INTERNATIONAL STANDARD

**ISO
16014-2**

First edition
2003-04-15

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

Part 2:
Universal calibration method

iTeh STANDARD PREVIEW

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

Partie 2: Méthode d'étalonnage universelle

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 16014-2:2003
https://standards.iteh.ai/catalog/standards/sist/42bbac80-ea2e-429e-ae8a-
ed5f2e6dfe8d/iso-16014-2-2003

Contents

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 16014-2:2003
https://standards.iteh.ai/catalog/standards/sist/42bbac80-ea2e-429e-ae8a-
ed5f2e6dfe8d/iso-16014-2-2003

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 16014-2 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*

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

Part 2:
Universal calibration method

1   Scope

This part of ISO 16014 specifies a method for determining the average molecular mass and the molecular mass distribution of polymers using size-exclusion chromatography (SEC). The average molecular mass and the molecular mass distribution are calculated using a universal calibration curve instead of the conventional calibration curve. The concept of the universal calibration method is based on a relationship by which the retention time in SEC depends on the size of the polymer molecule (the hydrodynamic volume) or on the product of the intrinsic viscosity $[\eta]$ and the molecular mass M. Many polymers classified as random-coil polymers (regardless of their chemical structure, degree of branching, composition or tacticity) have been experimentally confirmed as following this relationship. The universal calibration curve is constructed by plotting the logarithm of $[\eta]M$ versus the elution time t or elution volume V using polymer standards such as polystyrene with narrow molecular mass distributions. The molecular mass M_i of an unknown polymer sample can then be calculated from the value of $[\eta]M$ at each retention time using the universal calibration curve and $[\eta]$ or K and a in the Mark-Houwink-Sakurada equation ($[\eta] = KM^a \rightarrow [\eta]M = KM^{a+1}$), where K is a constant and a is an exponent depending on the experimental conditions. Therefore this test method is classified as a relative method as described in ISO 16014-1, but the average molecular masses and molecular mass distributions calculated by the method are equal to, or nearly equal to, the absolute values.

A list of documents related to this part of ISO 16014 is given in the Bibliography.

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 472:1999, *Plastics — Vocabulary*

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

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*

ISO 16014-4:2003, *Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography — Part 4: High-temperature 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. The definitions of the various types of average molecular mass are reproduced here for convenience.

Four types of average molecular mass are defined by the following equations, where N_i is the number of molecules of species i of molecular mass M_i and a is the exponent of the Mark-Houwink-Sakurada equation.

NOTE   Although the definitions are the same as in ISO 16014-1, the values of M_i in the equations are calculated using a universal calibration curve as described in Clause 4.

3.1
number-average molecular mass
M_n

$$M_n = \frac{\sum\limits_{i=1}^{\infty}(N_i \times M_i)}{\sum\limits_{i=1}^{\infty}N_i} \tag{1}$$

3.2
mass-average molecular mass
M_w

$$M_w = \frac{\sum\limits_{i=1}^{\infty}(N_i \times M_i^2)}{\sum\limits_{i=1}^{\infty}(N_i \times M_i)} \tag{2}$$

3.3
z-average molecular mass
M_z

$$M_z = \frac{\sum\limits_{i=1}^{\infty}(N_i \times M_i^3)}{\sum\limits_{i=1}^{\infty}(N_i \times M_i^2)} \tag{3}$$

3.4
viscosity-average molecular mass
M_v

$$M_v = \left[\frac{\sum\limits_{i=1}^{\infty}(N_i \times M_i^{a+1})}{\sum\limits_{i=1}^{\infty}(N_i \times M_i)}\right]^{1/a} \tag{4}$$

4 Principle of universal calibration method

In this part of ISO 16014, the experimental SEC procedures are the same as in ISO 16014-1, ISO 16014-3 and ISO 16014-4, but the molecular mass M_i at each elution time is calculated based on the universal calibration method. According to the theory, this method provides values for the average molecular mass and the molecular mass distribution that are equal to, or nearly equal to, the absolute values.

According to theory, the size of a polymer in solution, the hydrodynamic volume V_h, is proportional to the product of the intrinsic viscosity $[\eta]$ and the molecular mass M as given by Equation (5):

$$[\eta] \propto V_h / M \; \rightarrow \; [\eta]M \propto V_h \tag{5}$$

In SEC, many random-coil polymers, regardless of their chemical structure, degree of branching, composition, or tacticity, follow the same relationship, in which the retention time is proportional to the product of $[\eta]$ and M under the specific experimental conditions, including the column system, solvent and temperature. The relationship between the logarithm of $[\eta]M$ and the elution time is called the "universal calibration curve", and the SEC technique for the determination of average molecular masses and molecular mass distributions using this calibration curve is called the "universal calibration method".

As a first step, the universal calibration curve, retention time t versus the logarithm of $[\eta]M$, is constructed using polymer standards with narrow molecular mass distributions and the Mark-Houwink-Sakurada equation:

$$[\eta]_s = K_s M_s^{a_s} \tag{6}$$

where the subscript "s" denotes "polymer standard".

Direct measurement of $[\eta]_s$ is also possible.

In the next step, the molecular mass M_i at each retention time t_i is calculated using the universal calibration curve and the Mark-Houwink-Sakurada equation for the polymer sample:

$$[\eta] = KM^a \tag{7}$$

$$[\eta]_{s,i} M_{s,i} = [\eta]_i M_i = KM_i^{a+1} \tag{8}$$

Again, direct measurement of $[\eta]$ is possible.

Lastly, the average molecular mass and the molecular mass distribution are calculated from the molecular mass M_i and peak height H_i at each retention time, using the equations given in 9.2, 9.3, and 9.4.

For additional information on the universal calibration curve and the use of a conventional calibration curve based on universal calibration theory, see 9.1 and A.2.1.

For additional information on the intrinsic viscosity $[\eta]$, see A.2.2.

The values of K and a in the Mark-Houwink-Sakurada equation for several polymers are given in Annex B.

5 Reagents

See ISO 16014-1:2003, Clause 5.

6 Apparatus

See ISO 16014-1:2003, Clause 6.

7 Procedure

See ISO 16014-1:2003, Clause 7.

8 Data acquisition and processing

See ISO 16014-1:2003, Clause 8.

9 Expression of results

9.1 Construction of universal calibration curve

The universal calibration curve is constructed by plotting the logarithm of $[\eta]_{s}M_{s}$ against the elution time for a number of polymer standards. The value of $[\eta]_{s}$ for each polymer standard may be calculated using the Mark-Houwink-Sakurada equation or measured directly under the specific elution conditions.

For information on the molecular masses of commercially available polymer standards, see ISO 16014-1:2003, Annex B.

For the expression of the universal calibration curve, polynomials containing terms up to the third power of the elution time t are widely used. The addition of subsequent higher-power terms may improve the fit of the calibration curve.

$$\lg([\eta]_{s}M_{s}) = A_0 + A_1 t \tag{9}$$

$$\lg([\eta]_{s}M_{s}) = A_0 + A_1 t + A_2 t^{2} + A_3 t^{3} \tag{10}$$

where

$[\eta]_{s}$ is the intrinsic viscosity of the polymer standard eluting at time t;

M_{s} is the molecular mass of the polymer standard eluting at time t;

A_0, A_1, A_2, A_3 are coefficients.

An example of a universal calibration curve is shown in Figure 1. Elution time can be replaced by elution volume V_{e} ($V_{e} = t \times Q$ where Q is the flow rate).

For the use of a conventional calibration curve based on universal calibration theory, see A.2.1 and Figure 2.

9.2 Calculation of average molecular mass

Calculate the molecular mass M_i of the polymer sample at elution time t_i using $[\eta]_{s,i}M_{s,i}$ at elution time t_i and K and a in the Mark-Houwink-Sakurada equation or $[\eta]$ determined for the polymer sample from Equation (13).

$$[\eta] = KM^{a} \quad \text{(polymer sample)} \tag{11}$$

$$[\eta]_{s,i}M_{s,i} = [\eta]_{i}M_{i} = KM_{i}^{a+1} \tag{12}$$

$$M_i = ([\eta]_{s,i}M_{s,i}/K)^{1/(a+1)} = ([\eta]_{s,i}M_{s,i})/[\eta]_{i} \tag{13}$$

Calculate the signal intensity H_i at each elution time t_i using the corrected test sample chromatogram for which the baseline and the calculation range have been determined as specified in ISO 16014-1:2003, Subclauses 8.3.1 and 8.3.2.
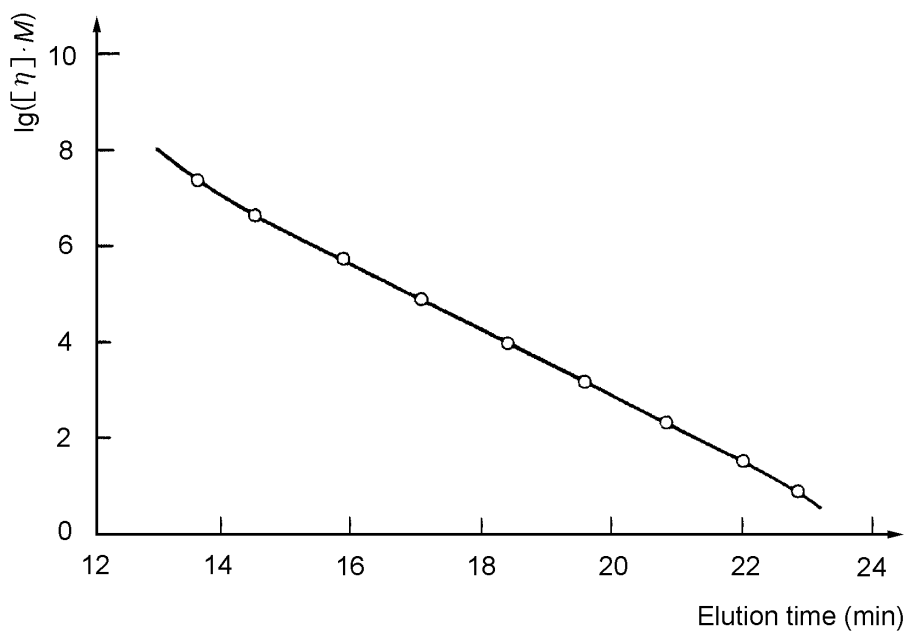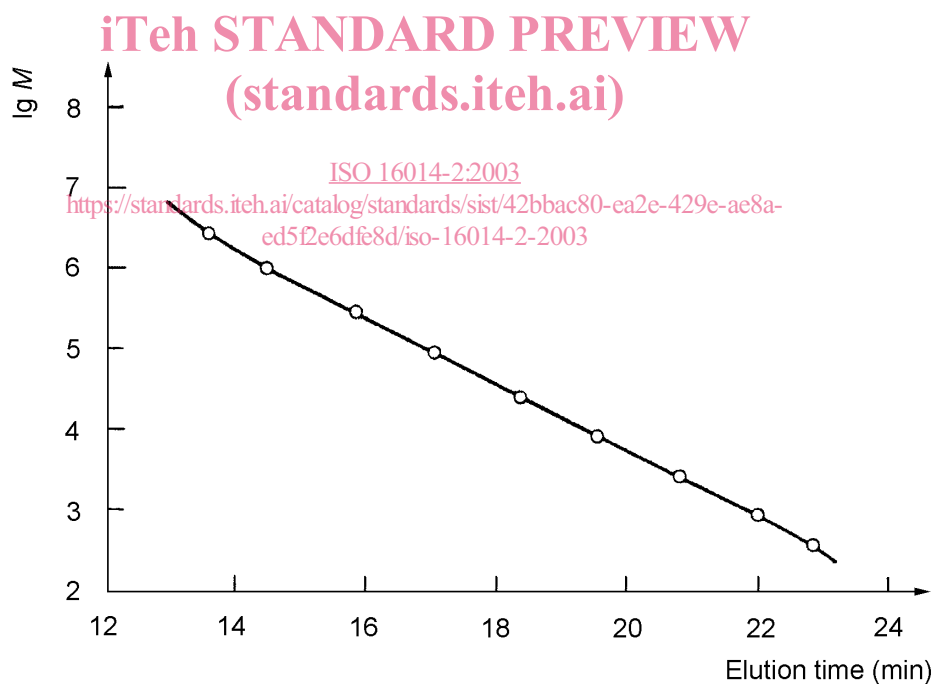
Figure 1 — Universal calibration curve

Figure 2 — Conventional calibration curve for a polymer sample
[molecular mass M of polymer calculated from Equation (27) or (29)]