



A Honeywell Company

Linear Alkylbenzene Isomer Distribution in Detergent Alkylate by GC

UOP Method 673-12

Scope

This method is for determining the isomer distribution in C₁₅ through C₂₀ mono-substituted linear alkylbenzenes (LABs). The 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 mass-%.

Components other than linear alkylbenzenes are not normally determined by this method; however, an estimate of the total LAB content of the sample may be obtained by measuring the components present in the sample other than the LABs. A calculation is included to determine the number average molecular weight of the LABs in the sample, if needed.

Reference

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a fused silica capillary column. The mass-% distribution of LABs is obtained by the internal normalization technique of quantitation wherein the peak areas of the LABs are normalized to 100%. By summing the non-LAB components, an estimate of the linearity of the detergent alkylate may be obtained.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Chromatographic column, 30 m of 0.32-mm ID fused silica capillary, internally coated to a film thickness of 0.25 µm with DB-17 bonded (50%-phenyl)-methylpolysiloxane, Agilent Technologies, Cat. No. 123-1732

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert and equipped with a flame

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ionization detector (FID), Agilent Technologies, Model 7890A, with autosampler capable of injecting a repeatable 0.2- μ L volume of sample, Agilent Technologies, Model 7693A

Data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from the use of a capillary column can be accurately measured. Agilent Technologies, ChemStation.

Leak detector, gas, Grace Davison, Cat. No. 60229

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Gas purifier, for hydrogen, to remove oxygen and moisture from carrier gas, VICI Mat/Sen, Cat. No. P200-1, and (optional) indicating oxygen trap, Restek, Cat. No. 22010, see *Procedure, Chromatographic Technique*, Step 1

Hydrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Nitrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Syringe, replacement, for recommended sample injector, 10- μ L, Agilent Technologies, Cat. No. 5181-1267

Vials, autosampler, for recommended sample injector, with caps, Agilent Technologies, Cat. No. 5182-0864

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if the gas purifier is not used. Replace the gas purifier at intervals determined by good laboratory practice. An indicating oxygen trap may be placed downstream of the gas purifier. When the indicator shows one-half used, replace both the gas purifier and the indicating trap.
2. Install the fused silica capillary column in the gas chromatograph according to the column and gas chromatograph manufacturer's instructions.
 - CAUTION: Hydrogen leakage into the confined volume of the column oven can cause a violent explosion. Therefore, it is mandatory to check for leaks each time a connection is made and periodically thereafter.

3. Establish the recommended operating conditions as given in Table 1.
 - Different conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (see Figure).
4. Program the column oven to 250°C (see Table 1) and maintain this temperature until a stable baseline has been obtained at the required sensitivity.

Table 1
Recommended Operation Conditions

Carrier gas	hydrogen
Mode	constant flow
Flow rate	1.4 mL/min flow rate
Column head pressure @ 140 °C	38 kPa gauge (5.5 psig)
Linear velocity	32.5 cm/sec
Split flow rate	280 mL/min
Injection port temperature	240 °C
Column temperature program	
Initial temperature	140 °C
Initial time	0 min
Programming rate	1 °C/min
Final temperature	170 °C
Final hold time^a	5 min
Detector	flame ionization
Detector temperature	240 °C
Hydrogen flow rate^b	30 mL/min
Air flow rate^b	300 mL/min
Makeup gas	nitrogen
Makeup flow rate^b	30 mL/min
Sample size	0.2 µL

^aThe final hold time may need to be adjusted to ensure that all heavies elute and response returns to baseline. If heavy components continue to elute for an extended period, the column temperature may be raised rapidly to up to 250°C to shorten the total analysis time. This increase in column temperature must be started after a flat baseline is established following the elution of the LABs.

^bConsult the manufacturer's instrument manual for suggested flow rates.

5. Cool the column oven to a stabilized 140°C.
6. Inject nominally 0.2 µL of the sample and immediately start the data system and column temperature programming sequence.
 - The use of an autosampler automates the injection of the sample into the GC, starts the data system, and the GC oven program simultaneously.
7. Identify the components by comparing the chromatogram obtained to the Typical Chromatogram shown in the Figure. The LAB peaks are identified in Table 2.
 - To ensure accuracy, the chromatographic baseline must be straight, without drift, from beginning to end. The parameters of the integrator must also be adjusted so that a continuous, straight baseline is followed, and the integrator must separate the areas defined as the LAB with a perpendicular drop, not a tangent skim.
8. Determine the area of each LAB peak. If an estimate of the linearity of the detergent alkylate is desired, sum the areas of all the non-LAB peaks.

Table 2
LAB Components

<u>Peak No.</u>	<u>Component</u>	<u>Peak No.</u>	<u>Component</u>
1	5-Phenylnonane	14	6-Phenyldodecane
2	4-Phenylnonane	15	5-Phenyldodecane
3	3-Phenylnonane	16	4-Phenyldodecane
4	2-Phenylnonane	17	3-Phenyldodecane
5	5-Phenyldecane	18	2-Phenyldodecane
6	4-Phenyldecane	19	7- & 6-Phenyltridecane
7	3-Phenyldecane	20	5-Phenyltridecane
8	2-Phenyldecane	21	4-Phenyltridecane
9	6-Phenylundecane	22	3-Phenyltridecane
10	5-Phenylundecane	23	2-Phenyltridecane
11	4-Phenylundecane	24	7-Phenyltetradecane
12	3-Phenylundecane	25	6-Phenyltetradecane
13	2-Phenylundecane	26	5-Phenyltetradecane
		27	4-Phenyltetradecane
		28	3-Phenyltetradecane
		29	2-Phenyltetradecane

Calculations

Because all components in the sample are similar, the flame ionization detector responds equally on a mass basis to the components determined; therefore, no response factors are required. Calculate the isomer distribution of the LABs, to the nearest 0.1 mass-%, using Equation 1.

$$\text{Component, mass-\%} = \frac{100 E}{S} \quad (1)$$

where:

E = peak area of each linear alkylbenzene isomer
S = sum of all recorded LAB peak areas
100 = factor to convert to mass-%

If an estimate of the linearity of the detergent alkylate is desired, calculate the estimated linearity using Equation 2.

$$\text{Estimated linearity, mass-\%} = \frac{100 S}{T} \quad (2)$$

where:

S = sum of all recorded LAB peak areas
T = sum of all recorded LAB peak areas and non-LAB peak areas
100 = factor to convert to mass-%

If the average molecular weight of the LABs in the sample is desired, calculate the number average molecular weight of the LABs in the sample using Equation 3.

$$\text{Number average molecular weight of the LABs in the sample} = \frac{100}{\sum_{i=1}^n \frac{M_i}{G_i}} \quad (3)$$

where:

G_i = molecular weight of component i, see Table 3, g/mol
 i = each component
 M_i = mass-% of component i
 n = number of components
 100 = conversion from mass-%

Table 3
Molecular Weights of LABs, g/mol

Phenylnonane	204.35
Phenyldecane	218.38
Phenylundecane	232.41
Phenyldodecane	246.44
Phenyltridecane	260.46
Phenyltetradecane	274.49

Precision

Precision statements were determined using UOP Method 999 from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining LAB isomer distribution in a detergent alkylate sample with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests on each day. The total number of tests for each component was eight. The precision data are summarized in Table 4. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 4 are a short-term estimate of repeatability and site precision. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term intermediate precision.

Reproducibility

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

Time for Analysis

The elapsed time for one analysis is 0.7 hour. The labor requirement is 0.3 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610, USA (302-633-8000)
www.agilent.com

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA (847-948-8600)
www.discoverysciences.com

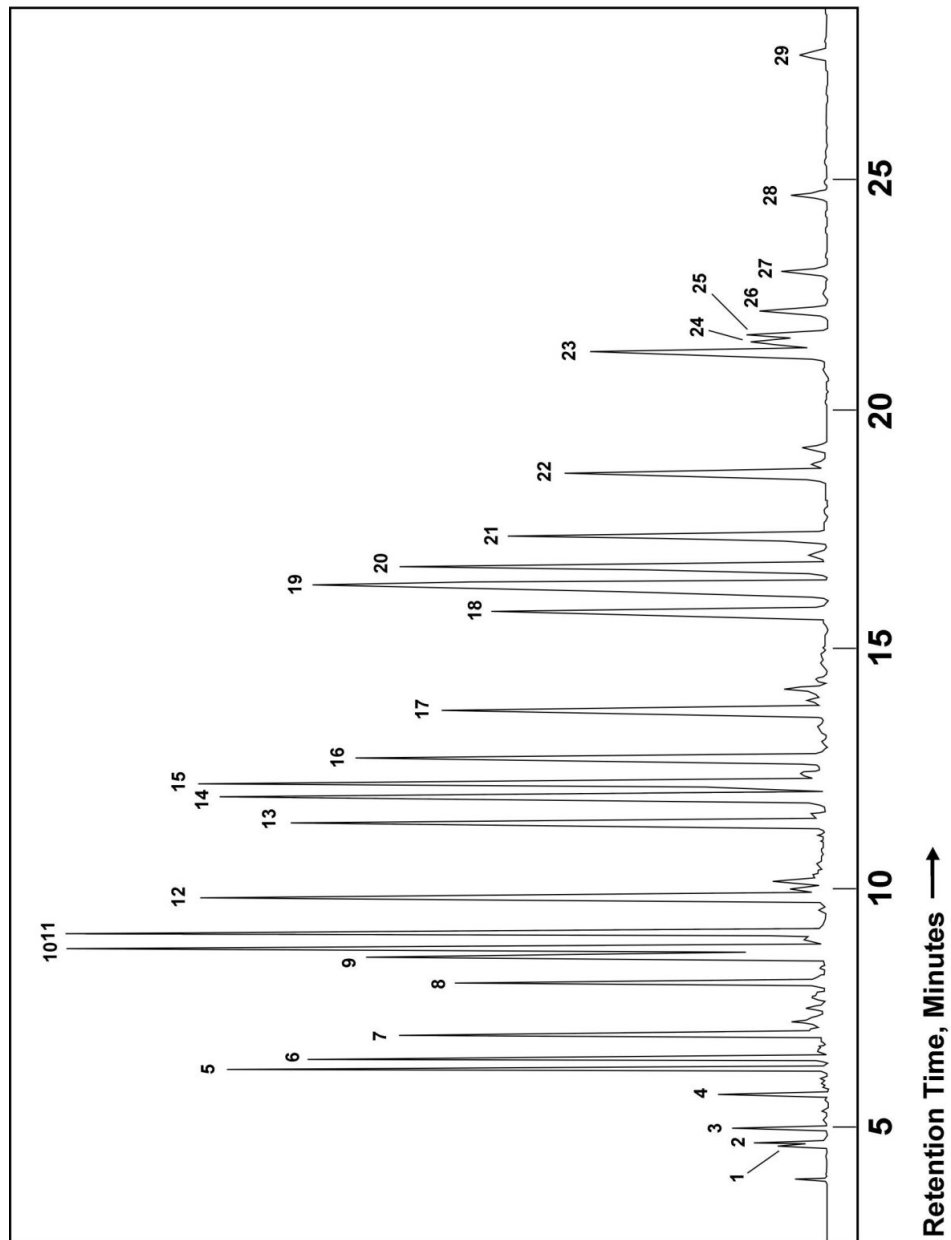
Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936, USA (215-648-4000)
www.mathesontrigas.com

Restek, 110 Benner Circle, Bellefonte, PA 16823, USA (814-353-1300) www.restek.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055, USA (713-688-9345) www.vicimatsen.com

Table 4
Repeatability and Site Precision, mass-%

<u>Component</u>	<u>Mean Conc.</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
5-Phenyldecane	2.58	0.004	0.01	0.006	0.04
4-Phenyldecane	2.46	0.004	0.02	0.005	0.02
3-Phenyldecane	3.04	0.014	0.08	0.019	0.08
2-Phenyldecane	4.46	0.009	0.03	0.012	0.05
6-Phenylundecane	2.99	0.021	0.08	0.030	0.12
5-Phenylundecane	5.90	0.008	0.03	0.010	0.04
4-Phenylundecane	5.61	0.005	0.02	0.005	0.02
3-Phenylundecane	6.91	0.008	0.03	0.010	0.04
2-Phenylundecane	9.62	0.016	0.06	0.022	0.09
6-Phenyldodecane	5.04	0.004	0.01	0.006	0.04
5-Phenyldodecane	5.18	0.004	0.01	0.004	0.01
4-Phenyldodecane	4.88	0.004	0.02	0.005	0.02
3-Phenyldodecane	6.08	0.004	0.01	0.004	0.01
2-Phenyldodecane	8.51	0.005	0.02	0.005	0.02
7- & 6-Phenyltridecane	5.84	0.005	0.02	0.005	0.02
5-Phenyltridecane	4.05	0.003	0.01	0.004	0.01
4-Phenyltridecane	3.73	0.005	0.02	0.005	0.02
3-Phenyltridecane	4.65	0.007	0.03	0.009	0.03
2-Phenyltridecane	6.75	0.023	0.09	0.106	0.65
7-Phenyltetradecane	0.08	0.007	0.03	0.111	0.21
6-Phenyltetradecane	0.28	0.004	0.01	0.004	0.01
5-Phenyltetradecane	0.31	0.011	0.04	0.015	0.06
4-Phenyltetradecane	0.28	0.008	0.03	0.011	0.04
3-Phenyltetradecane	0.32	0.008	0.03	0.011	0.04
2-Phenyltetradecane	0.48	0.015	0.06	0.017	0.08



Figure

Typical Chromatogram

UOP Method 673