SIST

SLOVENSKI STANDARD

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^Y`ca YYbUË`8c`c YjUb^Y`658; 9ž6:8; 9`]b`b^]\ cj]\ `\]Xfc_g]`]b`_`cf]fUb]\
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Materials and articles in contact with foodstuffs - Certain epoxy derivatives subject to limitation - Determination of BADGE, BFDGE and their hydroxy and chlorinated derivatives in food simulants

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Bestimmte Epoxyderivate, die Beschränkungen unterliegen - Bestimmung von BADGE, BFDGE und deren Hydroxy - und Chlorderivaten in Prüflebensmitteln

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Matériaux et objets en contact avec les denrées alimentaires - Dérivés époxy soumis a des limitations - Détermination du BADGE, du BFDGE et de leurs dérivés hydroxylés et chlorés dans les simulants d'aliments

Ta slovenski standard je istoveten z: **EN 15136:2006**

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67.250

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EUROPEAN STANDARD

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EN 15136

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English Version

Materials and articles in contact with foodstuffs - Certain epoxy derivatives subject to limitation - Determination of BADGE, BFDGE and their hydroxy and chlorinated derivatives in food simulants

Matériaux et objets en contact avec les denrées alimentaires - Dérivés époxy soumis à des limitations - Détermination du BADGE, du BFDGE et de leurs dérivés hydroxylés et chlorés dans les simulants d'aliments

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Management Centre: rue de Stassart, 36 B-1050 Brussels

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Foreword

This document (EN 15136:2006) 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of an identical text or by endorsement, at the latest by September 2006, and conflicting national standards shall be withdrawn at the latest by September 2006.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.

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Introduction

2,2-Bis(4-hydroxyphenyl)propane bis(2,3-epoxypropyl)ether (BADGE) and bis(hydroxyphenyl)methane bis(2,3-epoxypropyl)ether (BFDGE) are monomers used in the manufacture of certain polymeric food contact materials and articles.

The main application of these monomers is in epoxy coatings for cans and ends. The substances may also be used in organosol coatings.

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

The analytical method described allows for the determination of BADGE, BFDGE and their reaction products in aqueous and fatty food simulants.

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1 Scope

This European standard describes a method for the determination of BADGE, BFDGE and their reaction products in food simulants: distilled water, 3 % w/v aqueous acetic acid, 10 % v/v aqueous ethanol solution and olive oil or sunflower oil.

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

The method is capable of determining BADGE and its derivatives at a minimum level of 0,05 µg/ml food simulant.

BFDGE and its derivatives can be determined at a minimum level of 0,1 µg/ml food simulant.

Direct HPLC analysis of the migration solutions may result in chromatograms difficult to interpret, due to interference from other components or the instability of the monomers 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 relevant substances is simplified and in addition the identities of the substances are indicatively confirmed.

NOTE In this European standard the term "BADGE, BFDGE and their derivatives" refers to the substances listed in Directive 2002/16/EC [1] and its amendment, Directive 2004/13/EC [2]. These substances are listed in 4.1.

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2 Normative references

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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 food and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants*

ISO 648, *Laboratory glassware – One-mark pipettes*

3 Principle

3.1 Determination of BADGE, BFDGE and their derivatives in food simulants

Proper quantification of the sum of BADGE, BFDGE and/or their derivatives is obtained by analysing the simulants twice: a first analysis of the simulant as obtained from the migration is performed and, if necessary, the substances are fully hydrolysed and the hydrolysed substances are determined in a second HPLC analysis. This second analysis is used for confirmation and final quantification of the sum of BADGE or BFDGE and their derivatives as the bis(diol) derivatives.

In the first instance, after the migration period, samples from aqueous food simulants are directly injected into a reverse phase HPLC column and the substances are separated using a gradient elution profile. For fatty food simulants, the substances are extracted with acetonitrile followed by HPLC

analysis. Detection is performed by means of fluorescence detection. Identification is based on retention time and comparison with reference substances, fluorescence and UV detection. If it appears from this first analysis that the summed migration level of BADGE/BFDGE and/or their derivatives is >0.5 mg/kg, confirmation and final quantification of BADGE, BFDGE and their derivatives is performed by forced hydrolysis of the epoxy components and the chlorinated components. If the substance of interest contains either an epoxy group or a HCl adduct, then this component will hydrolyse to the bis(diol) components. Compared to the HPLC chromatogram prior to hydrolysis a simpler HPLC chromatogram is obtained after hydrolysis, containing fewer peaks because the peaks of BADGE, BFDGE and their adducts disappear; if the peak(s) remain(s) then this substance should be considered an interfering substance originating from the matrix. Forced hydrolysis is obtained by mixing the sample solution with buffer and hydrolysis at 100 °C. Then a second HPLC analysis is performed to determine the concentration of monomer.$2H_2O$.

3.2 Hydrolysis

BADGE, BFGDE and their 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 bis(diol) component. 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 bis(diol) substances are determined.

NOTE The structures of BADGE, BFDGE and their derivatives are included in Annex A as well as some derivatives that may be formed during contact with simulants. A flow chart showing the principle of the determination of BADGE, BFDGE and their derivatives in food simulants is given in Annex B.

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4 Reagents

4.1 Analytes

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NOTE See Annex A for molecular structures.

4.1.1 BADGE CAS no. 1675-54-3

4.1.2 BADGE.2HCl CAS no. 4809-35-2

4.1.3 BADGE.$2H_2O$ CAS no. 5581-32-8

4.1.4 BADGE.H_2O CAS no. 76002-91-0

4.1.5 BADGE.HCl CAS no. 13836-48-1

4.1.6 BADGE.H_2O.HCl CAS no. 227947-06-0

4.1.7 BFDGE CAS no. 2095-03-6

4.1.8 BFDGE.2HCl

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

4.1.10 BFDGE.HCl, prepared as follows:

Dissolve approximately 50 mg BFDGE (4.1.7) in 25 ml dioxane, add 10 µl concentrated hydrochloric acid and reflux for 10 min. Using a rotavapor evaporate the dioxane and dissolve the residue in 25 ml acetonitrile. The mixture should contain the isomers of each of three substances BFDGE, BFDGE.HCl and BFDGE.2 HCl. This mixture is only used for reference purposes.

4.1.11 BFDGE.H_2O, prepared as follows:

Dissolve 50 mg BFDGE in 25 ml dioxane, add 500 µl water and reflux for 10 min. Using a rotavapor evaporate the dioxane and dissolve the residue in acetonitrile. The mixture should contain the isomers of each of three substances BFDGE, BFDGE.H_2O and BFDGE.$2H_2O$. This mixture is only used for reference purposes.

NOTE BFDGE and its derivatives consists of a mixture of isomers (see annex A). The ratio of the various isomers may differ depending on the supply source.

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 Ethanol 100 %, distilled

4.2.4 Methanol, HPLC grade

4.2.5 Sodium hydroxide

4.2.6 Water deionised, HPLC grade

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4.3 Solutions

4.3.1 Borate buffer: 0,6 M

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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. Top up the volume to 250 ml with water.

4.3.2 Stock solutions of pure reference substances of BADGE, BFDGE and their derivatives in acetonitrile (500 µg/ml)

NOTE If the derivatives of BADGE and BFDGE only are used for establishing their retention times before hydrolysis, qualitative solutions may be prepared. If the solutions are used to quantify each of the derivatives in order to avoid the hydrolysis procedure (see scheme in Annex B), quantitative solutions should be prepared of each of the derivatives. However, quantitative solutions containing only BADGE and BFDGE should always be prepared.

Weigh to the nearest 0,1 mg approximately 50 mg of each of the relevant substances listed in 4.1 in a series of 100 ml volumetric flasks and add 80 ml acetonitrile (4.2.1). Place the flask for 5 min in an ultrasonic water-bath to dissolve the substances. Cool the solution to room temperature and fill the volumetric flask up to the mark with acetonitrile and mix carefully.

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

To dissolve the bis(diol) derivatives add first 20 ml of water and then make up to the mark with acetonitrile.

Repeat the procedure to obtain a second standard stock solution.

Check the two primary stock 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 stock 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 stock 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.

NOTE 1 Solubility of bis(diol) derivatives in pure acetonitrile is limited. When stored in a refrigerator the substances may crystallize. Addition of water to the acetonitrile as described will improve the solubility.

NOTE 2 The solutions may be stored for up to 6 months in a refrigerator.

4.3.3 Intermediate standard solution of BADGE, BFDGE and their derivatives in acetonitrile (10 µg/ml)

Into a series of 50 ml volumetric flask pipette 1,0 ml of each of the stock solutions (4.3.2) and fill the volumetric flask up to the mark with acetonitrile to give approximately 10 µg/ml of the relevant substance.

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

NOTE Either a mixture of standard substances or individual standard solution may be prepared by adding each of the stock solutions (4.3.2) to one and the same flask or to individual flasks. However, at least standards containing only BADGE and BFDGE shall be prepared for quantification purposes of the substances after hydrolysis.

4.3.4 Sodium hydroxide solution in water 4.5M

Dissolve 18 g of NaOH in 100 ml of water.

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5 Apparatus

5.1 HPLC vials.

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

5.3 Micro pipette.

5.4 Mixer of vortex type.

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

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

5.7 Pipettes, of 5 ml and 50 ml capacity, conforming to ISO 648.

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

5.9 C18 solid phase extraction cartridges (360 mg size) with Luer connection to a 5 ml syringe.

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5.10 HPLC apparatus

5.10.1 High performance liquid chromatograph preferably with 20 µl injection loop, 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.

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NOTE For the determination of BFDGE and its derivatives 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.

5.10.2 HPLC column, packed with C18 coated silica gel, capable of producing a symmetric peak of BADGE, and capable to separate from each other: BADGE, BFDGE and the hydrolysis and chlorohydrin reaction products of BADGE, BFDGE, as well as from peaks originating from simulants and/or solvents used.

For the determination of BADGE, BFDGE and their adducts a reverse phase HPLC procedure with a gradient profile is applied, using an analytical column and an optional pre-column.

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 : 30 °C
Flow : 1,1 ml/min
Eluent gradient : The following gradient profile, using a linear gradient in each step, is applied.

Table 1

Time (min)	% water	% acetonitrile
0	80	20
10	65	35
25	50	50
45	50	50
60	0	100
75	0	100
80	80	20
85	80	20

Depending on the composition of the samples injected, the final step(s) (from 60 min) 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 influence the retention times presented below.

Injection volume: 20 µl

Detection: See 5.10.1

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Under the conditions given above the following retention times were obtained from standard solutions. The retention times should be seen as indicative values as retention times may shift from one run to another.

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Typical chromatograms, containing the majority of the substances listed, are depicted in Annex C.

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Table 2

Component	**Retention time (min)**	**Component**	**Retention time (min)**
p,p-BFDGE.2H_2O	10,2	p,p-BFDGE.2HCl	28,9
o,p-BFDGE.2H_2O	11,4	o,p-BFDGE.2HCl	30,2
o,o-BFDGE.2H_2O	12,5	o,o-BFDGE.2HCl + p,p-BFDGE	31,6
BADGE.2H_2O	13,4	o,p-BFDGE	32,7
p,p-BFDGE.1H_2O	17,9	o,o-BFDGE	34,0
o,p-BFDGE.1H_2O	18,7	BADGE.2HCl_isom	35,8
o,o-BFDGE.1H_2O	19,5	BADGE.2HCl	36,6
BADGE.1H_2O. 1ether	21,5	BADGE.1HCl	38,7
BADGE.1HCl.1H_2O.	22,7	BADGE	41,0
BADGE.1H_2O	23,1		

Bisphenol A and p,p-Bisphenol F may appear at retention time 20,1 min and 15,2 min respectively.

Use of methanol as modifier in the elution solvent may cause a different order of elution.

Injection of acetonitrile solutions may influence the separation efficiency of short retention time substances. Dilution of the acetonitrile with water or buffer will avoid that problem.