Designation: D7704 – 16

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 of Detection (LOD) and Limit of Quantification (LOQ) is 0.0006 and 0.0020 weight %, respectively

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 %.

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:*[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

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.

[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.

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

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

6.9 *Thermometers,* capable of differentiating 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.

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 ($NH_2OH{\cdot}HCl$) 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 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 $AlCl_3$.

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 total aldehydes as benzaldehyde as follows:

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

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 weight %.

13. Precision and Bias

13.1 An ILS was conducted which included six laboratories analyzing four samples twice. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D16-1061.[5]

13.1.1 *Repeatability Limit (r):*

13.1.1.1 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.

13.1.2 *Reproducibility Limit (R):*

13.1.2.1 Results submitted by two laboratories should not be considered suspect unless they differ by more than R shown in Table 1. Results differing by less than R have a 95 % probability of being correct.

13.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

13.3 The precision statement was determined through statistical examination of 42 results, from a total of six laboratories, on four styrene materials.

[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.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1061. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Total Aldehydes (as benzaldehyde, weight %)

Material	Average[A] $\bar{X}$	Repeatability Limit r	Reproducibility Limit R
Styrene monomer + 0.0010 weight % benzaldehyde	0.0046	0.0011	0.0053
Styrene monomer + 0.0020 weight % benzaldehyde	0.0060	0.0016	0.0050
Styrene monomer + 0.0050 weight % benzaldehyde	0.0074	0.0010	0.0106
Styrene monomer + 0.0100 weight % benzaldehyde	0.0129	0.0006	0.0106

[A] The average of the laboratories' calculated averages.

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.

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

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D7704–12) that may impact the use of this standard. (Approved June 1, 2016.)

(1) Revised Section 1, Scope—Range of Concentration adapted to ILS RoC, Limit of Detection (LOD) and Limit of Quantification (LOQ) included.

(2) Weight % will be used as standard, not mass %.

(3) Updated Section 13, Precision and Bias statement with data from interlaboratory study #875 of Test Method D7704.