



Designation: D3238 – 22a

# Standard Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method<sup>1</sup>

This standard is issued under the fixed designation D3238; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This test method covers the calculation of the carbon distribution and ring content (Note 1) of olefin-free petroleum oils from measurements of refractive index, density, and molecular weight (n-d-M).<sup>2</sup> This test method should not be applied to oils whose compositions are outside the following ranges:

1.1.1 *In terms of carbon distribution*—up to 75 % carbon atoms in ring structure; percentage in aromatic rings not larger than 1.5 times the percentage in naphthenic rings.

1.1.2 *In terms of ring content*—up to four rings per molecule with not more than half of them aromatic. A correction must be applied for oils containing significant quantities of sulfur.

NOTE 1—The composition of complex petroleum fractions is often expressed in terms of the proportions of aromatic rings ( $R_A$ ), naphthene rings ( $R_N$ ), and paraffin chains ( $C_p$ ) that would comprise a hypothetical mean molecule. Alternatively, the composition may be expressed in terms of a carbon distribution, that is, the percentage of the total number of carbon atoms that are present in aromatic ring structures (%  $C_A$ ), naphthene ring structures (%  $C_N$ ), and paraffin chains (%  $C_p$ ).

1.2 The values stated in SI units are to be regarded as the standard.

1.2.1 *Exception*—The values in parentheses are for information only.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0K on Correlative Methods.

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<sup>2</sup> Van Nes, K., and van Westen, H. A., *Aspects of the Constitution of Mineral Oils*, Elsevier, New York, 1951.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>3</sup>

D1218 Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids

D1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer

D1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer

D1552 Test Method for Sulfur in Petroleum Products by High Temperature Combustion and Infrared (IR) Detection or Thermal Conductivity Detection (TCD)

D2502 Test Method for Estimation of Mean Relative Molecular Mass of Petroleum Oils from Viscosity Measurements

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *solvent refining, n—in lubricant manufacture*, a manufacturing process for the removal of most of the ring structures and aromatics from heavy distillates by liquid extraction.

3.2.1.1 *Discussion*—Common and suitable solvents for extraction are phenol, furfural and sulfur dioxide. Furfural is used as the extractant for the manufacture of paraffinic oils.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

\*A Summary of Changes section appears at the end of this standard

#### 4. Summary of Test Method

4.1 The refractive index and density of the oil are determined at 20 °C. The molecular weight is determined experimentally or estimated from measurements of kinematic viscosity at 37.8 °C and 98.89 °C (100 °F and 210 °F). These data are then used to calculate the carbon distribution (%  $C_A$ , %  $C_N$ , %  $C_P$ ) or the ring analysis ( $R_A$ ,  $R_N$ ) using the appropriate set of equations.

#### 5. Significance and Use

5.1 The carbon distribution and ring content serve to express the gross composition of the heavier fractions of petroleum. These data can be used as an adjunct to the bulk properties in monitoring the manufacture of lubricating oil base stocks by distillation, solvent refining or hydrogenation, or both, and in comparing the composition of stocks from different crude sources. Furthermore, the data can often be correlated with critical product performance properties.

#### 6. Measurement of Physical Properties

6.1 Determine the refractive index of the oil at 20 °C using Test Method **D1218**.

6.2 Determine the density at 20 °C using Test Method **D1480**, Test Method **D1481**, or Test Method **D4052**.

6.3 Determine the average molecular weight using Test Method **D2502**.

#### 7. Determination of Sulfur Content

7.1 Determine the percentage of sulfur in the oil using Test Methods **D1552**, **D2622**, or **D4294**.

#### 8. Calculation of Carbon Distribution and Ring Content

8.1 Calculate the factors  $v$  and  $w$  from the observed density ( $d$ ) and the observed refractive index ( $n$ ) using the following equations:

$$v = 2.51(n_D^{20} - 1.4750) - (d_4^{20} - 0.8510) \quad (1)$$

$$w = (d_4^{20} - 0.8510) - 1.11(n_D^{20} - 1.4750) \quad (2)$$

8.2 Calculate the percentage of aromatic carbon (%  $C_A$ ) from  $v$  and the molecular weight ( $M$ ) using one of the following equations:

$$\text{if } v \text{ is positive: } \% C_A = 430 v + 3660/M \quad (3)$$

$$\text{if } v \text{ is negative: } \% C_A = 670 v + 3660/M \quad (4)$$

8.3 Calculate the percentage of carbon in total (aromatic and naphthenic) ring structures (%  $C_R$ ) from  $w$  and the molecular weight.

$$\text{if } w \text{ is positive: } \% C_R = 820 w - 3 S + 10000/M \quad (5)$$

$$\text{if } w \text{ is negative: } \% C_R = 1440 w - 3 S + 10600/M \quad (6)$$

where:

$S$  = mass % sulfur.

8.4 Calculate the percentage of naphthenic carbon (%  $C_N$ ) and the percentage of paraffinic carbon (%  $C_P$ ) as follows:

$$\% C_N = \% C_R - \% C_A \quad (7)$$

$$\% C_P = 100 - \% C_R \quad (8)$$

8.5 Calculate the average number of aromatic rings per molecule ( $R_A$ ) from  $v$  and the molecular weight:

$$\text{if } v \text{ is positive: } R_A = 0.44 + 0.055 Mv \quad (9)$$

$$\text{if } v \text{ is negative: } R_A = 0.44 + 0.080 Mv \quad (10)$$

8.6 Calculate the average total number of rings per molecule ( $R_T$ ) from  $w$  and the molecular weight:

$$\text{if } w \text{ is positive: } R_T = 1.33 + 0.146 M (w - 0.005 S) \quad (11)$$

$$\text{if } w \text{ is negative: } R_T = 1.33 + 0.180 M (w - 0.005 S) \quad (12)$$

where:

$S$  = mass % sulfur.

8.7 Calculate the average number of naphthene rings per molecule ( $R_N$ ) by difference:

$$R_N = R_T - R_A \quad (13)$$

8.8 Report ring numbers to the nearest 0.01 ring and carbon distribution to the nearest 0.1 %.

#### 9. Precision and Bias

9.1 The precision of this test as obtained by statistical examination of interlaboratory test results is as follows:

9.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in 1 case in 20:

	Range	Repeatability
% $C_A$	2.7 to 34.6	0.6
% $C_N$	23.7 to 47.2	1.2
% $C_P$	32.3 to 68.6	1.0
$R_A$	0.12 to 1.69	0.04
$R_N$	1.61 to 2.90	0.08
$R_T$	1.73 to 3.77	0.08

9.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in 1 case in 20:

	Range	Reproducibility
% $C_A$	2.7 to 34.6	1.7
% $C_N$	23.7 to 47.2	3.6
% $C_P$	32.3 to 68.6	3.4
$R_A$	0.12 to 1.69	0.09
$R_N$	1.61 to 2.90	0.23
$R_T$	1.73 to 3.77	0.23

9.2 *Bias*—Bias cannot be determined because there are no reference materials suitable for determining the bias of this test method.

#### 10. Keywords

10.1 carbon distribution; density; molecular weight; petroleum oils; refractive index; ring content