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Plastics — Determination of residual styrene monomer in polystyrene (PS) and impact-resistant polystyrene (PS-I) by gas chromatography

Plastiques — Détermination du styrène monomère résiduel dans le polystyrène (PS) et le polystyrène résistant au choc (PS-I) par chromatographie en phase gazeuse

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

This fourth edition cancels and replaces the third edition (ISO 2561:2012), which has been technically revised.

The main changes-are as follows:

— adding headspace injection as another sample introducing option for gas chromatography.

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 residual styrene monomer in polystyrene (PS) and impact-resistant polystyrene (PS-I) by gas chromatography

1 Scope

This document specifies a method for the determination of the residual styrene monomer in polystyrene (PS) and impact-resistant polystyrene (PS-I) by gas chromatography. It can also be used for the simultaneous determination of other volatile aromatic hydrocarbons in PS and PS-I.

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*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

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

PS or PS-I sample is dissolved in solvent containing an internal standard. To obtain separation of styrene and other volatile materials, gas chromatography method is employed, in which three sample introducing options are available:

— Option A: a small volume of the polymer solution is injected directly into a gas chromatograph.

— Option B: a small volume of the supernatant solution remaining after precipitation of polymer by addition of a precipitator is injected into a gas chromatograph.

— Option C: a small volume of vapor of the polymer solution under thermal equilibrium is injected into a gas chromatograph.

5 Reagents and materials

Use only reagents of recognized analytical grade, unless otherwise specified.

5.1 Internal standard

The internal standard shall be selected based on consideration of the retention times of the materials contained in the polymer sample and solvent. Recommended candidates are n-butylbenzene, cyclopentanol, 1,2,4-trimetylbenzene and 1,4-diethylbenzene of sufficient purity for analytical use.

5.2 Solvent

Use dimethylformamide, butanone, dichloromethane, or tetrahydrofuran. Tetrahydrofuran is used only for method A. Only dimethylformamide is used in method C.

5.3 Precipitator

Use 2,2,4-trimethylpentane or ethanol.

5.4 Aromatic hydrocarbons

Use styrene and other aromatic hydrocarbons such as ethylbenzene, cumene or α-methylstyrene, if required. Styrene shall be checked for self-polymerizaiton before use. The criterion for acceptance is that the mixture of styrene and ethanol of the same volume shall be clear. When determining the content of other aromatic hydrocarbons in the sample, other aromatic hydrocarbons such as ethylbenzene, cumene or α-methylstyrene shall be used.

5.5 Carrier gases and fuel gases for gas chromatograph

Hydrogen, helium or nitrogen, according to the type of detector used, shall be used as carrier gas. Use hydrogen and air as fuel gases. If detectors are used which require carrier gases and fuel gases other than those mentioned, the carrier gases and fuel gases shall be specified.

WARNING — Strict observance of safety regulations is essential when using hydrogen.

6 Apparatus

6.1 General

Normal laboratory equipment and the following apparatus are required. Typical operating conditions are described in Annex A.

6.2 Gas chromatograph

6.2.1 Injection port. Use an injection port for liquid samples or gas samples. When using a capillary column, an injection port with splitter may be applicable.

6.2.2 Headspace sampler. only used in method C, including backflush capability, thermostated sample tray, and associated accessories fulfil these requirements while providing for automatic sequential sampling of headspace vapors.

6.2.3 Column. The column diameter and length, as well as the packing material and stationary phase shall be selected based on consideration of column resolution and calibration curve linearity. Both packed columns and capillary columns are acceptable. Capillary columns are recommended in the light of accuracy.

6.2.4 Detector. Use a suitable detector.

NOTE The most commonly used detector is a hydrogen flame ionization detector (FID).

6.3 Data processor

Use a recorder or microcomputer to record the signals from the detector.

6.4 Sample injection syringe

Use a micro-syringe of the 1 µl to 50 µl type. A micro-syringe integrated with the auto-injector may also be used.

6.5 Analytical balance

Shall be accurate to the nearest 0,1 mg.

6.6 Volumetric flasks

Volumetric flasks as standardized in ISO 1042 shall be used.

6.7 Headspace Vials

Vials matching the headspace sampler shall be used, including a lid with a sealing gasket and vial sealer.

NOTE The volume of headspace sample bottle is usually 10 ml, 20 ml or 22 ml.

7 Preparation of sample

The sample may be taken from material in the form of powder, pellets or moulded parts. In order to ensure the desired accuracy of the sample mass, large pieces of sample shall be reduced to smaller fragments.

8 Procedure

8.1 General

During the dilution processes described below, the temperature of each solution shall remain under 25 °C.

8.2 Preparation of internal-standard solution

Weigh 200 mg of internal standard (5.1), to the nearest 1 mg, into a 1 000 ml volumetric flask (6.6). Then add solvent (5.2) to make exactly 1 000 ml, stopper tightly and mix well.

8.3 Preparation of sample solution for sample introducing option A

Weigh 0,5 g of sample, to the nearest 1 mg, into a volumetric flask (6.6) having a volume between 25 ml and 100 ml. Using a syringe or a pipette, add 20 ml of the internal standard solution prepared in 8.2. Then stopper tightly and mix until dissolved.

8.4 Preparation of sample solution for sample introducing option B

Weigh 0,5 g of sample, to the nearest 1 mg, into a volumetric flask (6.6) having a volume between 50 ml and 100 ml.

Using either a syringe or a pipette, add 20 ml of the internal standard solution prepared in 8.2. Then stopper tightly and dissolve the sample (shake well, if necessary). After completely dissolving the sample, add 10 ml of precipitator (5.3) with a pipette. After vigorous shaking, allow the precipitate to

settle. The supernatant solution is used for injection into the gas chromatograph using a micro-syringe (6.4).

8.5 Preparation of sample solution for sample introducing option C

8.5.1 Prepare sample solution, see 8.3.

8.5.2 Using either a syringe or a pipette, transfer sample solution (8.5.1) into a headspace vial (6.7) and seal the vial. The recommended volume is half of the volume of the headspace vial and the same as the volume of the calibration solution used. Keep the headspace vial in headspace sampler (6.2.2) at 120 °C for 50 min.

8.6 Preparation of calibration solutions

8.6.1 General

The range of concentrations which can be analysed by gas chromatography using the internal-standard method is determined by the amounts of measured styrene and other aromatic hydrocarbons to be measured and the dilutions (see Table 1). A series of calibration solutions are prepared for each aromatic hydrocarbon to be analysed. The solutions are kept for injection into the gas chromatograph.

8.6.2 Calibration solutions for sample introducing option A

Weigh, to the nearest 0,1 mg, into separate volumetric flasks (6.6) (for the volume of the flasks, refer to Annex B) at least four of the amounts indicated in Table 1 of styrene and, if necessary, other aromatic hydrocarbons such as ethylbenzene, cumene or α-methylstyrene. Add internal-standard solution (8.2) to each flask, dissolve and make up to the mark with internal-standard solution. When determining the content of other aromatic hydrocarbons in the sample, other aromatic hydrocarbons such as ethylbenzene, cumene or α-methylstyrene shall be used.

8.6.3 Calibration solutions for sample introducing option B

Measure to the nearest 1 ml, 1 000 ml internal-standard solution (8.2) into a 2 000 ml flask. Then add 500 ml of precipitator (5.3), stopper tightly and mix well (this solution is hereafter called the precipitator solution). Weigh, to the nearest 0,1 mg, into separate 1 000 ml volumetric flasks (6.6) at least four of the amounts indicated in Table 1 of styrene and, if necessary, other aromatic hydrocarbons such as ethylbenzene, cumene or α-methylstyrene. Add the precipitator solution to each flask, dissolve and make up to the mark with precipitator solution. When determining the content of other aromatic hydrocarbons in the sample, other aromatic hydrocarbons such as ethylbenzene, cumene or α-methylstyrene shall be used.

NOTE For safety and economic reasons, there has been the case in which a smaller size glass container has been used instead of the 2 000 ml flask.

8.6.4 Calibration solution for sample introducing option C

8.6.4.1 Prepare calibration solution, see 8.6.2.

8.6.4.2 Using either a syringe or a pipette, transfer calibration solution (8.6.4.1) into a headspace vial (6.7) and seal the vial. The recommended volume is half of the volume of the headspace vial. Keep the headspace vial in headspace sampler (6.2.2) at 120 °C for 50 min.

Table 1 — Correlation between mass of aromatic hydrocarbon in calibration solution and concentration of aromatic hydrocarbon in sample solution

Mass of aromatic hydrocarbon in 1 000 ml of calibration solution Mg	Corresponding mass fraction of aromatic hydrocarbon in sample solution (sample = 0,5 g of polystyrene) µg/g
2,5	100
5,0	200
10,0	400
20,0	800
25,0	1 000
50,0	2 000

8.7 Gas-chromatographic procedure

8.7.1 Gas-chromatograph operating conditions

Select the gas-chromatographic conditions, solvent, and internal standard to give sufficient separation of styrene and the other eluted materials. If it is difficult to separate the peak corresponding to the internal standard from that corresponding to a target component, except styrene, use the standard addition method for analysis. If it is difficult to separate the peak corresponding to the internal standard from those due to impurities, increase the concentration of the internal standard to a level at which the peaks due to impurities become negligible.

Prepare a chromatogram satisfying the following requirements. The resolution R_e between the peaks corresponding to styrene, the internal standard and any other aromatic hydrocarbons (such as ethylbenzene, cumene or α-methylstyrene) and the peaks corresponding to the target components appearing just before or just after the former peaks shall be more than 1,0 and preferably 1,5, if possible. The resolution R_e between two peaks with the same area is defined as Formula (1):

$$R_e = 2 \times \frac{t_2 - t_1}{W_1 + W_2} \quad (1)$$

where

t_1 and t_2 are the retention times of the two peaks, expressed in min;

W_1 and W_2 are the respective widths of the peaks, expressed in min.

The gas-chromatographic conditions are chosen to give the above performance. Typical conditions are described in Table 2, and more detailed conditions for each method and column are described in Annex A.

Table 2 — Typical operating conditions

Item	Operating conditions
Column	Metal, glass tubing and fused silica capillary are typical.
Packed column	Pack with a commercial packing material and allow sufficient stabilization before use.
Capillary column	Choose a commercial capillary column coated with a suitable stationary phase inside of the tube and allow sufficient time for it to stabilize before use.

Table 2 *(continued)*

Item	Operating conditions
Column temperature	Isothermal or rising temperature can be used. It is not regulated but rising temperature condition is recommended in the light of time saving.
Temperature of injection port	200 °C to 250 °C.
Temperature of detector	Suitable for the type and design of detector used.
Carrier gas	Hydrogen, helium or nitrogen, according to the type of detector used. If detectors are used which require carrier gases other than those mentioned, the carrier gases shall be specified.
Carrier gas flow rate	Packed column: 25 cm^3/min to 90 cm^3/min. Capillary column: 2,5 cm^3/min to 10 cm^3/min.
Suitable detector	A high sensitivity of response. A linear response over the range of concentrations being measured. Only insignificant effects of small changes in flow rate on response or sensitivity.

NOTE 1 Use of sample introducing option A can cause that contamination of the injector with polymer and oligomers will occur over time, leading to erroneous results, and deposition of polymer on the column, making more frequent changes of the column necessary.

NOTE 2 Use of sample introducing option C can cause cross contamination of residual sample in the pipeline or the injection loop of headspace sampler, needing the headspace sampler inert, uniform high temperature and sufficient purging.

8.7.2 Recording the gas chromatograms of sample solutions and calibration solutions

Depending on the sensitivity of the gas chromatograph used, inject a suitable volume of the sample solution (prepared in accordance with 8.3 or 8.4 or 8.5) or the calibration solutions (prepared in accordance with 8.6). The volume of sample solution injected shall be identical to the volume of the corresponding calibration solutions injected. Record each chromatogram until all the materials such as solvent, styrene, ethylbenzene, other aromatic hydrocarbons being determined, and internal standard have been completely eluted.

8.7.3 Evaluation of the gas-chromatographic peaks

The relative retention times of styrene, the internal standard and any other aromatic hydrocarbons being determined shall be determined in advance.

Table 3 gives examples of the retention times of some of the most frequently occurring components. The exact values will depend upon the gas chromatograph and the operating conditions used.

Table 3 — Typical retention times of styrene and other aromatic hydrocarbons

Aromatic hydrocarbon MPa	Retention time min	Retention time relative to *n*-butylbenzene
Ethylbenzene	3,4	0,29
Cumene	4,7	0,39
n-Propylbenzene	5,9	0,50
Styrene	8,2	0,69
n-Butylbenzene (internal standard)	11,9	1,00
α-Methylstyrene	13,7	1,15
NOTE Annex A gives typical operating conditions and a typical gas chromatogram (see Figure A.1).		

Other components which might occur in smaller amounts are benzene, toluene, *o*-, *m*- and *p*-xylene, *o*-, *m*- and *p*-ethyltoluene and sec-butylbenzene.

The peak areas of the components and the internal standard can be determined using electronic integration.

9 Expression of results

9.1 Calculation of results from a calibration graph

When analysing an aromatic hydrocarbon using four or more calibration solutions having different concentrations, prepared by the procedure described in 8.6, first calculate, for each calibration solution, the peak area ratio Y' given by Formula (2):

$$Y' = \frac{A'_a}{A'_s} \tag{2}$$

where

A'_a is the peak area for styrene (or another aromatic hydrocarbon) in the calibration solution;

A'_s is the peak area of the internal standard in the calibration solution.

Then prepare a calibration curve by plotting the peak area ratio Y' against the concentration, in mg/ml, of the particular component being determined.

From the graph obtained, determine the linear regression using Formula (3):

$$Y' = a \times C'_a + b \tag{3}$$

where

Y' is the peak area ratio of the particular component being determined and the internal standard in the calibration solution, i.e. A'a/A's;

C'_a is the concentration, in mg/ml, of the component being determined in the calibration solution.

If the correlation coefficient is less than 0,995, consider using more calibration points or preparing the curve again.

When a sample solution is analysed, calculate the corresponding peak area ratio Y given by Formula (4):

$$Y = \frac{A_a}{A_s} \tag{4}$$

where

A_a is the peak area for styrene (or another aromatic hydrocarbon) in the sample solution;

A_s is the peak area of the internal standard in the sample solution.

The concentration of the component being determined is then calculated as Formula (5):

$$C_a = \frac{Y - b}{a} \tag{5}$$

where

C_a is the concentration of the component being determined, expressed in mg/ml;

Y is the peak area ratio for the component and the internal standard;

A is the slope of the linear regression line;

B is the Y-intercept of the linear regression line.

From Ca, calculate the mass fraction Pa of styrene or other aromatic hydrocarbon in the polystyrene sample, using Formula (6):

$$P_a = \frac{20 \times C_a}{m_p} \times 10^3 \quad (6)$$

where

m_p is the mass of the polystyrene sample, expressed in grams;

P_a is the content of styrene or other aromatic hydrocarbon in the sample, expressed in µg/g;

20 the amount of internal-standard solution, expressed in ml.

9.2 Acceptability of results and measurement sensitivity

The range of the results obtained from repeated determinations of styrene in the sample shall not exceed ±5 % of the arithmetic mean of P_a.

A detection limit of the order of 10 µg/g can be expected using the method described in this document.

10 Test report

The test report shall include the following particulars:

a) a reference to this document including its year of publication, i.e. ISO 2561:2023;

b) the type of polymer analysed and all details necessary for complete identification of the sample;

c) the sample introducing option (sample introducing option A or sample introducing option B or sample introducing option C) and the gas-chromatographic equipment and conditions used;

d) type and concentration of internal standard used;

e) concentration of styrene and type and concentration of other hydrocarbons in the calibration solution, if applicable;

f) the content of styrene (and other aromatic hydrocarbons, if also determined) in the sample, expressed as a mass fraction in µg/g to two significant figures;

g) the date of the analysis;

h) any deviations from the procedure;

i) any unusual features observed.

Annex A
(informative)

Examples of typical test conditions

A.1 Sample introducing option A

A.1.1 Chromatograph with packed column

1)	Column:	Glass tubing — Coated with 25 % PEG20M — Length 3,66 m, I.D. 4 mm, particle size 180 µm to 250 µm
2)	Column temp.:	110 °C (30 min)
3)	Injection temp.:	220 °C
4)	Detector temp.:	220 °C
5)	Carrier gas:	He at 90 cm^3/min
6)	Injection method:	Direct injection
7)	Injection volume:	3 µl
8)	Detector:	Flame ionization detector (FID)
9)	Solvent:	Dimethylformamide
10)	Internal standard:	Cyclopentanol
11)	Resolution (*Re*):	3,66 (styrene)

A.1.2 Chromatograph with capillary column (condition 1)

1)	Column:	Fused silica column — Film thickness 1 µm, length 15 m, I.D. 0,53 mm
2)	Column temp.:	130 °C (15 min)
3)	Injection temp.:	200 °C
4)	Detector temp.:	200 °C
5)	Carrier gas:	He at 5 cm^3/min
6)	Injection method:	Direct injection
7)	Injection volume:	1 µl
8)	Detector:	FID

9)	Solvent:	Dimethylformamide
10)	Internal standard:	*n*-Butylbenzene
11)	Resolution (*Re*):	2,80 (styrene)

A.1.3 Chromatograph with capillary column (condition 2)

1)	Column:	Fused silica column — TC-WAX (GL Science Ltd.) — PEG coating, thickness 0,5 µm — Length 30 m, I.D. 0,25 mm
2)	Column temp.:	60 °C - 100 °C raising rate 4 °C /min, 100 °C - 150 °C raising rate 10 °C / min
3)	Injection temp.:	220 °C
4)	Detector temp.:	220 °C
5)	Carrier gas:	He at 9 cm^3/min
6)	Injection method:	Direct injection
7)	Injection volume:	1 µl
8)	Detector:	FID
9)	Solvent:	Tetrahydrofuran
10)	Internal standard:	1,4-diethylbenzene
11)	Resolution (*Re*):	12,0 (styrene)

A.2 Sample introducing option B

A.2.1 Chromatograph with packed column

1)	Column:	Glass tubing — Coated with 10 % PEG20M — Length 3,66 m, I.D. 4 mm, particle size 180 µm to 250 µm
2)	Column temp.:	80 °C (40 min)
3)	Injection temp.:	150 °C
4)	Detector temp.:	150 °C
5)	Carrier gas:	He at 90 cm^3/min
6)	Injection method:	Direct injection
7)	Injection volume:	3 µl