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Plastics — Determination of ash —

Part 4: Polyamides

Plastiques — Détermination du taux de cendres —

Partie 4: Polyamides

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Foreword

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This document was prepared by Technical Committee ISO/TC 61, *Plastics,* Subcommittee SC 5, *Physical-chemical properties*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC249, *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 3451-4:1998), which has been technically revised.

The main changes are as follows:

— automatic device method (method D) has been added according to align with the revised ISO 3451-1:2019.

A list of all parts in the ISO 3451 series can be found on the ISO website.

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 — Determination of ash —

Part 4: Polyamides

WARNING — This document can involve hazardous chemicals, materials and operations. This document does not purport to address the safety problems associated with its use. It is the responsibility of the user to establish proper safety and health practices and determine any applicable regulatory limitations prior to use.

1 Scope

This document specifies methods for determination of the ash of polyamides, both filled and unfilled. It follows the general procedures given in ISO 3451-1.

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 3451-1:2019, *Plastics — Determination of ash — Part 1: General methods*

3 Terms and definitions

No terms and definitions are listed in this document.

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 Principle

4.1 General

For unfilled materials, method A and method D or method C of ISO 3451-1:2019 is used.

For filled and glass-fibre reinforced materials, method A and method D of ISO 3451-1:2019 is used.

For glass-fibre filled materials containing flame retardant, antimony trioxide, and/or other, volatilizable, additives such as pigment zinc sulfide, a modification is incorporated to remove these as volatile bromine component(s).

4.2 Unfilled materials

Direct calcination by burning the organic matter and treating the residue at a high temperature until constant mass is reached (ISO 3451-1:2019, method A and method D).

If the material contains metal halides and/or metals (especially in the presence of halogenated material) which are liable to evaporate during burning of the organic matter, calcination after sulfation can be applied (ISO 3451-1:2019, method C). This procedure is carried out by heating the organic matter together with concentrated sulfuric acid up to a temperature where fuming and subsequent burning of the organic matter occurs, and finally treating the residue at a high temperature until constant mass is reached.

4.3 Filled and glass-fibre reinforced materials

Direct calcination, by burning the organic matter and treating the residue at a high temperature until constant mass is reached (ISO 3451-1: 2019, method A and method D) (see 4.4.2).

4.4 Flame-retardant materials reinforced with glass fibre

4.4.1 Calcination by burning the organic matter in the presence of decabromobiphenyl (DBB) and finally treating the residue at a high temperature until constant mass is reached (ISO 3451-1:2019, method A and method D).

4.4.2 Some additives, for instance zinc sulfide, are also completely volatilized as bromides by burning the organic matter in contact with decabromobiphenyl (DBB). Information with respect to the additive(s) present in the material and the potential to evaporate during burning in contact with DBB should be requested from the supplier or obtained by testing on the pure chemical.

4.4.3 Flame retardants with a high bromine content, for instance ethylene bis(tetrabromophthalimide) or brominated polystyrene may also be used. The applicability and amount of chemical to be used can be determined by carrying out ash determinations in accordance with 7.5 with increasing amounts of flame retardant until a constant result is obtained. The chemical should be applied as a powder.

5 Reagents (method C or method A in the presence of DBB)

During the analysis, use only reagents of analytical grade or specified grade and only distilled water or water of equivalent purity.

5.1 Ammonium carbonate, anhydrous.

5.2 Ammonium nitrate, approximately a mass fraction of 10 % solution.

5.3 Sulfuric acid, ρ 1,84 g/ml.

5.4 Decabromobiphenyl (DBB), powder, technical grade or higher purity.

WARNING — The use of decabromobiphenyl can result in the formation of dioxins. Temperatures in the order of 600 °C to 850 °C are generally known as ideal temperatures for the formation of dioxins.

6 Apparatus

Apparatus specified in ISO 3451-1:2019, Clause 4 and in particular:

6.1 Crucibles of silica, porcelain or platinum, inert to the material tested, and typically of diameter (upper part) 50 mm to 60 mm and height equal to the diameter (see 4.4.3).

6.2 Muffle furnace, powered by electric resistance heating or by microwave heating, capable of being maintained at (600 ± 25) °C, (850 ± 50) °C or at a minimum temperature of 850 °C.

6.3 Fume cupboard.

7 Procedure

7.1 General

The material shall be in the form of small pieces of 1 cm × 0,5 cm × 0,2 cm or smaller, granules or powder. Filled or reinforced materials shall be dried before calcination, i.e. by heating at 100 °C until constant mass is reached.

7.2 Test portion

Take a quantity of the test sample sufficient to yield 5 mg to 500 mg of ash (see Table 1). In the case of reinforced materials, take a test portion of 1 g or more. If the likely quantity of ash is unknown, carry out a preliminary ash determination. According to the approximate ash content, choose the size of the test portion to be used from Table 1.

Table 1 — Mass of test portion

Approximate ash %	Test portion g	Mass of ash obtained mg
≤0,01	≥200	5 to 10
>0,01 to 0,05	100	10 to 50
>0,05 to 0,1	50	25 to 50
>0,1 to 0,2	25	25 to 50
>0,2 to 1	10	20 to 100
>1 to 10	5	50 to 500
>10 to 25	2	200 to 500
>25	1	>250

7.3 Unfilled materials

Follow the procedure specified in ISO 3451-1:2019, method A and method D, applying a calcination temperature of (850 ± 50) °C.

If the material contains metal halides or metals in the presence of halogenated material, liable to evaporate during the calcination procedure, or in those cases where “sulfated ash” is required, ISO 3451-1:2019, method C shall be applied.

7.4 Filled and glass-fibre reinforced materials

Follow the procedure specified in ISO 3451-1:2019, method A and method D, applying a calcination temperature of (850 ± 50) °C. If at that temperature glass fibres present become molten and thus prevent further calcination of the polymer, lower the temperature of calcination to (600 ± 25) °C and repeat the procedure with a fresh test portion.

7.5 Materials reinforced with glass fibre containing flame-retardant antimony trioxide and/or other volatilizable additives

The sample shall be ground or cut to pieces of 1 cm × 0,5 cm × 0,2 cm or smaller. Proceed as in ISO 3451-1:2019, 7.3.1 and 7.3.2 for method A and as in ISO 3451-1:2019, 7.6.1 to 7.6.3 for method D.

Add to the sample a quantity of DBB (5.4) equal to half the mass of the sample in grams and mix well in the crucible. Place the crucible in the muffle furnace, applying a calcination temperature of at least 850 °C. The muffle furnace shall be placed in a fume cupboard. Continue as directed in ISO 3451-1:2019, 7.3.4 of method A, and method D.

Directly placing the crucible into the muffle furnace is preferred. If direct calcination leads to large differences between repeated tests, for instance due to loss of ash-containing material, gently heat the crucible over a quiet flame until formation of fumes ceases. Make sure that the volatile components are properly drawn off by a fume cupboard. Place the crucible in the muffle furnace and apply a calcination temperature of at least 850 °C. Continue as directed in ISO 3451-1:2019, 7.3.4 of method A. Glass-fibre crucibles provided with two glass-fibre discs may also be used. The crucible shall be prepared by heating it in the muffle furnace at the test temperature and cooling it in a desiccator until constant mass is reached. Introduce the sample between the glass-fibre discs into the crucible. Place the crucible in the muffle furnace for 30 min. Allow the crucible to cool in a desiccator for 20 min.

For unground material the residue in the crucible shall be calcinated a second time according to the procedure specified in 2nd and 3rd paragraphs of 7.5. The amount of DBB added to the residue shall be 1 g.

8 Expression of results

The ash or sulfated ash, expressed as a percentage by mass, is given by Formula (1):

$$\frac{m_1}{m_0} \times 100 \tag{1}$$

where

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

m_1 is the mass, in grams, of ash obtained.

Calculate the average of two results and round off to the nearest 0,1 %.

9 Precision

Precision data of the ash determination are summarized in ISO 3451-1:2019, Clause 10 with the exception of the DBB method specified in 7.5. The precision data were determined with eight laboratories and eight materials.

For glass-fibre reinforced polyamides (PA/glass), the precision data given in Table 2 were obtained.

Table 2 — Precision data for PA/glass

Material/Filler	Mean ash %	s_r	s_R	r	R
PA/glass	33,16	0,272	0,282	0,760	0,790

where

s_r is the repeatability standard deviation;

s_R is the reproducibility standard deviation;

r is the repeatability value, comprising the value below which the absolute difference between two single test results obtained under repeatability conditions (same operator, same apparatus, same laboratory and within a short interval of time) may be expected to lie with a probability of 95 %;

R is the reproducibility value, comprising the value below which the absolute difference between two single test results obtained under reproducibility conditions (different operator, different apparatus, different laboratories) may be expected to lie with a probability of 95 %.

The precision of the direct calcination of glass-fibre-containing materials and the DBB method is not known because interlaboratory data are not available at the time of publication. However, the precision of these methods is expected not to deviate significantly from the known data. Interlaboratory data are being gathered and will be added at the next revision.