
**Rubber, raw synthetic — Determination of
antidegradants by high-performance
liquid chromatography**

*Caoutchouc synthétique brut — Détermination des agents de protection
par chromatographie en phase liquide à haute performance*



Reference number
ISO 11089:2010(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.

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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 11089 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This second edition cancels and replaces the first edition (ISO 11089:1997), which has been technically revised (*N*-phenyl- β -naphthylamine has been deleted from the antidegradants determined and precision data have been added as Annex A).

Rubber, raw synthetic — Determination of antidegradants by high-performance liquid chromatography

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 describes a procedure for the determination of the following antidegradants in raw synthetic rubbers:

- *N*-alkyl-*N'*-phenyl-*p*-phenylenediamine;
- *N*-aryl-*N'*-aryl-*p*-phenylenediamine;
- poly-2,2,4-trimethyl-1,2-dihydroquinoline.

Extender oils, when present, can interfere.

The method, with modification if necessary, can be applied to the determination of other amine antidegradants.

2 Principle

The antidegradant, following quantitative extraction from the rubber, is separated by high-performance liquid chromatography (HPLC) from other extracted components, and its component peaks detected and their areas measured. Its concentration in the rubber is calculated by comparison with the area of the antidegradant component peaks of a known amount of the same antidegradant analysed under the same analysis conditions.

NOTE Some antidegradants contain more than one component peak and the ratio of the areas of single component peaks may differ depending on the source of the antidegradant. The procedure described will give 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.

3 Materials

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

3.2 Eluent B: methanol (HPLC grade).

3.3 Extraction solvent: a 2:1 (by volume) mixture of isopropanol (HPLC grade) and dichloromethane (HPLC grade).

4 Apparatus

4.1 HPLC apparatus, with gradient elution capability, a 10 mm³ fixed-loop injector, a variable-wavelength ultraviolet-visible (UV-VIS) detector and a recording-integrator data system.

4.2 HPLC column, reverse-phase type.

Different columns may be used provided a good separation of antidegradant component peaks from other extracted components is obtained. The method has been tested using 5 µm particle size HYPERSIL ODS and SPHERI-5 ODS¹⁾ columns. However, the elution programme might need to be modified when columns different from the ones described in this International Standard are used.

4.3 Ultrasonic bath, typically of about 2 dm³ 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.

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

5 Chromatographic conditions

5.1 Pump A: Elution solvent A (3.1).

5.2 Pump B: Elution solvent B (3.2).

5.3 Flow rate: 0,25 cm³/min.

5.4 Column oven temperature: 40 °C.

5.5 Injection volume: 10 mm³ (10 µl).

5.6 Detector wavelength:

— poly-2,2,4-trimethyl-1,2-dihydroquinoline: 233 nm;

— all other antidegradants: 295 nm.

5.7 Reference wavelength: 550 nm.

5.8 Elution programme:

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

1) HYPERSIL ODS and SPHERI-5 ODS are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

6 Procedure

6.1 On a laboratory mill, thinly sheet, to about 0,25 mm to 0,5 mm thickness, a representative sample of the rubber to be analysed. Cut about 1 g of the thinly sheeted sample into small pieces about 5 mm square. Carry out the procedure in 6.2 to 6.10 twice, on duplicate test portions.

6.2 Weigh, to the nearest 0,1 mg, about 200 mg of the small pieces and place each test portion into a 20 cm³ flask.

6.3 Add accurately, by pipette, 10 cm³ of extraction solvent (3.3) and stopper the flask.

6.4 Extract in the ultrasonic bath (4.3) for 3 h at a temperature not exceeding 30 °C.

NOTE Should the bath temperature exceed 30 °C, the flask could rupture. Therefore it might be necessary periodically to add cold water to the bath during the extraction in order to maintain the bath below 30 °C.

6.5 Weigh, to the nearest 0,01 mg, a quantity of the reference antidegradant as close to the expected quantity of antidegradant contained in the test portion and place in a 20 cm³ flask.

6.6 Add accurately, by pipette, 10 cm³ of extraction solvent (3.3), stopper the flask and dissolve the reference antidegradant, using the ultrasonic bath below 30 °C, if necessary.

6.7 Inject into the HPLC column (4.2) a 10 mm³ volume of the rubber sample extract prepared in 6.4 and elute in accordance with the programme given in 5.8.

6.8 Record the areas of the sample antidegradant peaks.

6.9 Inject into the HPLC column a 10 mm³ volume of the reference antidegradant solution prepared in 6.6 and elute in accordance with the programme given in 5.8.

6.10 Record the areas of the reference antidegradant peaks.

7 Expression of results

Calculate the concentration of antidegradant in the sample for each of the two determinations, using the following equation:

$$\% \text{ antidegradant} = \frac{m_s \times A_c}{m_c \times A_s} \times 100$$

where

m_s is the mass, in milligrams, of the reference antidegradant test portion;

m_c is the mass, in milligrams, of the sample test portion;

A_s is the area of the reference antidegradant peaks;

A_c is the area of the sample antidegradant peaks.

Record the average of the two results.

8 Precision

See Annex A.

9 Test report

The test report shall include the following particulars:

- a) a reference to this International Standard;
- b) all details necessary for the identification of the sample;
- c) the concentration, in percent, of the antidegradant in the sample;
- d) the date of the test.

Annex A (informative)

Precision

A.1 General

An interlaboratory test programme (ITP) was conducted in 2008, using the precision procedures described in ISO/TR 9272:2005, *Rubber and rubber products — Determination of precision for test method standards*. Refer to this edition for further details of, and terminology used in, the determination of precision data.

The ITP was conducted on two different mixes obtained by the addition of 1 part (by mass) of antidegradant to 100 parts (by mass) of SBR 1500. One mix contained *N*-1,3-dimethylbutyl-*N'*-phenyl-*p*-phenylenediamine (6PPD) while the other mix contained *N,N'*-ditolyl-*p*-phenylenediamine (DTPD) (a single antidegradant in each mix). The mixes were prepared on a roll mill maintained at room temperature.

Seven laboratories participated in the ITP and, since the precision was determined directly on the target material with only limited preparation before the analysis, this ITP generated a type 1 precision.

A.2 Precision results

A.2.1 The precision results obtained for each of the two rubber mixes are given in Table A.1. These results were calculated using the outlier deletion procedures described in ISO/TR 9272:2005. Table A.1 also lists the number of laboratories remaining after the deletion of laboratories that had produced outliers. General statements on the use of the precision results are given in A.2.2 and A.2.3 for the absolute precision, r and R , and for the relative precision, (r) and (R) , respectively.

A.2.2 Repeatability: The repeatability, r , of the test method has been established as 0,24 percentage points. Two single test results, obtained under repeatability conditions, i.e. in the same laboratory, that differ by more than 0,24 percentage points should be considered as suspect, i.e. to have come from different populations, and should suggest that some appropriate investigative action be taken.

A.2.3 Reproducibility: The reproducibility, R , of the test method has been established as 0,36 percentage points. Two single test results, obtained under reproducibility conditions, i.e. in different laboratories, that differ by more than 0,36 percentage points should be considered as suspect, i.e. to have come from different populations, and should suggest that some appropriate investigative action be taken.

Table A.1 — Precision data for percentage of antidegradants in rubber

Material	Mean level %	Within laboratory			Between laboratories			No. of labs ^a
		s_r	r	(r)	s_R	R	(R)	
6PPD in SBR	1,04	0,06	0,16	15,4	0,15	0,41	39,5	6
DTPD in SBR	1,14	0,11	0,31	27,4	0,11	0,31	27,4	5
Average value ^b	1,09	0,08	0,24	21,4	0,13	0,36	33,4	
Notation used: s_r is the within-laboratory standard deviation (in measurement units); r is the repeatability (in measurement units); (r) is the repeatability (as a percentage of the mean level); s_R is the between-laboratory standard deviation (in measurement units); R is the reproducibility (in measurement units); (R) is the reproducibility (as a percentage of the mean level).								
^a Number of labs after deletion of outliers; three-step analysis; total of seven labs participated.								
^b Simple averages calculated.								

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