TECHNICAL REPORT

ISO/TR 16314

First edition
2010-11-01

Rubber — Measurement of the aromaticity of oil in reclaimed rubbers

Caoutchouc — Détermination de l'aromaticité des huiles dans les caoutchoucs régénérés

Reference number
ISO/TR 16314:2010(E)

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Foreword

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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.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

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ISO/TR 16314 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 — Measurement of the aromaticity of oil in reclaimed rubbers

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1 Scope

This Technical Report provides a method for the selective determination of polyaromaticity of oil in reclaimed rubbers. The method is based on nuclear magnetic resonance (NMR) spectrometry.

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 1407, *Rubber — Determination of solvent extract*

3 Terms and definitions

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

3.1
polycyclic aromatic hydrocarbon
PAH
organic compound consisting of two or more aromatic rings, certain carbon atoms of which are common to two or three rings

4 Reagents and materials

All reagents shall be of recognized analytical grade unless otherwise specified.

4.1 Extraction solvent

4.1.1 Acetone.

4.2 Sample preparation reagents

4.2.1 *n*-Hexane.

4.2.2 Methylene chloride.

4.2.3 **Nitrogen**, purity $> 99{,}9$ %, for protecting the extract from oxidation during drying.

4.2.4 **$CDCl_3$**, 99,9 %, NMR grade.

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

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 5.4.5:

5.4.1 **2 cm^3, 5 cm^3 and 25 cm^3 or 30 cm^3 syringes**, with conical end fittings, compatible with solid-phase extraction (SPE) columns for manual purification operations.

5.4.2 **SPE cartridge containing 500 mg of silica gel.**[1)]

5.4.3 **Laboratory glassware**.

5.4.4 (Optional) **Solid-phase extraction equipment**, connected to a vacuum pump, for simultaneous purification of many extracts.

5.4.5 **Disposable needles**.

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

- probe: ^1H;
- 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 laboratory sample shall be of sufficient size to provide at least 350 mg of extracted oil.

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.

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1) VARIAN BOND ELUT JR-SI, 500 mg, part number 12162037B, is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product. Equivalent products may be used.

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 (4.2.3) to prevent oxidation.

6.2 Purification of extract

6.2.1 Weigh, to the nearest 0,1 mg, 100 mg ± 5 mg of dry extract into a vial and dissolve it in 1 cm^3 of methylene chloride (4.2.2). There may be some insoluble matter.

6.2.2 Condition the SPE cartridge (5.4.2) by injecting 5 cm^3 of *n*-hexane (4.2.1) onto it using a 5 cm^3 syringe (5.4.1).

6.2.3 When nearly all the *n*-hexane has drained out, transfer quantitatively the methylene chloride solution onto the SPE cartridge and start collecting the eluate in a beaker or glass bottle. Use an additional 0,5 cm^3 of methylene chloride to rinse the vial and ensure complete transfer of the evaporation residue to the cartridge.

6.2.4 When nearly all the methylene chloride solution has been absorbed onto the SPE cartridge, start eluting the non-polar fraction with 25 cm^3 of hexane. 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*-hexane has been added to the SPE cartridge.

6.2.6 Evaporate the eluate to dryness under a stream of nitrogen to prevent oxidation.

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

6.2.8 Repeat the extract purification procedure two more times, taking a fresh portion of extract each time.

6.2.9 Calculate the average of the three percentage recovery values. If the individual values obtained are within ±5 % of the average, proceed to 6.3. Otherwise, repeat the sample extraction and extract purification procedure until three values within ±5 % of the average are obtained.

6.3 NMR analysis

6.3.1 General

The aromatic character of the oil present in the dry residue obtained in 6.2.7 is determined by means of ^1H NMR spectroscopy.

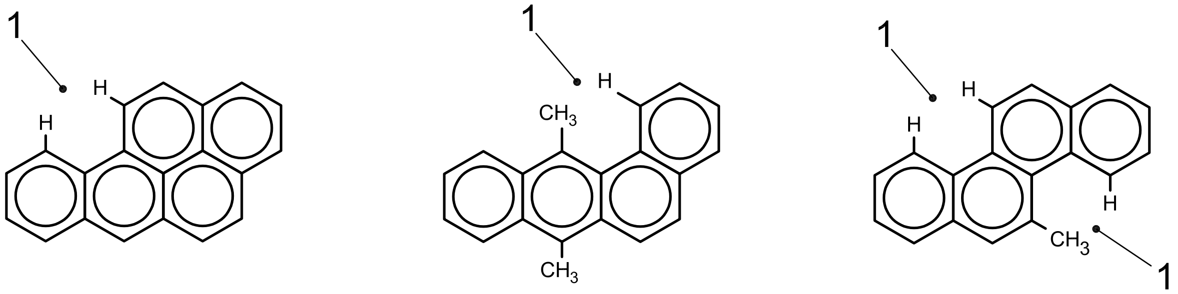
6.3.2 Principle

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

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

This method describes a procedure for determining the percentage of bay region hydrogens (% H_{Bay}) in a sample solution by ^1H NMR, thus giving an indication of the aromatic character of the oil.

The higher the percentage of bay region hydrogens, the higher the aromaticity.



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

Key

1 bay region

Figure 1

6.3.3 NMR measurement

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

6.3.3.2 Prepare the NMR tube by adding the sample solution prepared in 6.3.3.1 and a few drops of reference solvent, HMDS or TMS (4.2.5).

6.3.3.3 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. Adjust the resonance of the reference (HMDS or TMS) peak to 0,0 ppm.

6.3.3.4 Integrate the spectrum and record the following areas:

- I_0 the aromatic area, from 6,0 ppm to 9,5 ppm, including the $CHCl_3$ signal (impurity contained in $CDCl_3$);
- I_{CHCl_3} the $CHCl_3$ signal (located around 7,2 ppm);
- I_1 the pure aromatic area (= $I_0 - I_{CHCl_3}$);
- I_2 the area of the bay region from 8,3 ppm to 9,5 ppm;
- I_3 the area of the aliphatic and ethylenic regions from 0,2 ppm to 5,8 ppm.

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

7 Calculation

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

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

where the symbols are as defined in 6.3.3.4.

8 Test report

The test report shall include the following information:

a) a reference to this Technical Report (ISO/TR 16314);

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

c) details of the silica gel used in the solid-phase extraction cartridge (5.4.2);

d) the three percentage recovery values calculated in 6.2.7 and 6.2.8;

e) the average values of I_0, $I_{\mathrm{CHCl_3}}$, I_1, I_2, I_3 and % $\mathrm{H_{Bay}}$;

f) any unusual features noted during the determination;

g) details of any operation not included in this Technical Report, as well as details of any aspect regarded as optional, such as the NMR parameters in 5.5 if different from those specified;

h) the date of the test.

Annex A
(informative)

^{1}H NMR analysis results for typical reclaimed rubbers

Rubber	Type of oil	Bay region hydrogens %
Ecorr RNR30 B01 Rubber Resources (Netherlands)	Non-aromatic	0,15 ± 0,07
Green rubber (Malaysia)	Aromatic	0,57 ± 0,17
Jeng Yuan Tyrec M1 (Malaysia)	Aromatic	0,62 ± 0,18
Union Commercial UCD-103 (Thailand)	Aromatic	0,59 ± 0,18
RBR NE Rubber Resources (Netherlands)	Non-aromatic	0,13 ± 0,07

ICS 83.040.10

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