INTERNATIONAL STANDARD

ISO 21461

Third edition
2012-06-01

Rubber — Determination of the aromaticity of oil in vulcanized rubber compounds

Caoutchouc — Détermination de l'aromaticité des huiles dans les mélanges vulcanisés

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

Reference number
ISO 21461:2012(E)

© ISO 2012

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

COPYRIGHT PROTECTED DOCUMENT

© ISO 2012

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

© ISO 2012 – All rights reserved

Contents

Page

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

© ISO 2012 – All rights reserved

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 21461 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*.

This third edition cancels and replaces the second edition (ISO 21461:2009), which has been technically revised.

— In the reagents, *n*-hexane has been replaced by *n*-heptane and methylene chloride is no longer used.

— The precision data have been improved and transferred to an informative annex (Annex C).

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

© ISO 2012 – All rights reserved

Rubber — Determination of the aromaticity of oil in vulcanized rubber compounds

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all 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.

IMPORTANT — The electronic file of this document contains colours which are considered to be useful for the correct understanding of the document. Users should therefore consider printing this document using a colour printer.

1 Scope

This International Standard provides a method for the selective determination of polyaromaticity of oil in vulcanized rubber compounds. The method is based on nuclear magnetic resonance (NMR) spectrometry.

2 Normative references

iTeh STANDARD PREVIEW

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.

(standards.iteh.ai)

ISO 1407, *Rubber — Determination of solvent extract*

ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
PAH
polycyclic aromatic hydrocarbon
organic compounds consisting of two or more aromatic rings where certain carbon atoms are common to two or three rings

4 Reagents and materials

All reagents shall be of recognized analytical grade unless specified in a different way.

4.1 Extraction

4.1.1 Acetone.

4.2 Sample preparation reagents

4.2.1 *n*-Heptane, pa grade.

4.2.2 Nitrogen, purity required > 99,9 %, for protecting the extract from oxidation during the drying step.

4.2.3 Hexamethyldisiloxane (HMDS), 99,5 %, NMR grade, or **tetramethylsilane (TMS)**, 99,5 %, NMR grade.

© ISO 2012 – All rights reserved

4.2.4 Deuterated chloroform ($CDCl_3$), > 99,95 % deuteration degree, NMR grade containing 0,05 % TMS or 0,03 % HMDS (4.2.3). The resonance peak of either TMS or HMDS is used for the calibration of the horizontal scale of the spectrum.

4.2.5 Acetaldehyde, purity ≥ 99,5 %, may optionally be added at a concentration of 0,6 % to the deuterated chloroform containing the TMS or HMDS (4.2.4). The added acetaldehyde provides a resonance peak at around 9,8 ppm which is useful for a good phasing of the spectrum. The solution has to be prepared freshly in order to avoid interference from acetaldehyde decomposition products formed upon ageing.

5 Apparatus

5.1 Analytical balance, accurate to 0,1 mg.

5.2 Extraction apparatus, as specified in ISO 1407.

5.3 Steam bath.

5.4 Extract purification apparatus, consisting of the items specified in 5.4.1 to 5.4.4.

5.4.1 For single sample purification at one time (manually operated filtration):

a) **2 cm^3, 5 cm^3, 10 cm^3 and 25 cm^3 or 30 cm^3 syringes** with conical end fitting compatible with solid phase extraction (SPE) columns for manually operated purification.

b) **SPE cartridge containing 500 mg or 1 000 mg of silica gel**[1].

iTeh STANDARD PREVIEW
(standards.iteh.ai)

5.4.2 For simultaneous purification of multiple samples (optional):

ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-911bcadce7c6/iso-21461-2012

a) **2 cm^3, 5 cm^3, 10 cm^3 and 25 cm^3 or 30 cm^3 syringes** with conical end fitting compatible with Solid Phase Extraction (SPE) columns for manually operated purification.

b) **SPE cartridge containing 500 mg or 1 000 mg of silica gel**[2].

c) **Solid phase filtration equipment connected to a vacuum pump**, for simultaneous purification of many samples[3].

d) **Glass test tubes**, to collect the filtrate and compatible with the filtration device[4].

5.4.3 Laboratory glassware.

5.4.4 Disposable needle.

5.5 NMR spectrometer, at least 200 MHz, preferably with the following acquisition parameters:

— probe: ^1H;

---

1) Varian Bond Elut JR-SI, 1 000 mg, Part number: 12166008B or equivalent. This is an example of a suitable supplier. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this supplier.

2) Varian Bond Elut Mega BE-SI, 1 000 mg, Part number: 12256008 or equivalent. This is an example of a suitable supplier. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this supplier.

3) Varian Vac Elut 20 Manifold with tall glass basin, Part number: 12234104 or equivalent. This is an example of a suitable supplier. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this supplier.

4) For Varian Vac Elut 20, test tubes 16 mm diameter X 150 mm length.

© ISO 2012 – All rights reserved

— pulse phase: 30°;

— spectral width: – 2 ppm to + 12 ppm;

— number of scans: 256;

— relaxation delay: 2 s.

6 Procedure

6.1 Sample extraction

6.1.1 The compound sample shall be of sufficient size to provide at least 350 mg of extracted oil. In case of tyres, refer to Annex B for sample preparation.

6.1.2 Pass the sample between the rolls of a laboratory mill to reduce its thickness to less than 0,7 mm or, alternatively, cut the sample in pieces smaller than 1 mm × 1 mm × 2 mm.

6.1.3 Wrap the sample in a small filter paper and insert it in the extractor (5.2) or fill the extractor with the small cut pieces. Fill the flask of the extractor with acetone (4.1.1) and extract for 8 h.

6.1.4 Evaporate the extract to dryness under a stream of nitrogen (4.2.2) to prevent oxidation.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

6.2 Extract purification

6.2.1 Weigh the dried extract to the nearest 0,1 mg. Add the amount of *n*-heptane (4.2.1) necessary to bring the concentration to 100 mg/cm^3. There may be some insoluble matter. Prepare three vials containing 1 cm^3 each of the *n*-heptane solution.

ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

6.2.2 Condition the SPE cartridge (see 5.4.1 or 5.4.2) by eluting 5 cm^3 or 10 cm^3 of *n*-heptane (4.2.1) using the 5 cm^3 or 10 cm^3 syringe (see 5.4.1 or 5.4.2).

6.2.3 When the *n*-heptane is nearly completely eluted, transfer quantitatively the *n*-heptane solution from one vial (6.2.1) onto the SPE cartridge and start the collection in a beaker or glass test tube. Use an additional 0,5 cm^3 *n*-heptane portion to rinse the vial and ensure complete transfer of the evaporation residue.

6.2.4 When the *n*-heptane solution is nearly absorbed onto the SPE cartridge, elute the non-polar fraction with 25 cm^3 of *n*-heptane. During the elution, maintain a constant solvent flow not exceeding a rate of 5 cm^3/min.

6.2.5 Stop collecting the purified fraction when all of the 25 cm^3 of *n*-heptane has been added to the SPE cartridge.

6.2.6 Evaporate the eluted residue to dryness under a stream of nitrogen (4.2.2) to prevent oxidation. In order to accelerate the final drying step, the sample can be put in a vacuum oven at 50 °C for 2 h to 3 h.

6.2.7 Weigh the dry residue to the nearest 0,1 mg and calculate the percentage of recovery.

6.2.8 Repeat the extract purification procedure two more times, using the other two vials prepared in advance in step 6.2.1.

6.2.9 Calculate the average value of the three percentages of recovery (from 6.2.7). If the individual values obtained are within ± 5 % of the average, proceed to 6.3. Otherwise repeat the sample preparation until three values are within ± 5 % of the average recovery.

© ISO 2012 – All rights reserved

6.3 NMR analysis

6.3.1 Principle

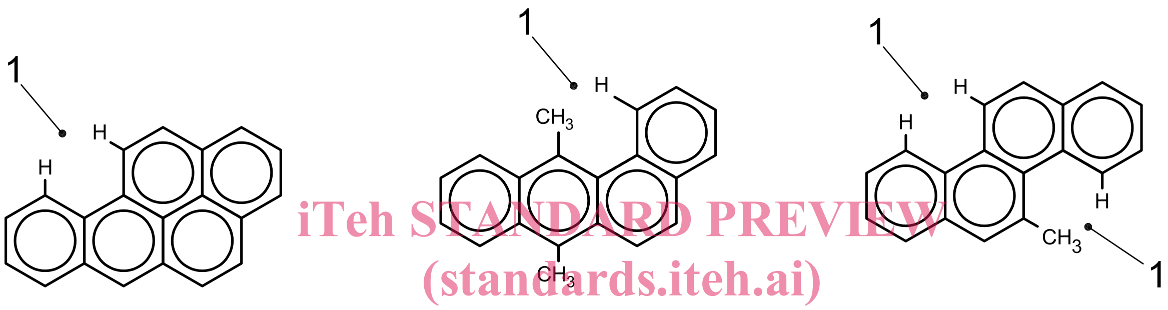
The aromatic character of the oil present in the dry residues obtained in 6.2.7 and 6.2.8 is determined by means of ^{1}H-NMR spectroscopy.

The molecular structure of non-linear PAH with three or more fused rings contains a characteristic three-sided concave area, located at the periphery of the aromatic hydrocarbon molecule: these specific hydrogen atoms in this area are called bay region hydrogens (see Figure 1).

^{1}H-NMR spectroscopy can identify and quantify selectively the hydrogen atoms in the bay region, which are characteristic for aromatic oils.

This method describes the procedure to determine the percentage of bay region hydrogens (% H_{Bay}) in a sample solution by ^{1}H-NMR, thus concluding on the aromatic character of the oil.

The higher the amount of bay region hydrogens, the higher is the aromaticity.



iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 21461:2012
https://stand... 5-b57b-4... 9118eadceb78/iso-21461-2012

a) Benzopyrene **b) 7,12-Dimethylbenzanthracene** **c) 5-Methylchrysene**

Key

1 bay region

Figure 1

6.3.2 NMR measurement

6.3.2.1 Dissolve one of the dry residues obtained in 6.2.7 and 6.2.8 in a glass vial [for example, about 1 cm^3 of $CDCl_3$ (4.2.4) for a 5 mm tube]. If necessary, enhance dissolution by using a small magnetic stirrer or mechanical shaker; if this is not enough, add more $CDCl_3$.

6.3.2.2 Acquire the free induction decay (FID) signal and apply a Fourier transform, multiplying by an exponential function (LB = 0,3 Hz) to obtain the spectrum (see the examples in Annex A). Adjust the resonance of the reference peak to 0,00 ppm for TMS, or to 0,06 ppm for HMDS, respectively.

6.3.2.3 Correct the baseline of the spectrum.

6.3.2.4 Correct the baseline by using a cubic spline correction, setting points for the correction at 11,5 ppm, 10,5 ppm, 6,0 ppm, −0,5 ppm and −1,5 ppm. An example of a spectrum after phase correction and after baseline correction is shown in Figure 2.

6.3.2.5 Integrate the spectrum and record the following areas:

 © ISO 2012 – All rights reserved

I_0 the aromatic proton area, from 6,0 ppm to 9,5 ppm, including the $CHCl_3$ signal (impurity contained in $CDCl_3$);

I_{00} the area of the aliphatic and ethylenic proton regions from 0,2 ppm to 5,8 ppm, including the water signal (water from $CDCl_3$) at around 1,5 ppm;

I_2 the area of the bay proton region from 8,3 ppm to 9,5 ppm.

6.3.2.6 As a solvent blank, measure the ^{1}H-NMR spectrum of the deuterated chloroform containing TMS or HMDS (4.2.4). Using this blank, the aromatic area I_0 and the aliphatic and ethylenic area I_{00} are corrected for the solvent impurity ($CHCl_3$) and the water content of the solvent.

The corrections above are done using the following equations:

$$I_1 = I_0 - \mathrm{CH_{blank}} \times \left(\frac{\mathrm{TMS}}{\mathrm{TMS_{blank}}} \right) \tag{1a}$$

or

$$I_1 = I_0 - \mathrm{CH_{blank}} \times \left(\frac{\mathrm{HMDS}}{\mathrm{HMDS_{blank}}} \right) \tag{1b}$$

$$I_3 = I_{00} - \mathrm{Water_{blank}} \times \left(\frac{\mathrm{TMS}}{\mathrm{TMS_{blank}}} \right) \tag{2a}$$

iTeh STANDARD PREVIEW
(standards.iteh.ai)

or

$$I_3 = I_{00} - \mathrm{Water_{blank}} \times \left(\frac{\mathrm{HMDS}}{\mathrm{HMDS_{blank}}} \right) \tag{2b}$$

ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

where

$\mathrm{CH_{blank}}$ is the integrated area from 6,0 ppm and 9,5 ppm in deuterated chloroform containing TMS or HMDS (4.2.4);

$\mathrm{Water_{blank}}$ is the integrated area from 1,0 ppm to 1,8 ppm in deuterated chloroform containing TMS or HMDS (4.2.4). This integrated signal intensity accounts for the water content in the solvent;

$\mathrm{TMS_{blank}}$ or $\mathrm{HMDS_{blank}}$ is the integrated signal intensity of TMS (or HMDS) in deuterated chloroform containing TMS or HMDS (4.2.4);

TMS or HMDS is the integrated signal intensity of TMS or HMDS in the sample solution (4.2.4).

6.3.2.7 Optional procedure using acetaldehyde:

In case of difficulties in obtaining a good phasing of the spectrum, it is permissible to add 0,6 % of acetaldehyde to the chloroform solution (see 4.2.5) to help phasing the spectrum: the phase correction is done using the peaks at around 9,8 ppm (acetaldehyde) and at 0,0 ppm (TMS) or at 0,06 ppm (HMDS). Processing is done in the same way as for the samples without acetaldehyde, with the following modifications.

— The integral I_{00} includes also the acetaldehyde aliphatic proton signal at around 2,2 ppm.

— The correction for the aliphatic protons of the acetaldehyde is done using the integrated signal intensity (AA) of the aldehydic proton (CHO at around 9,8 ppm) in the sample, as the concentration of acetaldehyde is likely to change with time due to the very low boiling point (21 °C).

— The additional correction to be applied to the integral I_3 to account for the presence of acetaldehyde is:

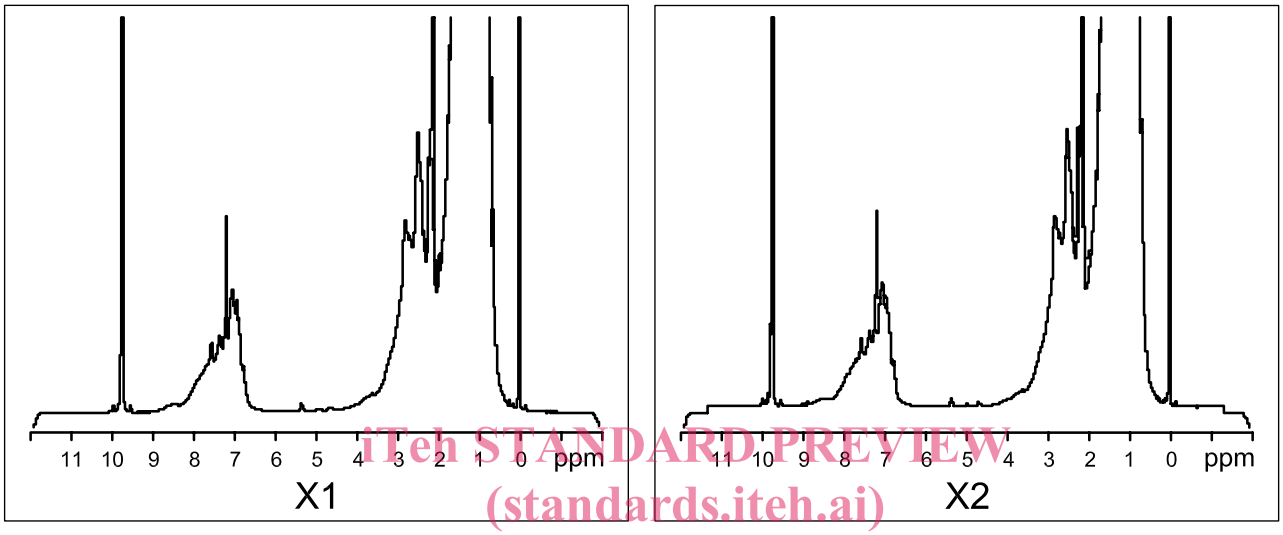
© ISO 2012 – All rights reserved

$$I_3 = I_{00} - \text{Water}_{\text{blank}} \times \left(\frac{\text{TMS}}{\text{TMS}_{\text{blank}}} \right) - 3 \times AA \quad (2c)$$

or

$$I_3 = I_{00} - \text{Water}_{\text{blank}} \times \left(\frac{\text{HMDS}}{\text{HMDS}_{\text{blank}}} \right) - 3 \times AA \quad (2d)$$

6.3.2.8 Perform NMR measurements on each of the three purified extracts obtained in 6.2.7 and 6.2.8.



iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/3781485-1b57b-4284-aacb-9118eadceb78/iso-21461-2012

a) After phase correction **b) After baseline correction**

Figure 2

7 Calculation

For each of the three purified extracts, calculate the percentage of bay region hydrogens (% H_{Bay}) within two decimals using the following equation:

$$\%\, H_{Bay} = \frac{I_2}{I_1 + I_3} \times 100$$

where the symbols are as defined in 6.3.2.6 (or 6.3.2.7).

8 Test report

The test report shall include the following information:

a) a reference to this International Standard (ISO 21461);

b) all details necessary for the identification of the rubber sample(s);

c) detailed information on silica gel for solid phase extraction (SPE) in (5.4.1 or 5.4.2);

d) each value of the three percentages of recovery in (6.2.7 and 6.2.8) and the average in (6.2.9);

e) the average values of I_1, I_2, I_3 and percentage of H_{Bay};

© ISO 2012 – All rights reserved

f) any unusual features during the determination;

g) any operation not included in this International Standard, or any operation regarded as optional such as the NMR parameters in (5.5) if different from the specified one;

h) the date of the test.

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 21461:2012
https://standards.iteh.ai/catalog/standards/sist/378148f5-b57b-4284-aacb-9118eadceb78/iso-21461-2012

© ISO 2012 – All rights reserved