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Vulcanized rubbers — Determination of antidegradants by high-performance liquid chromatography

Caoutchouc vulcanisés — Détermination des agents de protection par chromatographie en phase liquide à haute performance

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Vulcanized rubbers — Determination of antidegradants by high-performance liquid chromatography

WARNING 1 — Persons using this document should be familiar with normal laboratory practice. This document 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 determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document might involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document describes a procedure for the determination of the following antidegradants in vulcanized rubbers:

- aminoketone group;
- naphthylamine group;
- diphenylamine group;
- p-phenylenediamine;
- monophenol group.

The groups of antidegradants are summarized in Table A.1 with the chemical names, the abbreviated terms and the CAS registry numbers.

Extender oils, when present, can interfere.

For poly-2,2,4-trimethyl-1,2-dihydroquinoline, the method provides only an approximation because of its polymeric nature.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The antidegradant, following quantitative extraction from the rubber, is separated by high-performance liquid chromatography (HPLC) from other extracted components. Its component peaks are detected and their areas are measured. Its concentration in the rubber is calculated by using standard calibration curve.

NOTE Some antidegradants contain more than one component peak and the ratio of the areas of component peaks can differ depending on the source of the antidegradant. The procedure described gives accurate results providing the composition of the reference antidegradant and the antidegradant being analysed contain the same number of component peaks with the same area ratios. Inaccurate results are obtained when this condition is not satisfied, with the extent of the error being dependent on the difference in composition between reference and sample antidegradants.

5 Materials

5.1 Eluent A: a 1:1 (by volume) mixture of methanol (HPLC grade) and a 0,01 mol/l aqueous solution of ammonium acetate (AR grade).

5.2 Eluent B: methanol (HPLC grade).

5.3 Extraction solvent: a 2:1 (by volume) mixture of isopropanol (HPLC grade) and dichloromethane (HPLC grade) or any suitable solvents.

5.4 Single use PTFE filters: 25 mm diameter, 0,45 µm porosity.

6 Apparatus

6.1 HPLC apparatus, with gradient elution capability, a 10 µl fixed-loop injector, a variable-wavelength ultraviolet-visible (UV-VIS) detector and a recording-integrator data system.

6.2 HPLC column, reverse-phase type.

Different columns may be used provided that a good separation of antidegradant component peaks from other extracted components is obtained. The method has been tested using a 5 µm particle size column. A column RP C18 (150 mm × 4,6 mm) is usually appropriate. However, the elution programme may need to be modified when columns different from the ones described in this document are used.

6.3 Ultrasonic bath, typically of about 2 l capacity, operating at a frequency of 47,6 kHz ± 10 %.

An ultrasonic bath of different capacity and operating frequency may be used provided that extraction of the antidegradant is complete.

6.4 Analytical balance, capable of weighing to 0,01 mg.

7 Chromatographic conditions

7.1 Pump A: Eluent A (5.1).

7.2 Pump B: Eluent B (5.2).

7.3 Flow rate: 1,0 ml/min.

7.4 Column oven temperature: 40 °C.

7.5 Injection volume: 10 µl.

7.6 Detector wavelength:

- aminoketone group: 235 nm;
- all other antidegradants: 290 nm.

7.7 Elution programme.

Time min	Eluent A %	Eluent B %
0	100	0
20	0	100
40	0	100
50	100	0
55	End	

8 Procedure

8.1 Preparation of the calibration curve

Prepare standard solutions, for example from 2×10^{-4} mol/l to 10^{-3} mol/l (see Table B.1).

The concentration range shall be adapted depending on the requested quantification limit.

The calibration curve is obtained by plotting the peak area against the initial concentration of the antidegradant (see examples in Figures B.1 and B.2).

Check that the calibration curve is linear and the determination coefficient r^2 is greater than 0,99.

Repeat the injections twice and report the average of the two values.

NOTE Combination of antidegradants calibration can be used.

8.2 Preparation of the sample

8.2.1 Cut about 1 g sample into small pieces about 2 mm square.

8.2.2 Weigh, to the nearest 0,1 mg, about 200 mg of the small pieces and place each test portion into a 20 ml flask.

8.2.3 Add accurately, by pipette, 10 ml of extraction solvent (5.3) and stopper the flask.

8.2.4 Extract in the ultrasonic bath (6.3) for 3 h at a temperature not exceeding 30 °C.

If the bath temperature exceeds 30 °C, the flask may rupture. Therefore, it is necessary periodically to add cold water to the bath during the extraction, or to use a cooling system, in order to maintain the bath below 30 °C.

Filtrate with PTFE filter (5.4).

The tests shall be duplicated. Two test portions per sample are extracted.

8.3 Sample analysis

8.3.1 Filtrate at 0,45 µm and inject into the HPLC column (6.2) a 10 µl volume of the rubber sample extract prepared in 8.2 and elute in accordance with the programme given in 7.7.

Repeat the injections twice and report the average of the two values.

8.3.2 Record the areas of the sample antidegradant peaks. For examples of chromatograms and UV spectra, see Annex C.

9 Calculation

The concentration of the antidegradant in the sample (W, in %) shall be calculated by Formula (1), the formula of the calibration curve and the antidegradant area obtained for the test piece:

$$W = (C \times V \times M \times 100)/m \tag{1}$$

where

C is the antidegradant concentration in mol/l obtained by HPLC;

V is the volume of the solution obtained in l;

M is the molecular weight of the antidegradant, in g/mol;

m is the mass of the test piece, in g.

Record the average of the two results.

10 Precision

See Annex D.

11 Test report

The test report shall include the following information:

a) a full description of the product tested and its origin;

b) a reference to the test method used, i.e. the reference number of this document (ISO 23075:2021);

c) details of any procedures not specified in this document;

d) test results, i.e. the concentration, in percent, of the antidegradant in the sample;

e) the date of the test.

Annex A
(informative)

Antidegradants covered by this document

Table A.1 summarizes the chemical names, the abbreviated terms and the CAS registry numbers for the groups of antidegradants covered by this document.

Table A.1 — Names, abbreviated terms and CAS numbers of antidegradants covered by this document

Group	Name	Abbreviated term (see ISO 6472)	CAS
Aminoketone	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	ETMQ	91–53–2
	polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	TMQ	26780–96–1
Naphthylamine	*N*-phenyl-α-naphthylamine	PAN	90–30–2
	N-phenyl-β-naphthylamine	PBN	135–88–6
Diphenylamine	acetone-diphenylamine condensate	ADPA	68412–48–6
	4,4′-bis(α,α-dimethylbenzyl)-diphenylamine	CDPA	10081–67–1
	octylated diphenylamine	ODPA	106–67–7
	styrenated diphenylamine	SDPA	68442–68–2
p-Phenylenediamine	N-cyclohexyl-N'-phenyl-p-phenylenediamine	CPPD	101–87–1
	N,N'-bis(1-methylheptyl)-p-phenylenediamine	DMHPD	103–96–8
	N,N′-di-2-naphthyl-p-phenylenediamine	DNPD	93–46–9
	N,N′-diphenyl-p-phenylenediamine	DPPD	74–31–7
	N-isopropyl-N′-phenyl-p-phenylenediamine	IPPD	101–72–4
	N-1,3-dimethylbutyl-N′-phenyl-p-phenylenediamine	6PPD	793–24–8
	N-1,4-dimethylpentyl-N'-phenyl-p-phenylenediamine	7PPD	3081–01–4
	N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine	77PD	3081–14–9
	N-(1-methylheptyl)-N′-phenyl-p-phenylenediamine	8PPD	15233–47–3
	N,N'-dioctyl-p-phenylenediamine	88PD	1241–28–7
Monophenol	2,6-di-tert-butyl-4-methylphenol	BHT	128–37–0
	styrenated phenol	SPH	61788–44–1

Annex B
(informative)

Calibration

An example is given for preparation of 6PPD standard solutions from 2 × 10^{-4} mol/l to 10^{-3} mol/l.

The solutions are prepared by successive dilutions of a 6PPD solution of 10^{-3} mol/l, obtained by dissolving 5,37 mg of 6PPD (molecular weight M = 268,4 g/mol), in 20 ml of 2:1 (by volume) mixture of isopropanol (HPLC grade) and dichloromethane (HPLC grade).

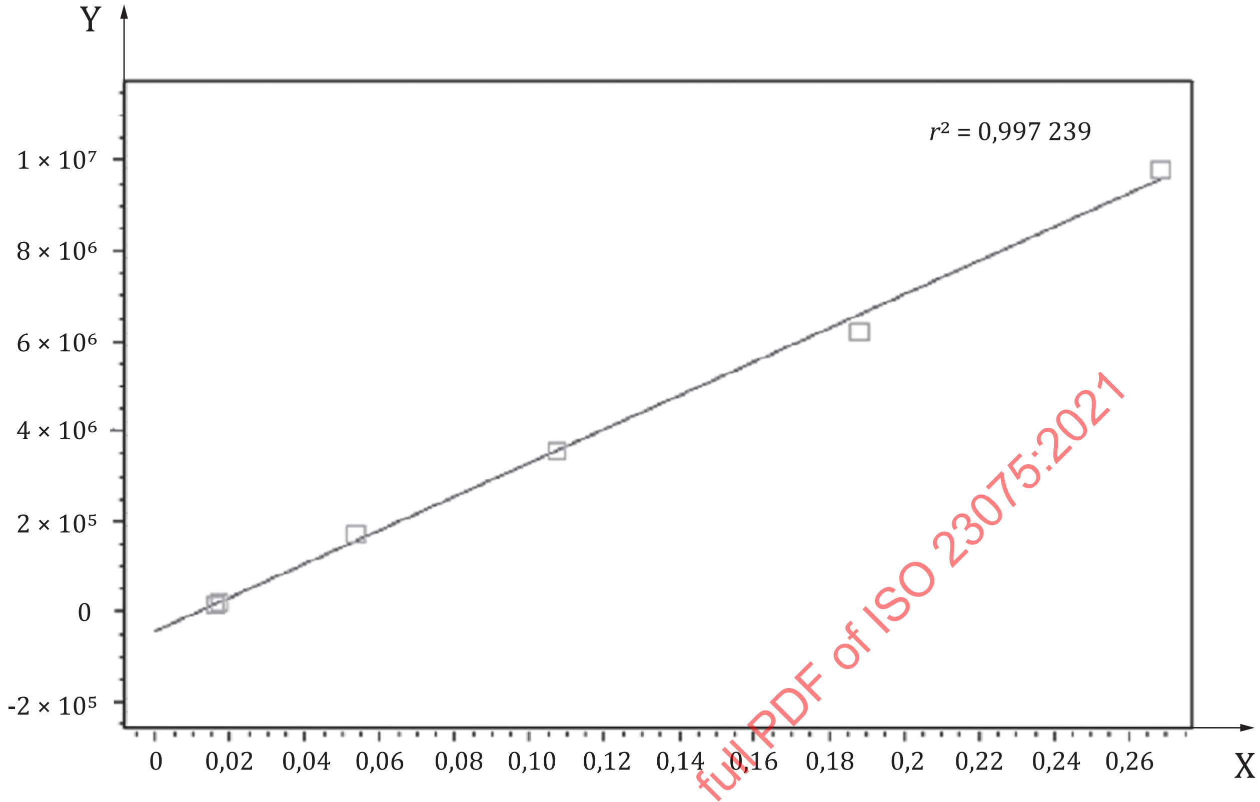
NOTE The order of injection of the standard solutions is generally from the less concentrated to the more concentrated.

Table B.1 provides information for preparation of the 6PPD standard solutions. Figures B.1 and B.2 provide examples of calibration curve of 6PPD and ODPA.

Table B.1 — Steps for preparation of the 6PPD standard solutions for the calibration range

Solutions	**6PPD concentration** mol/l
10 ml of 10^{-3} mol/l solution	1x10^{-3}
7ml of 10^{-3} mol/l solution, then complete up to 10 ml of 2:1 isopropanol: dichloromethane	7x10^{-4}
4 ml of 10^{-3} mol/l solution, then complete up to 10 ml of 2:1 isopropanol: dichloromethane	4x10^{-4}
2 ml of 10^{-3} mol/l solution, then complete up to 10 ml of 2:1 isopropanol: dichloromethane	2x10^{-4}

The injected volume is 10 µl.

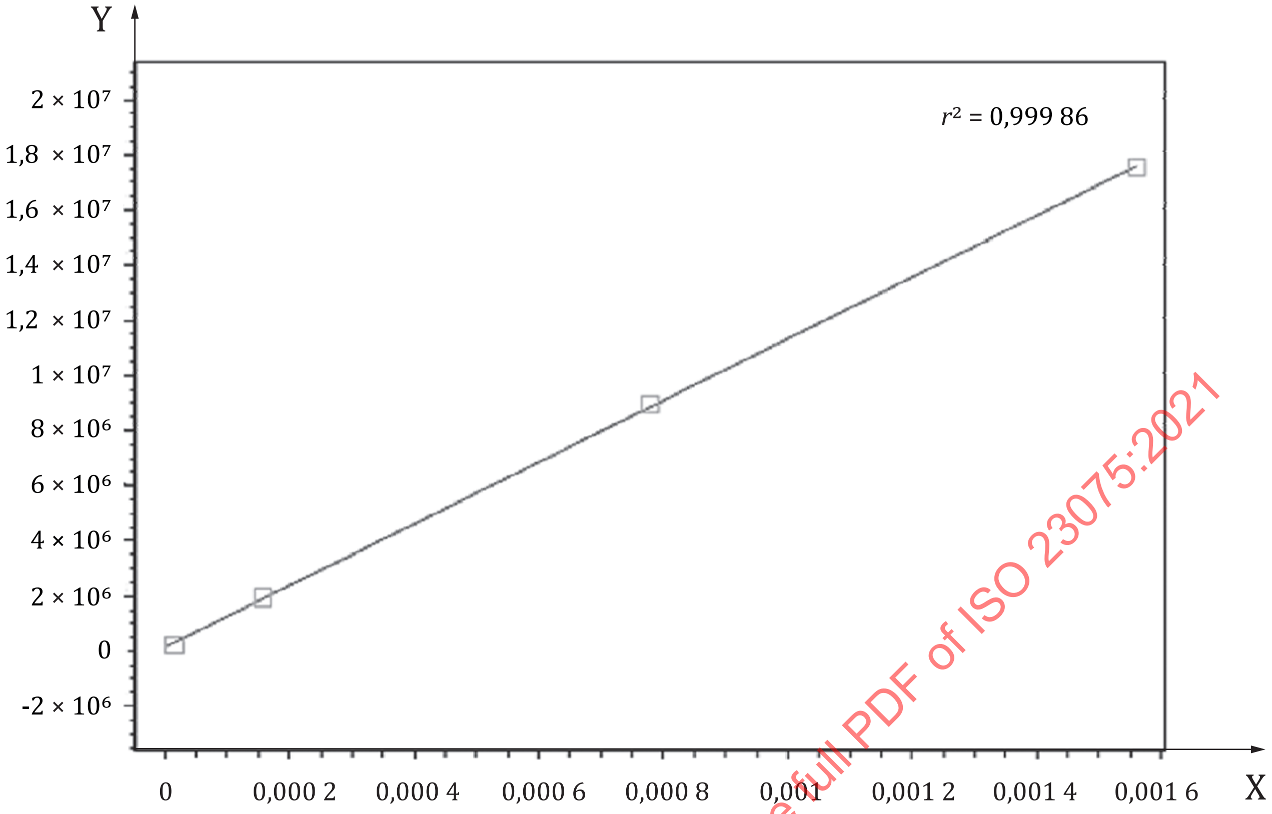


Key

X amount

Y area

Figure B.1 — Example of calibration curve for 6PPD



Key

X amount

Y area

Figure B.2 — Example of calibration curve for ODPA

Annex C
(informative)

Examples of chromatograms and UV spectra

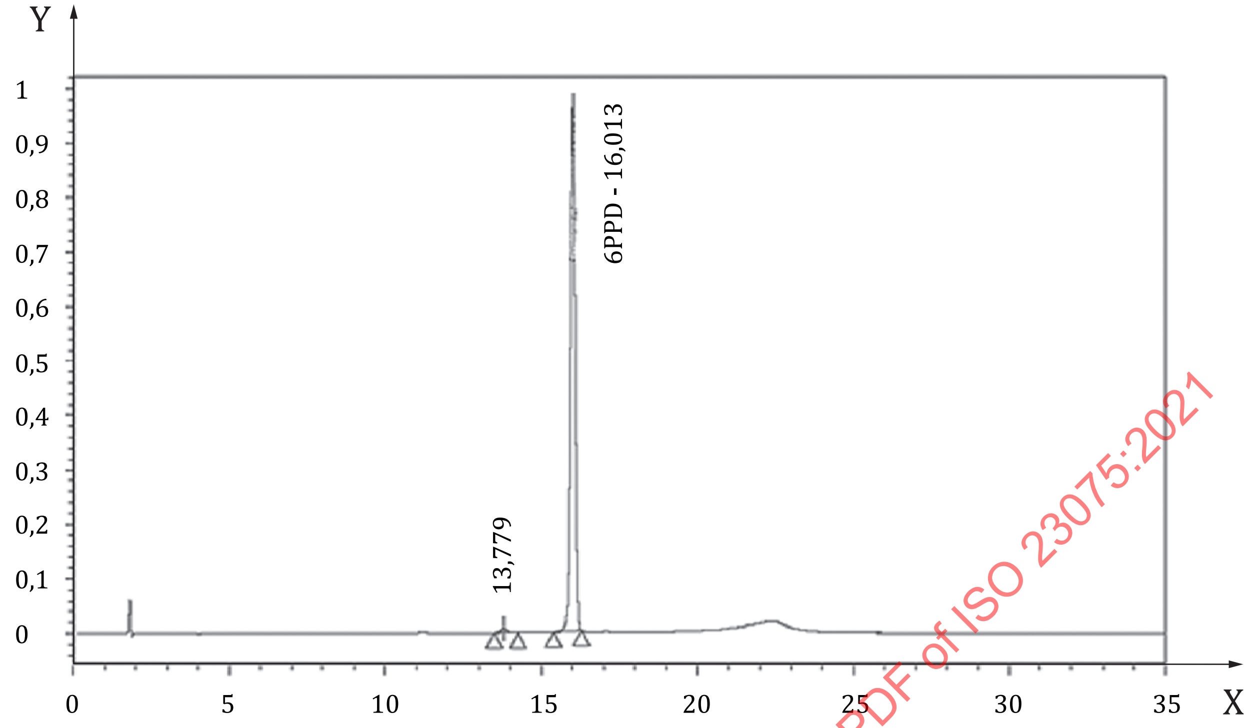
This annex provides examples of chromatograms and UV spectra.

Samples were obtained after extraction in a 2:1 (volume) of isopropanol:dichloromethane mixture. Separation was carried out on a C18 column (150 × 4,6 mm, 5 µm), with a flow rate of 1 ml/min using methanol (solvent B) as the mobile phase and a 1:1 (by volume) mixture of aqueous solution of ammonium acetate 0,01 mol/l and methanol (solvent A), according to the elution gradient shown in Table C.1.

Table C.1 — Operating conditions for external calibration

Time *t* min	**Solvent A** %	**Solvent B** %
0	100	0
20	0	100
40	0	100
50	100	0
55	100	0

Figures C.1 to C.8 are examples of chromatograms and UV spectra for 6PPD, IPPD, ODPA and TMQ. Detection was at 290 nm for 6PPD, IPPD or ODPA, and at 235 nm for TMQ.

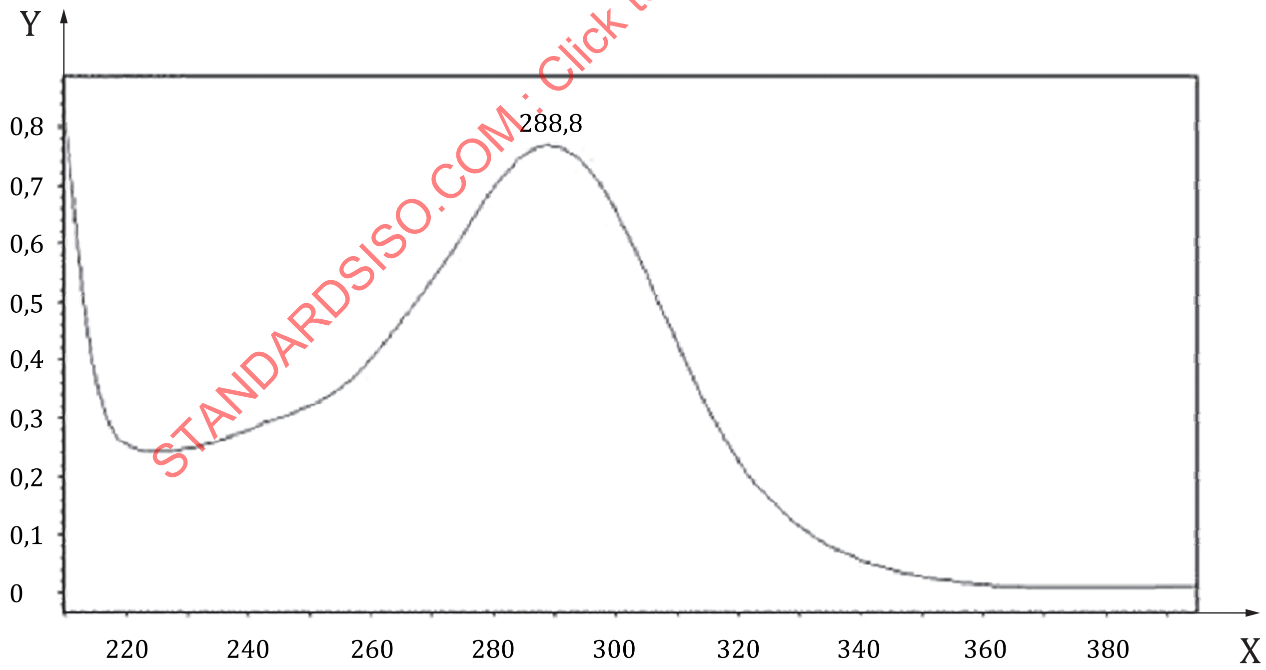


Key

X time (min)

Y absorbance unit

Figure C.1 — Chromatogram of 6PPD



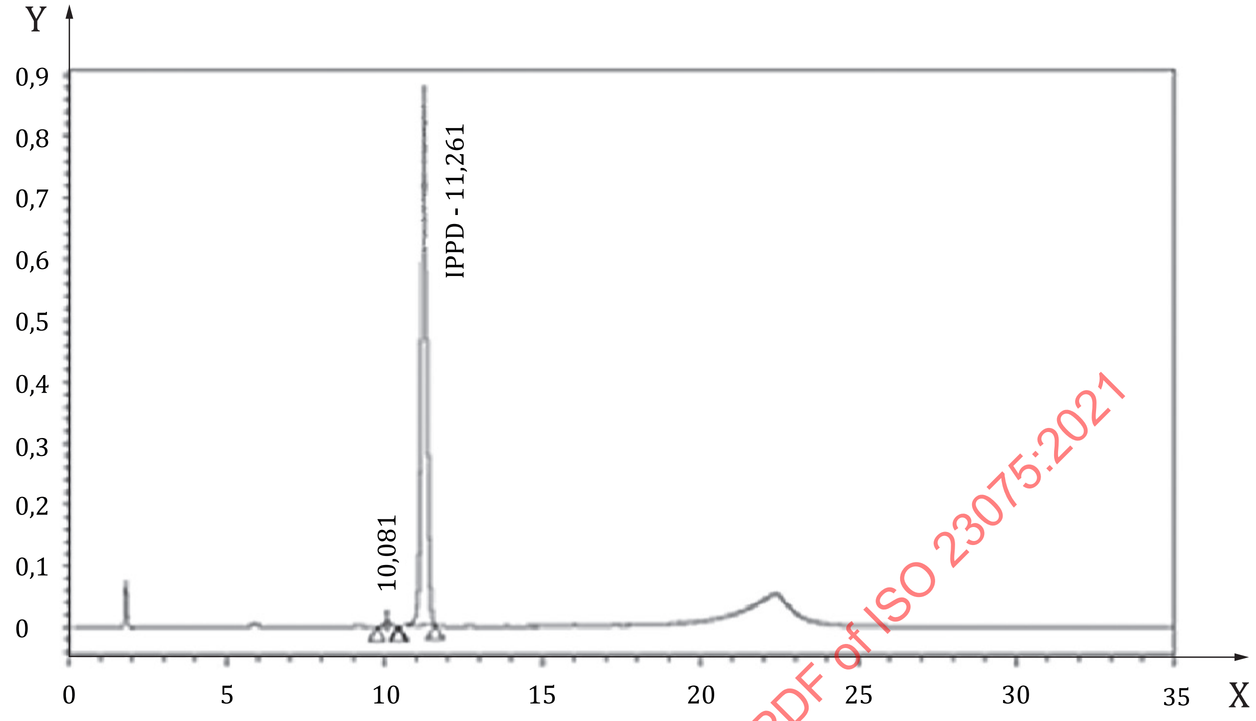
Key

X wavelength (nm)

Y absorbance unit

NOTE Time 16,075 extracted.

Figure C.2 — UV spectra of 6PPD

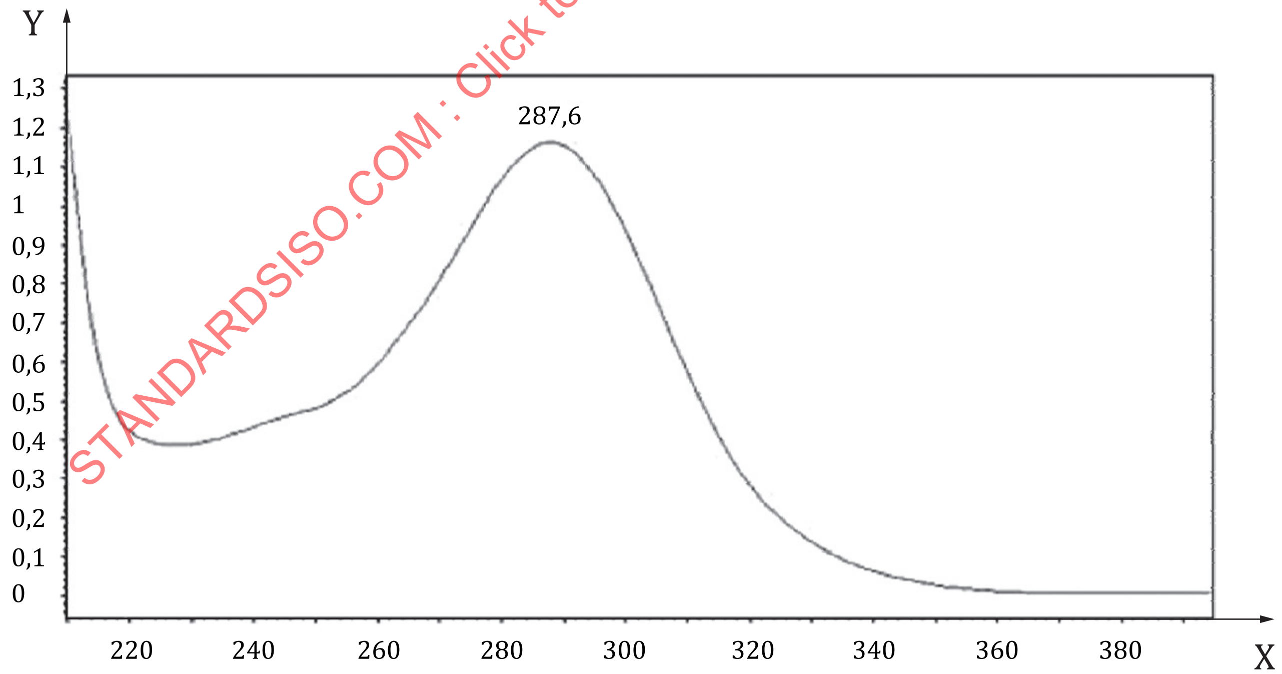


Key

X time (min)

Y absorbance unit

Figure C.3 — Chromatogram of IPPD



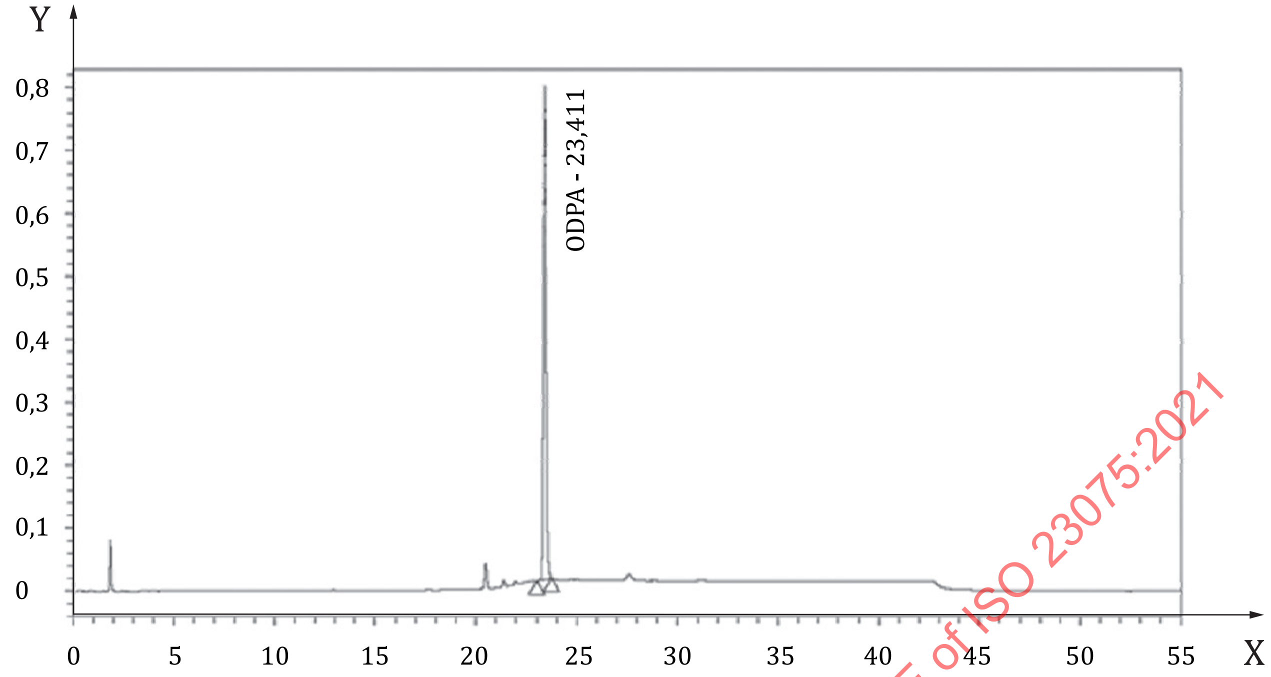
Key

X wavelength (nm)

Y absorbance unit

NOTE Time 11,945 extracted.

Figure C.4 — UV spectra of IPPD

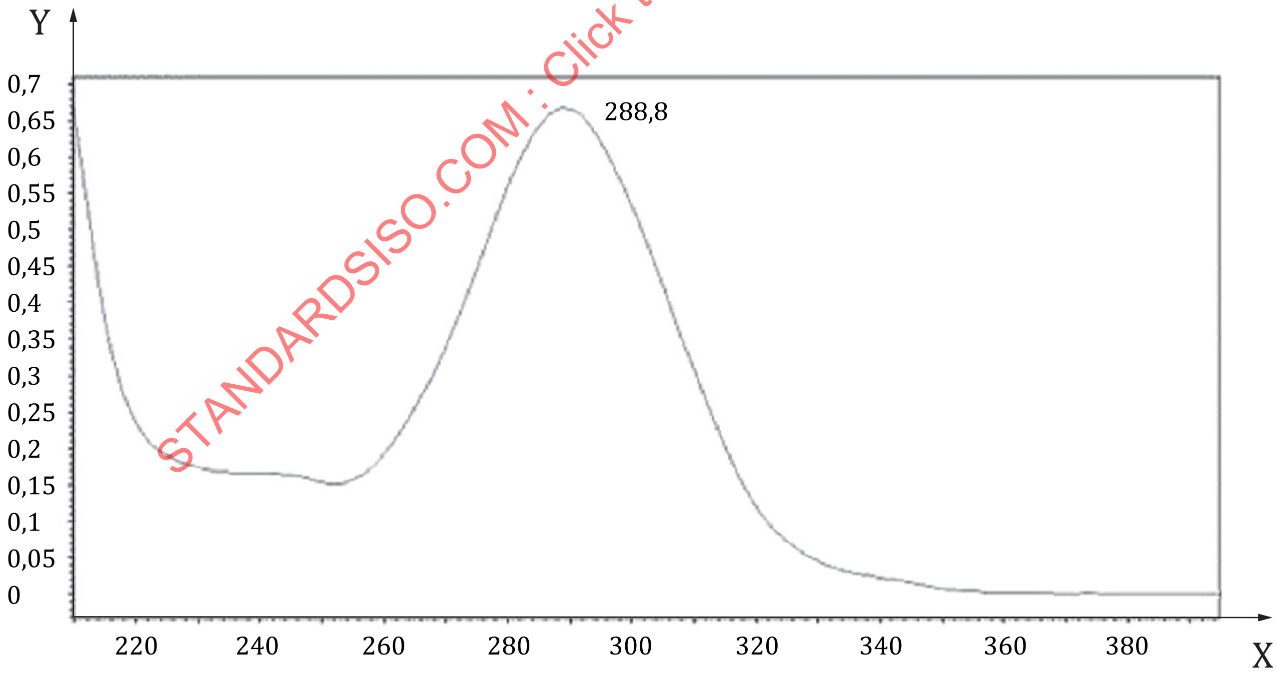


Key

X time (min)

Y absorbance unit

Figure C.5 — Chromatogram of ODPA



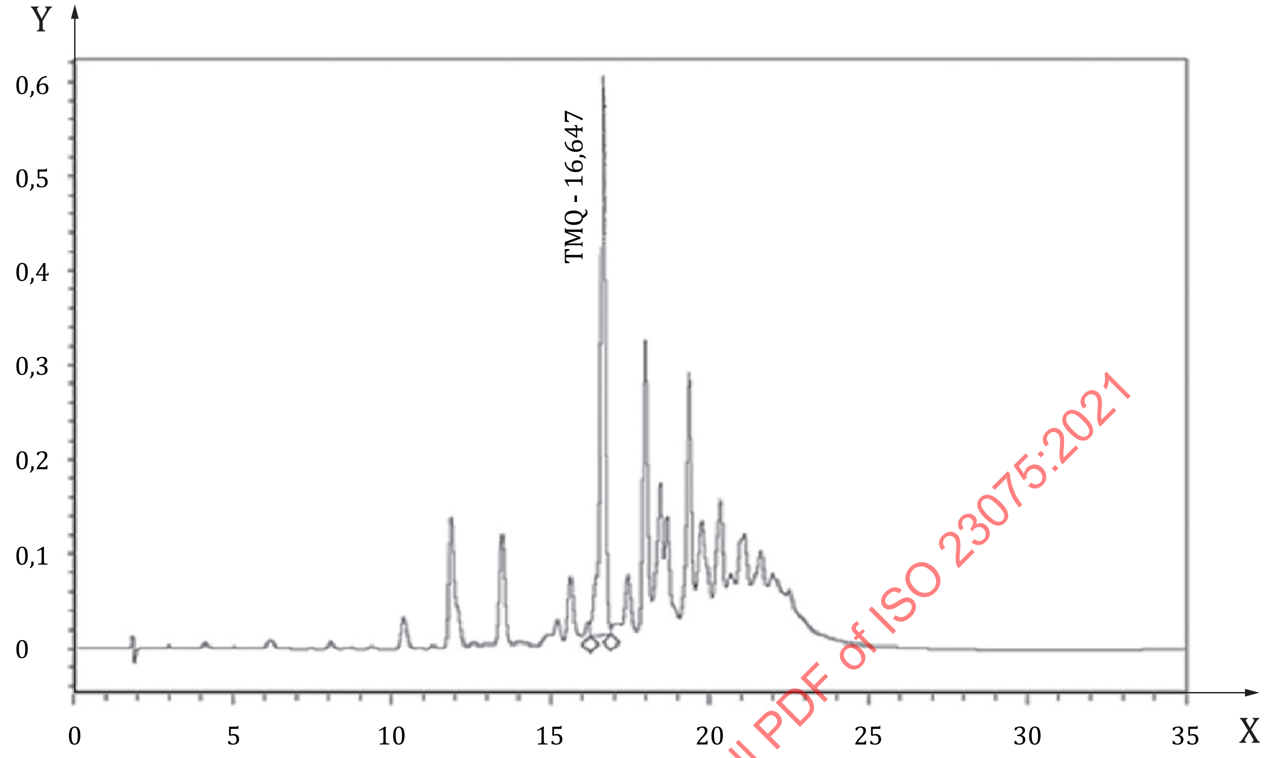
Key

X wavelength (nm)

Y absorbance unit

NOTE Time 23,431 extracted.

Figure C.6 — UV spectra of ODPA



Key

X time (min)

Y absorbance unit

Figure C.7 — Chromatogram of TMQ