Designation: D7883 – 13

Standard Test Method for Determination of 4-Carboxybenzaldehyde and *p*-Toluic Acid in Purified Terephthalic Acid by Weak Anion Exchange High Performance Liquid Chromatography[1]

This standard is issued under the fixed designation D7883; 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[2] covers the determination of the 4-Carboxybenzaldehyde (4-CBA) and *p*-Toluic acid (*p*-TOL) in purified terephthalic acid (PTA) by weak anion exchange high performance liquid chromatography (HPLC). This method is applicable for 4-CBA from 2 to 500 mg/kg and for *p*-TOL from 10 to 500 mg/kg, respectively.

1.2 In determining the conformance of the test results using this method to applicable specification, 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:*[3]

D1193 Specification for Reagent Water

D4790 Terminology of Aromatic Hydrocarbons and Related Chemicals

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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E682 Practice for Liquid Chromatography Terms and Relationships

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

2.2 *ISO Document:*[4]

EN ISO 8213 Chemical products for industrial use—Sampling techniques—Solid chemical products in the form of particles varying from powders to coarse lumps

2.3 *Other Document:*[5]

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Summary of Test Method

3.1 *Weak Anion Exchange HPLC Method*—PTA sample is dissolved in ammonium hydroxide solution. After pH adjustment, a fixed volume of this solution is injected into a high performance liquid chromatograph equipped with a UV detector. An anion-exchange column is used to separate the impurities 4-CBA and *p*-TOL from PTA. The external standard calibration is used for quantification.

4. Significance and Use

4.1 The presence of 4-CBA and *p*-TOL in PTA used for the production of polyester is undesirable because they can slow down the polymerization process, and 4-CBA is also imparting coloration to the polymer due to thermal instability.

4.2 Determining the amount of 4-CBA and *p*-TOL remaining from the manufacture of PTA is often required. This test method is suitable for setting specifications and could be used as an internal quality control tool where these products are produced or are used.

[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 D16.02 on Oxygenated Aromatics.

Current edition approved Aug. 1, 2013. Published October 2013. DOI: 10.1520/D7883-13.

[2] This standard is based on SH/T 1612.7-1995 Purified terephthalic acid for industrial use—determination of *p*-Toluic Acid, 4-Carboxybenzaldehyde-HPLC, copyright SINOPEC, 22 Chaoyangmen North Street, Chaoyang District, Beijing, China 100728. A copy of SH/T 1612.7-1995 may be obtained from China Petrochemical Press, www.sinopec-press.com.

[3] 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.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[5] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

5. Apparatus

5.1 *High Performance Liquid Chromatograph (HPLC)*—any HPLC capable of pumping the mobile phase at flow rates between 0.1 and 2.0 mL/min, with a pressure between 0 and 40 MPa and a pulsation of less than 1 % full scale deflection under the test conditions described in Table 1. The S/N (signal to noise) ratio should be 3:1 or greater for 2 mg/kg 4-CBA and 10 mg/kg *p*-TOL.

5.2 *Sample Injection System*—capable of injecting 1 to 25 µL, using either partial or full loop mode, with a repeatability of ±1 %.

5.3 *Detector, Variable Wavelength Ultraviolet Photometric Detector (VWD), Multi-wavelength Detector, or Photometric Diode Array Detector (PDA),* capable of operating at 236 and 258 nm.

5.4 *Column Oven*—any suitable HPLC column oven (block heating or air circulating) capable of maintaining a constant temperature of ±1°C within the range of 20 to 70°C.

5.5 *Chromatography Data System.*

5.6 *HPLC Columns:*

5.6.1 *Guard Column*—a stainless steel column placed in front of the analytical column is recommended. A column, packed with the same stationary phase as the analytical column, 3 to 5 mm ID and 50 to 100 mm length, has been found to be satisfactory. Other hydrophilic chemically-bonded silica stationary phases can also be used.

5.6.2 *Analytical Column*—a stainless steel HPLC column packed with amino-bonded silica stationary phase is suitable. See Table 1 for recommended operating conditions.

5.7 *Analytical Balance*—readable to ±0.0001 g.

5.8 *pH Meter.*

5.9 *Sample Filter*—a disposable syringe filter made of cellulose acetate, with a pore size between 0.22 and 0.45 µm, and is chemically inert to aqueous solutions, is recommended for the removal of particulate matter from the sample solution.

5.10 *Vacuum Filter*—capable of filtering mobile phase.

6. Reagents and Materials

6.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the reagent grade specification for analytical reagents of the American Chemical Society, where such specifications are available.[6] 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 performance or accuracy of the determination. Reagent chemicals shall be used for all tests.

NOTE 1—Calibration and detection limits of this test method can be biased by the purity of the reagents.

TABLE 1 Recommended Operating Conditions

Column	Weak Alkali Anion Exchange
Stationary phase	(-NMe_2) chemically bonded silica
Particle size	3 µm
Material of column	stainless steel
Length of column	50 mm
Inner diameter	4–5 mm
Mobile phase	0.1 mol/L $NH_4H_2PO_4$ solution:acetonitrile (or methanol) =9:1
Flow rate	0.8–1.2 mL/min
UV detector	258 nm for 4-CBA 236 nm for *p*-TOL
Injection amount	20 µL
Column temperature	30–40°C

6.2 *Ammonium Dihydrogen Phosphate*—(**Warning**—Ammonium dihydrogen phosphate may cause irritation with only minor residual injury.)

6.3 *Ammonium Hydroxide,* 25 to 28 % (wt).

6.4 *Phosphoric Acid,* ⩾82 % (wt).

6.5 *Acetonitrile*—HPLC grade. (**Warning**—Acetonitrile is flammable and hazardous in case of skin and eye contact, ingestion or inhalation.)

6.6 *Methanol*—HPLC grade. (**Warning**—Methanol is highly flammable and toxic by inhalation, ingestion or skin contact.)

6.7 *Water*—HPLC grade.

6.8 *Ammonium Hydroxide Solution*—ammonium hydroxide mixed with water as 1:1 (V:V).

6.9 *Phosphoric Acid Solution*—phosphoric acid mixed with water as 1:4 (V:V).

6.10 *PTA Calibration Standard*—A certified PTA calibration standard with known amounts of 4-CBA and *p*-TOL is required. If it is not commercially available, please refer to Annex A1 for determining the concentrations of 4-CBA and *p*-TOL in a PTA sample. The calibrated PTA sample can be served as a PTA calibration standard.

6.11 *Mobile Phase:*

6.11.1 *0.1 Mol/L $NH_4H_2PO_4$ Solution: Acetonitrile (or Methanol) = 9:1 (v/v)*—Dissolve approximately 11.50 g of ammonium dihydrogen phosphate in 850 mL of water, adjust pH to 4.3 by using phosphoric acid solution. Transfer the resulting solution to a 1000 mL volumetric flask, add 100 mL of acetonitrile or methanol, dilute with water to the mark.

NOTE 2—It is recommended to degas and filter the mobile phase before use. Degassing can be done conveniently, on-line or off-line by helium sparging, vacuum degassing or ultrasonic agitation.

7. Hazards

7.1 Consult current federal regulations, supplier's Material Safety Data Sheets, and local regulations for all materials used in this test method.

8. Sampling, Test Specimens, and Test Units

8.1 Use only representative samples obtained as described in EN ISO 8213, unless otherwise specified.

[6] *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.