



Standard Test Method for *p*-Phenylenediamine Antidegradants Purity by Gas Chromatography¹

This standard is issued under the fixed designation D 4937; 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 purity of Class I, II, and III *p*-phenylenediamine (PPD) antidegradants as described in Practice D 4676 by gas chromatography (GC) detection and area normalization for data reduction.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *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:

D 3853 Terminology Relating to Rubber and Rubber Latices—Abbreviations for Chemicals Used in Compounding²

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries²

D 4676 Classification for Rubber Compounding Materials—Antidegradants²

E 260 Practice for Packed Column Gas Chromatography³

2.2 ISO Standard:⁴

ISO 6472 Rubber Compounding Ingredients—Abbreviations

3. Terminology

3.1 Definitions:

3.1.1 *area normalization, n*—a method of calculating the percent composition by measuring the area of each observed peak and dividing each peak area by the total area. This assumes that all peaks are eluted and that each component has the same detector response.

3.1.2 *lot sample, n*—a production sample representative of a standard production unit, normally referred to as the sample.

3.1.3 *specimen, n*—the actual material used in the analysis. It must be representative of the lot sample.

3.2 *Abbreviations*: Abbreviations—The following abbreviations are in accordance with Terminology D 3853 and ISO 6472:

3.2.1 77PD—*N,N'*bis-(1,4-dimethylpenty)-*p*-phenylenediamine.

3.2.2 DTPD—*N,N'*-ditolyl-*p*-phenylenediamine.

3.2.3 IPPD—*N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine.

3.2.4 PPD—*p*-phenylenediamine.

3.2.5 6PPD—*N*-(1,3 dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine.

4. Summary of Test Method

4.1 The analysis is performed by temperature programmed GC utilizing either a packed column (Procedure A) or a capillary column (Procedure B). Quantification is achieved by area normalization using a peak integrator or laboratory data system.

5. Significance and Use

5.1 This test method is designed to assess the relative purity of production PPD's. These additives are primarily used as antiozonants for tires and other rubber or polymeric products.

5.2 Since the results of this test method are based on area normalization, it assumes that all components are eluted from the column and each component has the same detector response. Although this is not strictly true, the errors introduced are relatively small and much the same for all samples; thus, they can be ignored since the intent of the test method is to establish relative purity.

5.3 Although trace amounts of "low boilers" are present in production samples, they are disguised by the solvent peak when using packed columns (Procedure A).

6. Interferences

6.1 Utilizing the chromatographic conditions prescribed there are no significant co-eluting peaks; however, degradation of column performance could result in interference problems. Thus, when using the packed column it is essential that the total system be capable of 5000 theoretical plates before being

¹ This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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² *Annual Book of ASTM Standards*, Vol 09.01.

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ Available from the American National Standards Institute, 25 W. 43rd St., 4th Floor, New York, NY 10036.

used for this analysis. The evaluation of system efficiency is described in 7.4.

7. Apparatus

7.1 Gas Chromatograph:

7.1.1 *Procedure A: Packed Column*—Any high-quality temperature programmed gas chromatograph equipped with a thermal conductivity detector (see Note 1) is sufficient for this analysis.⁵ Refer to Practice E 260 for general gas chromatography practices.

NOTE 1—Although a thermal conductivity detector is recommended, a flame ionization detector can be used if appropriate adjustment is made for flow rate and specimen size. Since this probably would involve using a smaller diameter column, the adjustment in flow and injection volume should be proportional to the cross-sectional area of the column. A procedure for this calculation is included at the end of Section 9.

7.1.2 *Procedure B: Capillary Column*—A temperature programmable unit with flame ionization detector (FID) equipped for capillary columns. When utilizing the full capillary columns (0.25 mm), a split injection system is required; however a “cold on-column” injector is preferred for the wide bore (0.53 mm) capillaries. The FID should have sufficient sensitivity to give a minimum peak height response of 30 μ V for 0.1 mass % of 6PPD when operated at the stated conditions. Background noise at these conditions is not to exceed 3 μ V.

7.2 Gas Chromatographic Columns:

7.2.1 *Packed Column for Procedure A*—1.828 m \times 6.35 mm (6 ft \times ¼ in.) outside diameter \times 4 mm (0.16 in.) inside diameter glass columns packed with 10 % methyl silicone fluid (100 %)⁶ on 80/100 mesh acid washed and silanized diatomite support.⁷ The column should be conditioned with a helium flow of approximately 20 cm³/min by programming from ambient temperature to 350°C at the rate of 2 to 3°C/min and holding at 350°C overnight with the detector disconnected.

7.2.2 *Capillary Column for Procedure B*—(1) 30 m \times 0.25 mm ID fused silica capillary, internally coated to a film thickness of 0.25 μ m (bonded) with methyl silicone; (2) 15 m \times 0.53 mm fused silica (megabore) capillary with 3.0 μ m bonded film of 5 % phenyl silicone, HP-5 or equivalent.

7.3 *Integrator/Data System*, capable of determining the relative amount of each component by means of integration of the detector output versus time.⁸ When using capillary columns (Procedure B) the device must integrate at a sufficiently fast rate so that narrow peaks (one second peak width) can be accurately measured.

7.4 When using a packed column, a minimum of 5000 theoretical plates, as measured from the 6PPD peak, with the chromatographic conditions stated in 9.1 is required for analysis. Theoretical plates (*TP*) are determined by the following formula:

$$TP = 5.5 [X(R)/Y(0.5)]^2 \quad (1)$$

where:

$X(R)$ = retention time measured from the injection point to the apex of the 6PPD peak (adjust the attenuation to keep peak on scale), mm, and
 $Y(0.5)$ = 6PPD band width at half-height, mm.

8. Calibration and Standardization

8.1 When using the conditions described for Procedure A (packed column), the detector response of 6PPD for injections of 500 to 5000 μ g was found to be somewhat nonlinear (see X1.3). However, over the more limited range, 750 to 2500 μ g, the response was nearly linear (see X1.4). As a result, it is suggested that the samples be prepared so that 1250 to 1500 μ g injections are made.

8.2 Chromatograms from typical specimens run on the packed columns according to the prescribed procedure are given in Appendix X1.

9. Procedure

9.1 Procedure A—Chromatographic Conditions:

Helium flow rate	50 cm ³ /min
Injection port temperature	300°C
Initial column temperature	100°C
Heating rate	8°C/min
Final Temperature	350°C
Detector temperature	350°C
Detector: TC attenuation	8

9.1.1 Integrator/data system parameters are presented in X1.2.

9.1.2 *Specimen Preparation*—To ensure specimen homogeneity, lot samples of 6PPD should be ground with a mortar and pestle prior to weighing the test unit. In the case of liquid 6PPD where partial crystallization may have occurred resulting in fractionation, the lot sample should be melted in a 50° to 60°C oven with occasional stirring, prior to weighing the test unit.

9.2 Procedure A—Analysis:

9.2.1 Weigh 2.5 to 3.0 g specimen (to the nearest milligram) into a 10 cm³ volumetric flask, dilute to volume with methylene chloride, and shake well to dissolve.

9.2.2 When the instrument has equilibrated at the initial conditions described in 9.1, inject 5.0 mm³ (μ L) of sample solution and initiate the temperature program and data collection.

9.2.3 When the run is complete, inspect the chromatogram and output data for proper appearance and peak identification (see X1.1).

9.2.4 Repeat the run described in 9.2.2 on the same specimen.

NOTE 2—Specimen size and carrier gas flow rates should be adjusted in accordance with the cross-sectional area of the column utilized. For example, if a nominal ⅛ in. outside diameter column (1.87 mm inside diameter) is used rather than a ¼ in. outside diameter (3.54 mm inside diameter), the adjustment would be as follows: The ratio of cross-sectional areas is [3.54/1.87] squared, which equals 3.6. Thus, the sample size and helium carrier flow rate should be decreased by this factor; that is, the flow rate of 50/3.6 or 14 cm³/min and sample size to 5/3.6 or 1.4 mm³(μ L).

9.3 *Procedure B: Chromatographic Conditions*—The suggested operating conditions for the analysis using a capillary

⁵ A HP 5890A 6C, available from Hewlett-Packard, P.O. Box 3640, Sunnyvale, CA 94088, was used for the work reported in their document.

⁶ OV-101, available from Supelco, Bellefont, PA, has been found satisfactory for this material.

⁷ Chromosorb W-HP has been found satisfactory for this material.

⁸ The HP 5890A gas chromatograph which has an output of 0 to 1 V is interfaced with an HP 3353E Laboratory Automation System (LAS) for the work reported here.

column are given in Table 1. Column (1) is for a standard capillary and Column (2) is for a megabore capillary.

9.4 Procedure B—Sample Analysis:

9.4.1 Prepare the sample as in 9.1.2 and the test specimen according to Table 1.

9.4.2 When the instrument has equilibrated at the initial conditions described in Table 1, inject the indicated amount of diluted test specimen and immediately start the recorder, integrator, and column temperature programming sequence.

9.4.3 When the run is complete, inspect the chromatogram and output data for proper appearance and peak identification. Typical chromatograms on the 0.53 mm megabore capillary is shown in Figs. X2.1-X2.4 (6PPD) respectively.

9.4.4 Repeat the run described in 9.4.2 on the same specimen.

10. Calculation

10.1 Calculate the relative area percent of 6PPD and the other identified components as follows:

$$A = (A_C/A_T) \times 100 \% \quad (2)$$

where:

A = area of 6PPD, %,

A_C = area of component, and

A_T = total area.

11. Report

11.1 Report the following information:

11.1.1 The combined area of all unidentified peaks as percent other,

11.1.2 All results to the nearest 0.1 %, and

11.2 The final report should include proper identification of the specimen and the data from the two individual injections plus their average.

TABLE 1 Procedure B—Chromatographic Conditions

Column	(1) 30 m × 0.25 mm	(2) 15 m × 0.53 mm	
Stationary Phase	bonded methyl silicone	bonded 5 % phenyl silicone	
Film thickness	0.25 μm	3.0 μm	
Carrier gas	(helium)	(helium)	
Linear velocity at 100°C	0.34 m/sec	NA	
Flow rate	1.0 cm ³ /min	30.0 cm ³ /min	
Head pressure	60 kPa, gauge (9 psig)	NA	
Detector	FID	FID	
Detector Temperature	300°C	300°C	
Injection Port Temperature	300°C	oven tracking	
Hydrogen Flow Rate ^A	30 cm ³ /min	30 cm ³ /min	
Air Flow Rate ^A	300 cm ³ /min	300 cm ³ /min	
Makeup Gas	Nitrogen or Helium	Nitrogen or Helium	
Makeup Flow Rate ^A	29 cm ³ /min	10 cm ³ /min	
Split Ratio	180:1	(no split)	
Column Temperature Program		Ramp A	Ramp B
Initial temperature	42°C	35°C	240°C
Program rate	9°C/min	15°C/min	8°C/min
Final temperature	300°C	240°C	290°C
Time at final temperature	22 min	3 min	17 min
Sample Size	0.4 mm ³ (μL)	1 mm ³ (μL)	
Solvent	methylene chloride	methylene chloride	
Sample Concentration	10 mg/cm ³	3 mg/cm ³	

^AConsult the manufacturer's manual for optimum selection of flow rates on different instruments.

12. Precision and Bias—Procedure A

12.1 This precision and bias section has been prepared in accordance with Practice D 4483. Refer to Practice D 4483 for terminology and other statistical details.

12.1.1 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials (antidegradants) used in the particular interlaboratory programs as described below. The precision parameters should not be used for acceptance/rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include this test method.

12.2 A Type 1 (interlaboratory) precision was evaluated in 1987. Both repeatability and reproducibility are short term. A period of a few days separates replicate test results. A test result is the mean value, as specified by this test method, obtained on two determinations or measurements of the property or parameter in question.

12.3 Four different materials were used in the interlaboratory program. These were tested in four laboratories on two different days.

12.4 The results of the precision calculations for repeatability and reproducibility are given in Table 2, in ascending order of material average or level, for each of the materials evaluated.

12.5 The precision of this test method may be expressed in the format of the following statements which use an "appropriate value" or r , R , (r), or (R), that is, that value to be used in decisions about test results (obtained with the test method). The appropriate value is that value of r or R associated with a mean level in Table 2 closest to the mean level under consideration at any given time, for any given material, in routine testing operations.

12.6 *Repeatability*—The repeatability, r , of this test method has been established as the appropriate value tabulated in Table 1. Two single test results, obtained under normal test method procedures, that differ by more than this tabulated r (for any given level) must be considered as derived from different or nonidentical sample populations.

12.7 *Reproducibility*—The reproducibility, R , of this test method has been established as the appropriate value tabulated in Table 2. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated R (for any given level) must be considered to have come from different or nonidentical sample populations.

12.8 Repeatability and reproducibility expressed as a percent of the mean level, (r) and (R), have equivalent application statements as above for r and R . For the (r) and (R) statements, the difference in the two single test results is expressed as a percent of the arithmetic mean of the two test results.

12.9 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (or true) test property value. Reference values have not been evaluated for this test method. Bias, therefore, cannot be determined.

TABLE 2 GC Purity of PPD'S, Percent (Procedure A)

Material	Average	Within Laboratory ^A			Between Laboratory ^A		
		S_r	r	(r)	S_R	R	(R)
M1-6PPD	97.09	0.1651	0.4673	0.481	1.926	5.45	5.61
M2-IPPD	96.05	0.2792	0.7900	0.822	1.239	3.50	3.65
M3-77PD	96.05	0.1121	0.3172	0.330	1.382	3.91	4.07
M4-DTPD	94.85	0.2894	0.8191	0.864	2.080	5.88	6.20
Pooled values ^B	96.01	0.2301	0.6512	0.678	1.6588	4.6943	4.889

^A

S_r = repeatability standard deviation.

r = repeatability = 2.83 times the square root of the repeatability variance.

(r) = repeatability (as a percent of material average).

S_R = reproducibility standard deviation.

R = reproducibility = 2.83 times the square root of the reproducibility variance.

(R) = reproducibility (as a percent of material average).

^BNo values omitted.

13. Keywords

13.1 antidegradant; antioxidant; antiozanant; gas chromatography; N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD); N-(1;3 dimethylbutyl)-N'-phenyl-p-

phenylenediamine (6PPD); N; N'bis-(1;4-dimethylpentyl)-p-phenylenediamine (77PD); N; N'-ditolyl-p-phenylenediamene (DTPD); phenylenediamene; p-phenylenediamene (PPD)

APPENDIXES

(Nonmandatory Information)

X1. GAS CHROMATOGRAPHY METHODS AND RESULTS

X1.1 Standard chromatograms obtained according to this procedure on 6PPD, IPPD, 77PD, and DTPD are presented in Figs. X1.1-X1.3, and Fig. X1.4, respectively.

X1.2 A method for the HP 3353E Laboratory Automation System used for this procedure is included as Fig. X1.5.

X1.3 A plot of detector response versus column loading between 500 and 5000 μg is shown in Fig. X1.6. Each point

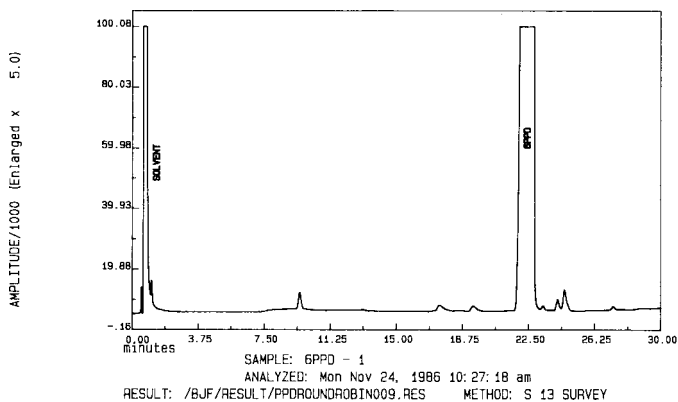


FIG. X1.1 6PPD Chromatogram (Procedure A)

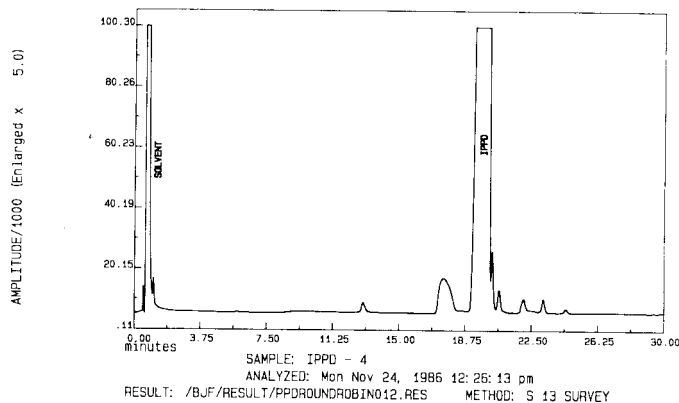


FIG. X1.2 IPPD Chromatogram (Procedure A)

represents the average of two injections.

X1.4 An expanded scale plot of detector response versus column loading between 750 and 2500 μg is shown in Fig. X1.7. The response is essentially linear between 1200 and 1700 μg .

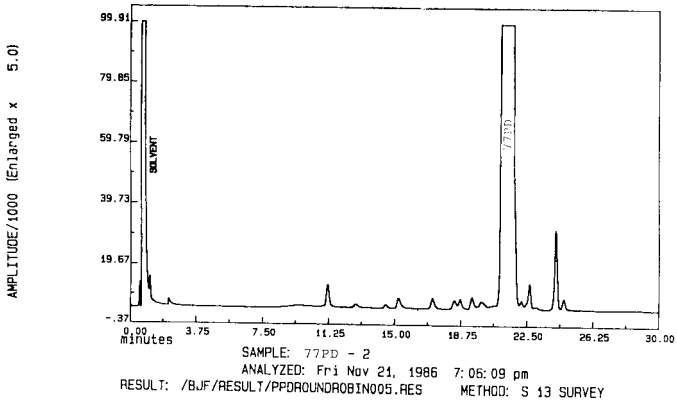


FIG. X1.3 77PD Chromatogram (Procedure A)

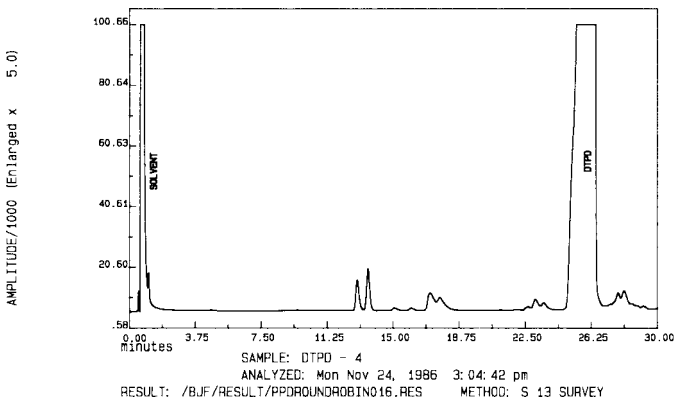


FIG. X1.4 DTPD Chromatogram (Procedure A)

METHOD HEADER

Method : /GC/METHOD/SIX_PPD_SURVEY.MTH
 Created : Mon Dec 2, 1985 9:16:59 am
 Updated : Mon Dec 2, 1985 9:22:29 am
 Instrmnt : H_5890A/D_GC
 Calc Type : APCT

COMMENT FIELDS

Comment 1 : 6 PPD AREA PERCENT NORMALIZATION
 Comment 2 :
 Comment 3 :
 Comment 4 :

DATA INPUT

Runtime : 30.00 Number Of Peaks : 100
 Delay Start : 3.00 Minimum Area : 4000.0
 Slope Sens. : 1.500 Bunch Mode : NONE
 Bunch Start : 2.00

DATA ANALYSIS

Area Calc : YES

USER PROGRAMS

Post Run :
 Dlg Prog :
 Parm File :
 Overlap : YES
 PEAK IDENTIFICATION

Ref Window : .100 Non-Ref Window : 3.000
 Resp Factor Unkn : 1.00000 Minimum Id Level : 0.0
 Dead Volume Time : 0.00

CALIBRATION FILE

File Name :

CALIBRATION TABLE

Time	Factor	Amount	Peak Name	Type	Grp
17.90	1.000000	1.000000	ADPA-4	R	
19.75	1.000000	1.000000	IPPD	R	
22.95	1.000000	1.000000	PPD-6	R	

REPORT SPECIFICATION

Fmt File : /GC/FORMAT/GC.FMT

Rpt Units : AREA %

REPORT DEVICES

Report Device Number Copies

1.	L1	1
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FIG. X1.5 Method for the HP 3353E Laboratory Automation System

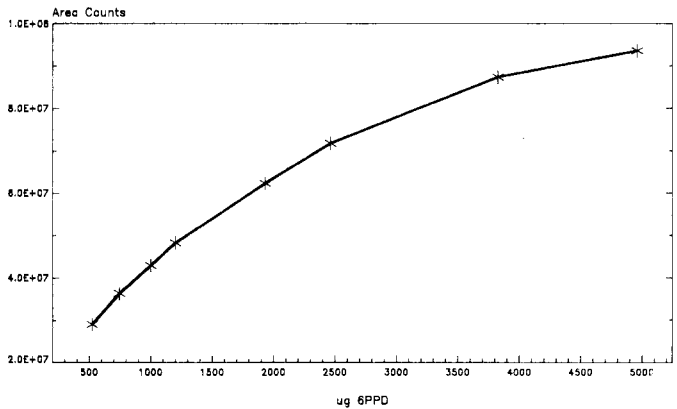


FIG. X1.6 TCD Linear Response for 6PPD Area Counts Versus ug 6PPD Injected

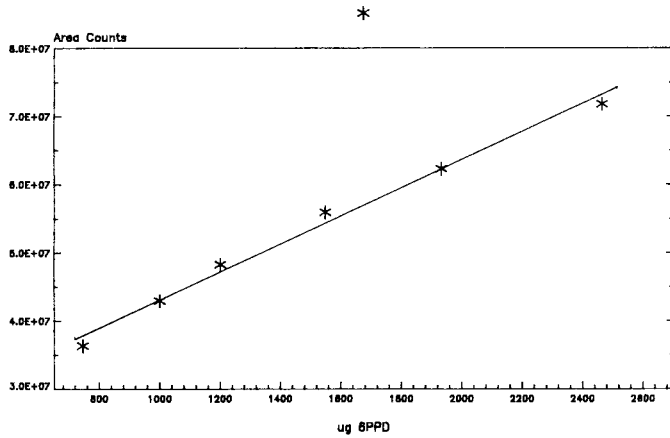


FIG. X1.7 TCD Linear Response for 6PPD Area Counts Versus ug 6PPD Injected

X2. CHROMATOGRAMS—PROCEDURE B

X2.1 Standard chromatograms obtained on Column (2) [megabore capillary] according to Procedure B on 6PPD, IPPD, 77PD, and DTPD are presented in Figs. X2.1-X2.4,

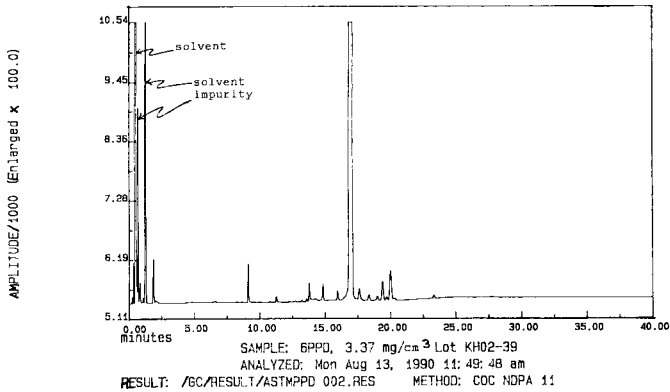


FIG. X2.1 6PPD Chromatogram—Procedure B

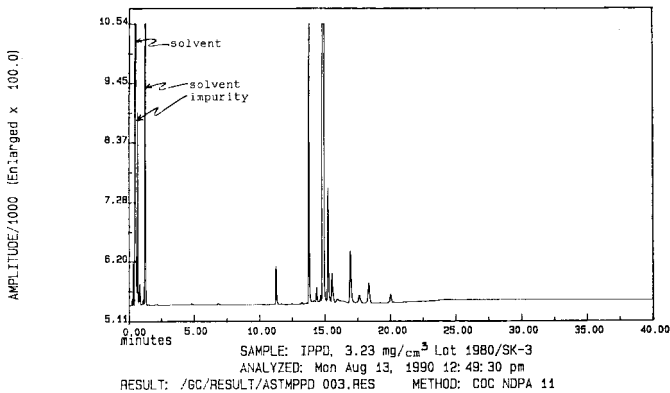


FIG. X2.2 IPPD Chromatogram—Procedure B

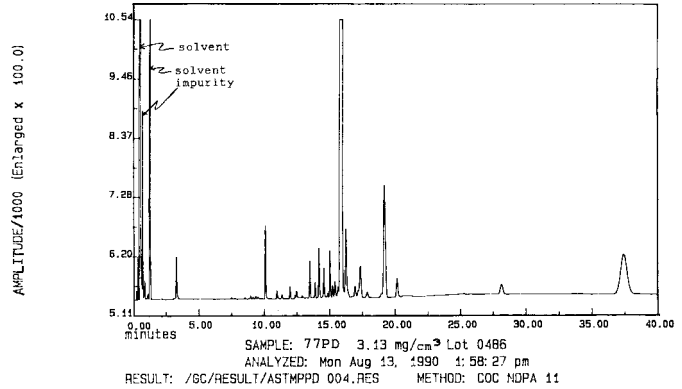


FIG. X2.3 77PD Chromatogram—Procedure B

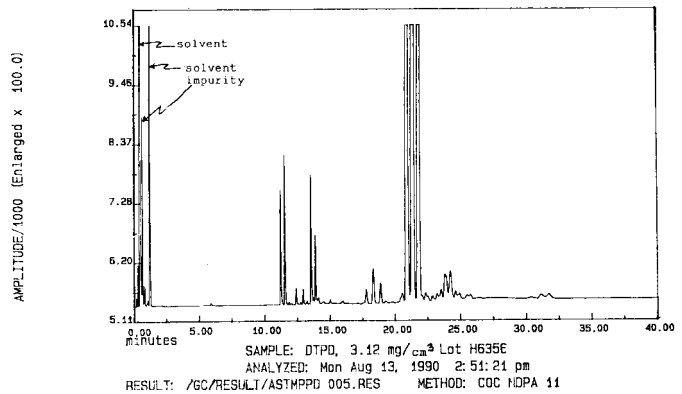


FIG. X2.4 DTPD Chromatogram—Procedure B

respectively.



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