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Plastics — Polyamides — Determination of ε-caprolactam and ω-laurolactam by gas chromatography

Plastiques — Polyamides — Détermination du ε-caprolactame et du ω-laurolactame par chromatographie en phase gazeuse

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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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This third edition cancels and replaces the second edition (ISO 11337:2010), which has been technically revised.

The main changes are as follows:

— isopropanol has been added as suitable internal standard for method A;

— the use of packed and capillary columns has been indicated specifically;

— the specification of suitable detectors has been opened.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Plastics — Polyamides — Determination of ε-caprolactam and ω-laurolactam by gas chromatography

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 determine the applicability of regulatory limitations prior to use.

1 Scope

This document specifies a method for determining ε-caprolactam and ω-laurolactam in polyamides by gas chromatography. It is applicable particularly to the determination of ε-caprolactam in polyamide 6 and ω-laurolactam in polyamide 12.

Two variants of the basic method are specified.

— Method A is an extraction method with boiling methanol, and the extract is injected into a gas chromatograph.

— Method B is a method using a solvent, and the solution is injected into a gas chromatograph.

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 amendment) applies.

ISO 472, *Plastics — Vocabulary*

ISO 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

3 Terms and definitions

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

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

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

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

4 Method A: Extraction method

4.1 Principle

A test portion is extracted with boiling methanol and a small volume of the extract is injected into a gas chromatograph equipped with a suitable detector to separate and detect the volatile components. The extract contains 1-dodecanol as an internal standard.

4.2 Reagents

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

4.2.1 Solvent, such as methanol.

4.2.2 Internal standard, such as 1-dodecanol or isopropanol.

4.2.3 ε-Caprolactam.

4.3 Apparatus and materials

Ordinary laboratory apparatus, plus the following.

4.3.1 Mill, for reducing the sample to the required grain size.

A mill in which the sample is ground at a low temperature is preferred. Large pieces may be reduced in size with a pair of scissors before they are fed to the mill.

4.3.2 Two sieves, with aperture sizes of 710 µm and 500 µm, respectively, in accordance with the requirements of ISO 565.

4.3.3 Extraction apparatus, that can accommodate an extraction crucible or porous ceramic thimble containing the test portion.

The apparatus shall be of such a design that the crucible or thimble is heated by the rising methanol vapour or the apparatus shall be constructed of an extraction flask with a Soxhlet-type reflux condenser.

Examples of suitable extraction apparatus designed along these lines are

EXAMPLE 1

— 250 ml extraction flask;

— extraction chamber to accommodate the extraction crucible so that it is enveloped on all sides by the rising methanol vapour and the condensed methanol drips through it continuously;

— glass triangle to support the crucible;

— reflux condenser;

— sintered-glass filter crucible, pore size 40 µm to 50 µm, capacity 30 ml;

— porcelain filter-plate of slightly smaller diameter than the crucible, with holes of diameter 0,4 mm.

EXAMPLE 2

— 250 ml extraction flask;

— jacketed Soxhlet extractor;

— reflux condenser;

— sintered-glass filter crucible, pore size 40 µm to 50 µm, capacity 30 ml, or a porous ceramic thimble of similar capacity (the dimensions shall be such that the crucible or thimble can be satisfactorily accommodated in the Soxhlet apparatus);

— porcelain filter-plate of slightly smaller diameter than the crucible or thimble, as appropriate, with holes of diameter 0,4 mm.

4.3.4 Heating device, suitable heating device for extraction apparatus.

4.3.5 Analytical balance, accurate to ±0,2 mg.

4.3.6 Liquid nitrogen or **solid carbon dioxide**, if necessary.

4.3.7 Gas chromatograph, with suitable detector.

Both, packed and capillary columns may be used.

a) Column

The following columns are suitable:

— a packed column, e.g. a glass column (3 mm Ø × 1,6 m), packed with acid-washed Chromosorb® W[1)] of particle diameter 0,149 mm to 0,177 mm (80 mesh to 100 mesh) coated with 10 % (by mass) poly(ethylene glycol) 20M;

— a capillary column, e.g. a megabore Carbowax™[1)] column (0,53 mm Ø × 15 m), of corresponding separation efficiency.

The method of packing is not specified but shall be such as to obtain satisfactory separation efficiency.

Other column dimensions may be used as long as a sufficient separation efficiency is achieved.

A capillary column may also be used.

Suggested operating conditions for using a glass column and an FID detector are shown in Table 1.

Table 1 — Operating conditions[a] for gas chromatograph with packed column and FID detector

Item	Value
Column temperature	200 °C
Injector temperature	250 °C
Detector temperature	250 °C
Carrier gas	Helium or nitrogen
Carrier gas flow rate	20 ml/min
[a] These values apply to the packed column indicated in 4.3.7 a)	

Other types of columns and/or detectors can require different operating temperatures and types and flow rates of carrier and makeup gas.

b) Detector

Use a suitable detector with adequate selection of operating temperature and type and flow rate of carrier and makeup gas so that:

— the sensitivity is high;

— the relationship between response and concentration is linear over the whole measurement range;

— small changes in flow rate produce only insignificant effects on response and sensitivity.

4.3.8 Microsyringes, with capacities from 1 µl to 10 µl.

4.4 Preparation of test sample

Take a representative sample of the polymer and grind it in the mill (4.3.1). Grind the material in small portions to prevent undue heat development (i.e. to avoid the temperature rising above about 40 °C), letting the mill cool down in between portions. Solid carbon dioxide or liquid nitrogen (4.3.6) may be ground together with the polymer to prevent heat build-up. With a large mill having a greater heat

1) Chromosorb® W and Carbowax™ are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

capacity, these precautions may not be required. Collect the fraction that passes through a sieve with mesh aperture 710 µm (4.3.2), but not through the one with mesh aperture 500 µm.

4.5 Procedure

4.5.1 Test portion

Weigh, to the nearest 0,001 g, (5 ± 0,5) g (mass m_0) of the test sample into the filter crucible or porous thimble (4.3.3). With low-concentration samples, it is preferable to increase the mass of the test portion so that it contains approximately 0,01 g to 0,05 g of ε-caprolactam.

Polyamides can contain a small amount of water, forming part of the mass of the test portion (m_0). This water shall not be considered in the calculation of the methanol-extractable matter content since its effect is small compared to the variance of the determination.

4.5.2 Extraction

Cover the test portion (see 4.5.1) with the filter-plate, pour about 50 ml of methanol (4.2.1) into the extraction flask, place the crucible or thimble containing the test portion in the extraction chamber and fit the condenser to the chamber. Heat the solvent in the flask until it is boiling. When the apparatus described in 4.3.3, Example 1, is used, adjust the rate of reflux to 1 to 2 drops per second and ensure that the drops fall into the crucible. When a Soxhlet extractor as described in 4.3.3, Example 2, is used, adjust the heating so that there are five to eight siphonings per hour.

Extract for a period of 3 h ± 5 min and then allow the extractor to cool to ambient temperature, overnight if necessary.

Detach the extraction flask with its contents and analyse by gas chromatography, using the procedure specified in 4.5.3 to 4.5.7.

4.5.3 Preparation of internal-standard solution

Weigh out, to the nearest 0,2 mg, (2 ± 0,2) g of 1-dodecanol (4.2.2) and transfer it to a 1 l volumetric flask. Dissolve in methanol and make up to the mark with the same solvent.

While 1-dodecanol is the preferred internal standard, it is also possible to use isopropanol.

4.5.4 Preparation of sample solution

Transfer the extract obtained in 4.5.2 to a 100 ml volumetric flask and add 10 ml of the internal-standard solution prepared in 4.5.3. Rinse the extraction flask with small amounts of methanol, add the rinsings to the volumetric flask and make up to the mark with methanol.

4.5.5 Preparation of calibration solution

Weigh, to the nearest 0,2 mg, (0,05 ± 0,005) g of ε-caprolactam (4.2.3) and transfer to a 100 ml volumetric flask. Add 10 ml of the internal-standard solution prepared in 4.5.3. Dissolve in methanol and make up to the mark with the same solvent.

4.5.6 Gas-chromatographic analysis of sample and calibration solutions

Inject a suitable volume between 1 µl and 10 µl (depending on the sensitivity of the detector used) of the sample solution prepared in 4.5.4 or the calibration solution prepared in 4.5.5.

When using a capillary column, it is recommended to limit the injection volume to 5 µl to avoid overloading the column.

The volume injected is not critical for the results, but shall be identical for corresponding sample and calibration solutions. Always record the calibration chromatogram at the same sensitivity setting as used for the corresponding sample chromatogram.

Multi-point calibration is recommended. For this, prepare a series of three calibration solutions with increasing concentrations in the range of the expected ε-caprolactam concentration in the sample solution. Express the result as the mean of the three calibration factors obtained.

Continue to record the chromatogram until the ε-caprolactam and internal standard have been completely eluted, then flush the column with carrier gas until the normal baseline is restored.

4.5.7 Evaluation of gas chromatographic peaks

The retention times of ε-caprolactam, methanol and 1-dodecanol shall be known, at least relative to each other. The values are dependent on the column length, the column temperature and other parameters, and they vary according to the density of the column packing and the age of the column. Determine the areas of the ε-caprolactam and 1-dodecanol peaks by electronic or graphical integration.

The method of peak evaluation chosen shall be identical for corresponding peaks of sample and calibration solutions.

4.6 Expression of results

The ε-caprolactam content, w, in the sample analysed is calculated, as a percentage by mass, from Formula (1):

$$w = \frac{A_{s'} \times A_a \times m_{a'}}{A_s \times A_{a'} \times m_0} \times 100 = \frac{A_a \times f_{s'} \times m_{s'}}{A_s \times f_{a'} \times m_0} \times 100 \quad (1)$$

where

A_s is the area of the 1-dodecanol peak from the test solution;

$A_{s'}$ is the area of the 1-dodecanol peak from the calibration solution;

A_a is the area of the ε-caprolactam peak from the test solution;

$A_{a'}$ is the area of the ε-caprolactam peak from the calibration solution;

$m_{a'}$ is the amount of ε-caprolactam, in grams, weighed into the calibration solution in 4.5.5;

$m_{s'}$ is the amount of 1-dodecanol, in grams, weighed into the calibration solution in 4.5.5;

m_0 is the mass, in grams, of the test portion;

$f_{s'}$ is the calibration factor for ε-caprolactam:

$f_{s'} = A_{s'}/m_{s'}$

$f_{a'}$ is the calibration factor for 1-dodecanol:

$f_{a'} = A_{a'}/m_{a'}$

4.7 Precision

The precision of this method is not available at the time of publication.

4.8 Test report

The test report shall include the following particulars:

a) a reference to this document, including the year of publication, i.e. ISO 11337:2023;

b) all details necessary for complete identification of the polyamide tested;

c) the manufacturer and specifications of the gas-chromatographic equipment used, including test conditions;

d) the ε-caprolactam content, expressed as a percentage by mass;

e) any deviations from the procedure;

f) any unusual features observed;

g) the date of the test.

5 Method B: Dissolution method

5.1 Principle

A small quantity of the sample to be analysed (about 0,5 g) is dissolved in an appropriate quantity of a suitable solvent containing an adequate quantity of internal standard.

A suitable volume of the solution thus obtained is then injected into a gas chromatograph to separate the ε-caprolactam or ω-laurolactam from the internal standard and allow the peak areas to be determined.

This method uses ε-caprolactam or ω-laurolactam as an internal standard, so it is important to be sure before the determination that the sample does not itself contain the internal standard used.

When analysing blends or copolyamides containing both ε-caprolactam and ω-laurolactam, 1-dodecanol, 2-azacyclononane or 2-azacyclooctanone may be used as internal standard instead of ε-caprolactam or ω-laurolactam.

5.2 Reagents

During the analysis, use only reagents of analytical grade or the grade specified.

5.2.1 2,2,2-Trifluoroethanol (TFE).

5.2.2 Trichloromethane (chloroform).

5.2.3 ε-Caprolactam, minimum purity 99,5 %.

5.2.4 ω-Laurolactam, minimum purity 99,5 %.

5.2.5 If applicable, **1-dodecanol, 2-azacyclononane or 2-azacyclooctanone** may be used as internal standard.

5.2.6 Anhydrous ethanol.

5.2.7 Anhydrous methanol.

5.3 Apparatus

Ordinary laboratory apparatus, plus the following.

5.3.1 Gas chromatograph, equipped with an injector for liquid samples and with a ground-glass liner (removable for periodic cleaning) that can eliminate non-volatile polymeric residues; a suitable detector and a recorder (or, better, a computer-integrator).

a) Column

A packed column such as a glass column (2 mm Ø × 1 m) packed with Chromosorb® W[2)] (80 mesh to 100 mesh) coated with 10 % (by mass) poly(ethylene glycol) 20M is suitable.

Other, similar, columns of corresponding separation efficiency may also used.

The use of a capillary column should be avoided as the polyamide remaining in the glass liner generates a large number of volatile impurities at the high temperatures used, dramatically reducing the lifetime of the column.

The method of packing is not specified but shall be such as to obtain satisfactory separation efficiency.

Other column dimensions are permissible, but only if they have been proved to give the same results.

Suggested operating conditions are shown in Table 2.

The temperatures and temperature-increase rate suggested are not the only possible ones. Any other temperature and temperature-increase rate that will give good separation of the solvent, ε-caprolactam and ω-laurolactam, and at the same time good peak shapes, is acceptable.

Table 2 — Operating conditions[a] for gas chromatograph with packed column and FID detector

Item	Value
Oven temperature	Hold at 175 °C for 5 min. Then increase at 10 °C/min. Hold at 205 °C for 7 min.
Injector temperature	300 °C
Detector temperature	300 °C
Carrier gas	Nitrogen
Carrier gas flow rate	35 ml/min to 60 ml/min
Injection volume	2 µl
Detector sensitivity	Has to be chosen as a function of the instrument and as a function of the lactam concentration in the sample or in the calibration solution.

[a] These values apply to the packed column indicated in 5.3.1 a)

b) Detector

Use a suitable detector with adequate selection of operating temperature and type and flow rate of carrier and makeup gas so that:

— the sensitivity is high;

— the relationship between response and concentration is linear over the whole measurement range;

— small changes in flow rate produce only insignificant effects on response and sensitivity.

2) Chromosorb® W is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

Every 10 injections, it is recommended that the column be cleaned with an injection of 2 µl of anhydrous ethanol.

5.3.2 Microsyringes, with capacities from 5 µl to 10 µl and with a needle without an internal wire (in order to avoid polymer blocking in the needle itself).

5.3.3 Analytical balance, accurate to ±0,2 mg.

5.3.4 Distillation apparatus.

It is possible to use a simple Claisen distillation flask with a short column (of, for instance, the Vigreux type) 400 mm to 600 mm in length.

5.3.5 Stirring device, capable of being heated to at least 70 °C.

This may be a shaking system immersed in a water bath or mounted on a hotplate heated to the required temperature, equipped with a series of magnetic stirrers.

5.4 Preparation of internal-standard solutions

5.4.1 General

For calibration solutions, methanol (5.2.6) may be used as the solvent instead of 2,2,2-trifluoroethanol (5.2.1). The internal standards (see 5.4.2, 5.4.3 and 5.4.4) shall be prepared using 2,2,2-trifluoroethanol, however.

5.4.2 Internal standard for unextracted polyamide 6

In a small weighing bottle, weigh, to the nearest 0,2 mg, 5,0 g of ω-laurolactam and transfer it to a 1 l volumetric flask. Dissolve in 2,2,2-trifluoroethanol and make up to the mark with the same solvent. This solution (solution S_A) is the internal standard to be used with polyamide 6, or its copolymers not containing polyamide 12, which have not yet been subjected to the extraction process for the elimination of the residual ε-caprolactam (ε-caprolactam content >5 %).

5.4.3 Internal standard for extracted polyamide 6

Weigh, to the nearest 0,2 mg, 0,25 g of ω-laurolactam (5.2.4) and transfer it to a 1 l volumetric flask. Dissolve in 2,2,2-trifluoroethanol and make up to the mark with the same solvent. This solution (solution S_B) is the internal standard to be used with polyamide 6, or its copolymers not containing polyamide 12, which have been subjected to the extraction process for the elimination of the residual ε-caprolactam (ε-caprolactam content <1 %).

5.4.4 Internal standard for polyamide 12

Weigh, to the nearest 0,2 mg, 0,25 g of ε-caprolactam (5.2.3) and transfer it to a 1 l volumetric flask. Dissolve in a solvent prepared by mixing together 60 parts by volume of 2,2,2-trifluoroethanol and 40 parts by volume of chloroform and make up to the mark with the same solvent. This solution (solution S_C) is the internal standard to be used with polyamide 12, or its copolymers not containing polyamide 6.