Designation: ~~D7884 – 19~~ D7884 – 20

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

This standard is issued under the fixed designation D7884; 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 determination of the 4-Carboxybenzaldehyde (4-CBA) and *p*-Toluic acid (*p*-TOL) in purified terephthalic acid (PTA) by reverse phase 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:*[2]

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:*[3]

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] 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 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:*[4]
OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Summary of Test Method

3.1 *Reverse Phase HPLC Method*—PTA sample is dissolved in ammonium hydroxide solution, and a fixed volume of this solution is injected into a high performance liquid chromatograph equipped with a UV detector. A C18 chemically bonded 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 imparts 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 for use as an internal quality control tool where these products are produced or are used.

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 240 and 254 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 A stainless steel HPLC column packed with an octadecylsilane (C18) chemically bonded silica stationary phase is suitable. See Table 1 for recommended operating conditions.

TABLE 1 Recommended Operating Conditions

Column	C18
Stationary phase	Octadecylsilane chemically bonded silica
Particle size	5 µm
Material of column	stainless steel
Length of column	150 mm
Inner diameter	4–5 mm
Mobile phase	0.06 % H_3PO_4 solution: acetonitrile = 82:18
Flow rate	1.0 mL/min
UV detector	254 nm for 4-CBA 240 nm for *p*-TOL
Injection amount	20 µL
Column temperature	40°C

[4] 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.

5.6.2 A C18 column with different dimensions (inner diameter, length, particle size, etc.) that provides adequate resolution to quantitate 4-CBA and *p*-TOL in a PTA sample can also be used.

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

5.8 *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.

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.[5] 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 Hydroxide*—25 to 28 %.

6.3 *Phosphoric Acid*—HPLC grade.

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

6.5 *Water*—HPLC grade.

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

6.7 *PTA Standard for Calibration*—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.

6.8 *Mobile Phase:*

6.8.1 *0.06 % H_3PO_4 Solution:Acetonitrile = 82:18*—Pipette 0.6 mL H_3PO_4 into a 1000 mL volumetric flask with 900 mL of water and make up to the mark with water to give 0.06 % H_3PO_4 solution. Mix 820 mL of H_3PO_4 solution and 180 mL of acetonitrile. Methanol could be used as an alternative to acetonitrile in the mobile phase.

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.

[5] *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.

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 recommended 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, 4 to 6 hours of equilibration time may be required.

NOTE 3—Separation between peaks of 4-CBA and PTA can be optimized by carefully varying the aqueous-organic ratio and flow rate.

NOTE 4—It has been found for a reverse-phase HPLC, separation between 4-CBA and PTA can be improved by adding a certain amount of trifluoroacetic acid (TFA) in acetonitrile water solution as a mobile phase.

NOTE 5—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. Then accurately transfer the resulting solution to a 250 mL volumetric flask, and dilute with water to the mark. Inject 20 µL of the calibration standard solution into chromatograph for analysis. Record chromatogram and peak area values for 4-CBA and *p*-TOL respectively with data system.

NOTE 6—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 of 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,

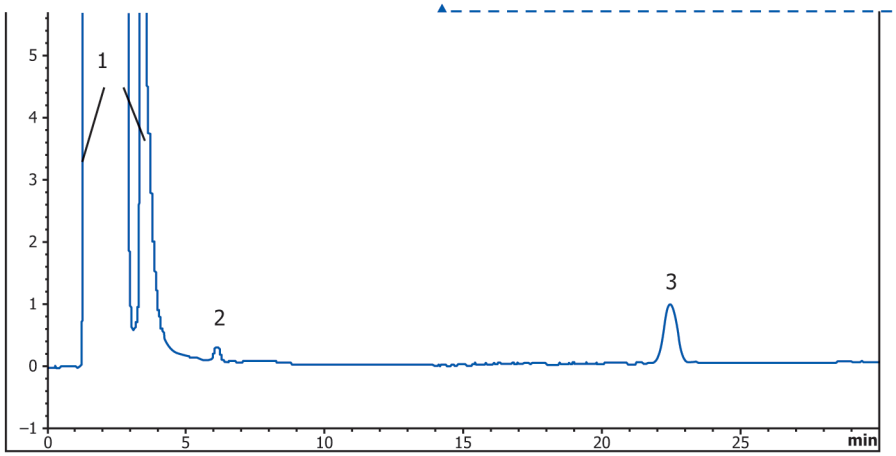

FIG. 1 Chromatogram of a PTA Sample (Reverse Phase HPLC)
1–PTA, 2–4-CBA, 3—*p*-TOL

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[6]

14.1 An ILS was conducted which included 3 laboratories analyzing 5 samples 2 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:D16-1073.~~RR:D16-2003. 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.

TABLE 2 Repeatability and Reproducibility

Analyte	Average (mg/kg) $\bar{x}$	Repeatability Limit r	Reproducibility Limit R
~~4-CBA~~	~~11.63~~	~~0.48~~	~~0.91~~
~~14.68~~	~~0.26~~	~~1.15~~	
~~24.45~~	~~0.95~~	~~3.43~~	
~~4.67~~	~~1.56~~	~~1.67~~	
~~1.53~~	~~0.14~~	~~0.31~~	
~~P-TOL~~	~~210.40~~	~~1.13~~	~~2.02~~
~~90.92~~	~~0.47~~	~~5.59~~	
~~120.72~~	~~3.52~~	~~8.74~~	
~~148.50~~	~~2.03~~	~~7.79~~	
~~64.47~~	~~0.56~~	~~6.03~~	

TABLE 2 Repeatability and Reproducibility

Analyte	Average (mg/kg) $\bar{x}$	Repeatability Limit r	Reproducibility Limit R
4-CBA	11.39	0.85	1.84
P-TOL	127.00	1.91	6.46

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report ~~RR:D16-1073~~RR:D16-2003. Contact ASTM Customer Service at service@astm.org.

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.

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; reverse-phase HPLC

ANNEX

(Mandatory Information)

A1. RECOMMENDED PROCEDURE FOR CALIBRATION OF PTA SAMPLE

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 steps in 10.1 to dissolve PTA samples. Then accurately transfer the solutions to five 250 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 flasks and dilute with water to the mark. The concentrations of 4-CBA and *p*-TOL added in 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

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:

$$A = a + bC \tag{A1.1}$$

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.