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

This standard is issued under the fixed designation D 2503; 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 (e) indicates an editorial change since the last revision or reapproval.

This test method has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This test method covers the determination of the average relative molecular mass (molecular weight) of hydrocarbon oils. It can be applied to petroleum fractions with molecular weights (relative molecular mass) up to 3000; however, the precision of the method has not been established above 800 molecular weight (relative molecular mass). The method should not be applied to oils having initial boiling points lower than 220°C.

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

1.3 This standard does not purport to address all of the safety problems, 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. For specific hazard statements, 5.2.1, 5.2.3, and 5.2.3.

2. Summary of Test Method

2.1 A weighed portion of the sample is dissolved in a known quantity of appropriate solvent. A drop of this solution and a drop of solvent are suspended, side by side, on separate thermistors in a closed chamber saturated with solvent vapor. Since the vapor pressure of the solution is lower than that of the solvent, solvent condenses on the sample drop and causes a temperature difference between the two drops. The resultant change in temperature is measured and used to determine the relative molecular mass (molecular weight) of the sample by reference to a previously prepared calibration curve.

3. Significance and Use

3.1 Relative molecular mass (molecular weight) is a fundamental physical constant that can be used in conjunction with other physical properties to characterize pure hydrocarbons and their mixtures.

3.2 A knowledge of the relative molecular mass (molecular weight) is required for the application of a number of correlational methods that are useful in determining the gross composition of the heavier fractions of petroleum.

4. Apparatus

4.1 Vapor Pressure Osmometer, with operating diagram.

5. Reagents and Materials

5.1 Purity of Reagents—Reagent grade chemicals shall be 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, 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.

5.2 Solvents—Solvents that do not react with the sample must be used. Since many organic materials exhibit a tendency to associate or dissociate in solution, it is desirable to use polar solvents for polar samples and nonpolar solvents for nonpolar samples. The solvents listed have been found suitable for hydrocarbons and petroleum fractions.

5.2.1 Benzene

NOTE 1: Warning—Poison. Carcinogen. Harmful if swallowed. Extremely flammable. Vapors may cause flash fire. Vapor harmful, may be absorbed through skin.

5.2.2 Chloroform

NOTE 2: Warning—May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned.

5.2.3 1,1,1-Trichloroethane

NOTE 3: Warning—Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.

NOTE 4: The precision data given in 10.1 and 10.2 will apply only when benzene is used as the solvent. There is also some evidence that determinations on the same oil sample carried out in different solvents will produce results that differ somewhat in absolute magnitude of apparent molecular weight (relative molecular mass).

5.3 Reference Standards—A calibration curve must be constructed for each new lot of solvent using a pure compound whose relative molecular mass (molecular weight) is

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This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.


1 A vapor pressure osmometer is available from H. Kaauer and Co., Berlin, West Germany. The manufacture of the Mechrolab instrument previously referred to in this footnote has been discontinued. However, some models may be available from stocks on hand at laboratory supply houses, or as used equipment from laboratory instrument exchanges.

2 "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."
accurately known. Compounds that have been used success-
fully include benzil (210.2), n-octadecane (254.5), and
squalane (422.8).

6. Sampling

6.1 The sample must be completely soluble in the selected
solvent at concentrations of at least 0.10 M, and it must not
have an appreciable vapor pressure at the test temperature.

7. Preparation and Calibration of Apparatus

7.1 Prepare standard 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1
M solutions of the calibrating compound in the solvent
selected.

7.2 Remove the upper sample chamber assembly. Rinse
the solvent cap with the solvent to be used. Install a vapor
wick in the cup and fill with solvent to the bottom of the
notches in the inner wick. Place the cup in the chamber base
recess, align the vapor wick openings with the viewing tubes,
and replace the upper assembly. Take care that the guide
pins properly engage matching holes in the thermal block
and that the matching surfaces of the base and block are
clean. Be careful not to allow the thermistor beads to touch
the cup or wicks as they may be bent out of alignment. Turn
on the thermostat and allow the temperature of the sample
chamber to reach equilibrium at 37°C.

Note 5—If the block is at room temperature, 2 to 3 h will be
required. To avoid such delay, it is desirable to always leave the
thermostat switch in the "on" position. If the chamber is at equilibrium
and is opened briefly, 30 to 45 min will generally be required before
temperature stabilization is regained. The exchange or refilling
of syringes does not necessitate any waiting period.

7.3 Thoroughly rinse all syringes with the solvent being
used and allow to dry.

7.4 Fill the syringes from guide tubes "S" and "6" with the
solvent. Fill the syringes for guide tubes "1" through "4" with the
standard solutions in order of increasing concentration.

7.5 Insert the syringes into the thermal block, keeping the
guide pins pointed away from the probe. Turn on the "Null
Detector" switch (Note 6). Set the sensitivity control to
sufficient gain so that a 1.0-Ω shift in the "Dekastat"
produces one major division shift of the meter needle.

Note 6—No measurements should be attempted until the "Null
Detector" switch has been on for at least 30 min.

7.6 Turn on the "Bridge" switch and turn the "T-AT"
switch to "T". Approximately zero the meter with the "T"
potentiometer and observe the drift of the needle. If the solvent
chamber is at equilibrium, the needle should not drift
more than 1 to 2 mm during one complete heating cycle; a
steady drift to the right indicates that the chamber is still
warming up; if "T" is stable, switch the selector to the "AT"
position.

7.7 While observing the thermistors in the viewing mirror,
lower the syringe in position "S", by rotating the knurled
collar of the holder fully clockwise. With the end of the
needle directly above the reference thermistor, turn the feed
screw and rinse the thermistor with about 3 to 4 drops of solvent.
Finally, deposit a drop of solvent on the thermistor bead and
raise the syringe by rotating the knurled collar in a counter-
clockwise direction. Rinse the sample thermistor with
solvent from syringe "6" and apply a drop approximately
the size of the drop on the reference thermistor. Depress the zero
button, and zero the meter with the "Zero" control. Set the
decade resistance to zero, and balance the bridge using the
"Balance" control. Repeat the balancing of the bridge with
fresh drops of solvent on each thermistor to assure a good
reference zero.

7.8 Lower syringe "1" and rinse the sample thermistor
with 3 to 4 drops of solution, finally applying one drop to the
bead. Start the stop watch. Center the meter by means of the
decade dials and take readings at 1-min intervals until two
successive readings do not differ by more than 0.01 Ω. Record
the ΔR value, estimating to the nearest 0.001 Ω from
the meter. Record the time required to reach this steady
state, and use this time for all subsequent readings for the
solvent used.

7.9 Upon completing each series of sample readings, rinse
the sample thermistor with solvent, deposit a drop, and
recheck the zero point. The meter should reproduce the
original indication within 0.5 mm. If the needle shows a
negative deflection, the sample thermistor should be rinsed
again. If it shows a positive deflection, the drop on the
reference thermistor should be replaced.

7.10 Plot the ΔR values for each concentration of stan-
dard against the molarity of the standard for the solvent
used.

Note 7—The calibration must be repeated for each of the solvents to
be employed and separate working curves constructed. Recalibration
is necessary each time a new batch of solvent is put into use.

8. Procedure

8.1 Select the solvent to be used and fill the solvent cup as
described in 7.2. Weigh into a 25-mL volumetric flask the
amount of sample suggested in the following table (Note 5):

<table>
<thead>
<tr>
<th>Estimated Relative Molecular Mass</th>
<th>Sample Size, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 200</td>
<td>0.3</td>
</tr>
<tr>
<td>200 to 500</td>
<td>0.3 to 0.6</td>
</tr>
<tr>
<td>500 to 700</td>
<td>0.6 to 0.9</td>
</tr>
<tr>
<td>700 to 1000</td>
<td>0.9 to 1.3</td>
</tr>
</tbody>
</table>

Record the weight to the nearest 0.1 mg and dilute to volume
with solvent.

Note 8—If the amount of sample is limited, weigh the sample into a
5 or 1-mL volumetric flask, using one-fifth or one twenty-fifth respec-
tively of the amount indicated in the table. Weigh to the nearest 0.001
mg using a microbalance.

8.2 Fill syringes "S" and "6" with solvent and fill one of
the remaining syringes with the sample solution. With the
sample chamber at thermal equilibrium, balance the bridge
to establish the reference zero as described in 7.6 and 7.7.

8.3 Rinse the sample thermistor with 3 or 4 drops of the
sample solution and deposit 1 drop on the thermistor. Start
the stop watch. Center the meter with the decade dials and
record ΔR at the time interval determined during the
standardization for the solvent being employed (7.8). When
running a series of samples, check the zero point frequently as described in 7.9.

8.4 Using the appropriate calibration curve, obtain the molarity corresponding to the observed $\Delta R$ value.

9. Calculation

9.1 Calculate the relative molecular mass (molecular weight) of the sample as follows:

$$\text{Relative Molecular Mass (molecular weight)} = \frac{c}{m}$$

where:

$c = \text{concentration of sample solution, g/L}$ and

$m = \text{molarity of solution, as determined in 8.4.}$

10. Report

10.1 Report the result to the nearest whole number.

11. Precision and Bias

11.1 Precision—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.1 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 Table 1 only in one case in twenty.

11.1.2 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 Table 1 only in one case in twenty.

11.1.3 The precision was not obtained in accordance with Committee D-2 Research Report RR-D-2-1007, “Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants.”

11.3 Bias—Bias for this method has not been determined.

12. Keywords

12.1 hydrocarbons; molecular weight; osmometer; relative molecular mass; thermoelectric measurement; vapor pressure

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