Designation: D4471 – 22

Standard Test Method for Pyridine Bases in Cresylic Acid by Direct Titration[1]

This standard is issued under the fixed designation D4471; 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 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 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 8.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3852 Practice for Sampling and Handling Phenol, Cresols, and Cresylic Acid

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

2.2 *Other Document:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200 Air Contaminates – Table of Exposure Limits and Hazard Communication[3]

3. Terminology

3.1 For definitions of terms used in this test method see Terminology D4790.

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 half cell or combination glass pH and Ag/AgCl reference 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. For low pyridine base concentrations: 10 mL burette that reads to 0.05 mL.

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty 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, Mail Stop: SDE, Washington, DC 20401.

*A Summary of Changes section appears at the end of this standard

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.[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.

7.2 *Perchloric Acid Titrant* (0.02 *N* in glacial acetic acid)—Add 1.8 mL of 70 % perchloric acid ($HClO_4$) 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* ($KH\ C_8H_8O_4$), 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 (CH_3CO_2H) 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 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 D3852.

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. See Fig. 1, Fig. 2, and Fig. 3.

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 $\Delta E/\Delta V$ 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.

13.2 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method for measuring pyridine bases, bias has not been determined.

13.3 *Additional Information:*

13.3.1 A single lab analyzed a quality control sample 101 times. The average was 0.00465 wt. %. The standard deviation was 0.00007 wt. %. Repeatability was 0.00019.

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

14. Quality Guidelines

14.1 Laboratories shall have a quality control system in place.

14.1.1 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.

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

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

14.1.4 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.

14.2 *Interlaboratory Testing:*

14.2.1 A program that includes multiple laboratories analyzing the same samples is strongly encouraged. This program should allow labs to compare their results with other laboratories. This is particularly important when a plant is selling the product to customers or the laboratory is analyzing the products for acceptance. Producers and customers need to have confidence that results from different producers are comparable.

15. Keywords

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

FIG. 1 Pyridine
CAS [68391-11-7]