



Designation: D 4337 – 89 (Reapproved 1995)<sup>ε1</sup>

## Standard Test Methods for Analysis of Linear Detergent Alkylates<sup>1</sup>

This standard is issued under the fixed designation D 4337; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Keywords were added editorially in February 1995.

### 1. Scope

1.1 These test methods cover chemical and physical tests applicable to linear detergent alkylates, evaluating those properties which characterize linear detergent alkylates with respect to its suitability for desired uses.

NOTE 1—Linear detergent alkylates comprises linear alkylbenzenes prepared by varying processes of varying linear alkyl chain length. The alkylate is sulfonated for surfactant use, the largest application being in detergent products. Careful control of linear detergent alkylate characteristics is desired; during sulfonation, variations of the sulfonate can occur that may result in either desirable or undesirable end-use properties.

1.2 The test methods appear as follows:

	Section
Composition by Gas Chromatography	7-15
Chlorides	16-27
Color	28-30
Refractive Index	31-33
Specific Gravity	34-36
Water	37-39

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage. See also Note 1 and Section 21.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 270 Method of Sampling Petroleum and Petroleum Products<sup>2</sup>
- D 1122 Test Method for Specific Gravity of Engine Coolant Concentrates and Engine Coolants by the Hydrometer<sup>3</sup>
- D 1193 Specification for Reagent Water<sup>4</sup>

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-12 on Soaps and other Detergents and are the direct responsibility of Subcommittee D12.12 on Analysis of Soaps and Synthetic Detergents.

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<sup>2</sup> Discontinued, see 1984 Annual Book of ASTM Standards, Vol 05.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 15.05.

<sup>4</sup> Annual Book of ASTM Standards, Vol 11.01.

D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)<sup>5</sup>

D 1218 Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids<sup>6</sup>

D 1364 Test Method for Water in Volatile Solvents (Fischer Reagent Titration Method)<sup>5</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

### 3. Significance and Use

3.1 These test methods are suitable for setting specifications on linear detergent alkylates and for quality control where these alkylates are manufactured or are used in a manufacturing process.

3.2 The gas chromatography test is useful in identifying linear detergent alkylates produced by the various manufacturing processes and for determining the applicability of a linear detergent alkylate to a particular end use. Test conditions have been optimized for resolution of the C-9 to C-15 linear detergent alkylates and the presence of higher or lower chain lengths will be readily apparent but may produce erroneous results. The tetralin structures have not been sufficiently identified to allow determination of tetralins, and small unidentified components are reported as tetralins and unidentified.

3.3 Some linear detergent alkylates use a manufacturing process with an organic chloride as a precursor. This test may be used to ensure that the chloride content of the alkylate is not excessive for a particular end use.

3.4 The platinum-cobalt color test is useful in determining that the color of the linear detergent alkylate will not contribute to the color of the end use product.

3.5 The refractive index and specific gravity tests are possible aids in the identification of linear detergent alkylates and in evaluating alkylates for gross contaminants.

3.6 The water test is suitable for determining that linear detergent alkylates do not contain amounts of water deleterious to further processing.

### 4. Purity of Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be

<sup>5</sup> Annual Book of ASTM Standards, Vol 06.04.

<sup>6</sup> Annual Book of ASTM Standards, Vol 05.01.

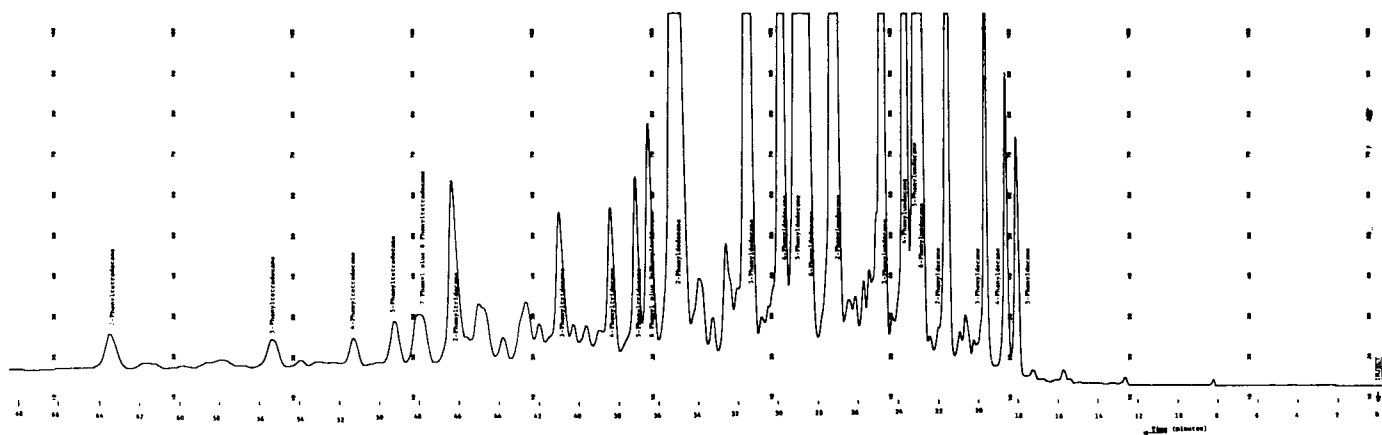


FIG. 1 Typical Gas Chromatic Scan of an Alkylate

used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,<sup>7</sup> where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean Type III water conforming to Specification D 1193.

## 5. Precautions

5.1 Consult the latest OSHA regulations regarding all reagents and materials used in these test methods.<sup>8</sup>

## 6. Sampling

6.1 Unless otherwise indicated in a specific test method, sample the material in accordance with Method D 270, with special application of Sections 41 and 42 pertaining to industrial aromatic hydrocarbons, Section 12 pertaining to Bottle or Beaker Sampling, and Section 15 pertaining to Tap Sampling. Samples must be taken and stored in amber, screw-cap, glass bottles to protect them from light.

## COMPOSITION BY GAS CHROMATOGRAPHY

### 7. Scope

7.1 The gas chromatography test was developed to allow determination of C-9 through C-15 linear detergent alkylate isomer distribution before sulfonation. The analyses of stocks having a chain length distribution above or below the interval covered in this test method will require a different set of operating conditions. If water, extremely high boiling components, or unusual impurities are present in the linear detergent

alkylate, this test would not necessarily detect them and may produce erroneous results.

### 8. Summary of Test Method

8.1 A sample is injected by means of a microsyringe into a vaporization chamber of a gas chromatograph. A stream splitter allows the majority of the sample to be vented into the atmosphere through a valve that is incorporated in the vaporization chamber. A small portion of the sample is then swept by the carrier gas into a capillary column that has been coated with a thin layer of the stationary phase. A hydrogen flame ionization detector provides a very sensitive means of detecting the extremely small concentrations of separated vapor components as they elute from the column. An electrometer-amplifier converts the detector signal into a suitable signal that can be recorded on a standard strip-chart recorder and integrated by a suitable integration device. The concentrations of the components are obtained by normalizing the integrated areas, based on the assumption that all components of the mixture are eluted under the conditions used.

### 9. Apparatus

9.1 *Gas Chromatograph*, with the following characteristics:

9.1.1 *Sample Injection Port*, operable at 250°C and containing a stream splitter capable of linearly splitting sample injections up to 1000 to 1.

9.1.2 *Column Oven*, capable of temperature programming from 120 to 165°C at a rate of 1 or 2°C per min.

9.1.3 *Flame Ionization Detector*, capable of operating at 300°C.

9.2 *Recorder*, 0 to 1 mv range with 0.1 second full scale deflection.

9.3 *Integration Device*, capable of accurately measuring areas of up to 250 components.

9.4 *Column*, 150 ft (45.7 m) by 0.01 in. (0.25 mm) inside diameter stainless steel wall; open tubular capillary column coated with phenyl methyl silicone DC-550<sup>9</sup> or other column that will perform required separation as indicated in Fig. 1.

<sup>7</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>8</sup> Available from Occupational Safety and Health Review Commission, 1825 K Street, Washington, DC 20006.

<sup>9</sup> Capillary column, Part 009-0354, available from Perkin-Elmer Corporation, Norwalk, CT, has been found satisfactory.

9.5 Syringe, 10- $\mu$ L capacity with fixed 2-in. (5.1 cm) needle.<sup>10</sup>

## 10. Reagents

- 10.1 Carrier Gas, high-purity nitrogen.
- 10.2 Hydrogen, 99.996 mol % pure.
- 10.3 Compressed Air.

## 11. Calibration

11.1 No calibration or correction factors are necessary as the response of the flame ionization detector is essentially constant for aromatic hydrocarbons. The individual peak area percentages may be regarded as the actual weight percent in the sample.

## 12. Procedure

12.1 Adjust the chromatograph to the following conditions:

Column temperature, °C (Note 2)	120 programmed to 160 at 1 to 2°C per min
Injection port temperature, °C	250
Detector temperature, °C	300
Carrier gas pressure, lbf	60
Sample size (Note 3), $\mu$ L	0.5 to 1
Chart speed, cm/min	1
Hydrogen flow (Note 4), mL/min	30
Air flow (Note 4), mL/min	240
Range	X1
Attenuator setting	X4
Splitter (Note 3)	1000/1

NOTE 2—These conditions should give adequate separation. It may be necessary to adjust conditions slightly to meet the separation criteria of the sample chromatogram (Fig. 1), depending upon the performance of the capillary column.

NOTE 3—Sample size and splitter ratio should be adjusted to obtain a peak height of 10 to 15 mV for the largest components.

NOTE 4—Hydrogen and air flows should be adjusted to give maximum detector sensitivity. See instructions in instrument instruction manual.

12.2 When a new column is installed, leak-test the plumbing connections by applying the operating carrier gas pressure. The air and hydrogen connections to the detector should be leak tested periodically. In particular, the hydrogen supply should be leak-tested at the cylinder each time the cylinder is changed, due to the hazardous nature of hydrogen gas.

12.3 Wet and rinse the syringe with the sample and draw an excess of liquid into the syringe barrel. Exercise caution that all air bubbles are excluded from the liquid in the syringe. Carefully depress the plunger until the exact amount of liquid desired is contained in the syringe.

12.4 Open the split valve and quickly pierce the septum, thrusting the needle of the syringe completely into the inlet. In the same motion quickly and completely depress the plunger. Immediately withdraw the syringe and start the column oven temperature program sequence. The split valve may be closed 1 min after the injection of the sample, but it must always be closed at exactly the same time after injection.

12.5 Compare the sample chromatogram with the standard chromatogram (Fig. 1) and from the retention times of the components identify all straight chain alkyl benzene isomers.

Label all peaks whose identity has been established. Many unidentified minor peaks will appear as minor constituents of the sample and may be attributed to tetralin structures. Include these peaks in the calculations and report in a pooled percentage as tetralins and unknowns.

## 13. Calculations

13.1 Calculate the percentage for each component by dividing the area of each component by the total area of all components and multiplying by 100.

13.2 Calculate the total 2-phenyl isomer by summing together the 2-phenyl isomers for all chain lengths.

13.3 Calculate the chain length distribution by summing together all percentages for the identified linear alkyl benzene isomers of each chain length.

13.4 Calculate lights (components eluting before C<sub>10</sub> alkyl benzene) by summing together the percentages of all the components eluting before 5-phenyldecane.

13.5 Calculate heavies (components eluting after C<sub>14</sub> alkyl benzene) by summing together all the percentages of the components eluting after 2-phenyltetradecane.

13.6 Calculate tetralins and unknowns by summing together the percentages of all unidentified peaks eluting between the 5-phenyldecane peak and the 2-phenyltetradecane peak.

13.7 Determine the average molecular weight by assuming the tetralins and unknowns to have a molecular weight of 244. The average molecular weight is calculated to the third decimal place using the following equation:

$$\begin{aligned} \text{Average molecular weight} = & [100 - (\text{lights} \\ & + \text{heavies})][(\sum C_{10} \text{ isomers}/218) \\ & + (\sum C_{11} \text{ isomers}/232) + (\sum C_{12} \text{ isomers}/246) \\ & + (\sum C_{13} \text{ isomers}/260) + (\sum C_{14} \text{ isomers}/274) \\ & + (\sum \text{tetralins} + \text{unknowns}/244)] \end{aligned} \quad (1)$$

## 14. Report

14.1 Report the components and average molecular weight as specified in Table 1. Duplicate runs that agree within the checking limits shown in Table 1 are acceptable for averaging (95 % confidence level).

## 15. Precision and Bias

15.1 The following criteria should be used for judging the acceptability of results:

15.1.1 *Repeatability (Single Analyst)*— The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value shown in Table 1 with the indicated degrees of freedom. Two such results should be considered suspect (95 % confidence level) if they differ by more than the values in Table 1.

15.1.2 *Reproducibility (Multilaboratory)*— The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value shown in Table 1 with the indicated degrees of freedom. Two such results should be considered suspect (95 % confidence level) if they differ by more than the values shown in Table 1 (Note 5).

NOTE 5—The preceding precision estimates are based on an interlaboratory study of six samples of linear detergent alkylates. A total of eight

<sup>10</sup> Microsyringe No. 701, available from Hamilton Co., P. O. Box 307, Whittier, CA, has been found satisfactory.