INTERNATIONAL STANDARD

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Plastics — Aromatic isocyanates for use in the production of polyurethanes — Determination of hydrolysable chlorine

Plastiques — Isocyanates aromatiques pour utilisation dans la production de polyuréthannes — Détermination du chlore hydrolysable

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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

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Foreword

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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 on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 15028:2004), which has been technically revised.

Introduction

No International Standard for the determination of hydrolysable chlorine in isocyanates has been published. The main sources of hydrolysable chlorine in isocyanates are carbamoyl chloride and dissolved phosgene from the manufacturing process. Both of these compounds react with alcohols and water, forming ureas, carbamates, carbon dioxide and hydrochloric acid. These acidic materials neutralize basic catalysts used in polyurethane production, thus adversely affecting processing properties. This test method is based on and is technically equivalent to ASTM D 4663.

Plastics — Aromatic isocyanates for use in the production of polyurethanes — Determination of hydrolysable chlorine

SAFETY STATEMENT — 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 of the hydrolysable-chlorine content of toluene-2,4-diisocyanate, toluene-2,6-diisocyanate or mixtures of the two. This test method may also be applied to other isocyanates of suitable solubility, such as crude or refined polymeric isocyanates.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

ISO 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
polyurethane
polymer prepared by the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

3.2
hydrolysable chlorine
organic or inorganic chlorine compounds formed in the production of isocyanates that react with methanol under the conditions of the test to liberate hydrogen chloride

4 Principle

The hydrolysable chlorine reacts with methanol, liberating hydrogen chloride. The titratable chlorides are then determined potentiometrically using a standard silver nitrate solution.

5 Interference

Thiocyanate, cyanide, sulfide, bromide, iodide and other substances capable of reacting with silver ions, as well as substances capable of reducing silver ions in acid solution, will interfere with the determination.

6 Sampling

Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling methods (for example sampling an open drum with a thief), even when conducted rapidly, can cause contamination of the sample with insoluble ureas; therefore, blanket the sample with a dry inert gas (e.g. nitrogen, argon or dried air) at all times.

WARNING — Organic isocyanates are hazardous when absorbed through the skin, or when the vapours are breathed in. Provide adequate ventilation and wear protective gloves and eyeglasses.

7 Test conditions

Since isocyanates react with moisture, keep the laboratory humidity low preferably below 50 % relative humidity.

NOTE If the relative humidity is greater than 50 % relative humidity, work quickly to minimize exposure of the sample to the air.

8 Reagents

Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of ISO 6353-2. Other grades may be used, provided that it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean grade 2 water as defined by ISO 3696:1987.

8.1 Concentrated nitric acid, HNO_3, specific gravity 1,42, conforming to ISO 6353-2.

8.2 Methanol, CH_3OH, conforming to ISO 6353-2.

8.3 Silver nitrate, standard solution (0,01 M).

Standardize with standard hydrochloric acid, either gravimetrically or potentiometrically, frequently enough to detect changes of 0,000 5 M.

9 Apparatus

9.1 Titrator, automatic (preferred) or manual, equipped with a silver/silver chloride electrode pair and a 50 ml burette, the latter conforming to ISO 385.

9.2 Pipette, 50 ml, one-mark, conforming to ISO 648.

9.3 Beakers, 400 ml, conforming to ISO 4787.

9.4 Magnetic stirrer, equipped with an inert stirring bar, **or equivalent stirrer**.

9.5 Laboratory balance, capable of weighing out test portions to within ± 0,01 g.

10 Procedure

10.1 Weigh (by difference to the nearest 0,01 g) 9 g to 11 g of the sample (or 18 g to 22 g of the sample if the hydrolysable-chlorine content is expected to be less than 0,01 %) from a sampling weighing bottle into a clean, dry 400 ml beaker. Add 50 ml of methanol and stir. Stir continually while the reaction starts, at which point the beaker will become warm and crystals may form on the sides of the beaker (see the Note). Fill the beaker half-full with water (add the water quickly to keep the reactants from solidifying and to minimize the loss of HCl) and boil gently for 30 min.

NOTE Some isocyanates will not react readily and slight warming may be necessary to initiate the reaction. Other isocyanates may react, as indicated by warming of the reactants, but may not form crystals.

10.2 Wash the sides of the beaker with water and remove and rinse the stirring bar, adding the rinsings to the beaker. Cool the beaker in an ice bath to about 10 °C and add 10 drops of HNO_3. Titrate potentiometrically with 0,01 M $AgNO_3$ (8.3) using a silver/silver chloride electrode pair (see 9.1) **with stirring.** If the chloride content is greater than 0,2 %, use 0,1 M instead of 0,01 M $AgNO_3$ solution.

Statistical data were developed in a round robin in which cooling to 10 °C was used. Other laboratories report that cooling to about 20 °C is sufficient. A temperature of 20 °C may be used if it is established that the results do not differ statistically from results obtained with cooling to 10 °C.

11 Expression of results

Calculate the hydrolysable chlorine, as a percentage by mass, as follows:

$$\text{Hydrolysable chlorine} = 3{,}55 \times V \times c/m$$

where

V is the volume of $AgNO_3$ solution required to titrate the test portion, in ml;

c is the exact concentration of the $AgNO_3$ solution, in mol/l;

m is the mass of the test portion taken, in g;

3,55 is a constant combining the atomic mass of chlorine (35,5), the conversion from mg to g (1 000), and the conversion to percent (100).

12 Precision and bias

12.1 Precision

The precision statement is based on a limited round robin conducted among three laboratories; therefore, this test method should not be used as a referee test method in cases of dispute.

12.1.1 Repeatability

It is estimated that duplicate results obtained by the same analyst using the same equipment on the same day should be considered as suspect if they differ by more than 0,000 5 % at hydrolysable-chlorine concentrations of 0,001 % to 0,2 %.

12.1.2 Reproducibility

It is estimated that results reported by different laboratories should be considered as suspect if they differ by more than 0,003 % hydrolysable chlorine.