



Designation: D4423 – 00 (Reapproved 2006)

Standard Test Method for Determination of Carbonyls In C₄ Hydrocarbons¹

This standard is issued under the fixed designation D4423; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of carbonyls (ketones and aldehydes) in C₄ hydrocarbons. This test method was tested on polymerization-grade 1,3-butadiene.

1.2 The applicable range for this test method is 0 to 50 mg/kg carbonyls calculated as acetaldehyde.

1.3 Other C₄ hydrocarbons and their mixtures besides polymerization-grade 1,3-butadiene could be tested using this same test method. However, the precision section of this test method covers only carbonyls in applicable range as listed in 1.2, as found in polymerization-grade 1,3-butadiene.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D484 Specification for Hydrocarbon Dry Cleaning Solvents³

D1193 Specification for Reagent Water

E1 Specification for ASTM Liquid-in-Glass Thermometers

3. Summary of Test Method

3.1 A measured amount of sample is added to an alcoholic hydroxylamine hydrochloride solution that has been adjusted to a given coloration using either alcoholic acid or base. The carbonyls will react with the hydroxylamine hydrochloride

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0.04 on C₄ Hydrocarbons.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

releasing an equivalent amount of hydrochloric acid which is then back-titrated to the original coloration. A blank containing only methanol and sample is titrated and the sample's results are calculated using the blank adjustment. Results are reported as milligrams per kilogram carbonyls as acetaldehyde.

4. Significance and Use

4.1 The determination of the carbonyl content of polymerization-grade 1,3-butadiene is necessary, since in some polymerization reactions, the presence of carbonyls in excess over some specified amount can have a deleterious effect upon the polymer properties or the reaction itself, or both.

5. Apparatus

5.1 *Bunsen Valves*—A device constructed so that when used with an Erlenmeyer flask, the sample vapors can exit the flask while protecting the flask's liquid contents. See Fig. 1 for details.

5.2 *Cooling Coil*—Prepare a cooling coil by winding about 10 to 15 cm of seamless copper tubing (about 6-mm diameter) on a short length of pipe (about 1.5 to 2.0-cm diameter), allowing sufficient length of tubing at the end of the coil to connect it to the sample source. Attach a valve at a point that would not extend more than 8 cm above the surface of the cooling bath liquid. To the valve, attach a 6 to 8 cm length piece of tubing bent downward so that the hydrocarbon liquid can be directed into the receiving container.

5.3 *Dewar Flask*—The Dewar flask must be of sufficient volume to completely immerse the main portion of the cooling coil except for the extremities necessary for receiving and delivering the sample through the coil.

5.4 *Erlenmeyer Flasks*, 250-mL capacity.

5.5 *Volumetric Flasks*, 1-L capacity. These flasks should be Class A glassware.

5.6 *Graduated Cylinders*—100-mL capacity, glass cylinders, graduated in 1 or 2-mL divisions.

5.7 *Microburets*, 2.00 or 5.00-mL capacity. The microburets should be Class A glassware with 0.01 or 0.02-mL divisions or less. It is advisable to have the buret's tip end equipped with a syringe needle to dispense very small drops of titrant.

5.8 *Sample Cylinders*—These should be of sufficient volume to give the required amount of sample for testing. Stainless steel cylinders equipped with needle valves should be

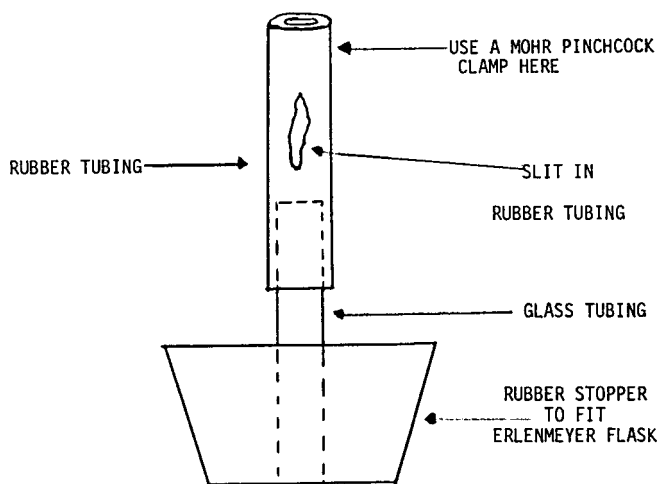


FIG. 1 Apparatus

used. It is suggested that a 500-mL-capacity cylinder be the minimum size to be used for butadiene.

5.9 *Thermometer*—For observing temperatures below -45°C . The Low Cloud and Pour Point Thermometer, conforming to the requirements for ASTM Thermometer 6C, as prescribed in Specification E1, is satisfactory. Thermometer 6C has a range from -80 to $+20^{\circ}\text{C}$.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ Other grades may be 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water conforming to Specification D1193.

6.3 *Alcoholic Hydrochloric Acid (0.05 N)*—Dilute 4.2 mL of concentrated hydrochloric acid (**Warning**—Poison. Corrosive. May be fatal if swallowed. Liquid and vapor cause severe burns. Harmful if inhaled.) to volume with anhydrous methanol in a 1-L volumetric flask. Use the alcoholic 0.05 N potassium hydroxide solution to standardize the HCl solution.

6.4 *Alcoholic Hydroxylamine Hydrochloride*—Dissolve 35.0 g of hydroxylamine hydrochloride (**Warning**—May be irritating to skin, eyes, or mucous membranes. Harmful if inhaled.) in 3.5 L of anhydrous methanol. (**Warning**—Flammable. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled. Cannot be made nonpoisonous.)

6.5 *Alcoholic Potassium Hydroxide (0.05 N)*—Dissolve 3.3 g of potassium hydroxide in anhydrous methanol.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

(**Warning**—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water.) Make to volume with methanol in a 1-L volumetric flask. Standardize against a primary standard, potassium acid phthalate.

6.6 *Dry Ice (Carbon Dioxide Solid)*—(**Warning**—Extremely cold (-78.5°C). Liberates heavy gas which may cause suffocation. Contact with skin causes burns or freezing, or both. Vapors may react violently with hot magnesium or aluminum alloys.)

6.7 *Stoddard Solvent*—Conforming to the specification listed in Specification D484. (**Warning**—Combustible. Vapor harmful.)

6.8 *Thymol Blue Indicator*—Dissolve 0.04 g of thymol blue in 100 mL of anhydrous methanol. (**Warning**—Flammable. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled. Cannot be made nonpoisonous.)

7. Preparation of Apparatus

7.1 *Dry Ice-Stoddard Solvent Bath*—Add a sufficient quantity of Stoddard solvent into the Dewar flask to ensure that the cooling coil will be submerged in the liquid plus dry ice (solid CO_2). (**Warning**—See 6.6 and 6.7.) Carefully add sufficient dry ice to the Stoddard solvent to obtain a temperature of at least -50°C . (**Warning**—Great care must be taken during this step. Do not add the dry ice all at once, but in small pieces, especially at the beginning. Wear protective gloves and adequate eye protection to prevent any contact with the extremely cold materials.) Attach the sample cylinder containing the butadiene (**Warning**—Extremely flammable gas under pressure. May form explosive peroxides upon exposure to air. Harmful if inhaled. Irritating to eyes, skin, and mucous membranes.) to the cooling coil and immerse the coil into the liquid. Support the sample cylinder in a cylinder rack or using a ring stand and appropriate clamps. Be sure the coil is positioned so that the delivery tip is free to dispense liquid butadiene into the Erlenmeyer flasks. After each use, be sure to clean the coil's interior with methanol. DO NOT USE ACETONE.

8. Procedure

8.1 Prepare a sample flask by pouring 50 mL of alcoholic hydroxylamine hydrochloride into a 250-mL Erlenmeyer flask.

8.2 Prepare a flask for use as a sample blank by pouring 50 mL of methanol into a 250-mL Erlenmeyer flask.

8.3 Add about 0.5 mL of thymol blue indicator solution to each flask.

8.4 Carefully add 0.05 N alcoholic KOH or alcoholic HCl to each flask until matching colors are obtained. The desired color is a yellow color with a slight, but distinct, orange coloration. It is important that this orange color is present at this point of the test. If the color is more yellow at this point, it would be easy to obtain a result of less than 1 mg/kg carbonyls on a sample containing over 100 mg/kg of carbonyls.

8.5 Stopper the flasks with the Bunsen valves. (This keeps the CO_2 vapor out of the flasks). Set the flasks on some crushed dry ice for a few minutes to cool the liquid contents. The color in the flasks may turn more yellow when cold, but this is not