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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).

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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.

8 Procedure

8.1 Gas chromatographic procedure

Select the gas chromatograph conditions, solvent and internal standard to give sufficient separation of acrylonitrile, styrene and internal standard. Chromatograph is to be prepared to satisfy the following resolution (Re) requirements. The resolution, Re, is evaluated between the peaks corresponding to styrene and the internal standard, acrylonitrile and the internal standard, any additional peaks due to solvent or internal standard and the peaks of interest (acrylonitrile, styrene and internal standard). Resolution (Re) shall be more than 1,0 and preferably 1,5, if possible. The resolution (Re) between two peaks with similar areas is defined as Formula (1):

$$Re = 2(t2 - t1)/(W1 + W2) \tag{1}$$

where

t1 and t2 are the retention times of the two peaks;

W1 and W2 are the respective widths of the peaks.

Representative conditions are given in Table 3, and more details conditions for each method are described in Annex A.

Table 3 — Representative gas-chromatographic analysis capabilities

		OT column	Packed column
Column temperature	Initiation temperature	60 °C to 150 °C	60 °C to 150 °C
	End temperature	200 °C to 260 °C	150 °C to 210 °C
	Rate of temperature increase	0 °C/min to 4 °C/min and 10 °C/min to 20 °C/min	0 °C/min to 5 °C/min and 10 °C/min to 20 °C/min
Temperature of injection port		200 °C to 280 °C	180 °C to 240 °C
Temperature of detector		210 °C to 300 °C	190 °C to 260 °C
Carrier gas		Helium or nitrogen	

NOTE 1 The column temperature and detector temperature are determined by checking the notes of the column, because the temperature limit of each column is different.

Adjust the hydrogen and air flow rates to give:

- a high sensitivity of response;
- a linear response over the range of concentrations being measured;
- only insignificant effects on response or sensitivity for small changes in flow rate.

NOTE 2 Because of contamination due to polymers or oligomers, regular cleaning or replacement of chromatographic columns or inserts are performed to maintain accurate results.

8.2 Measurement of sample solutions and calibration solutions

Inject a suitable volume of the calibration solutions (prepared in accordance with 7.2.1 or 7.3.2) or the sample solution (prepared in accordance with 7.2.3 or 7.3.3), depends on sensitivity of each equipment, into a gas chromatograph. The volume of the injected sample solution shall be identical to the volume of the injected corresponding calibration solutions. Record each chromatogram until all the materials, such as acrylonitrile, styrene, solvent and internal standard, have been completely eluted.

Examples of suitable volumes are 1 µL for OT column, 1 µL to 5 µL for packed column.

8.3 Evaluation of gas chromatographic peak

The relative retention times of acrylonitrile, styrene, internal standard and solvent have to be determined in advance.

NOTE Table 4 gives examples of the retention times of acrylonitrile, styrene, internal standards, and solvents for conditions given in Annex A. The exact values depend upon the gas chromatograph, the column and the operating conditions.

Table 4 — Typical retention times of acrylonitrile, styrene, internal standard and solvent

Detection materials	OT column min	Packed column min
methanol	2,9	2,2
toluene	4,4	4,9
acrylonitrile	3,7	3,8
tetrahydrofuran	2,8	2,3
ethylbenzene	6,0	7,1
bromobenzene	12,5	15,8
2-methyl-1-propanol	5,0	5,1
styrene	9,2	11,6
N, N- dimethylformamide	12,0	14,2
dipropylene glycol monomethyl ether	18,1/18,5/20,5	21,4/23,6/24,9

NOTE Annex A and Annex B give typical operating conditions and a typical gas chromatogram (see Figure B.1 and B.2 for typical chromatograms.).

9 Expression of the results

9.1 Preparation of the calibration curve

Prepare a calibration curve by injecting identical volumes of the corresponding calibration solutions into the gas chromatograph. The calibration curve consists of concentrations of each component and the peak area ratio by gas chromatograph of each component against the internal standard. For each calibration solution, the peak area ratio Y given by Formula (2):

$$Y = A_a / A_s \tag{2}$$

where

Y is the peak area ratio for the component (such as acrylonitrile and styrene) and internal standard in the calibration solution;

A_a is the peak area for acrylonitrile (or styrene) in the calibration solution;

A_s is the peak area for internal standard in the calibration solution.

For each calibration solution, the concentration ratio X given by Formula (3):

$$X = C_a / C_s \tag{3}$$

where

X is the concentration ratio for the component and the internal standard in the calibration solution;

C_s is the concentration of internal standard in the calibration solution;

C_a is the concentration of acrylonitrile (or styrene) in the calibration solution.

Then prepare the calibration curve for each component by plotting the peak area ratio Y, against the concentration ratio, X of each component C_a in the calibration solution.

From the obtained graph, determine the linear regression formula and the contribution ratio using Formula (4):

$$Y = a \times X + b \quad (4)$$

where

a is the slope of the linear regression line;

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

If the coefficient of determination (R^2) is 0,995 or less, increase number of calibration points or re-prepare the curve.

9.2 Calculation of results from a calibration graph

From the peak areas of the gas chromatogram for sample solution, calculate the corresponding peak area ratio Y', given by following Formula (5):

$$Y' = A'_a/A'_s \quad (5)$$

where

Y' is the peak area ratio for the component (such as acrylonitrile and styrene) and internal standard in the sample solution;

A'_a is the peak area for acrylonitrile (or styrene) in the sample solution;

A'_s is the peak area for the internal standard in the sample solution.

The concentration of each component is calculated by following Formula (6):

$$X' = (Y' - b)/a \quad (6)$$

where

X' is the concentration ratio for each component and internal standard in the sample solution.

Assigning a concentration of the internal standard in the sample solution to the calculated value X', calculate the concentration of each component in the sample solution.

From X' calculate the mass fraction P_a of acrylonitrile or styrene in the polymer polyol sample, using the following Formula (7):

$$P_a = (X' \times C'_s/C_p) \times 10^3 \tag{7}$$

where

P_a is the content of acrylonitrile or styrene in polymer polyol, expressed in ppm (calculated as µg/g);

C'_s is the concentration of internal standard in the sample solution, expressed in mg/mL;

C_p is the concentration of the polymer polyol sample, expressed in g/mL.

If solutions were prepared by mass given in Formula (8):

$$P_a = (X' \times M'_s/M_p) \times 10^3 \tag{8}$$

where

M'_s is the mass of internal standard in the sample solution, expressed in mg;

M_p is the mass of the polymer polyol sample, expressed in grams (g).

If $C_s = C'_s$, then Formulae (3), (5) and (6) can be replaced to Formulae (9), (10) and (11)

$$Y = a \times C'_a + b \tag{9}$$

$$C'_a = (Y' - b)/a \tag{10}$$

$$P_a = (V_p \times C'_a/M_p) \times 10^3 \tag{11}$$

where

C'_a is the concentration of each component in the sample solution, expressed in mg/mL;

V_p is the volume of the sample solution, expressed in mL.

9.3 Calculation of results from a single-point calibration

Provided that a linear relationship exists between peak areas and respective concentration of acrylonitrile or styrene, P_a may be calculated using Formula (12):

$$P_a = \left[\left\{M'_a\left(A_a / A_s\right)\right\}\right] / \left[\left\{M_p / \left(A'_a / A'_s\right)\right\}\right] \times 10^3 \tag{12}$$

where

A_a, A_s, A'_a, A'_s, M_p and P_a	are as defined in 9.1 and 9.2;
M'_a	is the mass, in milligrams (mg), of acrylonitrile or styrene in the calibration solution (refer to 7.1 and 7.2).

9.4 Acceptability of results and measurement sensitivity

Repeatability of acrylonitrile and styrene in the sample should not exceed ±10 % of the arithmetic mean of variability of the results.

A determination limit of the order of 1 µg/g order acrylonitrile and 1 µg/g order styrene, by OT column, 2 µg/g order acrylonitrile and 2 µg/g order styrene, by packed column, can be expected using the method described this document.

10 Precision

Precision and bias, analysed in accordance with this method, are given in Annex C.

11 Test report

The test report shall include the following particulars;

a) a reference to this document, i.e. ISO 21257:2018;

b) details of sample (the type of polymer polyol analysed and all details necessary for complete identification of the sample);

c) the measured conditions (gas-chromatographic equipment conditions, internal standard and solvent);

If used, the typical conditions, given in Annex A may be referred to by subclause number;

d) the measurement results (each measurement result, arithmetic mean and standard deviation);

e) the date of analysis.

Annex A
(informative)

Typical analytical conditions

A.1 Condition of chromatograph with OT column

a) Gas chromatograph: GC 6890[1]

b) Column: DB-WAX (L: 30 m, D: 0,53 mm, T: 1 µm)

c) Column temperature: 90 °C – 2 °C/min to 130 °C – 20 °C/min – 200 °C (hold 30 min)

d) Injection temperature: 200 °C

e) Detector temperature: 210 °C

f) Carrier gas: He (Flow rate: 30 mL/min)

g) Injection method: split method (2: 1)

h) Injection volume: 1 µL

i) Detector: FID

j) Solvent: N, N-dimethylformamide (DMF)

k) Internal standard: Ethylbenzene

A.2 Condition of chromatograph with packed column

a) Chromatograph: GC-2014[2]

b) Column: Glass 2,1 m × 3,2 mmID

PEG20M 20 % Uniport B 60/80 mesh

c) Column temperature: 100 °C – 2 °C/min to 140 °C – 20 °C/min – 200 °C (hold 30 min)

d) Injection temperature: 200 °C

e) Detector temperature: 200 °C

f) Carrier gas: He (Flow rate: 40 mL/min)

g) Injection method: Direct injection

h) Injection volume: 5 µL

i) Detector: FID

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[1] GC 6890 is the trademark of a product supplied by Agilent Technologies. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

[2] GC-2014 is the trademark of a product supplied by Shimadzu. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

j) Solvent: N, N- dimethylformamide (DMF)

k) Internal standard: Ethylbenzene