Designation: ~~D7704 – 16~~ D7704 – 24

Standard Test Method for Total Aldehydes in Styrene Monomer by Potentiometric Titration[1]

This standard is issued under the fixed designation D7704; 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 wet chemical determination of total aldehydes in styrene monomer. Total aldehydes are calculated and reported as benzaldehyde. ~~The Range of Concentration for this test method is 0.004 weight % to 0.013 weight %.~~

1.2 ~~Limit~~ This test method is applicable to samples with aldehyde concentrations to 0.013 mass%. The Limit of Detection (LOD) ~~and~~ is 0.0006 mass% and the Limit of Quantification (LOQ) is ~~0.0006 and 0.0020 weight %, respectively~~ 0.0020 mass%. The LOD and LOQ were calculated based on the data in Table 1.

1.3 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.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this ~~standard with the exception: weight % should be used rather than mass %.~~standard.

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~~safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Section 8.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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

Current edition approved ~~June 1, 2016~~Jan. 1, 2024. Published ~~October 2016~~January 2024. Originally approved in 2011. Last previous edition approved in ~~2012~~2016 as ~~D7704 – 12.~~D7704 – 16. DOI: ~~10.1520/D7704-16.~~10.1520/D7704-24.

[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.

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

2.2 *Other Documents:*
OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200[3]

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:

$$RCHO + NH_2OH{\cdot}HCl \rightarrow RCHNOH + H_2O + HCl \quad (1)$$

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~~1 °C at ambient.

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.

---

[3] Available from DLA Document Services, Building 4/D, 700 Robbins Ave., Philadelphia, PA 19111-5094, http://quicksearch.dla.mil.

[4] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* 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.

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

7.3 *Hydroxylamine Hydrochloride Solution*—Dissolve 20 g of hydroxylamine hydrochloride (NH_2~~OH·HCl)~~ OH·HCl, CAS 5470-11-1) in 1 L of ~~methanol.~~ methanol (CAS 67-56-1). Take a portion of this volume (for example, 50 mL) and neutralize (to the first equivalency point) with potassium hydroxide ~~(KOH)~~ (KOH, CAS 1310-58-3) 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 mentioned 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 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 $AlCl_3$. Styrene also polymerizes exothermically in the absence of inhibitor (Tert Butyl Catechol, TBC) and in the absence of adequate oxygen in the liquid phase to support the inhibitor (TBC).

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~~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~~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 total aldehydes as benzaldehyde as follows:

$$Total Aldehydes, (as\ benzaldehyde), weight\ \% = [((A - B - C) \times N \times 0.106)/\ 25 \times D] \times 100 \quad (2)$$

where:

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