Designation: D8031 – 16

Standard Test Method for Acid Number of Terephthalic Acid (TA) by Automatic Potentiometric Titration[1]

1. Scope

1.1 This test method covers the determination of acid number in terephthalic acid (TA) by automatic potentiometric titration. As the index of TA purity, acid number is usually within 674 to 676 mg KOH/g.

1.2 In determining the conformance of the test results using this method, results shall be rounded off in accordance with the rounding-off method of Practice E29.

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

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration
D1193 Specification for Reagent Water
D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals
D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E300 Practice for Sampling Industrial Chemicals
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Document:*[3]

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Terminology

3.1 *Definitions:*

3.1.1 *acid number, n*—the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample that is required to titrate a sample in a specified solvent to a specified end point.

4. Summary of Test Method

4.1 A TA sample is dissolved in pyridine, diluted with water and titrated potentiometrically with standard sodium hydroxide solution, using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are plotted automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. The acid number is calculated as milligrams of KOH per gram of TA sample. Its theoretical value of TA sample is 675.5 mg KOH/g.

5. Significance and Use

5.1 An estimate of TA purity can be determined by titrating with KOH. As an index of TA purity, the acid number can be used as a guide in the quality control of TA production.

6. Apparatus

6.1 *Analytical Balance.*

6.2 *Automatic Potentiometric Titrator*—Automatic titration systems capable of adding fixed increments of titrant at fixed time intervals (monotonic) or variable titrant increments with electrode stability between increment additions (dynamic) with endpoint seeking capabilities as prescribed in the method. As a minimum, the apparatus shall meet the performance and specification requirements as warranted by the manufacturer.

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[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] 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] Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

6.2.1 A monotonic or dynamic mode of titrant shall be used. During the titration, the speed and volume of the addition may vary depending on the rate of change of the system. The recommended maximum volume increment is 0.5 mL and the recommended minimum volume increment is 0.05 mL.

6.2.2 *Buret,* capable of delivering titrant in 0.05 mL or larger increments. The buret tip should be able to deliver titrant directly into the titration vessel without exposure to the surrounding air. Burets with total capacities of 5 mL, 10 mL and 20 mL are typically available from commercial manufacturers of auto titrators and can be used if their specifications meet the criteria of 6.2.1 and 6.2.2.

6.2.3 *Titration Stand,* suitable for supporting the electrode, stirrer and buret tip.

6.3 *Sensing Electrode,* standard pH, suitable for nonaqueous titrations.

6.4 *Reference Electrode,* silver/silver chloride (Ag/AgCl) reference electrode, filled with 1M to 3M LiCl in ethanol.

7. Reagents

7.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the reagent grade specification of the Analytical Reagents of the American Chemical Society,[4] where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the performance or accuracy of the determination. Reagent chemicals shall be used for all tests.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type III of Specification D1193. Boil the water gently for 5 to 10 min to remove any CO_2 and cool the water to room temperature.

7.3 *Pyridine*—(**Warning—**Flammable and harmful if inhaled, swallowed or absorbed through the skin.).

7.4 *Oxalic Acid* (standard reagent, $H_2C_2O_4 \cdot 2H_2O$)—(**Warning—**Harmful if absorbed through the skin.).

7.5 *Sodium Hydroxide Solution* (0.5 M)—Weigh 20 g of sodium hydroxide (NaOH) (**Warning—**Highly corrosive to all body tissue.) in a beaker. Add 100 mL water (boiling gently for 5 to 10 min and cooling to room temperature, free of CO_2) to dissolve and cool the solution. Then quantitatively transfer the solution into a 1000 mL volumetric flask and dilute to volume with the above water. The NaOH solution should be stored in a plastic bottle and stopper must be stressed.

NOTE 1—After standardization, the NaOH solution should not be stored in a glass container because it will be slowly neutralized from exposure to a glass container. It will also "cement" a glass stopper into a glass container.

8. Hazards

8.1 Consult current federal regulations, supplier's Safety Data Sheets, and local regulations for all materials used in this test method.

9. Sampling, Test Specimens, and Test Units

9.1 Use only representative samples obtained as described in Practice E300, unless otherwise specified.

10. Preparation of Apparatus

10.1 Adjust the apparatus in accordance with the manufacturer's instructions.

10.2 *Preparation of Electrodes:*

10.2.1 When the Ag/AgCl reference electrode is used for the titration and it contains an electrolyte which is not 1M to 3M LiCl in ethanol, replace the electrolyte. Drain the electrolyte from the electrode, wash away all the salt (if present) with water and then rinse with ethanol. Rinse several times with the LiCl electrolyte solution. Finally, replace the sleeve and fill the electrode with the LiCl electrolyte to the filling hole. When refitting the sleeve, ensure that there will be a free flow of electrolyte into the system. A combination electrode shall be prepared in the same manner. The electrolyte in a combination electrode can be removed with the aid of a vacuum suction.

10.3 *Testing of Electrodes*—Test the meter-electrode combination when first put into use, or when new electrodes are installed, and retest at intervals thereafter. Rinse the electrodes with solvent then with water. Dip them into a pH 4 aqueous buffer solution. Read the mV value after stirring one minute. Remove the electrodes and rinse with water. Dip the electrodes in a pH 7 aqueous buffer. Read the mV value after stirring one minute. Calculate the mV difference. A good electrode system will have a difference of at least 158 mV (20 to 25°C). If the difference is less than 158 mV, lift the sleeve of the electrode and ensure electrolyte flow. Repeat the measurements. If the difference is still less than 158 mV, clean or replace the electrode(s).

10.3.1 When the sensing electrode and the reference electrode are separate, one pair of electrodes shall be considered as one unit. If one or the other is changed, it shall be considered as a different pair and shall be re-tested.

10.4 *Maintenance and Storage of Electrodes:*

10.4.1 Follow the manufacturer's instructions for storage and use of the electrode.

10.4.2 Prior to each titration soak the prepared electrode in water for at least 2 min. Rinse the electrode with deionized water immediately before use. The glass membrane needs to be rehydrated after titration on non-aqueous material.

10.4.3 When not in use, immerse the lower half of the combination electrode in LiCl electrolyte. Do not allow electrodes to remain immersed in a titrated sample for any appreciable period of time between titrations. While the electrodes are not extremely fragile, handle them carefully at all times.

11. Standardization of Titrant

11.1 Weigh, to the nearest 0.0001 g, 0.7 to 0.8 g of oxalic acid, into a 250-mL titration beaker.

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[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.

11.2 Add 100 mL of CO_2-free water to the beaker. Swirl the beaker periodically until the sample is entirely dissolved. Add 20 mL of pyridine to the beaker.

11.3 Immerse the electrode assembly into the sample solution. Start the stirrer at a rate to ensure rapid and efficient mixing without causing undue turbulence and splashing.

11.4 Titrate using the standard NaOH solution. The meter readings are plotted automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. Record the amount of titrant required.

11.5 Perform a blank titration by repeating the above steps without adding oxalic acid.

11.6 Calculate the molarity of the NaOH solution as follows:

$$C = \frac{m \times 1000}{M \times (V - V_0)} \quad (1)$$

where:

C = molarity of NaOH solution, mol/L,
V = NaOH solution required for titration of the oxalic acid (11.4), mL,
V_0 = NaOH solution required for titration of the blank (11.5), mL,
M = 63.04 g/mol, molar mass of the oxalic acid (7.4), and
m = mass of oxalic acid titrated, g.

12. Procedure

12.1 Weigh, to the nearest 0.0001 g, 0.8 to 1.5 g of TA sample, into a 250-mL titration beaker.

12.2 Add 20 mL of pyridine with swirling the beaker periodically. Stir the solution gently until the entire solid has dissolved. Add 100 mL of CO_2-free water.

12.3 Immerse the electrode assembly, as used in Standardization, into the sample solution. Start the stirrer at a rate to ensure rapid and efficient mixing without causing undue turbulence and splashing.

12.4 Titrate using the standard NaOH solution. The meter readings are plotted automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. Record the amount of titrant required.

12.5 Perform a blank titration by repeating the above steps without adding the TA sample.

13. Calculation

13.1 Calculate the acid number as follows:

$$\text{Acid number, mg of KOH/g} = \left[(A - B) \times C \times M\right] / W \quad (2)$$

where:

A = NaOH solution required for titration of the TA sample (12.4), mL,
B = NaOH solution required for titration of the blank (12.5), mL,
C = molarity of the NaOH solution (11.6), mol/L,
M = 56.11 g/mol, molar mass of the KOH, and
W = mass of TA sample titrated, g.

14. Report

14.1 Report the value of acid number, to the nearest 0.1 unit.

14.2 Report the following information in the report:
14.2.1 The complete identification of the sample tested.
14.2.2 Any deviation from the procedure specified (for example, operating conditions).
14.2.3 Results of the test.
14.2.4 Any abnormal situations observed during the test.

15. Precision and Bias

15.1 The precision of this test method is based on an intralaboratory study of Test Method D8031 conducted in 2015. One laboratory tested one TA sample for acid number by automatic potentiometric titration. Every test result represents an individual determination. The laboratory reported 20 replicate results for each analysis/material combination in order to estimate the repeatability limits of the standard. Practice E691 was followed for the design and analysis of the repeatability data; the details are given in Research Report RR:D16-1057.[5]

15.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

15.1.1.1 Repeatability limits are listed in Table 1.

TABLE 1 Repeatability Limits (TA)

Automatic Potentiometric Titration	Average (mg KOH/g) $\bar{X}$	Repeatability Standard Deviation Sr	Repeatability Limit r
acid number	675.1	1.16	3.25

15.1.2 Reproducibility has not been determined and will be determined within five years.

15.2 *Bias*—At the time of the study, the test specimens chosen for analysis were not accepted reference materials suitable for determining the bias for this test method, therefore no statement on bias is being made.

16. Quality Guidelines

16.1 Laboratories shall have a quality control system in place.

16.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1057. Contact ASTM Customer Service at service@astm.org.

16.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

16.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

16.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

17. Keywords

17.1 acid number; automatic potentiometric titration; terephthalic acid (TA)

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