



# 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 D 3238; 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. 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 and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

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

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

Current edition approved Nov. 1, 2005. Published November 2005. Originally approved in 1973. Last previous edition approved in 2000 as D 3238 – 95 (2000) $\epsilon^1$ .

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

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

**D 1218** Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids

**D 1480** Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer

**D 1481** Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer

**D 1552** Test Method for Sulfur in Petroleum Products (High-Temperature Method)

**D 2502** Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum Oils from Viscosity Measurements

**D 2503** Test Method for Relative Molecular Mass (Molecular Weight) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure

**D 2622** Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-Ray Fluorescence Spectrometry

## 3. Summary of Test Method

3.1 The refractive index and density of the oil are determined at 20°C. The molecular weight is determined experimentally or estimated from measurements of viscosity at 37.8 and 98.89°C (100 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.

## 4. Significance and Use

4.1 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.

## 5. Measurement of Physical Properties

5.1 Determine the refractive index of the oil at 20°C using Test Method **D 1218**.

5.2 Determine the density at 20°C using Test Method **D 1480** or Test Method **D 1481**.

5.3 Determine the average molecular weight using Test Method **D 2502** or Test Method **D 2503**.

## 6. Determination of Sulfur Content

6.1 Determine the percentage of sulfur in the oil using Test Methods **D 1552** or **D 2622**.

## 7. Calculation of Carbon Distribution and Ring Content

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

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

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

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

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

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

7.3 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.

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

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

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

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

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

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

7.6 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.

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

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

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

## 8. Precision and Bias

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

8.1.1 *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

8.1.2 *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

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

## 9. Keywords

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

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