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COMMISSION ON PHYSICOCHEMICAL MEASUREMENTS AND STANDARDS
SUB-COMMISSION ON CALIBRATION AND
TEST MATERIALS

RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

(Recommendations 1975)

EDITOR: E. F. G. HERINGTON

SECTION: MOLECULAR WEIGHT

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INTRODUCTION

REFERENCE MATERIALS FOR MOLECULAR WEIGHT MEASUREMENTS

The relative molecular mass of a substance ("molecular weight") is the ratio of the average mass per molecule of a specified isotopic composition of a substance to 1/12 of the mass of an atom of the nuclide ^{12}C. It is dimensionless.

Molecular weight may be measured by several methods, each with its characteristic range of application and need for calibration and test materials. Samples of synthetic polymers are heterogeneous with respect to molecular weight, and methods are available which yield the molecular weight distribution (MWD) or one of its averages.

Those averages can be defined in terms of n_i, the number of molecules of molecular weight M_i, or in terms of $f(M)$, the molecular weight distribution treated as a continuous function such that the mass fraction of molecular weight between M_1 and M_2 is given by $\int_{M_1}^{M_2} f(M)\,dM$. The number-average molecular weight

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \int \frac{1}{(1/M) f(M)\,dM}$$

the weight-average molecular weight

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \int M f(M)\,dM$$

and the Z-average molecular weight

$$\bar{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\int M^2 f(M)\,dM}{\bar{M}_w}$$

are measurable instrumentally. The summations and integrations are over all the material present.

The following table lists methods of measurements, the quantities determined and their ranges and the upper temperature limits of the measurements.

Ranges of measurement given are accessible with apparatus available commercially or constructed simply. In favourable cases and with special equipment the scope of the colligative methods can be extended considerably.

Calibration materials are recommended for gel permeation chromatography, light scattering photometry and some colligative methods (vapour pressure osmometry, cryoscopy and ebulliometry). Test materials may be useful in commissioning membrane osmometry and ultracentrifugation, and one is suggested.

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Method	Quantity measured	Molecular weight	Upper temperature limit (°C)
Gel permeation chromatography	*MWD*	up to 10^7	140
Light scattering photometry	$\bar{M}_w$	10^4–10^7	160
Vapour pressure osmometry	$\bar{M}_n$	up to 4×10^4	130
Cryoscopy	$\bar{M}_n$	up to 5×10^4	165
Ebulliometry	$\bar{M}_n$	up to 4×10^4	120
Membrane osmometry	$\bar{M}_n$	2×10^4 to 10^6	130
Ultra-centrifugation	$\bar{M}_w$, $\bar{M}_z$	10^4–10^7	120

The following provisos apply to the information on Reference Materials: (a) the recommended materials have not been checked independently by IUPAC, (b) the quality of material may change with time: (c) the quoted sources of supply may not be exclusive sources because no attempt has been made to seek out all possible alternative sources; (d) IUPAC does not guarantee any material that is recommended.

I. REFERENCE MATERIALS FOR GEL PERMEATION CHROMATOGRAPHIC MEASUREMENTS

In gel permeation chromatography a dilute solution of the unknown is injected into a stream of solvent flowing continuously through columns containing microporous substrates; a detector, conventionally refractometric, provides a record of solute concentration vs elution volume. Determination of molecular weight averages and distributions requires the relation of elution volume to molecular weight by means of reference materials. The calibration should extend over a wide range of molecular weight and can be established[1] with reference materials of three kinds:

(i) A series of samples of narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 1.1$) centred about values which span the range of interest and certified as to M_0, the molecular weight corresponding to the peak of the chromatogram; calibration consists in relating that value to the observed peak volume.

(ii) A series of samples of certified number—and/or weight–average molecular weight; calibration consists in finding the relation between molecular weight and elution volume which best generates those values from the observed chromatograms.

(iii) A single sample of broad molecular weight distribution ($\bar{M}_w/\bar{M}_n > 3$) certified as to molecular weight distribution; calibration consists[2] in matching an integrated chromatogram with the certified integral molecular weight distribution. The following table lists reference materials and suppliers.

Preferably the reference material used should be a homologue of the sample to be analysed, but in the absence of such a material a universal[1] calibration may be employed.

1.2 *Materials and suppliers*

Material	Supplier	Calibration range	$\bar{M}_w/\bar{M}_n$	Certified quantities
Polyethylene	C	*ca.* 4×10^3–3.4×10^5	*ca.* 3.1	$\bar{M}_w$, *MWD*
Polypropylene	D	*ca.* 10^4–4×10^5	1.4–1.9	$\bar{M}_n$, $\bar{M}_w$
		ca. 10^4–4×10^5	*ca.* 3.7	*MWD*
Polystyrene	C	1.8×10^5–2.7×10^5	*ca.* 1.1 and 2.1	$\bar{M}_n$, $\bar{M}_w$
	D	1×10^4–1.5×10^6	*ca.* 3.4	*MWD*
	D	2.2×10^6–2.9×10^6	*ca.* 1.3	$\bar{M}_n$, $\bar{M}_w$
Polyvinylchloride	D	3×10^4–1.8×10^5	*ca.* 1.5	$\bar{M}_n$, $\bar{M}_w$
The following samples are available without full details of their characterization.				
Polystyrene	F	6×10^2–2×10^6	1.1–1.3	$\bar{M}_n$, $\bar{M}_w$, M_0
	H	2×10^3–9×10^5	1.009	M_0
Polyethylene	F	7×10^3–4×10^4	1.7–6	$\bar{M}_n$, $\bar{M}_w$, M_0
	G	10^4–5×10^5	*ca.* 1.1	M_0
Polyvinylchloride	A	2.5×10^4–1.3×10^5	2.4–2.9	$\bar{M}_n$, $\bar{M}_w$
Polydimethyl siloxane	H	50–10^4		M_0
Dextran	E	*ca.* 10^4–2×10^6		*MWD*

II. REFERENCE MATERIALS FOR LIGHT SCATTERING PHOTOMETRIC MEASUREMENTS

2.1 *Methods of measurement*

In light scattering photometry[3,4] a dilute solution of the unknown is illuminated monochromatically and the relative scattered irradiances are measured as a function of angle of scatter and concentration. The molecular weight of the solute ($\bar{M}_w$) is related to the excess reduced irradiance $R(\theta, c)$ at a distance r from the centre of the scattering volume $v(\theta)$ by the relation

$$R(\theta, c) = r^2[E(\theta, c) - E(\theta, 0)]/E_0 v(\theta)$$

where $E(\theta, c)$ is the irradiance of light scattered through an angle θ by a solution of concentration c, and E_0 is the incident irradiance.

Measurements are made by recording photomultiplier

outputs proportional to $E(\theta, c)$ and $E(\theta, 0)$ at a range of values of θ and c, and calibration with reference materials is necessary to find $R(\theta, c)$; it is common practice to include r and v in the calibration constant. The scattering volume is a function of the refractive indices of the scattering medium and the thermostatting liquid, if one is used, and a photometer should be calibrated under conditions as close to the experimental ones as possible.

Pure liquids are the preferred calibrants for work with a sensitive photometer near ambient temperatures; Rayleigh ratios $r^2E(90°, 0)/E_0v(90°)$ are tabulated[5] for a number of readily available liquids.

Solutions of 12-tungstosilicic acid in aqueous sodium chloride are convenient calibrants[6] for work on aqueous media.

For work on samples much above ambient temperatures solutions of standard polymer samples are recommended. Only those for which the characterization is described fully should be used, and the published procedure should be adhered to closely.

2.2 *Materials, data and suppliers*

Rayleigh ratios for carbon disulphide, benzene, toluene, carbon tetrachloride, methyl ethyl ketone and several aliphatic hydrocarbons are tabulated.[5]

Data and procedures for the use of 12-tungstosilicic acid are available.[6]

The above materials are available from laboratory suppliers. The following certified polymer samples are available from supplier (C).

Material	Sample number	$\bar{M}_w$
Polystyrene[7]	NBS SRM 705	179,300 ± 2220
Polyethylene[8]	NBS SRM 1475	52,000 ± 2000

III. REFERENCE MATERIALS FOR MEASUREMENTS BY COLLIGATIVE METHODS

Reference materials are required to relate to molality the difference in freezing point between solvent and solution (in cryoscopy),[9,10] in boiling point between solvent and solution (in ebulliometry)[11,12] or in steady-state temperature between drops of solvent and solution in saturated solvent vapour (in vapour pressure osmometry).[13,14] For the first two methods the calibration constant is calculable from the enthalpy of phase change of the solvent, but an empirical determination of the constant is preferred.

The reference material should be soluble, involatile and neither associated nor dissociated under the experimental conditions. Evidence is accumulating[15–17] that the calibration constants are dependent on molecular weight, and hence the reference material chosen should be close in molecular weight to the unknown.

The following table lists reference materials with their molecular weights. All are available from laboratory suppliers; recommended samples of certified purity are available from the sources indicated.

IV. REFERENCE MATERIALS FOR MEMBRANE OSMOMETRY AND ULTRACENTRIFUGATION

Calibration is not required for these methods;[18,19] however, the well-characterised polystyrene fraction, SRM 705 is recommended as a test material to check instrumental performance.

Reference materials and molecular weights

Material	Supplier	Molecular weight
Resorcinol		110.1
Benzoic acid	B,C	122.1
Naphthalene	D	128.2
Camphor		152.2
Mannitol		182.1
Dimethylterephthalate		194.2
2,4-Dinitrochlorobenzene		202.6
Benzil	D	210.2
2,2-bis(ethylsulphonyl) propane		228.3
Dibenzyldisulphide		246.4
Hexachlorobenzene		284.8
Cholesterol	C,D	386.7
2,6,10,15,19,23-Hexamethyltetracosane		422.8
Hexatriacontane		507
Glyceryl tristearate	D	891.5
Pentaerythrityl tetrastearate	D	1202

V. ADDITIONAL REFERENCE MATERIALS LISTED OCTOBER 1976

Supplier (C) has now announced certified samples of linear polyethylenes with values of $\bar{M}$ and $\bar{M}_w/\bar{M}_n$ as follows—SRM 1482; 13,600; 1.2: SRM 1483; 32,100; 1.1: SRM 1484; 119,600; 1.2. These reference materials are recommended for gel permeation chromatography and for light scattering photometry.

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