

MOLECULAR WEIGHT BY VAPOR PRESSURE OSMOMETRY

UOP Method 676-84

SCOPE

This method is for determining the average molecular weight of petroleum fractions having a minimum initial boiling point of 230 C as determined by ASTM Method D 86 or D 1160.

OUTLINE OF METHOD

A weighed amount of sample is diluted to a known volume with solvent. A drop of this solution and a drop of the pure solvent are placed on separate thermistors. The thermistors are contained in a closed chamber that is saturated with solvent vapor. Because the vapor pressure of the solution is lower than that of the pure solvent, solvent condenses on the sample drop and causes a temperature difference between the two drops. The resultant change in temperature is measured by a bridge circuit and used to determine the average molecular weight of the sample by reference to a previously prepared calibration curve.

APPARATUS

Balance, readability, 0.1-mg

Flasks, volumetric, 10- and 25-mL

Recorder, 10 mV, one-second full scale response, 28-cm chart width, Fisher Scientific, Cat. No. 13 939 14, or equivalent

Stopwatch, electric, Sargent-Welch Scientific, Cat. No. S-77507, or equivalent

Vapor pressure osmometer, Wescan Model 232A, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Benzil, 99.9% minimum purity

Chart paper, 28-cm width, Fisher Scientific, Cat. No. 13 939 40, or equivalent

Graph paper, linear 2 mm, 90 by 120 divisions, Codex Book Company. Cat. No. 31,233, or equivalent

Toluene, 99.9% minimum purity

PROCEDURE

Preparation of Apparatus

Refer to the manufacturer's instruction manual and set up the vapor pressure osmometer as directed. Connect the 10-mV recorder which is used as an aid in determining when the bridge circuit has stabilized. Clean and assemble the sample chamber. Turn on the heater and allow the temperature of the sample chamber to reach equilibrium at 50 ± 1 C, which usually requires about 3 hours. Saturate the sample chamber with toluene as directed.

Preparation of Calibration Curve

Using the following table prepare 0.005-, 0.01-, 0.02- and 0.03-*M* solutions of benzil (MW = 210.2) in toluene.

Molarity (<i>M</i>) of Solution	Mass of Benzil, g
0.005	0.0105
0.01	0.0210
0.02	0.0420
0.03	0.0630

Weigh the benzil into a 10-mL volumetric flask, record the mass to the nearest 0.1 mg and dilute to the mark with toluene. Determine the exact molarity of each calibration solution using the following equation:

$$M = \frac{W}{2.102}$$

where:

M = molarity of the solution, moles/L

W = mass of benzil, g

2.102 = factor to convert the molecular weight of benzil from g/10 mL to g/L

To determine the toluene blank, fill both the solvent and sample syringes with toluene and drop 0.03 ± 0.01 mL onto each thermistor. Wait until the instrument stabilizes as evidenced by the establishment of a stable recorder baseline (usually two or three minutes). If a stable baseline cannot be obtained, re-clean the cell. Record the reading on the indicating voltmeter of the instrument. Repeat the procedure to obtain a total of four readings. Successive readings should not differ by more than 0.2 mV. Average the readings and record this value as *S* for toluene.

Fill the sample syringe with the appropriate solution and follow the above procedure to determine the *S* value for each of the benzil solutions in succession, starting with the most dilute. Calculate the ΔS value of

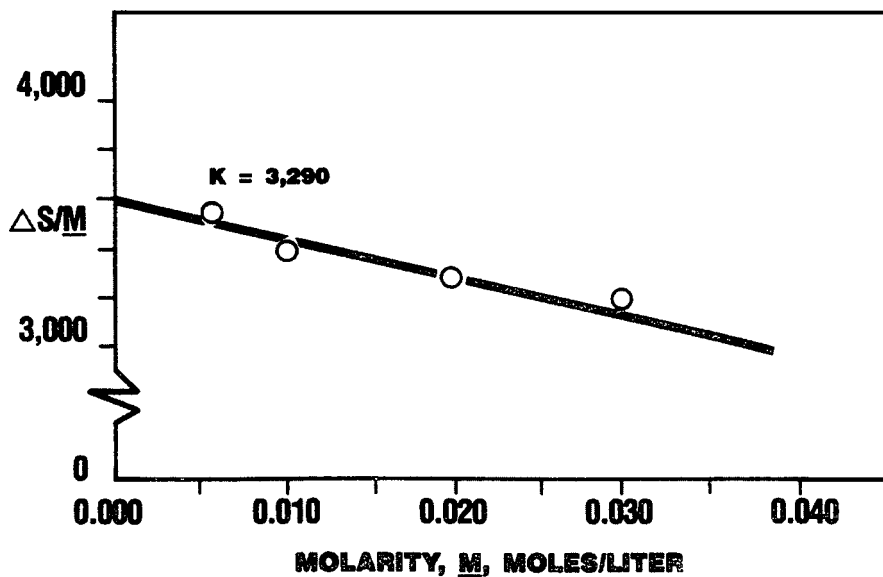
each calibration solution by subtracting the average toluene reading from the average calibration solution reading. Divide the ΔS values by the molarity, M , of each of the calibration solutions, respectively. The value of $\Delta S/M$ at infinite dilution (i.e., at zero concentration of benzil) is termed K . A graphical or computed procedure may be used to determine the value of K . A combination of both is recommended. The data may be plotted graphically with $\Delta S/M$ along the y-axis and M along the x-axis (see Figure). The y-intercept (K) can be read directly from the graph. The advantage of this technique is that the linearity of the data can be determined at a glance. The y-intercept (K) may be computed more exactly by using a least-squares regression equation as follows:

$$K = \lim_{M \rightarrow 0} (\Delta S/M) = \frac{\sum M^2 \sum (\Delta S/M) - \sum M \sum (\Delta S/M)}{n \sum M^2 - (\sum M)^2}$$

where:

- K** = the value of $\Delta S/M$ at infinite dilution
- M** = previously defined
- n** = number of data points used ($n = 4$)
- ΔS** = average meter reading of the solution minus the average meter reading of the solvent

The established K value should remain constant but must be checked each day the instrument is used. The $\Delta S/M$ value determined on one standard calibration blend may be used for verification. If results of this test deviate significantly from the previously established calibration curve, the K value must be reestablished using a freshly prepared set of standard benzil calibration solutions.



Typical Calibration Curve

Sample Analysis

A minimum of three dilutions is required although additional dilutions may be prepared if desired. Weigh into 25-mL volumetric flasks the amounts of sample suggested in the following table:

<u>Estimated Molecular Weight</u>	<u>Sample Weight, g</u>
200 - 500	0.0375, 0.075, 0.15
500 - 1000	0.2, 0.25, 0.5

Record the mass to the nearest 0.1 mg. Dilute to the mark with toluene and calculate the exact concentration (see *CALCULATIONS*).

Determine the ΔS values for each sample solution using the same procedure described under *Preparation of Calibration Curve*.

If a stable instrument response is not obtained, that is, if the meter and recorder trace continue to drift slowly in one direction, a reading must be taken at a specified time. To determine this time, start a stopwatch at the time the sample solution is dropped on the thermistor and record readings each minute for 10 minutes. Repeat this procedure twice. From this data determine the point when minimum change occurs and use this time for all subsequent readings.

Divide the ΔS values by the concentration in grams per liter for each sample solution, respectively, and plot this ratio, $\Delta S/C$, versus concentration, g/L. Extrapolate to zero molarity to determine A at infinite dilution using a least squares regression equation (see *CALCULATIONS*).

CALCULATIONS

Calculate the exact concentration of each sample solution using the following equation:

$$C = 40 D$$

where:

C = concentration, g/L

D = mass of sample, g

40 = factor to convert g/25 mL to g/L

Calculate the exact value for A using the following equation:

$$A = \lim_{C \rightarrow 0} (\Delta S/C) = \frac{\sum C^2 \sum (\Delta S/C) - \sum C \sum (\Delta S/C)}{n \sum C^2 - (\sum C)^2}$$

where:

A = the value of $\Delta S/C$ at infinite dilution

C, **n** and ΔS are as previously defined

Calculate the average molecular weight of the sample as follows:

$$\overline{M}_w = \frac{K}{A}$$

where:

$\overline{M}_w$ = average molecular weight

A and K are as previously defined

PRECISION

Based on 6 replicate determinations using a Hitachi-Perkin Elmer Model 115 instrument, the estimated standard deviation (esd) for molecular weight at the 615 level was calculated to be 5.5. Duplicate results by the same operator should not differ by more than 20 (95% probability).

TIME FOR ANALYSIS

The elapsed time and labor requirement for a single analysis, after calibration, are identical, 1.25 hours.

SUGGESTED SUPPLIERS

Codex Book Company, 76 Broadway, Norwood, MS 02062

Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

Wescan Instruments, Inc., 3018 Scott Blvd., Santa Clara, CA 95050