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

**Part 4:  
High-temperature method**

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

*Partie 4: Mesurage aux températures élevées*



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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 16014-4 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

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

## Part 4: High-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 temperatures between 60 °C and 180 °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).

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

ISO 16014-2, *Plastics — Determination of average molecular mass and molecular mass 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 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 above 60 °C, see Annex B.

## 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 diphenylmethane when 1,2-dichlorobenzene is used as eluent or ethylbenzene when 1,2,4-trichlorobenzene 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.

An example of a compound suitable for use as a flow rate marker is 2,6-di-*tert*-butyl-4-methylphenol when 1,2-dichlorobenzene or 1,2,4-trichlorobenzene is used as eluent.

## 5.5 Additives

Phenol-type antioxidants such as 2,6-di-*tert*-butyl-4-methylphenol should preferably be added to avoid degradation of the polymer sample. For further examples of antioxidants, see Annex B.

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## 6 Apparatus

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### 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 between 60 °C and 180 °C. However, the temperature of components connected upstream of the injector, such as the eluent reservoir, the pumping system and the tubing, are not kept at the same temperature as the columns.

The use of a commercially available SEC system is recommended because of the difficulty involved in assembling a system operating at such high temperatures.

### 6.2 Eluent reservoir

See ISO 16014-1:2003, Subclause 6.2.

As mentioned in 6.1 above, it is not necessary to keep the eluent 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 constant 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 ensure that the polymer solution remains clear, without any precipitation, the injector temperature-control equipment shall be capable of keeping the injector at the same temperature, to within  $\pm 1\text{ }^{\circ}\text{C}$ , as the columns. As manual injection is impossible at such temperatures, an automatic injection system shall be used.

### 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 except that, when analysing high molecular mass and/or shear-sensitive polymers, the particle size shall be large enough for no rupture of the polymer chain to occur during elution of the polymers.

The set of columns used shall have a theoretical plate number greater than 12 000/m 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  $\pm 0,5\text{ }^{\circ}\text{C}$  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  $\pm 0,5\text{ }^{\circ}\text{C}$  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 and high enough 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 unit

One of the important factors in SEC is that all components need to be kept at a constant temperature and, with the method described in this part of ISO 16014, some of them need to be kept at a high 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, a pressure monitor, a pulse damper or other related components can 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 and a universal calibration curve constructed for this different type of polymer (see 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 mass standards are as follows:

$M_p < 5 \times 10^4$	0,4 mg/cm <sup>3</sup>
$5 \times 10^4 \leq M_p < 10^6$	0,2 mg/cm <sup>3</sup>
$10^6 \leq M_p$	0,1 mg/cm <sup>3</sup>

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 cm<sup>3</sup> to 50 cm<sup>3</sup> 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 10<sup>5</sup> 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.



If solid material is observed on the filter, indicating incomplete dissolution, repeat the dissolution process. Following preparation, transfer sample solutions to vials and store at room temperature.

The sample must be heated sufficiently to dissolve it completely. Excessive or long heating shall be avoided, however, as this may lead to thermal or oxidative degradation. The optimum dissolution temperature and time shall be determined experimentally. For example, except for high molecular mass or high-density samples, polyethylene can be dissolved in 1,2-dichlorobenzene by heating at 140 °C for 1,5 h. Polyethylene with a molecular mass greater than  $10^6$  is more difficult to dissolve, requiring higher temperatures and longer times.

Before injection, sample solutions may be kept at a temperature between room temperature and the dissolution temperature. The temperature of the injector shall be sufficiently high, and the dwell time of the solution in the injector sufficiently long, to ensure that the sample remains dissolved and no precipitate forms, but the temperature shall not be so high, or the dwell time so long, that degradation of the sample occurs.

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/cm<sup>3</sup> 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 cm<sup>3</sup>/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 maximum injection volume shall be less than 0,01 cm<sup>3</sup> 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 recommended injection volume of the solution of low molecular mass compound is the same as that of the sample solution.