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Rubber compounding ingredients — *p*-Phenylenediamine (PPD) antidegradants — Test methods

Ingrédients de mélange du caoutchouc — Antidégradants du type p*-phénylènediamine (PPD) — Méthodes d'essai*

Reference number
ISO 11236:2000(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 11236 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

Rubber compounding ingredients — *p*-Phenylenediamine (PPD) antidegradants — Test methods

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard applies to a variety of substituted *p*-phenylenediamine (PPD) antidegradants used in the rubber industry. The three general classes of PPD are dialkyl, alkyl-aryl and diaryl, which are used to impart ozone resistance to rubber. The test methods of greatest significance in assessing the purity of production PPDs, and hence their suitability for use in rubber, are specified in this International Standard.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*.

ISO 1772:1975, *Laboratory crucibles in porcelain and silica*.

ISO 6472:1994, *Rubber compounding ingredients — Abbreviations*.

ISO/TR 9272:1986, *Rubber and rubber products — Determination of precision for test method standards*.

ISO 15528:—[1], *Paints, varnishes and raw materials for paints and varnishes — Sampling*.

3 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply:

3.1
area normalization
method of calculating the percent composition by measuring the area of each component peak observed in a chromatogram and dividing the area of the peak by the total peak area for all the components observed

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[1] To be published. (Revision of ISO 842:1984 and ISO 1512:1991)

3.2
lot sample
production sample representative of a standard production unit

3.3
test portion
actual material used in the analysis

NOTE The test portion must, of course, be representative of the lot sample.

4 Abbreviations

The following abbreviations, taken from ISO 6472, are used in the text:

77PD	*N*,*N*′-bis(1,4-dimethylpentyl)-*p*-phenylenediamine
DTPD	*N*,*N*′-ditolyl-*p*-phenylenediamine
IPPD	*N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine
PPD	*p*-phenylenediamine
6PPD	*N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine

5 Use and classification

PPDs represent the primary additive used in tyres and other mechanical rubber goods to impart ozone protection and to improve resistance to fatigue cracking. PPDs are also used as antioxidants in a number of applications.

Although all PPDs exhibit similar performance characteristics, particular types are frequently preferred for certain end-use conditions, for example the type and degree of flexing experienced by the rubber article.

PPDs are classified into the following types:

Type I: *N*,*N*′-dialkyl PPDs (see Figure 1)

R and R' are secondary alkyl groups, usually C_6 or larger. These materials are generally liquids at ambient conditions and consist for the most part (> 90 %) of a single chemical component.

Type II: *N*-alkyl-*N*′-aryl PPDs (see Figure 2)

R is a secondary alkyl group and R' is an aryl substituent (usually phenyl). These materials generally consist of a single component or a mixture containing two or more major components (mainly isomers).

Type III: *N*,*N*′-diaryl PPDs (see Figure 3)

R and R' can be the same aryl group or different (usually phenyl or *p*-tolyl) and can be single components or mixtures of three or more isomers. This type of PPD is generally solid at ambient conditions.

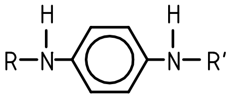


Figure 1 — Type I: *N*,*N*′-dialkyl *p*-phenylenediamines

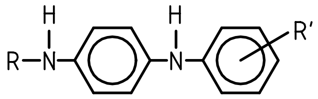


Figure 2 — Type II: *N*-alkyl-*N*′-aryl *p*-phenylenediamines

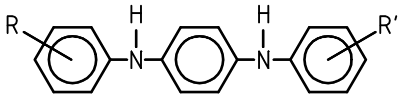


Figure 3 — Type III: *N*,*N*′-diaryl *p*-phenylenediamines

6 Sampling and repeat determinations

Carry out sampling in accordance with ISO 15528. To ensure homogeneity, blend at least 250 g of the lot sample thoroughly prior to removing any test portions.

If the difference between the results of duplicate determinations exceeds the repeatability given for the method concerned, repeat the test. If no repeatability figure is given for a particular method, report the results of both determinations.

7 Determination of purity by gas chromatography (GC)

7.1 General

This method is designed to assess the relative purity of production PPDs by determining the purity of type I, II and III PPDs using temperature-programmed gas chromatography with either a packed column (procedure A) or a capillary column (procedure B). Quantification is achieved by area normalization using a peak integrator or chromatography data system.

Since the results are based on area normalization, the method 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 method is to establish relative purity.

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

7.2 Interference

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 5 000 theoretical plates. Evaluation of system efficiency is described in the note to 7.3.2.

7.3 Apparatus

7.3.1 Gas chromatograph.

Procedure A: Any high-quality temperature-programmed gas chromatograph equipped with a thermal-conductivity detector and a peak integrator or chromatography data system is sufficient for this analysis.

Although a thermal-conductivity detector is recommended, a flame-ionization detector (FID) can be used if appropriate adjustment is made for flow rate and sample size. This will probably involve using a smaller-diameter column, in which case the adjustment in flow rate and injection volume shall be proportional to the cross-sectional area of the column.

Procedure B: Any high-quality temperature-programmed gas chromatograph with a flame-ionization detector and equipped for capillary columns is suitable. When utilizing standard 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 shall have sufficient sensitivity to give a minimum peak-height response of 30 µV for 0,1 mass % of 6PPD when operated at the stated conditions. Background noise at these conditions shall not exceed 3 µV.

7.3.2 Gas-chromatographic columns.

Procedure A: Use a 1,8 m × 6,4 mm outside diameter × 4 mm inside diameter glass column packed with 10 % methyl silicone fluid (100 %) on a 0,15/0,08 mm (80/100 mesh) acid-washed and silanized diatomite support. Condition the column with a helium flow of approximately 20 cm^3/min by programming from ambient temperature to 350 °C at the rate of 2 °C/min to 3 °C/min and holding at 350 °C overnight with the detector disconnected.

NOTE When using a packed column, a minimum of 5 000 theoretical plates, as measured from the analyte peak, under the chromatographic conditions stated in Table 1, is required for analysis. The number of theoretical plates (TP) is determined by the following equation:

$$\text{TP} = 5{,}5\,[X(\text{R})/Y(0{,}5)]^2$$

where

$X(\text{R})$ is the retention time measured from the injection point to the apex of the 6PPD peak (adjust the attenuation to keep peak on scale) in mm;

$Y(0{,}5)$ is the 6PPD peak width at half height, in mm.

Procedure B: Use a 30 m × 0,25 mm fused-silica capillary internally coated to a film thickness of 0,25 µm (bonded) with methyl silicone (column 1), or a 15 m × 0,53 mm fused-silica (megabore) capillary coated with a 3,0 µm bonded film of 5 % phenyl silicone, HP-5 or equivalent (column 2).

7.3.3 Integrator/data system, capable of determining the relative amount of each component by integration of the detector output as a function of time. When using capillary columns (procedure B), the equipment shall be capable of integrating at a sufficiently fast rate so that narrow peaks (1 s peak width) are accurately measured.

7.3.4 Volumetric flask, capacity 10 cm^3, meeting the requirements of ISO 1042.

7.3.5 Mortar and pestle.

7.3.6 Precision balance, accurate to ± 1 mg or better.

7.3.7 Syringe, of suitable size (see relevant procedure).

7.4 Calibration and standardization

Chromatograms from typical PPD antidegradants run on the packed columns in accordance with the prescribed procedure are given in Figures 4 and 5.

NOTE When using the conditions described for procedure A (packed column), the detector response for injections of 500 µg to 5 000 µg of 6PPD was found to be somewhat non-linear. However, over the more limited range 750 µg to 2 500 µg, the response was nearly linear. It is important that the samples be prepared so that 1 250 µg to 1 500 µg injections are made.

7.5 Procedure

7.5.1 Sample preparation

To ensure homogeneity, grind lot samples of 6PPD with a mortar and pestle prior to weighing out the test portion. In the case of liquid 6PPD where partial crystallization may have occurred resulting in fractionation, melt the lot sample in an oven at 50 °C to 60 °C, with occasional stirring, prior to weighing out the test portion.

7.5.2 Procedure A

7.5.2.1 Use the following 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 attenuation	8

7.5.2.1 Weigh a 2,5 g to 3,0 g test portion (to the nearest milligram) into a 10 cm^3 volumetric flask, dilute to volume with methylene chloride, and shake well to dissolve.

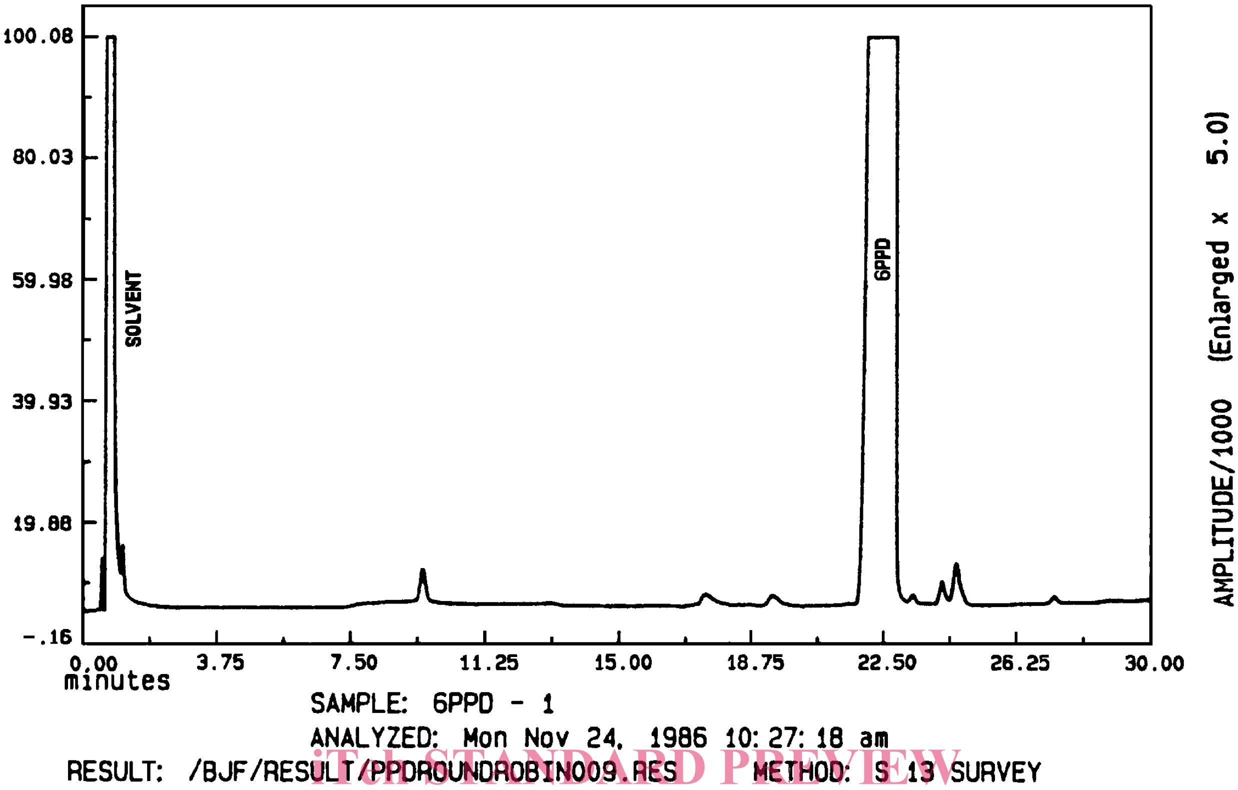
7.5.2.2 When the instrument has equilibrated at the initial conditions described above, inject 5,0 mm^3 (µL) of sample solution (7.5.2.1) and initiate the temperature programme and data collection.

Sample size and carrier-gas flow rates shall be adjusted according to the cross-sectional area of the column utilized. For example, if a nominally 3,2 mm outside diameter column (1,87 mm inside diameter) is used rather than a 6,4 mm outside diameter column (3,54 mm inside diameter), the adjustment would be as follows: the ratio of the cross-sectional areas is $(3{,}54/1{,}87)^2$, which equals 3,6. Thus, the sample size and helium-carrier flow rate must be decreased by this factor, i.e. the sample size to 5/3,6 or 1,4 mm^3 (µL) and the flow rate to 50/3,6 or 14 cm^3/min.

7.5.2.3 When the run is complete, inspect the chromatogram and output data for proper appearance and peak identification (see Figure 4).

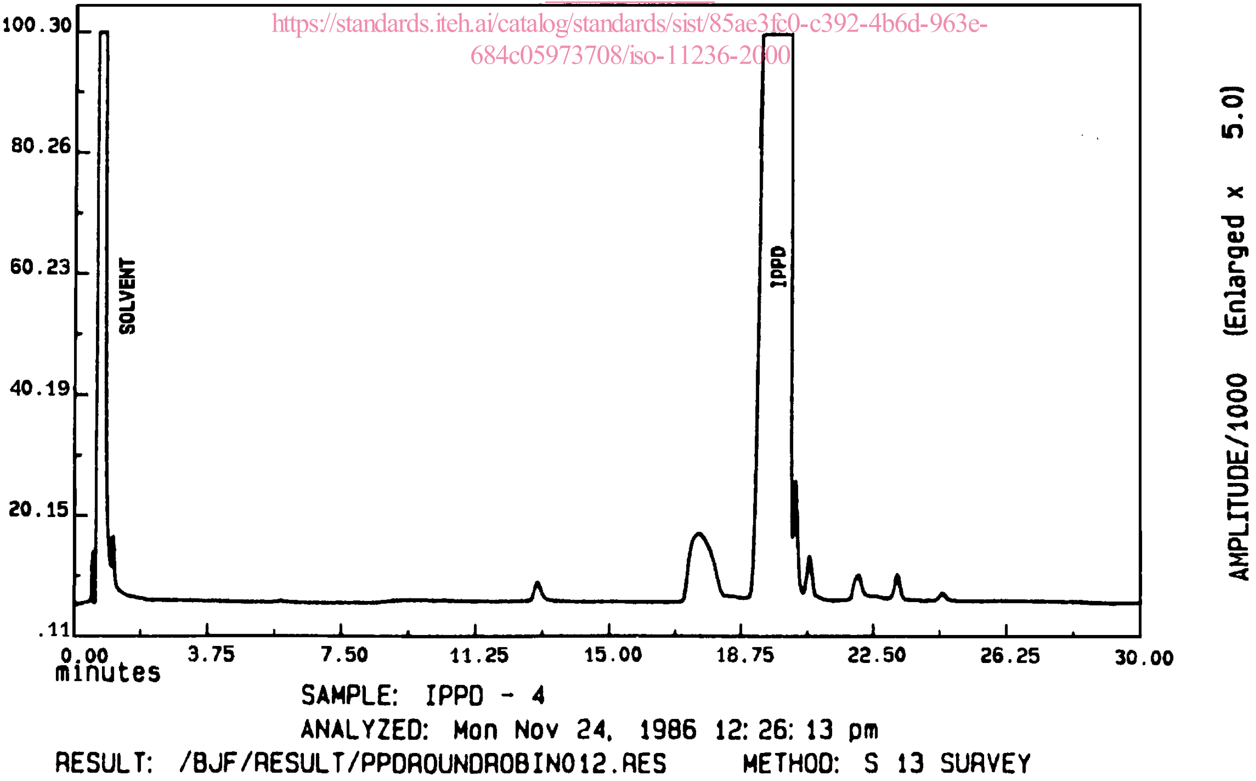
7.5.2.4 Repeat the run described in 7.5.2.2 on the same sample.

7.5.2.5 Typical chromatograms obtained by procedure A for 6PPD, IPPD, 77PD and DTPD are shown in Figures 4 a) to 4 d), respectively.



```
SAMPLE:  6PPD - 1
ANALYZED:  Mon Nov 24, 1986 10:27:18 am
RESULT:  /BJF/RESULT/PPDROUNDROBIN009.RES     METHOD:  S 13 SURVEY
```

a) 6PPD



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SAMPLE:  IPPD - 4
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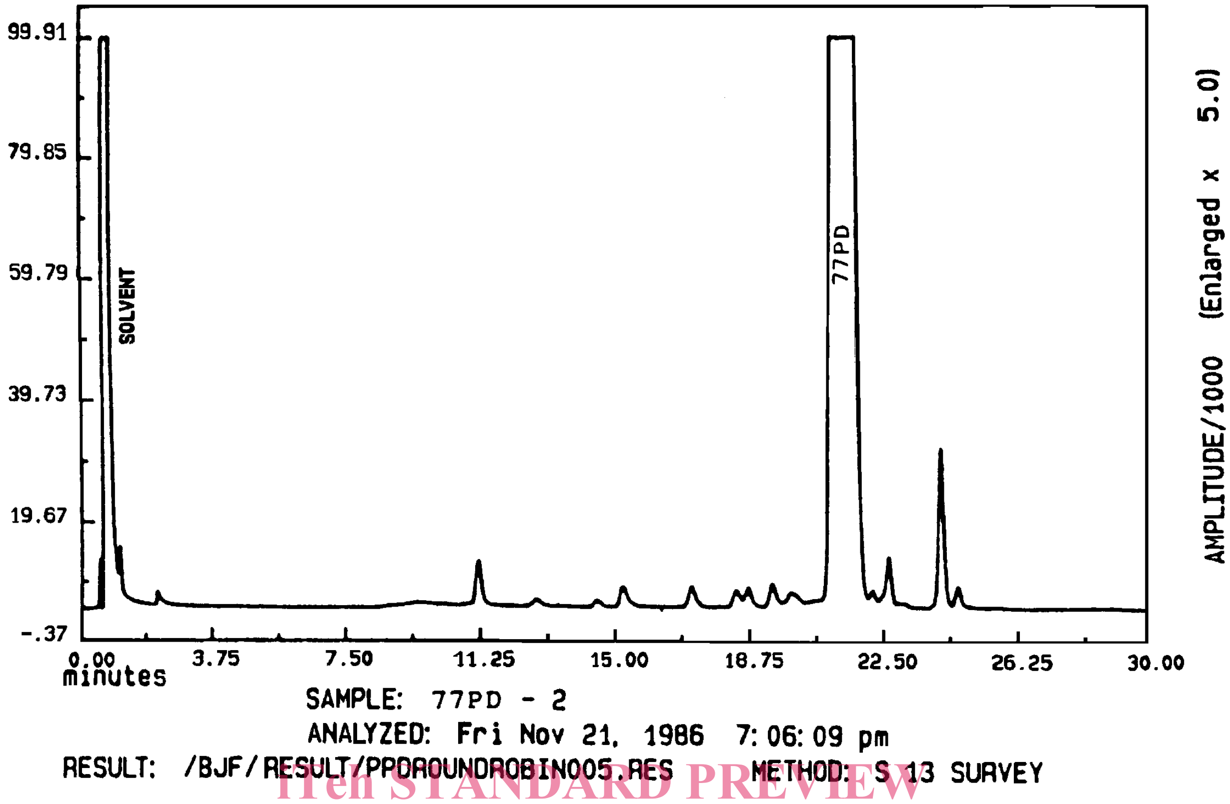
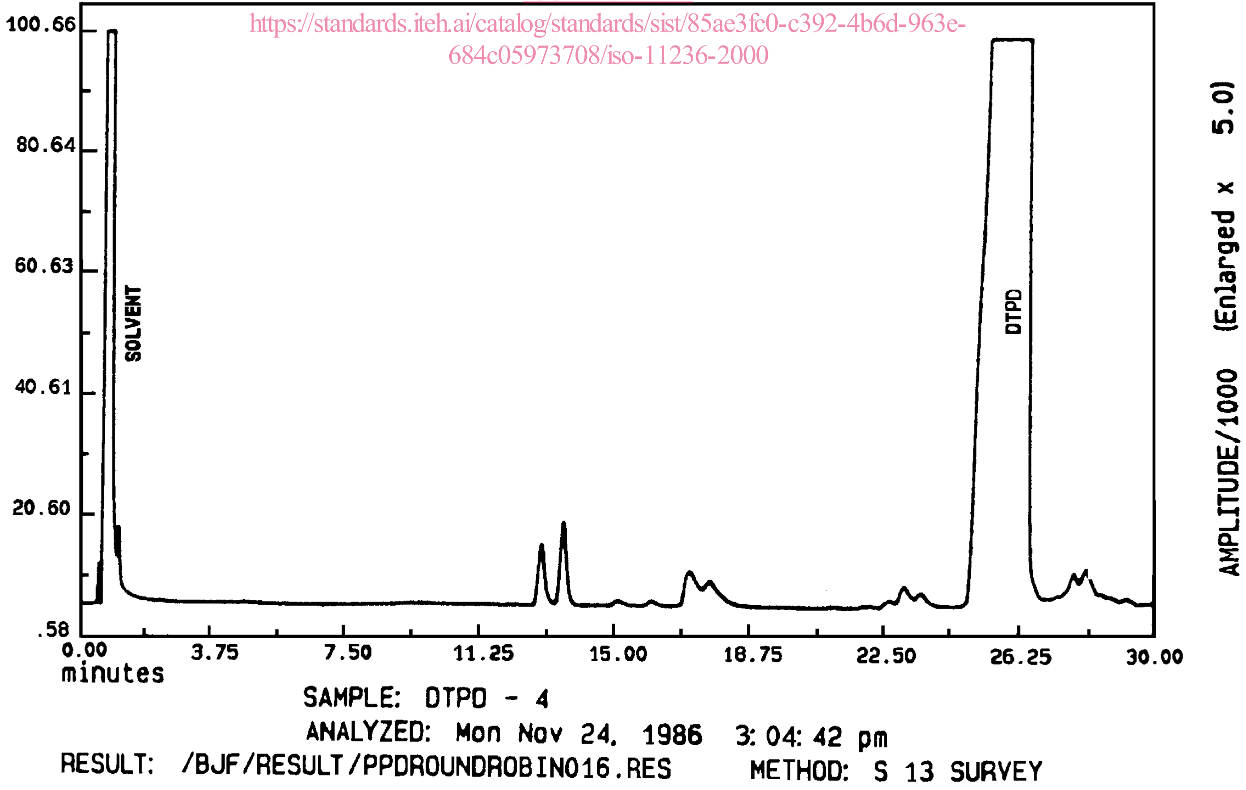
b) IPPD



c) 77PD



d) DTPD

Figure 4 — Chromatograms obtained using procedure A