
**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

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 15033 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This second edition cancels and replaces the first edition (ISO 15033:2000), which has been technically revised.

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Introduction

The basic method specified in this International Standard can be used for HPLC determination of the cyclic oligomers of caprolactam 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, on-line 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 ($n = 6$).

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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 ensure compliance with any regulatory requirements.

1 Scope

This International Standard describes an HPLC (high-performance liquid chromatography) 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.

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* <https://standards.iteh.ai/catalog/standards/sist/86b97796-7707-4d30-ae1d-8fb786589e4b/iso-15033-2007>

3 Terms and definitions

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

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-litre 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.

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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 litre and saturate with helium (5.16).

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 litres 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 PA6 by preparative HPLC, using the HPLC method described here. The purity of the dimer and the possible presence of other oligomers can be checked using the method described in this International Standard.

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 100 bar.
- **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.

And 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 20 bar.
- **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 B.