



Designation: ~~D7883~~—19 ~~D7883~~ – 20

Standard Test Method for Determination of 4-Carboxybenzaldehyde and *p*-Toluic Acid in Purified Terephthalic Acid by Weak Anion Exchange High Performance Liquid Chromatography¹

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 method² 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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:³

D1193 Specification for Reagent Water

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

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

¹ This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.02 on Oxygenated Aromatics.

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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.

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

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.

5. Apparatus

5.1 *High Performance Liquid Chromatograph (HPLC)*—~~any~~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%~~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*—~~System~~ capable of injecting 1 to 25 μ L, using either partial or full loop mode, with a repeatability of ~~±1%~~±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*—~~Oven~~, any suitable HPLC column oven (block heating or air circulating) capable of maintaining a constant temperature of $\pm 1^\circ\text{C}$ within the range of 20 to 70°C.

5.5 *Chromatography Data System.*

5.6 *HPLC Columns:*

TABLE 1 Recommended Operating Conditions

Column	Weak Alkali Anion Exchange
Stationary phase	(-NMe ₂) chemically bonded silica
Particle size	3 μ m
Material of column	stainless steel
Length of column	50 mm
Inner diameter	4–5 mm
Mobile phase	0.1 mol/L NH ₄ H ₂ PO 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 <i>p</i> -TOL
Injection amount	20 μ L
Column temperature	30–40°C

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>.

5.6.1 *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*—*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*—*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~~Ammonium hydroxide mixed with water as 1:1 (V:V).

6.9 *Phosphoric Acid Solution*—~~phosphoric~~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 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.

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 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.

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 μ L 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.

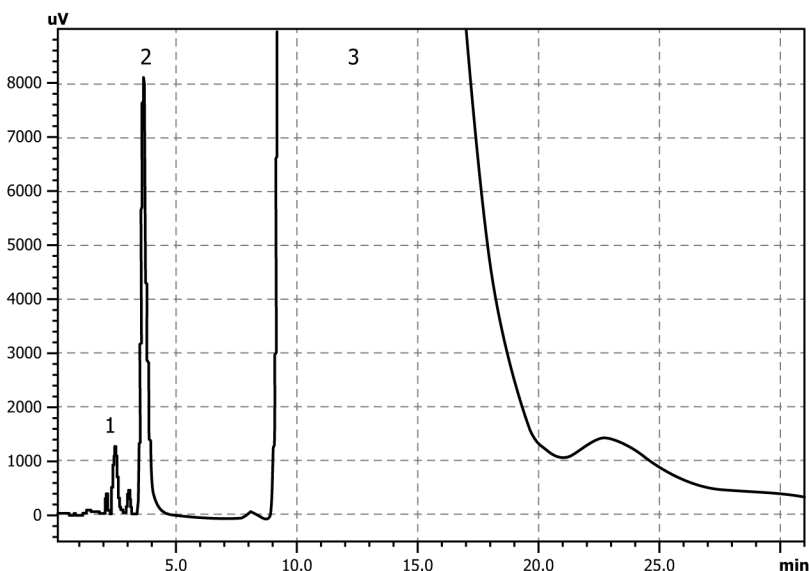


FIG. 1 Chromatogram of a PTA Sample (weak anion exchange HPLC)
1–4-CBA, 2–*p*-TOL, 3–PTA

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 Bias⁷

14.1 An ILS was conducted which included five laboratories analyzing five samples two times in 2012. Practice E691 was followed for the design and analysis of the data. This ILS did not meet Practice E691 minimum requirements of six laboratories, four materials and two replicates. The detailed results are given in Research Report ~~RR:D16-1072~~ RR:D16-2002. The outliers were identified and removed using the t test.

14.2 *Repeatability (r)*—Results should not be suspect unless they differ by more than shown in Table 2. Results differing by less than *r* have a 95 % probability of being correct.

14.3 *Reproducibility (R)*—Results submitted by two labs should not be considered suspect unless they differ by more than shown in Table 2. Results differing by less than *R* have a 95 % probability of being correct.

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

15. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report ~~RR:D16-1072~~ RR:D16-2002. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Repeatability and Reproducibility

Analyte	Average (mg/kg) \bar{x}	Repeatability Limit r	Reproducibility Limit R
4-CBA	10.77	0.67	2.43
12.69	0.94	4.13	
22.83	1.01	5.06	
4.69	0.57	1.47	
2.22	0.26	0.34	
P-TOL	204.21	13.83	27.94
89.64	2.07	9.99	
120.34	4.40	14.15	
146.29	5.16	10.40	
64.24	1.18	8.70	

TABLE 2 Repeatability and Reproducibility

Analyte	Average (mg/kg) \bar{x}	Repeatability Limit r	Reproducibility Limit R
4-CBA	10.64	0.74	3.19
P-TOL	124.94	6.97	15.90

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.

15.2 *Interlaboratory Testing:*

15.2.1 A program that includes multiple laboratories analyzing the same samples is strongly encouraged. This program should allow labs to compare their results with other laboratories. This is particularly important when a plant is selling the product to customers or the laboratory is analyzing the product for acceptance. Producers and customers need to have confidence that results from different producers are comparable. ASTM currently has a Proficiency Testing Program that sends a sample of mixed xylenes, p-xylene, and benzene to multiple labs twice a year for testing. Other programs are acceptable.

16. Keywords

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

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 $\mu\text{g/mL}$)*—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 $\mu\text{g/mL}$ 4-CBA stock solution. Then dilute with water 50 times to 10 $\mu\text{g/mL}$.

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 $\mu\text{g/mL}$)*—Weigh, to the nearest 0.0001 g, about 0.0200 g of *p*-TOL following steps in [A1.2.1](#) to give a 400 $\mu\text{g/mL}$ *p*-TOL stock solution. Then dilute with water five times to 80 $\mu\text{g/mL}$.

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:

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