Designation: D3546 – 05 (Reapproved 2011)

Standard Test Method for Formic Acid in Glacial Acetic Acid[1]

1. Scope*

1.1 This test method covers the determination of the formic acid (and other reducing substances) content of glacial acetic acid by oxidation with lead tetraacetate.[2]

1.2 For purposes of determining conformance of an observed or a calculated value using this test method to relevant specifications, test result(s) 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 E29.

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 For hazard information and guidance, see the supplier's Material Safety Data Sheets.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1193 Specification for Reagent Water

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Summary of Test Method

3.1 In an aqueous acetic acid solution each molecule of formic acid is oxidized to one molecule of carbon dioxide by reduction of one molecule of lead tetraacetate. The amount of lead tetraacetate remaining is then determined by adding potassium iodide and titrating the liberated iodine with standard sodium thiosulfate solution to the starch end point.

4. Significance and Use

4.1 This test method is useful for determining the formic acid content of glacial acetic acid by chemical means.

4.2 Low molecular weight organic acids (such as acetic and propionic), aldehydes (including formaldehyde and acetaldehyde), ketones, and alcohols (including methyl alcohol) do not interfere with the test.

4.3 Formic acid (and other reducing substances) may be present as a result of contamination during storage, distribution, and manufacture. This test method may be used in assessing compliance with a specification.

5. Reagents

5.1 *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.

5.2 *Purity of Water*—Unless otherwise indicated reference to water shall be understood to mean reagent water conforming to Type IV of Specification D1193.

5.3 *Lead Tetraacetate Solution*—Dissolve completely 40.0 g of sodium acetate in 1 L of glacial acetic acid and then dissolve 40.0 g of lead tetraacetate.

5.4 *Sodium Thiosulfate Standard Solution* (0.1 *N*)—Prepare and standardize 0.1 *N* sodium thiosulfate ($Na_2S_2O_3$) as described in Practice E200.

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[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates.

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[2] Perlin, A. S., "Determination of Formic Acid by Oxidation with Lead Tetraacetate," *Analytical Chemistry*, Vol 26, 1954, pp. 1053–1054.

[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.

[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 *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.

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

5.5 *Starch Indicator Solution*—Prepare the starch indicator solution as described in Practice E200.

5.6 *Stopping Solution*—Dissolve 100 g of potassium iodide and 500 g of sodium acetate in 1 L of water.

6. Procedure

6.1 Pipet 25 mL of the lead tetraacetate solution into each of two 500-mL Erlenmeyer flasks. Pipet the specimen (Note 1) into one of the flasks, swirl, and allow to stand for 20 to 30 min. The second flask is the blank.

NOTE 1—The following are suggested specimen sizes for varying concentrations of formic acid:

Formic Acid, %	Specimen Size, mL
0.0 to 0.10	25
0.10 to 0.30	10
0.30 to 0.60	5
0.60 to 1.00	3
1.00 to 2.00	2
2.00 to 3.00	1

6.2 Add to each flask a slight excess of the stopping solution as indicated by the formation of the yellow lead iodide precipitate. Add enough water just to dissolve the yellow precipitate. This usually requires about 200 mL.

6.3 Titrate the solution in both flasks with standard 0.1 *N* $Na_2S_2O_3$ solution to a pale yellow color. Add 1 mL of starch indicator and continue the titration until the blue color just disappears. If the specimen titration is less than 10 mL, discard and repeat with a smaller specimen.

7. Calculation

7.1 Calculate the weight percent of formic acid, *A*, as follows:

$$A = \frac{(B - V) \times N \times 2.3}{D \times S} \quad (1)$$

where:

B = $Na_2S_2O_3$ solution required for titration of the blank, mL,
V = $Na_2S_2O_3$ solution required for titration of the specimen, mL,
N = normality of the $Na_2S_2O_3$ solution,
D = specific gravity of the sample at test temperature,
S = specimen size, mL, and

$$2.3 = \frac{\text{equivalent weight of formic acid } (23) \times 100}{1000}$$

8. Report

8.1 Report the concentration of formic acid determined to the nearest 0.001 weight % absolute. Duplicates that agree within 0.0031 % are acceptable for averaging (95 % confidence level).

9. Precision and Bias

9.1 On the basis of an interlaboratory study of this test method in which operators in eight laboratories analyzed in duplicate on each of two different days two samples of acetic acid with mean contents of 0.050 % and 0.172 % formic acid, the pooled within-laboratory standard deviation was estimated to be 0.0016 % absolute with 13 df, and the between-laboratory standard deviation was estimated to be 0.0105 % absolute with 6 df. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

9.1.1 *Repeatability*—Two results, each the mean of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 0.005 % absolute.

9.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.036 % absolute.

9.2 *Bias*—Any material or contaminant that will react with lead tetraacetate under the test conditions will affect the results.

9.2.1 Various reducing materials may be present. As a result, this test method is sometimes used to measure "reducing substances, as formic acid."

10. Keywords

10.1 formic acid content ; glacial acetic acid

SUMMARY OF CHANGES

Committee D01.35 has identified the location of selected changes to this standard since the last issue (D3546 – 90 (1999)) that may impact the use of this standard.

(1) Added reference to Practice E29 in 1.2 of the Scope section.

(2) Added Practice E29 to list of Referenced Documents.

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