INTERNATIONAL STANDARD

ISO 4901

Second edition
2011-08-15

Reinforced plastics based on unsaturated-polyester resins — Determination of the residual styrene monomer content, as well as the content of other volatile aromatic hydrocarbons, by gas chromatography

Plastiques renforcés à base de résines de polyesters non saturés — Détermination du styrène monomère résiduel, ainsi que d'autres hydrocarbures aromatiques volatils, par chromatographie en phase gazeuse

Reference number
ISO 4901:2011(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 4901 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 4901:1985), which has been technically revised (for details, see the Introduction).

Introduction

During the 25 years since publication of the first edition of this International Standard, ISO 4901:1985, significant advances have been made in analytical techniques such as gas chromatography. The standard has therefore been completely revised. The following are the main changes which have been made:

a) In addition to a gas-chromatographic method, the first edition of ISO 4901 included, as an alternative, a classical method, Wijs' method, based on an iodometric titration. This method had been included in the first edition for laboratories in which gas chromatography was not available. As, nowadays, chromatography is considered to be a routine analytical tool, Wijs' method has been removed from the standard.

b) Packed gas-chromatography columns have generally been replaced by open, tubular columns which operate under completely different conditions. In the revised test method, therefore, only an open, tubular column is used.

c) In addition, the gas-chromatographic method has been extended to cover not only styrene but also other aromatic hydrocarbons which might have been used as solvents or starting materials in producing the unsaturated polyester resin.

INTERNATIONAL STANDARD **ISO 4901:2011(E)**

Reinforced plastics based on unsaturated-polyester resins — Determination of the residual styrene monomer content, as well as the content of other volatile aromatic hydrocarbons, by gas chromatography

WARNING — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any regulatory requirements.

1 Scope

This International Standard specifies a method for the determination, by gas chromatography, of the residual styrene monomer in reinforced plastics based on unsaturated polyester (UP) resins in the polymerized state. The residual styrene monomer content is an important criterion in evaluating the degree of cure of UP resins in the polymerized state. The method can also be used for the simultaneous determination of other volatile aromatic hydrocarbons in UP resins.

The method is not applicable to UP resins of high chemical resistance.

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*

ISO 1172, *Textile-glass-reinforced plastics — Prepregs, moulding compounds and laminates — Determination of the textile-glass and mineral-filler content — Calcination methods*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 apply.

4 Principle

Styrene is extracted from the UP resin in the polymerized state using dichloromethane. The styrene in the extract is determined by gas chromatography, using an internal standard and a calibration curve.

5 Materials

5.1 ***n*-Butylbenzene**, analytical grade, for use as an internal standard.

5.2 **Dichloromethane**, analytical grade, for use as the extraction solvent.

WARNING — Dichloromethane is harmful when swallowed, inhaled or absorbed through the skin. It affects the central nervous system, the liver, the cardiovascular system and the blood. It causes irritation of the skin, eyes and respiratory tract. It is also a suspected cancer hazard, the risk of cancer depending on the level and duration of exposure.

NOTE In view of the toxicity and suspected carcinogenic characterics of dichloromethane, acetone and ethyl acetate are being tested as replacements. If the results of this work demonstrate conclusively that either one or both of these solvents are suitable, this International Standard will be revised accordingly.

5.3 **Styrene**, analytical grade, and, if relevant, **other aromatic hydrocarbons**, such as toluene, ethylbenzene and α-methylstyrene, also analytical grade.

NOTE An aromatic hydrocarbon is considered to be relevant if it is used as a solvent or starting material in the UP resin production process.

5.4 **Carrier gas and FID fuel gases**:

- carrier gas: helium or nitrogen;
- FID fuel gases: hydrogen and air.

6 Apparatus

Normal laboratory equipment and the following apparatus are required:

6.1 **Cutting device**, equipped with a water-cooled diamond blade, for cutting the UP resin into strips of width 1 mm to 2 mm.

6.2 **Gas chromatograph**, including the following components:

6.2.1 **Injection port**, equipped with a splitter, for use with liquid samples.

6.2.2 **Open, tubular column**, e.g. meeting the specifications given in Annex A.

6.2.3 **Flame ionization detector (FID)**.

A typical instrument setup and typical operating conditions are given in Annex A. Other setups and operating conditions may be used provided that the chromatograms obtained comply with the requirements given in 8.6.1.

6.3 **Data processor**, e.g. a computer (or the equivalent), to record the signals from the detector.

6.4 **Sample injection syringe**, i.e. a 1 µl microsyringe, either as a separate item of apparatus or incorporated in the auto-injector of the gas chromatograph.

6.5 **Analytical balance**, accurate to 0,1 mg.

7 Preparation of sample

Polymerized UP resin pieces of any shape that will permit the production of strips of width 1 mm to 2 mm may be used. Cut the polymerized pieces into strips of width 1 mm to 2 mm. Dry the strips and break them into pieces of length approximately 10 mm. During cutting and drying, avoid any operation that could affect the styrene and/or volatile-hydrocarbon content.

8 Procedure

8.1 General

Three test portions of the sample (see Clause 7) shall be analysed.

During the preparation, dilution and extraction processes described below, the temperature of all solutions shall remain ≤25 °C.

8.2 Preparation of extraction solvent

Weigh, to the nearest 0,1 mg, (250 ± 50) mg of *n*-butylbenzene (5.1) into a 1 000 ml volumetric flask containing approximately 500 ml of dichloromethane (5.2). Make up to the mark with dichloromethane (see, however, next paragraph) and mix.

Alternatively, acetone (see Note to 5.2) may be used instead of dichloromethane, provided that the results can be demonstrated to be equivalent to those obtained with dichloromethane. In cases of dispute, dichloromethane shall be used.

8.3 Preparation of test solution

Weigh, to the nearest 0,1 mg, into a 50 ml conical flask a test portion of a size depending on the styrene monomer content expected (see Table 1). Add 15,00 ml of extraction solvent (see 8.2), close the flask with a suitable stopper and allow the suspension to stand for 15 h to 20 h with occasional shaking.

After shaking for the last time, allow the precipitate to settle. The supernatant solution is used for injection into the gas chromatograph.

Table 1 — Size of test portion as a function of expected styrene monomer concentration

Expected styrene monomer concentration % by mass	**Size of test portion** mg
≤0,5	1 000
>0,5 but ≤1	500
>1 but ≤1,5	250
>1,5 but ≤3	150
>3	100

8.4 Determination of glass and mineral content

If the content of styrene or another aromatic hydrocarbon is to be calculated on the basis of the resin content of a UP resin containing glass and/or a mineral filler, calcine a portion of the sample (see Clause 7) in accordance with ISO 1172 and determine the glass content, the filler content or both, as applicable.

8.5 Preparation of calibration solutions

8.5.1 General

The range of concentrations of the calibration solutions which will need to be prepared will depend on the expected styrene content of the sample and the expected content of any other aromatic hydrocarbons to be determined, as well as on the size of the test portion taken (see Table 1). A series of calibration solutions shall be prepared for each aromatic hydrocarbon to be determined.

8.5.2 Preparation of styrene stock solution

Weigh, to the nearest 0,1 mg, (250 ± 10) mg of styrene (see 5.3) into a 250 ml volumetric flask containing 100 ml of extraction solvent (see 8.2). Make up to the mark with extraction solvent and mix.

Using the same procedure, prepare stock solutions of any other aromatic hydrocarbons to be determined.

8.5.3 Preparation of calibration solutions

Prepare at least five different calibration solutions in accordance with the dilution scheme given in Table 2, taking the volume of stock solution indicated in a 50 ml volumetric flask and making up to the mark with extraction solvent (see 8.2) and mixing.

Table 2 — Preparation scheme for calibration solutions

Styrene concentration in calibration solution[a] mg/l	Volume of stock solution taken ml	Volumetric flask used ml
0	Undiluted extraction solvent (see 8.2)	
$0{,}02 \times m_a$	0,25	50
$0{,}08 \times m_a$	1	50
$0{,}2 \times m_a$	2,5	50
$0{,}4 \times m_a$	5	50
$0{,}8 \times m_a$	10	50
$1{,}2 \times m_a$	15	50
$1{,}6 \times m_a$	20	50
$2 \times m_a$	25	50

[a] m_a is the actual amount of styrene, in milligrams, weighed out in 8.5.2.

8.6 Gas-chromatographic procedure

8.6.1 Gas-chromatograph operating conditions

It is important that the gas-chromatographic conditions give sufficient separation of styrene and the other compounds eluted. The chromatograms prepared shall therefore satisfy the following requirement. The peak resolution R_e between the target peaks (i.e. those corresponding to styrene, any other aromatic hydrocarbons to be determined and the internal standard) and the peaks corresponding to components appearing just before or just after the target peaks shall be more than 1,5.

The resolution R_e between two peaks of the same area is defined as follows:

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

where

t_1 and t_2	are the retention times for the two peaks, in seconds;
W_1 and W_2	are the respective peak widths at the base of the peaks, in seconds.

The gas-chromatographic conditions shall be optimized to give the performance specified above. General details of the gas-chromatographic setup are given below. Typical operating conditions are described in Annex A.

Column:	open, tubular fused-silica column.
Carrier gas:	helium or nitrogen.
Detector	FID with a hydrogen/air flame.

Adjust the rates of flow of the hydrogen and air to the FID to give:

- a high sensitivity of response;
- a linear response over the concentration range used;
- only insignificant effects of small changes in flow rate on response and sensitivity.

8.6.2 Recording the gas chromatograms of test solution and calibration solutions

Inject a suitable volume, which will depend on the sensitivity of the gas chromatograph used, of the test solution prepared in accordance with 8.3 and of each of the calibration solutions prepared in accordance with 8.5. The volume of test solution injected shall be identical to the volume of each of the corresponding calibration solutions injected. Continue to record each chromatogram until all components, such as solvent, styrene, other aromatic hydrocarbons to be determined and internal standard, have been completely eluted.

8.6.3 Evaluation of the gas-chromatographic peaks

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

The peak areas of all components shall be determined using electronic integration.

Examples of the retention times of some of the most frequently determined components are given in Table 3. The exact values will depend on the gas chromatograph and the operating conditions used.

Table 3 — Typical retention times of styrene, other aromatic hydrocarbons and the internal standard (*n*-butylbenzene)

Component	Retention time min	Retention time relative to the internal standard (*n*-butylbenzene)
Toluene	2,8	0,48
Ethylbenzene	3,7	0,64
Styrene	4,0	0,69
α-Methylstyrene	5,0	0,86
n-Butylbenzene (internal standard)	5,8	1,00
NOTE The retention times given in this table were determined using the operating conditions given in Annex A.		

9 Expression of results

9.1 Calculation of results from a calibration graph

From the chromatograms produced for the calibration solutions, calculate for each calibration solution the peak area ratio Y', normalized to an internal standard concentration of 250 mg/l, by means of the following equation:

$$Y' = \frac{A_\text{a}'}{A_\text{s}'} \times \frac{m_\text{is}}{250}$$

where

A_a' is the peak area for styrene (or another aromatic hydrocarbon being determined) in the calibration solution;

A_s' is the peak area for the internal standard (*n*-butylbenzene) in the calibration solution;

m_is is the mass of internal standard, in milligrams, used in the preparation of the extraction solvent.

NOTE All peak area ratios are normalized to an internal standard concentration of 250 mg/l. In this way, extraction solvents with different internal standard concentrations can be used simultaneously. For instance, calibration solutions prepared with extraction solvent A (containing a given concentration of internal standard) can be used together with test solutions prepared with extraction solvent B (containing a different concentration of internal standard).

Prepare a calibration curve by plotting the peak area ratios Y' against the concentrations, in milligrams per litre, of styrene or another aromatic hydrocarbon being determined.

From the graph obtained, determine the linear-regression equation

$$Y' = a \times c_\text{a}' + b$$

where

Y' is the normalized peak area ratio for styrene (or another aromatic hydrocarbon) and the internal standard (*n*-butylbenzene) in the calibration solution, i.e. A_a'/A_s';

c_a' is the concentration, in milligrams per litre, of styrene (or another aromatic hydrocarbon) in the calibration solution;

a is the slope of the linear-regression line;

b is the Y-axis intercept of the linear-regression line.

If the correlation coefficient is less than 0,995, use more calibration points or prepare the curve again starting with freshly prepared calibration solutions.

From the chromatogram produced for the test solution, calculate the corresponding peak area ratio Y, normalized to an internal standard concentration of 250 mg/l, by means of the following equation:

$$Y = \frac{A_\text{a}}{A_\text{s}} \times \frac{m_\text{is}}{250}$$

where

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

A_s is the peak area for the internal standard in the test solution;

m_is is the mass of internal standard, in milligrams, used in the preparation of the extraction solvent.

The concentration of styrene (or another aromatic hydrocarbon) in the test solution is calculated using the equation:

$$c_\text{a} = \frac{\left(Y - b\right)}{a}$$

where

c_a is the concentration of styrene (or another aromatic hydrocarbon) in the test solution, expressed in milligrams per litre;

Y is the normalized peak area ratio of styrene (or another aromatic hydrocarbon) and the internal standard;

a is the slope of the linear-regression line;

b is the Y-axis intercept of the linear-regression line.

9.2 Calculation of the content of styrene (or another aromatic hydrocarbon) in the original UP resin sample

From c_a, calculate the concentration P_a of styrene (or another aromatic hydrocarbon) in the original UP resin sample, using the equation:

$$P_\text{a} = \frac{1{,}5 \times c_\text{a}}{m_\text{p}}$$

where

P_a is the content of styrene (or another aromatic hydrocarbon) in the original UP resin sample, expressed as a percentage by mass;

c_a is the concentration of styrene (or another aromatic hydrocarbon) in the test solution, expressed in milligrams per litre;

m_p is the mass of the original UP resin sample, expressed in milligrams.

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

NOTE The factor 1,5 in the equation originates from the test solution preparation, where 15,00 ml of extraction solvent is added to the test portion (see 8.3). The factor 1,5 is the result of the conversion of c_a from mg/l to mg/15 ml (i.e. 15/1 000 × 100), followed by expression as a percentage by mass.

9.3 Calculation of the content of styrene (or another aromatic hydrocarbon) in the pure UP resin

For glass- and/or mineral-filled UP resins, calculate from c_a the concentration P_a of styrene (or another aromatic hydrocarbon) in the pure UP resin, using the equation:

$$P_a = \frac{1{,}5 \times c_a \times 100}{m_p \times \left(100 - m_{\text{glass}} - m_{\text{filler}}\right)}$$

where

P_a is the content of styrene (or another aromatic hydrocarbon) in the pure UP resin, expressed as a percentage by mass;

c_a is the concentration of styrene (or another aromatic hydrocarbon) in the test solution, expressed in milligrams per litre;

m_p is the mass of the original UP resin sample, expressed in milligrams;

m_{glass} is the glass content of the original UP resin sample, expressed as a percentage by mass;

m_{filler} is the mineral filler content of the original UP resin sample, expressed as a percentage by mass.

NOTE For an explanation of the origin of the factor 1,5 in the equation, see the Note to 9.2.

10 Test report

The test report shall include the following information:

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 gas-chromatographic equipment and operating conditions used;

d) the content of styrene (or another aromatic hydrocarbon) in the sample, expressed as the arithmetic mean of the three determinations, in percent by mass, to two significant figures;

e) in the case of glass- and/or mineral-filled material, also give the content of styrene (or another aromatic hydrocarbon) with respect to the pure UP resin;

f) any deviations from this International Standard;

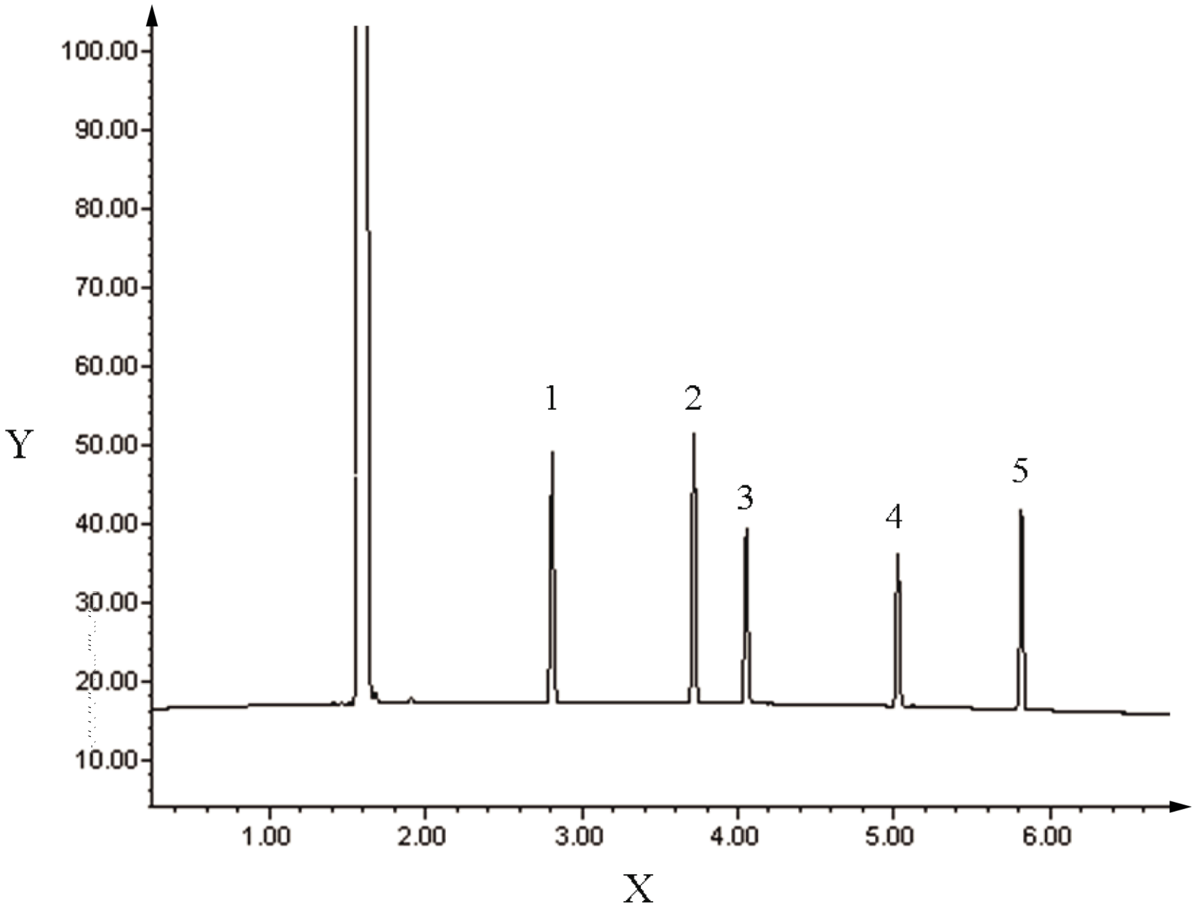
g) the date of the analysis.

Annex A
(informative)

Typical operating conditions

Chromatograph:	Agilent 6890
Column:	Open, tubular column — CP-Sil-8 CB (Varian) — film thickness 0,15 µm, length 15 m, I.D. 150 µm
Temperature programme:	Hold at 50 °C for 1 min, increase to 220 °C at 15 °C/min, hold at 220 °C for 1,66 min
Injection temperature:	250 °C
Detector temperature:	225 °C
Carrier gas:	He at 0,3 cm^3/min
Injection method:	Split injection (split ratio 1:100)
Injection volume:	1 µl
Detector:	FID
Solvent:	Dichloromethane
Internal standard:	*n*-Butylbenzene

A typical chromatogram is shown in Figure A.1.



Key

X time (minutes)

Y peak area (arbitrary units)

Peak No.	Retention time	Compound
1	2,8	Toluene
2	3,7	Ethylbenzene
3	4,0	Styrene
4	5,0	α-Methylstyrene
5	5,8	*n*-Butylbenzene

Figure A.1 — Typical gas chromatogram for styrene and other aromatic hydrocarbons
(obtained using the conditions given in this annex)

ICS 83.120

Price based on 10 pages