

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

Part 1: Tetrahydrofuran (THF) as eluent

ICS 87.060.20,

National foreword

This British Standard is the UK implementation of ISO 13885-1:2008. It supersedes BS6782-14:1999 and which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee STI/3, Paints, media and related products.

A list of organizations represented on this committee can be obtained on request to its secretary.

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 November 2008
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ISBN 978 0 580 59785 5

Amendments/corrigenda issued since publication

Date	Comments

INTERNATIONAL STANDARD

ISO
13885-1

Second edition
2008-08-01

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
ISO 13885-1:2008(E)

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Published in Switzerland

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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:

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

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

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

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:

$$0,2 \leq \frac{k_i}{k_j} \leq 5 \quad (3)$$

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.