SLOVENSKI STANDARD
SIST ENV 13130-8:2000

01-april-2000

Materiali in predmeti v stiku z živili - Snovi v plastičnih masah, katerih koncentracija je omejena - 8. del: Določevanje izocianatov v plastičnih masah

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 8: Determination of isocyanates in plastics

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 8: Bestimmung von Isocyanaten in Kunststoffen

Matériaux et objets en contact avec les denrées alimentaires - Matieres plastiques soumises a des limitations - Partie 8: Détermination des isocyanates dans les matieres plastiques

Ta slovenski standard je istoveten z: **ENV 13130-8:1999**

ICS:

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

SIST ENV 13130-8:2000 **en**

EUROPEAN PRESTANDARD
PRÉNORME EUROPÉENNE
EUROPÄISCHE VORNORM

ENV 13130-8

March 1999

ICS 67.250

English version

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 8: Determination of isocyanates in plastics

Matériaux et objets en contact avec les denrées alimentaires - Matières plastiques soumises à des limitations - Partie 8: Détermination des isocyanates dans les matières plastiques

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 8: Bestimmung von Isocyanaten 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.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

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

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

Ref. No. ENV 13130-8:1999 E

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 od 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 13130-6	Determination of vinylidene chloride in plastics
ENV 13130-7	Determination of monoethylene glycol and diethylene glycol in food simulants

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: Isocyanates are hazardous substances, and some (e.g. 2,4 and 2,6-toluene diisocyanate) are carcinogenic. They are also suspected of causing sensitization. Handling and preparation of standard solutions should be undertaken in a fume hood. Skin and eye contact with isocyanates and inhalation of vapour, should be strictly avoided.

0 Introduction

Isocyanates, characterised by the -NCO group, are monomers used for the manufacture of materials and articles intended to come in contact with food. During manufacture residual isocyanates can remain in the polymer and may migrate into food coming into contact with the polymer

1 Scope

This Part of this European Prestandard describes a method for the determination of individual and total levels of residual isocyanates in plastics materials and articles.

This method is applicable to the analysis of polyurethane polymers. The total level of isocyanate monomers in materials and articles determined according to the procedure described in this prestandard is given in milligrams of NCO per kilogram of material or article. The method is capable of quantitative determination of individual isocyanates measured as NCO at 0,04 mg/kg and total isocyanates at 1,0 mg/kg.

NOTE: The method has been applied to the analysis of 9 isocyanate monomers listed in 3.1. It has not been applied to the analysis of octadecyl isocyanate, diphenylether-4,4'-diisocyanate or 3,3'-dimethyl-4,4'-diisocyanatobiphenyl as samples of these monomers have not been obtained. There is no reason to anticipate that the method may not be suitable for the analysis of these monomers also.

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 procedure consists of two parts: screening and, if necessary, quantitative determination. Quantitative determination is applied only if isocyanates are detected by the screening procedure.

Materials and articles are initially screened for residual isocyanates by solvent extraction with dichloromethane and concurrent derivatisation with 9-(methylaminomethyl)anthracene. 1-Naphthyl isocyanate is used during the screening procedure to check that the derivatization procedure has been successful. The resultant fluorescent derivatives are analysed by high performance liquid chromatography with fluorescence detection.

Materials found to contain residual isocyanates are quantified by standard addition to the material or article under test, using 1-naphthyl isocyanate as internal standard.

If interferences are experienced with the internal standard then calibration is carried out by standard addition omitting the internal standard, as described in annex A.

Confirmation of isocyanate levels is carried out by re-analysing the sample extracts on an HPLC column with different elution characteristics.

4 Reagents

NOTE: Isocyanates react extremely rapidly with moisture. Suitable precautions should be taken to ensure all glassware is dry. All laboratory glassware should be rinsed with diethyl ether (4.2.2) and baked at 105°C overnight before use. After baking, vials should be placed in a desiccator and stored until required. Isocyanate standards should be protected from moisture and stored under refrigeration at -20 °C.

All reagents should be of recognised analytical quality, unless otherwise specified.

4.1 Analytes

4.1.1 2,6-toluene diisocyanate $CH_3C_6H_3(NCO)_2$

4.1.2 diphenylmethane-4,4'-diisocyanate $OCNC_6H_4CH_2C_6H_4NCO$

4.1.3 2,4-toluene diisocyanate $CH_3C_6H_3(NCO)_2$

4.1.4 hexamethylene diisocyanate $OCNC_6H_{12}NCO$

4.1.5 cyclohexyl isocyanate $C_6H_{11}NCO$

4.1.6 1,5-naphthalene diisocyanate $C_{10}H_6(NCO)_2$

4.1.7 diphenylmethane-2,4'-diisocyanate $OCNC_6H_4CH_2C_6H_4NCO$

4.1.8 2,4-toluene diisocyanate dimer

4.1.9 phenyl isocyanate C_6H_5NCO

4.1.10 1-naphthyl isocyanate (internal standard, $C_{10}H_7NCO$), which contains no impurity at > 1 % by area which will elute at the same retention time as any of the nine individual isocyanate derivatives.

All standards should be of > 99 % purity.

4.2 Reagents

4.2.1 Dichloromethane (DCM, CH_2C_{12}), <30 ppm H_2O, containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks. DCM should be dried over a bed of molecular sieve (5 Å) for 24 h prior to use.

4.2.2 Diethylether ($(C_2H_5)_2O$), at least 99 % purity.

4.2.3 9-(Methylaminomethyl)anthracene (MAMA, $CH_3NHCH_2C_{14}H_9$), containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks.

4.2.4 N,N'-Dimethylformamide ($HCON(CH_3)_2$), containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks.

4.2.5 Individual stock standard solutions (1000 µg/ml)

Weigh 0.01 g of isocyanate standard (4.1), to an accuracy of 0,1 mg, in a 10 ml volumetric flask. Rapidly make-up to the mark with DCM (4.2.1) and shake thoroughly. Ultrasonification may be used as an aid to dissolution. Repeat the procedure to provide a second stock solution.

4.2.6 Individual intermediate standard solutions (100 ug/ml)

Put approximately 5 ml DCM (4.2.1) into a 10 ml volumetric flask. Using a 1000 µl syringe, dispense 1000 µl of stock solution (4.2.5) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly. Repeat the procedure using the second stock solution (4.2.5) to provide a second intermediate standard solution.

4.2.7 Individual dilute standard solutions (1 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 100 µl syringe, dispense 100 µl of intermediate standard solution (4.2.6) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

NOTE: Individual dilute standard solutions should be prepared for each isocyanate (4.1).

4.2.8 Internal standard stock solution (1000 µg/ml).
Weigh 0,01 g of 1-naphthyl isocyanate (4.1.10), to an accuracy of 0,1 mg, into a 10 ml volumetric flask. Rapidly make-up to the mark with DCM (4.2.1) and shake thoroughly. Ultrasonification may be used as an aid to dissolution.

4.2.9 Intermediate internal standard solution (100 µg/ml).

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 1000 µl syringe, dispense 1000 µl of internal standard stock solution (4.2.8) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

4.2.10 Dilute internal standard solution (1 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 100 µl syringe, dispense 100 µl of intermediate internal standard solution (4.2.9) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

NOTE: Stock and standard solutions (4.2.5 to 4.2.10) should be stored with the exclusion of light and moisture at - 20 °C. They are stable for up to 1 month under these conditions.

4.2.11 Derivatization reagent solution (0,26 mg/ml)

Weigh 0,013 g of MAMA (4.2.3), to an accuracy of 0,1 mg, into a 50 ml volumetric flask. Make-up to the mark with DCM (4.2.1) and shake thoroughly.

NOTE: Derivatization reagent has to be prepared fresh daily, because of the photo-instability of MAMA, and stored with the exclusion of light.

4.2.12 Derivative dissolution solvent

Using a measuring cylinder, dispense 50 ml N,N'-dimethylformamide (4.2.4) into a 100 ml volumetric flask, make-up to the mark with the requisite HPLC mobile phase (7.1.5) and mix thoroughly.

4.2.13 Preparation of individual isocyanate derivatives for HPLC peak assignment

Using a 100 µl syringe, dispense 100 µl of dilute isocyanate standard solution (4.2.7) into a vial (5.3). Using a 1 ml syringe dispense 1 ml of derivatization reagent solution (4.2.11) into the same vial. Cap, gently agitate to mix the contents, and allow to stand for 60 min with the exclusion of light. Evaporate the vial contents to dryness under a stream of nitrogen, add 10 ml derivative dissolution solvent (4.2.12) and mix thoroughly. Ultrasonification may be used as an aid to dissolution.

Repeat for each isocyanate, using the individual dilute solutions (4.2.7).

NOTE: Derivative solutions should be stored with the exclusion of light at ambient temperature. They are stable for up to two weeks under these conditions.

Repeat the procedure with the dilute internal standard solution (4.2.10).

5 Apparatus

An instrument or piece of apparatus is mentioned only if it is special, or made to particular specifications. Usual laboratory equipment is assumed to be available.

NOTE: The MAMA-isocyanate derivatives are not sensitive to moisture and so glassware used for operations involving the derivatives need not be especially dried before use.

5.1 High performance liquid chromatograph, equipped with a fluorescence detector

Excitation Wavelength - 254 nm
Emission Wavelength - 412 nm

5.2 Chromatographic column

The column has to permit the separation of each of the MAMA derivatives of the nine individual isocyanates from one another as well as from that of the MAMA derivative of the internal standard. The peaks of the isocyanate standard derivatives and that of the internal standard derivative shall not overlap by more than 1 % of peak area with each other and with peaks resulting from other compounds.

The following are examples of HPLC columns found suitable for analysis of isocyanate derivatives:

a) 250 mm x 4,6 mm stainless steel column packed with silica, 5 µm particle size, 80 Å pore size, 220 m²/g surface area, octadecyl silyl bonded phase, 7 % carbon loading, partially end-capped;

b) 125 mm x 3,0 mm stainless steel columns packed as for a);

c) 250 mm x 4,6 mm stainless steel column packed with silica, 5 µm particle size, 120 Å pore size, 200 m²/g surface area, octadecyl silyl bonded phase, 11 % carbon loading, end-capped;

d) 250 mm x 4,0 mm stainless steel column packed as for c);

e) 125 mm x 4,0 mm stainless steel column packed with silica 5 µm particle size, 60 Å pore size, 220 m²/g surface area, octasilyl bonded phase, 11.5 % carbon loading, partially end-capped.

5.3 Glass vials

20 ml capacity with polytetrafluoroethylene-faced butyl rubber septa and aluminium crimp caps. Vials should be rinsed with diethyl ether (4.2.2), baked at 105 °C overnight and then stored in a desiccator until required for use.

NOTE: Erlenmayer flasks, with a capacity of 25 ml, with ground glass joints may be used instead of 20 ml vials. They should be washed, dried and stored as for glass vials.

5.4 Glass sample vials suitable for the HPLC system employed.

5.5 Glass barrel syringes with needles, with capacities of 5 µl, 10 µl, 50 µl, 100 µl, 250 µl, 500 µl and 1000 µl.

6 Samples

The laboratory samples of polymer materials or articles, to be analysed are obtained and stored as described in Part 1 of this prestandard.

The samples of plastics to be analysed have to be representative of the material, or article, presented for analysis.

The following precautions are advisable:

a) to avoid cross contamination, carry out preparation of the polymer samples in an area remote to that used for handling isocyanate and MAMA solutions;

b) to avoid loss of isocyanates through hydrolysis, carry out preparation of the polymer samples in an area of low relative humidity and away from sources of moisture;

c) ensure that all glassware and syringes are dry before use.

7 Procedure

7.1 Test sample screening

7.1.1 Test sample extraction and derivatization

Using a representative sample, weigh 1 g, to an accuracy of 5 mg, of the test material or article into a vial (5.3), cutting into small pieces where possible. Add 10 ml of DCM (4.2.1) followed by 80 µl of dilute internal standard solution (4.2.10) and 1 ml of derivatizing reagent (4.2.11). Seal the vial and shake for 12 h on an orbital shaker. Using a Pasteur pipette, transfer the solvent extract to a clean dry vial and reduce in volume to about 5 ml under a gentle stream of nitrogen. Seal the vial and store at - 20 °C. Add a further 10 ml of DCM to the extracted test pieces, seal the vial and shake for a further 12 h on an orbital shaker. Remove the solvent extract and combine with the first extract. Evaporate the vial contents to dryness under a gentle stream of nitrogen. Add 10 ml of derivative dissolution solvent (4.2.12) and mix thoroughly. Ultrasonification may be used to aid dissolution. Filter through a 0,45 µm syringe filter (pre-purged with 2 ml HPLC mobile phase (7.1.5)) and transfer to an HPLC sample vial.

Prepare a second derivatized sample extract.

NOTE: The MAMA derivatization reagent is photosensitive. Conduct the concurrent extraction/derivatization with the exclusion of light.

7.1.2 Preparation of reagent blank sample

Prepare as in 7.1.1 but omit the addition of the polymer sample.

7.1.3 Preparation of internal standard check sample

Prepare as in 7.1.1 but omit the addition of the internal standard.

7.1.4 Preparation of un-derivatized sample blank

Prepare as in 7.1.1 but omit the addition of the derivatizing reagent and the internal standard.

7.1.5 Chromatographic determination

Depending on the type of chromatograph, column and detector used for the determination, the appropriate operational parameters should be established.

NOTE 1: The range of parameters which has been employed for the column a) (5.2) is as follows:

Mobile phase: Prepare a solution of 3 % triethylamine ($(C_2H_5)_3N$) w/v in water. Mix with acetonitrile to give 80/20 v/v acetonitrile(CH3CN)/water. Adjust to pH 3,0 with orthophosphoric acid (H_3PO_4).

Flow rate	1 ml/min
Injection volume	20 µl
Temperature	ambient

Other conditions which have been found to be suitable for the chromatographic separation of isocyanates are as follows:

Column: d) (5.2)

Mobile phase A - 90/10 v/v water/acetonitrile (0,2 % tetrabutylammoniumhydrogen sulphate).

Mobile phase B - 10/90 v/v water/acetonitrile (0,2 % tetrabutylammoniumhydrogen sulphate).

Flow rate	1,5 ml/min.
Injection volume	10 µl

For advice on a suitable gradient profile see figure C.

NOTE 2: If problems are experienced with stabilisation of retention times, the HPLC column may be operated in an oven or heating block at 40 °C.

7.1.5.1 Inject the individual isocyanate derivatives (4.2.13) to establish retention times of analytes and the internal standard derivative (4.2.13) under the chosen conditions.

NOTE 1: A typical chromatogram is shown in figure B.

Inject the reagent blank sample (7.1.2), the internal standard check samples (7.1.3) and the un-derivatized sample blank (7.1.4) under the same chromatographic conditions.

NOTE 2: If peaks from the reagent blank sample (7.1.2) and the un-derivatized sample blank (7.1.4) co-elute with those of the isocyanate derivatives, adjust the mobile phase to effect separation. Use caution when making adjustments as small changes, e.g.> 2 %, in composition can have a large effect on the elution time of some isocyanate derivatives. Separation may also be effected by using an alternative HPLC column.

7.1.5.2 Inject the derivatized sample extracts (7.1.1) and establish from retention times whether one or more of the isocyanate derivatives are present. The signal:noise ratio for the internal standard derivative has to exceed 3:1 as an indication that the derivatization and analysis has been successful.

If one or more isocyanate(s) is/are identified, it/they have to be quantified by the method of standard addition (7.2).

If isocyanate derivatives are identified in the sample and the internal standard check sample shows an interference at the retention time of the internal standard, isocyanates shall be quantified by standard addition, omitting the internal standard (see annex A).

NOTE: If no isocyanate derivative peaks are detected at the expected retention times of the standard isocyanate derivatives and the derivatization has been shown to be successful then the test sample may be assumed to contain no individual isocyanate (as NCO) at > 0,04 mg/kg.