Designation: D7252 – 22

Standard Test Method for
Polyurethane Raw Materials: Determination of Monomer and Isomers in Isocyanates[1]

1. Scope*

1.1 This test method determines the percent by weight of monomeric isomers and total monomer in crude or modified isocyanates. The test method is applicable to methylene di(phenylisocyanate) (MDI) and polymeric (methylene phenylisocyanate) (PMDI). (See Note 1.)

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is no known ISO equivalent to this standard.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D883 Terminology Relating to Plastics
E456 Terminology Relating to Quality and Statistics
E682 Practice for Liquid Chromatography Terms and Relationships
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E2935 Practice for Evaluating Equivalence of Two Testing Processes

3. Terminology

3.1 For definitions of terms used in these test methods see Terminology D883, unless otherwise specified. For terms relating to precision and bias and associated issues, the terms used in this standard are defined in accordance with Terminology E456.

4. Summary of Test Method

4.1 The sample is reacted (derivatized) with methanol to form a mixture of methyl urethanes. The urethanes mixture is then separated by normal phase high performance liquid chromatography (HPLC). The separated, derivatized isomers are quantified through the use of an internal standard.

5. Significance and Use

5.1 This test method is used for research or for quality control to characterize isocyanates used in polyurethane products.

6. Apparatus

6.1 *High Performance Liquid Chromatograph,* consisting of:

6.1.1 *Binary (or greater) solvent pump,* capable of maintaining a pulse-free flow rate of 1-3 milliliters per minute

6.1.2 *Sample injector,* automatic or manual, capable of reproducibly injecting a 2 microliter volume

6.1.3 *Column heater,* capable of maintaining a temperature of 30 ± 0.2°C

6.1.4 *UV detector,* capable of measurements at 235 nm.

6.1.5 *Chart recorder or Data system,* capable of peak area integration.

6.2 *HPLC analytical column,* 250 mm by 4.6 mm by 5 μm cyano stationary phase.

NOTE 2—Other chromatographic columns are used provided it is ascertained that similar chromatographic performance is obtained.

6.3 *Magnetic Stirring Hotplate.*

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent-grade chemicals are to be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on

A Summary of Changes section appears at the end of this standard

Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades are used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1 *Acetanilide,* 99.9 % purity, to be used as an internal standard.

7.1.2 *Acetonitrile,* dry. Dry this and reagents below over molecular sieve for twenty-four hours.

7.1.3 *Ethanol,* dry. Use of ethanol denatured with methanol (such as SDA-30) is used if more readily available.

7.1.4 *Hexane,* dry.

7.1.5 *Methanol,* dry.

7.1.6 *Eluent solution,* Mix 1:1 by volume of dry methanol and ethanol.

7.1.7 *Internal Standard and derivatization solution,* Dissolve 0.20 g of acetanilide in 1 L of dry methanol.

8. Hazards

8.1 **Warning**—Diisocyanates are eye, skin and respiratory irritants at concentrations above the occupational exposure limit (TLV or PEL). Diisocyanates can cause skin and respiratory sensitization (asthma) in some people. Once sensitized, it is essential to limit further exposure to diisocyanates. Use a combination of engineering controls and personal protective equipment, including respiratory, skin and eye protection, to prevent over-exposure to diisocyanates. Consult the product suppliers' Safety Data Sheet (SDS) for more detailed information about potential health effects and other specific safety and handling instructions for the product.

9. Sampling

9.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling methods, even when conducted rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times. (**Warning**—see Section 8, Hazards, for handling concerns.)

10. Instrument Preparation

10.1 The instrument settings here are to be used as a guide for laboratory specific instrument-column combinations, which are to be adjusted to provide adequate separation and sensitivity as described in Practice E682.

10.1.1 *Pump*
Flow = 1.5 mL/min
Eluent A (hexane) = 90 %
Eluent B (1:1 by volume ethanol:methanol) = 10 %

10.1.2 *Detector*
Wavelength = 235 nm
Output Range = 2.000 au full scale

10.1.3 *Additional Settings*
Injection volume = 2 µL
Column Temperature = 30°C
Stop Time = 25 minutes
Post Run Time = 10 minutes

10.1.4 *Solvent Program*

10.1.4.1 After the components of interest have eluted, it is desirable to flush the remainder of the material from the column to avoid interference with subsequent analyses. A solvent program such as the one below is used for analysis and cleanup:

(1) Initial
Eluent A = 90 %
Eluent B = 10 %
Hold for 15 minutes.
(2) Column Flush
Eluent A = 0 %
Eluent B = 100 %
Hold for 10 minutes.
(3) Re-equilibration
Eluent A = 90 %
Eluent B = 10 %
Hold for 2.5 minutes

11. Calibration and Standardization

11.1 The primary standard consists of monomeric material of sufficient purity and containing all isomers of interest. The concentrations of the isomers in the standard are to be in the same ranges as those expected in samples to be analyzed. Because of the difficulty in obtaining primary standards for this test, agreement on the standard material to be used in testing must be obtained between the testing laboratory and the recipient of the final test results. Several strategies in obtaining suitable standard material have been used.

11.1.1 Several isomer blends of suitable purity are available from several isocyanate manufacturers. These blends are combined to produce a primary standard with isomers in the same range as the samples.

11.1.2 Alternatively, monomer of suitable purity consisting of unknown quantities of the isomers of interest is analyzed by gas chromatography with a flame ionization detector. An area percent technique is employed to determine the isomer content. Again, agreement between the testing laboratory and the recipient of the final test results must be obtained for the specific conditions of the gas chromatographic determination.

11.2 Regardless of which of the strategies above is used, the primary standard is prepared and analyzed as described in the following sections.

12. Procedure

12.1 *Sample Preparation*

12.1.1 Weigh the sample to be analyzed in a 250 mL beaker. Use the formula below to determine the correct weight. Record actual weight to the nearest 0.1 milligram.

$$Weight\ of\ sample\ (milligrams) = \frac{5000}{Expected\ wt\%\ monomer\ in\ sample}$$

(1)

12.1.2 Dissolve the sample in 20 mL of dry acetonitrile and add exactly 100 mL of the (Internal Standard and derivatization) solution. Add a stirring bar, cover with watch glass and heat on hotplate/stirrer for fifteen minutes. The hotplate temperature must be set such that the sample solution begins to boil in 7-10 minutes.

12.1.3 Remove the sample solution from heat and allow to cool to room temperature.
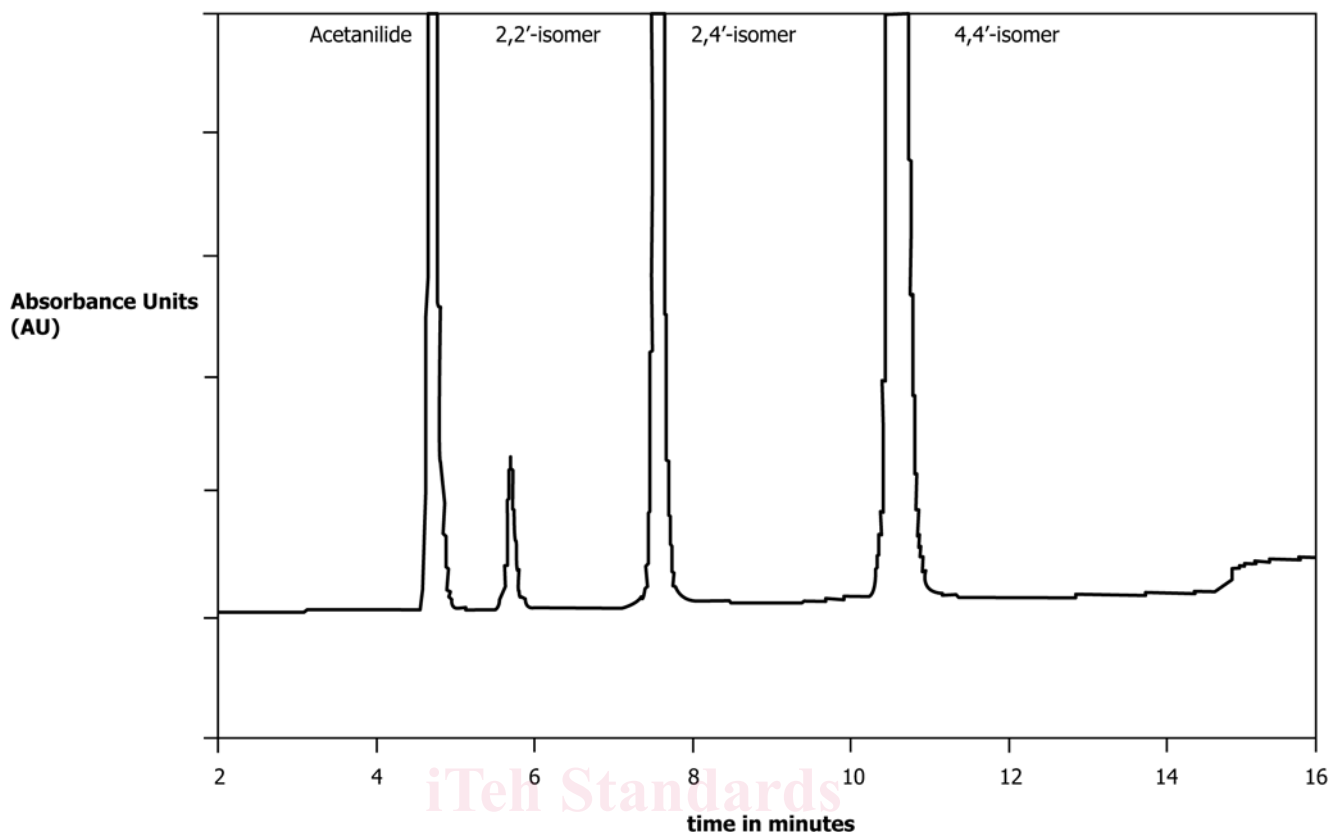
FIG. 1 Example of a Standard Solution Chromatogram

12.2 Analysis

12.2.1 Prior to injecting any sample, allow the chromatographic system to equilibrate by pumping the initial eluent through the column for at least 20-30 minutes. When a stable baseline is observed, analyze an aliquot of the derivatized sample solution. After all isomers of interest have eluted, flush the column as specified by the solvent program above.

13. Calculation

13.1 Calculate the weight percent of isomer "i" as follows:

$$Isomer\ i, \% = \frac{A_i^{sample}\ A_{IS}^{std}\ W_i^{std}\ 100}{A_i^{std}\ A_{IS}^{sample}\ W_{sample}} \qquad (2)$$

A_i^{sample} = the area of the "i" isomer peak in the sample chromatogram (see Fig. 1)

A_{IS}^{std} = the area of the internal standard peak in the standard chromatogram (see Fig. 2)

A_i^{std} = the area of the "i" isomer peak in the standard chromatogram

A_{IS}^{sample} = the area of the internal standard peak in the sample chromatogram

W_i^{std} = the weight of the "i" isomer in the standard solution in milligrams

W_{sample} = the weight of the sample in milligrams

13.2 Calculate the percent monomer in the sample by:
Monomer, % = Sum of all isomers, %.

14. Report

14.1 Report the weight percent of each isomer and of the monomer to the nearest 0.1%.

15. Precision and Bias[3]

15.1 *Precision*—Attempts to develop a precision and bias statement for this test method have not been successful. For this reason, only estimates of data on precision and bias are given. Because this test method does not contain an acceptable numerical precision and bias statement, it shall not be used as a referee test method in case of dispute. Anyone wishing to participate in the development of precision and bias data is to contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

15.1.1 A limited round robin was performed with three laboratories. Tables 1-4 are based on a round robin conducted in 2004 in general accordance with Practice E691, involving six materials tested by three laboratories. Each test result was the average of two individual determinations. Each laboratory made duplicate determinations on each material on each of two days. (**Warning**—The following explanations of *r* and *R* (15.1.2-15.1.3) are only intended to present a meaningful way of considering the approximate precision of this test method. The data in Tables 1-4 must not be rigorously applied to the acceptance or rejection of material, as those data are specific to the limited round robin and will not be representative of other lots, conditions, materials, and laboratories. Users of this test method must apply the principles outlined in Practice E691 to generate data specific to their laboratory and materials, or

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1243.
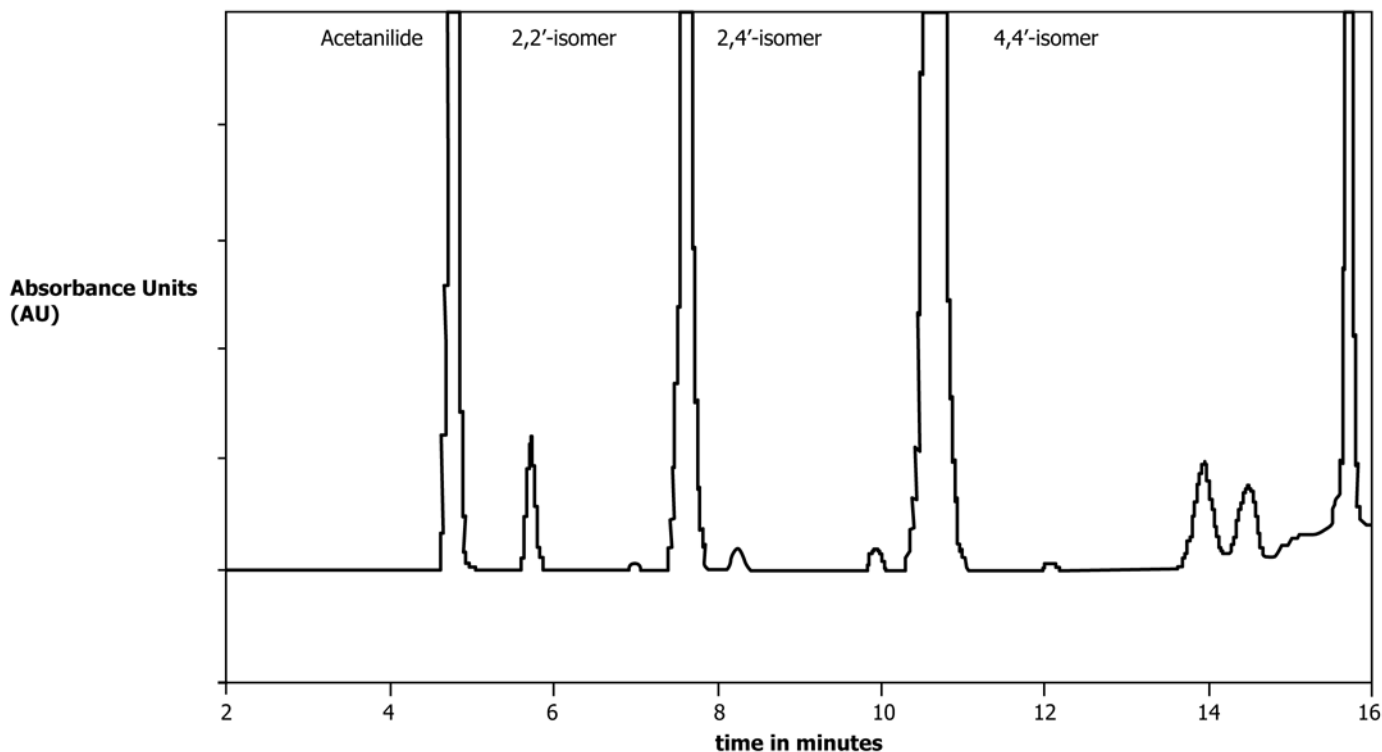
| Acetanilide | 2,2'-isomer | 2,4'-isomer | 4,4'-isomer |

FIG. 2 Example of a Sample Solution Chromatogram

TABLE 1 Estimated Precision for 2,2'- Isomer

	Weight % 2,2'- MDI					
Material	Average	S_r^A	S_R^B	r^C	R^D	n^E
1	3.05	0.08	0.09	0.21	0.26	3
2	0.13	0.01	0.12	0.02	0.33	3
3	0.00	0.00	0.00	0.00	0.00	3
4	0.13	0.02	0.11	0.06	0.31	3
5	0.77	0.03	0.03	0.09	0.10	2
6	1.33	0.04	0.05	0.11	0.15	
Pooled data		0.04	0.08	0.11	0.23	. . .

[A] S_r = within-laboratory standard deviation of the replicates.
[B] S_R = between-laboratory standard deviation of the averages.
[C] r = within-laboratory repeatability limit = 2.8*S_r.
[D] R = between-laboratory reproducibility limit = 2.8*S_R.
[E] n = number of laboratories contributing valid data for this material.

TABLE 2 Estimated Precision for 2,4'- Isomer

	Estimated Precision for 2,4'- Isomer Weight % 2,4'- MDI					
Material	Average	S_r^A	S_R^B	r^C	R^D	n^E
1	50.47	0.89	0.89	2.49	2.49	3
2	4.16	0.08	0.08	0.22	0.22	3
3	1.24	0.02	0.02	0.07	0.07	3
4	2.84	0.06	0.06	0.15	0.15	3
5	13.36	0.38	0.38	1.06	1.06	3
6	22.67	0.31	0.31	0.86	0.86	2
Pooled data		0.42	0.42	1.19	1.19	

[A] S_r = within-laboratory standard deviation of the replicates.
[B] S_R = between-laboratory standard deviation of the averages.
[C] r = within-laboratory repeatability limit = 2.8*S_r.
[D] R = between-laboratory reproducibility limit = 2.8*S_R.
[E] n = number of laboratories contributing valid data for this material.

between specific laboratories. The principles of 15.1.2-15.1.3 would then be valid for such data.)

15.1.2 *Repeatability, r*—It has been determined that the maximum expected difference between two test results for the

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