
**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*



PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO 11344:2004

© ISO 2004

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword	iv
1 Scope	1
2 Normative references	1
3 Principle	1
4 General	1
5 Reagents and materials	2
6 Apparatus	3
7 Analytical conditions	4
8 Procedure	4
9 Expression of results	7
10 Precision (only for instrumental software procedure)	8
11 Test report	9
Annex A (informative) Molecular-mass parameters determined by instrumental software	11
Annex B (informative) Calculation of molecular-mass parameters by manual procedure	15
Annex C (informative) Comparison of results obtained by automatic procedure (software) and manual procedure	19
Annex D (informative) Guidance for using precision results	20

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*.

STANDARDSISO.COM : Click to view the full PDF of ISO 11344:2004

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 5×10^3 to 1×10^6 .

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.

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 mm³ (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 5×10^2 to 1×10^7 (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 mm³/s to 165,0 mm³/s with a high degree of precision.

6.1.4 Injector or automatic sampler, with a 100 mm³ (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 = 10⁻¹⁰ 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 10³ Å, 10⁴ Å, 10⁴ Å and 10⁵ 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 cm³ (10 ml) and 250 mm³ (250 µl) syringes.

6.4 Autocollector (optional), with glass vials.

6.5 Mixer.

7 Analytical conditions

Flow rate: 17 mm³/s.

Injection volume: 100 mm³ (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.

8 Procedure

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 dm³ 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 cm³ of solution 5.2) for molecular masses around 1 000 000, 5 g/l (0,125 g in 25 cm³ 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 cm³ 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 α ($= 0,700$).

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 ³ 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

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 mm³ (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.

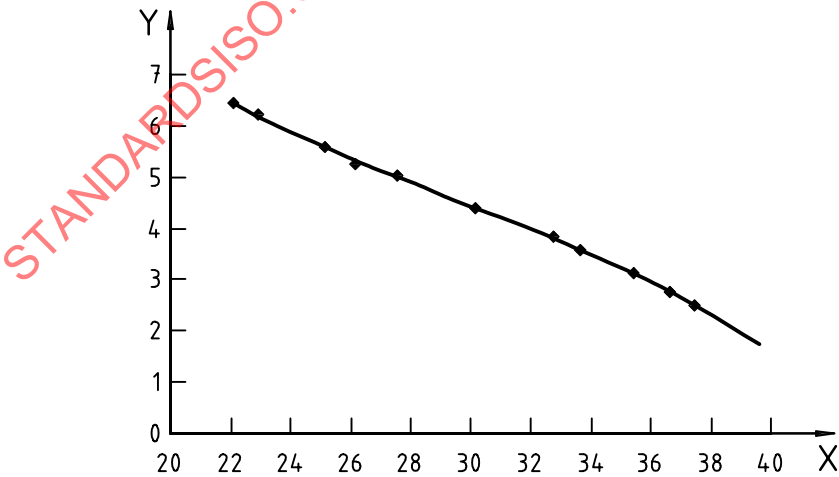
For the data plotted in Figure 1, the best-fit line is given by the following third-degree polynomial:

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

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 cm³ graduated flask and add roughly 35 cm³ 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 cm³ with filtered *o*-dichlorobenzene solution.

8.4 Analysis

8.4.1 Pass solvent through the columns (flow rate 17 mm³/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 cm³ 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 mm³ (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 ± 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 $D (= M_w/M_n)$;

- e) the peak molecular mass M_p ;
- f) the percentage peak area corresponding to the molecular fractions present.

9.5 When suitable software is unavailable, the results may be obtained by using the procedure given in Annex B (manual procedure).

9.6 Comparison of the results obtained by the automatic procedure (software) and the manual procedure is shown in Annex C.

10 Precision (only for instrumental software procedure)

10.1 The precision was determined by means of an inter-laboratory trials programme. Two test specimens of butadiene-styrene block copolymer (solution SBR), with a bimodal molecular-mass distribution, were used in the programme:

- S.SBR1 (97) linear butadiene-styrene block copolymer;
- S.SBR2 (97) radial butadiene-styrene block copolymer.

For each material, the samples were drawn from a uniform and homogeneous lot.

The molecular-mass distribution (triplicate analysis of each sample) was determined in six laboratories on two different days one week apart.

For repeatability purposes, the three test results were obtained with the same method on nominally identical test materials under the same conditions (same operator, apparatus and laboratory) and within a specified time period.

For reproducibility purposes, the three test results were obtained with the same method on nominally identical test materials under different conditions (different operator, apparatus and laboratory) and within a specified time period.

10.2 The parameters calculated were:

- the mass-average molecular mass M_w ;
- the number-average molecular mass M_n ;
- the polydispersity $D (= M_w/M_n)$.

10.3 The precision calculations to express the repeatability and reproducibility were performed in accordance with ISO/TR 9272. Consult this for precision concepts and nomenclature. Annex D gives guidance on the use of repeatability and reproducibility.

10.4 The precision results are given in Tables 6, 7 and 8. Unless stated otherwise, the probability is 95 %.

10.5 In order to obtain the precision given in Tables 6, 7 and 8 in other analyses, careful attention is necessary in the selection of the columns used.

Table 6 — Mass-average molecular mass $M_w \times 10^{-3}$ — Precision results

Rubber material	Average value	Within-lab			Between labs		
		s_r	r	(r)	s_R	R	(R)
S.SBR1 (97)	167,67	2,06	5,84	3,48	2,97	8,40	5,01
S.SBR2 (97)	361,22	3,85	10,90	3,02	5,60	15,85	4,39
Pooled values	264,44	2,96	8,37	3,16	4,28	12,12	4,59

Table 7 — Number-average molecular mass $M_n \times 10^{-3}$ — Precision results

Rubber material	Average value	Within-lab			Between labs		
		s_r	r	(r)	s_R	R	(R)
S.SBR1 (97)	138,42	1,57	4,44	3,20	25,43	71,97	52,00
S.SBR2 (97)	268,47	8,44	23,88	8,90	42,65	120,71	44,96
Pooled values	203,44	5,00	14,16	6,96	34,04	34,04	47,36

Table 8 — Polydispersity M_w/M_n — Precision results

Rubber material	Average value	Within-lab			Between labs		
		s_r	r	(r)	s_R	R	(R)
S.SBR1 (97)	1,11	0,01	0,03	2,33	0,05	0,15	13,73
S.SBR2 (97)	1,26	0,03	0,07	5,71	0,11	0,30	24,11
Pooled values	1,19	0,02	0,05	4,13	0,08	0,23	19,26

11 Test report

The test report shall include the following information:

- a reference to this International Standard;
- all details necessary for the identification of the sample analysed;
- the type and number of columns used;
- the type of detector used;
- the set of polystyrene standards used;
- the molecular-mass results obtained, particularly:
 - the mass-average molecular mass M_w ,
 - the number-average molecular mass M_n ,
 - the polydispersity $D (= M_w/M_n)$;

- g) any deviations from the procedure specified;
- h) any operation not included in this International Standard or regarded as optional;
- i) the date of the analysis;
- j) the procedure used (software or manual).

STANDARDSISO.COM : Click to view the full PDF of ISO 11344:2004

Annex A (informative)

Molecular-mass parameters determined by instrumental software

A.1 General

Instrumental software allows calculation of molecular-mass parameters that characterize a polymer from its GPC chromatogram and the use of a specific calibration curve obtained in accordance with the procedure outlined in 8.2.

A.2 Chromatogram acquisition

Set the chromatogram acquisition parameters and start the analysis. During the analysis, the GPC curve is shown in real time on the computer screen (see Figure A.1).

A.3 Chromatogram analysis

A.3.1 At the end of the run (run time 55,0 min), the molecular parameters are computed by the software, after setting the following parameters:

- a) A baseline time-frame that includes all the peaks in the chromatogram.

NOTE In the example in Figure A.2, the baseline time-frame is from 22,0 min to 29,5 min.

- b) An appropriate number of data points around the baseline time-frame extremes that allow the software to draw a straight line from one extreme to the other to eliminate noise.

- c) The exit time of the reference peak, with the maximum variation range (window) allowed to consider the chromatogram acceptable.

NOTE In the example in Figure A.2, the exit time of the reference peak is 45,41 min, with a time tolerance (window) of ± 30 s. The tolerance of ± 30 s is the limit imposed for the calculation. However, in practice a narrower tolerance of ± 20 s is used.

- d) The start and end points for the integration of the chromatogram.

NOTE In the example in Figure A.2, the start point is 23,54 min and the end point is 28,30 min.

- e) The total number of chromatogram time-slices between the start and end points defined in d).

NOTE In the example in Figure A.2, the number of time-slices is equal to 30; generally, the optimum number of time-slices is 150.

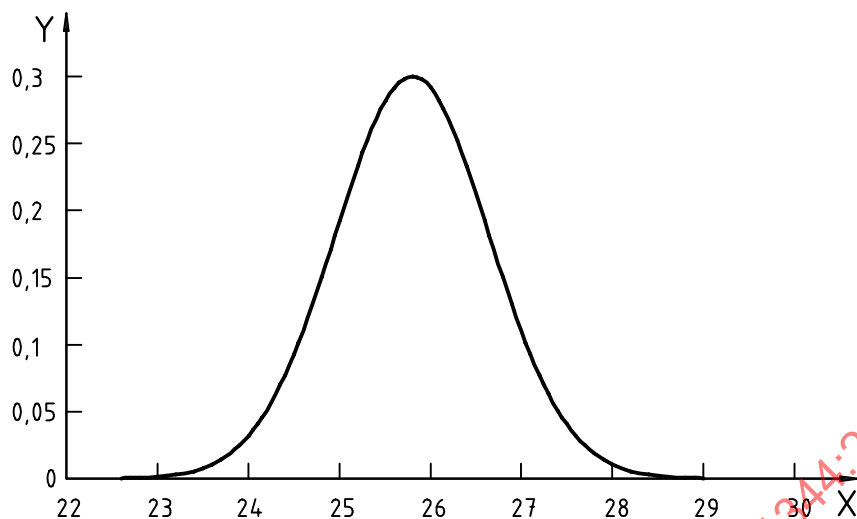
- f) The Mark-Houwink constants K and α .

NOTE In the example in Figure A.2, the K and α values used in the calculations are $K = 0,000\ 160\ 0$ and $\alpha = 0,700$.

Figure A.2 shows the chromatogram after slicing. Table A.1 shows all the parameters of each time-slice making up the chromatogram.

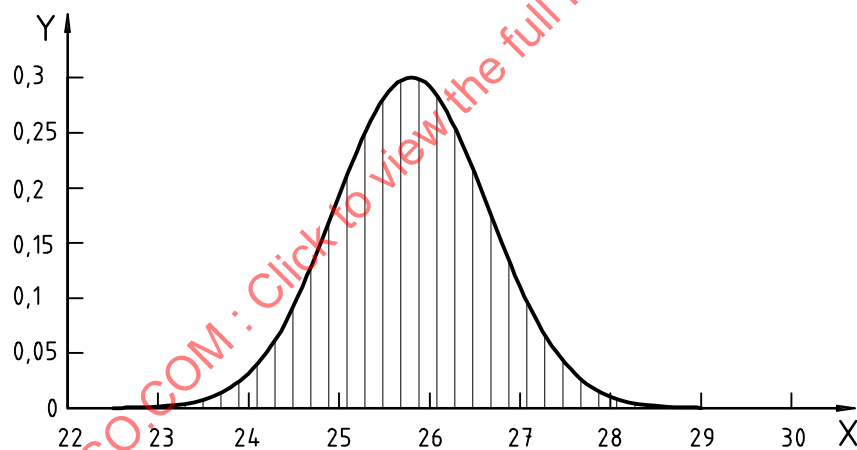
Table A.1 — GPC chromatogram time-slices

Retention time t_i (at centre of time-slice) min	Area of time-slice	$M_i[\eta]_i \times 10^{-3}$ ^a	M_i ^b
23,621 9	4 306	986	573 977
23,780 5	4 043	893	541 346
23,939 1	3 862	809	510 849
24,097 7	4 875	734	482 327
24,256 3	15 380	666	455 633
24,414 9	72 628	605	430 631
24,573 5	268 561	550	407 199
24,732 1	708 384	500	385 222
24,890 7	1 395 968	456	364 596
25,049 3	2 135 893	415	345 225
25,207 9	2 553 702	379	327 022
25,366 4	2 316 451	346	309 904
25,525 0	1 578 818	316	293 796
25,683 6	859 802	288	278 630
25,842 2	420 762	264	264 341
26,000 8	210 947	241	250 871
26,159 4	119 798	221	238 165
26,318 0	78 122	202	226 173
26,476 6	55 340	185	214 848
26,635 2	40 511	170	204 147
26,793 8	30 408	156	194 030
26,952 4	23 412	143	184 460
27,111 0	18 926	131	175 403
27,269 5	15 512	120	166 827
27,428 1	12 895	110	158 701
27,586 7	10 632	101	151 000
27,745 3	8 459	93	143 696
27,903 9	6 722	86	136 767
28,062 5	5 232	79	130 189
28,221 1	3 764	72	123 943
^a Determined from calibration curve (see Figure 1).			
^b Determined from Mark Houwink equation with $K = 0,000\ 16$ and $\alpha = 0,700$.			

**Key**

X retention time (min)

Y detector response

Figure A.1 — GPC chromatogram acquisition**Key**

X retention time (min)

Y detector response

Baseline:	Start: 22,00	End: 29,50
Number of data points in baseline region:	44	
Reference peak time:	45,41 min	Window: 30 s
Reference peak found at:	45,42 min	
Processing:	Start: 23,54 min	End: 28,30 min
Number of slices:	30	
Mark-Houwink equation:	Start time: 0,00	K: 0,000 160 0 α : 0,700 000

Figure A.2 — GPC chromatogram analysis

A.4 Results of GPC analysis

The final GPC analysis results are shown in Table A.2.

Table A.2 — Results of GPC analysis

Number-average molecular mass M_n	316 343	Intrinsic viscosity	1,146 0
Mass-average molecular mass M_w	322 380	Polydispersity M_w/M_n	1,019 1
z-Average molecular mass M_z	327 646	M_z/M_w	1,016 3
Peak molecular mass M_p	323 115		

STANDARDSISO.COM : Click to view the full PDF of ISO 11344:2004

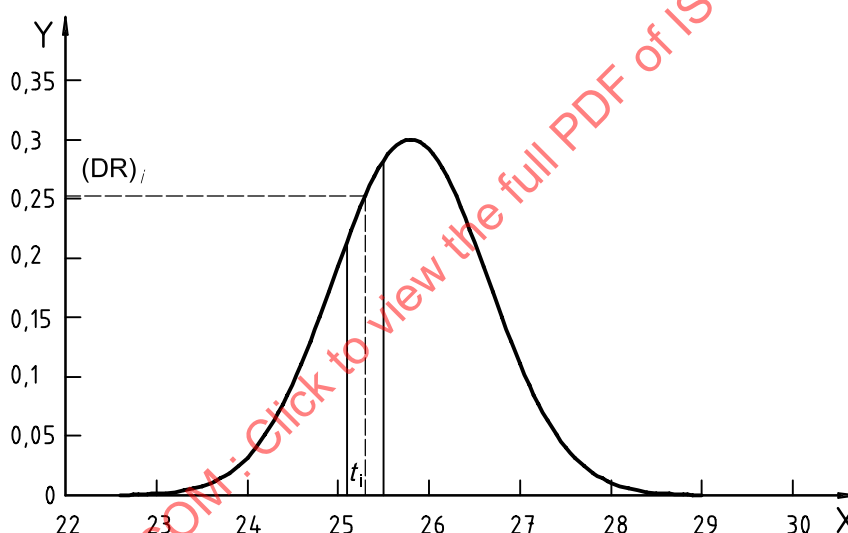
Annex B (informative)

Calculation of molecular-mass parameters by manual procedure

B.1 When software is not available, the results may be obtained by using the procedure given in B.2 to B.9:

B.2 Divide the chromatogram shown in Figure A.1, which is a plot of detector response against retention time in minutes, into equal time-slices. In the example given below, the chromatogram has been divided into 16 slices (the difference between the retention times of adjacent slices being equal to 0,158 6 min, corresponding to 9 516 ms).

B.3 For each of the time-slices, draw a vertical line from the central point on the retention time axis to intersect the chromatogram curve. Determine the detector response at the point of intersection and multiply this value by 1 000 to give $(DR)_i$ (see Figure B.1 for an example).



Key

X retention time (min)
Y detector response

Figure B.1 — Example of manual chromatogram analysis

B.4 Record the time, in minutes, to the central point of each time-slice and convert the value into milliseconds.

B.5 For each of these times, calculate the value of $\log(M_i[\eta]_i)$, using the equation, given in 8.2.4.6, of the calibration curve shown in Figure 1:

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

B.6 Using the Mark-Houwink equation, appropriately rearranged, determine the molecular mass at the central point of each time-slice:

$$[\eta]_i M_i = K M_i^{(1+\alpha)}$$

$$[\eta]_i M_i = 0,000\,16 M_i^{1,7}$$

$$Z_i = 10^{\log(M_i[\eta]_i)}$$

$$M_i = 10 \exp \left[\frac{\log \left(\frac{Z_i}{0,000\ 16} \right)}{1,7} \right]$$

Table B.1 gives a summary of the above parameters.

B.7 Calculate the area A_i of each time-slice as follows:

$$A_i = \Delta(t_i) \times (\text{DR})_i$$

where

$\Delta(t_i)$ is the time difference between slices (= 9 516 ms);

$(\text{DR})_i$ is the detector response.

B.8 For each slice, determine the values of A_i/M_i and A_iM_i as shown in Table B.2.

B.9 By using the following equations (see Table 1), calculate the number-average molecular mass, the mass-average molecular mass and the polydispersity, as follows:

$$M_n = \frac{\sum A_i}{\sum \frac{A_i}{M_i}} = 318\ 085$$

$$M_w = \frac{\sum (A_i M_i)}{\sum A_i} = 322\ 666$$

$$\text{Polydispersity } D = M_w/M_n = 1,014$$