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Plastics — Determination of ash —

Part 1:
General methods

Plastiques — Détermination du taux de cendres —

Partie 1: Méthodes générales

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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 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 5, *Physical-chemical properties*.

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.

This fifth edition cancels and replaces the fourth edition (ISO 3451-1:2008), which has been technically revised by adding an automated instrument method (Method D).

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

Plastics — Determination of ash —

Part 1:
General methods

SAFETY PRECAUTIONS — 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.

1 Scope

This document specifies general methods, with suitable test conditions, for the determination of the ash of a range of plastics. The particular conditions chosen can be included in the specifications for the plastic material in question.

Particular conditions applicable to poly(alkylene terephthalate) materials, unplasticized cellulose acetate, polyamides and poly(vinyl chloride) plastics, including some specific filled, glass-fibre-reinforced and flame-retarded materials, are specified in ISO 3451-2, ISO 3451-3, ISO 3451-4 and ISO 3451-5.

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:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Principle

It is possible to determine the ash of an organic material by four main methods (methods A, B, C and D).

a) Direct calcination, i.e. by burning the organic matter and heating the residue at high temperature until constant mass is reached, which may be carried out by two different procedures:

  - burning with, for example, a Bunsen burner and one or more calcining steps in a muffle furnace (method A);
  - burning and calcining as one single step in a muffle furnace (method A — rapid ashing), if it can be demonstrated that the rapid ashing yields the same results as method A.

b) Calcination after sulfation, which may be carried out by two different procedures:

- with sulfuric acid treatment after burning, i.e. by burning the organic matter, transforming the inorganic residue into sulfates with concentrated sulfuric acid and heating the residue at high temperature until constant mass is reached. This is the common method of obtaining “sulfated ash” (method B);
- with sulfuric acid treatment before burning, i.e. by heating the organic matter together with concentrated sulfuric acid up to temperatures where fuming and subsequent burning of the organic matter occur, and finally heating the residue at high temperature until constant mass is reached (method C). This procedure may be used if volatile metal halides are liable to evaporate during burning of the organic matter. It is not applicable to silicones or fluorine-containing polymers.

c) Automated instrument method (method D).

In each case, the final step of the procedure is calcination at a pre-defined temperature (see 7.2).

NOTE The mass of the ash can vary with the temperature of calcination. For example, higher temperatures such as 850 °C convert calcium carbonate and other carbonates to their oxides and thus give lower values for the ash.

5 Reagents (for methods B and C only)

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

5.1 Ammonium carbonate, anhydrous.

5.2 Ammonium nitrate, approximately 10 % (by mass) solution.

5.3 Sulfuric acid, concentrated 98 %, $\rho = 1{,}84\ \text{g/cm}^3$.

WARNING — Highly corrosive. Handle with suitable skin and eye protection in a fume cupboard. Reacts exothermically with water.

5.4 Sulfuric acid, 50 % (by volume) solution.

WARNING — Handle with care. Prepare by slowly adding the concentrated acid to water.

6 Apparatus

some of the listed items may not be necessary for each method.

6.1 Crucible, made of silica, porcelain, ceramics, fibres, quartz, glass or platinum, thereof, inert to the material tested and suitable for the temperatures used. The use of a crucible lid/watch-glass may be beneficial for samples producing a fine particulate ash.

6.2 Gas burner, or other appropriate heat source.

6.3 Muffle furnace, powered by electric resistance heating or by microwave heating, capable of being maintained at (600 ± 25) °C, (750 ± 50) °C, (850 ± 50) °C or (950 ± 50) °C, as appropriate.

6.4 Analytical balance, accurate to 0,1 mg.

6.5 For **automated instruments**, the following requirements apply:

- fully automatic analysis instrument with integrated drying oven, muffle furnace, analytical balance and a sample turntable;
- loss of weight during the drying and ashing process is continuously monitored during the ashing process;
- the built-in analytical balance can weigh each sample in turn, and the results recorded by the software;
- instrument shall have a method to correct the mass difference caused by buoyancy, thus the weighing can be taken at different temperature, samples do not need to be cooled down during test;
- having a furnace that operates at the prescribed temperature, capable of being maintained at (600 ± 25) °C, (750 ± 50) °C, (850 ± 50) °C or (950 ± 50) °C, as appropriate;
- having a holder for one or more crucibles, e.g. by using a turntable, or an automatic way to introduce and extract the crucibles consecutively into and from the furnace;
- temperature and sample mass ranges in accordance with the experimental requirements;
- recording device capable of automatically recording the sample mass versus temperature and time;
- measurement of temperature signals with an accuracy of ±2 % or better;
- measurement of mass with an accuracy of ±0,1 mg or better.

NOTE Automatic ash determination equipment, in line with the specifications prescribed in this document, is produced by several equipment manufacturers.

6.6 **Pipettes**, of suitable capacity (for methods B and C only).

6.7 **Desiccator**, containing an efficient desiccant which does not interact with the ash.

NOTE In certain cases, the ash can have a greater affinity for water than some substances commonly used as desiccants.

6.8 **Weighing bottle.**

6.9 **Fume cupboard** or other suitable means of ventilation.

7 Procedure

7.1 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 according to Table 1. If the likely quantity of ash is unknown, carry out a preliminary ash determination. Depending on the approximate ash content, choose the size of the test portion to be used from Table 1, the mass of the test portion may have a direct effect on the result.

Table 1 — Mass of test portion

Approximate ash %	Test portion g	Mass of ash obtained mg
≤0,01	≥200	approximately 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

For plastics yielding very low ash, it is necessary to use larger test portions. When it is impossible to burn the whole test portion at one time, weigh the required quantity in a suitable weighing bottle and introduce it into the crucible (6.1) in convenient amounts for a succession of burnings until the whole test portion has been burnt.

7.2 Test conditions

Calcine again under the same conditions until constant mass is reached, i.e. until the results of two consecutive weighings do not differ from each other by more than 0,5 mg.

The choice of the calcination temperature and the use of the sulfation method depend on the nature of the plastic and any additives it may contain. If a choice exists between different satisfactory conditions, choose those that allow the attainment of constant mass preferably in less than 3 h. A higher temperature or the use of sulfation generally shortens the duration of the calcination.

Whichever method (A, B, C or D) is used, choose one of the following temperature ranges for the final (calcination) step, unless other temperatures are requested for special technical or commercial reasons:

— (600 ± 25) °C;

— (750 ± 50) °C;

— (850 ± 50) °C; or

— (950 ± 50) °C.

Use a fume cupboard or other suitable means for ventilation for the ashing procedure, if not required otherwise by the furnace being used (e.g. for furnaces with an integrated exhaust system that shall not be operated in a fume cupboard).

For method A, if it can be conclusively demonstrated for a particular sample type that direct ashing in a muffle furnace without preheating/igniting the sample over a Bunsen flame or equivalent gives the same result, then this version of method A (rapid ashing) is permitted. The use of this rapid ashing method shall be included in the test report.

NOTE The precision and reproducibility of the ashing procedure depends on the temperature at which the burning and/or calcination process in the furnace (ohmic resistance heating or microwave heating) is performed.

Efficient ventilation of the furnace is equally important, especially if the furnace is used for burning and calcination (rapid ashing method).

To ensure a constant quality of the ashing procedure, the lab shall verify the operation of the furnace at regular intervals. This verification shall include:

- calibration of the furnace temperature using a reference traceable to a national standard according to a validated calibration procedure;
- check of the efficiency of the furnace ventilation.

Especially for plastics containing fillers that decompose under elevated temperatures, such as calcium carbonate, a precise and constant temperature in the furnace is important to ensure precise and reproducible results.

7.3 Method A — Direct calcination

7.3.1 Crucibles (6.1) shall be prepared by heating in the furnace (6.3) at the test temperature or by another suitable method until constant mass is reached. Allow to cool, preferably in a desiccator. Crucibles can be stored until needed, provided that they are kept clean and dry. Suitable storage methods are, for example, in a desiccator or a heating cabinet at a minimum temperature of 70 °C. Cool down to room temperature and weigh on the analytical balance (6.4) to the nearest 0,1 mg.

7.3.2 Introduce into the tared weighing bottle (6.8) a test portion (pre-dried as described in the corresponding material specification) of mass in accordance with Table 1. Weigh again to the nearest 0,1 mg or to 0,1 % of the mass of the test portion. If the test portion corresponding to the amount of ash specified in Table 1 does not more than half fill the crucible, this quantity may be placed directly into the crucible and weighed in it. The procedure described below assumes that this will not be the case, however. High-bulk materials may be compressed into tablets, which may then be broken up into fragments of appropriate size.

7.3.3 Introduce into the crucible enough of the test portion to not more than half fill the crucible. Heat the crucible in the muffle furnace or directly on the burner or other suitable heating device (6.2). If the furnace (6.3) is equipped with an adequate exhaust system, the furnace itself can be used as the heating device to burn slowly until volatile products have been driven off. Repeat the operation until the whole test portion is well charred.

7.3.4 Introduce the crucible into the muffle furnace preheated to the prescribed temperature and calcine for 30 min.

7.3.5 Place the crucible in the desiccator, allow it to cool for 1 h, or until room temperature is reached, and weigh on the analytical balance to the nearest 0,1 mg.

7.3.6 Calcine again under the same conditions until constant mass is reached, i.e. until the results of two consecutive weighings do not differ from each other by more than 0,5 mg.

7.3.7 If a laboratory can document that their procedure for time and temperature of a single calcination on a given material results in constant mass, then this so-called “rapid method” shall be permitted and the test report shall note a single calcination. Rapid ashing may include shorter calcining than stated in 7.3.4. In the event of a dispute, the referee method shall be calcination to constant mass.

7.4 Method B — Calcination following sulfuric acid treatment after burning

7.4.1 Proceed as specified in 7.3.1, 7.3.2 and 7.3.3.

7.4.2 After cooling, add sulfuric acid solution (5.4) drop by drop with a pipette of suitable capacity (6.6) to moisten the residue completely and heat until fuming ceases, avoiding too vigorous boiling.

7.4.3 If traces of carbonaceous materials remain after cooling, add 1 to 5 drops of ammonium nitrate solution (5.2) and heat until the evolution of white fumes ceases completely.

7.4.4 In order to reconvert metal oxides formed during the preceding steps into sulfates, add, after cooling, about 5 drops of concentrated sulfuric acid (5.3) and heat until there is no further evolution of white fumes, avoiding vigorous boiling or the loss of ash by excessive fuming.

7.4.5 After cooling, add 1 g to 2 g of solid ammonium carbonate (5.1) and heat, avoiding loss of ash, until the fuming has ceased. Then, place the crucible in the muffle furnace preheated to the indicated temperature and proceed as specified in 7.3.4, 7.3.5 and 7.3.6.

7.5 Method C — Calcination following sulfuric acid treatment before burning

7.5.1 This method shall never be used with silicones or fluorine-containing polymers.

7.5.2 Proceed as specified in 7.3.1 and 7.3.2.

7.5.3 Introduce into the crucible enough of the test portion to half fill the crucible. Add with a pipette (6.6) a sufficient amount of concentrated sulfuric acid (5.3) to moisten the material completely. Cover the crucible with a watch-glass. Heat the crucible directly on the burner over a low flame until the organic material begins to decompose.

Continue heating carefully, adjusting the watch-glass so as to allow the acid to be fumed off and making sure that no ash-containing material is lost. With plastics which have a tendency to lose ash-containing material, it is recommended that the crucible with its contents be placed into a holed board made of fireproof material (e.g. ceramic fibre) and heated with a low flame only so that the organic matter smoulders rather than burns. If the initial charge in the crucible was insufficient to yield an acceptable mass of ash, allow the crucible to cool, add more of the test portion and repeat the operations described above until the whole test portion has been burnt. Remove the watch-glass, making sure that no solid particles are adhering to it.

In cases where the sulfuric acid tends to creep over the lip of the crucible or where, despite precautions, some of the test portion tends to be lost by violent reaction (frequently in the case of PVC), the concentrated sulfuric acid may be replaced by a mixture of concentrated acetic and sulfuric acids. The use of these mixed acids shall be agreed between the interested parties and reference made to it in the test report.

7.5.4 Proceed as specified in 7.4.3, 7.4.4 and 7.4.5.

7.6 Method D — Automated instrument method

7.6.1 An automated procedure shall follow the general outline of method A. Any design that is capable of fulfilling the requirements specified in method A in an automated manner is acceptable.

7.6.2 Prepare the automatic ash determination equipment by setting the required test temperature (see 7.2), test time and the constant mass condition. If pre-ashing is required, the pre-ashing temperature should also be set. Prepare the crucibles (6.1) by heating them in the instrument chamber (6.3) at the test temperature until constant mass is reached.

NOTE Fully automatic analysis instruments typically carry out a number of ash determinations in one run.

7.6.3 Introduce the test portions of the samples, in accordance with Table 1, into the crucibles located in turn-table of the automatic instrument (6.5). The instrument will automatically determine and deduct the crucible tare weight to the nearest 0,1 mg and will automatically display net sample weight to the nearest 0,1 mg. If the test portion corresponding to the amount of ash specified in Table 1 more than half fill the crucible, need to set the pre-ashing procedure in instrument before the test.

NOTE High-bulk materials can be compressed into tablets, which can then be broken up into fragments of appropriate size.The samples can be dried according to the corresponding material specification.

7.6.4 After introducing the samples, start the ash determination program (see 7.6.2), the instrument is started and begins the heating cycle to the pre-set temperature. The loss of weight of each sample is recorded during the ashing process until two weighings with a time interval of 30 min do not differ from each other by more than 0,5 mg.The ash determination is finished after all samples have reach the constant mass condition.

The ash content of all samples is automatically calculated and reported by the instrument.

NOTE An instrument can be designed in such a way that it can only accommodate part of the test portion masses given in Table 1 in order to increase efficiency.

8 Number of tests

The number of tests and the permissible scatter of results should normally be stated in the particular standard for each material. If such information is not available, carry out two determinations, repeating the test as necessary until the results of two successive determinations do not differ from each other by more than 10 % of their mean. A single test can be performed if agreed upon among the parties involved.

9 Expression of results

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

$$\frac{m_1}{m_0} \times 100\% = \text{A}\% \tag{1}$$

where

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

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

A% is the result of ash content.

For A > 1, A should be reported in 2 decimals.

For A < 1, A should be reported in 3 decimals.

10 Precision

Precision data have been determined by testing involving eight laboratories and eight different materials. The results are summarized in Table 2.