SLOVENSKI STANDARD
SIST ENV 13130-4:2000

01-april-2000

Materiali in predmeti v stiku z živili - Snovi v plastiļnih masah, katerih koncentracija je omejena - 4. del: Doloļevanje 1,3-butadiena v plastiļnih masah

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 4: Determination of 1,3-butadiene in plastics

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Grenzwerten unterliegen - Teil 4: Bestimmung von 1,3-Butadien in Kunststoffen

Matériaux et objets en contact avec les denrées alimentaires - Matieres plastiques soumises a des limitations - Partie 4: Détermination du 1,3-butadiene dans les matieres plastiques

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English version

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 4: Determination of 1,3-butadiene in plastics

Matériaux et objets en contact avec les denrées alimentaires - Matières plastiques soumises à des limitations - Partie 4: Détermination du 1,3-butadiène dans les matières plastiques

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Grenzwerten unterliegen - Teil 4: Bestimmung von 1,3-Butadien 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
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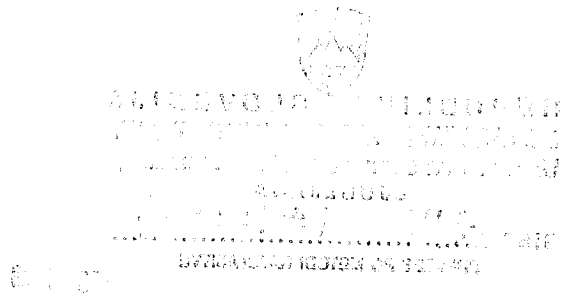

Foreword

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 13130-5	Determination of vinylidene chloride in food simulants
ENV 13130-6	Determination of vinylidene chloride in plastics
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).

Annexes A and B to this prestandard are 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: 1,3-Butadiene is a hazardous substance (carcinogenic) and gaseous at room temperature (boiling point - 4,4 °C/1013 mbar). All processes in which 1,3-butadiene can be liberated should therefore be carried out in a fume cupboard. Skin and eye contact with 1,3-butadiene solutions or the inhalation of 1,3-butadiene vapour should be avoided. Stock solutions and standard solutions should be prepared and stored in closed containers.

0 Introduction

1,3-Butadiene, CH_2=CH-CH=CH_2, is a monomer used in the manufacture of certain plastics materials and articles intended to come into contact with foodstuffs. During the manufacture of 1,3-butadiene copolymers, residual 1,3-butadiene monomer can remain in the polymer and can migrate into food coming into contact with the polymer.

The method described in this Part of this prestandard is to be used in conjunction with Part 1 of this prestandard, which describes the procedure required prior to determination of 1,3-butadiene. The method has been validated by a collaborative trial using acrylonitrile-butadiene-styrene copolymer (ABS).

1 Scope

This Part of this European Prestandard specifies a method for the determination of butadiene monomer in polymers.

The method is applicable to acrylonitrile-butadiene-styrene copolymer (ABS) and to high-impact polystyrene (HIPS) as well as to other 1,3-butadiene polymers and copolymers where these are soluble in N,N-dimethylacetamide or finely dispersed, swollen suspensions in N,N-dimethylacetamide. The level of 1,3-butadiene monomer determined is expressed as milligrams of 1,3-butadiene per kilogram of polymer. The method is appropriate for the quantitative determination of 1,3-butadiene at a level of 0,1 mg/kg in the polymer.

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 1,3-butadiene in a polymer is determined by headspace gas chromatography of the polymer sample dissolved in N,N-dimethylacetamide, applying automated sample injection and using flame ionization detection (FID). Quantification is achieved using n-pentane as an internal standard with calibration against polymer samples fortified with 1,3-butadiene according to the standard addition procedure.

If interferences are experienced with the internal standard, n-pentane, calibration is carried out by the external standardization as described in annex A.

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

Confirmation of 1,3-butadiene levels is carried out by combined gas chromatography/mass spectrometry (GC/MS).

4 Reagents

4.1 1,3-Butadiene, $CH_2=CH-CH=CH_2$, purity greater than 99.5 % (w/w).

4.2 n-Pentane, $CH_3-(CH_2)_3-CH_3$ containing no impurity at > 1 % by area which will elute at the same GC retention time as 1,3-butadiene.

4.3 N,N-Dimethylacetamide, $CH_3-CO-N(CH_3)_2$, $d^T = 0{,}9600 - 0{,}00094 * T$ (T: temperature in °C). The N,N-dimethylacetamide shall be free of any interferences (< 1 %) which elute at the same retention times as 1,3-butadiene and n-pentane peaks.

4.4 Prepare stock solutions of 1,3-butadiene in N,N-dimethylacetamide with defined concentrations in the range 5 mg/g to 10 mg/g as follows:

a) Weigh a 50 ml sample vial (5.4) including septum and cap to an accuracy of 0,01 mg. Pipette 50 ml N,N-dimethylacetamide (4.3) into the vial (5.4), close and weigh again to 0,01 mg. Insert hollow needles for introducing 1,3-butadiene and venting air and weigh again to 0,01 mg. Introduce, under a fume hood, 0,3 g to 0,5 g 1,3-butadiene (4.1) by bubbling through the N,N-dimethylacetamide. Re-weigh the vial plus needles to an accuracy of 0,01 mg and remove then the needles. Calculate the concentration in milligrams of 1,3-butadiene per gram of solution.

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

NOTE: The stock solutions may be stored at - 20 °C up to eight weeks protected from light in septum capped glass vials with minimum headspace; storage at 4 °C with the exclusion of light should not exceed one week.

4.5 Prepare standard solutions of 1,3-butadiene in N,N-dimethylacetamide with defined concentrations in the range of 0,01 mg/ml to 0,5 mg/ml corresponding to 0,2 µg/20 µl to 10 µg/20 µl (see NOTE: in 6.2.2) as follows:

a) Weigh a sample vial (5.3), including septum and cap, to an accuracy of 0,01 mg. Pipette 15 ml to 20 ml N,N-dimethylacetamide into the vial, close and weigh again to 0,01 mg. Add 0,2 ml to 5 ml of stock solution (4.4), mix thoroughly and re-weigh to an accuracy of 0,01 mg. Calculate the concentration in micrograms of 1,3-butadiene per gram of solution or in micrograms of 1,3-butadiene per 20 µl solution (calculate using density according to 4.3). To prepare diluted standard solutions repeat step 4.5.

b) Repeat item a) using the second stock solution prepared in 4.4b) to provide a second set of diluted standard solutions.

4.6 Dilute standard solution of n-pentane (4.2) in N,N-dimethylacetamide (4.3), with a known concentration of approximately 0,5 mg/ml to 2 mg/ml corresponding to 10 µg/20 µl to 40 µg/20 µl, prepared by following an analogous procedure to that described in 4.4 and 4.5.

4.7 Nitrogen, purified, 99,9999 %.

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 flame ionization detector and fitted with an automatic headspace sampler.

5.2 Gas chromatographic column, capable of the separation of N,N-dimethylacetamide from 1,3-butadiene and n-pentane such that the peaks of 1,3-butadiene and n-pentane 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 1,3-butadiene analysis:

a) 10 m x 0,32 mm internal diameter porous layer open tubular fused silica capillary column with 10 µm film thickness;

b) Packed pre-column 1 m x 2 mm uncoated silica beads, 100 mesh to 150 mesh, coupled with two packed columns in series 2 m x 2 mm, graphitized carbon (surface area approximately 10 m^2/g), 80 mesh to 100 mesh with 0,19 % picric acid;

c) 30 m x 0,53 mm internal diameter gas-solid capillary.

5.3 Glass sample vials, of 20 ml capacity or of another size suitable for the particular autosampler employed, with polytetrafluoroethylene-coated butyl or silicone rubber septa and aluminium crimp-closures.

5.4 Glass sample vials, of 50 ml capacity, with closures as in 5.3.

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

6 Samples

6.1 The laboratory samples of polymeric consumer articles to be analysed are obtained and stored as described in Part 1 of this prestandard.

6.2 Sample preparation for gas chromatography

NOTE: Since the determination of 1,3-butadiene in the polymer is to be performed only slightly above 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 (4.3) with purified nitrogen before filling with polymer and N,N-dimethylacetamide; b) store N,N-dimethylacetamide to be used for dissolving the polymer sample in a different laboratory to that used for preparation of stock and standard solutions to avoid cross-contamination by volatilization.

6.2.1 Test samples

Weigh a sample vial (5.3) including septum and cap to an accuracy of 1 mg. Weigh into the vial 1,00 g ± 0,01 g of sample material. Pipette into the vial 5,00 ml of N,N-dimethylacetamide, add then 20 µl internal standard solution (4.6) to the N,N-dimethylacetamide in the vial using the 50 µl syringe (5.5) and close the vial with septum and cap. To dissolve the sample, let the vial stand over night at room temperature under gentle shaking, if necessary followed by warming up.

6.2.2 Calibration samples for the standard addition method

Proceed as described in 6.2.1. Prior to dissolving the sample by shaking, use the 50 µl syringe to introduce 20 µl of standard 1,3-butadiene solution (4.5) through the septum and mix thoroughly.

NOTE: To make sure that the calibration range has a reasonable order of magnitude compared to the sample concentrations, 20 µl of the highest concentrated standard solution should contain not more than 10 µg 1,3-butadiene.

6.2.3 Blank samples

To a sample vial (5.3) add 5,00 ml of N,N-dimethylacetamide. Seal vial with cap and septum.

7 Procedure

7.1 GC preparation

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

NOTE: For guidance, the parameters established for a GC equipped with column a), see NOTE under 4.2, are given:

Transfer line temperature	150 °C
Column oven temperature	isothermal at 50 °C for 10 min, 50 °C to 220 °C at 5 °C/min, isothermal at 220 °C for 15 min
Detector temperature	250 °C
Carrier gas	Helium Column pre-pressure 0,6 bar Volume from split outlet 20 ml/min
FID gases optimized according to the manufacturer's specifications	

7.2 Performance of GC measurements

Each sample has to be determined at least in duplicate, i.e. as a pair of measurements.

The same conditions shall be maintained throughout the measurement of all samples prepared in 6.2.

When starting measurements, baseline stability and response linearity of the detector shall be examined.

Equilibrate the sample solutions prepared according to 6.2 in the thermostat of the automated headspace sampler for 60 min at 90 °C ± 1 °C before sampling (time 12 sec) and commencing the analysis programme.

Identify the 1,3-butadiene and n-pentane peaks on the basis of their retention times and measure the respective peak heights or read the computer print-out peak areas.

Under the conditions given in 7.1, the retention time of 1,3-butadiene was 15 min and that for n-pentane 24 min.

When assigning the peaks, attention has to be paid to possible interference with other C4-compounds. In preliminary experiments, it was observed that the 1,3-butadiene peak can be overlapped by:

- trans-butene when the packed column described in NOTE b) to 5.2 is used;

- 1-butene and iso-butane when the capillary column described in NOTE a) to 5.2 is used for the described method.