BRITISH STANDARD

BS EN
14981:2006

Surface active agents — Determination of content of high boiling solvents in liquid detergents by GLC

The European Standard EN 14981:2006 has the status of a British Standard

ICS 71.100.40

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee CII/34, Methods of test for surface active agents.

A list of organizations represented on CII/34 can be obtained on request to its secretary.

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EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 14981

October 2006

ICS 71.100.40

English Version

Surface active agents - Determination of content of high boiling solvents in liquid detergents by GLC

Agents de surface - Détermination de la teneur en solvants à point d'ébullition élevé dans les détergents liquides par chromatographie en phase gazeuse

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes an hochsiedenden Lösemitteln in flüssigen Reinigungsmitteln durch GLC

This European Standard was approved by CEN on 28 August 2006.

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Foreword

This document (EN 14981:2006) has been prepared by Technical Committee CEN/TC 276 “Surface active agents”, the secretariat of which is held by AFNOR.

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of an identical text or by endorsement, at the latest by April 2007, and conflicting national standards shall be withdrawn at the latest by April 2007.

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1 Scope

This European Standard specifies a method for the identifying and quantifying of high boiling point solvents in finished liquid detergents and raw materials.

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.

ISO 607, *Surface active agents and detergents - Methods of sample division*

3 Term and Definition

For the purposes of this European Standard, the following term and definition applies.

high boiling solvent
solvent, mainly a glycol and glycol ether product, with a boiling point significantly higher than water (100° C)

4 Principle

The organic solvents are determined by gas chromatography. The sample is dissolved in ethanol and injected into a polar phase capillary column and the unknown solvent is identified by its retention time. After qualitative determination, the solvent is quantified using (-) Carvone (2-Methyl-5-(1-methylethenyl)-2-cyclohexene-1-one) as internal standard.

5 Reagents

During the analysis, unless otherwise specified, use only reagents of recognized analytical grade that have been checked in advance so as not to interfere with the analytical results.

WARNING Some reagents used throughout this procedure are toxic. Care should be taken not to inhale the vapours. Contact with the skin should also be avoided. Safety glasses and gloves should be worn when handling the reagents. Waste solvent disposal should be carried out in accordance with safety and environmental regulations.

5.1 Ethanol (CAS number: 64-17-5).

5.2 (-) Carvone (2-Methyl-5-(1-methylethenyl)-2-cyclohexene-1-one), minimum purity 99,5 %
(CAS number : 6485-40-1)

5.3 Solvents to be determined (see example in Annex A)

WARNING Some solvents may exist as different isomers.

5.4 Carrier gas for gas chromatography

5.5 Auxiliary gas for gas chromatography

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6 Apparatus

Ordinary laboratory apparatus and the following:

6.1 Gas chromatograph equipped with split/splitless injection port and flame ionization detector (FID).

6.2 Electronic integrator or, preferably, a suitable data acquisition system.

6.3 Capillary column, capable of the separation characteristics shown in Figures A.1 and A.2.

6.4 Glass tube, with a capacity of at least 40 ml.

NOTE A 30 m x 0,25 mm internal diameter, fused silica capillary column (film thickness 0,25 µm) with 100 % polyethylene glycol stationary phase is advisable.

7 Sampling and preparation of the sample

The laboratory sample shall be prepared and stored in accordance with ISO 607.

8 Procedure

8.1 Gas chromatographic conditions

The following GC conditions have been found to be suitable. At least the quality of separation shown in Figures A.1 and A.2 shall be achieved.

- Oven temperature programs:
  - qualitative analysis: 60°C (5 min) to 240°C (5 min) at 5°C/min;
  - quantitative analysis: 60°C to 240°C (5 min) at 20°C/min;
- Injection: split ratio at 100:1 and temperature at 225°C;
- Detection : flame ionization detector (FID) at 275°C with nitrogen as make up gas at 25 ml/min;
- Carrier gas: hydrogen at 50 kPa head pressure.

8.2 Preparation of solutions

8.2.1 Solvent reference solution 1

Into a glass tube (6.4), weigh approximately 20 mg of each solvent as listed on chromatogram 1. Add 30 ml of ethanol and mix well.

8.2.2 Solvent reference solution 2

Into a glass tube (6.4), weigh approximately 20 mg of each solvent as listed on chromatogram 2. Add 30 ml of ethanol and mix well.

Inject 1 µl of the solvent reference solutions 1 and 2 into the gas chromatograph. Refer to the annexed chromatograms 1 and 2 for peak identities.

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8.2.3 Stock solution for calibrations

Weigh to the nearest 0,1 mg, approximately 250 mg of each of the solvent(s) of interest into a 100 ml volumetric flask. Dilute to volume with ethanol, and mix well.

8.2.4 Carvone internal standard solution

Weigh to the nearest 0,1 mg, approximately 500 mg of carvone into a 100 ml volumetric flask. Dilute to volume with ethanol and mix thoroughly (5,0 mg/ml of carvone).

8.3 Calibration

Using precision glass pipettes, transfer 5,0 ml, 7,0 ml, 10,0 ml, 12,0 ml, and respectively 15,0 ml of the stock solution for calibrations into a series of glass tubes (6.4).

Using a volumetric glass pipette, add 5,0 ml of the carvone internal standard solution, make up to 30 ml with ethanol and mix well.

Inject 1 µl of each solution into the gas chromatograph.

Record the peak areas of the peaks of interest and carry out a regression analysis of (Area of solvent/Area of internal standard) versus (mass of solvent/mass of internal standard), for each solvent(s).

The response factor, K_i, for each solvent i, is the slope of the calculated regression curve.

If a correlation factor of less than 0,98 is obtained prepare new calibration solution and re-inject.

If a data acquisition system is not available, calculate the response factor for all the standard solutions according to the following formula:

$$K_{\mathrm{i}} = \frac{m_{\mathrm{s}} \times f_s \times A_{\mathrm{i}}}{m_{\mathrm{i}} \times f_i \times A_{\mathrm{s}}} \qquad (1)$$

where

m_s is the mass, in milligrams, of the internal standard ;

f_{s} is the purity of the internal standard, in % (m/m);

fi is the purity of the solvent i, in % (m/m);

A_{i} is the peak area of the solvent i;

m_{i} is the mass, in milligrams, of the solvent i;

A_{s} peak area of the internal standard.

Calculate the mean response factor of all K_i for each solvent and the relative standard deviation. If the relative standard deviation (RSD) of K_{i} is > 3 %, repeat the calibration procedure.

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8.4 Sample analysis

8.4.1 Solvent identification

Into a glass tube (6.4), weigh 1g to 2 g of sample.

Add 30 ml of ethanol and mix thoroughly. Inject 1 µl of the obtained solution into the GC and allow the chromatogram to develop. Identify the solvent(s) present in the sample by comparing the retention time(s) with the reference chromatogram.

Spike the sample with 20 mg of each of the identified solvent(s). Mix the solution thoroughly and inject 1 µl of this new solution into the GC. Allow the chromatogram to develop.

Confirm the identification of the solvent(s).

8.4.2 Solvent quantification

Into a glass tube (6.4) accurately weigh sufficient sample to contain approximately 25 mg of solvent.

Using a volumetric glass pipette, add 5,0 ml of the carvone internal standard solution followed by 25 ml of ethanol and mix well.

Inject 1 µl of the ethanolic solution into the gas chromatograph.

Record the peak areas of the peaks of interest and calculate the results according to clause 9.

9 Calculation and expression of results

The content of solvent i, w_i, expressed in grams per 100 grams is calculated according to the following equation:

$$w_{\mathrm{i}} = \frac{m_0 \times f_o \times A_{\mathrm{i}}}{m \times A_0 \times K_{\mathrm{i}}} \qquad (2)$$

where

m_0 is the mass, in milligrams, of the internal standard;

f_0 is the purity of the internal standard, expressed in % (m/m);

A_{i} is the peak area of the solvent i in the sample analysis;

m is the mass, in milligrams, of the sample;

A_0 is the peak area of the internal standard in the sample analysis;

K_{i} is the response factor for solvent i, calculated in 8.3.

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10 Precision

10.1 Repeatability limit

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will not exceed the repeatability limit, r, in more than 5 % of cases.

Precision data are given in Annex B.

10.2 Reproducibility limit

The absolute difference between two independent single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will not exceed the reproducibility limit, R, in more than 5 % of cases.

Precision data are given in Annex B.

11 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample tested;

b) reference to this European Standard (EN 14981);

c) method used;

d) test results;

e) details of any operation not specified in this European Standard or in the European Standards to which reference is made, and any operations regarded as optional, as well as any incidents likely to have affected the results.

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Annex A
(informative)

Examples of chromatogram

A.1 Solvent identification

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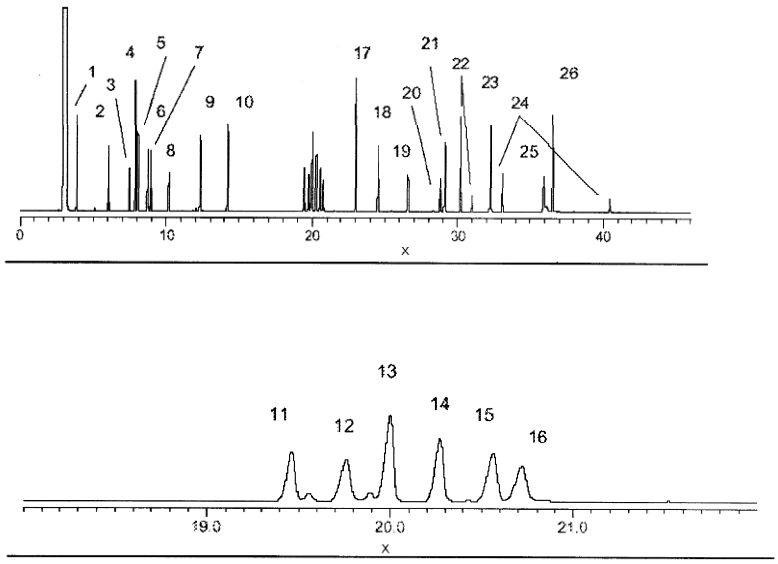

Key – Peak Identification

1	Ethylene glycol diethyl ether (CAS Number:629-14-1)	14	Diethylene glycol monoethyl ether (CAS Number:111-90-0)
2	Propylene glycol monomethyl ether (CAS Number: 107-98-2)	15	Ethylene glycol (CAS Number:107-21-1)
3	Ethylene glycol monomethyl ether (CAS Number:109-86-4)	16	Hexylene glycol (2-methyl-2,4-pentanediol) (CAS Number:107-41-5)
4	Limonene (CAS number:5989-27-5)	17	(-)Carvone (CAS Number:6485-40-1)
5	Propylene glycol tert-butyl ether (CAS Number:57018-52-7)	18	Diethylene glycol monobutyl ether (CAS Number:112-34-5)
6	Ethylene glycol monoethyl ether (CAS Number:110-80-5)	19	Benzyl alcohol (CAS Number:100-51-6)
7	Ethylene glycol monoisopropyl ether (CAS Number:109-59-1)	20	Diethylene glycol (CAS Number:111-46-6)
8	Propylene glycol monoisobutyl ether (CAS Number:80783-53-5)	21	Diethylene glycol monohexyl ether (CAS Number:112-59-4)
9	Propylene glycol monobutyl ether (CAS Number:5131-66-8)	22	Propylene glycol monophenyl ether (CAS Number:770-35-4)
10	Ethylene glycol monobutyl ether (CAS Number:111-76-2)	23	Ethylene glycol monophenyl ether (CAS Number:122-99-6)
11	Diethylene glycol monomethyl ether (CAS Number:111-77-3)	24	Triethylene glycol monobutyl ether (CAS Number:143-22-6)
12	1,2- Propanediol (CAS Number:57-55-6)	25	Glycerol (CAS Number:56-81-5)
13	Ethylene glycol monohexyl ether (CAS Number:112-25-4)	26	Diethyl phthalate (CAS Number:84-66-2)
		X	Time (min)

NOTE Chromatography
Column: 30 m x 250 µm internal diameter. x 0,25 µm of 100% polyethylene glycol (i.e., Zebron ZB-WAX column from Phenomenex).[1)]
Oven: 60°C (5 min) then to 240°C (5 min) at 5°C/min.
Injection: 225°C split ratio at 100:1
Detection: FID at 275°C.
Carrier gas: hydrogen at 50 kPa head pressure (or helium at 94 kPa).

Figure A.1 - Chromatogram 1 - High boiling point solvents – Solvent reference solution1 (one peak solvents)

1) "ZEBRON ZB-WAX is the trade name of a product supplied by Phenomenex. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results."

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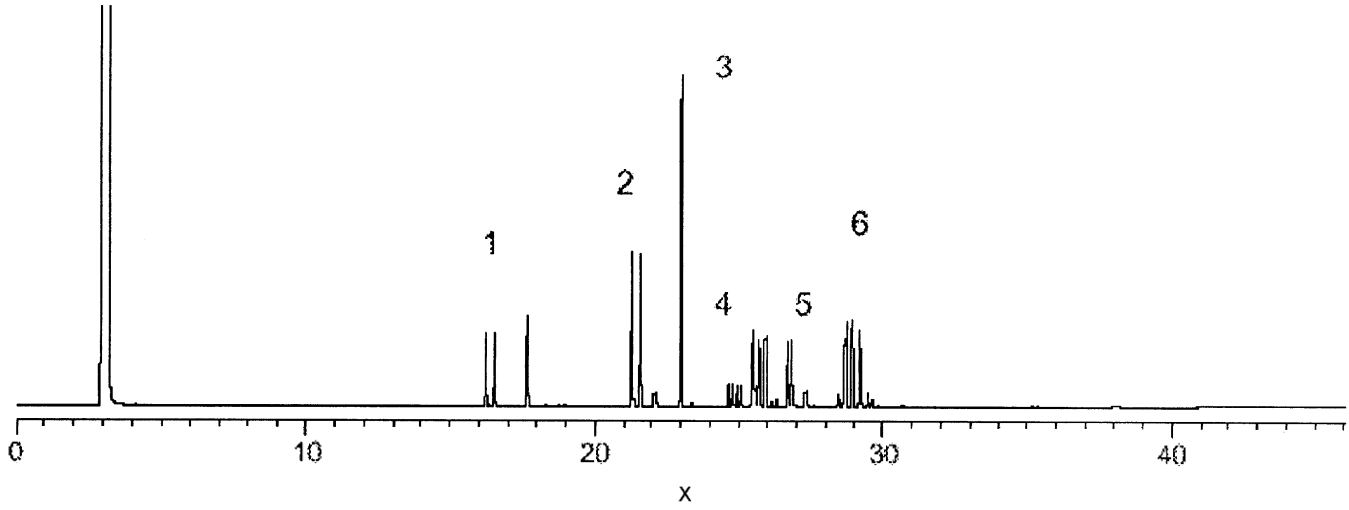

Key

Peak identification

1 Dipropylene glycol monomethyl ether (CAS Number:34590-94-8)

2 Dipropylene glycol monobutyl ether (CAS Number:29911-28-2):

3 (-)Carvone (CAS Number:6485-40-1)

4 Tripropylene glycol monomethyl ether (CAS Number:25498-49-1)

5 Dipropylene glycol (CAS Number:25265-71-8)

6 Tripropylene glycol monobutyl ether (CAS Number:55934-93-5)

X Time (min)

NOTE Chromatography: identical to chromatogram 1

Figure A.2 - Chromatogram 2 - High boiling point solvents – Solvent reference solution 2 (Multiple peak solvents)

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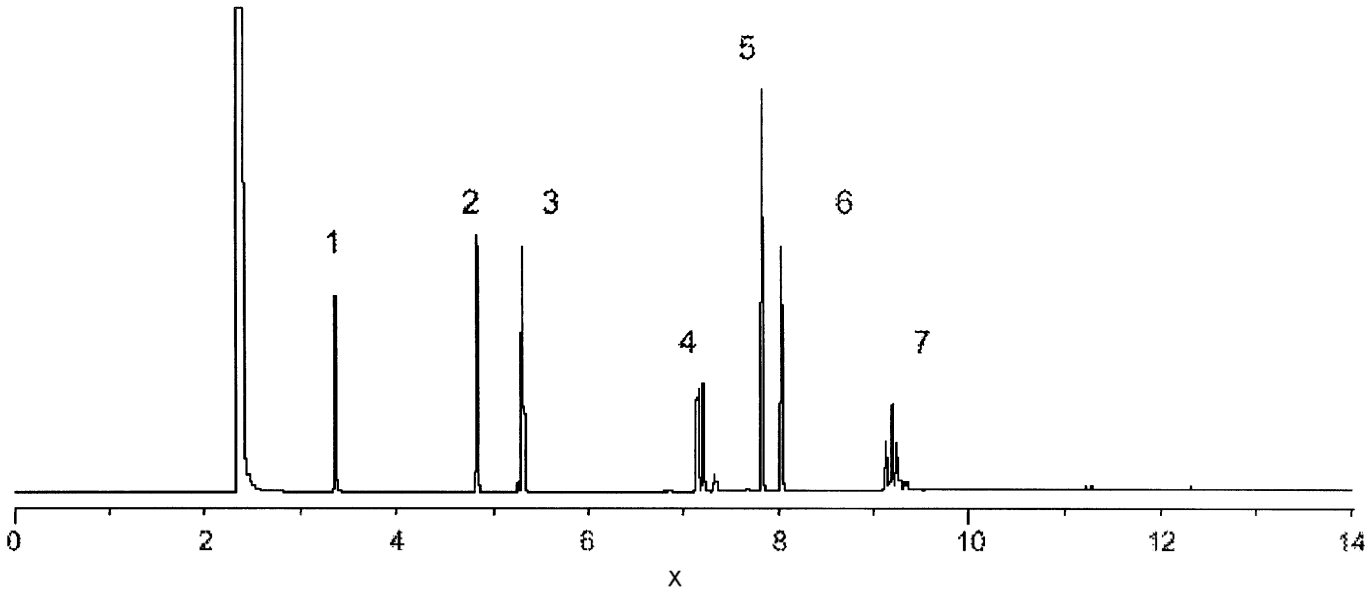
A.2 Solvent quantification



NOTE Chromatography
Column: 30 m x 250 µm internal diameter. x 0,25µm df of 100% polyethylene glycol (i.e., Zebron ZB-WAX column from Phenomenex).[2)]
Oven: 60°C to 240ºC(5 min) at 20°C/min
Injection: 225°C, split ratio at 100:1
Detection: FID at 275°C.
Carrier gas: hydrogen at 50 kPa head pressure (or helium at 94 kPa).

Key

Peak identification

1 Propylene glycol monomethyl ether (CAS Number: 107-98-2)
2 Propylene glycol monobutyl ether (CAS Number:5131-66-8)
3 Ethylene glycol monobutyl ether (CAS Number:111-76-2)
4 Dipropylene glycol monobutyl ether (CAS Number : 29911-28-2)
5 (-)Carvone (Internal Standard) (CAS Number:6485-40-1)
6 Diethylene glycol monobutyl ether (CAS Number:112-34-5)
7 Tripropylene glycol monobutyl ether (CAS Number:55934-93-5)

X Time (min)

Figure A.3 - Chromatogram 3 - High boiling point solvents – Quantification (example)

2) "ZEBRON ZB-WAX is the trade name of a product supplied by Phenomenex. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results."

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Annex B
(informative)

Statistical and other data derived from the results of inter-laboratory tests

The interlaboratory test was carried out in 2003 by CESIO (Comité Européen des agents de Surface et de leurs Intermédiaires Organiques)/AISE (International Association for Soaps, Detergents and Maintenance Products) WG "Surfactant Analysis". The results of the interlaboratory test were evaluated in accordance with ISO 5725-2.

Table B.1 - Results of interlaboratory test

	Propyleneglycol monomethyl ether	Propyleneglycol monobutyl ether	Diethyleneglycol monobutyl ether
Number of participating laboratories	8	7	8
Number of accepted test results	23	18	23
Mean value (% w/w)	1,99	1,99	2,00
Repeatability standard deviation (s_r)	0,024	0,021	0,013
Repeatability coefficient of variation	1,2%	1,0%	0,7%
Repeatability limit (r) (2,8 x s_r)	0,068	0,058	0,037
Reproducibility standard deviation (s_R)	0,053	0,047	0,069
Reproducibility coefficient of variation	2,7%	2,4%	3,5%
Reproducibility limit (R) (2,8 x s_R)	0,150	0,133	0,194

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Bibliography

[1] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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