

Standard Test Method for Acetaldehyde Content of Vinyl Acetate¹

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1. Scope

1.1 This test method covers the determination of trace quantities of acetaldehyde, in the range from 0.00 to 0.05 %, contained in 99 % grade vinyl acetate.

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.* For specific hazard statements see Section 8.

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water²

3. Summary of Test Method

3.1 The acetaldehyde present in the specimen is reacted with a measured excess of sodium bisulfite. The amount of sodium bisulfite consumed, determined by titrating the excess with a standard iodine solution, is a measure of the acetaldehyde present in the vinyl acetate.

4. Significance and Use

4.1 This test method provides a measurement of acetaldehyde content in vinyl acetate. The results of these measurements can be used for specification acceptance.

5. Interference

5.1 Ketones and other aldehydes, if present, cause a positive interference.

6. Apparatus

6.1 *Buret*, 50-mL capacity, graduated in 0.1-mL subdivisions, with a funnel or flared top and a ground-glass stopcock.

6.2 *Erlenmeyer Flask*, 500-mL capacity, glass-stoppered.

6.3 *Pipet*, 50-mL capacity.

6.4 *Pipet*, 100-mL capacity.

7. Reagents

7.1 *Purity of Reagents*—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.³ Other grades may be used provided that it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type IV of Specification D 1193.

7.3 *Iodine, Standard Solution (0.1 N)*—Dissolve 35.0 g of potassium iodide (KI) and 13.0 g of resublimed iodine in water, and dilute to 1 L with water. Store this solution in a dark bottle and standardize each day, as required, against a standard 0.1 N sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution. (See standardization procedure, 9.3 and 9.4.)

7.4 *Potassium Iodate (KIO₃)*, primary standard.

7.5 *Sodium Bisulfite Solution (0.44 %)*—Dissolve 4.4 g of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) in 1 L of water. This solution should be prepared fresh daily or just before using.

7.6 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Weigh to 0.1 g 24.8 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) crystals and dissolve in 500 mL of water. Dilute this solution to 1 L with water. Add 0.5 mL of chloroform per litre of solution as a preservative, and store in a clean dark bottle. This solution should be standardized weekly, as required, against potassium iodate (KIO₃). (See standardization procedure, 9.1 and 9.2.)

7.7 *Starch Indicator*—Make a paste of 6 g of powdered soluble starch in water, and dilute to 1 L with water, stirring to produce a suspension. While stirring, add 20 g of potassium hydroxide (KOH) pellets, and continue stirring until the KOH is dissolved. Let stand for 2 h and add 27.5 mL of hydrochloric acid (HCl). Adjust the mixture to a pH of 6.0 ± 0.1 by adding small increments of HCl or KOH as required. Add 6 mL of glacial acetic acid as a preservative.

7.8 *Sulfuric Acid (1 N)*—Place approximately 700 to 800 mL of water in a 1-L volumetric flask. Add slowly and with constant stirring 27.2 mL of concentrated sulfuric acid (H_2SO_4 ,

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 *Annual Book of ASTM Standards*, Vol 11.01.

³ *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.

sp gr 1.84). Allow the solution to cool to room temperature, and adjust the volume to the 1-L mark with additional water.

8. Hazards

8.1 Vinyl acetate is flammable and hazardous; use special precautions when handling it. Avoid eye and skin contact and the inhalation of its vapors.

9. Standardization

9.1 To standardize the 0.1 *N* Na₂S₂O₃ solution, first dry for 6 h approximately 3 g of the KIO₃ primary standard in a drying oven maintained at a temperature of 110 ± 5°C. Place the dried KIO₃ in a desiccator until cool. Weigh 0.14 to 0.15 g of the dried KIO₃ to 0.1 mg, and transfer to a 250-mL Erlenmeyer flask. Add 25 mL of water to the flask to dissolve the KIO₃. To this solution, add 2 g of KI crystals and 10 mL of the 1 *N* H₂SO₄, and thoroughly mix. Fill a 50-mL buret with the Na₂S₂O₃ solution to be standardized and titrate the KIO₃ solution until the brown color of the iodine has been reduced to a pale yellow color. At this point, add 0.5 mL of the starch indicator, and continue the titration until the color changes sharply from blue to colorless.

NOTE 1—When titrating excess iodine with sodium thiosulfate, the starch indicator should be added only when near the end point as noted by the fading of the brown color of the iodine. Starch reacts with iodine in the presence of iodide to form an intensely blue color absorption complex, and if added to a solution containing free iodine, a stable complex is formed, that would give erroneous results.

9.2 Calculate the normality *N* of the Na₂S₂O₃ solution as follows:

$$N = (W \times P)/(V \times 0.035669)$$

where:

W = weight of KIO₃ used, g

P = correction for purity of KIO₃ standard, and

V = volume of Na₂S₂O₃ required for titration of the KIO₃, mL.

9.3 Fill the funnel-topped 50-mL buret with the 0.1 *N* iodine solution to be standardized. Measure approximately 40 mL of the iodine solution into a 250-mL Erlenmeyer flask, and read the buret to the nearest 0.1 mL. Add approximately 50 mL of water to the flask containing the iodine solution, and titrate with the standardized 0.1 *N* Na₂S₂O₃ solution as described in 9.1.

9.4 Calculate the normality *N*₁ of the iodine solution as follows:

$$N_1 = (V \times N)/V_1 \quad (1)$$

where:

V = volume of Na₂S₂O₃ required for titration of the iodine solution, mL,

N = normality of the Na₂S₂O₃ solution, and

*V*₁ = volume of iodine solution used for standardization, mL.

10. Procedure

10.1 Pipet 50 mL of Na₂S₂O₅ solution (7.5) into each of two glass-stoppered 500-mL Erlenmeyer flasks. Add approximately 25 g of clean chipped ice to each flask and into one of the flasks

pipet 100 mL of the sample. Grease the stoppers and place the flasks on a mechanical shaker, allowing them to shake for 10 ± 1 min.

10.2 At the end of the 10-min reaction period, add 0.5 mL of starch indicator to the blank and specimen. Titrate the excess sodium bisulfite with the standard iodine solution. The end point is when the first permanent blue color is obtained.

NOTE 2—In order to maintain good drainage of the iodine solution, care should be taken to always use a clean buret which should be filled with the iodine solution just before beginning each series of titrations.

11. Calculation

11.1 Calculate the weight percent aldehyde content of the vinyl acetate, as acetaldehyde, *A*, as follows:

$$A = [(B - V_2) \times N_1 \times 0.02202]/(D \times M) \times 100 \quad (2)$$

where:

B = volume of iodine required for the titration of the blank, mL,

*V*₂ = volume of iodine required for titration of the specimen, mL,

*N*₁ = normality of the iodine solution,

D = specific gravity of the sample, and

M = volume of sample used, mL.

12. Report

12.1 Report the following information: weight percent acetaldehyde to the nearest 0.001 %. Duplicate runs that agree within 0.003 % are acceptable for averaging (95 % confidence level).

13. Precision and Bias

13.1 *Precision*—The following criteria should be used for judging the acceptability of results at the 95 % confidence level:

13.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same analyst should be considered suspect if they differ by more than 0.006 % absolute.

13.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by analysts in different laboratories should be considered suspect if they differ by more than 0.008 % absolute.

NOTE 3—The above precision estimates are based upon an interlaboratory study on four samples of vinyl acetate containing 0.01, 0.02, 0.03, and 0.05 % acetaldehyde. Two analysts in each of three different laboratories performed duplicate determinations on each sample on two successive days making a total of 96 determinations.

13.2 *Bias*—Bias has not been determined for this test method because there is no appropriate standard available.

14. Keywords

14.1 acetaldehyde; vinyl acetate

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