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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

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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.

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ISO 11337 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

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

WARNING — This International Standard may involve hazardous chemicals, materials or operations. It does not purport to address all of the safety problems, 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 regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for determining ε-caprolactam and ω-laurolactam in polyamides by gas chromatography. It is suitable particularly for the determination of ε-caprolactam in polyamide 6 and ω-laurolactam in polyamide 12. Bearing in mind that gas chromatography offers a wide range of possible conditions, the method specified is that shown to have been suitable in practice.

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.

Method A is suitable for the determination of ε-caprolactam and method B for ε-caprolactam and ω-laurolactam.

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*

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

3 Terms and definitions

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

4 Method A: Extraction method

4.1 Principle

A test portion is extracted with boiling methanol and a small volume of the extract injected into a gas chromatograph equipped with a flame-ionization 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 Methanol.

4.2.2 1-Dodecanol.

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 can 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, complying with the requirements of ISO 565.

4.3.3 Extraction apparatus, that will 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 Suitable heating device for extraction apparatus.

4.3.5 Analytical balance, accurate to 0,000 2 g.

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

4.3.7 Gas chromatograph, with flame-ionization detector.

a) Column

The following columns are suitable:

— a glass column (3 mm $\phi \times$ 1,6 m), packed with acid-washed Chromosorb W 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 fused-silica capillary column (0,31 mm $\phi \times$ 30 m), liquid phase 95 % dimethyl, 5 % diphenyl polysiloxane, film thickness 0,25 µm;

— a megabore carbowax column (0,53 mm $\phi \times$ 15 m) of corresponding separation efficiency.

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

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

Suggested operating conditions are shown in Table 1.

Table 1 — Operating conditions for gas chromatograph

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

b) Detector

Use a flame-ionization detector in which the hydrogen and air flow rates can be adjusted so that:

— 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 400 °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 capacity, these precautions may not be required. Collect the fraction that passes through the sieve with mesh aperture 710 µm (see 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 (see 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.

NOTE Polyamides may contain a small amount of water, forming part of the mass of the test portion (m_0). This water is not allowed for in the calculation of the methanol-extractable matter content since its effect is small compared with 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 to 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 following procedure:

4.5.3 Preparation of internal-standard solution

Weigh out, to the nearest 0,000 2 g, 2 g of 1-dodecanol and transfer it to a 1 l volumetric flask. Dissolve in methanol and make up to the mark with the same solvent.

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 amount 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 0,000 2 g, 0,05 g of ε-caprolactam and transfer to a 100 ml volumetric flask. Add 10 ml of the internal-standard solution prepared in 4.5.3. Dissolve. Make up to the mark with methanol.

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.

NOTE When using a capillary column, it is advisable 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 that 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, column temperature and other parameters, and they vary according to the density of the column packing and the age of the column. Typical values of retention times are shown in Table 2.

Table 2 — Typical values of retention times

Substance	Retention time in minutes	Retention time relative to 1-dodecanol
Methanol	2,80	0,21
ε-Caprolactam	5,14	0,39
1-Dodecanol	13,17	1,0

Determine the areas of the ε-caprolactam and 1-dodecanol peaks by:

c) electronic integration;

or

d) estimation using the following equation: peak area = peak height × width at half-height.

Use of method b) is recommended only for peaks with a horizontal baseline and having a shape as close as possible to that of an isosceles triangle, in order to minimize the inaccuracy of measurement. 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 the equation:

$$w = \frac{A_{s'} \times A_a \times m_{a'}}{A_s \times A_{a'} \times m_0} \times 100 = \frac{A_a \times A_{a'} \times m_{s'}}{A_s \times f \times A_{s'} \times m_0} \times 100$$

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 is the ratio of the calibration factors for ε-caprolactam ($f_{a'}$) and 1-dodecanol ($f_{s'}$) in the calibration solution:

$$f = \frac{f_{a'}}{f_{s'}} = \frac{A_{a'} \times m_{s'}}{A_{s'} \times m_{a'}}$$

4.7 Precision

The precision of this method is not known because inter-laboratory data are not available. Inter-laboratory data are being obtained and will be added at the next revision.

4.8 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

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

c) any deviation from the specifications for the gas-chromatographic equipment or from the procedure given in this International Standard;

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

e) the date of the determination.

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.

NOTE 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.

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 Anhydrous ethanol.

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 flame-ionization detector (FID) and a recorder (or, better, computer-integrator).

a) Column

A glass column (2 mm φ × 1 m) packed with Chromosorb W (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 (e.g a capillary 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 3.

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 3 — Operating conditions for gas chromatograph

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
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 reference solution.