BRITISH STANDARD

BS EN 13405:2002

Surface active agents — Determination of dialkyl-tetralins content in linear alkylbenzene by high performance liquid chromatography (HPLC)

The European Standard EN 13405:2002 has the status of a British Standard

ICS 71.100.40

British Standards

National foreword

This British Standard is the official English language version of EN 13405:2002.

The UK participation in its preparation was entrusted to Technical Committee CII/34, Methods of test for surface active agents, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
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This British Standard, having been prepared under the direction of the Materials and Chemicals Sector Policy and Strategy Committee, was published under the authority of the Standards Policy and Strategy Committee on 20 December 2002

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English version

Surface active agents - Determination of dialkyl-tetralins content in linear alkylbenzene by high performance liquid chromatography (HPLC)

Agents de surface - Détermination de la teneur en dialkyltétralines dans les alkylbenzènes linéaires par chromatographie liquide à haute performance (CLHP)

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes von Dialkyltetralin in linearem Alkylbenzol mittels Hochleistungs-Flüssigchromatographie (HPLC)

This European Standard was approved by CEN on 23 October 2002.

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Contents

Foreword

This document (EN 13405:2002) 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of an identical text or by endorsement, at the latest by June 2003, and conflicting national standards shall be withdrawn at the latest by June 2003.

Annex A is informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a method for the determination of dialkyl-tetralins (DAT), being 1,4-dialkyl-2,3-dihydro-naphthalene in linear alkylbenzene (LAB) in the range of the mass fraction of 0,5 % to 10 %.

2 Normative reference

This European Standard incorporates by dated or 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 or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN ISO 3696:1995, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987).*

3 Principle

The sample is analysed by isocratic high performance liquid chromatography (HPLC) using a micro-particulate silica stationary phase, 2,2,4-methylpentane mobile phase and ultra-violet absorbance detection at 254 nm. Quantification is made by using a "modified" external standard technique. Pure standard dialkyl-tetralins (DAT) are not available, therefore the molar response of DAT is assumed to be the same as the commercially available tetrahydronaphthalene (THN) used as external standard.

4 Reagents

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

4.1 **Water**, complying with grade 3 as defined in EN ISO 3696:1995.

4.2 **2,2,4-trimethylpentane** (iso-octane), C_8H_{18}, HPLC grade, with a water content less than 100 mg/kg.

NOTE Care should be taken when using iso-octane, which is highly flammable.

4.3 **Tetrahydronaphthalene** (THN), $C_{10}H_{12}$, minimum purity 96 % (determination by gas chromatography area standard technique).

NOTE Care should be taken when using tetrahydronaphthalene which can be irritating to eyes and skin.

4.4 **Hexane**, C_6H_{14}.

4.5 **Toluene**, C_7H_8.

5 Apparatus

Ordinary laboratory apparatus and glassware together with the following.

5.1 **High performance liquid chromatograph**, suitable for analysis according to the operating instructions given in Table 1.

5.2 Chromatographic column, normal phase, 250 mm length, 4 mm internal diameter containing micro-particulate silica.

5.3 Suitable means, for determining peak area, e.g. integrator or computer.

5.4 Disposable filter, 0,5   m pore diameter.

6 Procedure

6.1 Preliminary test

The column length (1 column or 2 columns in series) and the flow rate shall be arranged in order to optimise the efficiency and resolution (see Table 2 for column details). One way to test this is to run an HPLC chromatogram using a standard solution containing approximately 100 mg of toluene (4.5) and 10 mg of tetrahydronaphthalene (4.3) (THN) in 100 ml of hexane (4.4). An example of a chromatogram is given in Figure 1.

Do not wash the columns with any polar solvent otherwise the original separation factor is not to be restored any more.

From this chromatogram determine the net retention time (t') and the capacity factor (k') of both THN and toluene and calculate the relative separation factor ( ).

NOTE Typical values for two Lichrosorb Si 60 columns and 1 ml/min flow rate are shown in Table 1.

Table 1 - Net retention time and capacity factor for toluene and THN for two Lichrosorb Si 60 columns and a flow rate of 1 ml/min

Reagent	Net retention time (min) $t' = t \quad t_o$	Capacity factor $k' = \frac{t \quad to}{t_o}$
Toluene	4,8	0,94
THN	6,3	1,24
NOTE t_o is the duration of elution at the dead volume. A typical value of t_o for n-hexane is 5,1 min.		

The calculated separation factor, $= \frac{k'_2}{k'_1}$, is:

$$= \frac{k'_{THN}}{k'_{Toluène}} = 1{,}32$$

A reproducible and correct DAT analysis in LAB samples requires that the HPLC conditions are set up so that   is greater than or equal to 1,20.

6.2 Calibration

Prepare a solution of 0,1 g/l of THN in 2,2,4-trimethylpentane (4.2) by weighing 100 mg of the tetrahydronaphthalene (4.3) to the nearest 0,1 mg and making up to volume in an 1 l volumetric flask or by dilution of a more concentrated solution.

NOTE A reference sample of LAB containing 1,2 % DAT is available from ECOSOL 1) for checking the calibration of the method.

Analyse the solution by HPLC according to the conditions given in Table 2. The peak area for the THN peak is used for the calculation in clause 7.

If the mean molar mass is unknown, determine the carbon number distribution of the *LAB* sample to be analysed by a gas chromatography peak area normalisation technique, for example, as described in Annex A.

Calculate the average molar mass, M_{DAT}, of the DAT in the sample as follows:

$$M_{DAT} = \frac{100}{\sum_{i=8}^{15} \frac{W_{LAB}(i)}{M_{DAT(i)}}} \qquad (1)$$

where

$W_{LAB(i)}$ is the mass fraction of LAB at carbon number i of the alkyl chain, in percent;

$M_{DAT(i)}$ is the molar mass of DAT at carbon number i of the alkyl chain, in grams per mole.

6.3 Determination

Prepare a solution of 10 g/l of the sample in 2,2,4-trimethylpentane (4.2) by weighing 250 mg of the sample to the nearest 0,1 mg and making up to volume in a 25 ml volumetric flask.

Filter approximately 5 ml of the above solution through the disposable filter (5.4).

Analyse the filtered solution by HPLC according to the conditions given in Table 2.

NOTE An example of a chromatogram is given in Figure 2.

Use tangent skim technique for determining the area of the DAT peak.

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1) ECOSOL is a sector group of CEFIC/CESIO (Avenue E. VAN NIEUWENHUYSE 4, bte 2 B - 1160 Brussels, Belgium).

Table 2 - Operating instructions

Column	
Material	Stainless steel
Length x internal diameter	250 mm x 4 mm
Packing	Microparticulate silica, 5 m
Mobil phase	
Solvent	2,2,4-trimethylpentane
Flow rate	0,5 ml/min - 1 column (see clause 6)
	1,0 ml/min - 2 columns (see clause 6)
Programme	Isocratic for 30 min
Detector system	
Type	Ultra-violet absorbance
Wavelength	254 nm
Temperature	Room temperature
Injection volume	20 µl

7 Calculation

Determine the content of DAT, W_{DAT}, expressed as mass fraction in percent, in the sample as follows :

$$W_{DAT} = \frac{A_s}{A_{THN(c)}} \times \frac{THN(c)}{s} \times \frac{100}{R} \qquad (2)$$

where

As	is the peak area for DAT obtained by analysing the filtered solution by HPLC in 6.3 ;
$THN(c)$	is the mass concentration of THN in the calibration solution as prepared in 6.2, in grams per litre ;
R	is the molar mass ratio $= \frac{M_{THN}}{M_{DAT}} = \frac{132}{M_{DAT}}$;
$A_{THN(c)}$	is the peak area for THN obtained by analysing the solution using HPLC as specified in 6.2, same arbitrary units as A_s ;
s	is the mass concentration of the sample in the solution as prepared in 6.3, in grams per litre.

The result shall be given to one decimal place.

8 Precision

8.1 General

The precision data were obtained by statistical evaluation of the results of an interlaboratory test carried out by ECOSOL [1)] in 1992. Five laboratories took part in this interlaboratory test where three samples in the range of mass fractions from 0,5 % to 3,0 % were analysed.

8.2 Repeatibility 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.

In a ring test, the following repeatability limits, r, were obtained :

¾ less than or equal to 0,1 % at mass fractions up to 2 % ; and

¾ less than or equal to 0,2 % at mass fractions greater than 2 %.

8.3 Reproducibility limit

The absolute difference between two 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.

In a ring test, the following reproducibility limits, R, were obtained :

¾ less than or equal to 0,4 % at mass fractions up to 0,5 % ;

¾ less than or equal to 0,6 % at mass fractions greater than 0,5 % to 1,5 % ; and

¾ less than or equal to 0,8 % at mass fractions greater than 1,5 %.

9 Test report

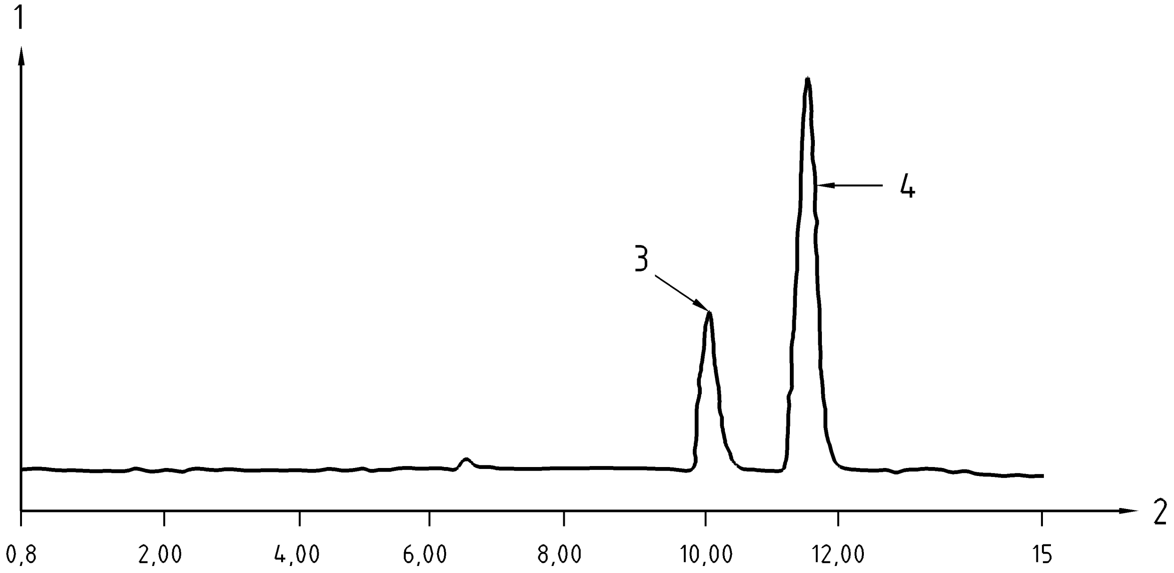
The test report shall include the following information:

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

b) a reference to this European Standard ;

c) the results obtained and the units in which they are expressed ;

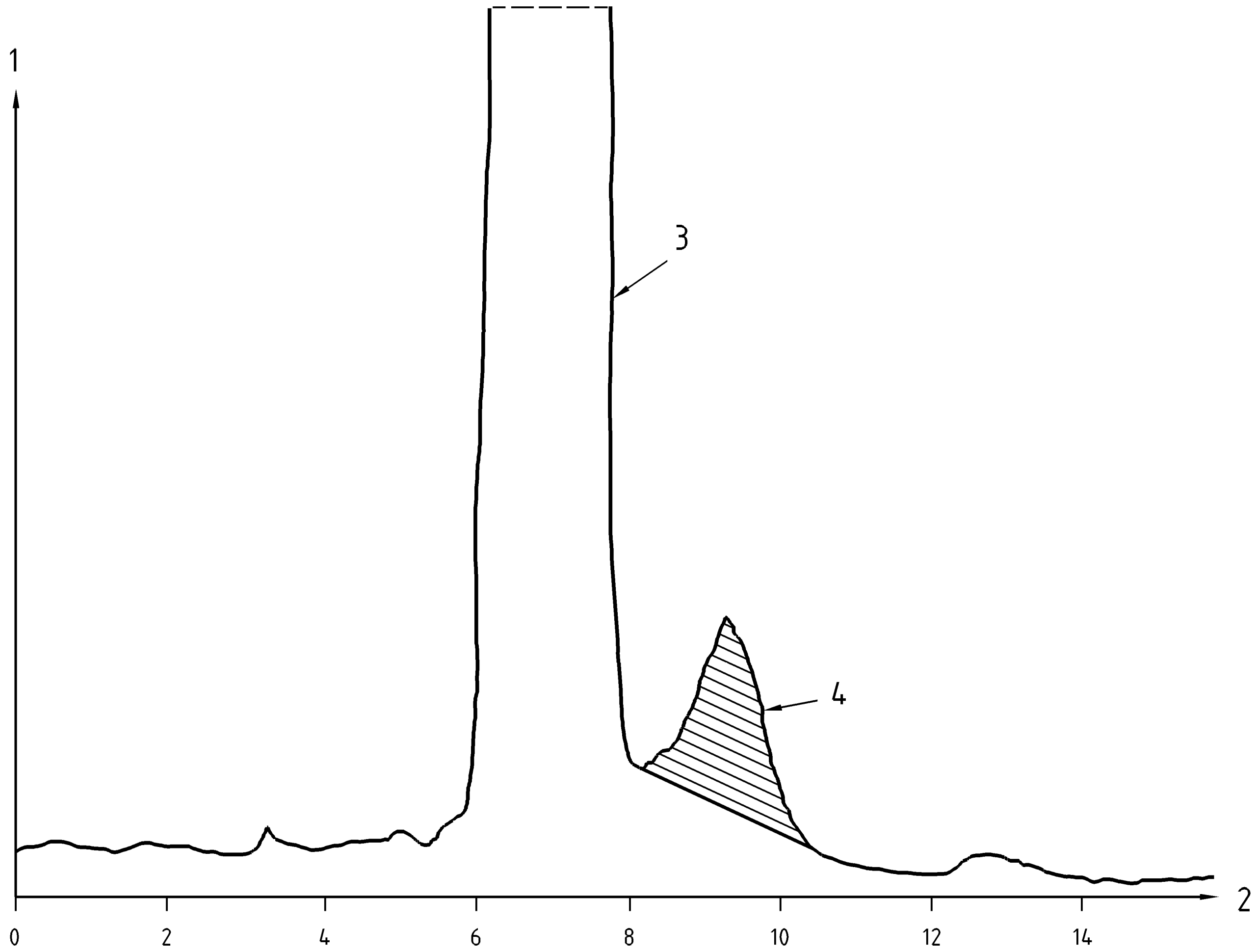
d) any operational details in this European Standard to which reference is made, as well as any operational details regarded as optional, plus details of any incidents likely to have affected the results.



Key

1 Area units
2 Time in minutes
3 Toluene
4 THN

Figure 1 - Example chromatogram - Resolution check



Key

1 Area units
2 Time in minutes
3 LAB
4 DAT

Figure 2 - Example chromatogram ECOSOL1) reference sample (w_{DAT} = 1,2 %)

Annex A
(informative)

Method of determination of the carbon number distribution of the LAB sample (UOP [2] Method 673-88)

A.1 General

This method is for determining the isomer distribution in C_{15} through C_{20} mono-substituted linear alkylbenzenes (LAB) 6-phenyltridecane and 7-phenyltridecane isomers are not resolved from each other and are determined as a composite. The lower limit of detection for a single component is 0,1 %.

Components other than linear alkylbenzenes are not determined by this method.

A.2 Principle

The sample to be analysed is injected into a gas chromatograph that is equipped with a fused silica capillary column. The composition of the sample in percent as mass fraction is obtained by the internal standard technique of quantification wherein the peak areas are first corrected for differences in response and then standardized to 100 %.

A.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and water conforming to grade 3 in accordance with EN ISO 3696:1995.

A.3.1 **Air**, total hydrocarbons less than 2,0 mg/kg as methane.

A.3.2 **Hydrogen**, total hydrocarbons less than 0,5 mg/kg as methane or helium as carrier gas.

A.3.3 **Nitrogen**, total hydrocarbons less than 0,5 mg/kg as methane.

A.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

A.4.1 **Analytical balance**, reading to the nearest 0,1 mg.

A.4.2 **Chromatographic column**, for example 30 m of length and 0,32 mm for internal diameter fused silica capillary, internally coated to a film thickness of 0,25 μm with DB-17 [3] bonded methylphenylpolysiloxane.

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[2] UOP = Universal Oil Products; company with worldwide locations, see www.uop.com

[3] DB-17 is the trade name of a product supplied by J&W Scientific (91 Blue Ravine Road, Folsom, CA 95630-4714). 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.

A.4.3 Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass insert, and equipped with a flame ionization detector that gives a minimum peak height response of 30 µV for 0,1 % of 5-phenyldecane when operated at the stated conditions. Background noise at these conditions shall not exceed 3 µV.

A.4.4 Integrator, electronic, or equivalent equipment for obtaining peak areas. This device shall integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from a capillary column can be accurately measured.

A.4.5 Regulator, air.

A.4.6 Regulator, hydrogen, two stages.

A.4.7 Regulator, nitrogen, two stages.

A.4.8 Sample injector, any syringe or injector capable of injecting a 0,2 µl volume of sample.

A.5 Procedure

WARNING - Effective health and safety practices should be followed when utilizing this procedure. Failure to utilize this procedure in the manner prescribed herein can be hazardous.

A.5.1 Chromatographic conditions

The recommended operating conditions for this analysis are listed in Table A.1. Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the typical chromatogram (see Figure A.1).

Table A.1 - Operating conditions

Carrier gas	Hydrogen or helium
Carrier gas velocity	0,28 m/s (1,4 ml/min flow rate)
Detector	Flame ionization
Detector temperature	240 °C
Injection port temperature	240 °C
Hydrogen flow rate [a]	30 ml/min
Air flow rate [a]	300 ml/min
Make up gas	Nitrogen
Make up flow rate [a]	30 ml/min
Split ratio	200 to 1
Column temperature programme	
Initial temperature	140 °C
Programming rate	1 °C/min
Final temperature	170 °C
Final time	5 min
Chart speed	1 cm/min
Sample volume	0,2 µl

[a] Consult the manufacturer's instrument manual for suggested flow rates.

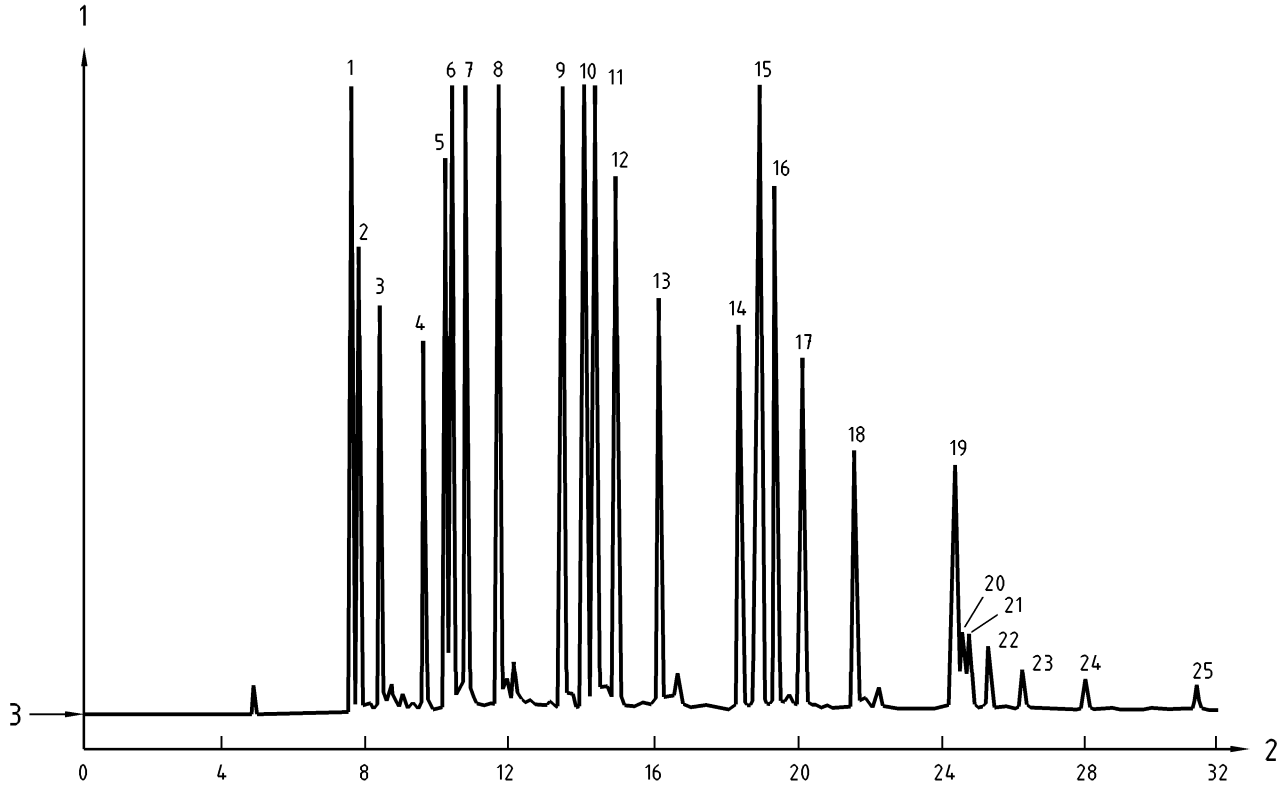
A.5.2 Determination

Install the fused silica capillary column in the gas chromatograph and establish the recommended operating conditions. Establish hydrogen or helium carrier gas flow.

WARNING - Leakage of hydrogen into the confined volume of the column compartment can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made and periodically there-after.

Programme the column oven to 170 °C. Maintain this temperature until a stable baseline has been obtained at the required sensitivity. Cool the column oven to 140 °C. Inject a sample and immediately start the temperature programmer, integrator and recorder.

NOTE 1 A typical chromatogram is shown in Figure A.1. Relative retention times of typical sample components are listed in Table A.2.



Key

1 Area units
2 Retention time in minutes
3 Injection

Figure A.1 - Typical chromatogram for a linear alkylbenzene product

Table A.2 - Relative retention times

Peak n°	Component	Relative retention times
1	5-Phenyldecane	0,41
2	4-Phenyldecane	0,43
3	3-Phenyldecane	0,46
4	2-Phenyldecane	0,53
5	6-Phenylundecane	0,56
6	5-Phenylundecane	0,57
7	4-Phenylundecane	0,59
8	3-Phenylundecane	0,64
9	2-Phenylundecane	0,73
10	6-Phenyldodecane	0,77
11	5-Phenyldodecane	0,78
12	4-Phenyldodecane	0,81
13	3-Phenyldodecane	0,87
14	2-Phenyldodecane	1,00
15	7/6-Phenyltridecane	1,03
16	5-Phenyltridecane	1,06
17	4-Phenyltridecane	1,09
18	3-Phenyltridecane	1,18
19	2-Phenyltridecane	1,33
20	7-Phenyltetradecane	1,34
21	6-Phenyltetradecane	1,35
22	5-Phenyltetradecane	1,38
23	4-Phenyltetradecane	1,43
24	3-Phenyltetradecane	1,53
25	2-Phenyltetradecane	1,70

The exact retention times shall be checked on each individual instrument by comparing a run to the typical chromatogram in Figure A.1. Determine the peak areas of the linear alkylbenzene components.

NOTE 2 For the purposes of this method, components other than linear alkylbenzenes are not quantificated.

A.5.3 Time for analysis

The elapsed time for one analysis is approximately 0,7 h. The labour requirement is approximately 0,3 h.

A.6 Calculations

The content of each linear alkylbenzene, w_i expressed as mass fraction in percent, is calculated to the nearest 0,1 % by the equation (A.1) :

$$w_i = 100 \frac{A}{S} \tag{A.1}$$

where

A	is the peak area of the ith component ;
S	is the sum of all A of all linear alkylbenzene peaks ;
100	is the factor to convert to percent.

The average linear alkylbenzene molar mass of the sample, M_P, expressed in grams per mole, is calculated by the equation (A.2) :

$$Mp = \frac{100}{\sum_{i=1}^{N} \frac{w_i}{M_i}} \tag{A.2}$$

where

M_i	is the molar mass of the ith component, in grams per mole ;
W_i	is the mass fraction of the ith component, in percent ;
N	is the number of components ;
100	is the factor to convert to percent.

A.7 Precision

A.7.1 Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in Table A.3. Two tests performed in one laboratory by different analysts on different days shall not differ by more than the allowable difference values listed in Table A.3 at the concentrations listed.

Table A.3 - Estimated standard deviations (esd) and allowable differences for several linear alkylbenzene isomers

Component	Concentration	Within-lab esd	Allowable difference, 95 % probability
	%	%	%
2-Phenyldecane	2,5	0,02	0,06
3-Phenylundecane	5,2	0,02	0,1
4-Phenyldodecane	4,5	0,02	0,1
5-Phenyltridecane	5,1	0,02	0,1
6-Phenyltetradecane	0,9	0,01	0,1

A.7.2 Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Bibliography

ASTM D 4307:1994, Practice for preparation of liquid blends for use as analytical standards.

UOP Method 673-88, Linear alkylbenzene isomer distribution in detergent alkylate by gas chromatography.

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