

# AMERICAN SOCIETY FOR TESTING MATERIALS

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## *Standard Method of Test for* CARBONYL CONTENT OF BUTADIENE<sup>1</sup>



ASTM Designation: D 1089-59 (73XR78)

ADOPTED, 1953; REVISED, 1959.<sup>2</sup>

This Standard of the American Society for Testing Materials is issued under the fixed designation D 1089; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

### Scope

1. This method is intended for the determination of the carbonyl content in liquid C<sub>4</sub> hydrocarbons containing less than 2500 ppm. Acid or alkaline materials, if present, interfere and are determined by a blank titration.

### Outline of Method

2. A measured quantity of liquid C<sub>4</sub> hydrocarbon is added to a cork stoppered narrow-mouthed bottle containing aqueous hydroxylamine hydrochloride reagent and Stoddard solvent. The carbonyl content is determined from the increase in the acidity of the resulting solution by titrating with a standard base, using a pH meter to determine the end point.

<sup>1</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-2 on Petroleum Products and Lubricants.

The method was derived from the one developed and cooperatively tested by the Butadiene Producers' Committee on Specifications and Methods of Analysis of the Office of Rubber Reserve which appears in the Butadiene Laboratory Manual as method 2.1.5.1.

<sup>2</sup> Prior to its adoption as standard, this method was published as tentative from 1950 to 1953.

In 1959, a new Note 2 was added and the section on Precision was revised.

### Apparatus

3. (a) *Bottles*, narrow-mouthed, 500-ml. fitted with cork stoppers.

(b) *Thermometer*.—For observing temperatures below -45 C, the Low Cloud and Pour Thermometer, having a range of -80 to 20 C or -112 to 70 F and conforming to the requirements for thermometer 6 C or 6 F as prescribed in the ASTM Specifications E 1<sup>3</sup> is satisfactory.

(c) *Bomb Rack* for supporting the sample bomb in an upright position.

(d) *Copper Cooling Coil*.—Prepare a cooling coil by winding 4 in. of  $\frac{1}{4}$ -in. seamless copper tubing on a short length of  $\frac{3}{4}$ -in. pipe, allowing sufficient length of tubing at the end of the coil to connect it to the sample source. Attach a  $\frac{1}{4}$ -in. valve on the outlet at a point that would not extend more than 3 in. above the surface of the bath liquid. To the valve attach a 3-in. piece of tubing bent for carrying the liquid into the required apparatus.

(e) *pH Meter*, having an accuracy of plus or minus 0.05 pH units.

(f) *Buret*, 10-ml. with 0.02-ml. divisions.

(g) *Buret*, 50-ml. with 0.1-ml. divisions.

<sup>3</sup> Appears in this publication, see Contents in Numeric Sequence of ASTM Designations at front of book.

### Reagents

4. (a) *Stoddard Solvent*, conforming to A.S.T.M. Specifications D 484.<sup>4</sup>

(b) *Hydroxylamine Hydrochloride Reagent (2 per cent)*.—Dissolve 20 g. of c. p. hydroxylamine hydrochloride in distilled water and dilute to 1 liter.

NOTE 1.—Hydroxylamine hydrochloride solutions are known to cause dermatitis. Rubber gloves should be worn whenever handling this substance and all contact of it with the skin should be avoided.

(c) *Sodium Hydroxide Solution (0.05 N)*.

(d) *Sulfuric Acid Solution (0.05 N)*.

### Test Sample

5. Set the sample bomb in an upright position in the bomb rack. Place the copper cooling coil in a dry ice-Stoddard solvent bath and connect the coil to the lower valve of the bomb. Purge the line with some of the sample before taking the sample to be tested. Cool a 100-ml. graduated cylinder in the dry ice-Stoddard solvent bath and withdraw the required amount of sample into it. Cool the sample to  $-45^{\circ}\text{C}$ . ( $-49^{\circ}\text{F}$ .) and record the volume. A 100-ml. sample is required for samples containing less than 100 ppm. carbonyl and a 50-ml. sample for higher concentrations.

NOTE 2.—Low results may be expected if the sample is not analyzed within 8 hr.

### Procedure

6. (a) *Carbonyl Determination*.—Cool a 500-ml. bottle by placing it in a dry ice-Stoddard solvent bath for 1 or 2 min. Remove the bottle from the bath and add 25 ml. of distilled water, 25 ml. of hydroxylamine hydrochloride reagent, and 150 ml. of Stoddard solvent previously cooled in a dry ice-Stoddard solvent bath. Add the cold sample to the bottle (Note 3). Stopper the bottle and shake it vig-

orously for 1 min. Transfer the contents of the bottle to a 500-ml. beaker and wash the bottle with 75 ml. of distilled water, catching the rinsings in the beaker. Place the beaker on the titrating stand of the pH meter and titrate the solution with standard 0.05 N NaOH to an end point of pH 3.85. Stir the solution continuously during the titration.

NOTE 3.—Use a 100-ml. size sample when less than 100 ppm. carbonyl content is present in the material being tested and a 50-ml. sample for higher concentrations.

(b) *Blank Determination for Hydroxylamine Hydrochloride Reagent and Stoddard Solvent*.—Add to a 500-ml. bottle 25 ml. of distilled water, 25 ml. of hydroxylamine hydrochloride reagent, and 150 ml. of Stoddard solvent. Stopper the bottle and shake it vigorously for 1 min. Transfer the contents of the bottle to a 500-ml. beaker and wash the bottle with 75 ml. of distilled water, catching the rinsings in the beaker. Place the beaker on the titrating stand of the pH meter and titrate the solution with standard 0.05 N NaOH to an end point of pH 3.85. Stir the solution continuously during the titration.

(c) *Blank Determination for Free Acid or Base in the Sample*.—Cool a 500-ml. bottle by placing it in a dry ice-Stoddard solvent bath for 1 or 2 min. Add to the bottle 50 ml. of distilled water and 150 ml. of Stoddard solvent previously cooled in a dry ice-Stoddard solvent bath. Add the same volume of cold sample to the bottle as was used in the carbonyl determination described in Paragraph (a). Stopper the bottle and shake it vigorously for 1 min. Transfer the contents of the bottle to a 500-ml. beaker and wash the bottle with 75 ml. of distilled water, catching the rinsings in the beaker. Place the beaker on the titrating stand of the pH meter and titrate the free acid or free base with standard 0.05 N NaOH or standard 0.05 N  $\text{H}_2\text{SO}_4$  to an end point

<sup>4</sup> 1958 Book of ASTM Standards, Part 7.