Designation: D1385 – 07

An American National Standard

Standard Test Method for Hydrazine in Water[1]

This standard is issued under the fixed designation D1385; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers[2] the colorimetric determination of hydrazine in boiler feed waters, condensates, natural, and well waters that have been treated with hydrazine (N_2H_4). This test method is usable in the range from 5.0 to 200 µg/L (ppb) hydrazine. The range is for photometric measurements made at 458 nm in 50 mm cell. Higher concentrations of hydrazine can also be determined by taking a more diluted sample.

1.2 It is the users' responsibility to ensure the validity of this test method for untested types of waters.

1.3 *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 precautionary statements, see 5.3, Note 1, *and Footnote 8.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D3370 Practices for Sampling Water from Closed Conduits
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 When a solution of p-dimethylaminobenzaldehyde in methyl alcohol and hydrochloric acid is added to hydrazine in diluted hydrochloric acid solution, a characteristic yellow color of p-dimethylaminobenzalazine is formed. The yellow color formed is proportional to the hydrazine present and is in good agreement with Beer's law in the range from 5.0 to 200 µg/L (ppb) hydrazine.

5. Significance and Use

5.1 Hydrazine is a man-made chemical and is not found in natural waters. The determination of hydrazine is usually made on boiler feedwaters, process waters, and other waters that have been treated with hydrazine (N_2H_4) for the purpose of maintaining residuals to prevent corrosion by dissolved oxygen. This reducing chemical reacts with dissolved oxygen to form nitrogen and water. However, under certain conditions it can also decompose to form ammonia and nitrogen. Hydrazine is used extensively as a preboiler treatment chemical for high-pressure boilers to scavenge small amounts of dissolved oxygen that are not removed by mechanical aeration. It has the advantage over sulfite treatment in that it does not produce any dissolved solids in the boiler water. Hydrazine is often determined in concentrations below 0.1 mg/L. However, in layup solutions for the protection of idle boilers, hydrazine may be present in concentrations as high as 200 mg/L.

5.2 Additionally, hydrazine provides protection where reducing conditions are required, particularly in mixed metallurgy systems for the protection of the copper alloys.

5.3 Hydrazine is a suspected carcinogen and a threshold limit value in the atmosphere of 1.0 mg/L has been set by OSHA. When in an aqueous solution, hydrazine will oxidize to nitrogen and water in the presence of air over a relatively short period of time.

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water

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[2] For further information on this test method, the following references may be of interest: Watt, G. W., and Chrisp, J. D., "Spectrophotometric Method for the Determination of Hydrazine," *Analytical Chemistry*, Vol 24, No. 12, 1952, pp. 2006–2008, and Wood, P. R., "Determination of Maleic Hydrazide Residues in Plant and Animal Tissue," *Analytical Chemistry*, Vol 25, No. 12, 1953, pp. 1879–1883.

[3] 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.

6. Interferences

6.1 The substances normally present in industrial water do not interfere with the test; however, the hydrazine content may be diminished by oxidizing agents, such as chlorine, bromine, and iodine, collected with the sample or absorbed by it prior to testing.

6.2 Colors in the prescribed wavelengths also interfere, as do other dark colors or turbidities that cannot be overcome.

6.3 Aromatic amines, such as aniline, will also interfere.

7. Apparatus

7.1 *Photometer*—A spectrophotometer suitable for measurements at 458 nm and capable of holding cells with a light path of 50 mm should be used. Filter photometers and photometric practices prescribed in this test method shall conform to Practice E60, and spectrophotometers to Practice E275.

7.2 Certain photoelectric filter photometers are capable of measurement at 425 nm, but not at 458 nm. Measurements may be made at 425 nm with a reduction in sensitivity of approximately 50 % of that possible at 458 nm.

7.3 Instruments that read out in direct concentration can also be used. Manufacturer's instructions should be followed.

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.[4] Other grades may be used, provided it is first ascertained that the reagent is sufficiently high in purity to permit its use without lessening the accuracy of the determinations.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the requirements in Specification D1193, Type III.

8.3 *Hydrazine Solution, Stock* (1.0 mL = 100 µg N_2H_4)—Dissolve 0.328 g of hydrazine dihydrochloride ($HCl{\cdot}NH_2 \cdot NH_2{\cdot}HCl$) in 100 mL of water and 10 mL of HCl (sp gr 1.19). Dilute with water to 1 L in a volumetric flask and mix (**Warning**, see Note 1).

8.4 *Hydrazine Solution, Standard* (1.0 mL = 0.500 µg N_2H_4)—Dilute 5.0 mL of hydrazine stock solution to 1 L with water and mix. Prepare as needed.

NOTE 1—**Warning:** Hydrazine is a suspected carcinogen and should be handled with care.[5]

8.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

8.6 *p-Dimethylaminobenzaldehyde Solution*—Dissolve 4.0 g of p-dimethylaminobenzaldehyde [$(CH_3)_2NC_6H_4CHO$] in 200 mL of methyl alcohol (CH_3OH) and 20 mL of HCl (sp gr 1.19). Store in a dark bottle out of direct sunlight.

9. Sampling

9.1 Collect the sample in accordance with Practices D3370 or Practice D1066, whichever is applicable (**Warning**, see Note 1).

9.2 Acidify and dilute the sample as soon as taken by adding 1 mL of concentrated HCl (sp gr 1.19) to a 100-mL volumetric flask and then pipetting 50 mL of the sample into the flask and diluting to 100 mL. Prepare a blank with water at the same time.

9.3 A smaller sample aliquot should be taken if the hydrazine concentration is greater than 200 µg/L.

10. Calibration

10.1 Prepare a series of standard hydrazine solutions by pipetting 0.0, 5.0, 10.0, 25.0, 50.0, 100.0, and 200.0 mL of hydrazine standard solution (1.0 mL = 0.500 µg N_2H_4) into 500-mL volumetric flasks. Add 5 mL of HCl (sp gr 1.19) to each flask and dilute with water to 500 mL and mix well. This will give standard solutions containing 0, 5.0, 10.0, 25.0, 50.0, 100, and 200 µg/L (ppb) of hydrazine.

10.2 Pipet 50.0-mL portions of the hydrazine standard solutions into clean, dry 100-mL beakers or flasks and proceed as directed in 11.2. Plot absorbance on the ordinate and micrograms per litre of hydrazine on the abscissa of linear graph paper.

10.3 A separate calibration curve must be made for each photometer and a recalibration must be made if it is necessary to change the cell, lamp, or filter, or if any other alterations of instrument or reagents are made. Check the curve for each series of tests by running two or more solutions of known hydrazine concentrations.

11. Procedure

11.1 Pipet 50.0 mL of the blank, standard solutions, and acidified diluted sample solutions into clean, dry 100-mL beakers or flasks.

11.2 Add 10.0 mL of p-dimethylaminobenzaldehyde solution with a pipet to each beaker or flask and mix well.

11.3 After a minimum of 10 min, but no longer than 100 min, measure the color absorbance of each solution at 458 nm in a 50 mm cell with a spectrophotometer, using the blank as reference solution for the initial instrument setting at zero absorbance. The instrument may be calibrated with the standard solutions to read directly in concentration if such capabilities are available.

11.4 Determine the micrograms per litre of hydrazine by referring the absorbance obtained for the sample to the calibration curve or reading hydrazine concentration directly.

[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 *Annual 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.

[5] MacEwen, J. D., Vernot, E. H., Haun, C. C., and Kinkead, E. B., "Chronic Inhalation Toxicity of Hydrazine: Onconogenic Effects," in cooperation with the University of California (Irvine) and the Airforce Aero Medical Research Laboratory.