INTERNATIONAL STANDARD ISO 2561

Plastics — Determination of residual styrene monomer in polystyrene by gas chromatography

Matières plastiques — Détermination du styrène monomère résiduel dans le polystyrène par chromatographie en phase gazeuse

First edition — 1974-08-01

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up has the right to be represented on that Committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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.

International Standard ISO 2561 was drawn up by Technical Committee ISO/TC 61, *Plastics*, and circulated to the Member Bodies in January 1972.

It has been approved by the Member Bodies of the following countries :

Austria	Ireland	South Africa, Rep. of
Belgium	Israel	Spain
Canada	Italy	Sweden
Czechoslovakia	Japan	Switzerland
Egypt, Arab Rep. of	Netherlands	Thailand
France	New Zealand	Turkey
Germany	Poland	United Kingdom
Hungary	Portugal	U.S.A.
India	Romania	U.S.S.R.

No Member Body expressed disapproval of the document.

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

Plastics — Determination of residual styrene monomer in polystyrene by gas chromatography

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for the determination of the residual styrene monomer in polystyrene by gas chromatography; it may be used also for the simultaneous determination of other volatile aromatic hydrocarbons in polystyrene. It is applicable both to styrene homopolymers and to butadiene modified polystyrene.

2 PRINCIPLE

Dissolution of the polymer sample in chloroform or dichloromethane. Precipitation of the polymer by the addition of methanol and injection of a small volume of the remaining solution into a gas chromatograph to obtain separation of styrene and other volatile aromatic hydrocarbons. The solvent contains a known amount of *n*-butylbenzene as an internal standard for quantitative evaluation.

3 REAGENTS

3.1 Chloroform or **dichloromethane**, analytical grade. A small amount of ethanol which may be contained in the chloroform for stabilization does not affect the determination.

3.2 Methanol, analytical grade.

3.3 *n*-Butylbenzene, of sufficient purity for analytical use.

3.4 Styrene and (if required) other aromatic hydrocarbons such as ethylbenzene, cumene or alpha-methylstyrene of sufficient purity for calibration. Styrene must be freshly distilled and stored at 0 °C until required for use. When mixed with an equal volume of methanol, the styrene shall give a clear mixture.

3.5 Polyethylene glycol, molecular mass 15 000 to 20 000. (Carbowax 15 to 20 M has been found satisfactory.)

3.6 Diatomaceous earth, particle size 210 to 250 μm. (Celite, acid-washed grade, has been found satisfactory.)

3.7 Helium, hydrogen, and **air** as carrier and fuel gases for gas chromatography. For use with the flame ionization detector, nitrogen may be applied as the carrier gas instead of helium.

NOTE — Changes in carrier gas are permissible only if this has proved to give the same results.

4 APPARATUS

Normal laboratory equipment and

4.1 Gas chromatograph, with injection port for liquid samples, flame ionization detector, and recorder. Some other type of ionization detector may be used, and, in exceptional cases, a thermal conductivity detector. The latter, however, entails lower sensitivity.

4.2 Micro-syringe, 1 to 50 μl.

4.3 Analytical balance.

5 PREPARATION OF SAMPLES

The sample may be taken from material in the form of a powder, pellets or moulding. Large pieces shall be reduced to fragments sufficiently small for weighing a sample amount as close as possible to 1,5 g.

6 PROCEDURE

6.1 Preparation of solvent for the sample

Weigh 900 ± 1 mg of *n*-butylbenzene (3.3) into a 25 ml flask, transfer quantitatively into a 1 000 ml volumetric flask, and dilute to 1 000 ml with chloroform or dichloromethane (3.1). During the dilution process, maintain the liquid at a temperature of 20 ± 0,5 °C.

6.2 Preparation of the sample solution

Weigh, to the nearest 1 mg, 1,5 g of the polymer sample and transfer to a 100 ml conical flask, preferably with a serum cap closure. Add from a pipette exactly 10 ml of the solvent prepared according to 6.1 and kept at 20 ± 0,5 °C. After closing the flask, allow the polymer to dissolve, with shaking if necessary. After complete dissolution, add exactly 5 ml of methanol (3.2) kept at 20 ± 0,5 °C, either by a syringe or from a pipette. After vigorous shaking,

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allow the precipitate to settle. For injection into the gas chromatograph, extract the required amount with the syringe (4.2) from the supernatant solution.

6.3 Preparation of calibration solutions

Prepare solutions for calibration by weighing 600 ± 0,5 mg of *n*-butylbenzene together with an appropriate amount of styrene or (if required) of another hydrocarbon to be determined, and diluting in a volumetric flask to 1 000 ml with a mixture of chloroform (or dichloromethane) and methanol in a volume ratio of 2:1. Appropriate amounts of hydrocarbon are recommended as follows :

- 100, 200, 500, 800 and/or 1 000 mg of styrene;

- 10, 20, 50, 80 and/or 100 mg of other hydrocarbons.

All hydrocarbons are to be weighed to the nearest 0,5 mg. The temperature of the liquids should be 20 ± 0,5 °C. A separate calibration solution, or a series of calibration solutions, is to be prepared for each single hydrocarbon to be determined. The solutions are kept for injection into the gas chromatograph.

6.4 Gas chromatographic procedure

6.4.1 *Gas chromatographic operating conditions*

Column : metal or glass tubing, 4,5 m (15 ft) length, 4 mm internal diameter, is recommended. The column is packed with a support medium of diatomaceous earth (3.6) which is coated with 10 % (*m/m*) polyethylene glycol (3.5).

NOTE — Methods of coating and packing are not specified, but may be chosen so as to obtain satisfactory separating efficiency of the column. The column shall be aged for 24 h at 150 °C with gas flow. Changes in column materials or column dimensions are permissible only if this has proved to give the same results.

Column temperature : 80 °C isothermal.

Temperature of injection port : 150 °C.

Temperature of detector compartment : 150 °C.

Carrier gas : Helium (or nitrogen under the conditions indicated in 3.7).

Flow rate of carrier gas : 100 cm³/min.

Flame ionization detector, in which the hydrogen and air flow rates are adjusted to give :

1) high sensitivity of response;

2) linear response over the range of concentrations being measured;

3) only insignificant effect of small changes in flow rates on response or sensitivity.

Recorder speed : 0,5 cm/min (0.2 in/min) is recommended.

6.4.2 *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 6.2) or the calibration solution (prepared according to 6.3). The injected volume is not critical for the calculation of results, but shall be identical for corresponding sample and calibration solutions.

Develop the gas chromatogram until the *n*-butylbenzene is completely eluted, or, if hydrocarbons with higher retention times are to be determined, until complete elution of these.

6.4.3 *Evaluation of gas chromatographic peaks*

The retention times of styrene, *n*-butylbenzene, and (if required) of other hydrocarbons to be determined must be known, at least relative to each other.

NOTE — In the following table approximate values of the retention time are given for some of the most frequently occurring components. The exact values vary according to the density of the column packing, the age of the column, and other gas chromatographic parameters.

Component hydrocarbons	Retention time min	Retention time relative to *n*-butylbenzene
Ethylbenzene	9	0,44
Cumene	10,5	0,51
n-Propylbenzene	12,5	0,61
Styrene	16,5	0,80
n-Butylbenzene (standard)	20,5	1
α-Methylstyrene	25	1,22

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 to be determined and of *n*-butylbenzene are determined by

1) electronic integration; or

2) area estimation on the basis of the formula :

area (*A*) = peak height X halfwidth[1]; or

3) planimetry.

Use of method 2 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. In most cases, method 2 is only applicable to the peaks of the major components, i.e. styrene and *n*-butylbenzene. For routine determinations, peak height measurements of both sample and calibration

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1) For terms and definitions see : "Preliminary recommendation on nomenclature and presentation of data in gas chromatography", issued by the International Union of Pure and Applied Chemistry, *Pure and Applied Chemistry*, Vol. 1, 1960, pp. 177 to 186.

chromatograms will be sufficient. The method of area evaluation chosen must be identical for corresponding peaks of sample solution and calibration solution.

7 EXPRESSION OF RESULTS

7.1 Calculation of results from a calibration graph

If several calibration solutions with different concentrations of one single aromatic hydrocarbon are available, a calibration graph is drawn 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, the concentration of the substance to be determined in the sample solution, c_a, may be taken from the calibration graph. From c_a, the percentage (m/m) of aromatic hydrocarbon in the polystyrene sample, P_a, is calculated according to the relation :

$$P_a = \frac{1,5 \, c_a}{m_p}$$

Symbols used :

A'_a is the peak area of styrene or other hydrocarbon to be determined in the calibration solution;

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

A_a is the peak area of styrene or other hydrocarbon to be determined in the sample solution;

A_s is the peak area of the internal standard (n-butylbenzene) in the sample solution;

c_a is the concentration of styrene or other hydrocarbon in the sample solution, expressed in milligrams per millilitre;

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

P_a is the content of styrene or other volatile aromatic hydrocarbon compound in the sample, expressed in percent (m/m).

If m_p amounts to exactly 1,5 g, as specified in this method, the numerical value of c_a as taken from the calibration graph is identical to the numerical value of P_a.

7.2 Calculation of results from a single point calibration

Provided a linear relationship exists between peak areas and respective concentrations of styrene or other hydrocarbons determined, the following relation may be applied;

$$P_a = 1,5 \frac{m'_a \, A_a/A_s}{m_p \, A'_a/A'_s}$$

where

$A'_a, A'_s, A_a, A_s, m_p$ and P_a are as in 7.1;

m'_a is the mass of styrene or other hydrocarbon weighed into 1 000 ml calibration solution (see 6.3).

NOTE — If the internal standard is present as a component in the polymer, as may be seen from a blank run of the sample solution, i.e. without internal standard added, then the monomer content may be determined by the internal addition method.

7.3 Precision of measurement and sensitivity

The dispersion of results on repeated measurement of one aromatic hydrocarbon, for example styrene, in the sample may not exceed 0,01 units of P_a around the arithmetic mean.

A lower limit of detection of the order of 10 ppm may be expected from the method.

8 TEST REPORT

The test report shall include the following particulars :

a) type and identification characteristics of the polymer tested;

b) any deviation of the gas chromatographic equipment and procedure from the standard equipment with flame ionization detector and procedure described herein;

c) content of styrene monomer (and other volatile aromatic hydrocarbons, if determined) expressed as a percentage by mass of the polymer sample and rounded off to the nearest 0,01 %.

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