BRITISH STANDARD

BS EN
13130-3:2004

Materials and articles in contact with foodstuffs — Plastics substances subject to limitation —

Part 3: Determination of acrylonitrile in food and food simulants

The European Standard EN 13130-3:2004 has the status of a British Standard

ICS 67.250

BSI
British Standards

National foreword

This British Standard is the official English language version of EN 13130-3:2004. It supersedes DD ENV 13130-3:1999 which is withdrawn.

The UK participation in its preparation was entrusted by Technical Committee CW/47, Materials and articles in contact with foodstuffs, to Subcommittee CW/47/1, Migration from plastics, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled "International Standards Correspondence Index", or by using the "Search" facility of the *BSI Electronic Catalogue* or of British Standards Online.

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 17 June 2004

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 18, an inside back cover and a back cover.

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Amendments issued since publication

Amd. No.	Date	Comments

ISBN 0 580 43948 8

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.

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

Contents

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.

The two sets of calibrant solutions made from independently prepared stock solutions shall be cross-checked by generating two calibration curves which, on the basis of peak area measurement, shall agree to ± 5 % of one another.

The standard signal shall be significantly higher than possible control samples at the same retention time. On the other hand, because of possible non-linearity of the nitrogen detector response, acrylonitrile and propionitrile concentrations shall be similar. For these two reasons, with respect to calibration, standard acrylonitrile solutions shall not be applied with higher concentrations (mass/volume) than given in this method.

7.2 Performance of GC measurements

NOTE For the method described, two response factors, one due to the nitrogen detector and the other to the volatility coefficients of acrylonitrile and propionitrile in the sample solutions, together make up the calibration factor. This requires the maintenance of the same conditions for the measurement of all sample solutions prepared in 6.2.1.

When starting measurements, particularly in the case of standard addition calibration according to annex A, baseline stability and response linearity of the detector should be examined.

As nitrogen specific detector sensitivity could change with time, sometimes in a different way for acrylonitrile and propionitrile, it is necessary to measure the three calibration solutions both before and after the series of samples. In addition, a medium-concentration sample solution (6.2.3) as well as a control solution (6.2.4) shall be analysed after every five sample injections.

Equilibrate the sample solutions prepared according to 6.2.1 in the thermostat of the automated headspace sampler for 2 h at 70 °C ± 1 °C before commencing the analysis programme.

Identify the acrylonitrile and propionitrile peaks on the basis of their retention times and measure the respective peak heights or areas.

8 Expression of results

8.1 General

NOTE The following calculations assume that for all measurements exactly the same volume or mass of food, or food simulant, has been used and, for the internal standard, that the same volume of standard solution has been added.

8.2 Method of calculation

8.2.1 GC interferences

If the control sample with propionitrile omitted shows an interference in the propionitrile region of the chromatogram exceeding 10 % of the area of propionitrile in the calibration samples, and if the analysis of replicate control samples reveals that this interference varies by more than ± 20 % in absolute size, then the method of external calibration given in annex B shall be used. Similarly, if the analysis of the control sample with acrylonitrile omitted 'blank food' shows an acrylonitrile peak corresponding to more than 0,01 mg/kg when calculated according to 8.2.2 or 8.2.3, then the method of standard addition given in annex A shall be used.

8.2.2 Graphical determination

Construct the calibration graph plotting acrylonitrile/propionitrile peak height or area ratio obtained from the fortified calibration solutions versus the acrylonitrile concentration, in milligrams per litre or milligrams per kilogram in the food, or food simulant, in a double-logarithmic manner. Read the acrylonitrile concentration of the test sample solutions (6.2.2) from the calibration graph by interpolation of the corresponding peak area ratio, having regard to the note given under 7.2.

This procedure yields directly the acrylonitrile concentration in milligrams per litre for liquid foods and aqueous food simulants and milligrams per kilogram for solid foods, and for olive oil and simulants D.

8.2.3 Determination by calculation

Calculate a calibration factor as follows:

$$f_{is} = C_{AN,cal} \frac{Y_{PN,cal} - Y_{PN,ctrl}}{Y_{AN,cal} - Y_{AN,ctrl}} \quad (1)$$

where:

f_{is} is the calibration factor;

$C_{AN,\,cal}$ is the acrylonitrile concentration of the calibration solution (fortified sample solutions from 6.2.3) in milligrams per litre or milligrams per kilogram;

$Y_{PN,\,cal}$ is the peak height or area of the propionitrile peak;

$Y_{PN,\,ctrl}$ is the peak height or area of the propionitrile peak resulting from control samples;

$Y_{AN,\,cal}$ is the peak height or area corresponding to $C_{AN,cal}$;

$Y_{AN,\,ctrl}$ is the peak height or area resulting from control samples (6.2.4);

Calculate the sample acrylonitrile concentration as follows:

$$C_{AN} = f_{is} \frac{Y_{AN} - Y_{AN,ctrl}}{Y_{PN} - Y_{PN,ctrl}} \quad (2)$$

where:

C_{AN} is the concentration of acrylonitrile in the sample in milligrams per litre or milligrams per kilogram;

f_{is} is the calibration factor, as given in equation (1). Use the mean value obtained from several calibration solutions (6.2.3);

Y_{PN} is the peak height or area of the propionitrile peak from the sample;

$Y_{PN,\,ctrl}$ is the peak height or area of the propionitrile peak resulting from control samples;

Y_{AN} is the peak height or area corresponding to C_{AN};

$Y_{AN,\,ctrl}$ is the peak height or area resulting from control samples.

NOTE Commission Directive 2002/72/EC [1] states that the specific gravity of all simulants should conventionally be assumed to be ‘1’. Milligrams of substance released per litre of simulant will thus correspond numerically to milligrams of substance released per kilogram of simulant and, taking into account of the provisions laid down in Directive 82/711/EEC, to milligrams of substance released per kilogram of foodstuff.

The migration results obtained above as milligrams per litre equate numerically as milligrams per kilogram.

8.2.4 Calculation of the specific migration

Depending on the fill volume of the test material and on the surface area/food simulant ratio, the acrylonitrile concentration in the laboratory sample as determined according to clause 7 may need mathematical transformation in order to calculate the specific migration value to be compared with SML. For guidance see EN 13130-1:2004, clause 13.

8.3 Precision data and detection limit

8.3.1 Validation

For validation of this method a collaborative trial using fruit juice, red wine and sunflower oil was performed. Each participant in this trial obtained each of the acrylonitrile-free foods together with corresponding samples fortified with acrylonitrile concentrations of approximately 0,020 mg, 0,050 mg and 0,1 mg acrylonitrile per litre. Calibration solutions were prepared with comparable concentrations, so that the control sample values could be corrected.

8.3.2 Repeatability and reproducibility

Evaluation of the collaborative trial results at a concentration of 0,02 mg/l at the 95 % probability level yielded the following performance characteristics:

- repeatability, *r*, is 0,005 mg acrylonitrile per litre;
- reproducibility, *R*, is 0,011 mg acrylonitrile per litre.

There was no influence of the calibration method, using either an internal or an external standard, on the numeric values of *r* and *R*.

8.3.3 Detection limit

The detection limit (DL), based on a signal/noise ratio of 3 or on the six-fold standard deviation of the control sample, was found to be in the range 0,005 mg acrylonitrile per kilogram to 0,02 mg acrylonitrile per kilogram. Thus the method is capable of quantitative detection at a minimum value of 0,02 mg acrylonitrile per kilogram.

NOTE For laboratories that have difficulties in achieving a measured detection limit of 0,005 mg/kg to 0,01 mg/kg the following should be taken into account: due to the favourable solubility of acrylonitrile in all of the food simulants, a lower effective detection limit can be obtained in a migration test by application of a smaller ratio of food simulant volume to contact surface area. For instance, by reducing the food simulant volume ratio from 1000 ml/6 dm² to 500 ml/6 dm² a minimum effective, migration-relevant detection limit of 0,01 mg/kg is achievable by any laboratory. Further reduction of the volume to area ratio can lead to even lower values.

Those laboratories that can achieve the above mentioned detection limit range of 0,005 mg/kg to 0,01 mg/kg may, in this way, obtain migration-related detection limit values in the range of 0,005 mg/kg and lower.

9 Confirmation

9.1 Requirement for confirmation

In cases where acrylonitrile migration from materials and articles into foods, or food simulants, as determined according to 8.2, exceeds a restriction criterion, e.g. SML = not detectable (DL = 0,02 mg/kg), the determination shall be confirmed by one of either of the methods described in 9.2 or 9.3.

9.2 Confirmation by combined gas chromatography-mass spectrometry

In the selected ion mode, re-analyse the test sample(s), the calibration standards and the control samples (6.2.1). The ions monitored shall be m/z 53 for acrylonitrile and m/z 55 for propionitrile. The peaks attributed to acrylonitrile and propionitrile shall maximize within one-half peak width (measured at half-height, H/2) or within 2 % of the absolute retention time, of standards, whichever is the smaller. Use the peak area ratios so derived to calculate the level of acrylonitrile in the food, or food simulant, sample(s) according to clause 8. This acrylonitrile level shall be considered to be the true value.

9.3 Confirmation by re-analysis on a GC column of different polarity

Re-analyse the test sample(s), calibration samples and control samples (6.2.1) using an alternative GC phase of different polarity e.g. a less polar alkyl polysiloxane phase like 5 % phenyl, 95 % methyl or similar instead of a polar Carbowax 20M or similar phase, or vice versa. For each column, the peaks attributed to acrylonitrile and to propionitrile if employed in the calculations, shall maximize within one-half peak width (H/2) or within 2% of the absolute retention time, of the standard, whichever is the smaller. If the levels of putative acrylonitrile found using the two columns agree to within 10 %, then the average of the two values shall be considered to be the true value. If not, procedure 9.2 shall be followed.

10 Test report

The test report shall include the following particulars, where known:

a) a reference to this part of this standard;

b) all information necessary for complete identification of the sample;

c) form of the plastics;

d) use /class of food for which the sample is intended to contact, where known, and where possible food classification reference number as listed in Table 2 of EN 13130-1:2004;

e) intended conditions of use, where known;

f) conditions of the test;

1) foodstuffs or food simulants used;

2) duration and temperature, and relation with "Conditions of contact in worst foreseeable use", as defined in Table 3 of EN 13130-1:2004;

3) area and geometry of the test specimen;

4) volume of foodstuff or food simulant used were appropriate;

g) any departures from the standard method, reasons for the departures;

h) any particular requirements of the parts of this standard;

i) any relevant comments on the test results;

j) details of any confirmation procedure(s);

k) limitation on the substance, that not detected with a method with a detection limit of 0,02 mg acrylonitrile per kilogram of food or food simulant;

l) identity of the laboratory conducting the test and the name of the analyst;

m) date of sample arrival or sampling, the method of sampling, the date of the analysis, together with note on any intervening storage conditions;

n) individual test results, and the mean of two or more determinations satisfying the repeatability criterion of 8.3.2, expressed in milligrams of acrylonitrile per kilogram of food or food simulant.

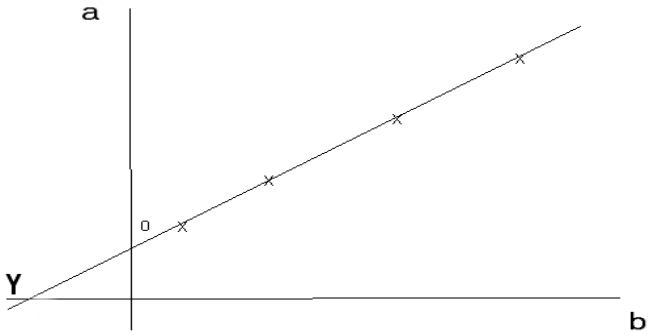
Annex A
(normative)

Method of standard addition

When acrylonitrile-free food or food simulant is not available the standard addition method is applied. In this case, in order to increase the precision of extrapolation, one amount of analyte added shall correspond to the unfortified sample solution, determined approximately in advance, and a second fortification shall approach three to four times this value.

Control samples inherently cannot be recognized, thus representing a possible source of error. Also constancy of the calibration factor over a long time cannot be presupposed, and therefore an analogous procedure to that given in 7.2 shall be followed with the standard addition method.

Evaluate according to the following Figure A.1.



Key

where:

a Y axis peak area ratio AN/PN

b X axis acrylonitrile added to sample milligrams per litre

o is the peak area ratio resulting from the sample solution (6.2.2);

x is the peak area ratio resulting from the fortified sample solutions (6.2.3);

Y is the intercept of calibration curve and x-axis.

Figure A.1 — Evaluation of results by the method of standard addition

This procedure yields, at intercept y, directly the acrylonitrile concentration in the sample in milligrams per litre or milligrams per kilogram.

NOTE When using the method of standard addition the performance values, particularly the critical difference value, will be higher than the numerical values given in clause 8.

Annex B
(normative)

Calibration via external standardization

In cases where interferences are experienced with the internal standard, calibration is carried out using an external standard. In this instance the acrylonitrile concentration of the calibration solution shall be comparable to that of the sample solution to be analysed.

Provided there is constancy of GC nitrogen detector sensitivity, calculate a calibration factor as follows:

$$f_{es} = \frac{C_{AN,cal}}{Y_{AN,cal} - Y_{AN,ctrl}}$$

where:

f_{es} is the calibration factor;

$C_{AN,\,cal}$ is acrylonitrile concentration of the calibration solution (fortified sample solutions from 6.2.3) in milligrams per litre or milligrams per kilogram;

$Y_{AN,\,cal}$ is the peak height or area corresponding to $C_{AN,cal}$;

$Y_{AN,ctrl}$ is the peak height or area resulting from control samples (6.2.4).

Calculate the acrylonitrile concentration of the test sample (6.2.2), in milligrams per litre or milligrams per kilogram, as follows:

$$C_{AN} = f_{es}(Y_{AN} - Y_{AN,ctrl}) \qquad \text{(B.1)}$$

where;

C_{AN} is the acrylonitrile concentration of the test sample in milligrams per litre or milligrams per kilogram;

f_{es} is the calibration factor, as given in equation (B.1). Use the mean value from several calibration solutions (6.2.3).

Y_{AN} is the peak height or area corresponding to C_{AN};

$Y_{AN,ctrl}$ is the peak height or area corresponding to the control.

When f_{es} is found to be concentration dependent apply an analogous graphical evaluation to Figure A.1 plotting the acrylonitrile peak area versus the acrylonitrile concentration, taking into consideration the note to 7.2.

Annex C
(normative)

Manual sample injection

In the case of non-availability of an automated headspace sampler, manual sample injection may be applied provided that the repeatability criterion stated in 8.3.2 is satisfied.

Performance of sample injection:

Equilibrate the sample solutions prepared according to 6.2.1 in a water bath for 2 h at a constant temperature between 55 °C and 70 °C (± 1 °C). Take an aliquot of 1 ml or 2 ml from the sample headspace with the aid of a prewarmed (100 °C) or heatable syringe pressing the plunger of the syringe when penetrating the septum and moving the plunger up and down several times before withdrawing the sample. Inject the aliquot into the GC. Keep the sample vial thermostated throughout this procedure.

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