# INTERNATIONAL STANDARD

# ISO 4581

Second edition
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# 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 voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 4581 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This second edition cancels and replaces the first edition (ISO 4581:1987), the annex of which has been technically revised.

Annex A forms an integral part of this International Standard.

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

## 1 Scope

This International Standard specifies a method for determining the content of residual acrylonitrile monomer in styrene/acrylonitrile copolymers and blends by gas chromatography. 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 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 2561:1974, *Plastics — Determination of residual styrene monomer in polystyrene by gas chromatography.*

## 3 Principle

A test portion is dissolved in dimethylformamide and a small volume of the solution injected into a gas chromatograph equipped with flame ionization detector to separate and detect the 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. To obtain a lower detection limit of the order of 0,3 ppm to 0,4 ppm, an alternative method is specified in annex A. In this method, the test portion is dissolved in propanediol-(1,2)-carbonate, and the solution is injected into a gas chromatograph equipped with a thermionic nitrogen detector. The solution 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, plus the following:

**5.1 Gas chromatograph**, with flame ionization detector and recorder.

**Gas-chromatographic operating conditions**

Column: Stainless-steel or glass tubing, 1 m to 2 m length, 3 mm to 4 mm internal diameter is recommended. The columm shall be packed with

Porapak Q[1] of particle size from 50 mesh 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 °C to 180 °C isothermal.

Temperature of injection port: 200 °C to 230 °C.

Temperature of detector compartment: 230 °C.

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

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

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

a) high sensitivity of response;

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

c) an only insignificant effect of small changes in flowrates on response and sensitivity.

Recommended recorder speed: 1,0 cm/min 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 Microsyringes**, of capacity of 1 µl 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 to permit a sample amount as close as possible to 1,0 g to be weighed out. 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 propionitrile (4.2) by means of a pipette into a 100 ml one-mark volumetric flask and dilute to the mark with dimethylformamide (4.1), both reagents having been kept at 20 °C ± 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 dimethylformamide. If necessary, further dilute this diluted solution with dimethylformamide, depending on the acrylonitrile concentration in the polymer sample, in order to be able to use the same detector sensitivity. During the dilution process, maintain the liquids at a temperature of 20 °C ± 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 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 in accordance with 7.1 and kept at 20 °C ± 1,0 °C, from a pipette and dilute to the mark with 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 acrylonitrile (4.3) together with an appropriate amount of dimethylformamide (4.1) into a 100 ml one-mark volumetric flask and dilute to the mark with dimethylformamide which has been kept at

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[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.

20 °C ± 0,1 °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 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 dimethylformamide, for the same reason as mentioned in 7.1. Maintain the temperature of the liquid at 20 °C ± 0,1 °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 volume of the acrylonitrile solution prepared in accordance with 7.3.1 and kept at 20 °C ± 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 dimethylformamide (4.1). As appropriate volumes of acrylonitrile solution (7.3.1), the following volumes are recommended:

0,5 ml – 1,0 ml – 1,5 ml and 2,0 ml

Keep the solutions for injection into the gas chromatograph.

## 7.4 Gas-chromatographic recording of sample and calibration solutions

Depending on the sensitivity of the gas chromatograph used, inject a suitable volume of the sample solution prepared in accordance with 7.2 or of the calibration solution prepared in accordance with 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,

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 baseline 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 shall 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

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

where

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

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

$A_a$ is the peak area for acrylonitrile in the sample solution;

$A_s$ is the peak area for 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:

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

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) a reference to this International Standard;

b) all details necessary for 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 of the method described in annex A of this International Standard has been applied;

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

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

# Annex A
(normative)

# Method for determining contents lower than 3 ppm by means of headspace gas chromatography using a thermionic nitrogen detector

## A.1 General

For toxicological reasons, acrylonitrile copolymers must contain the minimum possible amount of residual acrylonitrile monomer. In certain cases, a detection limit 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[2]; its lower limit of detection is expected to be between 0,3 ppm and 0,4 ppm. For the principle of the method, see clause 3.

## A.2 Reagents

For purity and safety precautions, see clause 4.

**A.2.1 Propanediol-(1,2)-carbonate (PC)**, boiling point between 241 °C and 243 °C.

**A.2.2 Propionitrile**.

**A.2.3 Acrylonitrile**.

**A.2.4 Reference polymer**, i.e. polymer powder, pellets or small fragments freed from acrylonitrile monomer by heat treatment in a vacuum oven at 100 °C for about 5 days.

## A.3 Apparatus

Ordinary laboratory apparatus, plus the following.

**A.3.1 Gas chromatograph**, with a thermionic nitrogen detector, heated injection port and/or automatic vapour-phase sample inlet.

**Gas-chromatographic operating conditions**

Column: Stainless steel of 4 m length and 2,5 mm internal diameter, with a packing of 15 % polyethylene glycol (molecular mass 1 500) on 50 mesh to 75 mesh kieselguhr. Other column packings of equal performance may be used.

Column temperature: 70 °C isothermal.

Temperature of injection port: 140 °C.

Temperature of detector block: 140 °C.

Carrier gas: helium.

Flowrate of carrier gas at 1,0 atm pressure: 25 ml/min, to be adjusted for optimum peak appearance consistent with rapid analysis. Under these conditions, the retention time of acrylonitrile is about 340 s, that of propionitrile about 420 s.

Thermionic nitrogen detector, in which the settings for air flow (at 1,5 atm pressure), hydrogen flow (at 2,0 atm pressure) and power supply shall be adjusted for maximum sensitivity with minimum noise.

To optimize the thermionic-detector signal, the manufacturer's instructions shall be followed. The sensitivity of this detector is adversely affected by increasing amounts of substance passing through it. For this reason, the choice of solvents is rectricted to those having low volatility. The head of the detector, which is composed of an alkali-metal salt, shall be renewed as soon as the signal/noise ratio at an acrylonitrile content of 0,5 ppm in the polymer has become less than 2,5.

Automatic sampling conditions for example:

Sampler temperature: 140 °C

Thermostat temperature: 70 °C

Thermostatic equilibration period: 16 h (i.e. overnight)

Sampling time[3]: 5 s

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[2] The method is taken from the *39. Mitteilung des Bundesgesundheitsamtes zur Untersuchung von Kunststoffen*, Bundesgesundheitsblatt, **20**, 162 (1977).

[3] These settings may vary according to the type of instrument used.

Purge time[3]: 30 s

Reset interval[3]: 30 s

**A.3.2 Sample vials**, with septa (butyl type) and aluminium crimp-on caps, 25 ml capacity for automatic sampling, 50 ml capacity for manual sampling.

**A.3.3 Crimper and decapper** for crimp-on caps.

**A.3.4 Microsyringe**, of 10 µl capacity (0,1 µl graduation marks).

**A.3.5 Gas syringe**, of 1 ml capacity (for manual sampling).

**A.3.6 Semi-microbalance**, capable of weighing to 0,01 mg.

## A.4 Preparation of test sample

This clause corresponds to clause 6 and applies both to the sample polymer and to the reference polymer (A.2.4). The mass of sample required is about 0,5 g.

## A.5 Procedure

### A.5.1 Preparation of the internal-standard solution

On the semi-microbalance, weigh out about 50 mg of propionitrile (A.2.2) and transfer to a 50 ml one-mark volumetric flask. Fill the flask to the mark with PC (A.2.1). Transfer exactly 10 ml of this solution, by means of a pipette, to a 1 000 ml volumetric flask and dilute to volume with PC (A.2.1).

### A.5.2 Preparation of acrylonitrile stock and calibration solutions

Weigh about 1,5 mg of acrylonitrile (A.2.3) to the nearest 5 mg into a 50 ml volumetric flask partially filled with PC (A.2.1) and fill to volume. For calibration, dilute this stock solution with PC in a volume ratio such that 5 µl of the final calibration solution will contain an amount of acrylonitrile which is about that expected in the polymer sample.

### A.5.3 Preparation of a reference-sample solution for calibration

Weigh about 0,5 g of monomer-freed reference polymer (A.2.4) to the nearest 0,2 mg into a 25 ml or 50 ml sample vial (A.3.2). Add, by means of a pipette, either 5 ml of PC (A.2.1) or 5 ml of internal standard solution prepared in accordance with A.5.1. Close the vial with a crimp-on cap. After closing, inject 5 µl of the calibration solution prepared in accordance with A.5.2 by means of a 10 µl microsyringe (A.3.4).

During injection of the acrylonitrile calibration solution, the tip of the syringe needle shall be immersed in the PC or the internal-standard solution in order to avoid stripping of acrylonitrile calibration solution when retracting the needle through the septum.

### A.5.4 Preparation of a zero-concentration sample solution

Dissolve monomer-freed reference polymer (A.2.4) in a 25 ml or 50 ml sample vial with either PC (A.2.1) or internal-standard solution (A.5.1) exactly as described in A.5.3, but do not inject acrylonitrile calibration solution into the closed vial.

### A.5.5 Preparation of the polymer-sample solution for acrylonitrile determination

Weigh about 0,5 g of the polymer sample to the nearest 0,2 mg into a 25 ml or 50 ml sample vial (A.3.2). Add either 5 ml of PC (A.2.1) or 5 ml of internal-standard solution prepared in accordance with A.5.1 by means of a pipette. Close the vial with a crimp-on cap.

### A.5.6 Preparation of a solvent blank sample

Transfer 5 ml of PC (A.2.1) or of internal-standard solution prepared in accordance with A.5.1 by means of a pipette into a 25 ml or 50 ml sample vial (A.3.2). Close the vial with a crimp-on cap.

### A.5.7 Gas-chromatographic analysis of solutions

Keep the vials containing sample solution (see A.5.5), reference-sample solution for calibration (see A.5.3), zero-concentration sample solution (see A.5.4) and blank solvent (see A.5.6) for 16 h at a temperature of 70 °C, either in a thermostat bath (when automatic sampling is used) or in an oven (when sampling is performed manually). An example for the settings of the automatic sampler is given in A.3.1. After conditioning, extract a 1 ml portion of the vapour phase from the vials by introduction of a needle through the septum and transfer into the gas chromatograph. In manual operation, the vapour-phase sample is extracted by means of the gas syringe (A.3.5) and injected into the gas chromatograph. Owing to the loss in sensitivity of the thermionic detector with time, zero-concentration sample solution (see A.5.4) and solvent blank (see A.5.6) are recorded before and after a series of 5 to 10 reference-sample solutions (see A.5.3) when establishing calibration graphs or values.

### A.5.8 Evaluation of gas-chromatographic peaks

In this method, peak heights, in millimetres, are determined instead of peak areas.

## A.6 Expression of results

### A.6.1 Calculation of results from a calibration graph

If several calibration solutions (see A.5.3) with different acrylonitrile concentrations are available, draw a calibration graph by plotting acrylonitrile peak heights $h'_a$, in millimetres, against amount of acrylonitrile $n'_a$, in micrograms, on a bilogarithmic plot. Read from the calibration graph, at the point corresponding to the peak height $h_a$, in millimetres, of the polymer sample solution (see A.5.5), the amount of acrylonitrile $n_a$, in micrograms, contained in the polymer sample. Determine, by the same procedure, from the acrylonitrile peak height $h''_a$, in millimetres, of the solvent blank sample (see A.5.6), the amount of acrylonitrile $n''_a$ contained in the solvent portion. Calculate the acrylonitrile content of the polymer sample $w_a$, expressed in parts per million (ppm) by mass, using the equation

$$w_a = \frac{n_a - n''_a}{m_p} \qquad \ldots (A.1)$$

where $m_p$ is the mass, in grams, of the test portion of polymer weighed out in A.5.5.

For this calculation, no internal standard is required. It is normally used only in cases where there is no linear relationship between the amount of acrylonitrile in the sample and the acrylonitrile peak height.

Symbols used:

| | |
|---|---|
| $h'_a$ | is the peak height, in millimetres, of acrylonitrile in the calibration solution prepared in accordance with A.5.3; |
| $h_a$ | is the peak height, in millimetres, of acrylonitrile in the sample solution prepared in accordance with A.5.5; |
| $h''_a$ | is the peak height, in millimetres, of acrylonitrile in the solvent blank sample prepared in accordance with A.5.6; |
| $n'_a$ | is the total amount, in micrograms, of acrylonitrile in a test portion of reference-sample solution for calibration, prepared in accordance with A.5.3 with varying amounts of acrylonitrile added, including minor amounts of acrylonitrile contained in the zero-concentration sample solution and measured separately; |
| $n_a$ | is the measured amount, in micrograms, of acrylonitrile in a test portion of polymer-sample solution prepared in accordance with A.5.5; |
| $n''_a$ | is the measured amount, in micrograms, of acrylonitrile in a test portion of solvent blank prepared in accordance with A.5.6; |
| $m_p$ | is the mass, in grams, of the test portion of polymer weighed out in A.5.5; |
| $w_a$ | is the acrylonitrile content of the polymer sample, expressed in parts per million (ppm) by mass. |

### A.6.2 Calculation of results from a single-point calibration

#### A.6.2.1 Without internal standard

Provided that a linear relationship exists between peak heights and respective amounts of acrylonitrile, calculate $w_a$ as follows:

$$w_a = \frac{n'_a}{h'_a - h'''_a \dfrac{m'_0}{m'''_0}} \times \frac{h_a - h''_a}{m_p} \qquad \ldots (A.2)$$

Symbols used in addition to those defined in A.6.1:

| | |
|---|---|
| $n'_a$ | is the amount, in micrograms, of acrylonitrile in a test portion of reference-sample solution for calibration as added by injection of calibration solution prepared in accordance with A.5.3; |
| $h'''_a$ | is the peak height, in millimetres, of acrylonitrile remaining in the degassed reference polymer as measured in the zero-concentration sample solution prepared in accordance with A.5.4; |
| $m'_0$ | is the mass, in grams, of the monomer-freed reference-polymer sample dissolved in the reference-sample solution for calibration prepared in accordance with A.5.3; |
| $m'''_0$ | is the mass, in grams, of the monomer-freed reference-polymer sample dissolved in the zero-concentration sample solution prepared in accordance with A.5.4. |