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Gel permeation chromatography (GPC) —

Part 1: Tetrahydrofuran (THF) as eluent

Chromatographie par perméation de gel (GPC) —

Partie 1: Utilisation de tétrahydrofurane (THF) comme éluant

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

This third edition cancels and replaces the second edition (ISO 13885-1:2008), which has been technically revised. The main changes compared to the previous edition are as follows:

— this document has been adapted to the actual state of the art, especially with regards to software engineering;

— the scope has been revised;

— the definition for gel-permeation chromatography has been revised;

— the text has been revised editorially.

A list of all parts in the ISO 13885 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Gel permeation chromatography (GPC) —

Part 1:
Tetrahydrofuran (THF) as eluent

WARNING — This document can 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.

1 Scope

This document specifies the determination of the molar-mass distribution and the average molar mass values M_n (number average) and M_w (weight average) of polymers that are soluble in tetrahydrofuran (THF) by gel permeation chromatography (GPC).

NOTE Also known as size exclusion chromatography (SEC).

Even though the chromatograms obtained show good repeatability, it is possible that this method cannot be used with certain polymer types because of specific interactions (e.g. adsorption) within the sample/eluent/column system.

The conditions specified in this document are not applicable to the GPC analysis of polymer samples with M_w values greater than 10^6 g/mol and/or of polymers with elution limits outside the calibration range (see 7.6 and Annex C).

This document includes no correction method (e.g. for the elimination of peak broadening. If absolute molar-mass values are required, an absolute method (e.g. membrane osmometry for M_n or light scattering for M_w) can be used.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 test samples*

ISO 4618, *Paints and varnishes — Terms and definitions*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
gel permeation chromatography
GPC
separation of molecules, mainly based on exclusion effects such as differences in the size and/or shape of molecules (size exclusion chromatography) or in charge (ion exclusion chromatography)

3.2
system peak
signal peculiar to the *gel permeation chromatography* (3.1) using a refractive index detector

Note 1 to entry: These signals appear at the total penetration limit of the columns and are not part of the sample, but of the overall system.

4 Principle

The dissolved (molecularly disperse) molecules of a polymer sample are fractionated on a porous column material, with separation taking place according to the size of the molecule (or, more precisely, the polymer coil size which forms in this eluent). 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 elution volume is solely a function of the coil size of the molecule.

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). With the aid of a calibration curve that has been determined for the particular GPC system, the relative molar-mass distribution, the relative quantities M_n and M_w and the heterogeneity or polydispersity M_w/M_n are calculated from the chromatogram obtained.

5 Apparatus

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

All the components which come into contact with the eluent or the sample solution shall be resistant and shall 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 connected to capillary tubes made of high-quality steel or titanium.

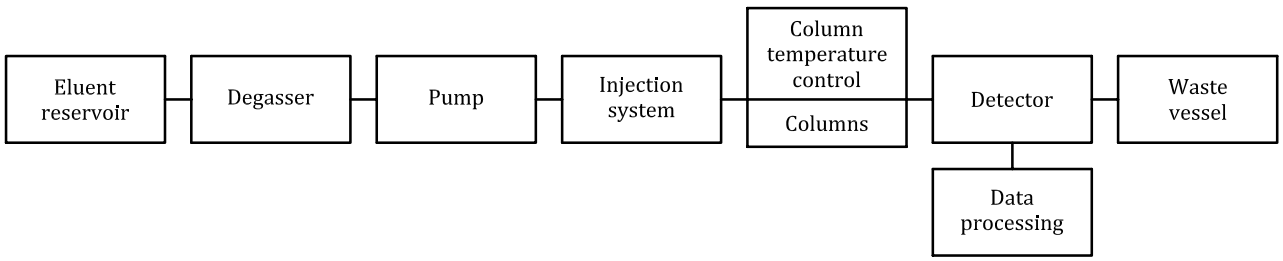


Figure 1 — Block diagram of a GPC apparatus

5.1 Eluent supply

The eluent reservoir shall adequately protect the eluent against external influences such as the atmosphere and light, if necessary by means of a blanket of inert gas above the liquid level.

The eluent reservoir shall contain a sufficient quantity of the eluent to bring the apparatus to equilibrium and to carry out several repeat analyses.

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.

5.2 Pump

The pump shall ensure that the eluent flow through the separation column is as smooth and pulse free as possible. The flow rate shall be 1 ml/min (see Annex A). To fulfil these requirements, the pump shall operate at optimum efficiency at this flow rate.

The flow rate of the pump used shall have a variation of max. 0,1 %.

5.3 Injection system

The injection system serves to introduce a given amount of the sample solution into the eluent stream in a rapid and smooth fashion. This introduction may be carried out either manually or automatically.

If the introduction is carried out manually, ensure that the sample loop is filled completely with solvent before loading with the sample.

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

5.4 Separation 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 copolymer (S/DVB), produced by a special polymerization process, which swells only slightly in the solvent and therefore cannot deform under the pressure developed at the set flow rate.

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 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 of such polymers by different laboratories, the laboratories shall agree on details of the test conditions that are not covered by this document.

For good repeatability of test results, 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 efficiency.

a) Number of theoretical plates

   The number of theoretical plates, N, shall be determined, for the apparatus used per metre of column used, from the peak width at half height (see Figure 2). Inject up to 20 µl of ethylbenzene (mass 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, using Formula (1):

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

where

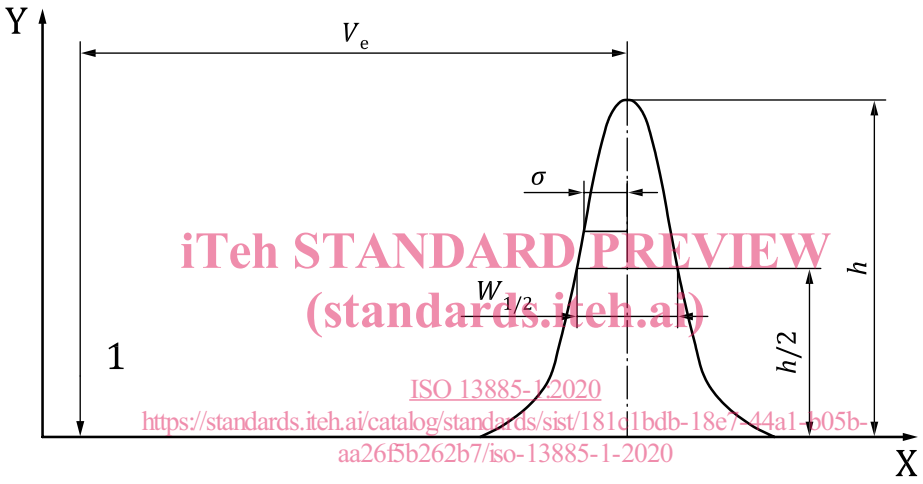
V_e is the elution volume at the peak maximum;

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

L is the length of the column (column combination), in centimetres.

Express as the result the number of theoretical plates per metre of column length. To conform to the requirements of this document, the column combination shall have at least 20 000 theoretical plates per metre.

NOTE See Annex C for tailing and fronting (asymmetry) of the peak used to calculate the plate count.



Key

X elution volume
Y peak intensity
1 injection
V_e elution volume at the peak maximum
$W_{1/2}$ peak width at the half maximum height of the peak
h maximum peak height
σ standard deviation

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

b) Separation efficiency

To ensure adequate resolution, the $\log_{10}M$ versus the elution volume, V_e, calibration curve for the column combination used shall not exceed a specified gradient. For the purposes of this document, the relation given in Formula (2) shall apply to the area of the peak maximum for the polymer sample under investigation:

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

where

V_{e,M_x} is the elution volume for polystyrene of molar mass M_x, in cubic centimetres;

$V_{e,(10\times M_x)}$ is the elution volume for 10 times that molar mass, in cubic centimetres;

A_c is the cross-sectional area of the column, in square centimetres.

M_x is the molar mass, that shall be selected such that the peak maximum for the polymer sample under investigation lies in approximately halfway between these two elution volumes.

5.5 Column temperature control

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

5.6 Detector

Use a differential refractometer detector. The cell volume shall not exceed 0,010 ml.

NOTE For the restriction to a single detector type, see Annex C.

If copolymer samples or polymer blends are 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 dn/dc), i.e. the relationship of the response factors k_i and k_j for components i and j respectively is as follows:

$$0{,}2 \le \frac{k_i}{k_j} \le 5 \tag{3}$$

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 suitable 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 Annex C.

The detector response obtained using the injection amounts specified in this document 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 are to be taken to maintain a constant temperature and to damp out pulses.

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

6 Reagents

The eluent shall consist of THF with the following specification:

THF	>99,5 % (mass fraction)
Water	<0,05 % (mass fraction)
Peroxide	<0,005 % (mass fraction)

THF may be stabilized with 2,6-di-*tert*-butyl-4-methylphenol (BHT) (up to a maximum of 0,250 g/l) to prevent the formation of peroxides.

The peroxide content of THF shall be checked before use (e.g. using test strips).

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

Discard the eluent used to condition the columns or to perform the analyses, and do not return it to the eluent reservoir.

7 Calibration of the apparatus

7.1 General

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

Calibrate the GPC apparatus with a series of unbranched polystyrene standards of narrow molar mass distribution (see Annex C) and 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 molar mass equivalent"[3].

7.2 Requirements for the calibration standards

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

$$\begin{cases} M_p < 2\,000\ \text{g/mol} & M_w/M_n \leq 1{,}2 \\ 2\,000\ \text{g/mol} \leq M_p < 10^6\ \text{g/mol} & M_w/M_n \leq 1{,}05 \\ 10^6\ \text{g/mol} \leq M_p & M_w/M_n \leq 1{,}2 \end{cases}$$

The empirical peak-asymmetry factor for each chromatogram, calculated from the peak widths A and B at half height before and after the perpendicular through the peak maximum, shall lie in the range given by Formula (4).

$$\frac{A}{B} = 1{,}00 \pm 0{,}15 \tag{4}$$

The widths A and B shall be determined from electronically acquired data on peaks defined by at least 60 measuring 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, shall be determined by an absolute method;

b) at least one method shall be used to determine the molar-mass distribution;

c) all the parameters involved in the method used shall be indicated;

d) the results and data for each batch analysed shall be presented in a comprehensible form for the user.

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

If 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.

