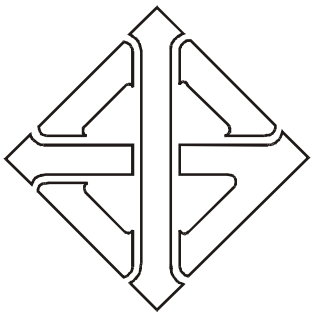

มาตรฐานผลิตภัณฑ์อุตสาหกรรม

THAI INDUSTRIAL STANDARD

มอก. 2250 เล่ม 1– 2548

ISO 16014 –1 : 2003

พลาสติก – การทดสอบหาค่าเฉลี่ยของมวลโมเลกุล และการกระจายมวลโมเลกุลของพอลิเมอร์ โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล

เล่ม 1 : หลักการทั่วไป

PLASTICS – DETERMINATION OF AVERAGE MOLECULAR MASS AND MOLECULAR MASS DISTRIBUTION OF POLYMERS USING SIZE– EXCLUSION CHROMATOGRAPHY–

PART 1 : GENERAL PRINCIPLES

สำนักงานมาตรฐานผลิตภัณฑ์อุตสาหกรรม

กระทรวงอุตสาหกรรม

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มาตรฐานผลิตภัณฑ์อุตสาหกรรม

พลาสติก – การทดสอบหาค่าเฉลี่ยของมวลโมเลกุล และการกระจายมวลโมเลกุลของพอลิเมอร์ โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล

เล่ม 1 : หลักการทั่วไป

มอก. 2250 เล่ม 1 — 2548

สำนักงานมาตรฐานผลิตภัณฑ์อุตสาหกรรม
กระทรวงอุตสาหกรรม ถนนพระรามที่ 6 กรุงเทพฯ 10400
โทรศัพท์ 0 2202 3300

ประกาศในราชกิจจานุเบกษา ฉบับประกาศและงานทั่วไป เล่ม 122 ตอนที่ 121ง
วันที่ 22 ธันวาคม พุทธศักราช 2548

หลักการทั่วไป เป็นเล่มหนึ่งในชุดมาตรฐานพลาสติก–การทดสอบหาค่าเฉลี่ยของมวลโมเลกุลและการกระจายมวลโมเลกุลของพอลิเมอร์ โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล จึงกำหนดมาตรฐานผลิตภัณฑ์อุตสาหกรรมพลาสติก – การทดสอบหาค่าเฉลี่ยของมวลโมเลกุล และการกระจายมวลโมเลกุลของพอลิเมอร์ โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล เล่ม 1 : หลักการทั่วไป ขึ้น

มาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้กำหนดขึ้นโดยรับ ISO 16014-1 : 2003 Plastics–Determination of average molecular mass and molecular mass distribution of polymers using size–exclusion chromatography–part 1 : General principle มาใช้ในระดับเหมือนกันทุกประการ (identical) โดยใช้ ISO ฉบับภาษาอังกฤษเป็นหลัก

มาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้กำหนดขึ้นเพื่อให้ทันกับความต้องการของผู้ใช้และจักได้แปลเป็นภาษาไทยในโอกาสอันสมควร หากมีข้อสงสัยโปรดติดต่อสอบถามที่สำนักงานมาตรฐานผลิตภัณฑ์อุตสาหกรรม

คณะกรรมการมาตรฐานผลิตภัณฑ์อุตสาหกรรมได้พิจารณามาตรฐานนี้แล้ว เห็นสมควรเสนอรัฐมนตรีประกาศตามมาตรา 15 แห่งพระราชบัญญัติมาตรฐานผลิตภัณฑ์อุตสาหกรรม พ.ศ. 2511

ประกาศกระทรวงอุตสาหกรรม

ฉบับที่ 3419 (พ.ศ. 2548)

ออกตามความในพระราชบัญญัติมาตรฐานผลิตภัณฑ์อุตสาหกรรม

พ.ศ. 2511

เรื่อง กำหนดมาตรฐานผลิตภัณฑ์อุตสาหกรรม

พลาสติก–การทดสอบหาค่าเฉลี่ยของมวลโมเลกุลและการกระจายมวลโมเลกุล

ของพอลิเมอร์โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล

เล่ม 1 : หลักการทั่วไป

อาศัยอำนาจตามความในมาตรา 15 แห่งพระราชบัญญัติมาตรฐานผลิตภัณฑ์อุตสาหกรรม พ.ศ. 2511 รัฐมนตรีว่าการกระทรวงอุตสาหกรรมออกประกาศกำหนดมาตรฐานผลิตภัณฑ์อุตสาหกรรม พลาสติก–การทดสอบหาค่าเฉลี่ยของมวลโมเลกุลและการกระจายมวลโมเลกุลของพอลิเมอร์ โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล เล่ม 1 : หลักการทั่วไป มาตรฐานเลขที่ มอก. 2250 เล่ม 1–2548 ไว้ ดังมีรายการละเอียดต่อท้ายประกาศนี้

ประกาศ ณ วันที่ 31 สิงหาคม พ.ศ. 2548

นายสุริยะ จึงรุ่งเรืองกิจ

รัฐมนตรีว่าการกระทรวงอุตสาหกรรม

มาตรฐานผลิตภัณฑ์อุตสาหกรรม
พลาสติก – การทดสอบหาค่าเฉลี่ยของมวลโมเลกุล และการกระจายมวลโมเลกุลของพอลิเมอร์ โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล
เล่ม 1 : หลักการทั่วไป

บทนำ

มาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้กำหนดขึ้นโดยรับ ISO 16014-1 : 2003 Plastics-Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography- part 1 : General principle มาใช้ในระดับเหมือนกันทุกประการ (identical) โดยใช้ ISO ฉบับภาษาอังกฤษเป็นหลัก

ขอบข่าย

มาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้เป็นข้อแนะนำหลักการทั่วไปเกี่ยวกับวิธีทดสอบหาค่าเฉลี่ยของมวลโมเลกุลและการกระจายมวลโมเลกุลของพอลิเมอร์ โดยใช้โครมาโทกราฟีคัดขนาดโมเลกุล มวลโมเลกุลและการกระจายมวลโมเลกุลคำนวณจากเส้นโค้งสอบเทียบสากลซึ่งสร้างจากพอลิเมอร์มาตรฐาน วิธีตามมาตรฐานนี้จำแนกเป็นวิธีสัมพัทธ์ (ดูที่ clause A.1ใน Annex A)

เอกสารอ้างอิง

ISO 472, Plastics – Vocabulary

บทนิยาม

ความหมายของคำที่ใช้ในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ใน ISO 16014-1 : 2003 ข้อ 3

หลักการ

หลักการในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ในข้อ ISO 16014-1 : 2003 ข้อ 4

สารเคมี

สารเคมีที่ใช้ในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ในข้อ ISO 16014-1 : 2003 ข้อ 5

เครื่องมือ

เครื่องมือที่ใช้ในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ใน ISO 16014-1 : 2003 ข้อ 6

การทดสอบ

การทดสอบที่ใช้ในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ใน ISO 16014-1 : 2003 ข้อ 7

การหาข้อมูล

การหาข้อมูลในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ในข้อ ISO 16014-1 : 2003 ข้อ 8

การแสดงผลลัพธ์

การแสดงผลลัพธ์ในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ใน ISO 16014-1 : 2003 ข้อ 9

ความเที่ยง

ความเที่ยงในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ในข้อ ISO 16014-1 : 2003 ข้อ 10

การรายงานผลทดสอบ

การรายงานผลทดสอบในมาตรฐานผลิตภัณฑ์อุตสาหกรรมนี้ให้เป็นไปตามที่ระบุไว้ใน ISO 16014-1 : 2003 ข้อ 11

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

Part 1:
General principles

1 Scope

This part of ISO 16014 specifies a general 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 from a calibration curve constructed using polymer standards. Therefore this method is classified as a relative method (see Clause A.1 in Annex A).

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, *Plastics — Vocabulary*

3 Terms and definitions

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

3.1
size-exclusion chromatography
SEC
a liquid chromatographic technique in which the separation is based on the hydrodynamic volume of molecules eluting in a column packed with porous non-adsorbing material having pore dimensions that are similar in size to the molecules being separated

NOTE The term gel permeation chromatography (GPC) should only be used where the porous non-adsorbing packing material is a gel; however, the term size-exclusion chromatography (SEC) is preferred.

3.2
molecular mass
M
sum of the masses of the atoms making up a molecule

NOTE Molecular weight is also used for molecular mass.

3.3 Average molecular mass

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.

3.3.1
number-average molecular mass
M_n

$$M_n = \frac{\sum_{i=1}^{\infty}(N_i \times M_i)}{\sum_{i=1}^{\infty} N_i} \quad (1)$$

3.3.2
mass-average molecular mass
M_w

$$M_w = \frac{\sum_{i=1}^{\infty}(N_i \times M_i^{\,2})}{\sum_{i=1}^{\infty}(N_i \times M_i)} \quad (2)$$

3.3.3
z-average molecular mass
M_z

$$M_z = \frac{\sum_{i=1}^{\infty}(N_i \times M_i^{\,3})}{\sum_{i=1}^{\infty}(N_i \times M_i^{\,2})} \quad (3)$$

3.3.4
viscosity-average molecular mass
M_v

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

4 Principle

A polymer sample is dissolved in a suitable solvent to make a dilute solution. This solution is injected into the mobile phase and onto the SEC column, which is packed with non-adsorbing material made up of small particles having pores of similar or varying size. As the polymer sample passes through the column, the polymer molecules are separated from each other according to the difference in their molecular masses, or more precisely, the difference in their molecular sizes (i.e. their hydrodynamic volume). In SEC, the larger-size molecules cannot permeate into the pores, and thus elute faster, while smaller molecules can permeate into the pores and elute more slowly. The polymer concentration in the eluate is continuously monitored by a concentration-sensitive detector to give an SEC chromatogram.

The molecular mass at any elution time on the SEC chromatogram is determined from a calibration curve which is constructed using reference polymer standards with a narrow molecular mass distribution. The average molecular mass and the molecular mass distribution is calculated by using the molecular mass and concentration data corresponding to each elution time.

5 Reagents

5.1 Eluent

The required purity of the eluent used for SEC varies with the application, but in general the solvent should be free of particulate matter and substances that react with the polymer or interfere with detection of the polymer. Additives such as antioxidants and salts can be used to prevent the degradation of the eluent, the aggregation of polymer molecules, the adsorption of the polymer on the packing material and for other purposes. A mixed eluent may also be used for SEC measurements to modify the solubility and the refractive index, or to reduce the cost of the mobile phase.

5.2 Reagent for column evaluation

A low molecular mass compound is used for the determination of the theoretical plate number, asymmetry factor and resolution factor of the column.

5.3 Molecular mass standards

This test method is not an absolute method but a relative one and requires a calibration curve for the calculation of the average molecular mass and the molecular mass distribution from the SEC chromatogram. The calibration curve is constructed by the use of standards of known molecular mass and narrow molecular mass distribution, the value of M_w and/or M_n of the standard being determined by an absolute method, such as light scattering, membrane osmometry, vapour pressure osmometry, ultracentrifugation, end-group analysis. The polydispersity M_w/M_n is calculated by dividing the absolute value of M_w by the absolute value of M_n. The polydispersity of the polymer standards shall lie within the following ranges:

$M_p < 2 \times 10^3$ $\quad M_w/M_n < 1{,}20$

$2 \times 10^3 \leqslant M_p < 10^6$ $\quad M_w/M_n < 1{,}10$

$10^6 \leqslant M_p$ $\quad M_w/M_n < 1{,}20$

where

M_w is the mass-average molecular mass;

M_n is the number-average molecular mass;

M_p is the molecular mass at peak maximum, calculated using Equation (5) if the molecular mass distribution of the polymer sample shows a logarithmic normal distribution (in the case of very efficient separation giving many peaks, use the highest peak):

$$M_p = (M_n \times M_w)^{1/2} \quad (5)$$

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

5.4 Reagent for flow rate marker (internal standard)

A low molecular mass compound is used to monitor the accuracy of the elution time, i.e. to evaluate whether or not the data are within the specification.

5.5 Additives

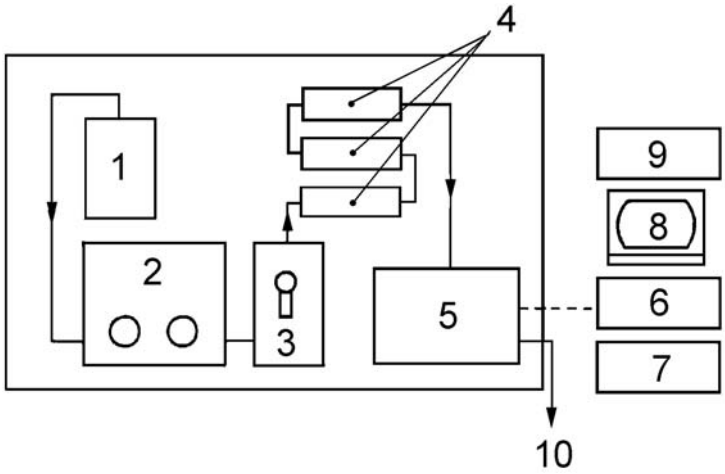
Additives to the eluents may be used to improve SEC performance and prevent sample degradation and the like.

6 Apparatus

6.1 General

A schematic diagram of an SEC system is shown in Figure 1. The essential components are an eluent reservoir, a pumping system, an injector, column(s), a detector, tubing, a recorder, a temperature-control system, and a data-processing system. Any component that meets the performance requirements specified for this method may be used.

Both commercially available SEC systems and SEC systems assembled in the laboratory may be used for this method, provided they meet the required levels of performance.



Key

1	eluent reservoir	6	computer
2	pump	7	recorder
3	injector	8	display
4	columns	9	plotter
5	detector	10	to waste

Figure 1 — Schematic diagram of SEC system

6.2 Eluent reservoir

The eluent reservoir shall have sufficient capacity to hold the amount of eluent required for column calibration and successive measurements. Dissolved air in the eluent shall be removed before use by placing the solvent in a suitable container designed to reduce the pressure and placing this container in an ultrasonic bath, or by using a vacuum degasser between the reservoir and the pumping system. Particles in the eluent may be removed by membrane filtration. It is desirable in addition to bubble an inert gas through the eluent in the reservoir and blanket the surface of the eluent with the gas, and to shield the reservoir from light.

6.3 Pumping system

A constant, pulseless flow of eluent through the column is desirable. It is recommended that the flow rate be adjusted to about 1 cm^3/min for a column of around 8 mm inner diameter. The SEC system shall have an overall flow-rate precision of within ± 0,3 %. Lower flow rates are recommended for high molecular mass and/or shear-sensitive polymers and viscous eluents. To keep the flow rate constant, temperature control providing stability to at least ± 1 °C is needed for the pumping system.

The flow rate shall be monitored frequently by the use of an internal standard, or by a direct method such as volume or mass measurements, and corrected in the event of significant deviations. In this test method, knowledge of the value of the flow rate is not required because the method is a relative one in which the result is calculated from a calibration curve constructed from measurements on molecular mass standards.

6.4 Injector

In addition to having an eluent bypass capability, the injector shall be able to hold the sample solution and inject the sample solution into the columns with minimum band broadening and minimum pressure change.

To maintain the required precise flow rate, temperature control equipment, or a precise air conditioner, is needed for the injection system.

6.5 Columns

6.5.1 General

The function of the columns is to separate the sample molecules according to differences in their molecular size (mass). Columns usually consist of a stainless-steel tube with end fittings, filters and a porous packing material. There is no limitation on the column length or diameter or on the packing-material particle size. The performance of the columns shall be such that they are suitable for use with an SEC system as specified in this part of ISO 16014.

6.5.2 Determination of theoretical plate number

Use a low molecular mass compound, such as ethylbenzene, to obtain a peak (see Figure 2) and calculate the theoretical plate number N of the set of columns from equation (6) or (7):

$$N = 5{,}55 \times (t_e / W_{1/2})^2 \quad (6)$$

$$N = 16 \times (t_e / W)^2 \quad (7)$$

where

t_e is the elution time to the peak maximum;

$W_{1/2}$ is the peak width at half height;

W is the difference between the intersection of the two tangents of the peak and the baseline.

6.5.3 Determination of resolution factor

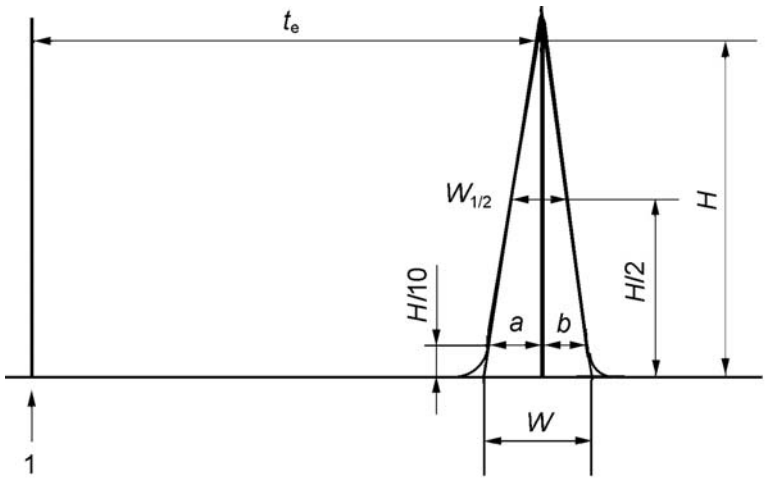
The resolution factor R of the set of columns can be calculated from Equation (8) by the use of the calibration curve (see 9.1 and Figure 5) and a molecular mass standard (see 5.3 and Figure 3) with a narrow molecular mass distribution that elutes at a point close to the apex of the sample peak:

$$R = 1/(D \times W_{STD}) \quad (8)$$

where

D is the slope of the calibration curve at the point corresponding to the apex of the sample peak;

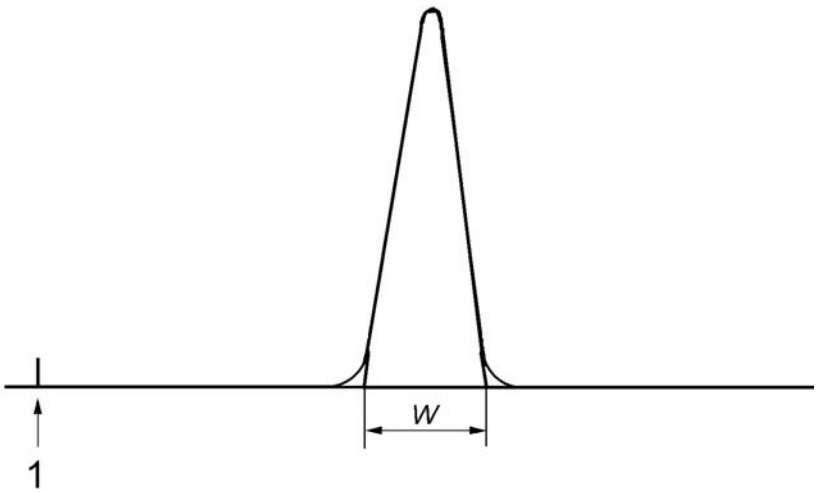
W_{STD} is the peak width at the baseline of the molecular mass standard.



Key

1 injection

Figure 2 — SEC chromatogram of a low molecular mass compound



Key

1 injection

Figure 3 — SEC chromatogram of a narrow molecular mass distribution standard

6.5.4 Determination of asymmetry factor

The asymmetry factor A_S of the set of columns can be calculated from Equation (9), using data obtained from the peak produced by a low molecular mass compound such as ethylbenzene (see Figure 2):

$$A_S = (a + b)/(2 \times a) \quad (9)$$

where

A_S is the asymmetry factor;

a is the width of the leading half of the peak at 10 % peak height;

b is the width of the trailing half of the peak at 10 % peak height.

6.6 Detector

The detector is used to continuously monitor the concentration of the polymer in the eluent coming off the columns. There are several types of commercially available concentration-sensitive detector, such as the refractive index detector, ultraviolet/visible detector, infrared detector, evaporative light-scattering detector and fluorescence detector.

The volume of the flow cell shall be sufficiently small so as to maintain the narrow molecular mass distribution of the molecules separated by columns and to maintain the overall theoretical plate number and the resolution factor of the set of columns determined in 6.5.2 and 6.5.3.

The sensitivity of the detector shall be such that it can detect a difference in refractive index of 10^{-8} or a difference in UV absorbance of 10^{-4}. The recommended signal/noise ratio is greater than 200. A lower ratio is admissible in the case of extremely broad molecular mass distributions or low-concentration measurements on extremely high molecular mass samples. In such cases, however, the signal/noise ratio should be greater than 20. Signal drift shall be less than 10 % of the peak height per hour, at the appropiate maximum sensitivity level.

6.7 Tubing

The inner diameter and length (including swage length) of the tubing used to connect the sample injector to the first column, the columns to each other and the last column to the detector shall be as small and short as possible to prevent the separated fractions from remixing and to ensure that the performance requirements specified in 6.5.1 are met. The inner diameter of the tubing used from the injector to the detector shall be 0,05 cm or less. Care shall be taken, however, not to use tubing of too small an inner diameter so as to avoid rupture of the polymer chain and turbulence in the detector cell.

6.8 Temperature control

The temperature of the columns, pumping system, injection system and tubing shall be kept constant within a narrow range as described in the appropriate subclause for each component. In the case of the detector, the temperature shall be controlled to meet the performance requirements for SEC.

6.9 Recorder and plotter

The SEC curve shall be recorded or plotted clearly enough to assess whether parameters such as peak height, baseline level, signal drift and peak separation are suitable for data processing.

6.10 Data-processing system

A data-processing system capable of data acquisition, generation of calibration curves, calculation of the required molecular masses and molecular mass distributions, and presentation of appropriate data and/or graphics is required. This system shall be capable of collecting, analysing and reporting data in the manner specified in this International Standard.

It is desirable that the SEC chromatogram is generated in real time, but the data may also be stored for subsequent processing off line.

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

The procedure includes setting up the SEC apparatus and the data acquisition and processing system, preparing solutions of molecular mass standards, test solutions, and solutions for determining column performance, filtering the solutions and injecting them.

Details of the exact procedure to be used are given in the relevant part of this International Standard.

8 Data acquisition and processing

8.1 Data acquisition

Data acquisition shall be carried out from the onset of sample elution to the end of the sample peak or when the signal drops back to the baseline. The number of data points or readings shall be at least 50 per decade of molecular mass. Care shall be taken to use enough data points so as to provide accurate estimates of the peak area and the elution time at the peak apex, as well as an accurate molecular mass distribution curve and average molecular mass derived from the curve.

8.2 Evaluation of data and correction of chromatograms

SEC chromatograms shall be monitored to determine whether the error in the elution time of the internal standard or that in the volume or mass of eluent is less than ± 0,3 % or between ± 0,3 % and ± 1,0 % or more than ± 1,0 % of the calibration value for each run.

No correction is required if the flow rate error is less than ± 0,3 %. If the error is between ± 0,3 % and ± 1,0 %, the flow rate shall be corrected. If the error is over the permitted limit (± 1,0 %), the data shall be rejected and the measurement repeated. Peak-broadening corrections are not required.

NOTE The elution-time and elution volume/mass monitoring methods are described in Clause A.2 of Annex A.

8.3 Data processing

8.3.1 Baseline determination

If the detector signal drops to the baseline before the system peak as shown in Figure 4 a), the baseline shall be assumed to be a straight line from t_a to t_b.

If the detector signal does not recover to the baseline before the system peak as shown in Figure 4 b), the baseline shall be assumed to be a straight line connecting the point t_a just before sample elution and the point t_c just after the system peak.

8.3.2 Determination of calculation range

If the sample does not contain components of molecular mass less than 1 000, as shown in Figure 4 a), the range between points t_a and t_b on the baseline shall be used for the calculation.

If the sample contains components of molecular mass less than 1 000, and these low molecular mass components make up less than 30 % of the total polymer peak area, as shown in Figure 4 b), one of the following two procedures shall be used for the calculation:

a) Calculate the area under the curve from point t_a to a point $t_{1\,000}$ corresponding to a molecular mass of 1 000.

b) Calculate the area from point t_a to t_d which covers the entire polymer, including oligomers and monomer but excluding additives. Point t_d is determined by producing a chromatogram of the eluent alone.

If the sample contains components of molecular mass less than 1 000, and these low molecular mass components make up more than 30 % of the total polymer peak area, as shown in Figure 4 c), the method described in this part of ISO 16014 cannot be used.

NOTE The detector response may vary at low molecular mass, and the presence of a significant proportion of low molecular mass material makes any calculation unreliable.

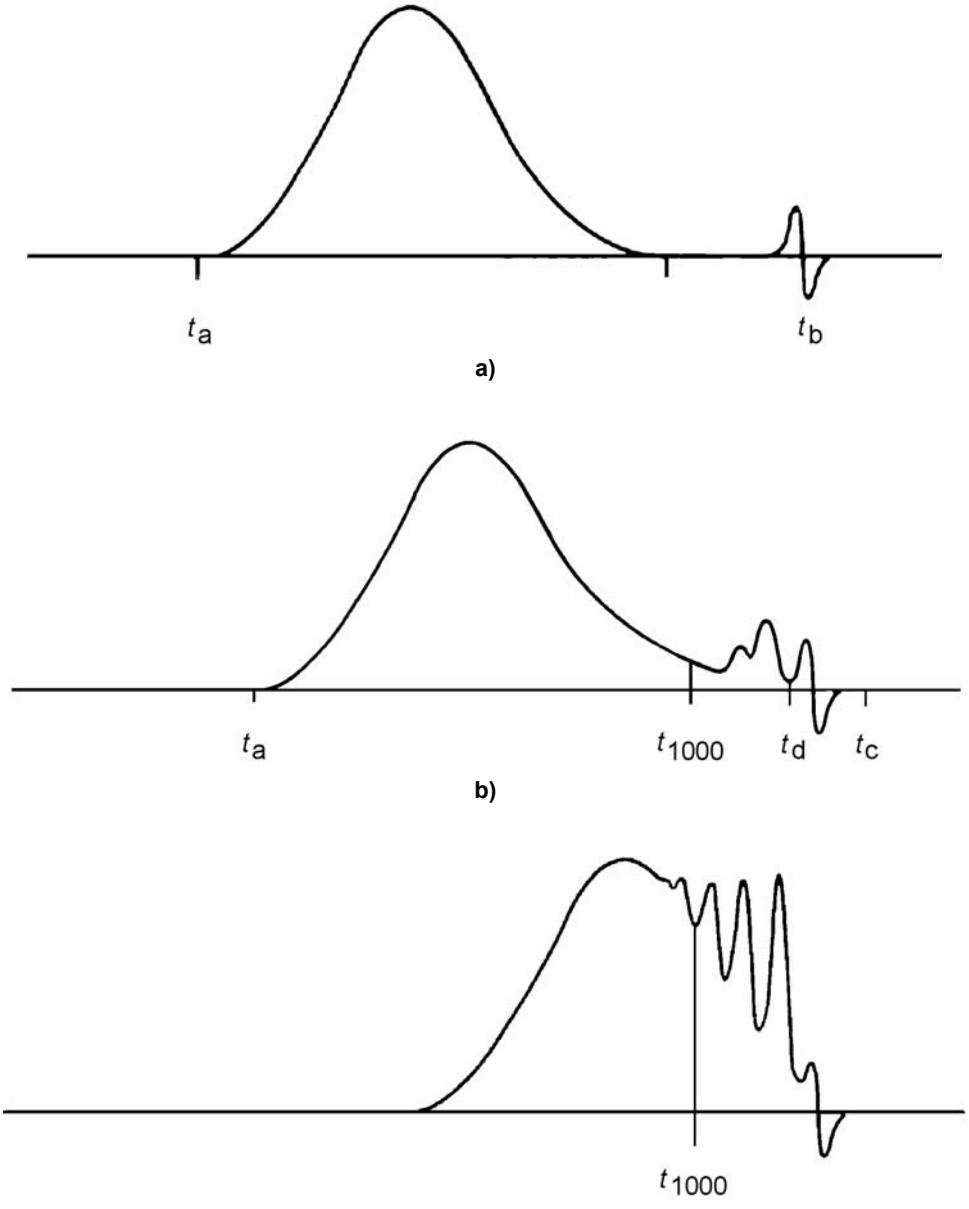


Figure 4 — Typical SEC curves

9 Expression of results

9.1 Calibration curve

The calibration curve is constructed by plotting elution times versus $\lg M_p$ as shown in Figure 5. The values of M_p are obtained in one of the following ways:

a) from the data sheets for the standard materials;

b) by calculation, using Equation (5), from the values of M_w and M_n given in the data sheets for the standard materials;

c) by calculation, using Equation (5), from the values of M_w or M_n and M_w/M_n given in the data sheets for the standard materials.

Polynomials containing terms up to the third power of the elution time t are widely used to describe calibration curves. The addition of higher powers may improve the fit of the curve to the data:

$$\lg M = A_0 + A_1 t \tag{10}$$

$$\lg M = A_0 + A_1 t + A_2 t^2 + A_3 t^3 \tag{11}$$

where

M is the molecular mass;

A_1, A_2, A_3 are coefficients;

t is the elution time.

Other methods, or a combination of methods, can be used to improve the fit.

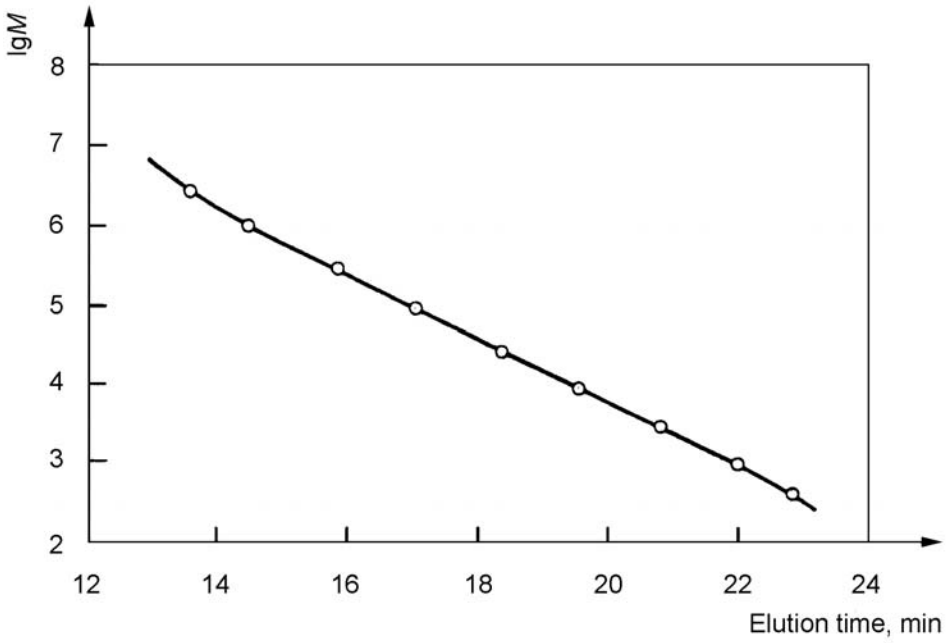


Figure 5 — Calibration curve

9.2 Calculation of average molecular mass

Calculate the molecular mass M_i and signal intensity H_i at each elution time using the calibration curve (see 9.1) and the SEC chromatogram of the polymer sample for which the baseline and the calculation range have been determined (see 8.3.1 and 8.3.2).

The average molecular mass and the polydispersity can be calculated from the values of M_i and H_i using equations (12) to (16), where n denotes the nth set of data:

$$M_{\mathrm{n}} = \frac{\sum_{i=1}^{n} H_i}{\sum_{i=1}^{n} (H_i / M_i)} \tag{12}$$

$$M_{\mathrm{w}} = \frac{\sum_{i=1}^{n} (H_i \times M_i)}{\sum_{i=1}^{n} H_i} \tag{13}$$

$$M_{\mathrm{z}} = \frac{\sum_{i=1}^{n} (H_i \times M_i{}^2)}{\sum_{i=1}^{n} (H_i \times M_i)} \tag{14}$$

$$M_{\mathrm{v}} = \left[\frac{\sum_{i=1}^{n} (H_i \times M_i{}^a)}{\sum_{i=1}^{n} H_i} \right]^{1/a} \tag{15}$$

Polydispersity = $M_{\mathrm{w}}/M_{\mathrm{n}}$ (16)

9.3 Differential molecular mass distribution curve

The differential molecular mass distribution curve is prepared by plotting $\mathrm{d}W_i/\mathrm{d}(\lg M_i)$ against $\lg M_i$ as shown in Figure 6. W_i is calculated from the following equations:

$$w_i = \frac{H_i}{\sum_{i=1}^{n} H_i} \tag{17}$$

$$W_i = w_i \times \frac{1}{I} \tag{18}$$

$$\frac{\mathrm{d}W_i}{\mathrm{d}(\lg M_i)} = -W_i \times \frac{\mathrm{d}t_i}{\mathrm{d}(\lg M_i)} \tag{19}$$

where I is the data acquisition interval, in minutes.

If the sample contains components of molecular mass less than 1 000, and these low molecular mass components make up less than 30 % of the sample, draw a vertical line at the point corresponding to $M_{1\,000}$.

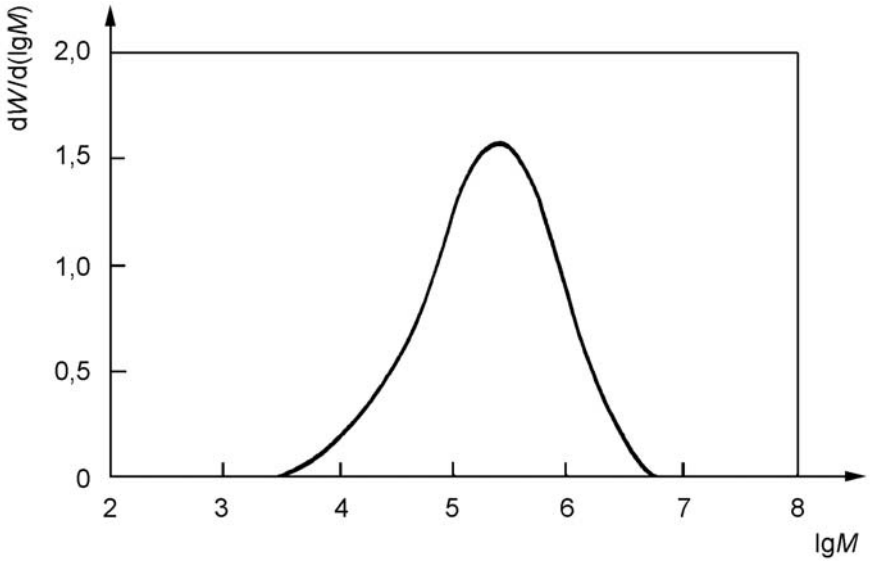


Figure 6 — Differential molecular mass distribution curve

9.4 Cumulative molecular mass distribution curve

The cumulative molecular mass distribution curve is prepared by plotting the mass fraction C_i versus lgM_i as shown in Figure 7, C_i being calculated from the following equation:

$$C_i = \sum_{j=1}^{i} (w_{j-1} + w_j)/2 \qquad (20)$$

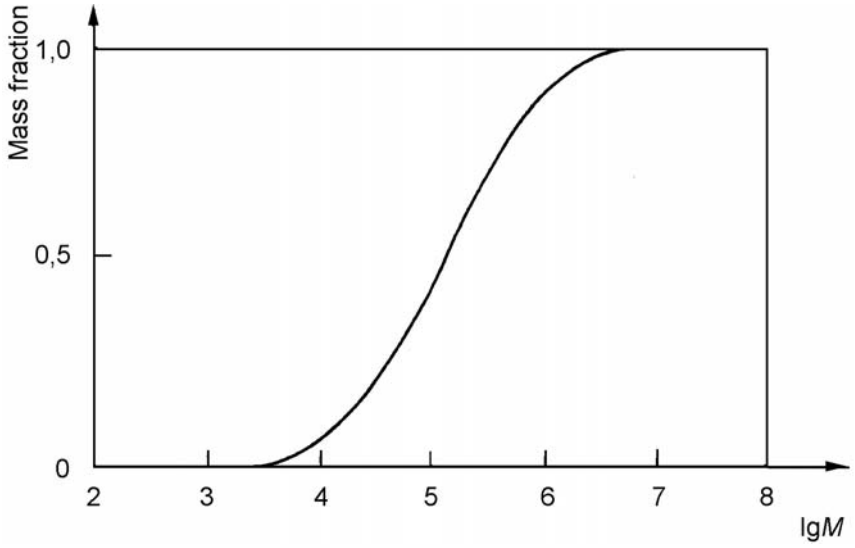


Figure 7 — Cumulative molecular mass distribution curve

10 Precision

The precision of this test method as obtained by interlaboratory testing is described in the other parts of ISO 16014.

11 Test report

11.1 General

The test report shall include the following information, as applicable:

a) a reference to relevant part of this International Standard and to any referring standards;

b) all details necessary for complete identification of the polymer analysed;

c) the date of the analysis and that of the calibration.

11.2 Apparatus and measurement parameters

Include the following information:

a) the type of SEC apparatus, the model and the manufacturer;

b) the type of column packing, its particle size and the name of the manufacturer;

c) the column temperature;

d) the theoretical plate number and resolution factor of the set of columns used, and the low molecular mass standard and narrow molecular mass distribution standard used to determine them;

e) the eluent, details of any additives, and the value of each flow rate used;

f) the type of detector, the model and the manufacturer;

g) the concentration of the polymer sample solution;

h) the type of data-processing system, the model and the manufacturer;

i) the version number of the software used.

11.3 Calibration of the system

11.3.1 Information on the molecular mass standards

Include the following information, in tabular form, for each calibration point:

a) the name of the standard;

b) the manufacturer of the standard;

c) the characteristic values of the standard, including the molecular masses M_n, M_w, M_z and the polydispersity, as stated by the manufacturer;

d) the injection volume and concentration;

e) the elution time or elution mass/volume.

11.3.2 Calibration curve

Include the following:

a) details of the method used to fit the curve to the data, including the equation;

b) a copy of the curve itself.

11.4 Results

Include the following:

a) the characteristic points on the chromatogram (t_a, t_b, t_c, t_d, $t_{1\,000}$, as applicable);

b) the calculated average molecular masses M_n, M_w, M_z, M_v and polydispersity M_w/M_n, indicating the calculation range used (see 8.3.2);

c) the SEC curve and, in tabular or graphical form, the differential molecular mass distribution and cumulative molecular mass distribution.

Annex A
(informative)

Supplementary information

A.1 Applicability of method (see Clause 1)

The method described in this part of ISO 16014 assumes the sample is a linear homopolymer. However, because it is a relative method, it is also applicable to non-linear homopolymers, such as branched, star-shaped, comb-like, stereo-regular and stereo-irregular polymers, and to other types of polymer, such as random, block, graft and heterophasic copolymers. The method is applicable to molecular masses ranging from that of the monomer to 3 000 000, but is not applicable to samples that contain more than 30 % of components having a molecular mass lower than 1 000.

The method cannot be used with water as eluent, i.e. for water-soluble polymers, or at column temperatures higher than 180 °C, or with polymers that exhibit appreciable secondary effects such as adsorption of the polymer molecules on the column packing material or repulsion between the polymer molecules and the packing material.

A.2 Evaluation of data (see 8.2)

SEC chromatograms are examined to assess whether the error in the elution time or in the elution volume or mass is within ± 0,3 %, between ± 0,3 % and ± 1,0 %, or more than ± 1,0 % of the calibrated elution time or elution volume or mass. If the error is more than 1,0 %, the run is repeated. The following three methods are recommended for monitoring and correcting any flow rate error.

a) Internal-standard method

Sulfur, for example, can be added to a solution of the sample in tetrahydrofuran and the solution injected onto the columns. Sulfur elutes from the columns after the system peaks or the ghost peaks. Ethylbenzene in *N*,*N*-dimethylformamide using polystyrene gel columns is another example.

b) Delayed-injection method

A low molecular mass compound, such as ethylbenzene, can be injected onto the columns using tetrahydrofuran at a given time after sample injection, so as to elute from the columns just after the system peaks or the ghost peaks.

c) Direct measurement

The volume or the mass of the elute can be measured directly with a graduated cylinder or balance.

Annex B
(informative)

Narrow molecular mass distribution standards

Examples of commercially available polymer standards with a narrow molecular mass distribution are given in Table B.1.

Table B.1 — Commercially available narrow molecular mass distribution standards

Polymer	Molecular mass range
Polystyrene	$5{,}0 \times 10^2$ to $2{,}0 \times 10^7$
Poly(1-methylstyrene)	$1{,}0 \times 10^3$ to $1{,}0 \times 10^6$
Poly(methyl methacrylate)	$2{,}0 \times 10^3$ to $1{,}5 \times 10^6$
Poly(ethylene glycol)	$2{,}0 \times 10^2$ to $2{,}2 \times 10^4$
Poly(ethylene oxide)	$2{,}0 \times 10^3$ to $1{,}0 \times 10^6$
Polyisoprene	$1{,}0 \times 10^3$ to $3{,}0 \times 10^6$
Poly(tetrahydrofuran)	$1{,}0 \times 10^3$ to $5{,}0 \times 10^5$
Polybutadiene	$1{,}0 \times 10^3$ to $1{,}0 \times 10^6$
Polyethylene	$1{,}0 \times 10^3$ to $1{,}2 \times 10^6$
Polypropylene	$4{,}8 \times 10^4$ to $3{,}5 \times 10^5$