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Plastics — Determination of bound acrylonitrile content in the continuous phase of acrylonitrile-butadiene-styrene (ABS) by Dumas combustion method

Plastiques — Détermination de la teneur en acrylonitrile lié dans la phase continue d'acrylonitrile-butadiène-styrène (ABS) par la méthode de combustion Dumas

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Foreword

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This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*.

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 bound acrylonitrile content in the continuous phase of acrylonitrile-butadiene-styrene (ABS) by Dumas combustion method

1 Scope

This document specifies a method for the determination of bound acrylonitrile content in the continuous phase of acrylonitrile-butadiene-styrene (ABS) copolymer using Dumas combustion method. This document is applicable to ABS resin with a mass fraction of bound acrylonitrile content in continuous phase between 5 % and 50 %.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes the 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 https://www.electropedia.org/

4 Principle

The ABS samples are dispersed in acetone. The dissolved continuous phase is separated from the dispersed elastomeric phase using a high-speed centrifuge. The separated supernatant is precipitated by methanol and then washed by *n*-hexane. The nitrogen content of the precipitate is determined through Dumas combustion method and the content of acrylonitrile in the continuous phase is calculated.

5 Reagents

5.1 Reference materials:

Combustible organic compounds with known nitrogen content, purity ≥ 99,99 %.

EXAMPLE Acetanilide, ethylenediaminetetraacetic acid (EDTA), aspartic acid, atropine, etc.

5.2 Oxygen gas, purity ≥ 99,99 % or in accordance with the analyser manufacturer's instruction.

5.3 Carrier gas, helium, argon or carbon dioxide, purity ≥ 99,995 % or in accordance with the analyser manufacturer's instruction.

5.4 Acetone, volume fraction ≥ 99,8 %.

5.5 Methanol, volume fraction ≥ 99,8 %.

5.6 N-hexane, volume fraction ≥ 95 %.

6 Apparatus

6.1 Automatic analyser

The automatic analyser consists of the following components:

a) a **combustion unit**, capable of complete combustion of the sample in an atmosphere of high-purity oxygen;

b) an **oxygen feeder**, capable of feeding enough high purity oxygen for complete combustion;

c) a **reduction unit**, capable of fully converting liberated nitrogenous compounds to nitrogen gas;

d) an **absorber** (or another type of separator) of by-products, capable of separating nitrogen from other combustion products;

NOTE 1 When helium or argon is used as the carrier gas, this unit normally separates nitrogen from carbon dioxide and water; when carbon dioxide is used as the carrier gas, this unit normally separates nitrogen from water.

e) a **thermal conductivity detector (TCD)**, capable of detecting nitrogen formed;

f) a **microprocessor**, capable of calibrating the apparatus with a reference material and of converting the detector response into the mass of nitrogen in the sample.

6.2 Tin boat, used in pair with the automatic analyser.

NOTE 2 Other sample containers provided by the automatic analyser manufacturer also apply.

6.3 Centrifuge, capable of centrifuging 50 ml tube with a speed of 18 000 r/min or higher while maintaining the temperature within 4 °C ± 0,1 °C.

6.4 Centrifuge tube, polycarbonate, 50 ml capacity, max acceleration tolerance ≥ 35 000 g.

6.5 Balance, depending on the typical specimen mass for the automatic analyser (6.1), choose one of the two following specifications: for specimen mass less than or equal to 50 mg, the balance shall be capable of weighing to the nearest 0,001 mg with a maximum capacity of no less than 2 g; for specimen mass more than 50 mg, the balance shall be capable of weighing to the nearest 0,01 mg with a maximum capacity of no less than 2 g.

6.6 Round bottom flask, condenser and hot plate stirrer, glass, round bottom flask with 250 ml capacity with proper joints with the condenser, the hot plate stirrer is capable of heating up to at least 200 °C.

6.7 Graduated cylinder, glass, 50 ml.

6.8 Pipette, 1 ml to 5 ml adjustable pipette with tips.

6.9 Buchner funnel, filter paper, filter bottle and pump, 60 ml capacity Buchner funnel and filter paper with 30 µm to 50 µm pore size, cut to proper shape and size to fit the funnel. A respective filter bottle and pump shall be prepared as well.

6.10 Vacuum oven, capable of maintaining a temperature of 60 °C ± 1 °C and pressure of 1 kPa ± 0,5 kPa.

7 Sampling and preparation of the specimen

WARNING — Centrifuge tubes shall be balanced before the centrifuge procedure.

7.1 Preparation of cold methanol and settlement of centrifuge

Mark two 50 ml centrifuge tubes with B1 and B2. Add 30 ml of methanol to each of them, then cool them to -10 °C or lower. Set temperature control of centrifuge to 4 °C ± 0,1 °C.

7.2 Sample dispersion

Prepare two round bottom flasks (6.6). To each flask, add a magnetic bar, 2,0 g (to the nearest 0,01 g) of dried particles of moulding compound (around 3 mm × 3 mm × 3 mm) and 70 ml of acetone. Set up the condenser and put the flasks on two hot plate stirrers. Reflux the mixture for at least 30 min, or until resin samples are well dispersed. The completely dispersed mixture shall be a milky, stable, homogeneous mixture. Extend the time of reflux if necessary. Remove the flasks from the hot plate stirrers and cool them to room temperature.

7.3 Centrifuge separation

After cooling, transfer 35 ml of the mixture from each flask prepared in 7.2 into two centrifuge tubes (6.4) marked with A1 and A2, respectively. Balance A1 and A2 with acetone. The masses difference between the two tubes after balancing shall be smaller than 10 mg, or any other value specified by the centrifuge manufacturer. Centrifuge A1 and A2 with a speed of 18 000 r/min for at least 30 min for complete separation. Extend the time of centrifuge if the supernatant is still opaque.

7.4 Precipitation of continuous phase

Dropwise pipette 3 ml of clear supernatant from each tube prepared in 7.3 into B1 and B2 prepared in 7.1, respectively, while gently shaking the tubes for complete precipitation. Balance B1 and B2 with cold methanol. The mass difference between the two tubes after balancing shall be smaller than 10 mg, or any other value specified by the centrifuge manufacturer.

7.5 Centrifuge and work-up

Centrifuge B1 and B2 prepared in 7.4 with a speed of 1 000 r/min for 5 min. Carefully decant and discard supernatant from both tubes. Add 35 ml *n*-hexane into B1 and B2. Stir the precipitate in B1 and B2 with a round-end glass rod for 1 min, and then filter the suspension. Without separating from filter paper, dry the precipitate under 60 °C and 1 kPa ± 0,5 kPa for 1 h. Remove dried precipitate from filter paper. The dried precipitate from both tubes are used as parallel specimens for Dumas test. Depending on the content of continues phase in the sample, the mass of the specimen prepared in this step is among 50 mg to 100 mg. Procedure from 7.4 to 7.5 can be repeated up to five times, and the specimen prepared can be combined to prepare specimen with larger mass.

NOTE Repetitive precipitation and work up is especially useful for Dumas test with larger mass of specimen, i.e. 100 mg and up.

8 Procedure

8.1 Calibration

8.1.1 General

The analyser shall be calibrated or adjusted before each batch of samples, taking into account the manufacturer's instructions.

8.1.2 Instrument set up

Set up and stabilize the automatic analyser (6.1) according to the manufacturer's instruction.

8.1.3 Setting up calibration curve

8.1.3.1 Choosing calibration points

Prepare a set of calibration samples using reference material (5.1). At least 5 calibration samples with different masses shall be prepared. The range of the sample set shall evenly expand in a way that the range of the absolute nitrogen content of the sample set well covers the potential target samples.

EXAMPLE When using acetanilide as reference material, a calibration curve prepared with the following set could serve the purpose in most cases: 0,5 mg, 0,8 mg, 1,2 mg, 1,7 mg, 2,3 mg and 3,0 mg. The mass selection of calibration samples could vary depending on the reference material and apparatus used.

8.1.3.2 Setting up calibration curve

Each calibration sample is prepared and tested according to the same procedure of 8.2 for at least three times in accordance with the instruction of the analyser manufacturer. Establish linear regression between the average nitrogen signal strength of each calibration sample and their absolute nitrogen contents. A valid calibration curve shall have a correlation coefficient no less than 0,995. This calibration curve is valid until the calibration factor calculated in 8.1.3.3 exceeds the range of 0,98 to 1,02.

8.1.3.3 Calibration factor determination

Calibration factor determination shall be carried out before testing every batch of specimens. To do so, three successive tests using reference material are carried out. The absolute nitrogen content of the three tests are calculated according to the calibration curve set up in 8.1.3.2. Calculate the nitrogen content of each sample of reference material by dividing the absolute nitrogen content by the mass of the sample. The mean result of three tests (w_{NC}) is compared with the labelled nitrogen content of the reference material (w_{NR}) according to Formula (1):

$$f = \frac{w_{NR}}{w_{NC}} \tag{1}$$

where:

f is the calibration factor;

w_{NR} is the labelled nitrogen content of the reference material used, in mass %;

w_{NC} is the mean result of nitrogen content of three tests using reference material samples, in mass %.

8.2 Measurement

8.2.1 Prepare the apparatus in accordance with the manufacturer's instructions. Proper calibration as described in 8.1 shall be carried out before the test. Table 1 gives an overview of recommended test parameters.

Table 1 — Recommended test parameters

Parameter	Unit	Value
Combustion temperature	°C	900 – 1 050
Reduction temperature	°C	550 – 700
Oxygen pressure	MPa	0,17 – 0,20
Carrier gas pressure	MPa	0,10 – 0,20

NOTE Test parameters can be adjusted according to the manufacturer's instructions for the apparatus.

8.2.2 Take part of the specimen prepared in 7.5 as the test portion, and weigh it to the nearest 0,001 mg for specimen masses less than or equal to 50 mg or 0,01 mg for specimen masses above 50 mg using balance (6.5) in a tin boat (6.2). The mass of the test portion shall fit the requirement of the manufacturer's instruction of the automatic analyser (6.1).

8.2.3 Flat, fold and carefully press the tin boat to drive out the air between the tin boat and the specimen, so that they are in close contact. Gently shake the folded tin boat to remove dust or dirt on the surface.

8.2.4 Place the tin boat with the specimen prepared in 8.2.3 in the automatic analyser (6.1) that has been readily set up. Start the analyser determination programme according to the manufacturer's instruction, and record the nitrogen content of the specimen w_N.

8.2.5 When conducting batch tests, the calibration factor should be re-calculated according to 8.1.3.3 for every ten unknown specimens.

8.3 Calculation

Calculate the bound acrylonitrile content $w_{AN,b}$ of the sample, in mass %, using Formula (2):

$$w_{AN,b} = w_N \times f \times 3{,}79 \quad (2)$$

where:

$w_{AN,b}$ is the content of bound acrylonitrile in continuous phase, in mass %;

w_N is the nitrogen content in continuous phase, in mass %;

f is the calibration factor.

The test result is the mean value from two successive tests of bound acrylonitrile content. Express the result in two decimal places.

9 Precision

9.1 General

Precision data have been determined by testing involving seven laboratories and nine different ABS samples The results, as determined by statistical examination according to ISO 5725-2[1], are given in 9.2 and 9.3. A summary of precision data can be found in Annex A.

9.2 Repeatability, *r*

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will not be greater than 0,64 % in more than 5 % of cases.

9.3 Reproducibility, *R*

The absolute difference between two independent single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will not be greater than 1,38 % in more than 5 % of cases.

10 Test report

The test report shall include the following information:

a) a reference to this document, including its year of publication, i.e., ISO 24048:2022;

b) full identification of the plastic sample tested;

c) full identification of the apparatus used;

d) reference material used and calibration factor;

e) test parameter used;

f) result of the test;

g) date of the test;

h) any deviations from the procedure;

i) any unusual features observed.

Annex A
(informative)

Summary of precision data

Precision data have been determined by testing involving seven laboratories and nine different ABS samples. All of the precision data have been calculated according to ISO 5725-2. The results of bound acrylonitrile content in the continuous phase are given in Table A.1.

Table A.1 — Precision data for bound acrylonitrile content in the continuous phase

No.	Sample	$w_{AN,b}$ %	s_r	s_R
1	ABS-1	27,53	0,344	0,517
2	ABS-2	25,25	0,211	0,420
3	ABS-3	24,42	0,129	0,392
4	ABS-4	27,82	0,190	0,520
5	ABS-5	24,62	0,460	0,654
6	ABS-6	23,52	0,146	0,420
7	ABS-7	23,98	0,086	0,380
8	ABS-8	24,45	0,177	0,454
9	ABS-9	26,27	0,281	0,605

No. is the experimental entry;

sample is the sample name;

$w_{AN,b}$ (%) is the general mean results of the content of bound acrylonitrile in continuous phase ;

s_r is the repeatability standard deviation;

s_R is the reproducibility standard deviation;

r (%) is the repeatability limit;

R (%) is the reproducibility limit.

An examination of the data in Table A.1 does not indicate any clear dependence and average values are used. The precision of the method, in mass fraction, is:

— repeatability standard deviation, s_r=0,225 %,

— reproducibility standard deviation, s_R=0,485 %,

— the repeatability limit under 95 % confidence: r=2,83 s_r =0,64 %,

— the reproducibility limit under 95 % confidence: R=2,83 s_R =1,38 %.