International Standard 4901

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Reinforced plastics based on unsaturated polyester resins — Determination of residual styrene monomer content

Plastiques renforcés à base de résines de polyesters non saturés — Détermination du styrène monomère résiduel

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Foreword

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Reinforced plastics based on unsaturated polyester resins — Determination of residual styrene monomer content

1 Scope and field of application

This International Standard specifies a method of determining the residual styrene monomer content in reinforced plastics based on unsaturated polyester resins in the polymerized state (hereinafter called *UP resins in the polymerized state*), by gas chromatography. The residual styrene monomer content is an important criterion in evaluating the degree of cure of UP resins in the polymerized state. This method is not applicable to UP resins of high chemical resistance.

NOTE — If other volatile aromatic hydrocarbon monomers are present in significant quantities, see ISO 2561 for the procedure to be followed in their determination.

This International Standard also specifies a method of determining residual styrene monomer by the Wijs method for laboratories in which gas chromatography is not available.

2 References

ISO 1172, *Textile glass reinforced plastics — Determination of loss on ignition.*

ISO 2561, *Plastics — Determination of residual styrene monomer in polystyrene by gas chromatography.*

3 Determination by gas chromatography

3.1 Principle

Extraction of the styrene from the UP resin in the polymerized state using dichloromethane, followed by determination by gas chromatography.

3.2 Reagents

During the analysis, use only reagents of recognized analytical grade.

3.2.1 Dichloromethane.

3.2.2 Methanol.

3.2.3 *n*-Butylbenzene.

3.2.4 Styrene, freshly distilled and stored at 0 °C until used.

When mixed with an equal volume of methanol, the styrene shall give a clear solution.

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

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

3.2.7 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 the replacement gas has been demonstrated to give the same results.

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Cutting device, consisting of a water-cooled diamond blade for cutting the UP resin in the polymerized state to strips of width 1 to 2 mm.

3.3.2 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, has lower sensitivity.

3.3.3 Microsyringe, of capacity 1 to 50 µl.

3.3.4 Analytical balance, accurate to 1 mg.

3.4 Preparation of sample

3.4.1 Cutting

Polymerized UP resin pieces of any shape that will permit the production of strips of width 1 to 2 mm may be used. Cut the polymerized pieces into strips of width 1 to 2 mm. Dry the strips and break into pieces of length about 10 mm. During cutting and drying, avoid any overheating which could modify the styrene monomer content.

3.4.2 Preparation of solvent for extraction

Weigh 600 ± 1 mg of *n*-butylbenzene (3.2.3) into a flask of capacity 25 ml, transfer quantitatively into a one-mark volumetric flask of capacity 1 000 ml, and dilute to the mark with dichloromethane (3.2.1). During the dilution process, maintain the liquid at 20 ± 0,5 °C.

3.4.3 Extraction of styrene

Depending on the styrene monomer content expected, weigh, to the nearest 1 mg, 1 to 2 g of the sample (3.4.1) and transfer into a conical flask of capacity 50 ml. Pour 15 ± 0,1 ml of the extraction solvent (3.4.2) over the sample and allow the suspension to stand for 15 to 20 h, with occasional shaking, keeping the flask closed. Then filter quickly, using a water-jet pump, and collect the filtrate.

3.4.4 Incineration of filtered residue

If the styrene monomer content is to be calculated on the resin content of UP resins in the polymerized state containing glass fibre or mineral fillers, incinerate the filtered residue (3.4.3) according to ISO 1172 (the final total mass after incineration is designated m_f).

If necessary, another piece of the test sample may be used instead of the filtered residue.

3.5 Procedure

Three test portions of the sample (3.4) shall be analysed.

3.5.1 Preparation of calibration mixtures for gas chromatography

Weigh, to the nearest 1 mg, 600 mg of *n*-butylbenzene with an appropriate amount of styrene and transfer quantitatively into a one-mark volumetric flask of capacity 1 000 ml and dilute to the mark with a mixture of 2 parts by volume dichloromethane (3.2.1), and 1 part by volume methanol (3.2.2). Recommended amounts of styrene are as follows : 100, 200, 500, 800 and 1 000 mg. During the dilution, maintain the liquid at 20 ± 0,5 °C.

3.5.2 Gas chromatographic operating conditions

Column : metal or glass tubing of length 4,5 m and inner diameter 4 mm are recommended. The column is packed with a stationary phase of diatomaceous earth (3.2.6) which is coated with 10 % (m/m) polyethylene glycol (3.2.5).

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 filling 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 3.2.7).

Flow rate of carrier gas : 100 ml/min.

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

a) high sensitivity of response;

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

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

Recorder speed : 0,5 cm/min is recommended.

3.5.3 Gas chromatogram of test and calibration mixtures

According to the sensitivity of the gas chromatograph used, inject a suitable volume of the test solution (prepared according to 3.4.3) or the calibration mixture (prepared according to 3.5.1). The injected volume is not critical for the calculation of results, but shall be identical for corresponding samples and calibration mixtures. Operate the gas chromatograph until the *n*-butylbenzene is completely eluted.

3.5.4 Evaluation of peaks of gas chromatogram

The retention times of styrene and *n*-butylbenzene shall be known, at least in relation to each other. The exact values vary according to the density of the column, the age of the column, and other gas chromatographic parameters.

NOTE — The approximate retention time of styrene at the conditions specified in 3.5.2 is 16,5 min and of *n*-butylbenzene (standard) is 20,5 min; the approximate retention time of styrene relative to *n*-butylbenzene is 0,80.

The peak areas of styrene and *n*-butylbenzene shall be determined by one of the following methods :

a) electronic integration;

b) estimation of area, A, on the basis of the equation[1]

$$A = hw_{1/2}$$

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[1] For terms and definitions see : IUPAC. Preliminary recommendation on nomenclature and presentation of data in gas chromatography. *Pure and Appl. Chem.* **1**, pp. 177-186 (1960).

where

h is the peak height,

$w_{1/2}$ is the width at half-height of the peak;

c) planimetry.

For routine determination, peak height measurements of both sample and calibration chromatograms will be sufficient. The method of area evaluation chosen shall be identical for corresponding peaks of sample solution and calibration mixture.

3.6 Expression of results

3.6.1 Calculation of results from a calibration graph

3.6.1.1 Drawing of the calibration graph

Draw a calibration graph by plotting the ratios of the peak areas

$$\frac{A'_a}{A'_s}$$

where

A'_a is the peak area of styrene in the calibration mixture;

A'_s is the peak area of the internal standard (*n*-butylbenzene) in the calibration mixture,

against the respective concentrations, expressed in milligrams per millilitre.

3.6.1.2 Determination of the percentage of styrene

With the corresponding ratios determined from the test solution

$$\frac{A_a}{A_s}$$

where

A_a is the peak area of styrene in the test solution;

A_s is the peak area of the internal standard (*n*-butylbenzene) in the test solution.

The concentration of styrene c_a, expressed in milligrams per millilitre, in the test solution may be taken from the calibration graph. From c_a the percentage by mass of styrene in the sample, P_a, is calculated from the equation

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

where m_p is the mass, in grams, of the sample.

3.6.2 Calculation of results from a single point calibration

Provided that a linear relationship exists between peak areas and respective concentration of styrene, the following equation may be applied :

$$P_a = 1{,}5 \left(\frac{m'_a A_a A'_s}{m_p A'_a A_s} \right)$$

where

A'_a, A'_s, A_a, A_s, m_p et P_a have the same meanings as in 3.6.1;

m'_a is the mass of styrene weighed into the 1 000 ml calibration mixture (3.5.1).

NOTE — If the internal standard is present as a component in the UP resin in the polymerized state (as may be seen from a blank run of the test solution, i.e. without internal standard added), then the monomer content may be determined by the internal addition method.

3.6.3 Calculation of the styrene monomer content

To calculate the styrene monomer content on the basis of the resin content of the material tested, substitute $m_p - m_f$ for m_p in the equations in 3.6.1.2 and 3.6.2, where m_f is the final total mass, in grams, after incineration (3.4.4).

3.6.4 Precision of measurement and sensitivity

The dispersion of results on repeated measurements of styrene in the same sample shall not exceed 0,01 units of P_a on both sides of the arithmetic mean.

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

4 Determination with Wijs' solution

4.1 Principle

Extraction of the styrene from the UP resin in the polymerized state by dichloromethane, followed by reaction with Wijs' solution. Iodometric determination of the excess of Wijs' solution. If the styrene content of a UP resin in the polymerized state is to be calculated on the resin content of the latter, the filter residue is incinerated according to ISO 1172 and subsequently the mass of the incinerated residue is determined.

Undecomposed peroxide initiator, which often may still be present in UP resins in the polymerized state, is also determined iodometrically and taken into account in calculating the styrene content.

NOTES

1 If the UP resin contains not only ethylenedicarboxylic acid, but also other unsaturated components, the reaction with Wijs' solution may be affected by substances extracted from these components; i.e. such a resin in the polymerized state may seem to have a styrene content that is higher than the actual content. This applies for instance to UP resins

containing tetrahydrophthalic acid, but not to those containing Het acid; in such cases, the actual styrene content has to be determined by gas chromatography.

2 In the presence of dimethylaniline or diethylaniline and the like, used as accelerators in quantities of 0,1 to 0,2 %, the styrene content will be about 0,05 to 0,1 % higher than the actual value because these amines also react with Wijs' solution.

3 The method as described is valid only for the determination of styrene. The presence of other monomers in the unsaturated polyester resin may give misleading results.

4 The effect of the presence of acrylic and methacrylic esters has not been taken into account.

4.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.2.1 Dichloromethane.

4.2.2 Glacial acetic acid, 99 to 100 % (*V*/*V*).

4.2.3 Potassium iodide, 100 g/l solution, free from iodates.

4.2.4 Wijs' solution.

Dissolve 8 ± 1 g of iodine trichloride and 9 ± 0,1 g of iodine in a mixture of 300 ml of carbon tetrachloride and 700 ml of glacial acetic acid. Iodine monochloride may be used in place of iodine trichloride.

The solution, which should be of a dark colour, is then filtered and stored in a dark cupboard. It shall not be used within 3 days of its preparation.

NOTE — Wijs' solution is also commercially available.

4.2.5 Sodium thiosulfate, standard solution, $c(Na_2S_2O_3 \cdot 5H_2O) \approx 0{,}05$ mol/l.

4.2.6 Starch solution, 10 g/l, stabilized with mercury(II) iodide (10 mg/l) or salicylic acid (1 mg/l).

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Cutting device, consisting of a water-cooled diamond blade for cutting the UP resin in the polymerized state to strips of width 1 to 2 mm.

4.3.2 Balance, accurate to 1 mg.

4.4 Preparation of sample

4.4.1 Cutting

Polymerized UP resin pieces of any shape that will permit the production of strips of width 1 to 2 mm may be used. Cut the polymerized pieces into strips of width 1 to 2 mm. Dry the strips and break into pieces of length about 10 mm. During cutting and drying, avoid any overheating which could modify the styrene monomer content.

4.4.2 Extraction of styrene

Depending on the styrene monomer content expected, weigh, to the nearest 1 mg, 0,5 to 2 g of the sample (4.4.1) for the determination of styrene content (initial total mass m_1) and 2 to 3 g of the sample for the determination of active oxygen content (initial total mass m_2), and transfer into a conical flask of capacity 500 ml.

With UP resins in the polymerized state reinforced with either glass fibres or fillers, the initial total mass shall be increased so that the resin contents of the initial total masses corresponds to 0,5 to 2 g and 2 to 3 g, respectively.

Pour 100 ml of dichloromethane (4.2.1) over the initial total mass and allow the suspension to stand for 15 to 20 h, with occasional shaking, keeping the flask closed. Then filter quickly using a water-jet pump and collect the filtrate in a conical flask of capacity 500 ml.

NOTE — If a water-jet pump is not available, the test can be carried out without separating the extracted UP resin in the polymerized state from the contents of the flask. However, the absorption of iodine on the surface of the resin may then lead to a slightly high result for the styrene content.

4.4.3 Incineration of filter residue

If the styrene monomer content is to be calculated on the resin content of UP resins in the polymerized state containing glass fibres or mineral fillers, incinerate the filter residues (4.4.2) according to ISO 1172 (final total mass after incineration m_3 or m_4, respectively).

4.5 Procedure

Three test portions of the sample (4.4) shall be analysed.

4.5.1 Reaction with Wijs' solution and titration

Add 10 ± 0,05 ml of Wijs' solution (4.2.4) to the filtrate for the styrene determination (4.4.2), stopper the conical flask and allow to stand in the dark at room temperature for 15 min at least, 45 min at most. Then add 20 ml of the glacial acetic acid (4.2.2) and 15 ml of the potassium iodide solution (4.2.3), stopper the flask loosely with the glass stopper and allow to settle in the dark for 30 min at least, 60 min at most, shaking two or three times during this period. After adding 100 ml of water, titrate with the sodium thiosulfate solution (4.2.5), shaking the flask vigorously. Towards the end of the titration, starch solution (4.2.6) may be added as in indicator.

Make a blank determination using the same quantities of reagents at the same time and under the same conditions. It is essential that the Wijs' solution used in the test and in the blank determination be at the same temperature.

If because of an excessively high styrene monomer content, less than 25 % of the Wijs' solution is back-titrated (the blank value is taken as 100 %) after reaction of the filtrate with the