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

Part 3:

Low-temperature method

iTeh STANDARD PREVIEW
(standards.iteh.ai)

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

<https://standards.iteh.ai/catalog/standards/sist/b467b4fe-0529-4aee-a5e0-237743e5b42d/iso-16014-3-2003>
Partie 3: Mesurage aux basses températures



PDF disclaimer

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

Adobe is a trademark of Adobe Systems Incorporated.

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

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[ISO 16014-3:2003](https://standards.iteh.ai/catalog/standards/sist/b467b4fe-0529-4aec-a5e0-237743e5b42d/iso-16014-3-2003)

<https://standards.iteh.ai/catalog/standards/sist/b467b4fe-0529-4aec-a5e0-237743e5b42d/iso-16014-3-2003>

© ISO 2003

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

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

Published in Switzerland

Contents

Page

Foreword.....	iv
1 Scope.....	1
2 Normative references	1
3 Terms and definitions	1
4 Principle	1
5 Reagents	2
6 Apparatus.....	2
7 Procedure.....	4
8 Data acquisition and processing.....	6
9 Expression of results.....	6
10 Precision	6
11 Test report.....	7
Annex A (informative) Further information on applicability of method	9
Annex B (informative) Further information on reagents	10

[ISO 16014-3:2003](https://standards.iteh.ai/catalog/standards/sist/b467b4fe-0529-4aec-a5e0-237743e5b42d/iso-16014-3-2003)

<https://standards.iteh.ai/catalog/standards/sist/b467b4fe-0529-4aec-a5e0-237743e5b42d/iso-16014-3-2003>

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 16014-3 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

ISO 16014 consists of the following parts, under the general title *Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography*:

- Part 1: General principles
- Part 2: Universal calibration method
- Part 3: Low-temperature method
- Part 4: High-temperature method

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[ISO 16014-3:2003](https://standards.iteh.ai/catalog/standards/sist/b467b4fe-0529-4aec-a5e0-237743e5b42d/iso-16014-3-2003)

<https://standards.iteh.ai/catalog/standards/sist/b467b4fe-0529-4aec-a5e0-237743e5b42d/iso-16014-3-2003>

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

Part 3: Low-temperature method

1 Scope

This part of ISO 16014 specifies a method for determining the average molecular mass and the molecular mass distribution of polymers by size-exclusion chromatography (SEC) using an organic eluent at a temperature lower than 60 °C. The average molecular mass and the molecular mass distribution are calculated from a calibration curve constructed using polymer standards. Therefore, this test method is classified as a relative method (see ISO 16014-1:2003, Annex A).

iTeh STANDARD PREVIEW

2 Normative references (standards.iteh.ai)

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 472, *Plastics — Vocabulary*

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 5725-2:1994, *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 16014-1:2003, *Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography — Part 1: General principles*

3 Terms and definitions

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

4 Principle

See ISO 16014-1:2003, Clause 4.

5 Reagents

5.1 Eluent

For a general discussion of eluents, see ISO 16014-1:2003, Subclause 5.1.

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

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

5.2 Reagent for column evaluation

See ISO 16014-1:2003, Subclause 5.2.

There are several low molecular mass 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.

5.3 Molecular mass standards

See ISO 16014-1:2003, Subclause 5.3.

Some examples of commercially available molecular mass standards are given in Annex B.

5.4 Reagent for flow rate marker (internal standard)

See ISO 16014-1:2003, Subclause 5.4.

It is often very difficult to find a low molecular mass 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, are used as additives in *N,N*-dimethylformamide to avoid aggregation of polyacrylonitrile, and sodium trifluoroacetate is added to hexafluoroisopropanol for SEC measurements on polyamide.

6 Apparatus

6.1 General

A schematic diagram of an SEC system is shown in ISO 16014-1:2003, Figure 1.

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

6.2 Eluent reservoir

See ISO 16014-1:2003, Subclause 6.2.

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

6.3 Pumping system

See ISO 16014-1:2003, Subclause 6.3.

In order to maintain the flow rate accurate to within $\pm 0,3$ %, 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

See ISO 16014-1:2003, Subclause 6.4.

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

6.5 Columns

See ISO 16014-1:2003, Subclause 6.5.

Organic or inorganic packing materials can be used, and there are no limitations on particle size or shape.

The set of columns used shall have a total theoretical plate number greater than 15 000 and the resolution factor R shall be greater than 1,5 close to the polymer peak. The asymmetry factor shall be within the range $1,00 \pm 0,15$. The set of columns used shall cover the whole range of molecular masses 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 16014-1:2003, Subclause 6.5.

The column temperature-control equipment shall be capable of keeping the columns within $\pm 0,5$ °C of the temperature set to ensure adequate reproducibility of the results.

6.6 Detector

See ISO 16014-1:2003, Subclause 6.6.

The detector temperature-control equipment shall be capable of keeping the detector within ± 1 °C 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

See ISO 16014-1:2003, Subclause 6.7.

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

6.8 Temperature control

One of the important factors in SEC is that all components need to be kept at a constant temperature. Therefore, an accurate temperature-control system is essential to meet the performance requirements for SEC.

6.9 Recorder and plotter

See ISO 16014-1:2003, Subclause 6.9.

6.10 Data-processing system

See ISO 16014-1:2003, Subclause 6.10.

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 mass standards

The molecular mass standards used to construct the calibration curve shall be selected so as to cover the range of molecular masses of the polymer being analysed and so that there are at least two standards in each molecular mass decade. Solutions may be prepared which contain more than one narrow molecular mass distribution standard, but only when the standards are perfectly separated from each other on the chromatogram. Solutions of standards of molecular mass greater than 1 000 000 shall be prepared separately.

If molecular mass standards having the same chemical structure as the polymer being analysed are not available, the calibration curve may be constructed using standards consisting of a different type of polymer.

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 mass 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 mass standard concentrations are required in the lower molecular mass region. Sample elution times shall 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 cm³ to 50 cm³ flask. Add eluent and, if necessary, an internal standard and dissolve, in the same way as for the molecular mass standard solutions, within 30 min. In general, samples with molecular masses greater than 10⁵ have a slow rate of dissolution, however, and it may 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:

$$M_w < 1 \times 10^5 \quad 5,0 \text{ mg/cm}^3$$

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

$$10^6 \leq M_w \quad 0,5 \text{ mg/cm}^3$$

7.3 Preparation of solutions for column performance evaluation

Prepare a 10 mg/cm³ solution of a suitable low molecular mass 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 cm³/min is recommended for a series of two or three high-performance columns of around 30 cm in length and 8 mm in diameter. For high molecular mass and/or shear-sensitive polymers, the flow rate shall 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 about 0,01 mg per cubic centimetre of empty column (without packing). The maximum mass injected shall be less than 0,1 mg per cubic centimetre of empty column.

The optimum sample solution injection volume has been found experimentally to be about 0,005 cm³ per cubic centimetre of empty column. The maximum injection volume shall be less than 0,01 cm³ per cubic centimetre of empty column.

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

The injection volume of the solution of low molecular mass compound shall be less than 0,005 cm³ per cubic centimetre of empty column.

7.5.3 Column temperature

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