INTERNATIONAL STANDARD

ISO 11236

First edition
2000-03-15

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)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

Contents

Page

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

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.

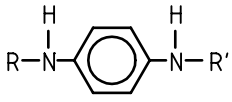


Figure 1 — Type I: *N*,*N*′-dialkyl *p*-phenylenediamines

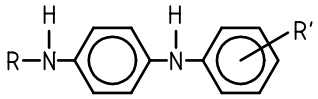


Figure 2 — Type II: *N*-alkyl-*N′*-aryl *p*-phenylenediamines

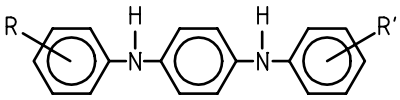


Figure 3 — Type III: *N*,*N′*-diaryl *p*-phenylenediamines

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:

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

where

$X(R)$ 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.

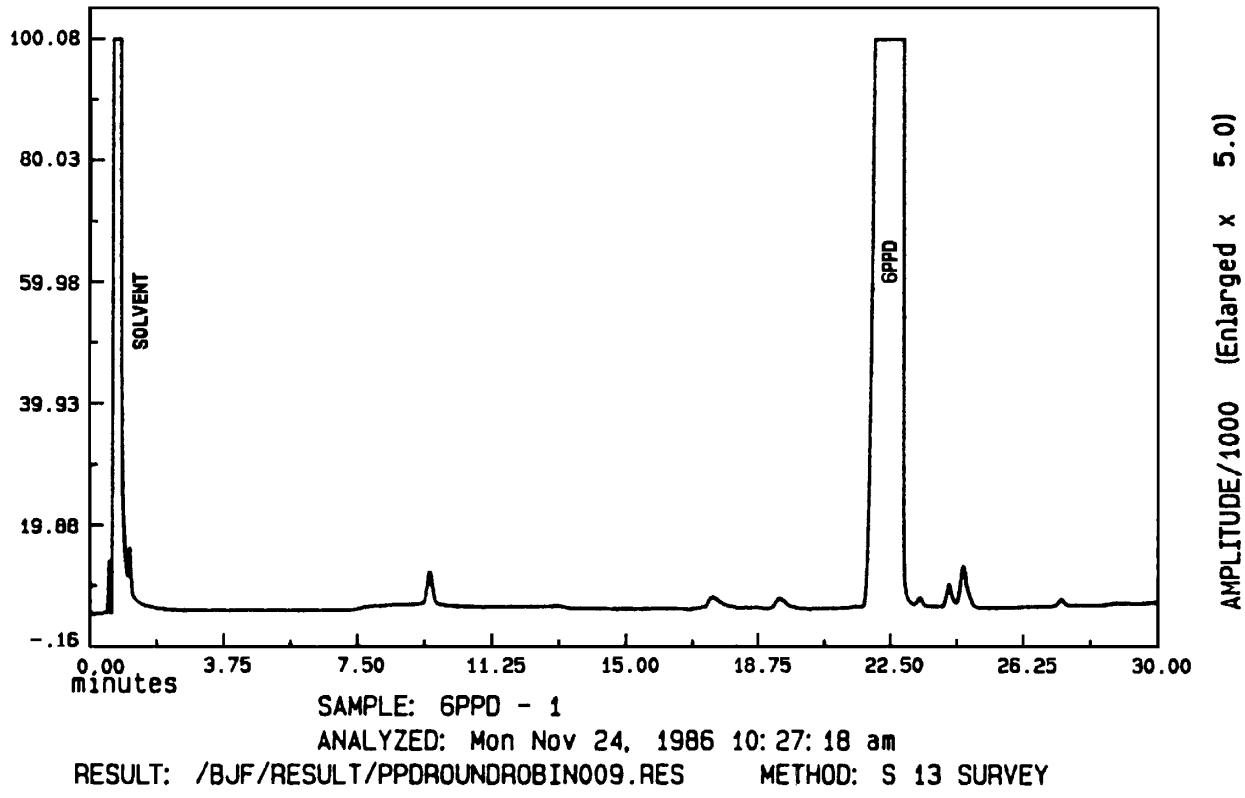
7.5.2.2 When the instrument has equilibrated at the initial conditions described above, inject 5,0 mm^3 (μL) of sample solution (7.5.2.1) and initiate the temperature programme and data collection.

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.

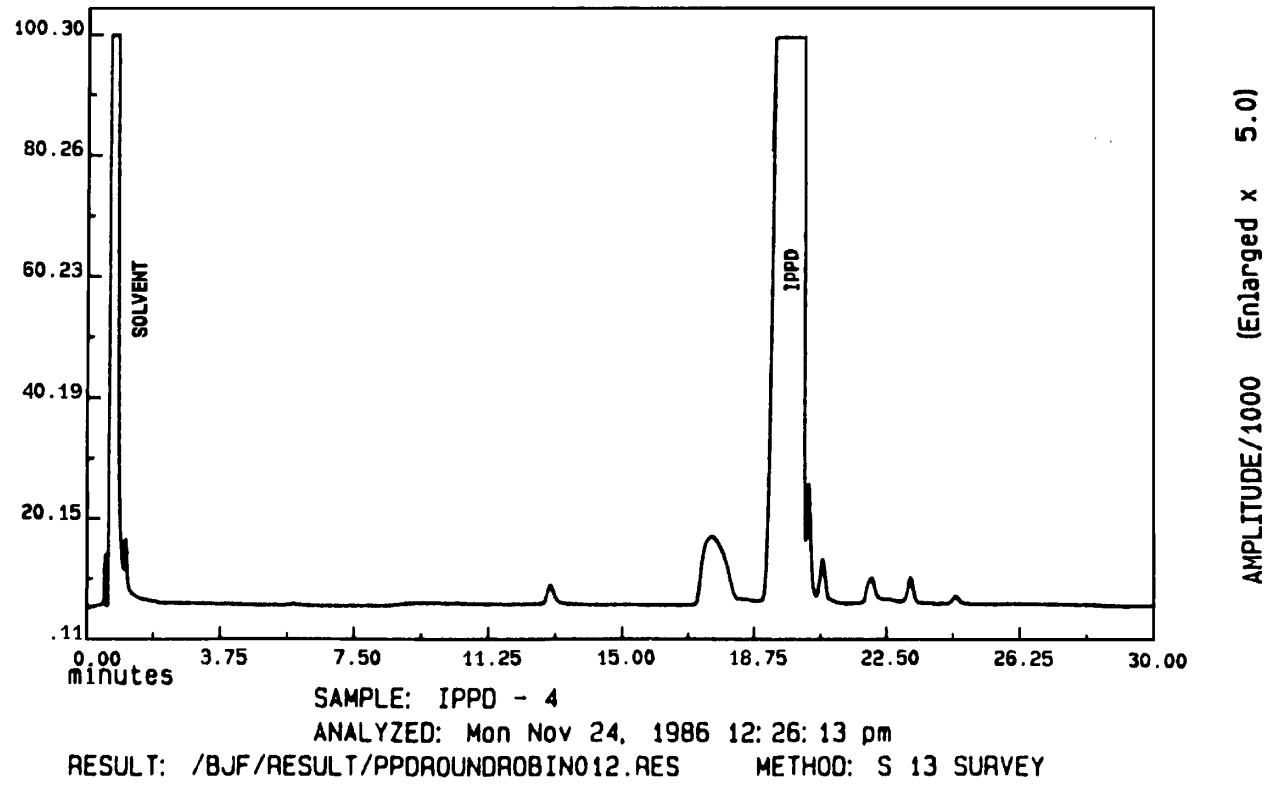
7.5.2.3 When the run is complete, inspect the chromatogram and output data for proper appearance and peak identification (see Figure 4).

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

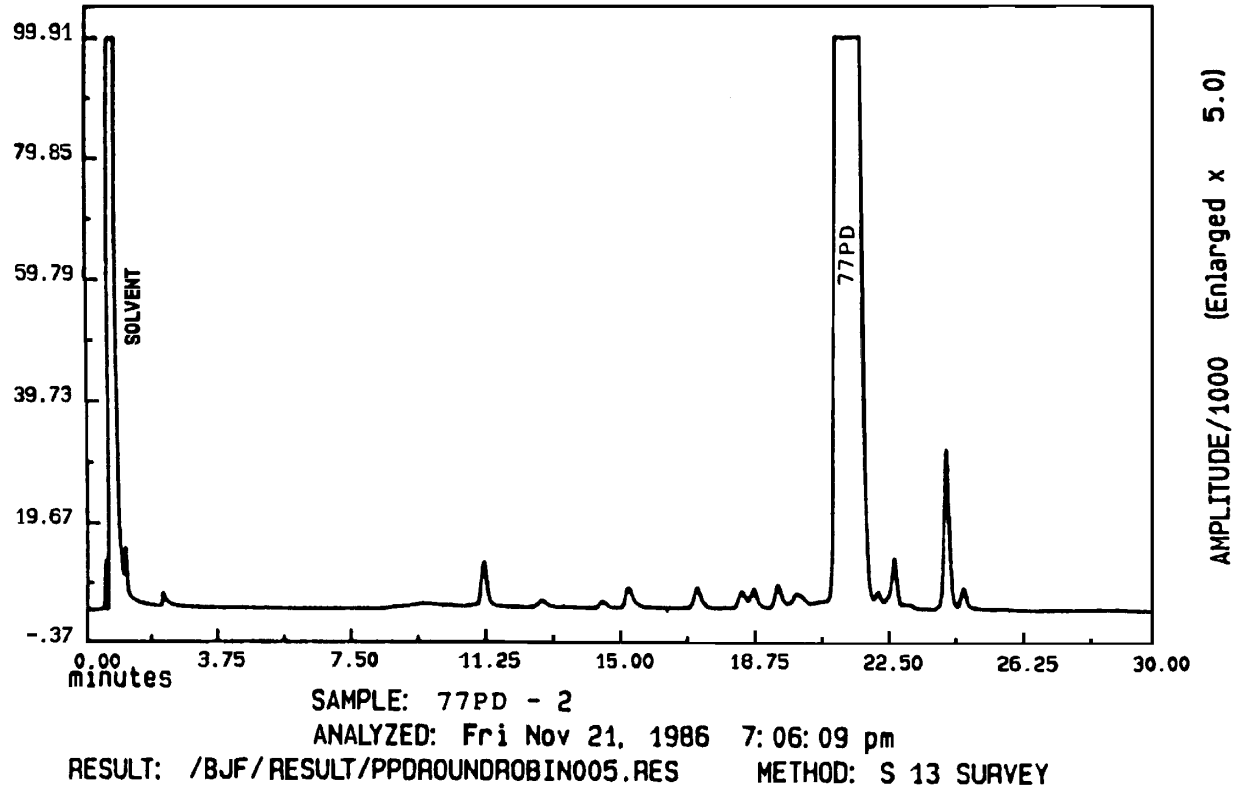
7.5.2.5 Typical chromatograms obtained by procedure A for 6PPD, IPPD, 77PD and DTPD are shown in Figures 4 a) to 4 d), respectively.



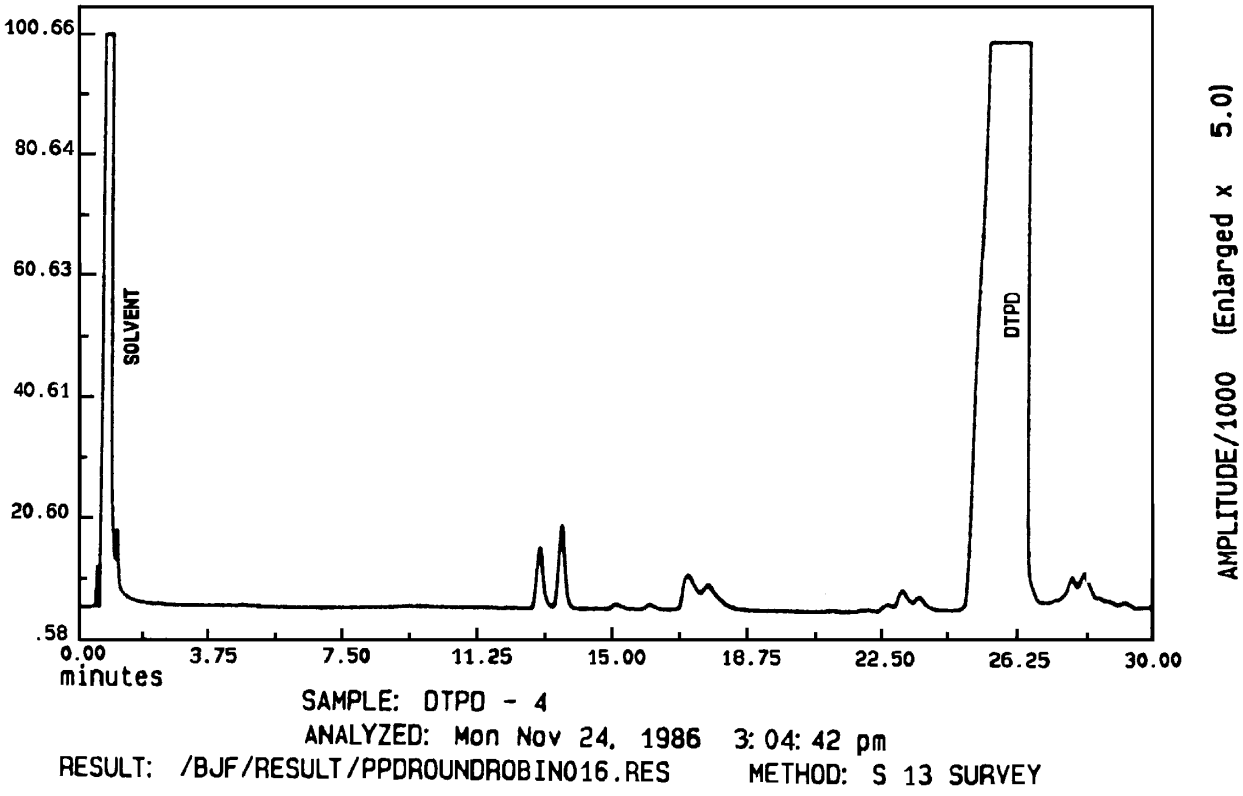
a) 6PPD



b) IPPD



c) 77PD



d) DTPD

Figure 4 — Chromatograms obtained using procedure A

7.5.3 Procedure B

7.5.3.1 The suggested operating conditions for the analysis using a capillary column are given in Table 1. Column 1 is a standard capillary and column 2 a megabore capillary.

Table 1 — Procedure B — Chromatographic conditions

	Column 1	Column 2	
Column size	30 m × 0,25 mm	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/s	NA	
Flow rate	1,0 cm^3/min	30 cm^3/min	
Head pressure, gauge	60 kPa	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	
Make-up gas	Nitrogen or helium	Nitrogen or helium	
Make-up gas flow rate[a]	29 cm^3/min	10 cm^3/min	
Split ratio	180:1	No split	
Column-temperature programme		Ramp A	Ramp B
Initial temperature	42 °C	35 °C	240 °C
Programme 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
Injection volume	0,4 mm^3 (μL)	1 mm^3 (μL)	
Solvent	Methylene chloride	Methylene chloride	
Test-portion concentration	10 mg/cm^3	3 mg/cm^3	

[a] Consult the manufacturer's manual for optimum flow rates on different instruments.

7.5.3.2 Prepare the test portion in accordance with Table 1.

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

7.5.3.4 When the analysis is complete, inspect the chromatogram and output data for proper appearance and peak identification.

7.5.3.5 Repeat the run described in 7.5.3.3 on the same sample.

7.5.3.6 Typical chromatograms obtained by procedure B using a megabore capillary for 6PPD, IPPD, 77PD and DTPD are shown in Figures 5a) to 5d), respectively.

7.6 Calculation

For each run, calculate the relative percent peak area for 6PPD and the other identified components as follows:

$$\text{Relative percent peak area} = (A_C/A_T) \times 100$$

where

A_C is the area count for the component in question;

A_T is the total area count for all the components.

7.7 Precision and bias

The data given in this subclause are applicable to procedure A only. They were determined using ISO/TR 9272 and give an estimate of the precision of this procedure with the materials used in the particular interlaboratory programme described below. The precision parameters shall 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.

Type 1 (interlaboratory) precision was determined. 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.

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

The results of the repeatability and reproducibility calculations are given in Table 2, in ascending order of the value obtained for the mean purity, for each of the materials evaluated.

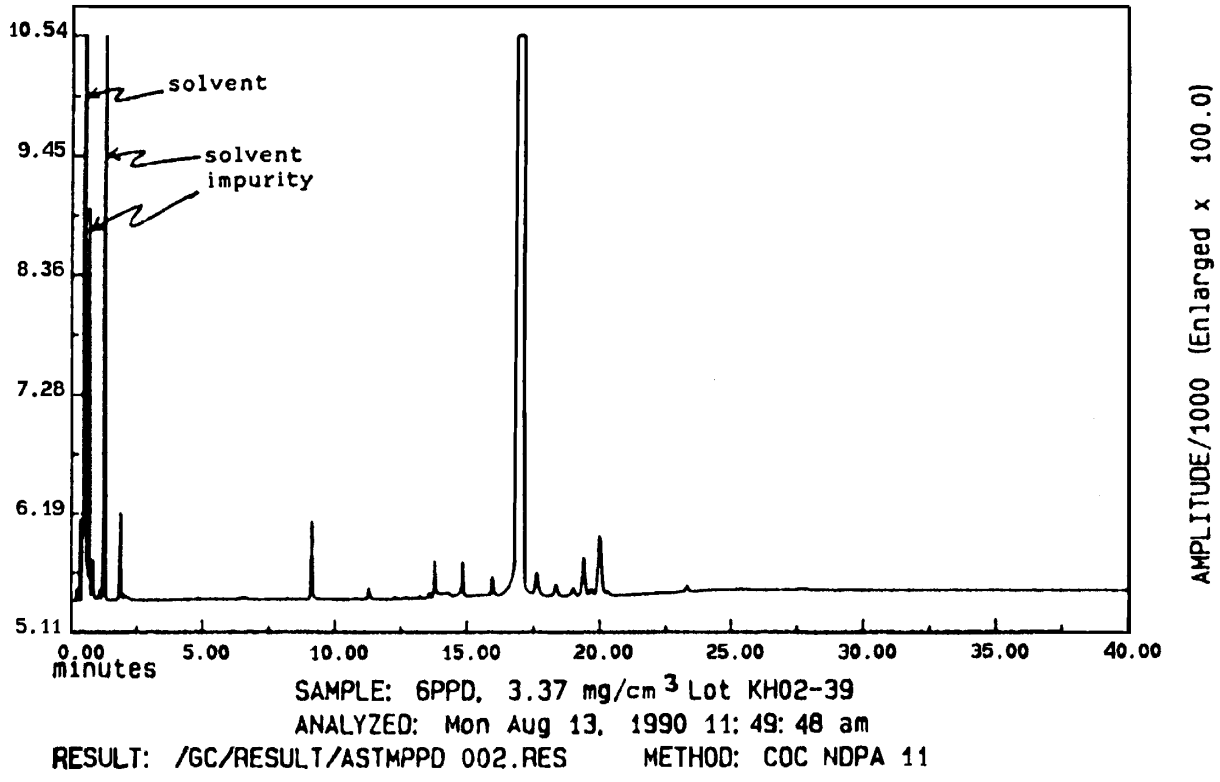
The precision of this test method may be expressed in the form of the following statements, which use an "appropriate value" of r, R, (r) or (R), i.e. that value to be used in decisions about test results (obtained with the test method). The appropriate value is that value of r or R associated with the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

Repeatability: The repeatability r of this test method has been established as the appropriate value tabulated in Table 2. Two single test results, obtained in the same laboratory under normal conditions, that differ by more than the tabulated value of r shall be considered to have come from different (non-identical) sample populations.

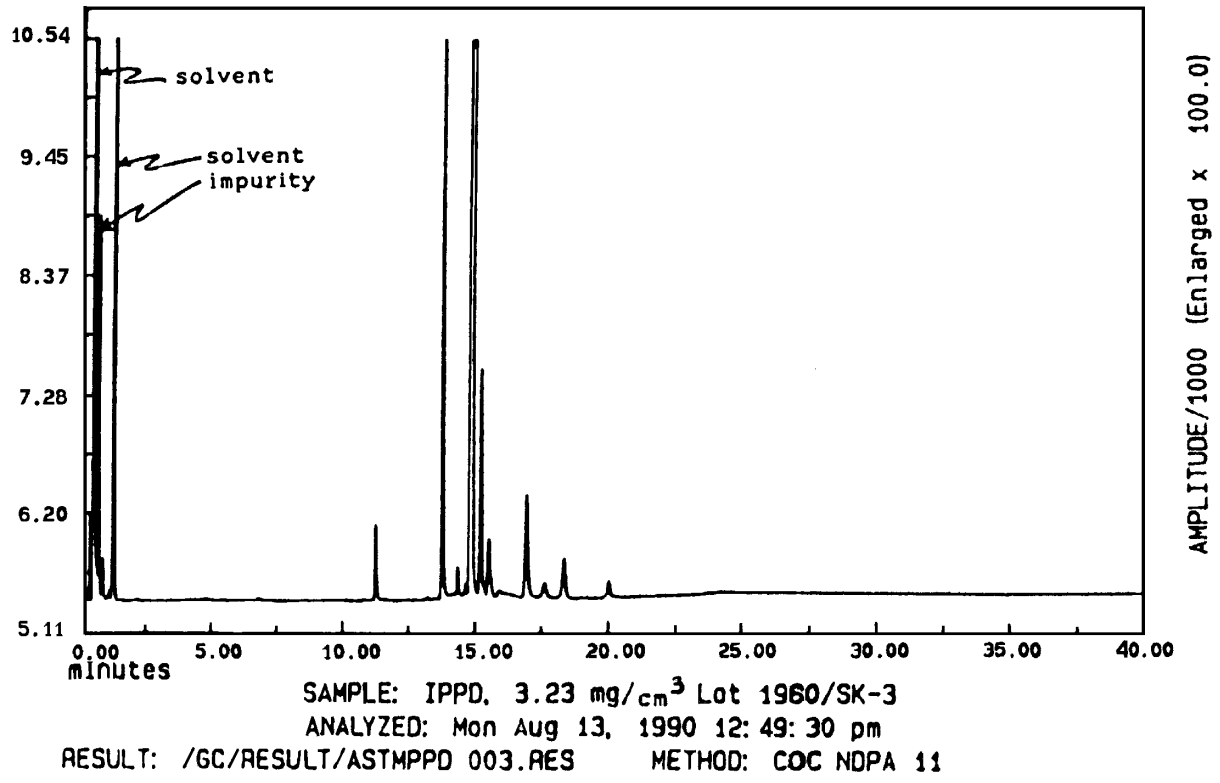
Reproducibility: The reproducibility R of this test method has been established as the appropriate value tabulated in Table 2. Two single test results, obtained in two different laboratories under normal conditions, that differ by more than the tabulated value of R shall be considered to have come from different (non-identical) sample populations.

The repeatability and reproducibility expressed as a percentage of the mean purity, (r) and (R), have application statements equivalent to those given above for r and R. For the (r) and (R) statements, the difference in the two single test results is expressed as a percentage of the arithmetic mean of the two test results.

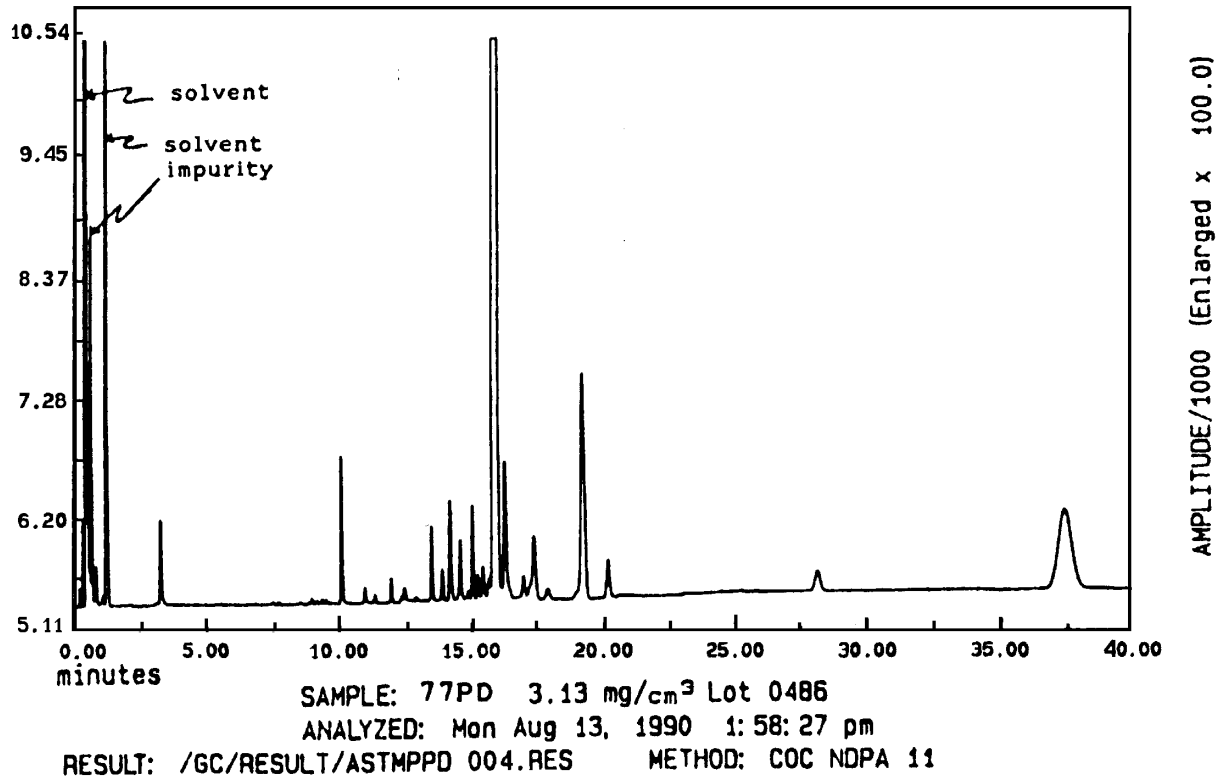
Bias: In test method terminology, bias is the difference between an average test value and the reference (or true) test-property value. Reference values have not been determined for this test method. The bias, therefore, cannot be determined.



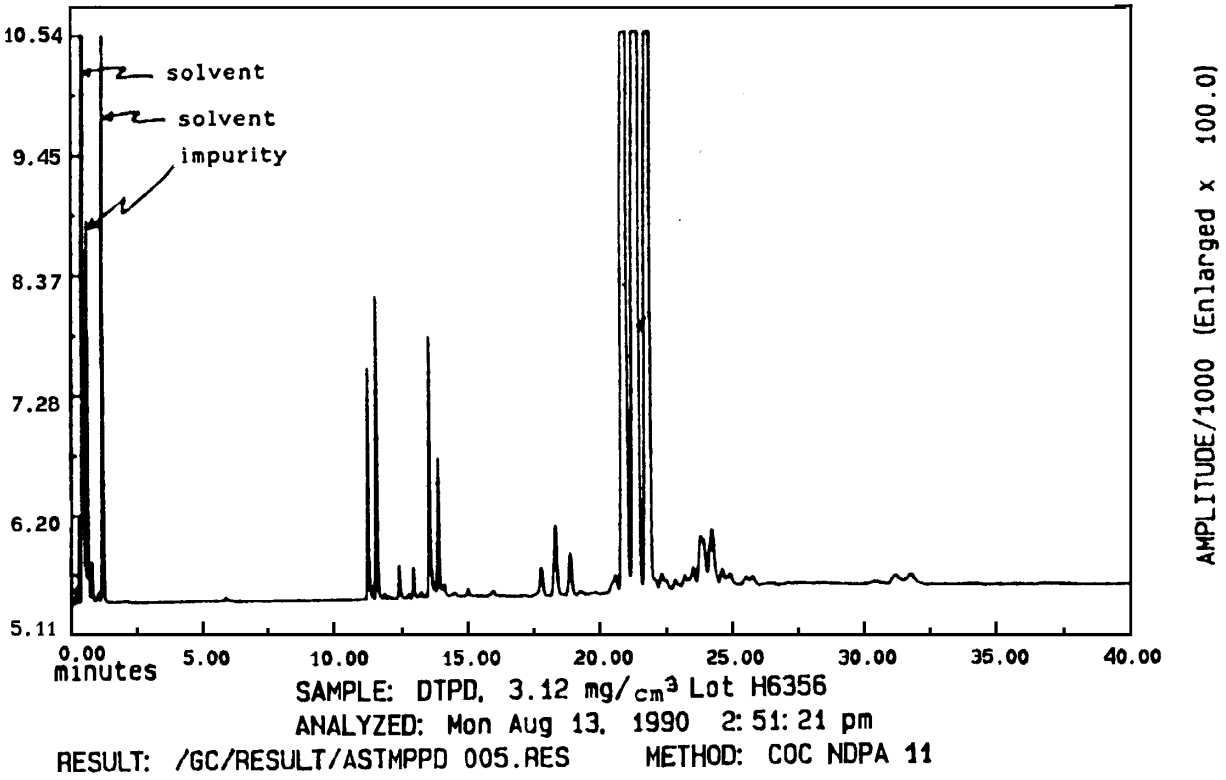
a) 6PPD



b) IPPD



c) 77PD



d) DTPD

Figure 5 — Chromatograms obtained using procedure B

Table 2 — Precision data for procedure A

Material	Mean purity	Within laboratory			Between laboratories		
		s_r	r	(r)	s_R	R	(R)
M1-6PPD	97,09	0,165	0,467	0,481	1,926	5,45	5,61
M2-IPPD	96,05	0,279	0,790	0,822	1,239	3,50	3,65
M3-77PD	96,05	0,112	0,317	0,330	1,382	3,91	4,07
M4-DTPD	94,85	0,289	0,819	0,864	2,080	5,88	6,20
Pooled values	96,01	0,230	0,651	0,678	1,659	4,69	4,89

s_r = repeatability standard deviation.

r = repeatability (= 2,83 times the square root of the repeatability variance).

(r) = repeatability (as a percentage of the mean for the material).

s_R = reproducibility standard deviation.

R = reproducibility (= 2,83 times the square root of the reproducibility variance).

(R) = reproducibility (as a percentage of the mean for the material).

7.8 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample;

c) the procedure used (A or B);

d) the result obtained from each of the two individual injections, plus the mean value, expressed to the nearest 0,1 %;

e) the combined area of all the unidentified peaks, expressed as "percent other";

f) details of any deviations from the procedure specified as well as details of any unusual incidents likely to have affected the results;

g) the date of the test.

8 Determination of purity by high-performance liquid chromatography (HPLC)

8.1 General

This method determines the purity of Type I, II and II PPD antidegradants by reverse-phase HPLC with UV detection. Quantification is achieved by using an external standard.

8.2 Apparatus

8.2.1 Precision balance, accurate to ± 0,1 mg.

8.2.2 Shaker or **ultrasonic bath.**

8.2.3 Volumetric flask, capacity 100 cm^3, meeting the requirements of ISO 1042.

8.2.4 Screw-cap vials, capacity 125 cm^3.

8.2.5 Syringe, capacity 2 cm^3.

8.2.6 Mortar and pestle.

8.2.7 High-performance liquid chromatograph: Any high-quality HPLC apparatus equipped with an autosampler or loop injector, a variable-wavelength UV detector and a peak integrator or chromatography data system is suitable for this analysis.

8.2.8 HPLC columns.

Precolumn: C_{18} silica, 35 μm to 50 μm diam.

Analytical column: C_{18} silica, 3 μm to 5 μm, 150 mm × 4,6 mm.

8.3 Reagents

8.3.1 HPLC-grade solvents.

8.3.2 Base salt.

8.3.3 Water, with a resistivity of > 200 MΩ·m (e.g. double-distilled).

8.3.4 PPD working standard, the purity of which is ensured by the use of an acceptable purification technique.

8.4 Procedure

8.4.1 Chromatographic conditions

Use the following conditions:

Eluent flow rate	1 cm^3/min
Column	C_{18} 150 mm × 4,6 mm
Injection volume	20 mm^3 (μL)
Detector wavelength	290 nm
Capacity factor k'	$3 < k' < 15$
Test portion	20 mg
Solvent	for example CH_3CN
Eluant	for example CH_3CN 65 %
	Water 35 %
	Ethanolamine 0,1 g/L

Samples shall be stored in the dark at a temperature < 5 °C

8.4.2 Preparation of test solutions

8.4.2.1 Using a mortar and pestle, grind at least 5 g of the lot test sample of the PPD to be analysed.

8.4.2.2 Perform the procedure described in 8.4.2.3 to 8.4.2.4 on duplicate test portions taken from the ground lot sample (8.4.2.1).

8.4.2.3 Into a tared 125 cm^3 screw-cap vial, weigh, to the nearest 0,15 mg, an amount (m_2) of the ground lot sample, so as to obtain a suitable detector response (see 8.4.5.3).

8.4.2.4 Add 100 cm^3 of a suitable solvent (for example CH_3CN for 6PPD) to each vial, cap the vials and dissolve the test portion by shaking or using an ultrasonic bath.

8.4.3 Preparation of reference solutions

Using the PPD working standard, prepare reference solutions in the same manner as the test solutions were prepared in 8.4.2.

8.4.4 Preparation of eluant

8.4.4.1 The eluant is a solvent or mixture of solvents which may or may not contain a base salt (see 8.4.1). Its composition is dictated by the capacity factor k' and resolution R of the apparatus (see 8.4.5.5).

8.4.4.2 Degas the eluant with helium or nitrogen before use.

8.4.5 HPLC analysis

8.4.5.1 Rinse and condition the precolumn at 25 °C ± 1 °C using the proper eluant for the product being analysed (for example CH_3CN, water and ethanolamine for 6PPD).

8.4.5.2 Using the eluant flow rate and detection wavelength given in 8.4.1, inject the reference solutions as follows:

8.4.5.2.1 Manual method: Using a 2 cm^3 syringe, make duplicate injections, each about 100 mm^3 (μL), of each of the reference solutions into the sample loop (i.e. a total of four injections).

8.4.5.2.2 Automatic method: Programme the autosampler to make duplicate injections, each about 100 mm^3 (μL), of each of the reference solutions (i.e. a total of four injections).

8.4.5.3 Calculate the response factors R_F and their mean $\overline{R_F}$, and check them as follows:

$$R_F = \frac{m_1}{A}$$

where

m_1 is the mass, in milligrams, of working standard in 100 cm^3 of reference solution;

A is the area of the peak produced by the working standard.

$$\text{Percentage dispersion} = \frac{W \times 100}{\overline{R_F}}$$

where

W is the range between a pair of duplicate determinations of the response factor;

$\overline{R_F}$ is the mean response factor.

8.4.5.4 Inject the test solutions as in 8.4.5.2.

8.4.5.5 Validate the chromatographic conditions by calculating the capacity factor k' and resolution R as follows:

$$k' = \frac{t_1 - t_0}{t_0}$$

where

t_1 is the retention time of the analyte;

t_0 is the column dead time.

The calculated value of k' shall be between 3 and 15.

$$R = 2\frac{t_1 - t_2}{tw_1 + tw_2}$$

where

t_1 is the retention time of the analyte;

t_2 is the retention time of a non-retained component;

tw_1, tw_2 are the corresponding peak widths at 10 % of peak height.

The calculated value of R shall be > 1.

8.5 Calculation

Calculate the percent PPD content as follows:

$$\% \text{ PPD} = \overline{R_F} \times \frac{A}{m_0} \times \frac{V_e}{V_r} \times 100 \times K$$

where

$\overline{R_F}$ is the mean response factor;

m_0 is the mass of the test portion, in milligrams;

V_e is the volume of the test solution, in cubic centimetres;

V_r is the volume of the reference solution, in cubic centimetres;

A is the area of the component peak;

K is the working-standard purity correction factor.

8.6 Precision and bias

No precision and bias data are currently available for this method.

8.7 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample;

c) the results obtained from the two individual determinations and their average, reported to the nearest 0,1 %;

d) details of any deviations from the procedure specified as well as details of any unusual incidents likely to have affected the results;

e) the date of the test.

9 Determination of ash

9.1 General

The ash is determined by heating a known mass of product over a gas burner to volatilize/pyrolyse the organic material, followed by ignition of the remaining carbonaceous material in a muffle furnace. The amount of ash remaining is expressed as a percentage of the original material.

The ash produced by a material is made up of all the components that remain after combustion, irrespective of chemical form. In effect, the determination measures inorganic impurities that can remain in the product at low levels following the manufacturing process.

Such impurities in accelerators or antidegradants can affect the performance of these additives in rubber if critical levels are exceeded.

9.2 Apparatus

9.2.1 Muffle furnace, capable of temperature regulation to ± 25 °C between 500 °C and 800 °C.

9.2.2 Laboratory gas burner.

9.2.3 Laboratory fume hood.

9.2.4 Porcelain crucible, high form, 15 cm^3 capacity, meeting the requirements of ISO 1772.

9.2.5 Clay triangle.

9.2.6 Steel crucible tongs.

9.2.7 Heat-resistant gloves.

9.2.8 Desiccator.

9.3 Procedure

9.3.1 Heat the 15 cm^3 crucible in the muffle furnace at 750 °C $\pm$ 25 °C for 30 min.

9.3.2 Transfer the crucible to the desiccator, allow to cool to room temperature, and weigh to the nearest 0,1 mg (m_1).

9.3.3 Weigh a nominally 2 g test portion to the nearest 0,1 mg into the crucible (m_2). Place the crucible in the clay triangle, and carefully heat the crucible and contents with the gas burner until all volatile material and pyrolysis products have been removed (gases may flame) and the residue has been carbonized.

9.3.4 Transfer the crucible to the muffle furnace and heat for 2 h at 750 °C ± 25 °C.

9.3.5 Carefully transfer the crucible containing the ash to the desiccator, allow to cool to room temperature, and reweigh to the nearest 0,1 mg (m_3).

Repeat the procedure on a second test portion.

9.4 Calculation

Calculate the percent ash to the nearest 0,01 % as follows:

$$\text{Percent ash} = [(m_3 - m_1)/(m_2 - m_1)] \times 100$$

where

m_1 is the mass of the crucible, in grams;

m_2 is the mass of the crucible plus test portion, in grams;

m_3 is the mass of the crucible plus ash, in grams.

9.5 Precision and bias

The data given in this subclause were determined using ISO/TR 9272 and give an estimate of the precision of this test method with the materials used in the particular interlaboratory programme described below. The precision parameters shall 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.

Type 1 (interlaboratory) precision was determined. 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.

Six different materials were used in the interlaboratory programme. These were tested in seven laboratories on two different days.

The results of the repeatability and reproducibility calculations are given in Table 3 for the mean ash, for each of the materials evaluated.

The precision of this test method may be expressed in the form of the following statements, which use an "appropriate value" of r, R, (r) or (R), i.e. 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 the mean ash in Table 3 closest to the mean ash under consideration at any given time, for any given material, in routine testing operations.

Repeatability: The repeatability r of this test method has been established as the appropriate value tabulated in Table 3. Two single test results, obtained in the same laboratory under normal conditions, that differ by more than the tabulated value of r shall be considered to have come from different (non-identical) sample populations.

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 conditions, that differ by more than the tabulated value of R shall be considered to have come from different (non-identical) sample populations.

The relative repeatability (r), and relative reproducibility (R) have been omitted from Table 3 since the level of ash determined was extremely low and approached the sensitivity limits of the test method. Under these circumstances, the relative values become negligible.

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 determined for this test method. The bias, therefore, cannot be determined.

Table 3 — Precision data for ash determination

Material	Mean ash	Within laboratory		Between laboratories	
		s_r	r	s_R	R
M1-6PPD	0,02	0,012	0,034	0,013	0,037
M2-IPPD	0,01	0,005	0,014	0,010	0,027
M3-77PD	0,01	0,008	0,021	0,012	0,034
M4-DTPD	0,02	0,006	0,016	0,007	0,020

s_r = repeatability standard deviation.

r = repeatability (= 2,83 times the square root of the repeatability variance).

s_R = reproducibility standard deviation.

R = reproducibility (= 2,83 times the square root of the reproducibility variance).

9.6 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample;

c) the results obtained from the two individual determinations and their average, reported to the nearest 0,01 %;

d) details of any deviations from the procedure specified as well as details of any unusual incidents likely to have affected the results;

e) the date of the test.

10 Determination of volatile matter

10.1 General

A test portion of the antidegradant is weighed before and after heating for 3 h at 70 °C. The measured difference in mass is the volatile-matter content.

The quantity of volatile matter in PPDs can affect the performance of these antidegradants in rubber if it exceeds critical levels.

10.2 Apparatus

10.2.1 Weighing bottle, low form.

10.2.2 Air-circulation oven, capable of being maintained at a temperature of 70 °C ± 2 °C.

10.2.3 Desiccator.

10.3 Preparation of sample

To ensure homogeneity, blend at least 250 g of the lot sample thoroughly prior to removing the test portion.

10.4 Procedure

10.4.1 Perform the following procedure (10.4.2 to 10.4.5) on duplicate test portions.

10.4.2 Dry a clean weighing bottle and stopper (with the stopper removed) for 30 min in the oven at 70 °C. Place the bottle and stopper in the desiccator and allow them to cool to room temperature. Weigh the bottle with its stopper to the nearest 0,1 mg (m_1).

10.4.3 Weigh a nominally 5 g test portion into the weighing bottle to the nearest 0,1 mg (m_2).

10.4.4 Place the weighing bottle containing the test portion, and the stopper (with the stopper removed), in the oven, equilibrated at 70 °C ± 2 °C, for 3 h.

10.4.5 After the heating period, replace the stopper and transfer the bottle to the desiccator for a period of time sufficient for the assembly to equilibrate at room temperature. Reweigh the bottle to the nearest 0,1 mg (m_3).

10.5 Calculation

Calculate the percent volatile-matter content to the nearest 0,1 % as follows:

$$\text{Percent volatile matter} = [(m_2 - m_3)/(m_2 - m_1)] \times 100$$

where

m_1 is the mass of the weighing bottle and stopper, in grams;

m_2 is the mass of the weighing bottle, stopper and test portion before heating, in grams;

m_3 is the mass of the weighing bottle, stopper, and test portion after heating, in grams.

10.6 Precision and bias

The data given in this subclause were determined using ISO/TR 9272 and give an estimate of the precision of this test method with the materials used in the particular interlaboratory programme described below. The precision parameters shall 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.

Type 1 (interlaboratory) precision was determined. 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.

Four different materials were used in the interlaboratory programme. These were tested in six laboratories on two different days.

The results of the repeatability and reproducibility calculations are given in Table 4, for the mean volatile-matter content, for each of the materials evaluated.

The precision of this test method may be expressed in the form of the following statements, which use an "appropriate value" of r, R, (r) or (R), i.e. 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 the mean volatile-matter content in Table 4 closest to the mean volatile-matter content under consideration at any given time, for any given material, in routine testing operations.

Repeatability: The repeatability r of this test method has been established as the appropriate value tabulated in Table 3. Two single test results, obtained in the same laboratory under normal conditions, that differ by more than the tabulated value of r shall be considered to have come from different (non-identical) sample populations.

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 conditions, that differ by more than the tabulated value of R shall be considered to have come from different (non-identical) sample populations.

The relative repeatability (r), and relative reproducibility (R) have been omitted from Table 3 since the level of ash determined was extremely low and approached the sensitivity limits of the test method. Under these circumstances, the relative values become negligible.

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 determined for this test method. The bias, therefore, cannot be determined.

Table 4 — Precision data for volatile-matter determination

Material	Mean volatile-matter content	Within laboratory		Between laboratories	
		s_r	r	s_R	R
M1-6PPD	0,06	0,022	0,062	0,029	0,083
M2-IPPD	0,08	0,004	0,012	0,027	0,076
M3-77PD	0,19	0,035	0,099	0,073	0,027
M4-DTPD	0,04	0,002	0,016	0,012	0,056

s_r = repeatability standard deviation.

r = repeatability (= 2,83 times the square root of the repeatability variance).

s_R = reproducibility standard deviation.

R = reproducibility (= 2,83 times the square root of the reproducibility variance).

10.7 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample;

c) the results obtained from the two individual determinations and their average, reported to the nearest 0,01 %;

d) details of any deviations from the procedure specified as well as details of any unusual incidents likely to have affected the results;

e) the date of the test.

ICS 83.040.20

Price based on 20 pages