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.

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.

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

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.

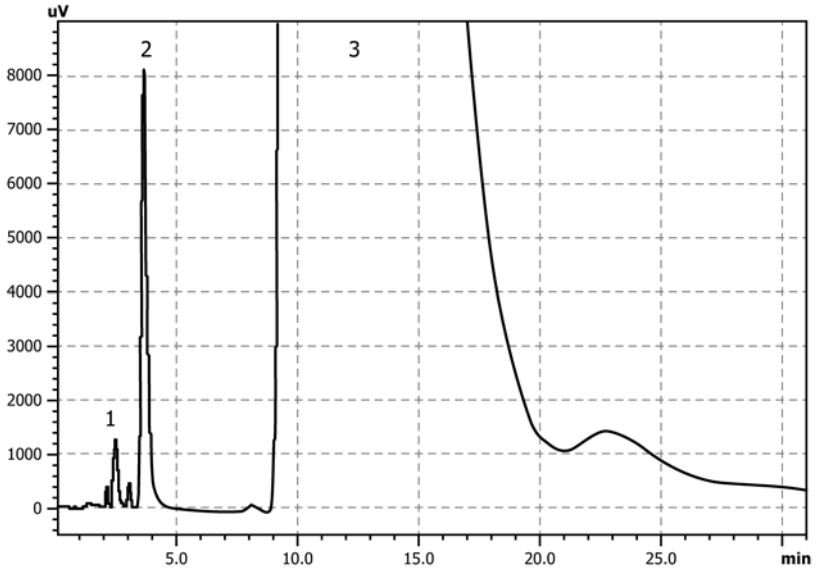

FIG. 1 Chromatogram of a PTA Sample (weak anion exchange HPLC)
1–4-CBA, 2–*p*-TOL, 3–PTA

9. Preparation of Apparatus

9.1 Set up the pump, sample injection system, column, oven, detector, and chromatography data system in accordance with the manufacturer's instructions. Adjust the instrument to the conditions described in Table 1, allowing sufficient time for the equipment to reach equilibrium which is indicated by a stable horizontal baseline. For a new column, four to six hours of equilibration time may be required.

NOTE 3—A gradient mobile phase can also be used for improving chromatograph.

10. Calibration

10.1 Weigh, to the nearest 0.0001 g, about 0.5 g of PTA standard in a 25 mL beaker, add 3 mL of ammonium hydroxide solution and 7 mL water, to dissolve PTA completely. Adjust the pH value of the solution to 6–7 by using the phosphoric acid solution. Then accurately transfer the resulting solution to a 50 mL volumetric flask, and dilute with water to the mark. When operating conditions are steady, inject 20 µL of the calibration standard solution into chromatograph for analysis. Record chromatogram and the peak area values for 4-CBA and *p*-TOL respectively with the data system.

NOTE 4—Care must be taken to ensure a quantitative transfer of the solution from the beaker, and also any material that is removed by the pH probe, into the 50 mL volumetric flask. It is recommended that a calibration standard be run after every ten samples to check the stability of the chromatograph system.

11. Procedure

11.1 Weigh, to the nearest 0.0001 g, about 0.5 g PTA sample, repeat the remaining steps in 10.1, and record peak area values of 4-CBA and *p*-TOL respectively. After each analysis, rinse the column with mobile phase until the baseline is stabilized for the next run. The representative chromatograms of a PTA sample is shown in Fig. 1.

12. Calculation

12.1 Calculate the concentration of 4-CBA or *p*-TOL in mg/kg, using the following equation:

$$X = \frac{m_s \cdot A \cdot C_s}{m \cdot A_s} \quad (1)$$

where:

X = concentration of 4-CBA or *p*-TOL in the PTA sample, mg/kg,
A = peak area of 4-CBA or *p*-TOL in the PTA sample,
m = weight of the PTA sample, g,
A_s = peak area of 4-CBA or *p*-TOL in the PTA standard,
C_s = concentration of 4-CBA or *p*-TOL in the PTA standard, mg/kg,
m_s = weight of the PTA standard, g.

13. Report

13.1 Report the value of 4-CBA or *p*-TOL content in mg/kg, to the nearest 1.0 mg/kg.

13.2 Report the following information in the report:

13.2.1 The complete identification of the sample tested.

13.2.2 Any deviation from the procedure specified (for example, detailed description of column and operating conditions).

13.2.3 Results of the test.

13.2.4 Any abnormal situations observed during the test.

14. Precision and Bias[7]

14.1 The precision of this test method is based on an intralaboratory study of Test Method D7883 conducted in

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1047. Contact ASTM Customer Service at service@astm.org.

2012. One laboratory tested one PTA sample and one qualified terephthalic acid (QTA) sample for 4-CBA and *p*-TOL. Every test result represents an individual determination. The laboratory reported 20 replicate results for each analysis/material combination in order to estimate the repeatability limits of the standard. Practice E691 was followed for the design and analysis of the repeatability data; the details are given in Research Report RR:D16-1047.

14.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between the two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

14.1.1.1 Repeatability limits are listed in Table 2.

TABLE 2 Repeatability Limits

Sample	Analyte	Average (wt. mg/kg)	Repeatability S_r	Repeatability Limit r
PTA	4-CBA	8.4	0.10	0.30
	p-TOL	136.1	1.86	5.27
QTA	4-CBA	229.5	2.23	6.30
	p-TOL	22.9	0.73	2.05

14.1.2 *Bias*—At the time of the study, the test specimens chosen for analysis were not accepted reference materials suitable for determining the bias for the test method, therefore no statement on bias is being made.

15. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

15.1.1 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.

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

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

15.1.4 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.

16. Keywords

16.1 purified terephthalic acid; 4-Carboxybenzaldehyde; *p*-Toluic acid; high performance liquid chromatograph; weak anion exchange HPLC

ANNEX

(Mandatory Information)

A1. RECOMMENDED PROCEDURE FOR CALIBRATION OF PTA SAMPLE

INTRODUCTION

When a PTA standard with known amounts of 4-CBA and *p*-TOL is not available, a PTA sample with granularity of 80 to 160 µm, containing 4-CBA and *p*-TOL at concentrations of 10 to 25 mg/kg and 100 to 200 mg/kg, respectively, may be analyzed to determine the concentrations of 4-CBA and *p*-TOL by using the following standard addition method. This PTA sample with calibrated concentrations of 4-CBA and *p*-TOL can be used as the PTA standard for sample analysis.

A1.1 Reagents and Materials

A1.1.1 *4-CBA*—Purity >98.0 %.

A1.1.2 *P-TOL*—Purity >98.0 %.

A1.2 Calibration Solutions

A1.2.1 *Calibration Standard 4-CBA (10 µg/mL)*—Weigh, to the nearest 0.0001 g, about 0.0250 g of 4-CBA in a 25 mL beaker, add some water and a few drops of ammonium hydroxide solution, and stir until 4-CBA is completely dissolved. Adjust the pH value of the solution to 6–7 by using phosphoric acid solution. Then accurately transfer the resulting solution to a 50 mL volumetric flask and dilute with water to the mark to give a 500 µg/mL 4-CBA stock solution. Then dilute with water 50 times to 10 µg/mL.

NOTE A1.1—Care must be taken to ensure a quantitative transfer of the solution from the beaker, and also any material that is removed by the pH probe, into the 50 mL volumetric flask.

A1.2.2 *Calibration Standard p-TOL (80 µg/mL)*—Weigh, to the nearest 0.0001 g, about 0.0200 g of *p*-TOL following steps in A1.2.1 to give a 400 µg/mL *p*-TOL stock solution. Then dilute with water five times to 80 µg/mL.

A1.2.3 *PTA Spiked Solutions*—Accurately weigh 0.500 ± 0.001 g of PTA in five 25 mL beakers each and follow the steps in 10.1 to dissolve PTA samples. Then accurately transfer these solutions to five 50 mL volumetric flasks. Add 0.00, 0.50, 1.00, 1.50, and 2.00 mL of calibration standard 4-CBA and calibration standard *p*-TOL to the above five flasks, and dilute with water to the mark. The concentrations of 4-CBA and *p*-TOL added into these PTA solutions are as follows:

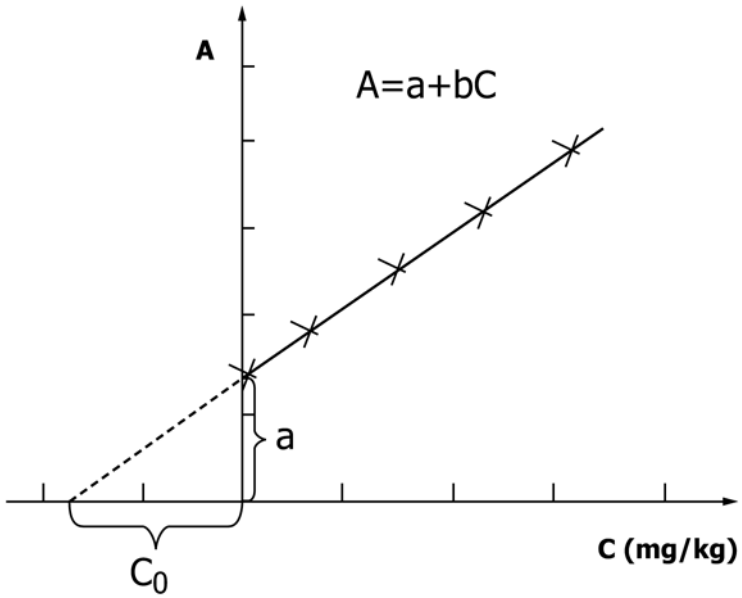

FIG. A1.1 Standard Addition Method for Calibration of 4-CBA or *p*-TOL in PTA
C = concentration of added 4-CBA or *p*-TOL in the PTA sample, mg/kg
A = average peak area of 4-CBA or *p*-TOL in the PTA sample

4-CBA (mg/kg): 0.0, 10.0*K, 20.0*K, 30.0*K, and 40.0*K

where:

K = weight of 4-CBA from A1.2.1/0.0250

p-TOL (mg/kg): 0.0, 80.0*J, 160.0*J, 240.0*J, and 320.0*J

where:

J = weight of *p*-TOL from A1.2.2/0.0200

A1.3 Procedure

A1.3.1 Follow steps in 10.1 to analyze the series PTA spiked solutions, and record the peak area values of 4-CBA and *p*-TOL respectively. Each sample should be run in duplicate to obtain an average value of peak area.

A1.4 Calculation

A1.4.1 Construct a calibration curve (see Fig. A1.1) by plotting the spiked concentration on the X-axis and the average peak area on the Y-axis based on the theory of least square linear regression. A linear calibration curve is required with a correlation coefficient (r^2) greater or equal to 0.99, otherwise the whole procedure should be repeated. A computer or data system may be used to interpret the calibration.

A1.4.1.1 The linear equation is as follows:

$$A = a + bC \quad \text{(A1.1)}$$

where:

C = spiked concentration of 4-CBA or *p*-TOL in the PTA sample, mg/kg,
A = average peak area of 4-CBA or *p*-TOL in the PTA sample,
b = slope obtained from Eq A1.1,
a = intercept obtained from Eq A1.1.

A1.4.1.2 Calculate the concentrations of 4-CBA and *p*-TOL in this PTA sample using the following equation:

$$C_0 = \frac{a}{b} \quad \text{(A1.2)}$$

where:

C_0 = concentration of 4-CBA or *p*-TOL in the PTA sample, mg/kg,
b = slope obtained from Eq A1.1,
a = intercept obtained from Eq A1.1.