



Standard Test Method for Estimation of Solubility of Water in Hydrocarbon and Aliphatic Ester Lubricants¹

This standard is issued under the fixed designation D 4056; 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.

1. Scope

1.1 This test method covers a procedure for estimating the equilibrium solubility of water and its vapor in hydrocarbon and aliphatic ester lubricants, at temperatures between 277 and 373 K. The test method is limited to liquids of low to moderate polarity and hydrogen bonding, with predicted solubilities not over 1000 ppm by weight in hydrocarbons, or 30 000 ppm by weight in oxygenated compounds, at 298 K.

1.2 Specifically excluded are olefins, nitriles, nitro compounds, and alcohols.

1.3 This test method is recommended only for liquids not containing widely different chemical species. This excludes blends of esters with hydrocarbons, and lubricants containing detergents, dispersants, rust preventives, or load carrying additives.

1.4 The values stated in SI units are to be regarded as the standard. Values in parentheses are given for information only.

1.5 *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:

- D 94 Test Method for Saponification Number of Petroleum Products²
- D 1218 Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids²
- D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method²
- D 2502 Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum Oils from Viscosity Measurements²

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.11 on Engineering Sciences of High Performance Fluids and Solids.

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² Annual Book of ASTM Standards, Vol 05.01.

D 3238 Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method³

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *charge transfer parameter*—the portion of the solubility parameter not attributed to London or Keesom forces.

3.1.1.1 *Discussion*—It includes hydrogen bonds, induced dipoles, and other quasichemical forces.

3.1.1.2 *Discussion*—The square of the solubility parameter equals the sum of the squares of the three partial parameters.

3.1.2 *dispersion parameter*—the portion of the solubility parameter attributed to London forces.

3.1.3 *polar parameter*—the portion of the solubility parameter attributed to Keesom (permanent dipole) forces.

3.1.4 *solubility parameter*—the square root of the cohesive energy density (heat of vaporization minus work of vaporization, per unit volume of liquid), at 298 K.

3.2 Symbols:

- C_A = percentage of aromatic carbons,
- C_N = percentage of naphthenic carbons,
- d = density of lubricant at 298 K, g/mL,
- G = solubility by weight, mg/kg (ppm),
- M = molecular weight of lubricant, g/mol,
- n_D = refractive index of lubricant at 298 K,
- RH = relative humidity, %,
- S = saponification number, mg of KOH/g of lubricant,
- T = system temperature, K,
- V = molar volume of lubricant, mL/mol,
- x = mole fraction of water in equilibrium mixture,
- y = Lorentz-Lorenz refractivity function,
- δ_d = dispersion parameter, (MPa)^{0.5},
- P = polar parameter, (MPa)^{0.5},
- H = charge transfer parameter, (MPa)^{0.5},
- ϕ_1 = volume fraction of lubricant in equilibrium mixture, and
- ϕ_2 = volume fraction of water in equilibrium mixture.

³ Annual Book of ASTM Standards, Vol 05.02.

4. Summary of Test Method

4.1 Data required are the density, refractive index, and molecular weight of a hydrocarbon. The saponification number is also required for an ester. From these are calculated the carbon distribution for a hydrocarbon, and then the partial solubility parameters. These in turn are used to calculate the volume fraction of water dissolved at 298 K at saturation. This is converted to mole fraction, and adjusted to system temperature. The mole fraction is then converted to solubility by weight. If the system atmosphere is not saturated, the solubility is multiplied by the relative humidity.

5. Significance and Use

5.1 Knowledge of the water content is important in lubrication, as large amounts of water can cause corrosion fatigue in steel bearings, and the complete absence of water can cause metal scuffing.

5.2 High water content has an accelerating effect on oxidation of lubricants, and can also contribute to foaming, especially at high altitude or temperature, or both.

6. Procedure

6.1 Calculate the molar volume of the lubricant as follows:

6.1.1 Determine the density at 298 K by Practice D 1298 or equivalent. If the density at 293 K is known (as required for Test Method D 3238) multiply it by 0.996 to obtain d with sufficient accuracy.

6.1.2 Determine the molecular weight by Test Method D 2502.

6.1.3 Calculate the molar volume as follows:

$$V = M/d \quad (1)$$

6.2 Calculate the dispersion parameter by these steps:

6.2.1 Determine the refractive index at 298 K by Test Method D 1218.

If a value at 293 K is known (as required for Test Method D 3238) multiply it by 0.998 to obtain n_D with sufficient accuracy.

6.2.2 Calculate the refractivity function as follows:

$$y = (n_D^2 - 1)/(n_D^2 + 2) \quad (2)$$

6.2.3 Calculate the parameter as follows:

$$\delta_d = 45 y^3 - 119 y^2 + 108 y - 4.58 \quad (3)$$

6.3 For hydrocarbons, calculate δ_d and P as follows:

6.3.1 Determine C_A and C_N by Test Method D 3238.

6.3.2 Calculate the parameters as follows:

$$P = 0.0143C_A \text{ and} \quad (4)$$

$$H = 0.0286C_A + 0.0143C_N \quad (5)$$

6.4 For esters, calculate P and H as follows:

6.4.1 Determine the saponification number by Test Method D 94.

6.4.2 Calculate the parameter as follows:

$$P = 0.00815 Sd \text{ and} \quad (6)$$

$$H = 0.00173 SM/V^{0.5} \quad (7)$$

6.5 Calculate the volume fraction of water at 298 K and saturation as follows:

$$\phi_2 = \exp [0.00726 \phi_1^2 ((18.00 - \delta_d)^2 + 2.39 (15.55 - P)^2 + 2.39 (16.27 - H)^2) + (1 - 18/V)\phi_1] \quad (8)$$

NOTE 1—For hydrocarbons, it may be safely assumed that $\phi_1 = 1.00$. However, that can introduce a significant error for some esters, so calculate ϕ_2 stepwise. Start with $\phi_1 = 1.00$, next step $\phi_1 = 1 - \phi_2$ from the first step, and so on until no further significant change is noted.

6.5.1 Rarely are more than three steps needed to obtain constancy to three significant figures. A small programmable calculator, which is strongly recommended for the whole procedure, can readily be set into the iterative cycle described.

6.6 Calculate the mole fraction at 298 K as follows:

$$x = V\phi_2/18 \quad (9)$$

6.7 Calculate the solubility by weight at 298 K, using Eq 10:

$$G = 18 \times 10^6 X/M(1 - X) \quad (10)$$

6.8 If the system was not saturated at equilibrium, with at least a trace of liquid water present, multiply X by $RH/100$; then convert to G as before. (Unless G is larger than 1000, this adjustment can be made directly on it.)

6.9 Multiply G by $RH/100$, if the system was not saturated, with at least a trace of liquid water present. If G is greater than 1000, multiply X by $RG/100$ before converting to G .

7. Precision and Bias

7.1 *Precision*—The repeatability and reproducibility intervals arise entirely from those of the experimental methods employed for n , S , C_A and C_N . The intervals due to the stated precision of Test Method D 1218 will both be 0.4 % of the calculated solubility. The effects of the intervals stated for Test Methods D 94 and D 3238 are such that no blanket statement can be made. However, the intervals for any specific lubricant can readily be calculated by processing the values of S , C_A and C_N through the equations alone and plus the intervals from the experimental methods.

7.1.1 Predictions have been made for all pure hydrocarbons for which solubilities of water at 298 K were listed, excepting the olefins, by API⁴, Riddick⁵, and Polak⁶. On aliphatics, Polak's values were chosen if available since they were carefully compared against the older data, giving 14 points. Riddick yielded three, and API two accepted, plus six rejected simply because they appeared "wild." All 18 points were predicted within ± 10 %. The API and Riddick values were similar on naphthenes; five values were predicted within 20 % and one within 50 %. Polak's six values for aromatics were predicted within 10 %, and five others from Riddick within 15 %. API had only one that was neither redundant nor wild; it was predicted within 10 %.

7.1.2 Predictions at elevated temperatures had to be checked against API data, and were within 10 % of the correct slope

⁴ API Technical Data Book, American Petroleum Institute, Washington, DC 1970.

⁵ Riddick, J. A., and Bunger, W. E., *Organic Solvents*, (Techniques of Organic Chemistry, Vol. 2, A. Weissberger, Ed.) Wiley-Interscience, John Wiley and Sons, New York, NY 1970.

⁶ Polak, J., and Lu, B. C.-Y., "Mutual Solubilities of Hydrocarbons and Water," Canadian Journal of Chemistry, Vol 51, 1973, pp. 4018-4023.

from 298 to 373 K for the three liquids covering this range. Most of the data stop at 323 K or less, and have not been analyzed.

7.1.3 API lists eight commercial oils with solubilities at elevated temperatures. Assigning plausible δ_d , C_A and C_N values gave predictions on five of these within 50 % or better for solubility, and 25 % or better for slope. The gasoline temperature range was too short to test, and the JP-3 and 4 data appeared wild.

7.1.4 Data by Cantley⁷ on a petroleum (SAE 5W) oil, a synthetic hydrocarbon, and two esters at 311 K were predicted

within 20 %, and the dependence on RH within 10 %. Other data also illustrate the problems caused by additives.

7.1.5 Riddick shows data on 34 esters. However, only 13 of those meet the criteria in the scope, and two of these were classified as wild because of obvious conflicts with close isomers. The remaining 11 were predicted within 50 % of the true value, and most within 30 %.

7.2 *Bias*—No general statement is made for bias for this test method since the data used to determine the correlation cannot be compared with accepted reference material.

8. Keywords

8.1 lubricants; solubility; water

⁷ Cantley, R. E., "The Effect of Water in Lubricating Oil on Bearing Fatigue Life," *ASLE Transactions*, Vol 20, 1977, pp. 244–248.

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