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Plastics — Polymer polyols for use in the production of polyurethane — Determination of the residual acrylonitrile and styrene monomer content by gas chromatography

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Polymer polyols are defined as very fine and stable dispersions of solid, vinylic polymers (for example, acrylonitrile/styrene copolymers are typical) in liquid polyether polyols.

Polymer polyol is used to improve the physical properties of seat cushions, especially hardness. Because the toxicity of acrylonitrile and styrene is high, it is important to establish an analytical method to determine residual amounts of these reactants.

The importance of residual toxicity has increased with the use of polyurethane foam, etc. which comes in contact with food and skin. This document is intended to help manufacturers evaluate the safety of their products.

Annexes A, B and C complement the main body of this document and not meant to be a normative part of this document.

Plastics — Polymer polyols for use in the production of polyurethane — Determination of the residual acrylonitrile and styrene monomer content by gas chromatography

1 Scope

This document specifies a method for the determination of the residual acrylonitrile monomer and styrene monomer in polymer polyols by gas chromatography.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The polymer polyol sample is dissolved in a suitable solvent. This sample solution is then analysed using gas chromatography with internal standardization. The amounts of residual acrylonitrile monomer and styrene monomer are determined from peak areas using a previously established calibration curve.

NOTE Because of the high molecular weight of substances which are part of the polymer polyol, and because these are injected directly into the chromatograph, injector contamination can occur which will lead to erroneous results.

Monitor the condition of the chromatographic parts and clean or replace as necessary.

An injector liner packed with glass wool has been used to improve vaporization and ease of cleaning.

5 Reagents and materials

5.1 Solvent, use analytical-grade methanol, N, N-dimethylformamide, tetrahydrofuran, dipropylene glycol monomethyl ether or toluene.

Other solvents can also be used if suitable results are obtained for the retention time, thermal stability and separation performance.

5.2 Internal standard, shall be selected based on the retention times of the volatile materials contained in the polymer polyol sample and the solvent.

Recommended combinations of solvent from 5.1 and internal standard are methanol and 2-methyl-1-propanol, N, N-dimethylformamide and ethylbenzene, dipropylene glycol monomethyl ether and bromobenzene.

Other combinations are also possible if the retention times, thermal stability and separation performance are suitable.

5.3 Carrier gases and fuel gases for gas chromatograph.

Use helium or nitrogen as carrier gas, hydrogen as fuel gas, dry air as supporting fuel gas.

6 Apparatus

Normal laboratory equipment and the following apparatus are required.

6.1 Gas chromatograph, with flame ionization detector and capable of employing packed or open tubular columns with either split or splitless injector. Typical operating conditions are described in Annex A.

6.1.1 Injection port, for liquid samples.

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

6.1.2 Column and packing material.

The column diameter and length, as well as the packing material and liquid phase, are to be selected based on consideration of column resolution (Re) and calibration curve linearity. Both packed columns and OT (capillary) columns (hereafter referred to as OT columns) are acceptable.

Typical columns are described in Annex A.

— OT columns: The OT column are to be selected from suitable manufacturer(s), and then shall be conditioned sufficiently.

— Packed columns: The packed column should be packed with the liquid phase and support particles from suitable manufacturer(s), and then conditioned sufficiently.

6.1.3 Detector, hydrogen flame ionization detector (hereafter referred to as FID).

6.2 Data processor, selected based on suitability for recording the signals from the detector and processing the chromatograms.

6.3 Sample injection syringe, micro-syringe with a volume range 1 µL to 50 µL. Manual and autoinjector syringes are suitable.

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

6.5 One-mark volumetric flasks (hereafter volumetric flasks), as specified in ISO 1042.

Needed volumes are 50 mL and 500 mL.

6.6 Single-volume pipettes (hereafter volumetric pipettes), as specified in ISO 648.

Needed volumes are 0,5 mL, 1,0 mL, 2,0 mL 5,0 mL and 10,0 mL.

NOTE Graduated pipettes (ISO 835) and piston pipettes (ISO 8655) are also suitable.

7 Preparation of calibration solution and sample solution

7.1 General

Two sample preparation methods are described in 7.2 and 7.3. Method A is to be used for an OT-column chromatograph and Method B is used for a packed-column chromatograph. The range of calibration concentrations should be selected based on expected levels of acrylonitrile and styrene monomers. Calibrations with 4 levels of each monomer are to be used.

7.2 Method A for using OT column

7.2.1 Preparation of internal standard solution

Into a 500 mL volumetric flask, weigh to the nearest 1 mg, the amount of internal standard specified in Table 1. Add solvent to make 500 mL, stopper tightly and mix well. This solution is hereafter called the internal standard solution.

7.2.2 Preparation of calibration solutions

Weigh the amounts of acrylonitrile and/or of styrene specified in Table 1, to the nearest 1 mg, into a 500 mL volumetric flask. Add solvent to make 500 mL, stopper tightly and mix well. This solution is hereafter called the acrylonitrile/styrene solution.

Into a 50 mL volumetric flask, pipet 0,5 mL of the acrylonitrile/styrene solution and 5,0 mL of the internal standard solution. Add solvent to make 50 mL, stopper tightly and mix well. Prepare three additional solutions by pipetting 2,0 mL, 5,0 mL and 10,0 mL of the acrylonitrile/styrene solution into separate 50 mL volumetric flasks. Add 5,0 mL of the internal standard to each flask. Then add solvent to volume, stopper tightly and mix well. These solutions are hereafter called the calibration solutions.

Table 1 — Recommended sample concentrations and solution conditions for OT-column chromatography

Concentration of acrylonitrile and/or styrene in sample ppm	Amount of internal standard substance for internal standard solution mg	Amount of acrylonitrile and/or styrene for acrylonitrile/styrene solution mg
<50	20,0	20,0
50 to 100	30,0	30,0
>100	60,0	60,0

7.2.3 Preparation of sample solution

Weigh 4,0 g sample, to the nearest 1 mg, into 50 mL volumetric flask and add 5,0 mL of internal standard solution into this 50 mL volumetric flask by using a 5,0 mL volumetric pipettes. Then add solvent to make 50 mL, stopper tightly and mix well. This solution is hereafter called the sample solution.

7.3 Method B for using packed column

7.3.1 Preparation of internal standard solution

Into a 500 mL volumetric flask, weigh to the nearest 1 mg, the amount of internal standard specified in Table 2. Add solvent to make 500 mL, stopper tightly and mix well. This solution is hereafter called the internal standard solution.

7.3.2 Preparation of calibration solutions

Weigh the amounts of acrylonitrile and/or of styrene that are specified in Table 2, to the nearest 1 mg, into a 500 mL volumetric flask. Add solvent to make 500 mL, stopper tightly and mix well. This solution is hereafter called the acrylonitrile/styrene solution.

Into a 50 mL volumetric flask, pipet 0,5 mL of the acrylonitrile/styrene solution and 5,0 mL of the internal standard solution. Add solvent to make 50 mL, stopper tightly and mix well. Prepare three additional solutions by pipetting 2,0 mL, 5,0 mL and 10,0 mL of the acrylonitrile/styrene solution into separate 50 mL volumetric flasks. Add 5,0 mL of the internal standard solution to each flask. Then add solvent to volume, stopper tightly and mix well. These solutions are hereafter called the calibration solutions.

Table 2 — Recommended sample concentrations and solution conditions for packed-column chromatography

Concentration of acrylonitrile and/or styrene in sample ppm	Amount of internal standard substance for internal standard solution mg	Amount of acrylonitrile and/or styrene for acrylonitrile/styrene solution mg
<50	50,0	50,0
50 to 100	75,0	75,0
>100	150,0	150,0

7.3.3 Preparation of sample solution

Weigh 10,0 g sample, to the nearest 1 mg, into 50 mL volumetric flask and add 5,0 mL of internal standard solution using a 5,0 mL volumetric pipette. Add solvent to make 50 mL, stopper tightly and mix well. This solution is hereafter called the sample solution.

NOTE 1 Preparing solutions of Clause 7 by mass (weight), each ingredient and whole, is also suitable.

NOTE 2 While preparing solutions of Clause 7, be careful with loss of each ingredient. Because, boiling point (BP) is rather low and tend to volatilize, especially acrylonitrile. BP of each substance shows in the following:

— ethylbenzene: 136 °C;

— acrylonitrile: 77 °C;

— styrene: 145 °C.