INTERNATIONAL STANDARD

ISO 13885-1

Second edition
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Binders for paints and varnishes — Gel permeation chromatography (GPC) —

Part 1: Tetrahydrofuran (THF) as eluent

Liants pour peintures et vernis — Chromatographie par perméation de gel (GPC) —

Partie 1: Utilisation de tétrahydrofurane (THF) comme éluant

Reference number
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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 13885-1 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 10, *Test methods for binders for paints and varnishes*.

This second edition cancels and replaces the first edition (ISO 13885-1:1998), which has been technically revised. In particular, the method has been brought into line with the current state of the art, especially as far as the software used is concerned, and the procedure for the manual evaluation of the results has been deleted.

ISO 13885 consists of the following parts, under the general title *Binders for paints and varnishes — Gel permeation chromatography (GPC)*:

— *Part 1: Tetrahydrofuran (THF) as eluent*

Binders for paints and varnishes — Gel permeation chromatography (GPC) —

Part 1: Tetrahydrofuran (THF) as eluent

WARNING — This part of ISO 13885 may involve hazardous materials, operations or equipment. It 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. A specific hazard statement appears in Clause 6.

1 Scope

This part of ISO 13885 describes the determination of the molar-mass distribution, number-average molar mass M_n and mass-average molar mass M_w of polymers that are soluble in THF (tetrahydrofuran) by gel permeation chromatography (GPC)[1)].

It is possible that, in spite of the good repeatability obtained with this method, it cannot be used with certain polymer types because of specific interactions, such as adsorption within the sample/eluent/column system.

The method is not an absolute one and requires calibration with commercially available unbranched-polystyrene standards that have been characterized by absolute methods. The results for samples of polymers other than polystyrene are therefore only comparable within groups of samples of the same type.

The conditions specified in this part of ISO 13885 are not suitable for the GPC analysis of polymer samples with M_w values greater than 10^6 (see Annex C).

No correction methods, e.g. for the elimination of peak broadening, are included in this part of ISO 13885. If absolute molar-mass values are required, an absolute method, e.g. membrane osmometry for M_n or light scattering for M_w, must be used.

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 1513, *Paints and varnishes — Examination and preparation of samples for testing*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

1) Also known as size exclusion chromatography (SEC).

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
gel permeation chromatography
chromatographic method in which the completely dissolved molecules of a polymer sample are fractionated on a porous column material, separation taking place according to the size of the molecule (or, more precisely, the size of the polymer coil which forms in this elution solvent)

NOTE 1 Small molecules diffuse into the pores of the column material more frequently and are therefore retarded more than large molecules. Thus large molecules are eluted earlier, small molecules later. Under the test conditions given, the retention volume is solely a function of the size of the molecule.

NOTE 2 This is a special form of liquid chromatography.

4 Principle

The polymer content of a sample is determined, the sample is then diluted with eluent to give a concentration of less than 5 g/l and an aliquot of the diluted sample is injected into the GPC system. The concentration of the molecules eluted from the column is measured in order of decreasing coil size with a concentration-sensitive detector, typically a differential refractometer. The molar-mass distribution, the quantities M_n and M_w and the heterogeneity or polydispersity M_w/M_n are calculated from the resultant chromatogram with the aid of a calibration curve that has been determined for the particular GPC system.

5 Apparatus

5.1 General

The apparatus shall consist of the components shown in Figure 1, which are described below.

It is essential that all components which come into contact with the eluent or the sample solution are resistant to them and do not exhibit adsorption or memory effects in any form. The individual components of the GPC apparatus, which in this case uses THF as eluent, shall be linked with stainless-steel or titanium capillary tubes.

5.2 Eluent supply

The eluent reservoir shall provide the eluent with adequate protection against external influences such as the atmosphere and light, if necessary by means of a blanket of inert gas over the surface of the liquid. The eluent reservoir shall have sufficient capacity to permit equilibrium to be established between the elution solvent and the surface of the column material and several analyses to be conducted.

The eluent shall be degassed, either before it is introduced into the reservoir or by use of a device fitted between the reservoir and the pump, to prevent malfunctions of the pump or the formation of bubbles in the detector. The method of degassing used, e.g. bubble trap, online purging with helium, or vacuum degassing, is open to choice.

5.3 Pump

The pump ensures that the eluent flow through the column is as smooth and pulse-free as possible. The flow rate shall be 1 ml/min (see, however, Annex A). The maximum permitted variation in the flow rate is 0,1 %. To fulfil these requirements, the pump shall operate at optimum efficiency at this flow rate.

5.4 Injection system

The injection system serves to introduce a predetermined, precise amount of the sample solution into the eluent stream in a rapid and smooth fashion.

When filling the sample loop with sample solution and subsequently introducing the sample solution into the eluent stream, the volume of liquid used shall be great enough to ensure that, even if laminar-flow effects occur, the sample loop is completely filled with the sample solution and subsequently completely flushed out.

Memory effects from the previous sample solution in the injection system shall be avoided by suitable design or by adequate flushing.

5.5 Columns

The apparatus shall have one or more columns connected in series and packed with spherical porous material, the diameter of the pores corresponding to the size of the polymer molecules being analysed.

The packing material typically consists of a styrene/divinylbenzene (S/DVB) copolymer, produced by a special polymerization process, which swells only slightly in the solvent and therefore will not normally deform under the pressure developed at the flow rate used.

In addition to these macroporous spherical S/DVB particles, packing materials based on other organic monomers or on silicon dioxide (silica) are also used. The criterion for their use is that no adsorptive interaction shall occur between their surface and the polymer molecules in the sample. Furthermore, the sample being analysed shall not be changed, either chemically or structurally, within the chromatographic system.

Certain polymers can interact with the surface of the packing material, e.g. by adsorption, and other effects can sometimes interfere with the GPC separation mechanism. Details of such effects and notes on possible remedies are discussed in Annex C. If it is intended to compare analyses by different laboratories of such polymers, the laboratories shall agree on details of the test conditions that are not covered by this part of ISO 13885.

One of the objectives of this part of ISO 13885 is to ensure that results obtained in different laboratories using different GPC apparatus for the same sample agree as well as possible. In order to meet this objective, it is necessary to adhere to the minimum requirements specified below with regard to peak broadening (expressed in terms of a number of theoretical plates) and separation performance.

a) Number of theoretical plates

The number of theoretical plates N shall be determined, for the apparatus used, from the peak width at half height (see Figure 2). Inject 20 µl of a solution of ethylbenzene (concentration 1 g/l) on to the column (see Annex A) and evaluate the chromatogram obtained under the same conditions as are used for analysing polymers, according to the following equation:

$$N = 5{,}54 \times \left(\frac{V_e}{W_{1/2}} \right)^2 \times \frac{100}{L} \qquad (1)$$

where

V_e is the retention volume to the peak maximum;

$W_{1/2}$ is the peak width at half height (see Figure 2) — use the same units for V_e and W;

L is the length, in cm, of the column/column system.

Express the result as the number of theoretical plates per metre of total column length. To meet the requirements of this part of ISO 13885, the column system shall have at least 20 000 plates/m.

Consult Annex C with regard to tailing and fronting (asymmetry) of the peak used to calculate the plate count.

b) Separation performance

To ensure adequate resolution, the $\log_{10}M$ versus retention volume V_e calibration curve for the column system used shall not exceed a specified gradient. This parameter should preferably be measured using a pair of polystyrene standards which elute in the area of the peak maximum for the polymer sample under investigation or be determined from the calibration curve and evaluated as

$$\frac{V_{e,\,M_x} - V_{e,\,(10\times M_x)}}{A_c} > 6{,}0 \qquad (2)$$

where

$V_{e,\,M_x}$ is the retention volume for polystyrene of molar mass M_x, in cm^3;

$V_{e,\,(10\times M_x)}$ is the retention volume for 10 times that molar mass, in cm^3;

A_c is the cross-sectional area of the column, in cm^2.

Select M_x such that the peak maximum for the polymer sample under investigation lies approximately halfway between these two retention volumes.

5.6 Column temperature control

Carry out the test at room temperature (15 °C to 35 °C) or at a higher temperature up to a maximum of 40 °C. The temperature of the column shall not change by more than 1 °C during the analysis (see Annex C).

5.7 Detector

Use a differential refractometer detector. The cell volume shall not exceed 0,010 ml (see Annex A).

NOTE 1 For the reasons for permitting only a single type of detector, see Annex C.

If samples consisting of copolymers or polymer blends are to be analysed, ensure that all the components give a similar response factor (ratio of detector signal to concentration of analyte in the eluate or, in the case of the differential refractometer, specific refractive index increment ν (usually expressed as dn/dc), i.e. mathematically:

$$0{,}2 \leqslant \frac{k_i}{k_j} \leqslant 5 \qquad (3)$$

where

k_i and k_j are the response factors for components i and j, respectively;

dn/dc is the change in the refractive index n related to the change of the concentration c.

If the ratio of the response factors does not fall within this range in the analysis of a set of samples, a different detector or combination of detectors may be used. If it is intended to compare the results obtained by different laboratories for such a set of samples, the type of detector shall be agreed upon. If a different detector is used, the reasons for using it shall be stated in the test report (see also Annex C).

The detector response obtained using the sample loadings specified in this part of ISO 13885 shall, at the lowest setting for electronic damping, exhibit a noise level of less than 1 % of the maximum height of the polymer peak. As the noise level is influenced by variations in pressure, temperature and flow rate, particularly in the differential refractometer, suitable measures shall be taken to maintain a constant temperature and to damp out pulses.

5.8 Data acquisition

The signals from the detector are recorded by means of an electronic data-acquisition system (see Clause 11 for details).

6 Eluent

The eluent shall consist of tetrahydrofuran (THF) with the following specification:

— assay > 99,5 %;

— water < 0,05 %;

— peroxides < 0,005 %.

It may be stabilized with up to a maximum of 250 ppm of 2,6-di-tert-butyl-4-methylphenol to prevent the formation of peroxides.

The peroxide level in the tetrahydrofuran shall be checked before use, e.g. with test strips.

WARNING — THF is highly flammable. The user of this part of ISO 13885 should refer to appropriate safe-handling procedures.

In exceptional cases, which shall be explained in the test report, it may be necessary to incorporate additives in the THF eluent, up to a maximum of 10 g/l, to avoid problems in the analysis of certain samples (see Annex C for details).

Discard the eluent after using it to condition the column and for the actual analyses, and do not return it to the eluent reservoir.

7 Calibration of the apparatus

7.1 General

Calibrate the GPC apparatus with a series of unbranched-polystyrene standards of narrow molecular-mass distribution (see Annex C) whose molar masses have been determined by independent, absolute methods. The result is a calibration curve for the evaluation of GPC analyses of polystyrene samples. If this calibration curve is used to analyse samples of other compositions, containing molecules with other structures, the results shall be expressed as the "polystyrene-equivalent molar mass" [1].

7.2 Specification for the calibration standard

The molar-mass distribution of the standard shall be narrower than the limits given below as a function of the peak-maximum molar mass M_p:

$M_p < 2\,000$ g/mol	$M_w/M_n \leqslant 1{,}20$
$2\,000$ g/mol $\leqslant M_p < 10^6$ g/mol	$M_w/M_n \leqslant 1{,}05$
10^6 g/mol $\leqslant M_p$	$M_w/M_n \leqslant 1{,}20$

The peak-asymmetry factor A/B for each chromatogram, calculated from the peak half-widths A and B at half height before and after the perpendicular through the peak maximum, shall lie in the range

$$\frac{A}{B} = 1{,}00 \pm 0{,}15 \qquad (4)$$

The half-widths A and B shall be determined from electronically acquired data on peaks defined by at least 60 data points.

The following minimum requirements shall be fulfilled in the characterization of each individual polystyrene standard used for calibration:

a) At least one average molar-mass value, M_n, M_w or M_z (see equations in 11.3), shall be determined by an absolute method. The M_p-values are used for calibration, but there is no absolute method of determining M_p, therefore the procedure for determining the M_p-values (e.g. calculation by M_n and M_w or iterative GPC calibration, starting with the M_w-values associated with the peak maximum and recalculating M_w) must be specified in the data sheet of the standard.

b) At least one method shall be used to determine the molar-mass distribution.

c) All the parameters involved in these methods and used in the calculations shall be stated in the test report.

d) The results and data for each batch analysed shall be presented in a form that will enable the data to be re-evaluated by the user.

NOTE An example of a data sheet of this type is given in Annex B.

Should the calibration standards give a shoulder on either side of the peak, pre-peaks or a tailing peak, the area represented by these anomalies shall be less than 2,0 % of the peak area, otherwise the calibration standard shall be rejected.

Hexylbenzene ($M = 162$) shall be used as the standard with the lowest molar mass on the calibration curve.

If the calibration standards in the low-molecular range are separated so well that the peaks of the individual oligomers can be recognized, their actual molar mass, including the terminal groups, shall be used in the calculations.

7.3 Preparation of the calibration solutions for injection

Shake the calibration standards in the eluent at room temperature, and store at room temperature.

Filter the solutions manually through a 0,45 µm membrane filter. If the filter shows signs of blocking, the solution is unsuitable for calibration purposes.

The solutions shall be used within 48 h.

Several calibration standards may be injected and analysed at the same time, as long as all the peaks are separated down to the baseline.

The concentration of the individual calibration standards in the injection solution, as a function of the peak-maximum molar mass, shall be

$M_p < 50\,000$ g/mol	1,0 g/l
$50\,000$ g/mol $\leqslant M_p < 10^6$ g/mol	0,5 g/l
10^6 g/mol $\leqslant M_p$	0,1 g/l

The quantities injected on to the column shall be matched to the capacity of the column by adjusting the injection volume, and not the concentration. The injection volumes determined in accordance with the requirements of Clause 10 shall be used both in calibration runs and in sample analyses.

7.4 Conditions for calibration runs

The conditions for a calibration run shall, with the exception of the concentration of the injection solutions, be identical to those for the sample analyses.

7.5 Measurement of retention volume/time

The retention volume V_e or retention time t_R shall be measured from the start of injection to the point on the baseline at which the peak reaches its maximum height. In determining this point, a baseline drift of 5 % of the peak height, measured from injection to after the impurity peaks, is acceptable. If the drift is greater or the baseline is unsteady in the area of the peak, the analysis shall be repeated.

The retention time can be measured and checked against an internal standard and, if necessary, a correction made.

7.6 Plotting the calibration curve

The calibration curve shall be plotted with $\log_{10} M_p$ as the ordinate and the retention volume V_e or retention time (or corrected retention time) t_R as abscissa. At least two calibration points shall be measured per decade of molar mass and there shall be at least five calibration points altogether. In the low molar mass range, the calibration curve shall be extrapolated from the hexylbenzene peak to the impurity peaks.

In the high molar mass range, the peak of the first calibration standard eluted shall lie before the high molar mass limit of the sample, and the retention volume corresponding to this limit shall be determined.

The results of the calibration runs can be fed into a computer or recorded in the form of a table or in the form of one or more regression curves. They shall be available at all times in the form of hard copy for direct checking. Since the evaluation of the chromatograms involves their conversion into differential distribution curves in which the reciprocal of the first derivative of the calibration curve is required (see 11.4), it shall be possible to differentiate the equation $\log_{10} M = f(V_e$ or $t_R)$.

To check how well the calibration curve thus produced fits the measurements, the percentage deviation for each calibration point, given by

$$\frac{M_{\text{p, calibration value}} - M_{\text{p, calculated}}}{M_{\text{p, calibration value}}} \times 100$$

shall be plotted against V_e or t_R. From this graph it should be possible to assess whether the positive or negative deviations are random along the V_e or t_R axis. Calibration-curve fits which exhibit trends in the deviation plot over particular elution ranges are unsuitable. If such distributions of residuals cannot be improved upon with the regression models (see Annex C) available in a laboratory, the results must be expected to contain greater errors and this shall be stated in the test report.

The test for the distribution of residuals need not be carried out on calibration curves obtained by methods in which the measured points and those of the calibration curve automatically coincide, as is the case with a connected series of straight lines and with uncompensated spline algorithms. With these methods, other means must be used to ensure that the calculated calibration curves contain no physically impossible areas, e.g. regions with a positive slope.

8 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528. Examine and prepare each sample for testing, as described in ISO 1513.

9 Preparation for the test

9.1 Preparation of the injection solution

Weigh an aliquot of the polymer sample and dissolve in eluent (see Clause 6) from the reservoir of the chromatograph in which the sample is to be analysed. Store the solution at room temperature.

The concentration of the injection solution is not an independent quantity. It depends on the total volume of the column used, and the injection volume. See Clause 10 for details.

Shake the solution at room temperature to ensure complete dissolution and homogenization; in the case of samples with a mean molar mass of less than 700 000 g/mol, a magnetic stirrer may be used. The use of ultrasound is not permitted because of the risk of degradation. The use of heat should preferably also be avoided. Exceptions, e.g. for PVC, shall be justified in the test report.

As a rule, polymer samples shall be weighed free of solvent. If the sample contains solvent and if it is sensitive, the original solution can be used at its original concentration, or it shall be concentrated carefully under vacuum at room temperature before weighing. The polymer content of the original solution shall be determined separately; the method used shall be stated in the test report. If such samples give overlapping solvent and polymer peaks, the evaluation shall be restricted to the unaffected area of the chromatogram and the limit of the evaluation stated in the test report in terms of molar mass. When several samples are analysed and compared, the evaluation limit selected shall be identical in each case.

Remove insoluble foreign matter, e.g. pigments, extender materials and high-impact components, from the injection solution by suitable methods, e.g. ultracentrifugation, filtration or membrane filtration. Even if the solution appears clear to the eye, filtration through membrane filters with a pore size between 2 µm and 0,2 µm is always recommended. These operations, as well as any precautions taken to ensure that the concentration of the injection solution is maintained, shall be recorded in the test report.

If the sample contains insoluble polymer particles, e.g. microgel, the test report shall expressly point out that the GPC results refer only to the soluble components. The appearance of such samples shall be described.

The injection solutions shall be used within 48 h.

9.2 Preparation of the apparatus

The apparatus shall be operated under the conditions given in Clause 10. First, pump eluent through the entire apparatus until the detector noise level reaches a minimum, preferably below that given in 5.7, and the baseline conditions specified in 7.5 can be expected to be maintained. At this point, the analyses or, if necessary, the control analyses can be carried out.

10 Conditions of analysis

The concentration of the sample solution injected shall be 0,1 g/l to 5,0 g/l.

The injection volume shall be matched to the set of columns used and shall be not more than 100 µl for a column volume of 300 mm × 7,8 mm (the volume of the reference column — see Annex A). The total injection volume shall not exceed 250 µl.

With narrow molar-mass distributions and high molar masses, the retention volume is very sensitive to the quantity of polymer injected. If anomalous peak shapes are observed with a particular sample, the concentration of the injection solution shall be repeatedly halved until the effective variation in the calculated M_w-value has been reduced to below 5 %.

If greater injection quantities are necessary for a particular polymer because of an unsuitable detector response factor, this shall be mentioned in the test report.

Several injections shall be made for each sample. The number of injections made shall be stated in the test report. The two last injections shall be evaluated individually and the results presented individually. Their position in the sequence of injections shall be evident.

When analyses carried out by different laboratories are to be compared, injections shall be made from at least two solutions that have been prepared separately.

Observations that indicate adsorptive interactions between the injected polymer and the column packing material as described in 5.5 shall be noted in the test report.

11 Data acquisition and evaluation

11.1 General

The chromatogram shall be recorded by means of an electronic data-acquisition system. Data shall be stored starting at a point before the evaluation limit (see 11.2.3) for the column system being used and continuing until the curve returns to the baseline after elution of the last system peak.

The number of the measured points, which shall be equidistant, shall be at least 20 per molar-mass decade of the calibration curve used, and a peak that is to be evaluated shall include at least 25 such points.

The dynamic range of the detector signal between the smallest detectable value and the highest peak in the chromatogram after subtraction of the baseline shall be at least 1 500.

The raw data from the sample and calibration analyses shall be stored for at least one year to permit re-evaluation if necessary.

11.2 Calculation of the net chromatogram from the raw data

11.2.1 Determination of the baseline

The zero signal of the detector (i.e. the baseline) shall be taken as the straight line between the zone preceding the evaluation limit and that following the last system peak, i.e. zones in which no elution will take place in an ideal GPC separation.

The baseline shall coincide with the detector signal in these zones for at least 10 % of the total analysis time, otherwise the analysis shall be discarded as unsuitable. If deviations from the baseline determined can be seen in this interval, the results shall also be rejected. The calculations themselves can be made at points along the baseline that lie within this range on the baseline thus determined.

The plot of the difference between each original data point and the interpolated baseline point at the same time or volume between the low and the high molar cut-off is referred to in the following discussion as the net chromatogram.

11.2.2 Correction of the measured values and of the net chromatogram

An adjustment or correction of the raw data or of the net chromatogram, e.g. elimination of peak broadening, correction for concentration shifts, is not covered by this part of ISO 13885.

Only smoothing measures such as the averaging of not more than five adjacent points, as well as indirect smoothing measures, such as are carried out in the interpolation of values for purposes of data compression or in matching points and calibration-curve matrices, are permissible; the necessary compensatory calculations for a point shall be restricted to an interval of less than 0,25 $\log_{10} M$ units. All such manipulations of data shall be recorded explicitly in the test report.

It is permissible to take the average of several results from repetitive analyses or to take the mean distribution curves in addition to the data in 13.3 g), e.g. co-addition of the chromatograms or averaging of the molar-mass averages; the methods used shall be described in full and the standard deviations determined and stated.

11.2.3 Evaluation limit

Before starting the analysis, determine the point at which the system or solvent peaks start to elute by injection of the solvent actually used as the mobile phase. This will be at the low-molecular end of the chromatogram. The elution volume corresponding to this point is the low-molecular evaluation limit. Its value shall be stated in the test report together with the corresponding molar mass read off the calibration curve.

Chromatograms that exhibit tailing of the sample peak such that it extends into the area of the impurity peaks cannot be evaluated in the way specified in this part of ISO 13885 and shall be rejected.

11.3 Calculation of the average values

With the measurement points spaced at intervals as specified in 11.1, the integrations normally required can be replaced by summations and the curve of the chromatogram can be represented as a series of slices.

The individual measurement points shall be situated in the middle of each slice and the molar mass determined from the calibration curve at the ith measurement point shall apply to the whole width of the ith slice.

As the measured points are assumed to be equidistantly spaced, the slice width cancels out in all the equations shown below and the slice areas can be represented directly by the measured ordinates, e.g. as h_i for the ith slice.

The average molar masses shall be calculated using the following equations:

Number average $$M_{\mathrm{n}} = \frac{\sum_{i=1}^{i=n} h_i}{\sum_{i=1}^{i=n} h_i / M_i} \tag{5}$$

Mass average $$M_{\mathrm{w}} = \frac{\sum_{i=1}^{i=n} h_i \times M_i}{\sum_{i=1}^{i=n} h_i} \tag{6}$$

z-average $$M_z = \frac{\sum_{i=1}^{i=n} h_i \times M_i^2}{\sum_{i=1}^{i=n} h_i \times M_i} \tag{7}$$

$(z+1)$-average $$M_{z+1} = \frac{\sum_{i=1}^{i=n} h_i \times M_i^3}{\sum_{i=1}^{i=n} h_i \times M_i^2} \tag{8}$$

where

h is the height of the chromatogram;

M_i is the molecular mass of species i.

The heterogeneity factor D is defined as the ratio of M_w to M_n. As no correction is made for peak broadening, this value is designated by the subscript GPC, i.e.

$$D = \left(\frac{M_w}{M_n} \right)_{GPC}$$

to be able to distinguish it from values calculated from molar masses measured by absolute methods.

M_p is defined as the molar mass at the slice at which the height H of the net chromatogram is the greatest.

The repeatability of these average values is expressed either as the standard deviation of repeated analyses or in terms of values obtained in the past for the GPC apparatus used.

There is no point in calculating the viscosity average M_v using the equation

$$M_v = \left(\frac{\sum_{i=1}^{i=n} h_i \times M_i^{\alpha}}{\sum_{i=1}^{i=n} h_i} \right)^{1/\alpha} \quad (9)$$

unless the sample and calibration polymers have identical structures or unless the same Mark-Houwink exponent α applies to both in the eluent used.

11.4 Calculation of the distribution curves

The cumulative percent mass fraction distribution curve $S(M)$ is obtained by summing the normalized slice areas. $S(M)$ shall be taken as the sum of all areas between the low molar mass evaluation limit and the point of intersection of the distribution curve and the abscissa M_i:

$$S(M_i) = \frac{\sum_{j=1}^{j=i} \left(h_{j-1} + h_j \right) / 2}{\sum_{j=1}^{j=n} h_j} \times 100 \quad (10)$$

where $j = 1$ at the low molar mass end of the curve and $j = n$ at the high molar mass end of the curve.

The form of the differential distribution curve $W(M)$ depends on the abscissa chosen. This plot of relative frequency of molecules W versus $\log_{10} M$ requires the use of one of the following equations to calculate W from the net chromatogram with the abscissa V_e or t_R:

$$W\left(\log_{10} M_i\right) = (-1) \times \frac{h_i}{\sum_{j=1}^{j=n} h_j} \times \left(\frac{dV_e}{d\log_{10} M} \right)_i \quad (11)$$

or

$$W\left(\log_{10} M_i\right) = (-1) \times \frac{h_i}{\sum_{j=1}^{j=n} h_j} \times \left(\frac{\mathrm{d}t_R}{\mathrm{d}\log_{10} M} \right)_i \qquad (12)$$

i.e. the normalized net chromatogram height is multiplied by the negative reciprocal of the first derivative of the calibration curve.

12 Precision

12.1 General

The precision of this method has been determined in several round-robin experiments (see Annex C for details).

If individual samples interact in a non-ideal manner with the surface of the column packing material — as described in 5.5 — the standard deviations can increase to a multiple of the values given.

12.2 Repeatability

Repeatability is, according to ISO 5725-1, the precision of a set of test results obtained by the same method carried out under conditions that are as constant as possible, i.e. at short intervals in the same place (in the same laboratory) by the same operator using the same equipment. The following repeatability standard deviations σ_r were determined as a percentage of the measured values:

for M_n: $\sigma_r = 3$ %

for M_w: $\sigma_r = 2$ %

for M_z: $\sigma_r = 3$ %

for M_w/M_n: $\sigma_r = 3$ %

for M_p: $\sigma_r = 2$ %

12.3 Reproducibility

Reproducibility is, according to ISO 5725-1, the precision of a set of test results obtained under comparable conditions, i.e. on the same sample material in different laboratories by different operators using different equipment but using the same method. The reproducibility standard deviations σ_R for the parameters M_n, M_w, etc., referred to in 12.2 were, on average, 5 times greater than the repeatability standard deviations σ_r.

The following values were obtained for the reproducibility standard deviation σ_R at different places on an average distribution curve calculated for all the laboratories:

in the low-molecular range from 0 % to 10 %: $\sigma_R = 50$ %

in the range from 10 % to 90 %: $\sigma_R = 11$ %

in the high-molecular range from 90 % to 100 %: $\sigma_R = 38$ %

The large differences between the values of the reproducibility standard deviation σ_R given above show that it would be possible to improve the comparability between different laboratories by agreeing to standardize additional aspects of the method currently not covered by this part of ISO 13885.

A serious source of differences between the individual laboratories proved to be their different assessment of the high- and low-molecular components in chromatograms with a tailing peak. Special attention shall therefore be paid to 11.2.3, first paragraph, and 11.2.1, particularly in plotting the baseline and determining the evaluation limits on a computer, either manually or automatically.

13 Test report

13.1 General

The test report shall contain a reference to this part of ISO 13885 plus the data required in 13.2 and 13.3 (it is necessary to give the data required in 13.2 only once for a series of samples analysed under the same conditions). Those items marked with an asterisk (*) shall be documented in the laboratory, but the information does not have to be stated in the test report.

13.2 General data on the equipment and settings

13.2.1 Data on the equipment used

a) Eluent reservoir, inert gas and degassing of the eluent, plus details of any additives in the eluent.

*b) Pump.

*c) Injection system.

d) Columns (manufacturer, packing material, pore size, separation range, and the number, dimensions and sequence of the columns in the column combination used).

e) Low-molecular evaluation limit determined in 11.2.3.

*f) Number of theoretical plates per metre of the column combination used, asymmetry of the plate-count peak, separation performance as determined in 5.5 b) in the area of the peak maxima for the samples analysed.

g) Column temperature.

*h) Means of maintaining this temperature.

*i) Detector (measurement principle, type, cell size).

*j) Data-acquisition and evaluation hardware and software (manufacturer, type, version number).

13.2.2 Calibration

*a) Full description of the method used for fitting the calibration curve to the measured values.

*b) Typical precision-data characteristic of this fitting method, e.g. sum of the squares of the errors, correlation coefficient, mean error in the individual measurements.

*c) Any assumptions made: e.g. extrapolation of the calibration curve, limiting constraints and additional nodes in spline curves, weighting of individual values.

*d) The values used to construct the calibration curve, listed in a table that gives the following data for each calibration point:

— name and batch number of the standard used;

— manufacturer of the standard;

— characteristic values M_p, M_n, M_w, and M_w/M_n given by the manufacturer or determined subsequently, with details of the method of determination;

— concentration of the solution injected, in g/l;

— injection volume, in µl;

— M_p-value used for calibration;

— elution volume V_e or corrected retention time t_R measured at the peak maximum;

— M_p-value calculated for the peak maximum;

— percentage error, given by

$$\frac{M_{\text{p, calibration value}} - M_{\text{p, calculated}}}{M_{\text{p, calibration value}}} \times 100$$

13.2.3 Evaluation

*a) For evaluation on the basis of time, a description of the measures taken to ensure the constancy and repeatability of the flow rate between the calibration and sample analyses (method of correction, standards, automatic or manual measurements, etc.).

b) For an incompletely evaluated polymer peak, the evaluation limits.

c) Details of direct or indirect smoothing procedures used.

*d) Details of co-addition of repeated analyses, if carried out.

13.3 Special data on the sample

a) Description of the product tested (name, batch number, date of manufacture).

b) Type of sample.

*c) Results of the determination of the non-volatile components, if carried out.

d) Sample preparation (pretreatment, form in which weighed, dissolution procedure, purification of the injection solution).

e) Any insoluble components observed in the sample.

f) Analysis parameters: injection volume in µl, injection concentration in g/l.

g) Test results:

Give the molar-mass averages M_n, M_w, $(M_w/M_n)_{GPC}$ and, optionally, M_z, M_{z+1}, M_p or M_v individually for each chromatogram determined. If M_v has been calculated, state the Mark-Houwink coefficients used. If known, state the repeatability standard deviation for the GPC apparatus used to investigate the particular polymer class.

All analyses conducted on samples in which the polymer is not 100 % polystyrene shall include a note that the values obtained are not absolute molar-mass values but “polystyrene molar-mass equivalents”.

Enclose the distribution curves found (differential mass fraction against $\log_{10}M$ or cumulative percent mass fraction against $\log_{10}M$) as a table or a figure.

Include the raw chromatograms, showing the baseline and the evaluation limit.

h) Any observations that indicate that the ideal GPC separation mechanism is overlaid by other effects.

i) Test conditions that deviate from those given in this part of ISO 13885.

j) Date of the test.

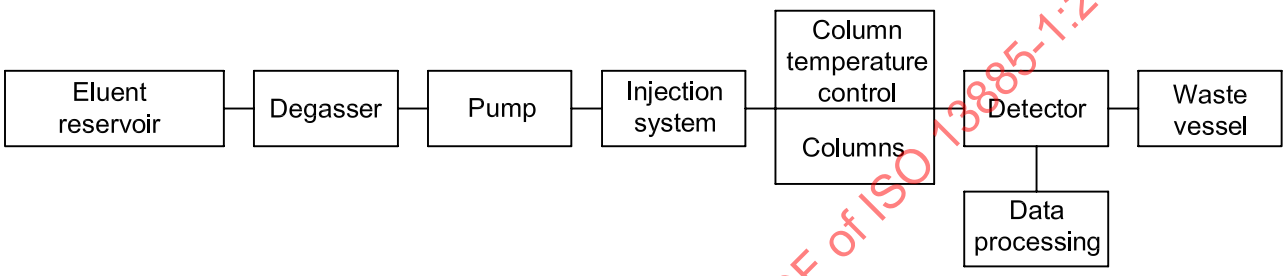
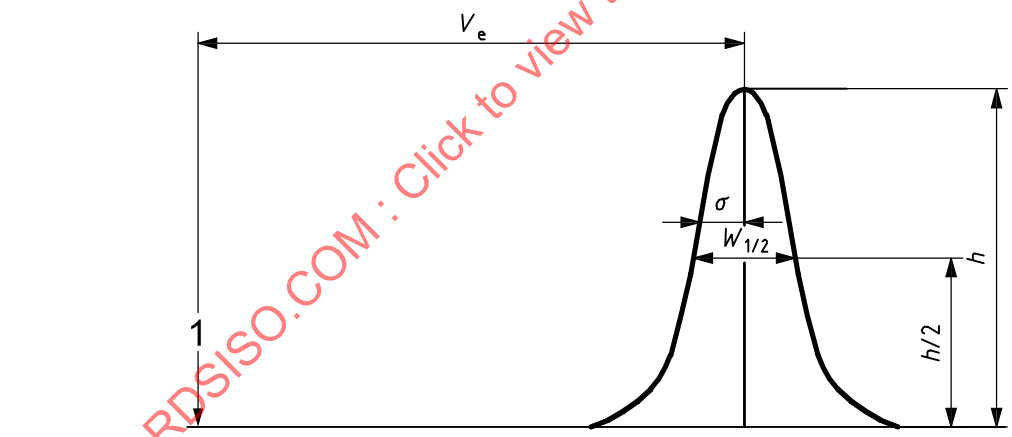


Figure 1 — Block diagram of a GPC apparatus



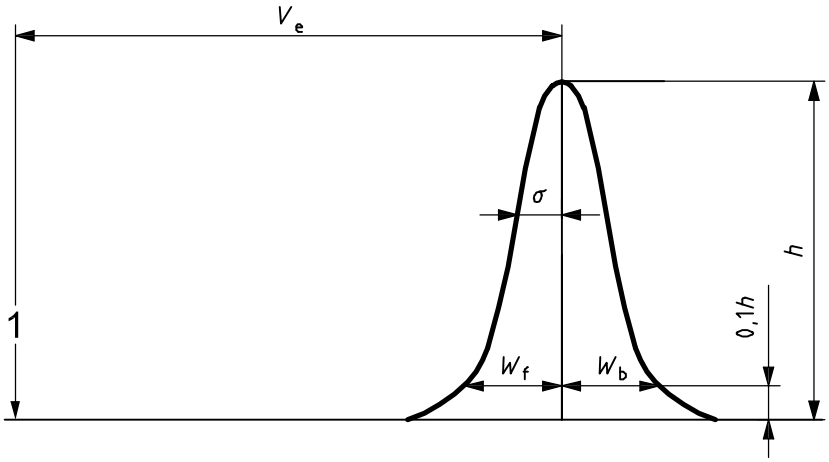
$$N = \left(\frac{V_e}{\sigma}\right)^2$$

$$= 5{,}54\left(\frac{V_e}{W_{1/2}}\right)^2 \times \frac{100}{L}$$

Key

1 injection

Figure 2 — Determination of the number of theoretical plates N by the half-height method



$$A = \frac{W_f}{W_b}$$

Key

1 injection

Figure 3 — Determination of the asymmetry A of a peak

Annex A
(normative)

Calculation of experimental parameters for different column sizes

The values of the flow rate, injection volume, injection mass and cell volume given in this part of ISO 13885 refer to columns of a size of 300 mm × 7,8 mm (referred to as the reference column). If the column volume differs from this value, the experimental parameters will need to be adjusted (see Table A.1).

For optimum separation, the linear flow speed has to be the same as in the reference column. The volume-flow rate F_1, in ml/min, can be calculated from Equation (A.1):

$$F_1 = F_2 \times \left(\frac{D_1}{D_2} \right)^2 \tag{A.1}$$

where

F_2 is the volume-flow rate through the reference column (= 1 ml/min);

D_1 is the diameter of the column used, in mm;

D_2 is the diameter of the reference column (= 7,8 mm).

To calculate the values required for the elution volume, injection mass and cell volume, the pore volume has to be considered. The injection volume can be calculated from Equation (A.2):

$$F_1 = F_2 \times \left(\frac{D_1}{D_2} \right)^2 \times \frac{L_1}{L_2} \tag{A.2}$$

where

L_1 is the length of the column used, in cm;

L_2 is the length of the reference column (= 30 cm).

Table A.1 — Experimental parameters referring to the size of the column

Size of column mm × mm	Volume-flow rate F ml/min	Maximum injection volume for determination of number of plates µl	Maximum injection mass for determination of number of plates µg	Maximum injection volume for the test sample per column µl
50 × 20	6,25	20	20	100
300 × 8,0	1,0	20	20	100
300 × 7,8	1,0	20	20	100
150 × 7,8	1,0	10	10	50
250 × 4,6	0,35	10	10	50
250 × 4[a]	0,25	5	5	25
250 × 3[a]	0,15	3	3	15
250 × 2[a]	0,05	1	1	5

[a] To reduce peak-broadening effects, columns of this size require a micro-cell in the detector used.

Annex B
(informative)

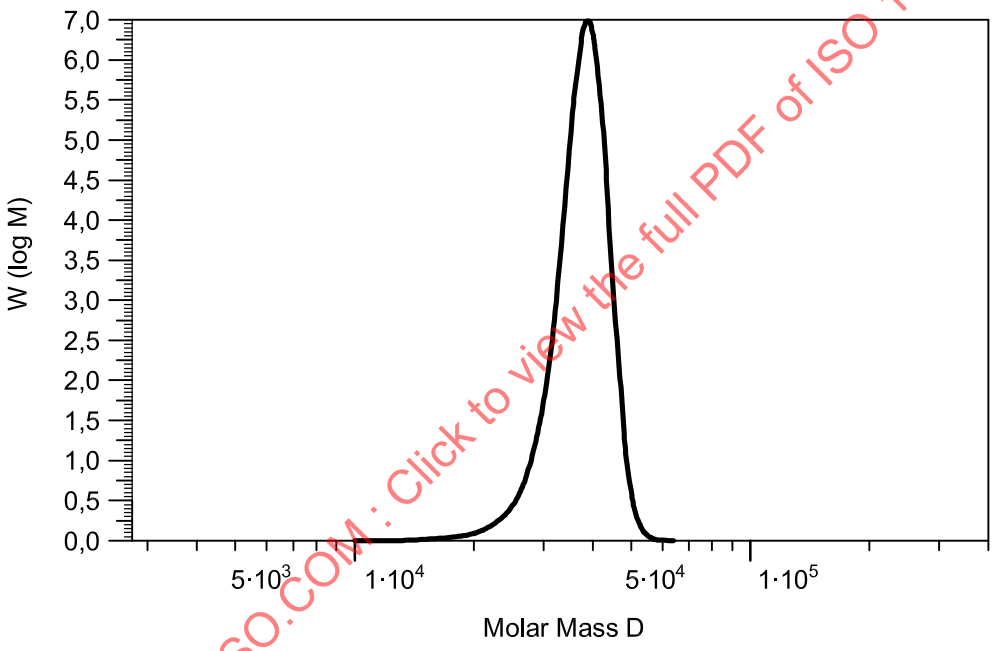
Example of a data sheet for a polymer standard

Quality certificate

Polymer type: Poly(styrene)

Lot No: ps15057

Molar-mass distribution



Parameters

Sample concentration	1,00 g/ml	Injection volume	20 µl
Solvent	THF	Flow rate	1,00 ml/min
Columns	PSS SDV 5 µm 10e3Å/10e5Å/10e6Å	Temperature	25 °C
Data acquisition software	PSS WINGPC 7	Operator	A.N. Other

Polymer characteristics

Detector	M_w (daltons)	M_n (daltons)	M_p (daltons)	D (M_w/M_n)
Shodex RI-71	37 600	36 500	39 200	1,03

M_w	mass-average molar mass	M_p	molar mass at peak maximum
M_n	number-average molar mass	D	polydispersity