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Naftni proizvodi - Določevanje aromatičnosti - Spektrometrijska metoda 13C z nuklearno magnetno resonanco (NMR)

Petroleum products - Determination of aromaticity - 13C nuclear magnetic resonance (NMR) spectrometric method

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ICS

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Petroleum products - Determination of aromaticity - ^{13}C nuclear magnetic resonance (NMR) spectrometric method

Produits pétroliers - Détermination de l'aromaticité - Spectrométrie de résonance magnétique nucléaire du carbone 13 (RMN)

This CEN Report was approved by CEN on 1 December 1999. It has been drawn up by the Technical Committee CEN/TC 19.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Foreword

This CEN Report has been prepared by Technical Committee CEN/TC 19 "Petroleum products, lubricants and related products" the Secretariat of which is held by the Netherlands Standardization Institute (NNI)).

Introduction

The aromaticity of a petroleum product is not related to the concentrations of individual aromatic compounds in the product, it represents only the sum of the aromatic substructures present in a particular sample.

In ^{13}C nuclear magnetic resonance spectroscopy, the distinction between olefinic and aromatic carbon is not made easily and, as the value of aromaticity determined by this technique includes carbon from olefins, it is not appropriate for hydrocarbon mixtures containing large amounts of olefinic products.

The method descibed in this Report is based on IP 392/90 [1]with some differences in, and addenda to, sample preparation and some restrictions in spectroscopic parameters.

1. Scope

This CEN Report describes a method of test which can be used for the determination of the aromaticity of petroleum products.

The method described is applicable to all hydrocarbon mixtures that are completely soluble in chloroform, including kerosines, middle distillates, gas oils, coal liquids and other distillate mineral oil fractions, and is not restricted to a particular boiling range.

The lower detection limit for aromaticity by the method is typically in the region of 0,5 %.

WARNING. The use of this method may involve hazardous materials, operations and equipment. This Report does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this Report to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

[1] IP 392/90: Determination of aromatic hydrogen and carbon content - High resolution nuclear magnetic resonance spectroscopy method.

2. Normative references

This CEN Report incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For date references, subsequent amendments to or revisions of any of these publications apply to this CEN Report only when incorporated in it by amendment ofrrevision. For undated references the latest edition of the publication referred to applies.

EN ISO 3170, *Petroleum liquids - Manual sampling.*

EN ISO 3171, *Petroleum liquids - Automatic pipeline sampling.*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods.*

EN ISO 4259, *Petroleum products - Determination and application of precision data in relation to methods of test.*

3. Definitions

For the purposes of this Report, the following definition applies:

3.1
aromaticity
molar ratio of aromatic carbon to total carbon, a dimensionless value usually given as a percentage.

4. Principle

Aromaticity is determined as the ratio of the integrated areas of aromatic and total carbons in the nuclear magnetic resonance (NMR) spectra of a sample evaluated at signal areas from 160 mg/kg to 100 mg/kg for aromatic carbon atoms, and from 60 mg/kg to 5 mg/kg for aliphatic carbon atoms, with the chemical shifts referring to the signal of tetramethylsilane fixed at 0 mg/kg.

5. Reagents

Use only reagents of recognized spectoscopic grade and water conforming to grade 3 of EN ISO 3696.

5.1 Chloroform.

5.2 Deuterochloroform.

5.3 Cr(III) acetylacetonate, as relaxation agent.

5.4 Carbondisulfide.

5.5 Tetramethylsilane (TMS), as internal reference.

CAUTION. These reagents are toxic and should be handled accordingly. Gloves should be worn when handling aromatic compounds.

6. Apparatus

Usual laboratory apparatus and glassware, together with the following:

6.1 Fourier Transform NMR spectrometer, employing the inverse gated pulse technique.

NOTE: A small amount of relaxation agent, e.g. Cr(III) acetylacetonate, is added to the sample solution in order to reduce the delay time between pulses. This delay time needs to be optimized, taking into consideration the relaxation time of the solvent relaxation process in the sample. The optimization of the pulse delay time has an influence on the repetition rate of scans, thus enhancing the signal to noise ratio for a given time of determination.

6.2 Ultrasonic bath.

7. Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171, and/or in accordance with the requirements of national standards or regulations for the sampling of the product under test.

8. Preparation of the test sample

8.1 Dissolve 40 g - 50 g of the sample in chloroform (5.1) containing the necessary amount deuterochloroform (5.2), using an ultrasonic bath (6.2) for 5 min to facilitate dissolution if necessary. In the case of heavy vacuum residues, use 30 g - 100 g of sample.

NOTE 1: The concentration range should not be altered between test samples.

NOTE 2: For some analyses, the sample solution will require filtering but, if this is carried out, there is no guarantee that the test sample will be representative. If the sample solution has been filtered, this should be reported with the results.

8.2 Add 20 mg of Cr(III) acetylacetonate (5.3) per gram of sample together with a small amount of carbondisulfide (5.4).

NOTE: Carbon disulfide generates an additional NMR signal for use as an aid in phase correction.

8.3 Use tetramethylsilane (5.5) as an internal spectral reference for chemical shifts.

9. Procedure

9.1 General

Set up the NMR spectrometer (6.1) in accordance with the manufacturer's instructions, with the magnetic field optimized and stabilized to obtain the best resolution and signal to noise ratio as possible. Optimize the tuning of the excitation and detection coils in the probe and introduce the test sample.

9.2 Quantitative measurements

Select the duration and spacing of the radiofrequency pulses so that a saturation of magnetization is effectively avoided. In order to suppress the unpredictable signal enhancement of the Nuclear Overhauser Effect (NOE) accompanying proton decoupling, use the inverse gated pulse decoupling technique. The NOE is effectively suppressed by applying proton decoupling only during acquisition and switching off of the decoupler at the beginning of the delay period.

9.3 Acquisition parameters

Adjust the spin rate, radiofrequency power, decoupling power, etc. according to the recommendations of the manufacturer of the spectrometer. For other parameters, follow the recommendations given below.

- Memory size:	minimum 16 k datapoints
- Spectral width:	50 mg/kg to 250 mg/kg, with the transmitter set to the centre frequency
- Proton decoupling:	broadband, centred at 5 mg/kg
- Filter width:	minimum value corresponding to the spectral width (optimum value is 1,5 times the spectral width)
- Pulse angle and pulse delay:	pulse angle 90 degrees and delay time 5 s (to avoid magnetic saturation)
- Number of scans:	minimum 1024 scans at 250 MHz proton frequency (for acceptable signal to noise ratio)

9.4 Manipulation of spectral data

Use zero filling to improve the digital solution.

In Gaussion multiplication of the free induction delay (FID), the presence of the relaxation reagent (Cr(III) acetylacetonate) results in a significant line broadening and care should be taken not to apply too rigorous multiplication at the cost of spectral resolution beyond this line broadening.

Carry out phase correction with extreme care, correcting the reference signals at both sides of the spectrum (left: carbondisulfide; right: TMS) to the best possible symmetry and testing the solvent signal also for symmetry.

> NOTE: Experimental experience shows that phase correction is one of the major sources of error in the determination of aromaticity.

Correct the baseline to be as flat as possible; in some cases it may be advantageous to restart processing raw data.

Carry out the integration with the use of separate scaling factors for the aromatic and the aliphatic region in order to produce integral curves as large as possible. Extend the integral curve to both sides of the corresponding region to allow better judgement for correct phase correction. Ensure that the curves are horizontal before and after the signals of the aromatic and aliphatic regions.

Determine the distance between the parallel integration lines corresponding to the signal areas to give the aromatic (*A*) and the aliphatic (*B*) signals and normalize these to the same expansion scale.