:	200 °C
Oven programme:	75 °C for 10 min, 20 °C/min to 200 °C, hold 5 min.
Detector (FID):	250 °C
Carrier gas and flow rate:	helium, 5 ml/min
Injection mode:	split (ratio = 4:1).

Electron capture detector optimization. If a capillary column is employed, it should be ensured that the detector has a make-up gas. Nitrogen or argon/methane (95 % / 5 %) is generally recommended and the flow should be optimized as recommended in the GC manufacturer's instructions. Gases should be purified of moisture, oxygen and electron capturing species by passage through suitable filters, to the level recommended by the detector manufacturer.

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

5.4 Microsyringes, of 50 µl, 100 µl and 200 µl capacity.

6 Samples

6.1 Laboratory samples

The laboratory samples of food simulant to be analysed are obtained as described in EN 13130-1. Samples shall be kept refrigerated at 5 °C with the exclusion of light, in glass, gas-tight containers with minimal headspace volume. Vinylidene chloride-free samples of simulant are also required for calibration purposes. The simulant shall be the same as that used for the exposure.

NOTE Since the determination of vinylidene chloride in food simulant is performed close to the limit of detection of the method, extreme care should be taken with respect to possible adventitious contamination during preparation of the test samples and standards and to loss by volatilization. The following precautions are advisable.

a) To avoid cross-contamination by volatilization, the migration test procedure and the preparation of the simulant test samples should be carried out in a remote area to that used for handling vinylidene chloride and 1-chloropropane solutions.

b) To avoid loss of standard solutions to the septum when making additions and subsequent loss during headspace equilibration, it is preferable to add solutions directly to the food simulant contained within the vial, rather than injecting them through the septum. The simulant should be cooled to 5 °C before addition.

c) To reduce volatilization, vinylidene chloride and internal standard should be added to simulant samples as quickly as possible, injecting solutions down the side of vials and sealing vials immediately after addition.

6.2 Preparation of test samples

6.2.1 General

Conduct all weighings to an accuracy of 0,1 mg.

6.2.2 Aqueous food simulants

To a sample vial (5.3), add 10 ml of food simulant and weigh. Then, weighing after each addition, add 20 µl N,N-dimethylacetamide and 20 µl of intermediate 1-chloropropane solution (4.3.4) and reweigh. Seal vial. Repeat this procedure to provide a duplicate test sample.

6.2.3 Fatty food simulant

Follow the procedure outlined in 6.2.2

6.3 Preparation of blank samples

To a sample vial, add 10 ml, as appropriate, of food simulant and 20 µl of N,N-dimethylacetamide. Seal vial. Prepare a duplicate blank sample.

6.4 Preparation of calibration samples

NOTE If vinylidene chloride-free food simulant is not available, the method of standard addition described in annex A should be employed.

To a sample vial (5.3), add 10 ml of aqueous food simulant and weigh. Then, weighing after each addition, add 20 µl of intermediate 1-chloropropane solution and 20 µl of the 5 mg/kg intermediate standard vinylidene chloride solution (4.3.2) in place of the N,N-dimethylacetamide. Seal the vial. Repeat the procedure using the 12,5 mg/kg, 25 mg/kg, 37,5 mg/kg, and 50 mg/kg intermediate vinylidene chloride standard solutions. Prepare a zero-point calibration standard using 10 ml of simulant, as appropriate, plus 20 µl internal standard and 20 µl N,N-dimethylacetamide. Prepare duplicates of each calibration sample.