SLOVENSKI STANDARD
SIST EN 13130-3:2004

01-september-2004

Nadomeģ a:
SIST ENV 13130-3:2000

Materiali in predmeti v stiku z ģivili - Snovi v polimernih materialih, katerih koncentracija je omejena - 3. del: Dolo ev anje akrilonitrila v ģivilih in modelnih raztopinah za ģivila

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 3: Determination of acrylonitrile in food and food simulants

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 3: Bestimmung von Acrylnitril in Lebensmitteln und Prüflebensmitteln

Matériaux et objets en contact avec des denrées alimentaires - Substances dans les matieres plastiques soumises a des limitations - Partie 3 : Détermination de l'acrylonitrile dans les aliments et les simulants d'aliments

Ta slovenski standard je istoveten z: **EN 13130-3:2004**

ICS:

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

SIST EN 13130-3:2004 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 13130-3

May 2004

ICS 67.250

English version

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 3: Determination of acrylonitrile in food and food simulants

Matériaux et objets en contact avec des denrées alimentaires - Substances dans les matières plastiques soumises à des limitations - Partie 3 : Détermination de l'acrylonitrile dans les aliments et les simulants d'aliments

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 3: Bestimmung von Acrylnitril in Lebensmitteln und Prüflebensmitteln

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.

CEN members are the national standards bodies of 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.

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 13130-3:2004: E

Contents

page

Foreword 3

1 Scope 6

2 Normative references 6

3 Principle 6

4 Reagents 6

5 Apparatus 7

6 Samples 8
6.1 Laboratory samples 8
6.2 Test sample preparation 8

7 Procedure 9
7.1 GC preparation 9
7.2 Performance of GC measurements 10

8 Expression of results 10
8.1 General 10
8.2 Method of calculation 10
8.3 Precision data and detection limit 12

9 Confirmation 12
9.1 Requirement for confirmation 12
9.2 Confirmation by combined gas chromatography-mass spectrometry 12
9.3 Confirmation by re-analysis on a GC column of different polarity 13

10 Test report 13

Annex A (normative) Method of standard addition 14

Annex B (normative) Calibration via external standardization 16

Annex C (normative) Manual sample injection 17

Bibliography 18

Foreword

This document (EN 13130-3:2004) 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 13130-3 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 4: *Determination of 1,3-butadiene in plastics*

Part 5: *Determination of vinylidene chloride in food simulants*

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

Acrylonitrile, CH_2=CH-CN, is a monomer used in the manufacture of certain plastics materials and articles intended to come into contact with foodstuffs. During the manufacture of acrylonitrile copolymers, residual acrylonitrile 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 acrylonitrile.

The method has been validated by collaborative trial using fruit juice, wine and sunflower oil.

1 Scope

This part of this European Standard specifies a method for the determination of acrylonitrile monomer in foods and 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, as well as to liquid and solid foodstuffs such as beverages and soft margarine. The level of acrylonitrile monomer determined is expressed as milligrammes of acrylonitrile per kilogram of food or food simulant.

The method is appropriate for the quantitative determination of acrylonitrile monomer at minimum levels of down to 0,01 mg/kg to 0,005 mg/kg, or lower, in food simulant, depending on the applied test conditions (see NOTE in 8.2.3). With regard to the performance in the mentioned foodstuffs, in general, a direct detection limit of 0,02 mg/kg is achievable.

NOTE This method was developed for the determination of acrylonitrile 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 acrylonitrile (AN) in a food, or a food simulant, is determined by headspace gas chromatography with automated sample injection, using nitrogen specific detection. Quantification is achieved using propionitrile (PN) as an internal standard with calibration against blank samples fortified with acrylonitrile. If blank samples 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 as described in annex B.

If automated headspace sampling cannot be performed, manual injection as described in annex C shall be applied.

Confirmation of acrylonitrile 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 Acrylonitrile, CH_2=CH-CN, purity greater than 99% (w/w).

4.2 Propionitrile, CH_3-CH_2-CN, containing no impurity at > 1 % by area which will elute at the same GC retention time as acrylonitrile.

4.3 Propylene carbonate, CH_3-CH-OCOO-CH_2, boiling point 240 °C to 243 °C at normal pressure, free of any interferences (< 1 % area) with the acrylonitrile and propionitrile peaks.

4.4 Nitrogen, purified to 99,9999 %.

4.5 Standard solutions of acrylonitrile in propylene carbonate with defined concentrations in the range 25 µg/ml to 25 µg/ml, prepared as described in 4.5.1 and 4.5.2.

4.5.1 Prepare concentrated standard acrylonitrile solutions at approximately 12,5 mg/ml as follows:

a) Fill a 100 ml volumetric flask with 50 ml propylene carbonate (4.3), close and weigh to an accuracy of 0,2 mg. Add to the propylene carbonate a quantity of approximately 1,5 ml (1,25 g) acrylonitrile (4.1) and shake the closed flask. Determine the exact mass of acrylonitrile added by re-weighing to an accuracy of 0,2 mg. Fill the flask to the 100 ml mark.

b) Repeat item a) to provide a second concentrated standard solution.

4.5.2 Prepare dilute standard acrylonitrile solutions as follows:

a) With an accuracy of 0,1 ml throughout, dilute one of the solutions prepared in 4.5.1 by a factor of 100 in two steps, taking for each step 10 ml acrylonitrile solution and 90 ml propylene carbonate, to give an intermediate standard solution of approximately 125 µg acrylonitrile per millilitre. Place 48 ml or 45 ml or 40 ml of propylene carbonate into three 55 ml glass vials and add 2 ml or 5 ml or 10 ml of the intermediate standard solution, respectively. Close the vials with a polytetrafluoroethylene (PTFE) seal and cap and shake thoroughly.

b) Repeat item a) using the second solution prepared in 4.5.1 to provide a second set of three dilute standard acrylonitrile solutions.

NOTE The standard solutions with known acrylonitrile concentrations of approximately 5 µg/ml, 12,5 µg/ml and 25 µg/ml, respectively, can be stored at 4 °C for up to four weeks.

4.6 Dilute standard propionitrile solution in propylene carbonate, with a known concentration of approximately 25 µg/ml of propionitrile (4.2) prepared by following an analogous procedure to that described in 4.5.

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 a nitrogen specific detector and fitted with an automatic headspace sampler.

5.2 Gas-chromatographic column, capable of the separation of propylene carbonate from acrylonitrile and propionitrile such that the peaks of acrylonitrile and propionitrile do not overlap by more than 1 % peak area with other compounds.

NOTE The following are examples of GC columns known to be suitable for acrylonitrile analysis:

a) 2 m x 3 mm internal diameter stainless steel column packed with 15 % polyethylene glycol 1500 on 60 mesh to 100 mesh diatomite support;

b) 1,8 m x 2 mm internal diameter stainless steel column packed with 0,2 % polyethyleneglycol 1500 on 80 mesh to 100 mesh graphitized carbon black USP (S7) solid support;

c) 3 m x 2 mm internal diameter glass column packed with 20 % polyethylene glycol 20 on 60 mesh to 80 mesh flux-calcined diatomite support;

d) 25 m x 0,32 mm internal diameter, fused silica capillary column with 1,2 µm film thickness of 100 % dimethylpolysiloxane;

e) 12 m x 0,20 mm internal diameter, fused silica capillary column with 0,33 µm film thickness of free fatty acid phase (modified polyethylene glycol).

5.3 Sample vials, 25 ml, or of another size suitable for the particular autosampler employed, with butyl rubber septa and crimp-closures.

NOTE The butyl rubber septa should not give rise to acrylonitrile or interference peaks and in some circumstances PTFE-faced septa are preferred.

5.4 Microsyringes, of 50 µl capacity and syringes, of 5 ml capacity.

6 Samples

6.1 Laboratory samples

The laboratory samples of food, or food simulant, to be analysed are obtained as described in EN 13130-1. Acrylonitrile-free samples of the same type as those to be analysed are also required for use for calibration purposes. Keep the samples refrigerated at 4 °C in closed containers with the exclusion of light.

NOTE Acrylonitrile losses are unlikely during sampling, losses during transport and short-term storage for up to 4 weeks are unlikely.

6.2 Test sample preparation

6.2.1 General

NOTE Since the determination of acrylonitrile in food or food simulant is performed close to the detection limit of the method, extreme care should be taken with respect to possible adventitious contamination during preparation of the test samples.

The following precautions are advisable:

a) purge the empty sample vials (5.3) with purified nitrogen before filling with food or food simulant;

b) to avoid cross-contamination by volatilization, carry out the migration test procedure and the preparation of the food or food simulant subsamples in a different laboratory to that used for handling acrylonitrile and propionitrile solutions;

c) to avoid loss of standard solutions to the septum when making additions, it is preferable, particularly with PTFE-faced septa, to add these directly to the food, or food simulant, contained within the vial, rather than injecting them through the septum.

6.2.2 Preparation of test sample solutions

For liquid foods, place 5,0 ml ± 0,1 ml of the food or aqueous food simulant, in a sample vial (5.3) using a 5 ml syringe (5.4). For solid foods, such as soft margarine and for olive oil and simulants D, weigh 5,0 g ± 0,1 g of food or simulant into the sample vial. Add 20 µl propylene carbonate (4.3) and 20 µl propionitrile

standard solution (4.6) to the food, or food simulant, using the 50 µl syringe (5.4) and close the vial with septum and cap.

6.2.3 Preparation of food, or food simulant calibration samples.

NOTE If the food or food simulant is not available free of acrylonitrile, the method of standard addition described in annex A should be used.

Follow the procedure described in 6.2.2 adding 20 µl of one of the dilute standard acrylonitrile solutions (4.5) in place of the propylene carbonate.

6.2.4 Preparation of blank samples

Follow the procedure described in 6.2.2 employing acrylonitrile-free food or food simulant, adding further propylene carbonate (20 µl) in place of the propionitrile.

7 Procedure

7.1 GC preparation

7.1.1 GC parameters

Depending on the type of gas chromatograph and column used for the determination, establish the appropriate GC parameters.

NOTE The range of parameters which may be employed for packed columns are as follows:

Temperature:	
Injector	140 °C to 200 °C
Column	80 °C to 90 °C (isothermal)
Detector	140 °C to 200 °C

Carrier gas and flow rate:	
Helium or nitrogen	20 ml/min to 40 ml/min.

7.1.2 Nitrogen specific detector optimization

Optimize the air and hydrogen flow rates according to the manufacturer's instructions.

NOTE As the influence of the carrier gas flow rate (see 7.1.1) on the detector sensitivity is low, hydrogen and air flow rates can in most cases be left unchanged after installation of a new rubidium bead. Any necessary change of detector sensitivity can be achieved by adjustment of detector voltage. The rubidium bead should be renewed if an acrylonitrile concentration of 20 µg/l in the sample solution yields a signal/noise ratio smaller than 3 and if the fault does not lie elsewhere.

7.1.3 Calibration

Each sample has to be determined at least in duplicate.

With the aid of the three dilute standard acrylonitrile solutions, establish a calibration curve based on fortification of acrylonitrile-free food or food simulant. For this calibration use aliquots of the same type of food or food simulant, as that to be analysed.