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Plastics — Determination of caprolactam and its cyclic and linear oligomers by HPLC

Plastiques — Détermination du caprolactame et de ses oligomères cycliques et linéaires par CLHP

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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*.

This third edition cancels and replaces the second edition (ISO 15033:2007), which has been technically revised to add method B.

Introduction

The method A specified in this document can be used for HPLC determination of the cyclic oligomers of caprolactam (n = 1) up to and including the hexamer (n = 6), using UV detection. If desired, after post-column reaction of the primary amine with 1,2-phthalic dicarboxaldehyde, online determination of the linear oligomers up to and including the hexamer can also be carried out.

The determination is not quantitative for oligomers higher than the hexamer (n > 6). In the determination of cyclic oligomers the sensitivity for the tetramer and higher oligomers is constant, which means that calibration should take place up to and including the tetramer (n = 4).

The linear oligomers are determined by the fluorescence of the iso-indole group, which is a product of the reaction between the primary amino group, 1,2-phthalic dicarboxaldehyde and 3 mercaptopropionic acid. The calibration with the linear oligomers should be carried out up to and including the hexamer (n = 6).

The method B included in this document is intended for the determination of caprolactam and its cyclic dimer only, following the same principle and using the same equipment as method A, but significantly faster.

Plastics — Determination of caprolactam and its cyclic and linear oligomers by HPLC

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

1 Scope

This document describes a high-performance liquid chromatography (HPLC) method for determining the concentrations of cyclic oligomers of caprolactam, from 0,01 % by mass upwards, and linear oligomers of caprolactam, from 5 mg/kg upwards, both up to and including the hexamer of caprolactam (n = 6), in samples of polyamide 6, caprolactam and mixtures of rearrangement products in water.

A second, significantly faster, HPLC method is included for determination of caprolactam and its cyclic dimer, based on the same principle and using the same equipment as the first method.

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*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 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 https://www.iso.org/obp

4 Principle

A test sample is dissolved in, or diluted with, formic acid and the oligomers separated in the presence of a low-pH mobile phase using a column filled with reversed-phase packing material. The cyclic oligomers are detected by UV absorption at 200 nm. If desired, the linear oligomers can be detected by fluorescence after post-column reaction of the primary amino group with 1,2-phthalic dicarboxaldehyde and 3-mercaptopropionic acid. The concentrations are calculated by comparison of the measured values with those of calibration solutions.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

5.1 Water, ultrapure or double-distilled.

5.2 Phosphoric acid, 85 % by mass.

5.3 Phosphoric acid, 1 mol/l. Introduce 68 ml of phosphoric acid (5.2) into a 1 l volumetric flask, make up to the mark with water (5.1) and mix well.

5.4 Acetonitrile.

5.5 Formic acid, concentrated.

5.6 Caprolactam.

5.7 Cyclic dimer of caprolactam, isolated by HPLC (see Note).

5.8 Cyclic trimer of caprolactam, isolated by HPLC (see Note).

5.9 Mixture of cyclic oligomers of caprolactam, isolated by HPLC (see Note).

5.10 ε-Aminocaproic acid.

5.11 Linear dimer of ε-aminocaproic acid.

5.12 Linear trimer of ε-aminocaproic acid.

5.13 Linear tetramer of ε-aminocaproic acid.

5.14 Linear pentamer of ε-aminocaproic acid.

5.15 Linear hexamer of ε-aminocaproic acid.

5.16 Helium.

5.17 Eluent.

— **Eluent A**

Add 10 ml of acetonitrile (5.4) and 10 ml of phosphoric acid (5.3) to 900 ml of water (5.1). Raise the pH of the solution to 2,6 using sodium hydroxide flakes (5.19). Make up to 1 l and saturate with helium (5.16).

— **Eluent B**

Add 10 ml of phosphoric acid (5.3) to 900 ml of water (5.1). Raise the pH of the solution to 2,6 using sodium hydroxide flakes (5.19). Make up to 1 land saturate with helium (5.16).

NOTE The analysis time for determination of caprolactam and its dimer using eluent B is significantly shorter than using eluent A.

5.18 Sodium tetraborate decahydrate.

5.19 Sodium hydroxide flakes.

5.20 1,2-Phthalic dicarboxaldehyde.

5.21 Methanol, 96 % by volume.

5.22 3-Mercaptopropionic acid.

5.23 Post-column derivatization reagent.

Dissolve 76 g of sodium tetraborate decahydrate (5.18) and 6 g of sodium hydroxide (5.19) in 2 l of water (5.1). Dissolve 1,6 g of 1,2-phthalic dicarboxaldehyde (5.20) in 40 ml of methanol (5.21) and add this solution to the sodium tetraborate decahydrate reagent. Add 1,5 ml of 3-mercaptopropionic acid (5.22) and mix well.

The stability of the post-column derivatization reagent is limited. Do not keep for longer than 3 days.

NOTE The cyclic dimer, the cyclic trimer and the mixture of cyclic oligomers of caprolactam can be isolated from a methanol extract of polyamide 6 (PA6) by preparative HPLC, using the HPLC methods described here. The purity of the dimer and the possible presence of other oligomers can be checked using the methods described in this document.

6 Apparatus

6.1 HPLC equipment, having the following specifications:

— **Eluent pump**, including mixer, damper and manometric module, giving an eluent flow rate of 0,51 ml/min and a pressure drop of approximately 10 MPa.

— **Injector**, e.g. an auto-sampler capable of 1 µl to 250 µl injections, equipped to carry out a variable injector programme (see Annex A). The injector shall be capable of accommodating at least three components in the sample loop, i.e. the injector programme shall be capable of controlling the "sandwich" injection of up to three components into the sample loop plus a solvent injection in one HPLC run.

— **Column**:

  — stainless steel;
  — inside diameter: 3 mm;
  — length: 250 mm;
  — temperature: 40 °C;
  — packing: reversed-phase C18 silica or equivalent;
  — particle size: 0,005 mm.

  The resolution of the column shall be such that baseline separation of the components of interest is obtained.

  The lifetime of the reversed-phase C18 column is very strongly influenced by the C18-silica bonding of the packing material. Therefore, columns equipped with a packing material containing monofunctional silanes with diisobutyl side-chain groups are preferred. These side groups sterically protect the key silanes from hydrolytic attack at low pH, making the stationary phase stable at such pH (pH 1).

— **UV detector**: wavelength 200 nm and 220 nm.

Additionally for determination of the linear oligomers:

— **Reagent pump**, including manometric module and pulse damper, giving a reagent flow rate of 0,25 ml/min and a reagent pressure drop of approximately 2 MPa.

— **Reaction coil**:

  — stainless steel or PEEK;
  — length: 3 m;

- inside diameter: 0,25 mm;
- temperature: 25 °C.

— **Fluorescence detector**:

- excitation: 330 nm;
- emission: 420 nm.

A schematic diagram of an HPLC apparatus is given in Annex C.

6.2 Microbalance, accurate to 0,1 mg.

6.3 Ultrasonic vibration bath.

6.4 Volumetric flask, capacity 25 ml.

7 Test sample

For polyamide 6 and caprolactam, the maximum test sample size shall be 0,5 g. For mixtures of rearrangement products in water, a maximum test sample size of 1,25 g shall be used. The stability of the dissolved samples is limited, since caprolactam is hydrolysed to ε-aminocapronic acid. Do not keep for longer than 6 days.

8 Procedure

8.1 Calibration

8.1.1 Method A

To calibrate the column for the cyclic oligomers, prepare a series of at least three calibration solutions with concentrations increasing from 100 mg/l to 1 500 mg/l by dissolution in formic acid (5.5) for caprolactam (5.6, n = 1), the cyclic dimer (5.7, n = 2), the cyclic trimer (5.8, n = 3) and the oligomer mixture (5.9, n = 4 to n = 6). To calibrate the column for the linear oligomers, prepare a series of three calibration solutions with concentrations increasing from 2 mg/l to 15 mg/l by dissolving in formic acid (5.5) for ε-aminocaproic acid (5.10) and each of the linear oligomers from the dimer (5.11) to the hexamer (5.15).

If possible, adjust the concentrations of the calibration solutions in such way that the concentrations of the substance(s) in the sample solutions to be determined (Clause 7) are not in the lowest or highest part of the relevant calibration series.

Pump eluent A (5.17) through the column at a rate of 0,51 ml/min. Starting with the lowest concentration of a calibration series, inject 2 µl of the calibration solution into the column in accordance with the injector programme given in Annex A. Elute in accordance with the gradient timetable in Annex A. Record the UV chromatogram. If applicable, immediately after UV detection, add the post-column reagent (5.23) at a rate of 0,25 ml/min, mixing the eluent and the reagent in the reaction coil. Record the fluorescence chromatogram. Measure the peak area of the component(s).

Repeat the calibration successively for the other calibration solutions of the same component and for the other calibration series.

NOTE Calibration can also be carried out using a commercially available PA6 polymer with a known concentration of cyclic and linear oligomers (see Reference [3]).

8.1.2 Method B

To calibrate the column for the caprolactam and its cyclic dimer, prepare a series of at least three calibration solutions with concentrations increasing from 100 mg/l to 1 500 mg/l by dissolution in formic acid (5.5) for caprolactam (5.6) and the cyclic dimer (5.7).

If possible, adjust the concentrations of the calibration solutions in such way that the concentrations of the substance(s) in the sample solution to be determined (Clause 7) are not in the lowest or highest part of the relevant calibration series.

Pump eluent B (5.17) through the column at a rate of 0,81 ml/min. Starting with the lowest concentration of a calibration series, inject 2 µl of the calibration solution into the column in accordance with the injector programme given in Annex B. Elute in accordance with the gradient timetable in Annex B. Record the UV chromatogram. Measure the peak area of the components.

Repeat the calibration successively for the other calibration solutions of the same component and for the other calibration series.

NOTE Calibration can also be carried out using a commercially available PA6 polymer with a known concentration of cyclic oligomers (see Reference [3]).

8.2 Determination

8.2.1 Method A

Introduce a test sample (see Clause 7) into a 25 ml volumetric flask. Add 20 ml of formic acid (5.5), close the flask and dissolve the sample, optionally by using ultrasonic vibration. Make up to the mark with formic acid (5.5). Pump eluent A (5.17) through the column at a flow rate of 0,51 ml/min. Inject 2 µl the sample solution into the column in accordance with the injector programme given in Annex A. Elute in accordance with the gradient timetable in Annex A. Record the UV chromatogram (see Figure 1). If applicable, immediately after UV detection, add the post-column reagent (5.23) at a flow rate of 0,25 ml/min, mixing the eluent and the reagent in the reaction coil. Record the fluorescence chromatogram (see Figure 2). Measure the peak areas of the cyclic oligomers (UV detection) and linear oligomers (fluorescence detection) up to and including the hexamer.

If necessary, e.g. if lower sensitivity is necessary due to high(er) concentrations, caprolactam can be detected by UV absorption at 220 nm instead of 200 nm.

NOTE The cyclic dimer of caprolactam elutes before caprolactam. See References [1], [2] and [3].