INTERNATIONAL STANDARD

ISO 16014-3

Third edition
2019-05

Plastics — Determination of average molecular weight and molecular weight distribution of polymers using size-exclusion chromatography —

Part 3: Low-temperature method

Plastiques — Détermination de la masse moléculaire moyenne et de la distribution des masses moléculaires de polymères par chromatographie d'exclusion stérique —

Partie 3: Mesurage aux basses températures

Reference number
ISO 16014-3:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 61, *Plastics,* Subcommittee SC 5, *Physical-chemical properties*.

This third edition cancels and replaces the second edition (ISO 16014-3:2012), which has been technically revised. The main changes compared to the previous edition are as follows:

— publication dates of references have been removed;

— molecular mass has been changed to molecular weight according to IUPAC rule.

A list of all parts in the ISO 16014 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.

Plastics — Determination of average molecular weight and molecular weight distribution of polymers using size-exclusion chromatography —

Part 3: Low-temperature method

1 Scope

This document specifies a method for determining the average molecular weight and the molecular weight distribution of polymers by size-exclusion chromatography (SEC) using an organic eluent at a temperature lower than 60 °C (see Annex A). The average molecular weight and the molecular weight distribution are calculated from a calibration curve prepared using polymer standards. Therefore, this test method is classified as a relative method (see ISO 16014-1).

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 472, *Plastics — Vocabulary*

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

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 16014-1, *Plastics — Determination of average molecular weight and molecular weight distribution of polymers using size-exclusion chromatography — Part 1: General principles*

ISO 16014-2, *Plastics — Determination of average molecular weight and molecular weight distribution of polymers using size-exclusion chromatography — Part 2: Universal calibration method*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 and in ISO 16014-1 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/

4 Principle

According to ISO 16014-1.

5 Reagents

5.1 Eluent.

For a general discussion of eluents, see ISO 16014-1.

For examples of eluents used for SEC measurements at temperatures < 60 °C, see Annex B.

NOTE Water is often used for SEC measurements on water-soluble polymers at temperatures < 60 °C, but it is not suitable for use in this method.

5.2 Reagent for column evaluation, according to ISO 16014-1.

There are several low molecular weight compounds that can be used, for example ethylbenzene when tetrahydrofuran is used as eluent or diethylene glycol when *N*,*N*-dimethylformamide is used as eluent (see Annex B).

5.3 Molecular weight standards, according to ISO 16014-1.

Some examples of commercially available molecular weight standards are given in ISO 16014-1:2019, Annex B.

5.4 Reagent for flow rate marker (internal standard), according to ISO 16014-1.

It is often very difficult to find a low molecular weight compound suitable for use as a flow rate marker because it should not co-elute with the polymer peak, the system peak or the solvent peak.

Examples of compounds suitable for use as a flow rate marker are sulfur when tetrahydrofuran is used as eluent and ethylbenzene when *N*,*N*-dimethylformamide is used as eluent.

5.5 Additives.

LiBr or LiCl, for example, is used as an additive in *N*,*N*-dimethylformamide to avoid aggregation of polyacrylonitrile, and sodium trifluoroacetate is added to 1,1,1,3,3,3-hexafluoroisopropanol for SEC measurements on polyamide.

6 Apparatus

6.1 General

A schematic diagram of an SEC system is shown in ISO 16014-1.

Either commercially available or assembled SEC systems may be used, provided they meet the component requirements specified and have the capability to maintain a constant column temperature < 60 °C.

6.2 Eluent reservoir, according to ISO 16014-1.

It is not necessary to keep the reservoir at the same temperature as the columns.

6.3 Pumping system, according to ISO 16014-1.

In order to maintain the flow rate accurate to within ±0,3 %, the pumping system shall be kept at a controlled temperature. It is, however, not necessary to keep the pumping system at the same temperature as the columns.

6.4 Injector, according to ISO 16014-1.

In order to maintain an accurately known flow rate, the injector temperature-control equipment shall be capable of keeping the injector at within ±1 K of the temperature set. It is not necessary to keep the injector at the same temperature as the columns.

6.5 Columns, according to ISO 16014-1.

Organic or inorganic packing materials may be used. There are no limitations on particle size or shape.

The set of columns used shall have a total theoretical plate number > 15 000, and the resolution factor R shall be > 1,5 close to the polymer peak. The asymmetry factor shall be within the range 1,00 ± 0,15. The set of columns used should preferably cover the whole range of molecular weights being determined, and the calibration curve shall be as linear as possible (the correlation factor shall be very close to 1). Determination of the theoretical plate number, the resolution factor and the asymmetry factor of the columns shall be carried out as described in ISO 16014-1.

The column temperature-control equipment shall be capable of keeping the columns within ± 0,5 K of the temperature set, to ensure adequate reproducibility of the results.

6.6 Detector, according to ISO 16014-1.

The detector temperature-control equipment shall be capable of keeping the detector within ± 1 K of the temperature set, in order to meet the requirements for flow rate and baseline stability (sensitivity). It is recommended that the columns and detector be kept at the same temperature.

6.7 Tubing, according to ISO 16014-1.

The temperature of the tubing shall be kept constant to ensure that the column performance requirements are met, but it is not necessary to keep the tubing at the same temperature as the column.

6.8 Temperature control.

Refer to 6.4 for the injector temperature-control equipment. And refer to 6.5 and 6.6 for the columns and detector.

One of the important factors in SEC is that all components need to be kept at a constant temperature.

6.9 Recorder and plotter, according to ISO 16014-1.

6.10 Data-processing system, according to ISO 16014-1.

6.11 Other components.

In addition to the components described above, a column guard filter, pressure monitor, pulse damper or related components may be used, if necessary.

7 Procedure

7.1 Preparation of solutions of molecular weight standards

The molecular weight standards used to prepare the calibration curve should preferably be selected so as to cover the range of molecular weights of the polymer being analysed and so that there are at least two standards in each molecular weight decade. Solutions may be prepared which contain more than one narrow molecular weight distribution standard, but only when the standards are perfectly separated from each other on the chromatogram.

A solution of mixed molecular weight standards containing standards of high molecular weight (>1 000 000) might give peaks which are retarded and/or deformed because of the high viscosity of the solution. In such cases, the solutions of high molecular weight standards shall be prepared separately.

If molecular weight standards having the same chemical structure as the polymer being analysed are not available, the calibration curve may be prepared using standards consisting of a different type of polymer, and a universal calibration curve prepared for this different type of polymer (according to ISO 16014-2).

If gentle shaking and/or stirring or heating is required to accelerate dissolution, the time shall be as short as possible to avoid any rupture of the polymer chains.

Filtration of the solutions is recommended to protect the column from clogging. In such cases, membrane filters or sintered-metal filters with a pore size between 0,2 µm and 1 µm shall be used. If solid material is observed on the filter, indicating incomplete dissolution, repeat the dissolution process. If a membrane filter is used, the membrane and backing shall be inert to the solvent being used.

In general, use solutions within 48 h of preparation. However, longer storage times are allowed if the solution is kept in a cool, dark place to prevent polymer degradation and solvent evaporation.

Recommended concentrations for solutions of molecular weight standards are as follows:

$M_p < 5 \times 10^4$ 0,4 mg/cm^3

$5 \times 10^4 \leq M_p < 10^6$ 0,2 mg/cm^3

$10^6 \leq M_p$ 0,1 mg/cm^3

If a viscometric detector is used, higher molecular weight standard concentrations are required in the lower molecular weight region. Sample elution times should preferably be measured at lower concentrations, however.

7.2 Preparation of sample solutions

Prepare sample solutions by weighing accurately 10 mg to 250 mg of sample into a 10 cm^3 to 50 cm^3 flask. Add eluent and, if necessary, an internal standard and dissolve, in the same way as for the molecular weight standard solutions (see 7.1), within 30 min. In general, however, samples with molecular weights > 10^5 have a slow rate of dissolution, and it might be necessary to continue beyond 30 min to ensure complete dissolution. Filtration of solutions is recommended to avoid clogging of the column.

Sample solution concentrations shall not exceed the following limits:

$M_w < 1 \times 10^5$ 5,0 mg/cm^3

$1 \times 10^5 \leq M_w < 10^6$ 2,0 mg/cm^3

$10^6 \leq M_w$ 0,5 mg/cm^3

7.3 Preparation of solutions for column performance evaluation

Prepare a 10 mg/cm^3 solution of a suitable low molecular weight compound to determine the theoretical plate number, asymmetry factor and resolution factor of the set of columns.

7.4 Setting up the apparatus

Place the amount of eluent required for the SEC measurements in the reservoir and degas. Flush all the SEC components, except for the columns, with fresh eluent. Connect the set of columns into the system. Inspect all connections for leakage under the test conditions.

Keep the system at the test conditions (e.g. flow rate, detection sensitivity and temperature) until a flat baseline is obtained, with no drift or noise.

7.5 Operating parameters

7.5.1 Flow rate

A flow rate of approximately 1 cm^3/min is recommended for a series of two or three high-performance columns of approximately 30 cm in length and 8 mm in diameter. For high molecular weight and/or shear-sensitive polymers, the flow rate should preferably be reduced so that no chain rupture will occur during elution of the polymer.

7.5.2 Injection masses and injection volumes

The mass of polymer sample and volume of sample solution injected depend on the column dimensions and the detector sensitivity. The optimum sample injection mass has been found experimentally to be approximately 0,005 mg/cm^3 of empty column (without packing). The maximum mass injected shall be less than 0,05 mg/cm^3 of empty column.

The optimum sample solution injection volume has been found experimentally to be approximately 0,005 cm^3/cm^3 of empty column. The maximum injection volume shall be < 0,01 cm^3/cm^3 of empty column.

The injection volumes of the solutions of molecular weight standards shall be the same as for the sample solution.

The injection volume of the solution of low molecular weight compound shall be < 0,005 cm^3/cm^3 of empty column.

7.5.3 Column temperature

The column temperature should preferably be selected based on the solubility of the sample, the viscosity and boiling point of the eluent, and the ambient temperature.

7.5.4 Detector sensitivity

The signal intensity depends on the amount of sample injected and on the specific refractive index increment d_n/d_c for an RI detector and the absorbance per unit mass concentration for a UV detector. The detector sensitivity should preferably be set to obtain a strong peak signal for the sample, to ensure accurate data handling.

The linear relationship between solute concentration and peak height shall be maintained by keeping the sensitivity at the same setting. Recommended sensitivities are approximately $1 \cdot 10^{-5}$ to $9 \cdot 10^{-4}$ RI units at full scale for a refractive index detector and approximately 0,1 to 0,9 absorbance units at full scale for a UV detector.

7.6 Number of determinations

Carry out at least two sample runs to demonstrate the repeatability of the positions and shapes of the peaks in the chromatogram. If the deviation in the flow rate between the two runs is > 0,3 %, the deviation in M_n > 3 % and the deviation in M_w > 2 %, the measurements shall be repeated.

8 Data acquisition and processing

According to ISO 16014-1.

9 Expression of results

According to ISO 16014-1.

10 Precision

10.1 General

The precision of this method has been determined in several interlaboratory tests carried out between 1995 and 1998 in accordance with ISO 5725-1 and ISO 5725-2.

10.2 Experimental conditions

The test samples, which included three types of polystyrene, one type of poly(methyl methacrylate) and one type of polyacrylonitrile, and the calibration standards of narrow molecular weight distribution were distributed to the participating laboratories by the organizer. The details of the interlaboratory tests are as follows:

1st round-robin (1995)

Polymer samples (three samples)	Polystyrene PS-1 Polystyrene PS-2 Polystyrene PS-3
Calibration	14 polystyrene standards
Column packing material	Polystyrene gel
Eluent	Tetrahydrofuran
Column temperature	40 °C
Number of laboratories	13

2nd round-robin (1996)

Polymer sample	Poly(methyl methacrylate) (PMMA)
Calibration	14 polystyrene standards
Column packing material	Polystyrene gel
Eluent	Tetrahydrofuran
Column temperature	40 °C
Number of laboratories	14

3rd round-robin (1997–1998)

Polymer sample	Polyacrylonitrile (PAN)
Calibration	a) 14 polystyrene standards b) 14 poly(ethylene glycol) and poly(ethylene oxide) standards