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)

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

Page

Foreword iv
Introduction v
1 Scope 1
2 Normative references 1
3 Terms and definitions 1
4 Principle 1
5 Materials 2
6 Apparatus 2
7 Preparation of sample 3
8 Procedure 3
8.1 General 3
8.2 Preparation of extraction solvent 3
8.3 Preparation of test solution 3
8.4 Determination of glass and mineral content 3
8.5 Preparation of calibration solutions 4
8.6 Gas-chromatographic procedure 4
9 Expression of results 6
9.1 Calculation of results from a calibration graph 6
9.2 Calculation of the content of styrene (or another aromatic hydrocarbon) in the original UP resin sample 7
9.3 Calculation of the content of styrene (or another aromatic hydrocarbon) in the pure UP resin 8
10 Test report 8
Annex A (informative) Typical operating conditions 9

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.

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.