



Designation: D 2930 – 94

Standard Test Method for Maleic Acid in Maleic Anhydride by Potentiometric Titration¹

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1. Scope

1.1 This test method covers the determination of free maleic acid in refined maleic anhydride by potentiometric titration.

1.2 This test method is applicable for all concentrations of maleic acid; however, it is primarily used for concentrations below 0.5 %.

1.3 The following applies to all specified limits in this standard: For purposes of determining conformance with this standard, an observed value or a calculated value shall be rounded off “to the nearest unit” in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

1.4 *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.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3438 Practice for Sampling and Handling Naphthalene, Maleic Anhydride, and Phthalic Anhydride³

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴

2.2 Other Documents:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200.⁵

3. Summary of Test Method

3.1 This test method is based on a direct titration of maleic acid using a tertiary amine as the base. The titration is carried out in an anhydrous solvent system and followed potentiometrically by means of a pH meter. Tertiary amines do not react

with anhydrides. Only one carboxylic acid group is titrated.

4. Significance and Use

4.1 The maleic acid content is usually an indication of exposure to moisture in air. Maleic anhydride reacts with moisture to form maleic acid.

5. Apparatus

5.1 *Titrimeter or pH meter*, equipped with glass and calomel electrodes. The pair of electrodes shall be mounted to extend well below the liquid level.

5.2 *Microburet*, 5 or 10-mL size, graduated 20 divisions/mL.

5.3 *Stirrer*, mechanical, that will furnish a rapid stirring action, but not such vigorous stirring that air bubbles will be drawn to the electrodes of the titrimeter or pH meter.

5.4 *Beaker*, 250-mL, tall-form.

5.5 *Automatic Titrator* can be used in place of the above apparatus.

6. Reagents

6.1 *Purity of 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 the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ 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 reagent water conforming to Type IV of Specification D 1193.

6.3 *Acetone*, dried over Linde Type 5A molecular sieves.⁷

6.4 *N-ethylpiperidine*⁸ (0.05 N in acetone)—Dissolve 5.65 g of *N*-ethylpiperidine in acetone and dilute to 1 L. Prepare fresh daily.

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.02 on Oxygenated Aromatics.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.04.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

⁶ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁷ Manufactured by Union Carbide Corp., Linde Div., 270 Park Ave., New York, NY 10017.

⁸ *N*-ethylpiperidine, Catalog No. EX828, available from Matheson Coleman & Bell, East Rutherford, NJ, has been found satisfactory for this purpose.



6.5 *Maleic Acid*⁹—Titrate with aqueous NaOH solution (0.5 N) to a phenolphthalein end point to obtain assay.

7. Hazards

7.1 Consult current OSHA regulations and supplier's Material Safety Data Sheets for all materials used in this test method.

7.2 In addition to other precautions, handling of maleic anhydride shall be done with care. Although it is a solid at ambient temperatures, its vapor pressure is high enough to cause objectionable fumes. The fumes and dust from maleic anhydride are local irritants to skin and mucous membranes especially in the presence of moisture.

8. Sampling

8.1 Sample the material in accordance with Practice D 3438.

9. Standardization of N-Ethylpiperidine Solution

9.1 Standardize the amine solution by titration with maleic acid. Calculate the normality *E* as follows:

$$E = (G \times P)/(M \times 11.6) \quad (1)$$

where:

G = maleic acid, g,

M = N-ethylpiperidine, mL, and

P = purity of maleic acid as obtained in 6.5, %.

NOTE 1—Only one carboxyl group titrates. The dissociation constant for the first hydrogen is approximately $10\Sigma^2$. The second hydrogen is too weak to titrate.

10. Procedure

10.1 It is desirable to take enough sample so that the solution contains approximately 0.002 mole of maleic acid. If the acid content is suspected to be lower than 0.5 %, use a 10-g specimen. (**Precaution**—See 7.2.)

10.2 Dissolve the specimen in 100 mL of dry acetone.

10.3 Set the beaker in place, insert the glass and calomel electrodes, start the stirrer, and commence the titration with the 0.05 N, N-ethylpiperidine solution. Conduct the titration in the manner of the usual potentiometric titration, taking readings of pH versus millilitres of titrant. The end point may be ascertained in the conventional manner as follows: Add the titrant in 0.01-mL increments. Allow the pH to reach stability and plot the pH readings against the millilitres of titrant used. The equivalence point is then taken as the end point.

11. Calculation

11.1 Calculate the percent maleic acid *A* as follows:

$$A = (M \times N \times 0.116 \times 100)/S \quad (2)$$

where:

M = N-ethylpiperidine, mL,

N = normality of N-ethylpiperidine, and

S = sample used, g.

12. Report

12.1 Report the percent maleic acid to the nearest 0.001 %.

13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of the results.

13.1.1 *Repeatability*—The standard deviation of single results, obtained by the same analyst on different days, has been estimated to be 0.004 % absolute at 28 df. Two such values could be considered suspect (95 % confidence level) if they differ by more than 0.012 % absolute.

13.1.2 *Reproducibility*—The standard deviation of single results, obtained by analysts in different laboratories, has been estimated to be 0.015 % absolute at 16 df. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.048 % absolute.

NOTE 2—These precision statements were developed at maleic acid concentrations between 0 and 0.5 %.

14. Keywords

14.1 maleic acid; maleic anhydride; titration

⁹ Maleic acid, Catalog No. 690, available from Fisher Scientific Co., Springfield, NJ 07081, has been found satisfactory for this purpose.

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