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

*Plastiques — Isocyanates aromatiques utilisés pour la production de  
polyuréthannes — Dosage du chlore total*

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## Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 26603 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

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## Introduction

Isocyanates are typically produced by phosgenation of an aromatic amine using chlorine-substituted benzenes (e.g. o-dichlorobenzene) as reaction solvents. ISO 15028 is used to determine the hydrolyzable chlorine content of the isocyanates. The test methods in this International Standard are used to determine the total chlorine content of aromatic isocyanates. The difference between the total chlorine content and the hydrolyzable chlorine content is a measure of the reaction solvents left in the product, and therefore is a useful tool for assessing product quality.

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

**SAFETY PRECAUTIONS** — Persons using this International Standard should be familiar with normal laboratory practice, if applicable. This International Standard 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 is used to determine the total chlorine content of aromatic isocyanates used in the preparation of polyurethanes. The difference between the total chlorine content and the hydrolyzable chlorine content (see ISO 15028) is a measure of the process solvents left in the product. Both test methods are applicable to a variety of organic compounds, including aliphatic isocyanates, but the amount of sample used might need to be adjusted. These test methods can be used for research or for quality control.

NOTE This International Standard is technically equivalent to ASTM D 4661-03.

## 2 Normative references

The following referenced documents are indispensable for the application 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 3696, *Water for analytical laboratory use — Specification and test methods*

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

ISO 6353-3, *Reagents for chemical analysis — Part 3: Specifications — Second series*

## 3 Terms and definitions

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

### 3.1 isocyanates

organic compounds containing one or more NCO groups

### 3.2 polyurethane

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

### 3.3 hydrolyzable chlorine

organic or inorganic chlorine compounds formed in the production of isocyanates that react with methanol under the conditions of ISO 15028 to liberate hydrogen chloride

**3.4 total chlorine**  
inorganic and organically bound chlorine present in isocyanates that is converted to titratable chlorides under the combustion conditions of the test

## 4 Principle

In each test method, the organic matter in the sample is destroyed by combustion with oxygen, thus converting the organically combined chlorine to ionic chloride. The chloride is determined potentiometrically by titration with silver nitrate ( $\text{AgNO}_3$ ) solution.

### 4.1 Test Method A

Combustion of the sample is done in a pressurized oxygen bomb.

### 4.2 Test Method B

Combustion is done at atmospheric pressure in a Schöniger oxygen flask.

NOTE For information on the Schöniger flask, refer to Reference [6].

## 5 Interferences

Thiocyanate, cyanide, sulphide, bromide, iodide or other substances capable of reacting with silver ion, as well as substances capable of reducing silver ion 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, even when conducted rapidly, can expose the isocyanate to moisture and 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.**

**CAUTION — Provide adequate ventilation and wear protective gloves and eyeglasses.**

## 7 Test Method A — Total chlorine by oxygen bomb

### 7.1 Reagents

#### 7.1.1 Purity of reagents

Reagent-grade chemicals shall be used in all tests. 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, it is intended that all reagents shall conform to the specifications of ISO 6353-2 and ISO 6353-3.

### 7.1.2 Purity of water

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

**7.1.3 Ethyl Alcohol** — Conforming to ISO 6353-2.

**7.1.4 Nitric acid (diluted)** — While stirring vigorously, add 100 ml of nitric acid ( $\text{HNO}_3$ , specific gravity 1,42) to 100 ml of water cooled in an ice bath.

**7.1.5 Oxygen** — Free of combustible materials and halogen compounds.

**7.1.6 Silver nitrate, standard solution (0,01 M)** — Prepare a 0,01 M silver nitrate ( $\text{AgNO}_3$ ) solution, and check frequently enough to detect changes of 0,000 5 M, either gravimetrically or potentiometrically, using standard hydrochloric acid (HCl).

**7.1.7 Sodium carbonate solution (50 g/l)** — Dissolve 135 g of sodium carbonate decahydrate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) in water and dilute to 1 l.

## 7.2 Apparatus

**7.2.1 Weighing bottle and balance** — suitable for weighing a liquid sample by difference to the nearest 0,5 mg.

**7.2.2 Oxygen bomb apparatus** — A corrosion-resistant steel reactor capable of being pressurized to 40 atmospheres of pure oxygen, followed by electrical ignition of the sample by use of an internal fuse wire. The bomb must be capable of withstanding the pressure build-up caused by the combustion of the sample. Parr Bomb No. 1108 is a suitable device (see Figure 1). Equivalent apparatus may be substituted with appropriate changes in the procedure.

**7.2.3 Fuse wire** — iron-nickel-chromium, No. 34 B & S gage.

**7.2.4 Titrimeter** — automatic (preferred) or manual, equipped with a silver/silver chloride electrode pair and a 10 ml capacity microburette.

**7.2.5 Bubble counter** — a 100 ml graduate and delivery tube, or a bent "L" glass tube connected to a piece of rubber tubing. The graduate is filled to the 50 ml mark with water to which 3 ml of 0,1 M  $\text{AgNO}_3$  and 1 drop of concentrated nitric acid have been added. Any turbidity that develops indicates that HCl gas is being lost when venting the bomb.

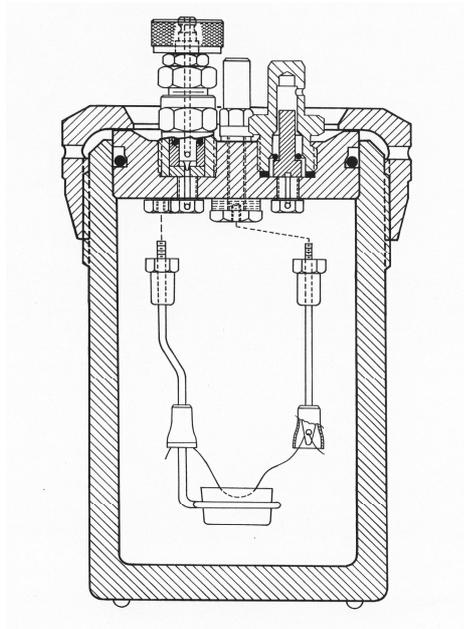


Figure 1 — Parr oxygen bomb

### 7.3 Procedure

7.3.1 Make certain that the bomb, oxygen lines, and fittings are free of oil and grease.

**WARNING — Small quantities of either oil or grease may cause a violent explosion.**

When the bomb is used repeatedly, a film may form on its inner surface. Remove this film by rotating the bomb on a lathe at about 300 rpm and polishing the inside surface with Grit No. 2/0 or equivalent paper coated with light machine oil, then with a paste made from grit-free chromic oxide and water. This procedure will remove all but very deep pits while polishing the surface. Before using the bomb, wash it with soap and water to remove residual cutting oil or paste. Bombs with pitted surfaces should not be used because they will retain chlorine from sample to sample.

7.3.2 Weigh a 0,9 g sample by difference to  $\pm 0,000\ 5\text{g}$  into the combustion capsule.

**WARNING — A severe safety hazard exists if more than 1 g of sample is used.**

7.3.3 Fit a 100 mm, iron-nickel fuse wire (7.2.3) onto the two electrodes. Place the combustion capsule on the loop electrode and adjust the fuse wire in the capsule so that it is under the surface of the sample but does not touch the capsule. Place about 5 ml of  $\text{Na}_2\text{CO}_3$  solution (7.1.7) in the bomb and, with a small rubber spatula, wet the interior surface of the bomb, including the head, as thoroughly as possible. Put the bomb head in the bomb cylinder and the contact ring on top of the bomb head, screwing the cap down finger-tight. Close the outlet valve securely with the special wrench provided and open the main oxygen cylinder slightly. Place the bomb in its bench-mounted holder and tighten the holder with a suitably sized hex wrench. Attach the union on the oxygen-filling connection to the inlet valve of the bomb. Admit oxygen slowly (to prevent blowing the sample from the cup) to 20 to 25 atmospheres (2,03 MPa to 2,53 MPa). Close the operating valve of the oxygen cylinder and observe the pressure on the bomb gage. If a leak is indicated by a gradual pressure drop, inspect and tighten all connections. Do not continue with the test until the leak is stopped and the bomb holds pressure. Release the pressure from the oxygen tank and disconnect the bomb. Place the valve thumb nut on the oxygen inlet valve and tighten finger-tight.

**WARNING — Exercise extreme caution from this point on until the bomb has been fired, cooled, and bled free of oxygen.**

**7.3.4** Pull the plug to the bomb ignition unit. Fill the bomb ignition receptacle three-quarters full of water. Submerge the bomb in the centre of the ignition receptacle and visually inspect it for oxygen leaks. If the needle valve is not gas tight, tighten the packing gland slightly. Do not fire the bomb until all leaks are repaired. Allow cooling water to circulate around the bomb the entire time the bomb is in the receptacle.

**WARNING — A serious shock hazard exists around the bomb ignition receptacle should the ignition unit be shorted. Always pull the electrical plug before touching this receptacle.**

**7.3.5** Connect the terminal at the top of the ignition receptacle to the terminal on the top of the bomb. Connect the plugs to the cooling receptacle, insert the plug to the ignition unit and fire the bomb. The red indicator light should flash on, then off, indicating that the bomb fired properly. Pull the electrical plug. If the bomb did not fire as indicated, carefully feel the bomb. If it is cold, this indicates that the test was incomplete, and that 7.3.1 to 7.3.5 must be repeated.

**7.3.6** Allow the bomb to cool at least ten min, then remove it from the receptacle and connect the bubble counter to the outlet valve. Release the pressure slowly and uniformly, taking at least 2 min. When all of the gas has bled, open the bomb and examine the contents. Traces of unburned sample or soot indicate incomplete combustion, and that the test must be repeated.

**7.3.7** Carefully wash the bomb head, the electrodes, the capsule, and the cylinder walls with water as follows: Rinse the walls of the cylinder with about 25 ml of reagent water and fill the capsule. Scrub both the interior of the bomb and the inner surface of the bomb cover with a small rubber spatula then rinse the spatula, catching the rinse water in the bomb. Rinse the bomb washings into a 250 ml beaker.

**NOTE** Because it is difficult to rinse the last traces of chloride from the walls of the bomb, residual chloride tends to carry over from sample to sample. Therefore, it is advisable to avoid alternating samples with high and low chlorine contents.

Evaporate the washings in the beaker to about 20 ml. Cool below 10 °C and acidify the solution to methyl red indicator by the dropwise addition of diluted HNO<sub>3</sub> (7.1.4). Insert silver/silver chloride electrodes and add 60 ml to 100 ml of ethyl alcohol to cover the electrode tips. Cool the solution to 10 °C, and titrate potentiometrically with 0,01 M AgNO<sub>3</sub>, adding the AgNO<sub>3</sub> solution in 0,1 ml increments near the end point.

**7.3.8** Titrate a blank exactly as described in 7.3.1 to 7.3.7, but without adding the sample.

## 7.4 Calculation

Calculate the total chlorine, in percent, by means of the formula

$$3,55(A - B)C / m$$

where

*A* is the AgNO<sub>3</sub> solution required for titration of the sample, ml;

*B* is the AgNO<sub>3</sub> solution required for titration of the blank, ml;

*C* is the molarity of the AgNO<sub>3</sub> solution;

*m* is the mass of the sample used, in g;

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

## 7.5 Precision and bias

A limited round robin was conducted among PURMAC laboratories. Results showed the following for precision and bias of the method.

### 7.5.1 Precision

**7.5.1.1** Duplicate results by the same analyst should be considered suspect if they differ by more than 0,015 % total chlorine.

**7.5.1.2** Results reported by different laboratories should be considered suspect if they differ by more than 0,03 % total chlorine.

### 7.5.2 Bias

Bias is the difference between the expectation of the test results and an accepted reference value. There are no recognized standards by which to estimate the bias of this test method.

## 8 Test Method B – Total chlorine by Schöniger oxygen flask

### 8.1 Reagents

**8.1.1 Nitric acid (diluted)** – While stirring vigorously, add 100 ml of nitric acid ( $\text{HNO}_3$ , specific gravity 1,42) to 100 ml of water cooled in an ice bath.

**8.1.2 Oxygen** – Free of combustible materials and halogen compounds.

**8.1.3 Silver nitrate, standard solution (0,01 M)** – Prepare a 0,01 M silver nitrate ( $\text{AgNO}_3$ ) solution, and check frequently enough to detect changes of 0,000 5 M, either gravimetrically or potentiometrically, using standard hydrochloric acid (HCl).

**8.1.4 Sodium carbonate solution (10 g/l)** – Dissolve 27 g of sodium carbonate decahydrate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) in water and dilute to 1 l.

### 8.2 Apparatus

**8.2.1 Schöniger combustion flask** – A chemically resistant, 1 000 ml narrow-mouth (24/40 standard taper joint) Erlenmeyer flask with a 100 mm (approximately 4 in) No. 18 platinum wire sealed into the glass stopper. Using tweezers to avoid contamination from fingerprints, make a basket from 45 mesh 0,20 mm (0,007 8 in) platinum gauze as follows.

NOTE Because small amounts of chloride are involved, contamination from fingerprints can be significant.

Fold over the edges of a (12,7 × 25,4) mm (0,50 × 1 in) piece of gauze about 1,6 mm (0,06 in) and crimp them to prevent the gauze from unravelling. Bend the last 25,4 mm (1 in) of the No. 18 wire at a right angle and place the gauze on the 25,4 mm (1 in) section. Bend the last half of the wire back over the gauze and crimp strongly to hold the gauze firmly in place. Bend the sides of the gauze to form an open basket.

**8.2.2 Absorbent cotton** – cut into squares weighing approximately 50 mg.

**8.2.3 Filter paper** – cut into (6,4 × 25,4) mm (0,25 × 1 in) pieces.

**8.2.4 Weighing burette or dropping bottle.**

**8.2.5 Tweezers** – for handling the cotton squares.

**8.2.6 Potentiometric titrator or pH meter** – with calomel and silver/silver chloride electrodes.

**8.2.7 Microburette** – 5 ml capacity, 0,01 ml graduations.

**8.2.8 Magnetic stirrer.**

### 8.3 Procedure

**8.3.1** Place 25 ml of Na<sub>2</sub>CO<sub>3</sub> absorbing solution in an empty combustion flask. Sweep the flask with a moderate stream of oxygen for about 30 s to displace air.

**8.3.2** While the flask is swept with oxygen, use tweezers to place an absorbent cotton square and filter paper strip (fuse) in the platinum basket. Add about 200 mg of sample to the absorbent cotton from a weighing burette containing a known amount of sample weighed to the nearest 0,000 5 g.

NOTE Throughout this procedure, handle cotton squares and filter paper strips with tweezers to avoid contamination from fingerprints.

**8.3.3** While holding the flask nearly horizontal in one hand and the stopper in the other, light the filter paper fuse with a Bunsen flame and quickly and smoothly insert the stopper. In the same motion and after the stopper is firmly seated, tilt the flask beyond the horizontal so that the liquid will run down and form a seal around the stopper. Hold the stopper firmly in place.

**WARNING — Ignition may cause a sudden build-up of pressure within the flask. While the sample is being combusted, handle the flask with leather or heavy vinyl gloves behind a safety shield. The combustion should be carried out in a safety cabinet such as the Schöniger combustion ignitor which uses an infra-red lamp to ignite black filter paper in the combustion flask.**

**8.3.4** After the combustion is complete, rotate the flask to wet the flask wall, being careful not to wet the platinum basket. Allow the flask to stand 5 min to 10 min.

**8.3.5** Remove the stopper, sweep the flask with oxygen, and burn two more 200 mg portions of the same sample in the same flask in accordance with 8.3.2 to 8.3.4. To the nearest 0,000 5 g, reweigh the weighing burette to determine accurately the total amount of sample burned. Transfer the solution into a 100 ml beaker. Rinse the flask with small portions of Na<sub>2</sub>CO<sub>3</sub> solution, adding the rinses to the 100 ml beaker. Acidify the solution to methyl red by adding HNO<sub>3</sub>(1+1) dropwise, then add 0,1 ml excess. Add a magnetic stirring bar and, using a 5 ml burette, titrate potentiometrically with standard 0,01 M AgNO<sub>3</sub> solution, using a silver/silver chloride electrode system.

**8.3.6** Titrate a blank exactly as described in 8.3.1 to 8.3.5, but without adding the sample.

### 8.4 Calculation

Calculate the total chlorine, in percent, by means of the formula

$$3,55(A - B)C / m$$

where

*A* is the AgNO<sub>3</sub> solution required for titration of the sample, ml;

*B* is the AgNO<sub>3</sub> solution required for titration of the blank, ml;

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