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Plastics — Determination of average molecular mass and mixture ratio of poly(ethylene glycol) and its derivatives by MALDI-TOF-MS

Plastiques — Détermination de la masse moléculaire moyenne et du rapport de mélange du poly(éthylène glycol) et de ses dérivés par MALDI-TOF-MS

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Foreword

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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).

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For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

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

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Introduction

For quality control and research of polymeric materials, it is important to know the composition of polymer mixtures with different terminal groups. In contrast to traditional methods such as liquid chromatography, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) is a rapid and effective method to characterize polymer mixtures because of its high mass resolution. It can also be applied to quantitation of mixtures of different polymers. Interlaboratory comparisons of quantitative MALDI-TOF-MS performed for mixtures of PEG and its derivatives can ensure standardized conditions of measurement. Standardization of quantitative MALDI-TOF-MS may promote increasing applications of this analytical technique.

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Plastics — Determination of average molecular mass and mixture ratio of poly(ethylene glycol) and its derivatives by MALDI-TOF-MS

1 Scope

This document specifies a general method for determining the average molecular mass and mixture ratio of poly(ethylene glycol) (PEG) and its derivatives with different end groups by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). It is applicable to PEG and its derivatives with molecular masses from 500 g mol^{-1} to 20 000 g mol^{-1}. The composition is calculated by means of a calibration curve constructed using standard polymer mixtures, where the peak area ratio is plotted versus the mass ratio. This document can be applied to other polymers with monomeric unit similar to PEG.

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 10927:2011, *Plastics — Determination of the molecular mass and molecular mass distribution of polymer species by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472, ISO 10927 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

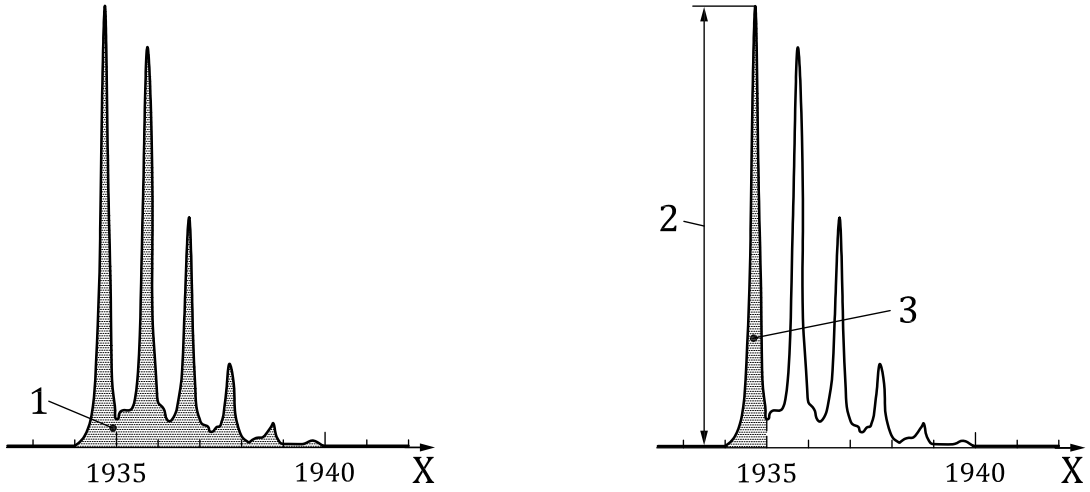
— ISO Online browsing platform: available at http://www.iso.org/obp

3.1
matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
MALDI-TOF-MS
technique in which the separation is based on different flight times in a field free flight tube depending on the mass of formed polymer ions after ionization by a laser, desorption and acceleration by high voltage

3.2
peak area
A
sum of peak areas, A_{ij}, where A_{ij} is an area under the curve of the mass, M_{ij}, associated with the *j*-th species of polymer *i*

Note 1 to entry: As Figure 1 a) shows, integration for peak area, A_{ij}, should be performed over all isotopes related to the *j*-th species. If the software is not able to integrate all isotopic peaks, the peak area of the most abundant isotopic peak can be used instead [see Figure 1 b)]. For data handling, see ISO 10927:2011, 6.7.

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a) Peak area of isotopic peaks

b) Peak area or peak height of the most abundant isotopic peak

Key

1 "peak area", A_{ij}

2 "peak height" of the most abundant isotopic peak of $[PEG(n = 43)+Na]^+$

3 "peak area" of the most abundant isotopic peak of $[PEG(n = 43)+Na]^+$

X mass/charge

Figure 1 — Definitions of peak area and peak height

3.3
molecular mass
M
sum of the masses of atoms

Note 1 to entry: The molecular mass of the j-th species, M_j, is also calculated as the average mass of isotopes.

Note 2 to entry: The terms "molecular weight" and "molar mass" are also used instead of "molecular mass".

3.4
number-average molecular mass
M_n
molecular mass defined as:

$$M_n \equiv \frac{\sum_j N_j M_j}{\sum_j N_j}$$

Note 1 to entry: N_j is the number of molecules of species j of molecular mass M_j.

3.5
weight-average molecular mass
M_w
molecular mass defined as:

$$M_w \equiv \frac{\sum_j \left(N_j \times M_j{}^2\right)}{\sum_j \left(N_j \times M_j\right)}$$

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3.6
z-average molecular mass
M_z
molecular mass defined as:

$$M_z \equiv \frac{\sum_j \left(N_j \times M_j{}^3 \right)}{\sum_j \left(N_j \times M_j{}^2 \right)}$$

4 Principles

The MALDI process involves the ablation and the ionization of an analyte dispersed in a small organic molecule matrix. The matrix shall be able to absorb the laser energy. A metal salt may be added to cationize the analyte. A polymer is co-crystallized or co-mixed with the matrix molecule and deposited on the target. A short duration UV laser pulse is used to ablate the matrix and the analyte. The laser energy is transferred to the matrix molecules, causing them to vaporize. Analyte and matrix molecules leave the target surface in a plume. Due to the very short desorption time, polymer molecules do not degrade. The polymer in the ablation plume gains a cation and is accelerated by a high voltage, drifts down the field free flight tube and is detected at the end of the flight tube. The time-of-flight of the species depends on their molecular masses, and needs to be calibrated with standards of known molecular masses. Biopolymers such as proteins are often used to this end.

Ideally, the product of the ratio between the total sum of peak areas and that between number-average molecular mass is proportional to the mass ratio, i.e.

$$\left(\frac{A_1}{A_0} \right) \cdot \left(\frac{M_{n,1}}{M_{n,0}} \right) = k_{10} \frac{W_1}{W_0} \tag{1}$$

where A_i, W_i and $M_{n,i}$ are sum of peak areas in MALDI-TOF-MS spectra, mass and number-average molecular mass of polymer i (i = 0 or 1), respectively. The proportionality constant, k_{10}, is experimental and generally depends on the combination of polymers with different chemical structures. Ideally, if no mass discrimination is observed, k_{10} = 1.

5 Reagents

5.1 Matrices.

α-Cyano-4-hydroxycinnamic acid (CHCA) and 1,8,9-trihydroxyanthracene (dithranol) are the recommended matrices for this method. Other matrices can be used after examining sufficient ionizing ability and solubility in solvents used. The procedure described in Clause 7 can be applied to examination of the ability and solubility. All materials should be at least 97 % pure. They should be stored in a freezer or refrigerator. They should be warmed up to room temperature right before use. Regulated reagents shall be handled in accordance with regulations.

5.2 Salts.

Lithium, sodium and potassium salts, e.g. iodides or trifluoroacetates, are recommended.

5.3 Solvents.

Methanol and tetrahydrofuran (THF) are recommended since they are good solvents of PEG and its derivatives. They also applied to polar polymers. The solvents should be at least 97 % pure. If the solvents are regulated, they should be treated safely.

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