



Standard Test Method for Formic Acid in Glacial Acetic Acid¹

This standard is issued under the fixed designation D 3546; 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 the formic acid (and other reducing substances) content of glacial acetic acid by oxidation with lead tetraacetate.²

1.2 *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.*

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

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water³

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis⁴

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.⁵ 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 D 1193.

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 ($\text{Na}_2\text{S}_2\text{O}_3$) as described in Practice E 200.

5.5 *Starch Indicator Solution*—Prepare the starch indicator solution as described in Practice E 200.

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

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

Current edition approved May 25, 1990. Published July 1990. Originally published as D 3546 – 76. Last previous edition D 3546 – 86.

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

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

⁵ *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

precipitate. This usually requires about 200 mL.

6.3 Titrate the solution in both flasks with standard 0.1 *N* Na₂S₂O₃ 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 = Na₂S₂O₃ solution required for titration of the blank, mL,

V = Na₂S₂O₃ solution required for titration of the specimen, mL,

N = normality of the Na₂S₂O₃ 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).

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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 glacial acetic acid; formic acid content