Designation: D1385 – 07 (Reapproved 2013)ε1

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 U.S. Department of Defense.

ε[1] NOTE—This standard was reapproved with editorial changes in January 2013.

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 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.* 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.

[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.

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.

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 quantitative requirements of Type III reagent water in Specification D1193.

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. Alternately, graph the data in an electronic spreadsheet or use an instrument that reads out in direct concentrations.

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.

[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.

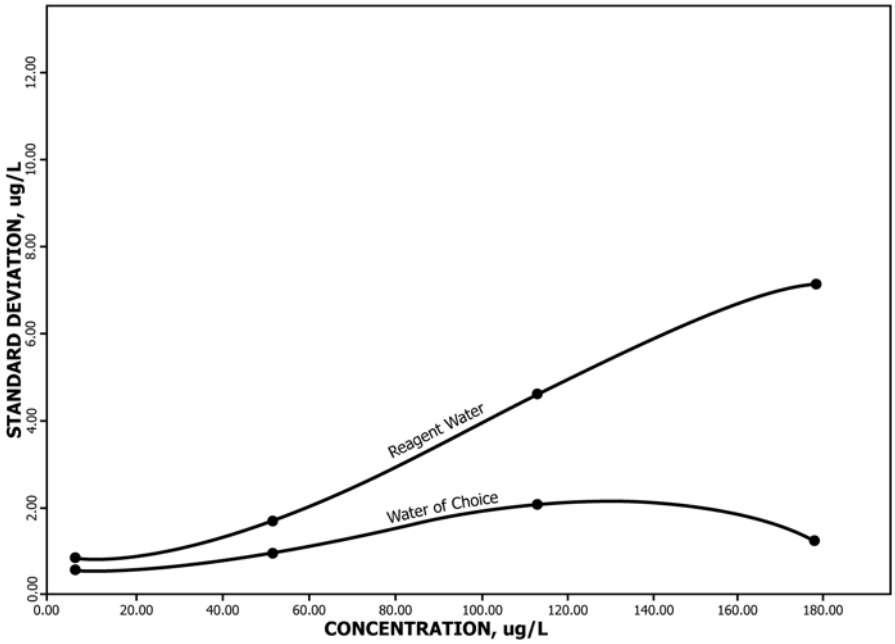

FIG. 1 Precision for Hydrazine

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.

12. Calculation

12.1 Calculate the concentration of hydrazine in micrograms per litre (parts per billion) in the sample by applying the following equation for the hydrazine determined in 11.4:

$$\text{hydrazine } (N_2H_4),\ \mu g/L\ (\text{ppb}) = A \cdot B/C$$

where:

A = hydrazine indicated by the calibration curve or read directly from the instrument, µg/L,
B = volume of the flask, µg/L, in which the sample was diluted in Section 9.2, mL, and
C = volume of the sample in Section 9.2, mL.

13. Precision and Bias[6]

13.1 The precision of this test method was tested by seven (7) laboratories in reagent water, condensate, well water, and natural water. Three laboratories reported data from two operators. Although multiple injections were reportedly made, the report sheets that were provided allowed only for reporting single values. Thus, no single operator precision can be calculated.

13.1.1 The overall precision of this test method, within its designated range for both reagent water and selected natural water matrices, varies with the quantity tested, as shown in Fig. 1.

13.1.2 Recovery and bias data for this test method are listed in Table 1.

TABLE 1 Recovery and Bias

Amount Added, µg/L	Amount Found, µg/L	% Bias	Statistically Significant, % (95 % Confidence Level)
	Reagent Water Type II		
6.041	5.891	−2.5	No
51.57	51.54	−0.1	No
177.8	178.1	0.2	No
112.9	113.2	0.3	No
	Selected Water Matrices		
6.041	5.935	−1.7	No
51.57	50.77	−1.6	No
177.8	176.2	−0.9	Yes
112.9	111.2	−1.5	No

13.2 These data may not apply to waters of other matrices; therefore, it is the responsibility of the analyst to ensure the validity of the test method in a particular matrix.

14. Quality Control

14.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1119. Contact ASTM Customer Service at service@astm.org.

confidence limits of the test, the following QC procedures must be followed when running the test.

14.2 *Calibration and Calibration Verification:*

14.2.1 When beginning use of this method, an initial calibration verification standard (CVS) should be used to verify the calibration standards and acceptable instrument performance. This verification should be performed on each analysis day. The CVS is a solution of the method analyte of known concentration (mid-calibration range) used to fortify reagent water. If the determined CVS concentrations are not within ±15 % of the known value, the analyst should reanalyze the CVS. If the value still falls outside acceptable limits, a new calibration curve is required that must be confirmed by a successful CVS before continuing with ongoing analyses.

14.2.2 One CVS should then be run with each sample batch (maximum of 20 samples) to verify the previously established calibration curves. If the determined analyte concentrations fall outside acceptable limits (±15 %) that analyte is judged out of control, and the source of the problem should be identified before continuing with ongoing analyses.

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 The laboratory using this test should perform an initial demonstration of laboratory capability. Analyze seven replicates of an initial demonstration of performance (IDP) solution. The IDP solution contains method analytes of known concentration, prepared from a different source to the calibration standards, used to fortify reagent water. Ideally, the IPD solution should be prepared by an independent source from reference materials. The level 2 spiking solution used for the precision and bias study is a suitable IDP solution. The mean and standard deviation of the seven values should then be calculated and compared according to Practice D5847.

14.4 *Laboratory Control Sample:*

14.4.1 One laboratory control sample (LCS) should be run with each sample batch (maximum of 20 samples). The LCS is a solution of method analytes of known concentration added to a matrix that sufficiently challenges the test method. A synthetic "water" matrix of relevance to the user (for example, drinking water or wastewater) spiked with the method analyte at the level of the IDP solution would be an example of an appropriate LCS. The analyte recoveries for the LCS should fall within the control limits of x ± 3S.

14.5 A reagent blank should be run when generating the initial calibration curves. A blank should also be run with each sample batch (maximum of 20 samples) to check for sample or system contamination.

14.6 *Matrix Spike:*

14.6.1 One matrix spike (MS) should be run with each sample batch (maximum of 20 samples) to test method recovery. The MS should be prepared in accordance with Guide D5810. Spike a portion of a water (or other) sample from each batch with the method analytes at the level of the IDP solution. The % recovery of the spike should fall within limits established from the interlaboratory precision and bias study data (assuming a background level of zero), according to Practice D5847.

14.7 *Duplicate:*

14.7.1 One matrix duplicate (MD) should be run with each sample batch (maximum of 20 samples) to test method precision. If non-detects are expected in all the samples to be analyzed, a matrix spike duplicate should be run instead. The precision of the duplicate analysis should be compared, according to Practice D5847, to the nearest tabulated S_0 value established from the interlaboratory precision and bias study data for each analyte.

14.8 *Independent Reference Material:*

14.8.1 In order to verify the quantitative values produced by the test method, an independent reference material (IRM), submitted to the laboratory as a regular sample (if practical), should be analyzed once per quarter. The concentration of the IRM should be within the scope of the method, as defined in 1.1. The values obtained must fall within the limits specified by the outside source.