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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Nitrobenzene in Aniline¹

This standard is issued under the fixed designation D 4589; 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 a polarographic procedure for the determination of nitrobenzene in aniline.

1.2 This test method has been found applicable to the determination of nitrobenzene in aniline containing concentrations of not more than 25 mg/kg nitrobenzene.

1.3 The following applies to all specified limits in this test method: for purposes of determining conformance with this test method, 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 10 and Note 3.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 1549 Test Method for Zinc in Lubricating Oils and Additives (Polarographic Method)³

D 3436 Practice for Sampling and Handling Aniline⁴

D 4790 Terminology of Aromatic Hydrocarbons and Related Chemicals⁴

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁵

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁶

2.2 Other Document:

OSHA Regulations, 29 CFR, paragraphs 1910.1000 and 1910.1200⁷

3. Terminology

3.1 See Terminology D 4790 for definition of terms used in this test method.

4. Summary of Test Method

4.1 Polarography is an electrochemical method of analysis. A quantitative evaluation of an electro-reducible material such as nitrobenzene can be determined by measuring the characteristic current flow, as a function of an increasingly applied voltage, resulting from the solution undergoing electrolysis.

4.2 The current flowing through the specimen during the analysis is in the microampere range so several polarograms can be obtained on the same specimen solution without significant differences.

4.3 The nitrobenzene content is determined by mixing four volumes of aniline with one volume of concentrated hydrochloric acid. The diffusion current of nitrobenzene is then measured by polarographic technique. A standard calibration graph is developed with various concentrations of nitrobenzene in aniline versus their diffusion currents. A reading of the diffusion current level of the test specimen from the calibration graph determines its nitrobenzene content.

5. Significance and Use

5.1 This test method gives a quantitative means of detection of nitrobenzene in industrial grade aniline both for quality control and quality assurance of the product.

6. Interferences

6.1 Since the diffusion coefficient for solutions of organic molecules can possibly increase up to 2 % per degree rise in temperature, the polarographic cell temperature should be relatively the same when comparing specimen analyses with standard calibration analyses.

6.2 The sensitivity of an analysis is affected by the dimensions of the dropping mercury electrode (DME) capillary and also by the height of the mercury column above the electrode. It is advisable to use the same DME capillary with a constant head of mercury that will yield a uniform dropping rate during a series of analyses. Recalibrate when the DME is changed.

6.3 Sudden or severe vibrations of the DME system can cause interferences in the resulting polarogram.

6.4 Residual dissolved oxygen in the specimen solution will interfere with the analysis. This test method includes a nitrogen purge to remove dissolved oxygen.

¹ This test method is under the jurisdiction of ASTM Committee D-16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.0D on Organic Nitrogen Compounds.

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² Annual Book of ASTM Standards, Vol 11.01.

³ Discontinued 1984; see 1984 Annual Book of ASTM Standards, Part 23.

⁴ Annual Book of ASTM Standards, Vol 06.04.

⁵ Annual Book of ASTM Standards, Vol 14.02.

⁶ Annual Book of ASTM Standards, Vol 03.05.

⁷ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

7. Apparatus

7.1 *Recording Polarograph*—However, a nonrecording polarograph may be adapted for this test method.

7.2 *Electrodes:*

7.2.1 *Dropping Mercury Electrode Capillary.*

7.2.2 *Electrolysis Vessel*, with a mercury pool reference electrode.

NOTE 1—Suitable electrolysis assemblies are shown in Test Method D 1549 and Practices E 50. Any other cell that will perform similarly may be used.

7.3 *Nitrogen Bubbler System and Purification Assembly.*

NOTE 2—If the nitrogen being used contains enough oxygen to interfere with the polarogram, it must be purified by passing the gas over copper turnings at 450°C.

7.4 *Tubing*, flexible, vinyl for connections. Rubber tubing should be avoided due to the possibility of oxygen permeation. Due to the weight and viscosity of mercury, suitable hose clamps must be used for tubing connections to withstand stresses.

8. Reagents

8.1 *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.⁸ 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.

8.1.1 *Aniline*, nitrobenzene-free and chemically pure (reagent grade) for calibration purposes.

8.1.2 *Hydrochloric Acid (HCl)*, concentrated and chemically pure with a specific gravity of 1.19.

8.1.3 *Mercury Metal*, triple distilled instrument grade.

8.1.4 *Nitrobenzene*, chemically pure (reagent grade) for calibration purposes.

8.1.5 *Nitrogen*, water-pumped and oxygen-free.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type IV of Specification D 1193.

9. Standards

9.1 Prepare a master solution by weighing 100 ± 1 mg of nitrobenzene into 1000 g of aniline. This master solution contains 0.0001 g of nitrobenzene per gram of aniline and is equal to 100 mg/kg of nitrobenzene. Prepare separate standards containing 5, 10, 15, 20, and 25 mg/kg of nitrobenzene by appropriately diluting aliquots of the above master solution by weight with aniline.

10. Hazards

10.1 Special attention must be given to ventilation, mercury

handling, and the immediate cleaning of mercury spills.

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

11. Sampling and Handling

11.1 Sample the material in accordance with Practice D 3436.

12. Calibration and Standardization

12.1 The DME capillary has an average length of approximately 80 mm and a bore of approximately 0.04 mm. The height of the mercury column and reservoir will normally vary from 400 to 800 mm. The exact length of the capillary and the height of the mercury column are determined by trial and error to give a mercury drop-time from 3 to 5 s/drop when it is immersed in a solution of the type to be tested.

12.2 Operate the polarograph in accordance with the instrument manufacturer's instructions. Adjust the polarograph to the following specific settings:

Direct-current electromotive force (EMF)	3V
Initial EMF	additive
Damping	off
Dropping mercury electrode	negative
Span voltage	2.0V
Initial voltage	0V
Sensitivity for standardization	0.010 μ A/mm
Percentage point span of applied EMF	10 to 50 %

12.2.1 The sensitivity setting may vary with individual instruments.

12.3 Develop polarograms for the series of standards in accordance with the analytical procedure described in Section 13.

12.4 Construct a calibration graph by plotting the wave height of the diffusion current curve *versus* the percentage value of the nitrobenzene in the standards on linear graph paper. The calibration curve is valid for comparisons with specimens if the standards and specimens are analyzed with the same set of instrument conditions, cell temperature, and a constant dropping rate of mercury.

13. Procedure

13.1 Pipet a 40.0-mL specimen into a beaker and add 10.0 mL of HCl by pipeting and then mix thoroughly.

NOTE 3—**Caution:** Prepare the mixture in a fume hood and wear standard protective safety equipment.

13.2 Transfer a sufficient quantity of specimen solution to the electrolysis vessel to immerse the DME capillary. Adjust the mercury head to a level predetermined to give the desired constant drop rate. Purge the specimen by bubbling oxygen-free nitrogen through the specimen for 10 min at a moderate rate.

13.3 Shut off the nitrogen purge and determine a polarogram of the test specimen while observing the specific instrument parameters given in 12.2.

NOTE 4—A nitrogen blanket above the specimen without disturbing the specimen is desirable.

13.4 Clean the electrolysis vessel with water, acetone, and again with water between analyses to prevent cross contamination.

⁸ *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.