



Standard Test Method for Pyridine Bases in Cresylic Acid by Direct Titration¹

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1. Scope

1.1 This test method covers the determination of pyridine and other basic nitrogen impurities in crude and refined cresylic acids streams, including mixtures.

1.2 This test method is applicable for pyridine base levels of 0.001 % to 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 8.

2. Referenced Documents

2.1 ASTM Standards:

D 3852 Practice for Sampling and Handling Phenol and Cresylic Acid²

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals²

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³

2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁴

3. Terminology

3.1 For definitions of terms used in this test method see Terminology D 4790.

4. Summary of Test Method

4.1 This test method is a direct, nonaqueous titration technique utilizing perchloric acid in acetic acid as titrant and the cresylic acid itself as titration solvent. Endpoints may be established potentiometrically as well as by indicator so that the method is applicable to highly colored as well as lighter colored materials. This test method will detect basic components other than pyridine bases should they be present. All basic compounds detected by this procedure are calculated and expressed as percent pyridine.

5. Significance and Use

5.1 The pyridine base content of cresylic acids is important in certain applications. This test method may be used as a tool for quality control and specification purposes by producers and users.

6. Apparatus

6.1 *Titrimeter or pH meter*, equipped with glass and calomel electrodes. The pair of electrodes shall be mounted to extend well below the liquid level. Storage in water between titrations is essential because prolonged immersion in nonaqueous medium significantly deadens response.

6.2 *Buret*, 50-mL capacity.

6.3 *Magnetic Stirrer*, with TFE-fluorocarbon or glass covered stirring bar.

6.4 *Autotitration Equipment* may be used if available.

7. Reagents

7.1 *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.⁵ 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.

7.2 *Perchloric Acid Titrant* (0.02 N in glacial acetic acid)—

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 06.04.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

⁵ *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.

Add 1.8 mL of 70 % perchloric acid (HClO₄) to 1 L of glacial acetic acid and mix well. To standardize, weigh accurately 0.0800 to 0.0950 g of primary standard potassium acid phthalate in glacial acetic acid and titrate potentiometrically or to the indicator endpoint, as described in 10.2. Calculate the normality, *N*, of the perchloric acid solution as follows:

$$N = \frac{W}{V \times 0.2041}$$

where:

W = weight of potassium acid phthalate, g, and
V = volume of perchloric acid titrant consumed, mL.

7.3 *Potassium Acid Phthalate* (KH C₈H₈O₄), primary standard—Dry for 2 h at 110°C.

7.4 *Quinaldine Red Indicator Solution*— Dissolve 0.2 g of quinaldine red indicator in 100 g of glacial acetic acid.

7.5 *Titration Solvent*—Glacial acetic acid (CH₃CO₂H) may be used as an additional titration solvent in order to decrease the viscosity of a particular sample or to keep it from freezing.

8. Hazards

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

9. Sampling

9.1 Samples of the material shall be taken in accordance with Practice D 3852.

10. Procedure

10.1 Weigh an appropriate amount of cresylic acid sample into the titration beaker. (A sample size of 100 g is suggested if the expected pyridine base content is in the range of 0.001 to 0.070 %.) Place a stirring bar in the beaker and, if desired, add about 100 mL of titration solvent.

10.2 The specimen is titrated with perchloric acid titrant and the endpoint determined by either of the following methods:

10.2.1 *Indicator*—A few drops of quinaldine red indicator is added to the solution. The titration is terminated when the red color disappears and the color of the sample returns to its original hue.

10.2.2 *Potentiometric*—The electrodes are inserted into the specimen and the observed potentials are plotted as a function of the titrant volume consumed. The point where Δ*E*/Δ*V* is the greatest is taken as the endpoint.

10.3 Repeat 10.1 through 10.2, but with no specimen to

obtain a reagent blank when titration solvent is used.

11. Calculation

11.1 Results are calculated as weight percent pyridine, *P*, as follows:

$$P = \frac{7.91 \times N \times (V_S - V_B)}{W}$$

where:

N = normality of the perchloric acid titrant,
V_S = titrant consumed for the sample, mL,
V_B = titrant consumed for the reagent blank, mL, and
W = specimen weight, g.

12. Report

12.1 Report the percent of pyridine bases to the nearest 0.001 %.

13. Precision and Bias

13.1 *Precision*—The following criteria shall be used for judging the acceptability of results.

13.1.1 *Intermediate Precision (within laboratory)*— When using the visual endpoint in this test method, results obtained by different analysts in the same laboratory should be suspect within 95 % confidence limits if they differ by more than 2.8 % of the average of values determined. When using the potentiometric endpoint in this test method, results obtained by different analysts in the same laboratory should be suspect within 95 % confidence limits if they differ by more than 2.2 % of the average of values determined.

13.1.2 *Reproducibility (between laboratories)*—When using the visual endpoint in this test method, results obtained by analysts in different laboratories should be suspect within 95 % confidence limits if they differ by more than 6.8 % of the average of values determined. When using the potentiometric endpoint in this test method, results obtained by analysts in different laboratories should be suspect within 95 % confidence limits if they differ by more than 13.9 % of the average of values determined.

13.1.3 *Bias*—The bias of this test method cannot be determined because no referee method is available to determine the true value.

14. Keywords

14.1 cresols; cresylic acids; nitrogen bases; phenol; pyridine bases; tar acids

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