



Standard Test Method for Total Aldehydes in Styrene Monomer by Potentiometric Titration¹

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1. Scope

1.1 This test method covers the wet chemical determination of aldehydes in styrene monomer. Aldehydes are calculated and reported as benzaldehyde. The range of concentration for this test method is 0.001 mass % to 0.030 mass %.

1.2 In determining conformance of the test results using this method to applicable specifications, results shall be rounded off 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 *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:²

D1193 Specification for Reagent Water

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

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

2.2 Other Documents:

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.07 on Styrene, Ethylbenzene and C9 and C10 Aromatic Hydrocarbons.

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² 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.

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200³

3. Summary of Test Method

3.1 An alcoholic solution of hydroxylamine hydrochloride is added to a specimen of styrene monomer. Active aldehydes present react in accordance with Eq 1:



The amount of hydrochloric acid released, which is equivalent to the aldehyde present in the sample, is titrated with standard alcoholic potassium hydroxide solution.

4. Significance and Use

4.1 This test method is suitable for determining the quantity of aldehydes, both for quality control and quality assurance of the product.

5. Interferences

5.1 Ketones, if present, interfere by partially reacting with the reagent.

5.2 Methanol used in this procedure may partially react with aldehydes to form (hemi)acetals.

6. Apparatus

6.1 *Titration Vessel*, 150 mL.

6.2 *Combined pH – Glass Electrode*, dedicated for non-aqueous liquids.

6.3 *Stirring Bar*, 30 mm.

6.4 *Titration Stand* with stirrer.

6.5 *Pipets*, 25 mL.

6.6 *Volumetric Flasks*, 100 mL.

6.7 *Burets*, 5 mL. (Microburets are preferred.)

6.8 *Exchange Unit*, 5 mL.

6.9 *Thermometers*, capable of differentiating 1°C at ambient.

³ Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098, <http://dodssp.daps.dla.mil>.

7. Reagents and Materials

7.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

7.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification D1193.

7.3 Hydroxylamine Hydrochloride Solution—Dissolve 20 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 1 L of methanol. Take a portion of this volume (for example, 50 mL) and neutralize (to the first equivalency point) with potassium hydroxide (KOH) in methanol (7.4). Record the amount of KOH required and the reading (in mV) of the electrode when neutralized. For accuracy, repeat this procedure with a second portion and average the amount of KOH required. Add neutralizing solution (KOH in methanol) to the remaining 900 mL of hydroxylamine solution based on the average amount that was calculated. Check neutrality regularly (for example, once a week) by either checking the reading of the electrode or by titration.

7.4 Methanol, free of acids. If necessary, neutralize with potassium hydroxide (KOH) solution (see 7.5), do not record volume. Use the same neutralizing method as mentions in 7.3 for hydroxylamine hydrochloride solution.

7.5 Potassium Hydroxide, Standard Solution in Methanol (0.1 N)—Dilute five times to a concentration of 0.02 N. Standardize against primary standard benzoic acid. Use a carbon dioxide scavenger (for example, sodalime) to prevent carbon dioxide from entering the KOH solution.

8. Hazards

8.1 Consult the latest OSHA regulations, supplier's Material Safety Data Sheets, and local regulations regarding all materials used in this test method.

8.2 Styrene monomer is flammable and polymerizes exothermally on contact with peroxides, mineral acids, and AlCl_3 .

9. Sampling and Handling

9.1 Collect the sample as directed in Practice D3437.

10. Procedure

10.1 Prepare the pH electrode according to the manufacturer's instructions.

10.2 Pipet 25.0 mL of the sample (**Warning**—see 8.2) and 25 mL of methanol (7.4) into a 150-mL titration vessel with stirring bar. Add 0.2 mL of water. Add 25 mL of the neutralized hydroxylamine hydrochloride solution and allow to stand 0.5 h

while stirring. Titrate with the 0.02 N KOH/methanol solution, dispensed from a 5-mL buret, until the first equivalence point, and record the volume used.

10.3 Since methanol may contain aldehydes, run a blank determination on 25 mL of methanol (7.4), record the volume used.

10.4 Since styrene may contain acids, run a blank determination by repeating 10.2 without adding the neutralized hydroxylamine hydrochloride solution, record the volume used.

11. Calculation

11.1 Calculate the percentage of aldehydes as benzaldehyde as follows:

$$\text{Aldehydes, mass \%} = [(A - B - C) \times N \times 0.106] / 25 \times D \times 100 \quad (2)$$

where:

A = KOH solution required for titration of the specimen, mL,

B = KOH solution required for titration of the methanol blank, mL,

C = KOH solution required for titration of styrene to check for acids, mL,

N = normality of KOH solution used, and

D = density of styrene monomer.

12. Report

12.1 Report the aldehydes content to the nearest 0.001 mass %.

13. Precision and Bias

13.1 Repeatability—Results should not be suspect unless they differ by more than shown in Table 1. Results differing by less than “*r*” have a 95 % probability of being correct.

TABLE 1 Repeatability^A

Aldehyde Content, mass %	Repeatability, mass %
0.004	0.0003
0.03	0.002

^A Based on 10 duplicate results obtained by the same operator on a single day.

13.2 Reproducibility—No data available.

13.3 Bias—Since there is no accepted reference material suitable for determining the bias in this test method for measuring aldehydes, bias has not been determined.

14. Quality Guidelines

14.1 Laboratories shall have a quality control system in place:

14.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

14.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

14.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

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.

14.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide **D6809** or similar statistical quality control practices.

15. Keywords

15.1 aldehyde content; aldehydes in styrene; benzaldehyde; styrene

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