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Rubber — Identification of antidegradants by gas chromatography/mass spectrometry

Caoutchouc — Identification des antidégradants par chromatographie en phase gazeuse/spectrométrie de masse

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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10638 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

Introduction

Most rubber products contain antidegradants to extend the life of the product, the type of antidegradant depending on the service conditions to which a particular product will be exposed. Doubts are increasingly being expressed about the negative impact which rubber containing certain antidegradants can have on the environment. However, demonstrating the presence of antidegradants in rubber products is not easy.

There are methods of qualitative analysis, specified in International Standards such as ISO 4645, which use thin-layer chromatography. This requires a highly skilled operator with a great amount of knowledge and experience, as well as the use of standard reference materials.

The gas chromatography/mass spectrometry technique specified in this International Standard is an efficient method suitable for identifying antidegradants contained in rubber products as well as in the raw-rubber and the unvulcanized-rubber compounds used to make such products.

Rubber — Identification of antidegradants by gas chromatography/mass spectrometry

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.

CAUTION — Certain procedures specified in this International Standard may 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 International Standard specifies a qualitative method, using gas chromatography/mass spectrometry, for the identification of antidegradants in raw rubbers, latices, unvulcanized-rubber compounds and vulcanized-rubber products. It is applicable to the 31 types of antidegradant listed in Annex A. Users should note that the method specified is a qualitative one and is not intended for quantitative analysis.

NOTE Persons using this International Standard are expected to be familiar with procedures of analysis using gas chromatography/mass spectrometry. In addition, it is assumed that the gas chromatograph/mass spectrometer is operated in accordance with the manufacturer's instruction manual and that it is maintained in an optimum condition. Detailed procedures for operation of the equipment are therefore not included.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 123, *Rubber latex — Sampling*

ISO 124, *Latex, rubber — Determination of total solids content*

ISO 1407, *Rubber — Determination of solvent extract*

ISO 1795, *Rubber, raw natural and raw synthetic — Sampling and further preparative procedures*

ISO 4661-2, *Rubber, vulcanized — Preparation of samples and test pieces — Part 2: Chemical tests*

3 Principle

Antidegradants are recovered from samples by thermal desorption or solvent extraction. The type of antidegradant recovered is identified by the mass spectrum that is produced after passing the antidegradant through a gas chromatograph and mass spectrometer connected in tandem. The retention index can be used as a supplementary means of identification if necessary.

4 Thermal-desorption method

4.1 Reagents and materials

4.1.1 Trap coolant, e.g. liquid nitrogen, used only when required by the particular thermal-desorption apparatus in use.

4.1.2 Gas chromatograph carrier gas: helium.

4.2 Apparatus

4.2.1 Thermal-desorption apparatus or equivalent, connectable to the gas chromatograph and which can be heated up to 340 °C.

NOTE An example of an equivalent apparatus is a pyrolyser in which the heating temperature is kept low.

4.2.2 Trap apparatus, used only when required by the particular thermal-desorption apparatus in use.

4.2.3 Gas chromatograph/mass spectrometer.

4.2.3.1 Gas chromatograph, as specified below:

— Column:

  — length: 25 m to 60 m;

  — diameter: 0,25 mm to 0,35 mm;

  — liquid phase: 5 % diphenyl-, 95 % polydimethylsiloxane;

  — film thickness: 0,20 µm to 0,35 µm.

Other types of column (e.g. 100 % polydimethylsiloxane) may be used if the retention index given in Annex A, or determined as described in Annex C, is not utilized in the analysis.

— Carrier gas flow rate: 1,0 ml/min to 2,0 ml/min.

— Injector temperature: 300 °C to 350 °C.

— Oven temperature programme: initial temperature 40 °C, heating at 20 °C/min up to 320 °C, maintained at 320 °C for 10 min.

4.2.3.2 Mass spectrometer: quadrupole mass spectrometer, magnetic-sector-type mass spectrometer or any other suitable type, having the characteristics specified below:

— interface temperature: 300 °C;

— ionization method: electron ionization;

— ion source temperature: 230 °C to 300 °C;

— ionizing voltage: 70 eV;

— scan range: mass/charge ratio (m/z): 50 to 600.

4.3 Sampling

4.3.1 In the case of latex, carry out sampling in accordance with ISO 123 and dry the sample in accordance with ISO 124.

4.3.2 In the case of raw rubber and rubber compounds, carry out sampling in accordance with ISO 1795 or ISO 4661-2, respectively.

4.4 Procedure

4.4.1 Put approximately 1 mg to 2 mg of sample into a sample holder (cup or tube).

4.4.2 Put this test sample in the thermal-desorption apparatus, maintained at 340 °C, and start the gas chromatography/mass spectrometry measurement in order to obtain the gas chromatogram and mass spectrum.

If a trap apparatus is used, heat the sample at 340 °C for 1 min and trap the volatile components generated during the heating period in the trap cooled by liquid nitrogen. On completion of the heating period, stop supplying the liquid nitrogen and start the gas chromatography/mass spectrometry measurement in order to obtain the gas chromatogram and mass spectrum.

5 Solvent-extraction method

5.1 Reagents and materials

5.1.1 **Extraction solvent**: acetone of analytical reagent grade.

5.1.2 **Gas chromatograph carrier gas**: helium.

5.2 Apparatus

5.2.1 **Soxhlet extractor**, as specified in ISO 1407.

5.2.2 **Gas chromatograph/mass spectrometer**, as specified in 4.2.3.

5.3 Sampling

See 4.3.

5.4 Procedure

5.4.1 Carry out a Soxhlet extraction, using acetone as solvent, on approximately 2 g of sample that has been cut into cubes measuring 2 mm or less, continuing the extraction for approximately 8 h.

If the 2 g sample does not give enough antidegradant, continue the extraction with more sample.

5.4.2 Concentrate the extract to between 10 ml and 20 ml and inject 1 µl of the concentrated extract into the gas chromatograph/mass spectrometer.

NOTE The amount of concentrated extract injected depends on the amount of antidegradant in the rubber.

If the raw-rubber or unvulcanized-rubber compound is soluble in acetone, the thermal-desorption method should be used instead of the solvent-extraction method.

6 Determination of gas-chromatographic retention index

See Annex C.

7 Analysis

Gas chromatograms and mass spectra of the antidegradants covered by this International Standard are shown in Figures B.1 to B.31, in which the gas-chromatographic peaks characteristic of each antidegradant are indicated. Further details of these peaks are given in Table A.1, including the identity of each component concerned, the retention index of the component and the mass/charge ratios (m/z) of the main peaks in the mass spectrum of each component.

For the particular antidegradant being analysed, display the mass spectrum corresponding to each of the characteristic peaks in the chromatogram and verify that these mass spectra are identical to the mass spectra shown in Annex B.

Note that the retention indices are given for guidance only. Although they are useful for predicting retention times, the identity of an antidegradant shall be confirmed primarily by checking the mass spectra obtained.

Some types of antidegradant are a mixture of several chemical compounds rather than a single compound. In such cases, the gas chromatogram will include more than one set of peaks. The ratios of the quantities of each compound present (which will affect the peak ratios) will depend on the manufacturer and the grade.

There are also cases in which only decomposition products of an antidegradant are detected. In such cases, it is necessary to identify the antidegradant by confirming the presence of a mass spectrum specific to each of the decomposition products of the antidegradant.

Another case which will need to be taken into consideration is that in which more than one antidegradant has been included in the rubber compound.

8 Test report

The test report shall include the following particulars:

a) a full description of the sample and its origin;

b) test method:

   1) a full reference to the test method used, i.e. the number of this International Standard;

   2) the procedure used to extract the antidegradant (thermal desorption or solvent extraction);

c) test details:

   1) the number of test samples analysed;

   2) details of any procedures not specified in this International Standard;

d) the test result (i.e. the identity of the antidegradant found);

e) the date of the test.

Annex A
(normative)

Antidegradants covered by this International Standard

The name, the abbreviation, the CAS registry number, the characteristic components as detected by gas chromatography, the mass/charge ratios of the main peaks in the mass spectrum of each of these components, and the retention indices of the characteristic components are summarized, for the antidegradants covered by this International Standard, in Table A.1.

Table A.1 — Details of antidegradants covered by this International Standard

Number[a]	Name	Abbreviation (see ISO 6472)	CAS RN	Peak number[a]	Component detected	Characteristic mass/charge ratio(s) *m/z*		Retention index
B1	polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	TMQ	26780-96-1	B1-1	2,2,4-trimethyl-1,2-dihydroquinoline	158	173	1 466
				B1-2	dimer	158	331	2 725
				B1-3	trimer	174	519	3 823
B2	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	ETMQ	91-53-2	B2-1	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	202	217	1 762
B3	acetone-diphenylamine condensate	ADPA	68412-48-6	B3-1	diphenylamine	169		1 645
				B3-2	isopropyl diphenylamine	196	211	1 911
				B3-3	9,9′-dimethylacridane	194	209	1 963
				B3-4	unknown	236	251	2 175
B4	reaction product of diphenylamine, aniline and acetone	—	—	B4-1	diphenylamine	169		1 644
				B4-2	9,9′-dimethylacridane	194	209	1 963
				B4-3	unknown	331	348	2 722
				B4-4	unknown	363	378	3 738
B5	*N*-phenyl-α-naphthylamine	PAN	90-30-2	B5-1	phenyl-1-naphthylamine	219		2 205
B6	alkylated diphenylamine	—	68921-45-9	B6-1	diphenylamine	169		1 645
				B6-2	4,4′-dibutyl-diphenylamine	210	281	2 326
				B6-3	4,4′-dioctyl-diphenylamine	322	393	3 004
B7	octylated diphenylamine	ODPA	106-67-7	B7-1	4,4′-dioctyl-diphenylamine	322	393	3 009
B8	4,4′-bis(α,α-dimethylbenzyl)-diphenylamine	—	10081-67-1	B8-1	4,4′-bis (α,α-dimethylbenzyl)-diphenylamine	390	405	3 655
B9	*p*-(*p*-toluenesulfonylamido)-diphenylamine	—	100-93-6	B9-1	*N*-phenyl-*p*-phenylenediamine	184		1 986
				B9-2	*p*-(*p*-toluenesulfonylamido)-diphenylamine	183	338	3 337
B10	*N*,*N*′-di-2-naphthyl-*p*-phenylenediamine	DNPD	93-46-9	B10-1	*N*,*N*′-di-2-naphthyl-*p*-phenylenediamine	360		4 124
B11	*N*,*N*′-diphenyl-*p*-phenylenediamine	DPPD	74-31-7	B11-1	*N*,*N*′-diphenyl-*p*-phenylenediamine	260		2 736

Table A.1 (*continued*)

Number[a]	Name	Abbreviation (see ISO 6472)	CAS RN	Peak number[a]	Component detected	Characteristic mass/charge ratio(s) *m/z*		Retention index
B12	*N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine	IPPD	101-72-4	B12-1	*N*-phenyl-*N*′-isopropyl-*p*-phenylenediamine	211	226	2 153
B13	*N*-1,3-dimethylbutyl-*N*′-phenyl-*p*-phenylenediamine	6PPD	793-24-8	B13-1	*N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine	211	268	2 391
B14	*N*-(1-methylheptyl)-*N*′-phenyl-*p*-phenylenediamine	—	15233-47-3	B14-1	*N*-(1-methylheptyl)-*N*′-phenyl-*p*-phenylenediamine	211	296	2 657
B15	mixed diaryl-*p*-phenylenediamine	—	68953-84-4	B15-1	*N*,*N*′-diphenyl-*p*-phenylenediamine	260		2 728
				B15-2	*N*,*N*′-dimethylphenyl-*p*-phenylenediamine	288		2 810
				B15-3	*N*,*N*′-dimethylphenyl-*p*-phenylenediamine (isomer)	288		2 880
B16	2,6-di-*tert*-butyl-4-methylphenol	BHT	128-37-0	B16-1	2,6-di-*tert*-butyl-4-methylphenol	205	220	1 528
B17	2,6-di-*tert*-butyl-4-ethylphenol		4130-42-1	B17-1	2,6-di-*tert*-butyl-4-ethylphenol	219	234	1 577
B18	styrenated phenol	SPH	61788-44-1	B18-1	α-methylbenzylphenol	183	198	1 744
				B18-2	di-α-methylbenzylphenol	287	302	2 530
				B18-3	tri-α-methylbenzylphenol	391	406	3 082
B19	*n*-octadecyl-3-(4-hydroxy-3′,5′-di-tert-butylphenyl) propionate	—	2082-79-3	B19-1	*n*-octadecyl-3-(4-hydroxy-3′,5′-di-*t*-butylphenyl) propionate	515	530	3 628
B20	2-*t*-butyl-6-(3-*t*-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate	—	61167-58-6	B20-1	2-*t*-butyl-6-(3-*t*-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate	361	394	2 608
B21	2,2′-methylene-bis(4-ethyl-6-*tert*-butylphenol)	*o*-MBp24	88-24-4	B21-1	2,2′-methylene-bis(4-ethyl-6-*tert*-butylphenol)	191	368	2 549
B22	2,2′-methylene-bis(4-methyl-6-*tert*-butylphenol)	*o*-MBp14	119-47-1	B22-1	2,2′-methylene-bis(4-methyl-6-*tert*-butylphenol)	177	340	2 457
B23	4,4′-butylidene-bis(6-*tert*-butyl-*m*-cresol)	*p*-BBp14	85-60-9	B23-1	4,4′-butylidene bis(3-methyl-6-*tert*-butylphenol)	339	382	2 736
B24	4,4′-thio-bis(2-*tert*-butyl-*m*-cresol)	*p*-TBp14	96-69-5	B24-1	4,4′-thio-bis(3-methyl-6-*tert*-butylphenol)	343	358	2 820
B25	butylated reaction product of *p*-cresol and dicydopentadiene	—	68610-51-5	B25-1	2,2′-cyclopentadiene-bis(4-methyl-6-*tert*-butyl-phenol)	445	460	3 746
B26	2,2′-methylene-bis[6-(1-methylcyclohexyl)-*p*-cresol]	*o*-MBp1(1C)	77-62-3	B26-1	2,2′-methylene-bis[6-(1-methylcyclohexyl-*p*-cresol)]	217	420	3 327
B27	2,5-di-*tert*-butyl-hydroquinone	DBHQ	88-58-4	B27-1	unknown	205	220	1 483
				B27-2	2,5-di-*tert*-butyl-hydroquinone	207	222	1 814
B28	2,5-di-*tert*-amyl-hydroquinone	DAHQ	79-74-3	B28-1	2,5-di-pentyl-*p*-benzoquinone	177	248	1 680
				B28-2	2,5-di-*tert*-amyl-hydroquinone	221	250	1 982

Table A.1 (*continued*)

Number[a]	Name	Abbreviation (see ISO 6472)	CAS RN	Peak number[a]	Component detected	Characteristic mass/charge ratio(s) *m/z*		Retention index
B29	tributyl thiourea	—	2422-88-0	B29-1	di-*n*-butylamine	86	129	960
				B29-2	butylisothiocyanate	72	115	1 003
B30	dilauryl thiodipropionate	DLTDP	123-28-4	B30-1	dilauryl thiodipropionate	329	514	3 629
B31	butyl hydroxyanisole	BHA	25013-16-5	B31-1	3-*tert*-butyl-4-hydroxyanisole	165	180	1 495

[a] See Annex B.

Annex B
(informative)

Chromatograms and mass spectra

Chromatograms and mass spectra of antidegradants covered by this International Standard are shown in Figures B.1 to B.31. The chromatograms and mass spetra were obtained under the following conditions:

a) Thermal-desorption apparatus: Frontier-LAB model PY-2020 iD:

   — thermal-desorption temperature: 350 °C.

b) Trap apparatus: not used.

c) Gas chromatograph/mass spectrometer: Agilent 6890 and Agilent 5973:

   — carrier gas flow rate: 1,0 ml/min;

   — total flow rate: 300 ml/min (split ratio 1/300);

   — injector temperature: 320 °C;

   — oven temperature programme: Initial temperature 40 °C, heating by 20 °C/min up to 320 °C, maintained at 320 °C for 10 min;

   — interface temperature: 300 °C;

   — ionization method: electron ionization;

   — ion source temperature: 250 °C;

   — ionizing voltage: 70 eV;

   — scan range: mass/charge ratio (m/z) 29 to 600.

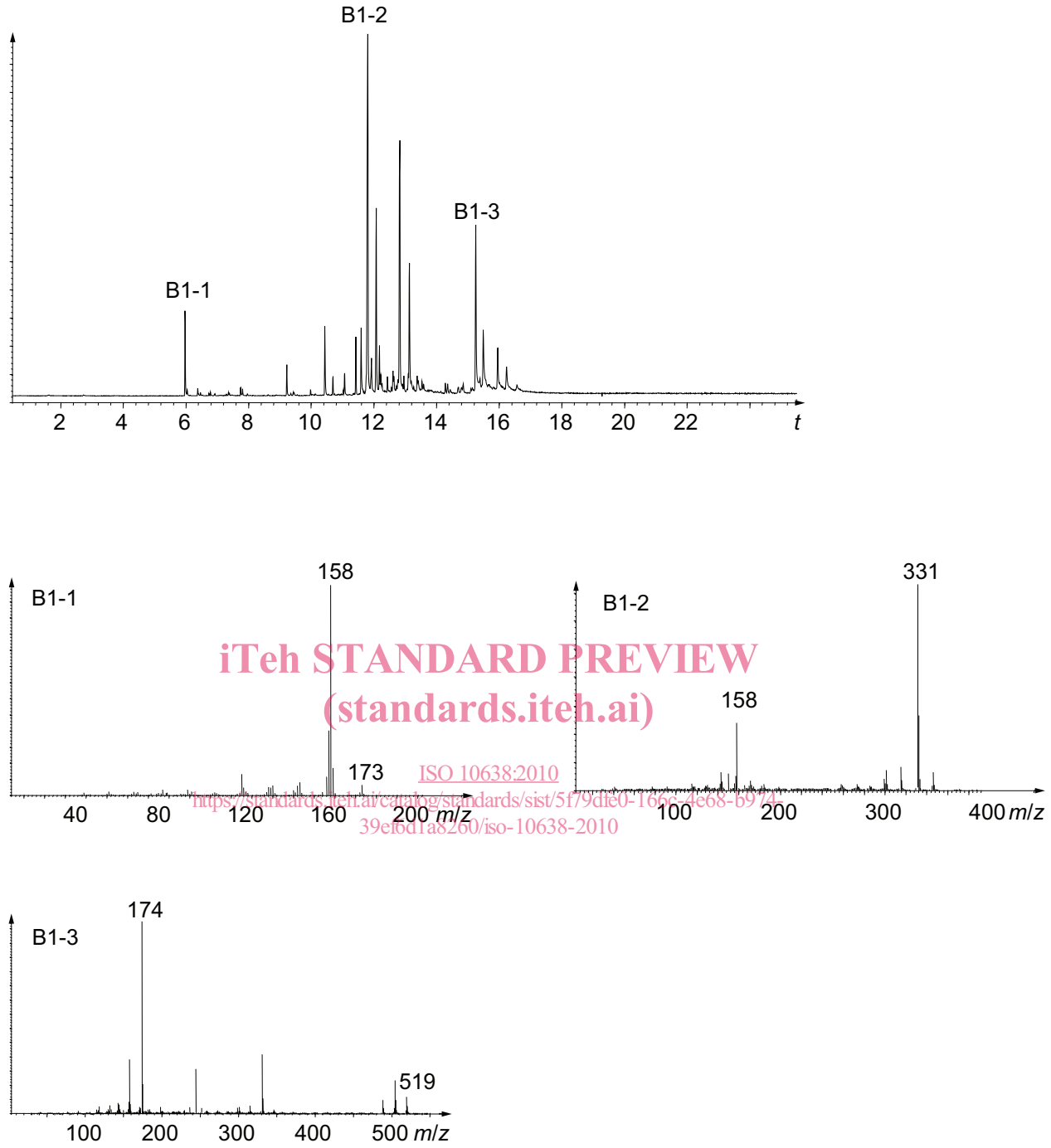
d) Column: Ultra ALLOY-5 (Frontier-LAB):

   — length: 30 m;

   — diameter: 0,25 mm;

   — liquid phase: 5 % diphenyl-, 95 % polydimethylsiloxane;

   — film thickness: 0,25 µm.



Key

t time (minutes)

m/z mass/charge ratio

Figure B.1 — Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline