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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 main task of technical committees is to prepare International Standards. 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.

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ISO 2561 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*.

This second edition cancels and replaces the first edition (ISO 2561:1974), which has been technically revised.

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

1 Scope

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

2 Normative references

The following referenced documents are indispensable for the application 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.

4 Principle

The polymer sample is dissolved in solvent, which for polystyrene contains an internal standard. Either a small volume of the polymer solution is injected directly into a gas chromatograph (method A) or a small volume of the supernatant solution remaining after precipitation of polymer by addition of a precipitator is injected (method B), in order to obtain separation of styrene and other volatile materials. Method A is simple and has much the same accuracy as method B. However, there is a possibility that contamination of the injector with polymer and oligomers will occur over time, leading to erroneous results.

5 Reagents and materials

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 and 1,2,4-trimethylbenzene, of sufficient purity for analytical use.

5.2 Solvent

Use analytical-grade dimethylformamide, butanone or dichloromethane.

5.3 Precipitator

Use analytical-grade 2,2,4-trimethylpentane or ethanol.

5.4 Aromatic hydrocarbons

Use analytical-grade styrene and (if required) other aromatic hydrocarbons such as ethylbenzene, cumene or α-methylstyrene. Styrene shall give a clear mixture when mixed with an equal volume of ethanol.

5.5 Carrier gases and fuel gases for gas chromatograph

Use helium or nitrogen as carrier gas. Use hydrogen and air as fuel gases.

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. When using an open tubular column (hereafter called an OT column), an injection port with splitter may be applicable.

6.2.2 Column: The column diameter and length, as well as the packing material and liquid phase, shall be selected based on consideration of column resolution and calibration curve linearity. Both packed columns and OT columns are acceptable.

6.2.3 Detector: Use 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 forming part of the auto-injector may also be used.

6.5 Analytical balance

A balance capable of measuring to 0,1 mg is required.

7 Preparation of sample

The sample can 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. Then add solvent (5.2) to make exactly 1 000 ml, stopper tightly and mix well.

8.3 Preparation of sample solution for method A

Weigh 0,5 g of sample, to the nearest 1 mg, into a 20 ml volumetric flask. Then add the internal standard solution prepared in 8.2 to make exactly 20 ml, stopper tightly and mix until dissolved.

8.4 Preparation of sample solution for method B

Weigh 0,5 g of sample, to the nearest 1 mg, into a 100 ml volumetric flask. 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.

8.5 Preparation of calibration solutions

8.5.1 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.

8.5.2 Calibration solutions for method A

Weigh, to the nearest 0,1 mg, into separate 1 000 ml volumetric flasks 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.

NOTE Alternative sizes of volumetric flask which can be used, together with the corresponding mass of aromatic hydrocarbon for each size, are given in Annex B.

8.5.3 Calibration solutions for method B

Measure, to the nearest 1 ml, 1 000 ml of 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 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 precipator solution to each flask, dissolve and make up to the mark with precipator solution.

NOTE See the Note to 8.5.2.

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

8.6 Gas-chromatographic procedure

8.6.1 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 follows:

$$R_e = 2(t_2 - t_1)/(W_1 + W_2)$$

where

t_1 and t_2 are the retention times of the two peaks;

W_1 and W_2 are the respective half-widths of the peaks.

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

Column: Metal, glass tubing and fused silica capillary are typical.

Packed column: Pack with a commercial packing material and allow sufficient stabilization before use.

OT column: Choose a commercial OT column with a suitable filler and allow sufficient time for it to stabilize before use.

Column temperature: 90 °C to 110 °C, isothermal.

Temperature of injection port: 200 °C to 250 °C.

Temperature of detector:	200 °C to 250 °C.
Carrier gas:	Helium or nitrogen.
Carrier gas flow rate:	Packed column: 25 cm^3/min to 90 cm^3/min.
	OT column: 2,5 cm^3/min to 10 cm^3/min.
FID:	Adjust the hydrogen and air flow rates to give:

— 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 Use of method A may cause deposition of polymer on the column, making more frequent changes of the column necessary.

8.6.2 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 the calibration solutions (prepared in accordance with 8.5). 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.

8.6.3 Evaluation of the gas-chromatographic peaks

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

NOTE Table 2 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 2 — Typical retention times of styrene and other aromatic hydrocarbons

Aromatic hydrocarbon	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 shall 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 8.5, first calculate, for each calibration solution, the peak area ratio Y' given by:

$$Y' = A'_a/A'_s$$

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 formula

$$Y' = a \times C'_a + b$$

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:

$$Y = A_a/A_s$$

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 follows:

$$C_a = (Y - b)/a$$

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 C_a, calculate the mass fraction P_a of styrene or other aromatic hydrocarbon in the polystyrene sample, using the equation

$$P_a = (20 \times C_a)/(m_p \times 10^3)$$

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.

9.2 Acceptability of results and measurement sensitivity

The range of the results obtained from repeated determinations of each aromatic hydrocarbon in the sample should 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 International Standard.

10 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

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

c) the method (method A or method B) and the gas-chromatographic equipment and conditions used (if used, the typical conditions given in Annex A may be referred to by subclause number);

d) 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;

e) the date of the analysis.

Annex A
(informative)

Typical analytical conditions

A.1 Method A

A.1.1 Chromatograph with packed column

1) Chromatograph: HP5890 (Hewlett Packard Ltd.)
2) Column: Glass tubing
   - Uniport HP (GL Science Inc.) coated with 25 % PEG2OM
   - Length 3,66 m, I.D. 4 mm, particle size 180 µm to 250 µm
3) Column temp.: 110 °C (30 min)
4) Injection temp.: 220 °C
5) Detector temp.: 220 °C
6) Carrier gas: He at 90 cm^3/min
7) Injection method: Direct injection
8) Injection volume: 3 µl
9) Detector: Flame ionization detector (FID)
10) Solvent: Dimethylformamide
11) Internal standard: Cyclopentanol
12) Resolution (R_e): 3,66 (styrene)

A.1.2 Chromatograph with open tubular column

1) Chromatograph: HP5890A (Hewlett Packard Ltd.)
2) Column: Fused silica column
   - DB-WAX (J&W)
   - Film thickness 1 µm, length 15 m, I.D. 0,53 mm
3) Column temp.: 130 °C (15 min)
4) Injection temp.: 200 °C
5) Detector temp.: 200 °C