SLOVENSKI STANDARD
SIST-TS CEN/TS 13130-20:2005

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Materiali in predmeti v stiku z živili - Snovi v polimernih materialih, katerih koncentracija je omejena - 20. del: Določevanje epiklorohidrina v polimernih materialih

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 20: Determination of epichlorohydrin in plastics

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 20: Bestimmung von Epichlorhydrin in Kunststoffen

Matériaux et objets en contact avec les denrées alimentaires - Substances dans les matieres plastiques soumises a des limitations - Partie 20 : Détermination de l'épichlorohydrine dans les matieres plastiques

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Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 20: Determination of epichlorohydrin in plastics

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This Technical Specification (CEN/TS) was approved by CEN on 16 December 2004 for provisional application.

The period of validity of this CEN/TS 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 CEN/TS can be converted into a European Standard.

CEN members are required to announce the existence of this CEN/TS in the same way as for an EN and to make the CEN/TS available promptly at national level in an appropriate form. It is permissible to keep conflicting national standards in force (in parallel to the CEN/TS) until the final decision about the possible conversion of the CEN/TS into an EN is reached.

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Foreword

This document (CEN/TS 13130-20:2005) 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 EN 13130 has been prepared within the Standards, Measurement and Testing project, MAT1-CT92-0006, “*Development of Methods of Analysis for Monomers*” and has been prepared by Subcommittee (SC 1) of TC 194 "Utensils in contact with food" as one of a series of test methods for plastics materials and articles in contact with foodstuffs.

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.

This part of EN 13130 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 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 3: *Determination of acrylonitrile in food and 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-trimethylolpropane in food simulants*

Parts 1 to 8 are European Standards. Parts 9 to 28 are Technical Specifications.

WARNING All chemicals are hazardous to health to a greater or lesser extent. It is beyond the scope of this Technical Specification to give instructions for the safe handling of all chemicals, that meet, in full, the legal obligations in all countries in which this Technical Specification may be followed. Therefore, specific warnings are not given and users of this Technical Specification should ensure that they meet all the necessary safety requirements in their own country.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this CEN Technical Specification: 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

Epichlorohydrin, 1-chloro-2,3-epoxypropane, C_3H_5OCl, PM/Ref. No 16750, is a monomer used in the manufacture of certain plastics materials and articles, but mainly coatings intended to come into contact with foodstuffs.

After manufacture residual epichlorohydrin can remain in the finished product and may migrate into foodstuffs coming into contact with that product.

This analytical method allows the determination of the residual content of epichlorohydrin in coatings.

The method has been pre-validated by collaborative trial with two laboratories.

NOTE A limit on the residual quantity of 1 mg/kg polymer in final product has been set. However, epichlorohydrin is mainly used in coatings on non-plastics substrates. The amount of coating on a final article, e.g. coated cans, cannot be determined with an acceptable accuracy. Therefore, the residual content of epichlorohydrin in coatings cannot be determined. The area of a coating is easy to determine and so the amount of residual epichlorohydrin content can be determined in milligrams per square decimetre.

1 Scope

This document, part of EN 13130, specifies an analytical procedure for the determination of residual epichlorohydrin in coatings.

The method is appropriate for the quantitative determination of epichlorohydrin in the analyte concentration range of 5 ng/ml to 80 ng/ml of extract. In general this allows for the detection of epichlorohydrin at the level of 1 mg/kg of polymer or in the case of coatings, where the amount of polymer cannot be determined, detection of 1 µg epichlorohydrin per square decimetre of coating is feasible.

In order to obtain reliable and reproducible results, it is essential that the method described in this part of EN 13130 is followed as closely as possible.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

To determine the residual amount of epichlorohydrin in a coating, the sample material is extracted with dioxane for 6 h at room temperature. Subsequently, the extract is distilled by means of a micro-distillation. The concentration of epichlorohydrin in the distilled fraction thus obtained is determined by derivatization of the epoxide with an aromatic sulfonic acid, i.e. 9,10-dimethoxyanthracene-2-sulfonic acid (DAS), followed by reversed phase high performance liquid chromatography (HPLC) with fluorescence detection. Depending on the quality and type of the HPLC column, it is possible to separate the two isomers that are formed in the derivatization reaction of epichlorohydrin with DAS. Quantification is achieved by means of external standard calibration using dioxane solutions fortified with known amounts of epichlorohydrin.

Confirmation of epichlorohydrin is carried out by normal phase HPLC with fluorescence detection.

4 Reagents

NOTE All reagents should be of recognized analytical quality unless otherwise stated.

4.1 Analyte

4.1.1 Epichlorohydrin (C_3H_5OCl), purity > 99 %.

4.2 Chemicals

4.2.1 Acetonitrile (HPLC grade).

4.2.2 9,10-Dimethoxyanthracene-2-sulfonic acid sodium salt, i.e. DAS-Na, $C_{16}H_{13}NaO_5S$.

4.2.3 Dioxane > 99,5 %, absolute; over molecular sieve (H_2O < 0,01 %).

4.2.4 Hexane

4.2.5 Cation exchange resin, strongly acid with sulfonic acids as functional groups, ion form H^+.

4.2.6 Isopropanol

4.2.7 Methanol

4.2.8 Water, deionized (HPLC quality).

4.3 Preparation of the DAS reagent

Dissolve approximately 100 mg DAS-Na (4.2.2) in 20 ml methanol/water (80/20). Heat the solution slightly to obtain a clear solution. In a glass beaker, wash an amount of the ion exchange resin (4.2.5) with methanol/water (80/20) and subsequently pour the slurry into a glass column with a diameter of 1 cm, until the resin has reached a height of ± 20 cm. Elute the DAS solution through the ion exchange resin and flush the column with a mixture of methanol/water (80/20). Start to collect the eluate at the moment the eluate has decreased to a pH of approximately pH 1 to pH 2. Continue collecting the eluate until the pH starts to increase. Evaporate the solution thus obtained to dryness by means of a nitrogen stream.

NOTE The dry residue should be protected from light and is stable for at least 1 year.

WARNING Do not deviate from the prescribed ratio of DAS-Na versus ion exchange resin.

4.4 Solutions

4.4.1 Stock solution of epichlorohydrin in dioxane (1 mg/ml)

Weigh to the nearest 0,1 mg approximately 50 mg of epichlorohydrin (4.1.1) in a 50 ml volumetric flask. Make up to the mark with dioxane (4.2.3) and mix thoroughly.

Calculate the exact concentration in milligrams of epichlorohydrin per millilitre of solution.

Repeat the procedure to obtain a second stock solution.

NOTE The solutions can be stored in closed containers in dark for a maximum period of 3 months at any temperature between - 20 °C and + 20 °C.

4.4.2 Diluted stock solutions of epichlorohydrin in dioxane (0,04 mg/ml)

Pipette 2 ml of the stock solution (4.4.1) into a 50 ml volumetric flask. Make up to the mark with dioxane and mix thoroughly.

Calculate the exact concentration in milligrams of epichlorohydrin per millilitre of solution.

Repeat the procedure using the second stock solution to obtain a second diluted stock solution.

4.4.3 Standard solutions of epichlorohydrin in dioxane

Pipette into a series of 25 ml volumetric flasks, 0 ml, 0,5 ml, 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of the diluted stock solution (4.4.2). Make up to the mark with dioxane and mix carefully.

The standard solutions thus obtained contain approximately 0 µg, 0,8 µg, 1,6 µg, 3,2 µg, 4,8 µg, 6,4 µg or 8,0 µg epichlorohydrin per millilitre.

Calculate the exact concentrations in micrograms of epichlorohydrin per millilitre of solution.

Repeat the procedure using the second diluted stock solution to obtain a second series of standard solutions.

4.4.4 DAS solution in acetonitrile (5 mg/ml)

Prepare from the DAS reagent (4.3) a solution in acetonitrile which contains approximately 5 mg DAS-reagent per millilitre of acetonitrile.

The DAS solution in acetonitrile shall be prepared freshly before use and protected against light. The solution is only stable for one day at room temperature.

5 Apparatus

NOTE An instrument or item of apparatus is listed only where it is special or made to a particular specification, the usual laboratory glassware and equipment being assumed to be available.

5.1 High performance liquid chromatograph (HPLC)

NOTE A chromatograph with an automatic injector or 20 µl injection loop, and a fluorescence detector, set to $\lambda_{excitation}$ 262 nm and $\lambda_{emission}$ 490 nm, connected to a strip chart recorder or integrator is preferred.

5.2 HPLC column, capable of producing a symmetric peak for epichlorohydrin, and capable of separating epichlorohydrin from peaks originating from solvents and excess of DAS.

Appropriate operating conditions have to be established for the specific equipment used for the determination.

NOTE The column and parameters established for the column used in the development of the method are given below.

Column: Stainless steel 250 mm x 4,6 mm, filled with C_8 coated silica, particle size 5 µm (load of 10 % carbon and end capped)

Column temperature: ambient
Eluent : acetonitrile (4.2.1)
water (4.2.8)

Gradient	time in min	% acetonitrile	% water
	0	55	45
	5	55	45
	15	70	30
	18	70	30
	21	55	45
	31	55	45

Flow rate: 2 ml/min
Injection volume: 20 µl
Detection: fluorescence
Wavelength: $\lambda_{excitation}$ = 262 nm
$\lambda_{emission}$ = 490 nm

5.3 Crimper, for sealing sample vials.

5.4 22 ml sample vials with polytetrafluoroethylene coated butyl rubber septa and aluminium crimp caps.

5.5 De-capper, for de-capping sample vials closed with an aluminium crimp cap.

5.6 Injection syringe, 50 µl.

5.7 Injection syringe, 100 µl.

5.8 Equipment for micro-distillation, as shown in Figure A.1.

6 Samples

6.1 General

Laboratory samples of the food simulant to be analyzed shall be obtained as described in EN 13130-1.

NOTE This method only describes the determination of epichlorohydrin from coatings, but is expected to be suitable for any other materials containing epichlorohydrin.

6.2 Preparation of test samples - extraction of epichlorohydrin from coated articles

NOTE 1 In general test samples are extracted with dioxane for 6 h at room temperature. In the case of very thick samples, the extraction time should be extended or carried out at elevated temperature using a closed system to avoid loss of epichlorohydrin.

For cans, fill a can with 50 ml dioxane, close the can with an epoxide-free coated end and extract for 6 h at room temperature on a roller bank.

NOTE 2 A typical surface to volume ratio is 2,5 dm²/50 ml.

For coated packaging material, cut 2 dm² coated material into pieces and immerse in 50 ml dioxane for a period of 6 h at room temperature.

Transfer 10,0 ml of the solution obtained into a 22 ml headspace vial, add a magnetic stirring bar and seal the vial with a polytetrafluoroethylene lined septum. This vial is known as vial A.