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**Rubber, raw synthetic — Determination  
of the molecular-mass distribution of  
solution polymers by gel permeation  
chromatography**

*Caoutchouc synthétique brut — Détermination de la répartition de la  
masse moléculaire pour les caoutchoucs polymérisés en solution par  
chromatographie par perméation de gel*

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11344 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

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# Rubber, raw synthetic — Determination of the molecular-mass distribution of solution polymers by gel permeation chromatography

**WARNING** — Persons using this International Standard should be familiar with normal laboratory practice. 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 to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

## 1 Scope

This International Standard describes a method for the determination of the molecular mass, expressed as polystyrene, and the molecular-mass distribution of polymers produced in solution which are completely soluble in tetrahydrofuran (THF) and which have a molecular-mass range from  $5 \times 10^3$  to  $1 \times 10^6$ .

It is not the purpose of this International Standard to explain the theory of gel permeation chromatography.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TR 9272, *Rubber and rubber products — Determination of precision for test method standards*

## 3 Principle

The molecular components of a polymer are separated on the basis of macromolecule size on a gel permeation column. A known quantity of a dilute solution of the polymer is injected into a stream of solvent, which carries it through the column at a constant rate. The concentration of the separated molecular components in the solvent stream is measured by a suitable detector. Through the use of a calibration curve, both the number-average molecular mass ( $M_n$ ) and mass-average molecular mass ( $M_w$ ) of the material analysed can be determined from the retention time and the corresponding concentration.

## 4 General

**4.1** Gel permeation chromatography (GPC), which is also known as size exclusion chromatography (SEC), is a particular type of liquid chromatography which allows the separation of the various components of a polymer based on macromolecule size.

**4.2** The molecules of a polymer do not all have the same mass, but comprise a range of different masses. For this reason, the usual concept of molecular mass is not applicable to polymeric materials. Instead, different average molecular masses are determined as shown in Table 1.

Table 1 — Definitions of various kinds of molecular mass

Mass-average molecular mass $M_w$	$= \Sigma(N_i M_i^2) / \Sigma(N_i M_i)$ $= \Sigma(A_i M_i) / \Sigma A_i$
Number-average molecular mass $M_n$	$= \Sigma(M_i N_i) / \Sigma N_i$ $= \Sigma A_i / \Sigma(A_i / M_i)$
z-Average molecular mass $M_z$	$= \Sigma(N_i M_i^3) / \Sigma(N_i M_i^2)$ $= \Sigma(A_i M_i^2) / \Sigma(A_i M_i)$
Peak molecular mass $M_p$	Molecular mass at peak maximum
where	
$N_i$	is the number of moles having a molecular mass of $M_i$ ;
$A_i$	is the area of the time-slice that corresponds to molecular mass $M_i$ .

The molecular-mass distribution is an important parameter in determining the properties of the polymer. It may be represented by the polydispersity  $D$  given by:

$$D = M_w / M_n$$

NOTE Polymers invariably consist of macromolecules with a range of molecular sizes. Even the so-called monodisperse polystyrenes have a polydispersity of 1,1 compared to a value of 1,0 for a pure compound with a single molecular mass. As the range of molecular sizes present within the polymer increases, so does the polydispersity.

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## 5 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

### 5.1 Tetrahydrofuran (THF), high-purity-grade solvent.

NOTE A large stock of THF is needed to avoid frequent refills. Changes in the quantity of dissolved air or impurities due to addition of fresh solvent cause significant variations in the refractive index and could also affect the retention time. Air bubbles at the pump head reduce the quantity of solvent pumped (leading to errors in retention volumes and times) and can block the pump if the volume of the air bubbles reaches excessive levels. After adding fresh solvent, it takes 2 to 3 hours to obtain a stable baseline.

**5.2 Solution of o-dichlorobenzene (internal retention time standard) in THF**, obtained by dilution of 250 mm<sup>3</sup> (250 µl) of o-dichlorobenzene with 1 l of THF.

**5.3 Set of certified polystyrene reference standards** (minimum 10), with molecular masses in the range  $5 \times 10^2$  to  $1 \times 10^7$  (depending on the sample molecular-mass range) and a very narrow molecular-mass distribution ( $D < 1,10$ ) (see Table 2 for an example of such a set, available from various chemical suppliers).

Table 2 — Set of polystyrene standards

Standard No.	Actual molecular mass $M_i$	$D (= M_w/M_n)$
1	1 030 000	1,05
2	770 000	1,04
3	336 000	1,03
4	210 000	1,03
5	156 000	1,03
6	66 000	1,03
7	30 300	1,03
8	22 000	1,03
9	11 600	1,03
10	7 000	1,04
11	5 050	1,05

## 6 Apparatus

Ordinary laboratory apparatus, plus the following:

**6.1 Gel permeation chromatograph**, consisting of the components specified in 6.1.1 to 6.1.8.

**6.1.1 Solvent reservoir**, of sufficient capacity to complete the analysis (see Note to 5.1) without refilling.

**6.1.2 Automatic on-line degassing system or helium sparging of solvent reservoir**, to stabilize the solvent flow, mainly to prevent formation of bubbles in the solvent.

**6.1.3 Pump**, to ensure that the THF solvent flows at a constant rate, programmable over the range 1,7 mm<sup>3</sup>/s to 165,0 mm<sup>3</sup>/s with a high degree of precision.

**6.1.4 Injector or automatic sampler**, with a 100 mm<sup>3</sup> (100 µl) injection loop.

**6.1.5 Columns**, packed with regular, rigid, porous spheres. The pore size of column packing material is expressed in Angstrom units (1 Å = 10<sup>-10</sup> m). The packing spheres are made of cross-linked polystyrene, obtained by polymerization of styrene with divinylbenzene. The spheres shall have a nominal diameter in the range 5 µm to 10 µm. The columns are generally 300 mm long. The pore size is selected depending on the range of molecular masses to be analysed.

NOTE Four columns with pore sizes 10<sup>3</sup> Å, 10<sup>4</sup> Å, 10<sup>4</sup> Å and 10<sup>5</sup> Å were used when the repeatability and reproducibility of the method described in this International Standard were determined. The solvent first enters the column with the lowest porosity and exits from the column with the highest porosity. Other suitable columns may be used. These types of column are available from many suppliers.

The recommended column characteristics are:

- linear range: 200 to 2 000 000;
- guaranteed column efficiency: > 50 000 plates/m;
- column arrangement: four columns (300 mm long and 4,6 mm to 8,0 mm ID).

**6.1.6 Detector.**

Various types of detector may be used, such as differential refractometer, UV or light-scattering.

**6.1.7 Integrator**, capable of integrating at least 150 time-slices during the elution of the polymer being analysed.

**6.1.8 Personal computer and software**, to avoid long and difficult manual calculations.

**6.2 PTFE filters**, having a pore size of 0,50 µm or 0,45 µm.

**6.3 10 cm<sup>3</sup> (10 ml) and 250 mm<sup>3</sup> (250 µl) syringes.**

**6.4 Autocollector** (optional), with glass vials.

**6.5 Mixer.**

## 7 Analytical conditions

Flow rate: 17 mm<sup>3</sup>/s.

Injection volume: 100 mm<sup>3</sup> (100 µl) of solution, or a quantity suitable for the volume of the column used.

Elution time of internal standard (*o*-dichlorobenzene): 45 min minimum.

Column temperature: (40 ± 1) °C.

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## 8 Procedure

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### 8.1 Solvent degassing

**8.1.1** Filter the solvent (5.1) by suction through a PTFE filter (6.2).

**8.1.2** Degas 1 dm<sup>3</sup> of solvent under vacuum and/or in an ultrasonic bath for about 30 min.

To obtain a constant baseline, degassing should preferably be done 12 h before use. From time to time, the columns should be flushed, for a period of 8 h, with THF solvent, degassed as specified in this subclause, to remove any peroxides left in the column.

If an automatic on-line degassing system is available, the degassing operation given in this subclause can be omitted.

### 8.2 Calibration

**8.2.1** Use polystyrene standards (5.3) dissolved in *o*-dichlorobenzene solution (5.2) for calibration purposes. To ensure constant peak size, weigh out a different amount of each individual standard as a function of its molecular mass, for example 1 g/l (0,025 g in 25 cm<sup>3</sup> of solution 5.2) for molecular masses around 1 000 000, 5 g/l (0,125 g in 25 cm<sup>3</sup> of solution 5.2) for molecular masses lower than 30 000. The calibration plot shall cover the entire range of molecular masses present in the polymer being analysed.

**8.2.2** Shake the solutions gently for about 1 h.

**8.2.3** Filter each solution through a PTFE filter (6.2) attached to a 10 cm<sup>3</sup> syringe.

NOTE The reference standard solutions can be kept in a refrigerator at 6 °C to 7 °C for a maximum of 3 months.



**8.2.4** The calibration procedure described in 8.2.4.1 to 8.2.4.6 is given by way of example.

**8.2.4.1** Prepare 11 solutions of polystyrene in accordance with Table 3.

**8.2.4.2** Calculate the intrinsic viscosity  $[\eta]_i$  for each standard by applying the Mark-Houwink equation ( $[\eta]_i = KM_i^\alpha$ ) and using the known values of  $K$  ( $= 0,000\ 16$ ) and  $\alpha$  ( $= 0,700$ ).

NOTE Table 4 shows the intrinsic viscosity of the polystyrene standard solutions given in Table 3.

**Table 3 — Solutions of polystyrene reference standards**

Solution No.	Concentration g in 25 cm <sup>3</sup> of o-dichlorobenzene solution (5.2)	Actual molecular mass $M_i$
1	0,025	1 030 000
2	0,025	770 000
3	0,030	336 000
4	0,050	210 000
5	0,050	156 000
6	0,075	66 000
7	0,125	30 300
8	0,125	22 000
9	0,125	11 600
10	0,125	7 000
11	0,125	5 050

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**Table 4 — Values of  $[\eta]_i$  for the solutions in Table 3**

Actual molecular mass $M_i$	Intrinsic viscosity $[\eta]_i$
1 030 000	2,588 8
770 000	2,111 9
336 000	1,181 8
210 000	0,850 5
156 000	0,690 7
66 000	0,378 3
30 300	0,219 3
22 000	0,175 3
11 600	0,112 0
7 000	0,078 6
5 050	0,062 6

**8.2.4.3** When using manual injection, draw off 250 mm<sup>3</sup> (250 µl) from each vial, flush the injection loop and then inject 100 µl. Read off the retention time corresponding to the peak for each standard. With an automatic sampler, follow the manufacturer's instructions. Repeat for a total of three times.

**8.2.4.4** Average the three retention times obtained for each standard and the retention times of o-dichlorobenzene averaged over all the runs (in this case a total of 33).

8.2.4.5 Plot the average retention time, in minutes, against the corresponding value of  $\log(M_i[\eta]_i)$  for each standard and calculate the best-fit line (see Figure 1).

8.2.4.6 The correlation coefficient shall be higher than 0,999 5. If not, repeat the calibration procedure for the standards that are causing imperfect alignment, found by computing the difference between the certified (actual) molecular masses and the molecular masses calculated (see Table 5) using the third-degree polynomial representing the best-fit line in Figure 1.

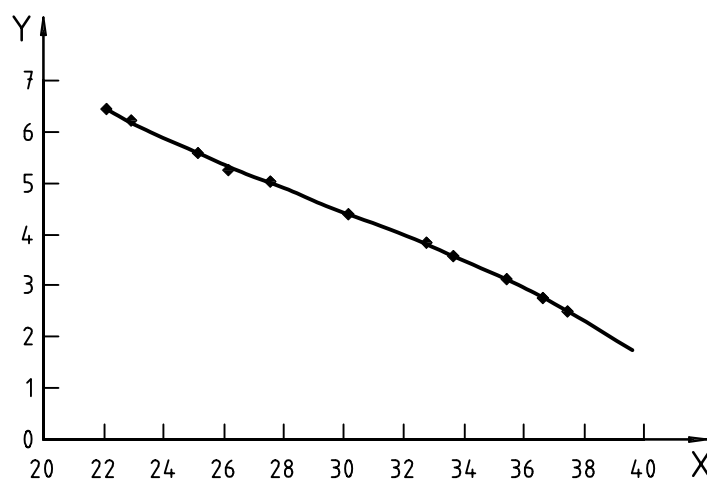
For the data plotted in Figure 1, the best-fit line is given by the following third-degree polynomial:

$$\log(M_i[\eta]_i) = 26,072\ 144\ 65 - 1,746\ 517\ 348\ t_i + 0,051\ 765\ 825\ t_i^2 - 0,000\ 585\ 847\ t_i^3$$

For these data, the correlation coefficient is 0,999 76.

Table 5 — Calibration data corresponding to plot in Figure 1

Actual molecular mass $M_i$	Retention time $t_i$ min	Intrinsic viscosity $[\eta]_i$	Calculated molecular mass
1 030 000	22,08	2,588 8	1 058 592
770 000	22,89	2,111 9	749 179
336 000	25,15	1,181 8	331 816
210 000	26,15	0,850 5	206 277
156 000	27,58	0,690 7	158 756
66 000	30,18	0,378 3	69 059
30 300	32,76	0,219 3	29 520
22 000	33,68	0,175 3	21 760
11 600	35,46	0,112 0	11 344
7 000	36,64	0,078 6	7 266
5 050	37,47	0,062 6	4 998



**Key**  
 X retention time (min)  
 Y  $\log(M_i[\eta]_i)$

Figure 1 — Calibration plot

### 8.3 Preparation of test solution

**8.3.1** The test solution concentration specified in 8.3.2 is suitable for most circumstances, but may be varied depending on the actual polymer being tested, the molecular-mass range expected, the volumes of the columns, the type of detector and the volume of solution injected.

**8.3.2** Place 0,075 g of the sample in a 50 cm<sup>3</sup> graduated flask and add roughly 35 cm<sup>3</sup> of filtered (see 8.2.3) *o*-dichlorobenzene internal-standard solution (5.2).

**8.3.3** Agitate the solution gently for roughly 1 h on a shaker to ensure the polymer has dissolved completely and then make up to 50 cm<sup>3</sup> with filtered *o*-dichlorobenzene solution.

### 8.4 Analysis

**8.4.1** Pass solvent through the columns (flow rate 17 mm<sup>3</sup>/s) until the baseline stabilizes.

NOTE With some detectors and column sets, this may take up to 7 h.

**8.4.2** When the baseline has stabilized, run the analysis as described below, under the conditions given in Clause 7.

**8.4.2.1** Using a syringe, draw off 10 cm<sup>3</sup> of the test solution prepared in 8.3.

**8.4.2.2** Filter it through a PTFE filter (6.2) connected to a second syringe, and transfer it to a vial.

**8.4.2.3** When using manual injection, inject 250 mm<sup>3</sup> (250 µl) to flush the injection loop and then inject 100 µl to start the analysis. Repeat the procedure for a total of three times.

**8.4.2.4** With an automatic sampler, follow the manufacturer's instructions. Repeat the procedure for a total of three times.

**8.4.2.5** The molecular parameters will normally be computed by an integrator (6.1.7), using the data stored from the calibration procedure.

## 9 Expression of results

**9.1** Results are acceptable if the elution time of the internal standard is within  $\pm 30$  s of the value obtained during the calibration stage (see 8.2). If this is not achieved, the columns shall be cleaned by flushing fresh solvent through them for at least 3 h and then the retention time of the *o*-dichlorobenzene internal-standard solution determined again.

**9.2** Should the anomalous retention time be confirmed, the system needs recalibration using the polystyrene standards (see 8.2).

**9.3** The instrument software allows calculation of a great deal of information about the molecular-mass distribution (see Annex A).

**9.4** Report the average of the three determinations of:

- a) the mass-average molecular mass  $M_w$ ;
- b) the number-average molecular mass  $M_n$ ;
- c) the z-average molecular mass  $M_z$ ;
- d) the polydispersity  $D (= M_w/M_n)$ ;