SLOVENSKI STANDARD
SIST ENV 13130-7:2000

01-april-2000

Materiali in predmeti v stiku z ģivili - Snovi v plastiļ nih masah, katerih koncentracija je omejena - 7. del: Doloļ evanje monoetilen glikola in dietilen glikola v modelnih raztopinah ģivil

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 7: Determination of monoethylene glycol and diethylene glycol in food simulants

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Grenzwerten unterliegen - Teil 7: Bestimmung von Monoethylenglycol und Diethylenglycol in Prüflebensmitteln

Matériaux et objets en contact avec les denrées alimentaires - Matieres plastiques soumises a des limitations - Partie 7: Détermination du monoéthylene glycol et du diéthylene glycol dans les simulants

Ta slovenski standard je istoveten z: **ENV 13130-7:1999**

ICS:

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

SIST ENV 13130-7:2000 **en**

EUROPEAN PRESTANDARD
PRÉNORME EUROPÉENNE
EUROPÄISCHE VORNORM

ENV 13130-7

March 1999

ICS 67.250

English version

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 7: Determination of monoethylene glycol and diethylene glycol in food simulants

Matériaux et objets en contact avec les denrées alimentaires - Matières plastiques soumises à des limitations - Partie 7: Détermination du monoéthylène glycol et du diéthylène glycol dans les simulants

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Grenzwerten unterliegen - Teil 7: Bestimmung von Monoethylenglycol und Diethylenglycol in Prüflebensmitteln

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
EUROPÄISCHES KOMITEE FÜR NORMUNG

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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 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 13130-4	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 13130-8	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).

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.

0 Introduction

Monoethylene glycol (MEG) is a monomer used in the manufacture of plastics materials and articles intended to come into contact with foodstuffs. Residues of monoethylene glycol and diethylene glycol can remain in the plastic after processing to form materials and articles for food contact use, and can migrate into foodstuffs. EC Directive 90/128/EEC lists a combined specific migration limit of 30 mg/kg (T) of monoethylene glycol and diethylene glycol in foods or food simulants.

1 Scope

This Part of this European Prestandard specifies methods for the determination of monoethylene glycol and diethylene glycol in the four conventional EC food simulants; water, 3 % w/v acetic acid, 15 % v/v ethanol and olive oil (or approved substitutes sunflower oil or mixture of synthetic triglycerides). The methods are capable of determining monoethylene glycol and diethylene glycol in food simulants separately, or combined, at the specific migration limit SML (T) of 30 mg/kg.

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.

ISO 385-1	Laboratory glassware - Burettes - Part 1: General requirements
ISO 385-2	Laboratory glassware - Burettes - Part 2: Burettes for which no waiting time is specified
ISO 385-3	Laboratory glassware - Burettes - Part 3: Burettes for which a waiting time of 30s is specified
ISO 648:1977	Laboratory glassware - One mark pipettes
ISO 1042:1983	Laboratory glassware - One neck volumetric flasks
ISO 4788:1980	Laboratory glassware - Graduated measuring cylinders
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

After addition of an internal standard the aqueous food simulants or the olive oil water extract is directly injected for gas chromatographic analysis using a cold on-column injector. Detection limits are approximately 1 mg/kg in the food simulants. The concentrations of monoethylene glycol and diethylene glycol are measured by comparison of peak height or area ratios against standards.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water of equivalent purity.

4.1 Methanol

4.2 Monoethylene glycol

4.3 Diethylene glycol

4.4 Butan-1,4-diol, internal standard

4.5 Water (HPLC or deionized)

4.6 Heptane

4.7 Prepare a monoethylene glycol and diethylene glycol standard stock solution as follows:

Weigh accurately about 0,75 g each of monoethylene glycol and diethylene glycol into a beaker, dissolve in methanol and transfer with washings to a 100 ml volumetric flask. Dilute to the mark with methanol. This solution is stable for 1 month if stored in the dark at 5 °C in a stopped flask. Prepare a second stock solution for validation purposes, see 7.2.2.

4.8 Prepare a butan-1,4-diol internal standard stock solution as follows:

Weigh about 1 g of butan-1,4-diol into a beaker, dissolve in methanol and make up to 100 ml mark with methanol in a volumetric flask. This solution is stable for 1 month if stored in the dark at 5 °C in a stoppered flask.

5 Apparatus

5.1 Analytical balance capable of weighing to 0,1 mg.

5.2 Graduated pipettes, conforming to the minimum requirements of ISO 835 and of 1 ml and 2 ml capacity.

5.3 Burette, conforming to the minimum requirements of ISO 385 and of 25ml capacity.

5.4 Volumetric flasks, conforming to the minimum requirements of ISO 1042 and of 25 ml, 50 ml and 100 ml capacity.

5.5 Separating funnels with polytetrafluoroethylene stopcock, of 250 ml capacity.

5.6 Glass syringe, of 50 ml capacity.

5.7 0,2 µm disposable HPLC filters, or disposable C18 solid phase extraction cartridges 400 mg size.

5.8 Measuring cylinders, conforming to the minimum requirements of ISO 4788 and of 25 ml and 50 ml capacity.

5.9 Gas chromatograph (GC) fitted with a flame ionization detector (FID) and a cold on-column injector.

NOTE: This method has been developed for use with cold on-column injectors, which are available from all major GC suppliers. Previous studies at other laboratories have shown that split/splitless

injection gives unreliable results. Higher than optimum carrier gas flow rates have been found to give less peak tailing and increased column lifetime for polyethylene glycol stationary phases. The GC column should be capable of resolving monoethylene glycol, diethylene glycol and butan-1,4-diol afrom each other, and from ethanol and acetic acid present in the simulants. GC capillary columns using a polyethylene glycol stationary phase have been found to be most suitable for example:

a) 15 m X 0,53 mm internal diameter, film thickness 1 µm;

Temperature	100 °C hold 2 min ramped to 150 °C at 10 °C/min, hold 4 min;
Carrier gas	Helium 50 KPa, 18 ml/min;
Detector	Flame ionization detector 250 °C;
Injector	Cold on-column.

The retention times are monoethylene glycol, 4,0 min, butan-1,4-diol , 7,5 min and diethylene glycol, 8,1 min.

b) 12 m X 0,32 mm internal diameter, film thickness 1 µm;

Temperature	100 °C hold 1 minute ramped to 200 °C hold 1 minute at 10 °C/min;
Carrier gas	Helium 70 KPa, 7 ml/min;
Detector	Flame ionization detector 250 °C;
Injector	Cold on-column.

The retention times are monoethylene glycol, 3,8 min, butan-1,4-diol, 7,0 min and diethylene glycol, 7,6 min, and a typical GC chromatogram is given in annex A.

6 Samples

The food simulant samples for testing shall have been prepared as described in Part 1 of this prestandard. Blank samples of the food simulants are also required.

For each simulant, 50 ml samples are required for each test.

7 Procedure

7.1 Preparation of standards

7.1.1 Intermediate standards

Into each of five 25 ml volumetric flasks pipette 2 ml of the stock butan-1,4-diol solution. Add, using a burette or graduated pipettes, 0,5 ml, 1,0 ml, 2,5 ml, 5 ml and 10 ml of the stock monoethylene glycol/diethylene glycol solution and dilute to the mark with methanol to give 150 mg/l, 300 mg/l, 750 mg/l, 1500 mg/l and 3000 mg/l monoethylene glycol and diethylene glycol respectively. These standards are stable for 1 month if stored in the dark at 5 °C in stoppered flasks.

7.1.2 Internal standard, 800 mg/l butan-1,4-diol

Pipette 2 ml of the stock butan-1,4-diol solution into a 25 ml volumetric flask and dilute to the mark with methanol. This solution is stable for 1 month if stored in the dark at 5 °C in a stoppered flask.

7.1.3 Working standards for aqueous simulants

Fill each of five 50 ml volumetric flasks to the graduation mark with water and add, by pipette, 1 ml of each intermediate standard. Mix thoroughly to give, nominally, working standards containing 3 mg/l, 6 mg/l, 15

mg/l, 30 mg/l and 60 mg/l monoethylene glycol and diethylene glycol respectively. To a further 50 ml volumetric flask filled to the mark with water add, by pipette, 1 ml of the internal standard 800 mg/l butan-1,4-diol and mix well to act as a blank.

7.1.4 Working standards for olive oil

Using a measuring cylinder, pour 50 ml ± 1 ml of the olive oil blank simulant into a 250 ml separating funnel. Add, by pipette, 1 ml of the first intermediate standard, mix well and add 50 ml ± 2 ml of heptane from the measuring cylinder (this transfers any remaining olive oil). Mix and add 20 ml ± 1 ml of water using a measuring cylinder, shake vigorously for 1 min and allow 5 min to 10 min for the layers to separate.

NOTE 1: This can be facilitated by holding the separating funnel at an angle of about 45 °C and slowly rotating it.

Run off the lower aqueous layer into a 100 ml beaker and re-extract the olive oil with a further 20 ml ± 1 ml of water. Allow the phases to separate and run off the lower layer into the beaker to combine the extracts. Pass about 2 ml of the aqueous solution through a disposable filter, using a syringe, and collect the filtrate.

Repeat this process for each intermediate standard and the internal standard to act as a blank. These standards correspond to 0 mg/l, 3 mg/l, 6 mg/l, 15 mg/l, 30 mg/l and 60 mg/l monoethylene glycol and diethylene glycol.

NOTE 2: A C18 solid phase extraction cartridge can also be effectively used for removal of oil droplets.

7.2 Preparation of calibration graphs

7.2.1 Injection of standards

Inject a suitable quantity, 0,5 µl to 1 µl, of each standard and measure the peak heights or areas. Divide the monoethylene glycol and diethylene glycol peak height/areas by the butan-1,4-diol peak height/area and plot this ratio against monoethylene glycol and diethylene glycol concentration. The calibration graph shall be linear with a correlation coefficient better than 0,998. Calculate the slope and intercept on the y axis from the line of best fit.

7.2.2 Validation of stock monoethylene glycol/diethylene glycol solution

Dilute the second stock standard monoethylene glycol/diethylene glycol prepared in 4.7 to give a 750 mg/l intermediate standard as described in 7.1.1, and dilute again to obtain a 15 mg/l working standard described in 7.1.3. Inject this working standard, in duplicate, for GC analysis and calculate the monoethylene glycol/butan-1,4-diol and diethylene glycol/butan-1,4-diol peak area ratios. Calculate the mean concentrations of monoethylene glycol and diethylene glycol found in the validation working standard using the slope and intercept values obtained in 7.2.1, correcting for the masses of monoethylene glycol and diethylene glycol used to prepare the first stock solution. The mean concentrations shall be within ± 1 mg/l of the actual monoethylene glycol and diethylene glycol concentrations present in the validation working standard calculated from the masses of monoethylene glycol and diethylene glycol used to prepare the second stock standard. If the concentrations found are not within ± 1 mg/l, reject all solutions and start again.

7.3 Extraction of olive oil simulant migration test samples

Pour the olive oil samples directly from the migration cell or containers into a dry 50 ml measuring cylinder until the 50 ml ± 1 ml mark is reached. Pour the olive oil into a 250 ml separating funnel. Add by pipette 1 ml of the internal standard solution (800 mg/l, butan-1,4-diol) and mix thoroughly. Rinse the measuring cylinder with 50 ml ± 2 ml heptane and transfer to the separating funnel. Extract twice with water as described in 7.1.4.