SLOVENSKI STANDARD

SIST EN 15137:2006

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Materiali in predmeti v stiku z ģivili ï Nekateri epoksi derivati, katerih koncentracija je omejena - Doloļ evanje NOGE in njihovih hidroksi in kloriranih derivatov

Materials and articles in contact with foodstuffs - Certain epoxy derivatives subject to limitation - Determination of NOGE and its hydroxy and chlorinated derivatives

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Bestimmte Epoxyderivate, die Beschränkungen unterliegen - Bestimmung von NOGE und dessen Hydroxy- und Chlorderivaten

Matériaux et objets en contact avec des denrées alimentaires - Dérivés époxy soumis a des limitations - Détermination des NOGE et de leurs dérivés hydroxylés et chlorés

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Materials and articles in contact with foodstuffs - Certain epoxy derivatives subject to limitation - Determination of NOGE and its hydroxy and chlorinated derivatives

Matériaux et objets en contact avec des denrées alimentaires - Dérivés époxy soumis à des limitations - Détermination des NOGE et de leurs dérivés hydroxylés et chlorés

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Bestimmte Epoxyderivate, die Beschränkungen unterliegen - Bestimmung von NOGE und dessen Hydroxy- und Chlorderivaten

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Foreword

This document (EN 15137:2006) has been prepared by Technical Committee CEN/TC 194 “Utensils in contact with food”, the secretariat of which is held by BSI.

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of an identical text or by endorsement, at the latest by September 2006, and conflicting national standards shall be withdrawn at the latest by September 2006.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex ZA, which is an integral part of this document.

This document should be read in conjunction with EN 13130-1.

WARNING: All chemicals are hazardous to health to a greater or lesser extent. It is beyond the scope of this European standard to give instructions for the safe handling of all chemicals, that meet, in full, the legal obligations in all countries in which this European standard may be followed. Therefore, specific warnings are not given and users of this European standard 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 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, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

NOGE (Novolac glycidyl ethers) is used as a monomer in the manufacture of certain polymeric food contact materials and articles.

The main application of NOGE is in epoxy coatings for cans and ends. The substance may also be used in organosol coatings.

After the manufacture, residues of NOGE or its reaction products can remain in the finished product and may migrate into foodstuffs coming into contact with that product.

The analytical method described allows for the determination NOGE and its reaction products in can coatings.

1 Scope

This European standard describes the determination of NOGE components with more than two aromatic rings (the two-ring NOGE is equal to BFDGE = Bis(2-hydroxyphenyl)methane bis(2,3-epoxypropyl)ether) and at least one epoxy group as well as their derivatives containing chlorohydrin functions and having a molecular mass less than 1000 Daltons in can coatings.

A high performance liquid chromatography (HPLC) method is employed based on reversed phase HPLC and fluorescence detection.

The method is capable of determining NOGE and its derivatives at a minimum level of 1 μg/ml in solution.

Direct HPLC analysis of the can coating extract may result in chromatograms difficult to interpret, due to interference from other components or the instability of the monomer resulting in a complex mixture of derivatives and/or reaction products. By forced hydrolysis of all epoxy groups and their reaction products, the quantification of the NOGE is simplified and the identities of the substances are indicatively confirmed.

NOTE In this European standard the term “NOGE and its derivatives” refers to the requirements of Directive 2002/16/EC [1] and its amendment, Directive 2004/13/EC [2]. This includes NOGE components with more than two aromatic rings and at least one epoxy group as well as their derivatives containing chlorohydrin functions and having a molecular mass less than 1000 Daltons.

2 Normative references

The following referenced documents are indispensable for the application of this European standard. 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 the 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

3.1 Determination of NOGE and derivatives in a can coating

Can coatings are extracted with acetonitrile for 24 h at room temperature. Then the extraction solvent is injected into a reverse phase HPLC column. The substances are separated using a gradient elution profile. Detection is performed by means of fluorescence detection. Identification is based on retention time and comparison with reference substances, fluorescence and UV detection response. For confirmation and quantification of NOGE and derivatives the epoxy and the chlorohydrin containing components are fully hydrolysed in alkaline medium at elevated temperature to form the diol components. The hydrolysed components (NOGE per H_2O) are separated by HPLC using fluorescence detection. The NOGE per H_2O components will appear early in the chromatogram due to the increased polarity of the hydrolysed components. Compared to the HPLC chromatogram prior to hydrolysis a simpler HPLC chromatogram is obtained after hydrolysis, containing fewer peaks because all epoxy components and chlorohydrin derivatives disappear; if a peak remains then this substance shall be considered an interfering substance originating from the matrix. To establish compliance with the restrictions set the total amount of diol substances is determined. If relevant, the total amount of NOGE per H_2O derivatives is reduced with the amount of NOGE per H_2O derivatives present initially, prior to hydrolysis.

3.2 Hydrolysis

NOGE and its partly hydrolysed adducts hydrolyse in aqueous neutral and acid conditions. The chlorinated adducts are stable in acid conditions and hydrolyse only slowly in neutral aqueous media. However, in slightly alkaline conditions all adducts (excepting ether derivatives) hydrolyse to the NOGE per H_2O components. To force complete hydrolysis of the epoxy and HCl adducts, the sample solutions are buffered at pH 8.5 and subsequently stored for a minimum of 20 h at 100 °C. After that period the NOGE per H_2O substances are determined.

NOTE 1 Some structures of NOGE and derivatives are shown in Annex A and B.

NOTE 2 A flow chart showing the principle of the determination of NOGE and derivatives in can coatings is given in Annex C.

4 Reagents

4.1 Analytes

4.1.1 Poly(phenyl glycidyl ether)-co-formaldehyde CAS no 28064-14-4
The analyte substance contains approximately 40% of NOGE with 3 – 6 aromatic rings, but batch and supplier variations may occur. Average Mn approximately 345; Average epoxy groups per molecule, 2.2.

4.1.2 BFDGE.$2H_2O$ CAS no 72406-26-9

4.1.3 BFDGE CAS no 2095-03-6

NOTE 1 NOGE and its derivatives consist of a mixture of isomers (see Annexes A and D). The ratio of the various isomers may differ, depending on the supply source. Also the composition of the reference material may vary, depending on supply source and Lot number.

NOTE 2 The substances of interest are those with more than two aromatic rings and at least one epoxy group as well as their derivatives containing chlorohydrin functions and having a molecular mass less than 1000 Dalton.

4.2 Reagents

NOTE During the analysis, unless otherwise stated, only reagents of recognized analytical grade and distilled water of equivalent purity should be used.

4.2.1 Acetonitrile, HPLC grade

4.2.2 Boric acid

4.2.3 Methanol, HPLC grade

4.2.4 Sodium hydroxide

4.2.5 Water deionised, HPLC grade

4.3 Solutions

4.3.1 Borate buffer: 0,6 M

Dissolve 9,28 g of boric acid in 220 ml of water. Add 4,5 M sodium hydroxide solution to a pH of 8,5. Fill the volume to 250 ml with water.

4.3.2 Reference solutions of NOGE in acetonitrile (4 mg/ml)

Weigh to the nearest 0,1 mg approximately 100 mg of NOGE (4.1) in a 25 ml volumetric flask. Fill the volumetric flask up to the mark with acetonitrile and mix carefully.

Calculate the concentration of the substance in milligrams per millilitre solution.

4.3.3 Intermediate reference solution of NOGE in acetonitrile (160 µg/ml)

Pipette 1,0 ml of the stock solution (4.3.2) into a 25 ml volumetric flask and fill the flask up to the mark with acetonitrile to give a solution containing approximately 160 µg/ml of NOGE.

NOTE 1 The solutions prepared contain approximately 40 % of the components of interest (NOGE with 3 to 6 aromatic rings).

NOTE 2 The solutions may be stored for up to 6 months in a refrigerator at a temperature between 4 ºC and 10 ºC.

4.3.4 Standard stock solutions of BFDGE in acetonitrile (500 µg/ml)

Weigh to the nearest 0,1 mg approximately 50 mg of BFGDE (4.1.3) in a 100 ml volumetric flask and add 80 ml acetonitrile (4.2.1), and mix thoroughly to dissolve the BFDGE. Fill the volumetric flask up to the mark with acetonitrile and mix carefully.

Calculate the actual concentration of BFDGE in micrograms per millilitre of solution.

Repeat the procedure to obtain a second standard stock solution.

Check the two primary standard solutions of analyte against one another. Check that the response factor, i.e. detector response divided by concentration of analyte solution, of the two primary standard solutions (or dilutions of that) does not differ by more than 5 %. If there is agreement within 5 %, make subsequent diluted standard solutions from only one of the primary standard solutions. If the levels of the two independently prepared stock solutions do not correspond to within ± 5 %, discard both stock solutions and prepare new solutions.

4.3.5 Intermediate standard solution of BFDGE in acetonitrile (10 µg/ml)

Into a 50 ml volumetric flask pipette 1,0 ml of the BFDGE stock solution (4.3.4) and fill the volumetric flask up to the mark with acetonitrile and mix carefully.

Calculate the actual concentration of BFDGE in µg/ml solution.

NOTE The solutions may be stored for up to 6 months in a refrigerator at a temperature between 4 ºC and 10 ºC.

4.3.6 Sodium hydroxide solution in water; 4,5 M

Dissolve 18 g of NaOH in 100 ml of water.

5 Apparatus

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

5.2 HPLC vials.

5.3 Headspace vials of suitable volume, with inert gas-tight closure capable of sustaining the build-up of pressure during the heating period.

5.4 Micro pipette.

5.5 Oven, capable of being maintained at 100 ºC ± 5 °C.

5.6 pH meter, accurate to within ± pH 0,1.

5.7 Mixer of vortex type.

5.8 Reaction-therm heating module with nitrogen gas flow supply and the temperature set to between 40 °C to 50 °C.

5.9 HPLC apparatus

5.9.1 High performance liquid chromatograph provided with an injector, 20 µl to 50 µl, a UV detector at 225 nm, and a variable fluorescence detector, set to λ_{ex} =275 nm and λ_{em} =305 nm, detectors should be connected to an integrator.

NOTE For the determination of NOGE the use of the prescribed fluorescence wavelengths is essential. Alternative wavelengths may provide better sensitivity but the response factor for the various isomers is different, making correct quantification impossible.

5.9.2 HPLC column, capable of producing symmetric peaks of NOGE, and capable of separating NOGE from the hydrolysis products of NOGE, as well as from peaks originating from the matrix/or solvents used.

For the determination of NOGE and adducts a reverse phase HPLC procedure with a gradient profile is applied, using an analytical column and a pre-column packed with C18 coated silica.

NOTE For guidance, the parameters which are found suitable for the analysis, using the column selected are given below. Other columns and dimensions have also been found to be suitable.

HPLC SYSTEM

Analytical Column : Stainless steel 250 mm x 4,6 mm, Spherisorb ODS2, partical size 5 µm

Pre Column : Stainless steel 30 mm x 4,6 mm, Hypersil ODS, partical size 5 µm

Column temperature : 40 °C

Flow : 1.1 ml/min

Eluent gradient : The following gradient profile, using a linear gradient in each step, is applied:

Time (min)	% water	% acetonitrile
0	80	20
60	0	100
75	0	100
80	80	20
85	80	20

Depending on the composition of the samples injected, the final step(s) in the gradient can be adapted or shortened. In case of strongly contaminated solutions it is advised to rinse the HPLC column properly with pure acetonitrile in between successive injections.

If mainly clean samples are injected then the pre column may not be required. This will reduce the retention times presented below.

Injection volume: 20 µl to 50 µl

Detection: See 5.9.1

Under the conditions given above the following retention times were obtained from standard solutions. Typical chromatograms are depicted in Figures 3 and 4.

Component	**Retention time (min)**	**Component**	**Retention time (min)**
p,p-BFDGE.2H_2O	10,5	p,p-BFDGE	29,6
o,p-BFDGE.2H_2O	11,9	o,p-BFDGE	30,4
o,o-BFDGE.2H_2O	13,0	o,o-BFDGE	31,3
p,p-BFDGE.1H_2O	17,9	3-ring NOGE_isomers	35,8 to 37,9
o,p-BFDGE.1H_2O	18,7	4-ring NOGE_isomers	37,9 to 42,0
o,o-BFDGE.1H_2O	19,5	5-ring NOGE_isomers	42,0 to 45,3
NOGE.per H_2O (3 ring isomers)	13,2 to 14,2	6-ring NOGE isomers	45,3 to 47,7
NOGE.per H_2O (4 ring isomers)	14,2 to 16,7		
NOGE.per H_2O (5 ring isomers)	16,7 to 22,5		
NOGE.per H_2O (56 ring isomers)	22,5 to 27,0		

6 Samples

6.1 Preparation of test samples from can coatings

6.1.1 Extraction of the can coating

Extract 1 dm² of can coating for 24 h at room temperature with 33 ml acetonitrile.

After extraction, fill a HPLC vial with the solution thus obtained and continue as described in 7.3.

NOTE 1 To confirm complete extraction a second extraction period for 24 h at room temperature using a fresh portion of acetonitrile is advised. When there is evidence that the extraction is completed within the 24 h extraction period, a second extraction is not required.