



Standard Test Method for Relative Molecular Mass (Molecular Weight) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure¹

This standard is issued under the fixed designation D2503; 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.

This standard has been approved for use by agencies of 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 this test method has not been established above 800 molecular weight (relative molecular mass). This test method should not be applied to oils having initial boiling points lower than 220°C.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.* 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.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0D on Physical and Chemical Methods.

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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 correlative 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.²

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.³ 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

² A vapor pressure osmometer is available from H. Knauer 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.

³ *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 *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

samples. The solvents listed have been found suitable for hydrocarbons and petroleum fractions.

5.2.1 *Benzene* (**Warning**—Poison. Carcinogen. Harmful if swallowed. Extremely flammable. Vapors may cause flash fire. Vapor harmful, may be absorbed through skin.)

5.2.2 *Chloroform* (**Warning**—May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned.)

5.2.3 *1,1,1-Trichloroethane* (**Warning**—Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.)

NOTE 1—The precision data given in 10.1 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 accurately known. Compounds that have been used successfully 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 2—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 “5” 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 3). 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 3—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-ΔT” 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 “ΔT” position.

7.7 While observing the thermistors in the viewing mirror, lower the syringe in position “5”, 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 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 counterclockwise 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 ohm. Record the Δ*R* value, estimating to the nearest 0.01 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 Δ*R* values for each concentration of standard against the molarity of the standard for the solvent used.

NOTE 4—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 2):

Estimated Relative Molecular Mass	Sample Size, g
Less than 200	0.3
200 to 500	0.3 to 0.6
500 to 700	0.6 to 0.9
700 to 1000	0.9 to 1.3

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

NOTE 5—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 respectively

of the amount indicated in the table. Weigh to the nearest 0.001 mg using a microbalance.

8.2 Fill syringes “5” 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 ΔR value.

9. Calculation

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

$$\text{Relative Molecular Mass (molecular weight)} = cm \quad (1)$$

where:

c = concentration of sample solution, g/L and
 m = 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

TABLE 1 Precision Data (Benzene Solvent)

Relative Molecular Mass (Molecular Weight) Range	Repeatability, g/mol	Reproducibility, g/mol
245 to 399	5	14
400 to 599	12	32
600 to 800	30	94

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 D02 Research Report RR-D02-1007, “Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants.”⁴

11.2 *Bias*—Bias for this test method has not been determined.

12. Keywords

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

⁴ Filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1007.

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