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МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Plastics — Styrene/acrylonitrile copolymers — Determination of residual acrylonitrile monomer content — Gas chromatography method

Plastiques — Copolymères styrène/acrylonitrile — Dosage de l'acrylonitrile monomère résiduel — Méthode par chromatographie en phase gazeuse

Reference number
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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Plastics — Styrene/acrylonitrile copolymers — Determination of residual acrylonitrile monomer content — Gas chromatography method

1 Scope and field of application

This International Standard specifies a method for determining the content of residual acrylonitrile monomer in styrene/acrylonitrile copolymers and blends by gas chromotography. Bearing in mind that gas chromatography offers a wide range of possible conditions, the method specified in this International Standard is that shown to have been suitable in practice.

2 Reference

ISO 2561, *Plastics — Determination of residual styrene monomer in polystyrene by gas chromatography.*

3 Principle

Dissolution of a test portion in dimethylformamide and injection of a small volume of the solution into a gas chromatograph equipped with flame ionization detector to obtain separation and detection of volatile components. The solvent contains a known amount of propionitrile or acetonitrile as an internal standard for quantitative evaluation. With this method, a lower detection limit of the order of 3 parts per million (ppm) of acrylonitrile in the copolymer may be expected. For obtaining a lower detection limit of the order of 1 ppm, an alternative method is specified in the annex. In this method, the test portion is dissolved in *N*,*N*-dimethylacetamide, propylene carbonate or ethylmethylketone, and the solution is injected into a gas chromatograph equipped with nitrogen-phosphorus detector. The solvent also contains propionitrile as an internal standard.

4 Reagents

During the analysis, use only reagents of recognized analytical grade. Special safety precautions shall be observed when handling the following reagents, especially acrylonitrile.

4.1 Dimethylformamide, of purity such that no impurity peaks occur within the range of retention times of the substances to be determined.

4.2 Propionitrile.

Acetonitrile may be used as internal standard instead of propionitrile, if it has been shown that the same results are obtained.

4.3 Acrylonitrile.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Gas chromatograph, with flame ionization detector and recorder.

Gas chromatographic operating conditions

Column : Stainless steel or glass tubing, 1 to 2 m length, 3 to 4 mm internal diameter is recommended. The column is packed with Porapak Q[1)] of particle size from 50 to 100 mesh. To prevent non-volatile material contained in the test solution from entering the column, suitable means shall be provided, such as a glass liner in the injection port or a pre-column of 5 cm length with the same packing as the column and mounted in such a way as to allow frequent renewal.

The method of packing is not specified, but shall be such as to obtain a satisfactory separation efficiency of the column. The column shall be aged for 24 h at 230 °C with gas flow. Change in column dimensions is permissible only if this has proved to give the same results.

Column and, if applicable, pre-column temperature : 160 to 180 °C isothermal.

Temperature of injection port : 200 to 230 °C.

Temperature of detector compartment : 230 °C.

Carrier gas : helium (or nitrogen) as specified in ISO 2561.

Flow rate of carrier gas : to be adjusted such that propionitrile is eluted in 5 to 10 min.

1) Porapak Q is the trade-name of a product of Millipore Corporation. This information is given for the convenience of the users of this International Standard and does not constitute an endorsement of this product by ISO. By agreement between the interested parties alternative products of equal performance may be used.

Flame ionization detector in which the hydrogen and air flow rates are adjusted such as to give

a) high sensitivity of response;

b) linear relationship between response and concentration in the measured range;

c) only insignificant effect of small changes in flow rates on response and sensitivity.

Recommended recorder speed : 1,0 or 1,27 cm/min.

The silicone rubber septum for injection shall have a layer of polytetrafluoroethylene on each side in order to delay attack by dimethylformamide. If the septa available have a protective layer on one side only, two shall be used. Even so, it will be necessary to renew them frequently.

5.2 Micro-syringes, of capacity 1 to 50 µl.

5.3 Analytical balance, accurate to within 0,5 mg.

6 Preparation of test sample

The sample may be taken from material in the form of powder, pellets, or a moulding. Large pieces shall be reduced to fragments sufficiently small for weighing a sample amount as close as possible to 1,0 g. This size reduction operation shall not cause the sample to become heated.

7 Procedure

7.1 Preparation of the internal standard solution

Transfer exactly 1 ml of the propionitrile (4.2) by means of a pipette into a 100 ml one-mark volumetric flask and dilute to the mark with the dimethylformamide (4.1), both reagents having been kept at 20 ± 1,0 °C. Transfer with a pipette exactly 5 ml of the solution thus obtained into another 100 ml one-mark volumetric flask and dilute to the mark with the dimethylformamide. If necessary, further dilute this diluted solution with dimethylformamide in compliance with the acrylonitrile concentration of the polymer sample, in order to obtain the same sensitivity of the detector. During the dilution process, maintain the liquids at a temperature of 20 ± 1,0 °C.

7.2 Preparation of the sample solution

Weigh, to the nearest 1 mg, approximately 1 g of the polymer sample and transfer to a 20 ml one-mark volumetric flask fitted with a ground glass stopper. Add approximately 15 ml of the dimethylformamide (4.1). After closing the flask, allow the polymer to dissolve, with shaking if necessary. After complete dissolution, add exactly 1 ml of the internal standard solution, prepared according to 7.1 and kept at 10 ± 1,0 °C, from a pipette and dilute to the mark with the dimethylformamide. Keep the solution for injection into the gas chromatograph.

7.3 Preparation of acrylonitrile solutions for calibration

7.3.1 Preparation of a stock standard solution

Weigh, to the nearest 1 mg, 0,1 ml of the acrylonitrile (4.3) together with an appropriate amount of the dimethylformamide (4.1) in a 100 ml one-mark volumetric flask and dilute to the mark with the dimethylformamide which has been kept at 20 ± 1,0 °C. Transfer with a pipette exactly 10 ml of the solution thus obtained into another 100 ml one-mark volumetric flask and dilute to the mark with the dimethylformamide. If necessary, transfer with a pipette exactly 20 ml of this diluted solution into another 100 ml one-mark volumetric flask and dilute to the mark with the dimethylformamide, for the same reason as mentioned in 7.1. Maintain the temperature of the liquid at 20 ± 1,0 °C during the dilution process. Weigh the acrylonitrile, which is very volatile, into the already weighed amount of dimethylformamide in order to reduce its vapour pressure.

7.3.2 Preparation of calibration solutions

Transfer an appropriate amount of the acrylonitrile solution prepared according to 7.3.1 and kept at 20 ± 1,0 °C into a 20 ml one-mark volumetric flask, add exactly 1 ml of the internal standard solution (7.1) and dilute to the mark with the dimethylformamide (4.1). As appropriate volumes of acrylonitrile solution (7.3.1), the following volumes are recommended :

0,5 — 1,0 — 1,5 and 2,0 ml

Keep the solutions for injection into the gas chromatograph.

7.4 Gas chromatographic recording of sample and calibration solutions

According to the sensitivity of the gas chromatograph used, inject a suitable volume of the sample solution prepared according to 7.2 or of the calibration solution prepared according to 7.3. The volume injected is not critical for the calculation of results, but shall be identical for corresponding sample and calibration solutions. Record the calibration gas chromatograms always with the same sensitivities for component and internal standard peaks as those used for the respective sample gas chromatograms.

Develop the gas chromatogram until acrylonitrile and the internal standard have been eluted completely, but not after the initial slope of the dimethylformamide peak appears. Then flush the column (no back-flushing operation is required with this method) until the normal baseline is restored.

7.5 Evaluation of gas chromatographic peaks

The retention times of acrylonitrile and propionitrile must be known, at least relative to each other. The values are dependent on column length, column temperature and other parameters, and they vary according to the density of the column packing and the age of the column.

The peak areas of acrylonitrile and propionitrile are determined by :

a) electronic integration, or

b) area estimation on the basis of the equation

area (A) = peak height × width at half-height (see ISO 2561), or

c) planimetry.

Use of method b) is recommended only for peaks with a horizontal base line and having a shape as close as possible to that of an isosceles triangle, in order to minimize the inaccuracy of measurement. This method has been found appropriate for the analytical procedure described herein. For routine determinations, peak height measurements of both sample and calibration chromatograms will be sufficient. The method of peak evaluation chosen must be identical for corresponding peaks of sample and calibration solutions.

8 Expression of results

8.1 Calculation of results from a calibration graph

If several calibration solutions with different concentrations of acrylonitrile are available, draw a calibration graph by plotting the ratios of peak areas, A'_a/A'_s, against the respective concentrations in milligrams per millilitre.

With the corresponding ratios determined from the sample solution, A_a/A_s, read the concentration of acrylonitrile in the sample solution, c_a, from the calibration graph. Calculate P_a, the content of acrylonitrile in the polymer sample expressed in parts per million (ppm) by mass, from c_a using the equation

$$P_a = \frac{2\,c_a}{m_p} \times 10^4 \qquad \dots (1)$$

where

A'_a is the peak area of acrylonitrile in the calibration solution;

A'_s is the peak area of the internal standard (propionitrile) in the calibration solution;

A_a is the peak area of acrylonitrile in the sample solution;

A_s is the peak area of the internal standard (propionitrile) in the sample solution;

c_a is the concentration, in milligrams per millilitre, of acrylonitrile in the sample solution;

m_p is the mass, in grams, of the polymer sample;

P_a is the content of acrylonitrile in the polymer sample, expressed in parts per million by mass, abbreviated as ppm.

For routine determinations, peak heights may be used instead of peak areas A'_a, A'_s, A_a and A_s, if this has been verified to lead to the same results.

8.2 Calculation of results from a single point calibration

Provided that a linear relationship exists between peak areas and respective concentrations of acrylonitrile, P_a may be calculated as follows :

$$P_a = \frac{m'_a\,(A_a/A_s)}{m_p\,(A'_a/A'_s)} \times 10^3 \qquad \dots (2)$$

where

A'_a, A'_s, A_a, A_s, m_p and P_a are as defined in 8.1;

m'_a is the mass, in milligrams, of acrylonitrile in 20 ml of the calibration solution (see 7.3).

8.3 Precision of measurement and sensitivity

The spread of results obtained from replicate measurements of acrylonitrile concentration in a calibration sample shall not exceed ± 20 % of the mean result or 5 ppm absolute, whichever is the greater. A lower limit of detection of the order of 3 ppm may be expected from the method.

9 Test report

The test report shall include the following particulars :

a) reference to this International Standard;

b) complete identification of the polymer tested;

c) any deviation of the gas chromatographic equipment and procedure from the standard equipment with flame ionization detector and procedure specified in the main part of this International Standard, especially if the method described in the annex of this International Standard has been applied;

d) content of acrylonitrile monomer, expressed as parts per million (ppm) by mass of the polymer sample and rounded off to an integral number;

e) the limit of error as determined from the spread of results (see 8.3).

Annex

Method for determining contents lower than 3 ppm

(This annex forms an integral part of the Standard.)

A.1 General

For toxicological reasons, acrylonitrile copolymers must contain the minimum possible amount of residual acrylonitrile monomer. In certain cases, a limit of detection lower than 3 ppm may therefore be required from the analytical method. For these cases, the method as specified in this annex may be applied; its lowest level of detection under optimum conditions is approximately 1 ppm.

A.2 Reagents (see clause 4)

Reagent grade chemicals shall be used in all tests. If these are not available, other grades may be used only if it has been ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Special safety precautions shall be observed when handling the following reagents, especially acrylonitrile.

A.2.1 ***N,N*-Dimethylacetamide (DMAC), propylene carbonate (PC)** or **ethylmethylketone,** as solvents.

NOTE — Prior to use, inject 5 µl of solvent and obtain a gas chromatogram under the conditions of A.5.4, to demonstrate absence of coeluting materials at the acrylonitrile or internal standard retention times under the conditions of analysis.

A.2.2 Propionitrile.

For the use of **acetonitrile** as internal standard, see 4.2.

A.2.3 Acrylonitrile.

A.3 Apparatus (see clause 5)

Ordinary laboratory apparatus and

A.3.1 Gas chromatograph, with nitrogen-phosphorus detector, heated injection port with removable glass liners, back-flush capability, and recorder.

Gas chromatographic operating conditions

Column : Two columns of stainless steel, 61 and 183 cm length, respectively, and 3,2 mm outer diameter. The 61 cm column is filled with 80/100 mesh Porapak QS[1], the 183 cm column with 80/100 mesh Porapak S[1]. Both columns are connected by means of a "tee" having 3,2 mm inner diameter and attached to a back-flush assembly as shown in the figure. The back-flush will be effective in the shorter column as soon as the on/off valve allows the carrier gas from line B to enter injector B, and the septum is removed from injector A. The column system shall be conditioned overnight at 190 °C.

NOTE — Other column packings may be used for substitution after suitable evaluation to determine that no interfering peaks occur. Use of more volatile solvents (for example ethylmethylketone) could avoid the necessity to back-flush.

Column temperature : 165 °C isothermal.

Temperature of injection port : 200 °C.

Temperature of detector block : 250 °C.

Carrier gas : helium (or nitrogen).

Flow rate of carrier gas : Optimize the carrier gas flow rate (20 to 30 ml/min) for minimum peak broadening consistent with fast analysis time. Adjust the carrier gas flow rate at the exit of the 183 cm column (using a soap film flowmeter and a stop-watch) to be identical in the forward flush and back-flush positions of the system.

Nitrogen-phosphorus detector in which the settings for air flow, hydrogen flow and feed power supply must be adjusted for maximum sensitivity with minimum noise.

Recorder sensitivity : 1 mV full scale.

A.3.2 Micro-syringes, of capacity 5 to 100 µl.

A.3.3 Analytical balance, capable of weighing to ± 0,1 mg.

A.3.4 Soap film flowmeter and **stop-watch.**

A.3.5 Laboratory shaker.

A.4 Preparation of test sample (see clause 6)

This clause corresponds to clause 6. The mass of sample required is 2 ± 0,1 g.

A.5 Procedure (see clause 7)

A.5.1 Preparation of the internal standard solution

Partially fill a 100 ml one-mark volumetric flask with the solvent (A.2.1). Weigh a micro-syringe (A.3.2) loaded with approximately 15 mg of the propionitrile (A.2.2). Transfer the contents

1) Porapak QS and Porapak S are trade-names of products of Millipore Corporation. This information is given for the convenience of the users of this International Standard and does not constitute an endorsement of these products by ISO. By agreement between the interested parties alternative products of equal performance may be used.

of the micro-syringe to the volumetric flask and immediately reweigh the micro-syringe to determine the mass of internal standard by difference. Dilute the flask contents to the mark with pure solvent and mix thoroughly. Dilute 10,0 ml of this solution to 1 litre with solvent.

A.5.2 Preparation of the sample solution

Weigh, to the nearest 1 mg, 2 ± 0,1 g of the polymer sample into a tared 25 ml bottle, add 20,0 ml of the internal standard solution prepared according to A.5.1 and cap the bottle immediately. Place the bottle on a mechanical shaker and mix until the sample has completely dissolved. Keep the solution for injection into the gas chromatograph.

A.5.3 Preparation of acrylonitrile solutions for calibration

A.5.3.1 Preparation of a stock standard solution

Weigh a 25 ml one-mark volumetric flask partially filled with solvent. Using a 50 µl micro-syringe, transfer 25 µl (approximately 20,2 mg) of the acrylonitrile (A.2.3) to the flask and reweigh. Dilute to volume with solvent and calculate the concentration of acrylonitrile, in milligrams per millilitre, of this stock standard. Prepare fresh stock standard every 7 to 10 days.

A.5.3.2 Preparation of calibration solution

Transfer exactly 20,0 ml of the internal standard solution prepared according to A.5.1 to a bottle equipped with a septum closure cap, and inject, using a 50 µl micro-syringe, exactly 25 µl of stock standard solution prepared according to A.5.3.1 through the cap. Keep the solution for injection into the gas chromatograph. Prepare a new calibration solution each time a fresh internal standard solution is prepared.

A.5.4 Gas chromatographic recording of sample and calibration solutions

Sub-clause 7.4 applies. In addition, back-flush technique is applied in order to avoid the full elution time of the solvent used. In the following description, reference is made to the figure.

Before injection, insert the septum and glass liner into injector A and switch the valve to the OFF position. Inject a suitable volume of the sample into injector A. At a pre-determined time (see the note), remove the septum of injector A and switch the valve to the ON position to connect the carrier line with injector B. The back-flush through the short column is now effective. Meanwhile, replace the glass injection port liner with a clean one. At the end of the back-flush time (which should be four times as long as the forward flush), switch the valve in carrier line B to the OFF position to stop the back-flush flow and replace the septum on injection port A. Allow at least 2 min for the baseline to equilibrate. Make a new injection as soon as the normal baseline is established.

NOTE — The optimum time for starting the back-flush is determined empirically by repeated injections of calibration solution with incresing back-flush times. The optimum is reached at a minimum time after which no increase in acrylonitrile or propionitrile response or further increase of back-flush time is observed.

A.5.5 Evaluation of gas chromatographic peaks

See 7.5.

A.6 Expression of results

P_a, the content of acrylonitrile in the polymer sample expressed in parts per million by mass, may be calculated from equation (2) in 8.2. A_a, A_s, A'_a, A'_s and m_p have the same meaning as indicated in 8.1; m'_a is the mass, in milligrams, of acrylonitrile injected into 20,0 ml of the internal standard solution when preparing the calibration solution according to A.5.3.2.

For applicability of equation (2), a constant ratio R of response factors for acrylonitrile and propionitrile must exist in sample and calibration solution :

$$R = \frac{\text{Peak area of acrylonitrile} \times \text{mass of propionitrile}}{\text{Peak area of propionitrile} \times \text{mass of acrylonitrile}}$$

If necessary, adjust the concentrations of propionitrile in the internal standard solution and of acrylonitrile in the calibration solution to closely approximate the range of acrylonitrile concentrations expected in the sample.

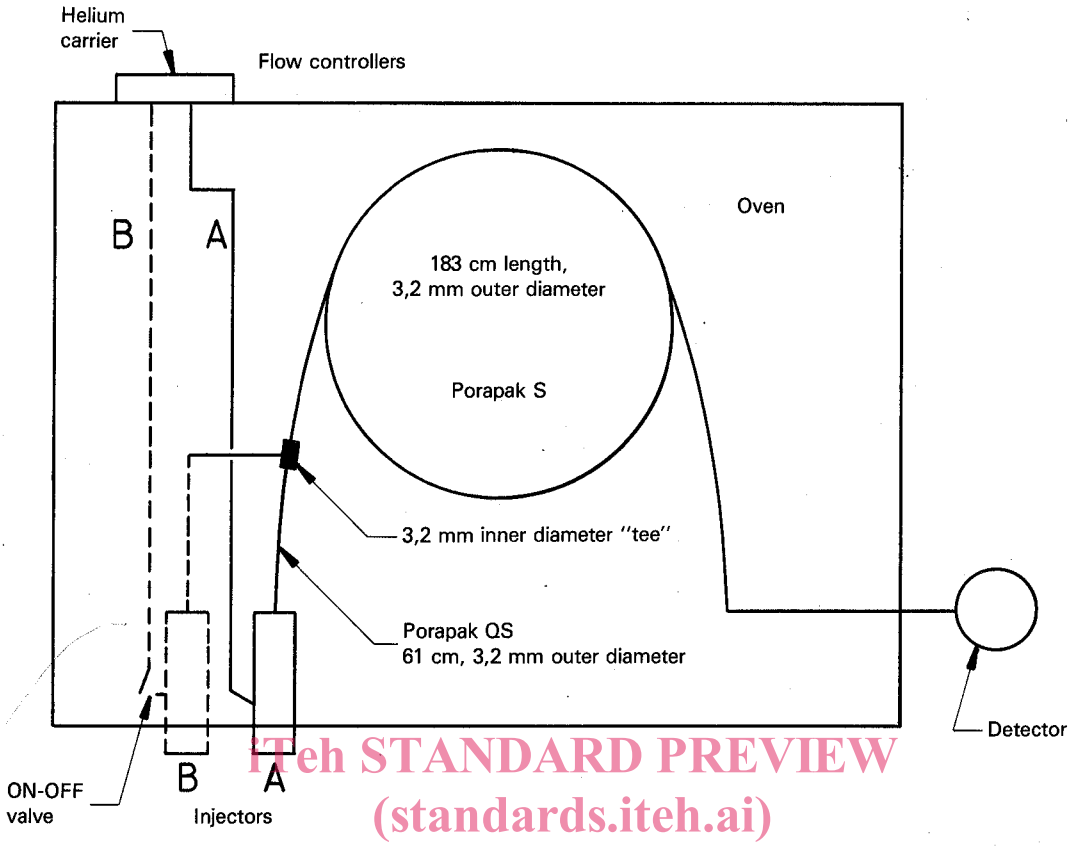

Figure — Typical back-flush assembly

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