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APPLICATION NOTE AN52979

Hydrogen content determination by picoSpin NMR

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Application benefit

The picoSpin 80 Series II NMR spectrometer serves as a cost-effective analytical tool for hydrogen content determination. The picoSpin NMR spectrometer has the advantage of increased functionality compared to time-domain instruments and a low cost of ownership compared to high-field NMR spectrometers.

Keywords

NMR, fuels, petroleum, hydrogen content

The Thermo Scientific picoSpin 80 Series II spectrometer.

Abstract

Nuclear Magnetic Resonance (NMR) is an important tool for measuring hydrogen content in fuel. However, time domain NMR instruments (described below) offer little flexibility, and high-field frequency domain NMR instruments (described below) can be prohibitively expensive. The Thermo Scientific™ picoSpin™ 80 Series II NMR spectrometer can serve as a flexible and economical alternative to time-domain and high-field NMR for this application. In this note, a range of reference compounds and fuel standards were analyzed using a picoSpin 80 Series II NMR spectrometer and the results were compared to their theoretical values as well as to those obtained experimentally using a high-field NMR. For hydrogen content determination, the picoSpin 80 Series II NMR spectrometer offers accuracy and precision comparable to the high-field NMR measurements described in the literature.

Introduction

The combustion of hydrocarbon containing fossil fuels currently serves as the largest source of energy worldwide. The more hydrogen attached to each carbon in the hydrocarbon, the lower the oxidation state of that carbon and the greater the energy released during combustion. Because of this, the hydrogen content is an important parameter of petroleum distillate products.[1]

A number of methods have been developed to determine the hydrogen content in petroleum products. ASTM D5291, a combustion method for determining the hydrogen content of petroleum fuels is limited in that it is not suitable for samples with a low boiling range and is also a destructive technique which restricts repeatability studies.[2] Nuclear Magnetic Resonance (NMR) has long been used for the determination of hydrogen content in petroleum hydrocarbons and various ASTM methods have been published. Earlier NMR methods (ASTM D3701 and ASTM D4808) made use of obsolete continuous-wave spectrometers.[3-4] Subsequently, an updated method ASTM D7171 was published for determining the hydrogen content of middle distillates using a pulsed time-domain (TD) NMR spectrometer.[5] TD-NMR quantifies materials using their different relaxation properties and is found in quality control labs in a variety of industries. However, it is inadequate for obtaining frequency spectra, thus is not capable of structural analysis like frequency-domain NMR spectrometers. Methods for determining hydrogen content in petroleum products have been developed for high-field NMR spectrometers as well, but these instruments are expensive to purchase and maintain, and require a specific NMR facility apart from the factory or testing laboratory.[1,6]

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In this application note, the picoSpin 80 Series II NMR spectrometer was used to determine the hydrogen content in a range of reference materials and petroleum fuel standards. The data shows that the picoSpin NMR spectrometer can serve as an effective, low-cost alternative to high-field NMR for hydrogen content determination.

Experimental

A picoSpin 80 Series II benchtop NMR spectrometer was used to acquire spectra for hydrogen content determination. The spectrometer is an 82 MHz, pulsed, Fourier transform ^{1}H NMR. The instrument contains a 2 Tesla temperature controlled permanent magnet heated to a temperature of 36 °C and is fitted with a 40 microliter capillary cartridge used for sample introduction into the spectrometer. All samples were purchased from Sigma Aldrich® and were used as received.

For hydrogen content determination, a vial was placed on an analytical balance and ~45mg of hexamethyldisiloxane (HMDSO) was added. The mass was recorded and the balance was tared. Then ~300mg of the sample was added to the same vial and the mass was recorded. The vial was capped and shaken until adequately mixed. Five runs were prepared for each sample. The samples were injected into the capillary cartridge using 1 mL slip-tip polypropylene syringes and 22 gauge blunt-tipped needles. All spectra were acquired using 16 scans, 4000 acquisition points and a recycle delay of 40 seconds.

Results and discussion

To determine hydrogen content using the pulsed picoSpin 80 NMR spectrometer, an appropriate internal standard was first selected. Hexamethyldisiloxane (HMDSO) was chosen for this application because it is chemically inert, has a high boiling point, has similar hydrogen content to relevant petroleum samples, and its ^{1}H NMR signal resonates in a region that does not overlap with the samples of interest.[1] Once the spectrum of the mixture containing the internal standard HMDSO and the sample of interest was obtained, the following equation was used to determine the hydrogen content of the sample.

$$H\ (wt\%) = \frac{I\ (Sample)}{I\ (HMDSO)} \times \frac{W\ (HMDSO)}{W\ (Sample)} \times H\ (wt\%)\ (HMDSO)$$

In this equation, the percent hydrogen by weight was determined using the recorded weight of the HMDSO and sample as well as the integration of the peak area of the HMDSO singlet and the combined peak areas of the sample signals. The percent hydrogen of HMSDO has a known value of 11.17% and was used in the equation. An example of a ^{1}H NMR spectrum used for calculating percent hydrogen content in this study is shown with the integrations labeled in Figure 1.

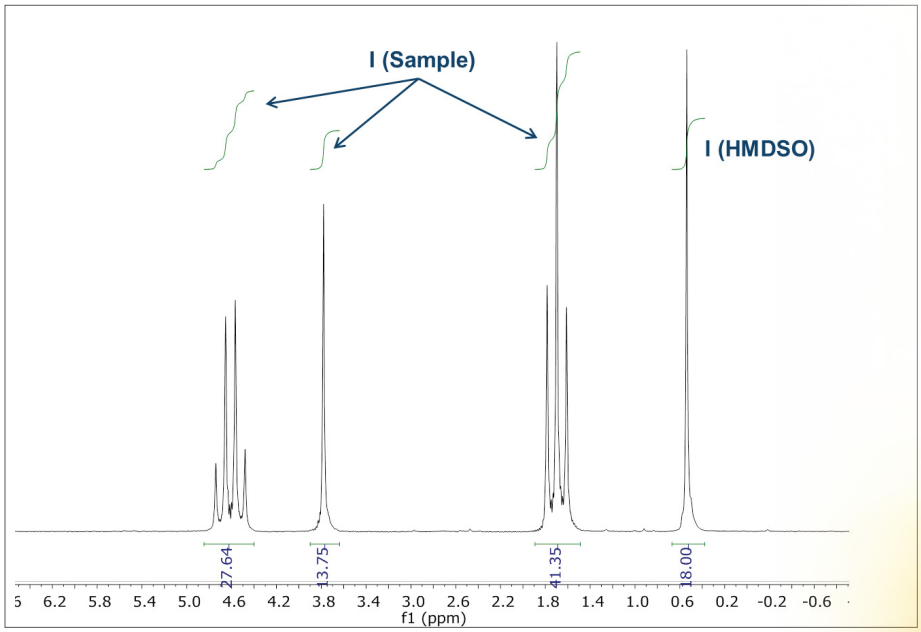

Figure 1: ^{1}H NMR spectrum of diethyl malonate with HMDSO internal standard

To examine the applicability of the picoSpin 80 NMR spectrometer for determining hydrogen content over a range of samples, several reference compounds with known hydrogen content, and published results from other NMR instruments were analyzed.[1,5,6] The reference compounds were first used to examine the precision of the hydrogen content measurement method. The six reference compounds selected represent a hydrogen content range from ~7-15 percent (Table 1). The reported "Ave %H" is an average of 5 runs and the percent relative standard deviation (%RSD) for each compound is shown. In all cases, the %RSD was below 1%. The average %RSD of the six compounds analyzed in this work was 0.44%, on par with the reported results using a high-field instrument.[1]

The accuracy of this method for determining hydrogen content was also examined by using the theoretical % hydrogen content to calculate the relative percent error for each sample. The 6 reference samples examined with the picoSpin spectrometer gave a range of relative error between 0.56% and 2.59%.

These relative error values generally track those reported using a high-field NMR spectrometer, which examined 25 reference samples and reported a range of relative error between -10.58% and 2.65%.[1] On average, the picoSpin method gave an average of 1.58% compared to the high-field instrument which reported 2.75% relative error. The results indicate the low-field picoSpin NMR spectrometer was able to measure hydrogen content of selected reference compounds with similar accuracy to a high-field instrument.[1]

Three ASTM fuel standards were then analyzed and results are summarized in Table 3.

Sample	Ave %H	%RSD
Diethyl Malonate	7.72	0.36
Toluene	8.80	0.32
Mesitylene	10.23	0.19
Cyclohexanone	10.44	0.44
2-Nonanone	13.09	0.41
Dodecane	15.51	0.89

Table 1: Average hydrogen content and % relative standard deviation of five runs per reference sample determined using picoSpin 80 NMR.

Sample	Ave %H	%H theoretical	%Relative error
Diethyl Malonate	7.72	7.55	2.22
Toluene	8.80	8.75	0.56
Mesitylene	10.23	10.06	1.68
Cyclohexanone	10.44	10.27	1.63
2-Nonanone	13.09	12.76	2.59
Dodecane	15.51	15.39	0.77

Table 2: Accuracy of picoSpin 80 NMR spectrometer for determining hydrogen content using five runs per reference sample.

Standard D5307	%H by NMR	Standard D5580	%H by NMR	Standard D5134	%H by NMR
Test 1	15.38	Test 1	14.36	Test 1	14.33
Test 2	15.31	Test 2	14.37	Test 2	14.38
Test 3	15.32	Test 3	14.60	Test 3	14.27
Test 4	15.23	Test 4	14.30	Test 4	14.14
Test 5	15.41	Test 5	14.38	Test 5	14.50
Average	15.33	**Average**	14.40	**Average**	14.32
Theoretical	15.18	**Theoretical**	14.61	**Theoretical**	14.38
%Relative Error	0.98	**%Relative Error**	-1.43	**%Relative Error**	-0.39
%RSD	0.41	**%RSD**	0.71	**%RSD**	0.83

Table 3: . Hydrogen content determination using fuel standards.

ASTM D5307 Crude Oil Internal Standard has a calculated theoretical hydrogen content of 15.18% and is made up of a mixture of C14-C17 hydrocarbons. This is comparable to diesel fuel which typically contains a mixture of C10-C19 hydrocarbons. The average percent hydrogen using the picoSpin spectrometer was determined to be 15.33% which gave a relative error of 0.98% when compared to the theoretical value. The ASTM D5580 Calibration Mix 4 is composed primarily of 2,2,4-trimethylpentane, an important component in gasoline. The picoSpin method yielded a hydrogen content of 14.40%, which gave a relative error of -1.43%. The final standard analyzed was ASTM D5134 Splitter Linearity Check Mix. The obtained hydrogen content of 14.32% also matched closely with its theoretical value of 14.38% with a relative error of -0.39%. ASTM D5580 contained a mixture of C6-C8 hydrocarbons, and ASTM 5134 contains a mixture of C6-C9 hydrocarbons, both of which are within the typical C4-C12 hydrocarbon range of gasoline.

Conclusions

Although there are existing ASTM methods for determining the hydrogen content of fuel and petroleum using NMR spectroscopy, the instruments involved are either obsolete, or limited in their applications. It has been previously shown that high-field NMR is capable of determining the hydrogen content of fuel samples.[1,6] In this work, six reference compounds representing a range of hydrogen contents were analyzed by the picoSpin 80 benchtop NMR spectrometer. The accuracy and precision of the measurement were found to be similar to those obtained with high field instruments.

Three fuel standards mimicking actual fuels were also analyzed, and the hydrogen content agree well with the theoretical and high-field NMR measurements. These results indicate that the picoSpin 80 spectrometer is capable of providing hydrogen content information with similar accuracy and precision to high-field instruments NMR at a significantly reduced cost of ownership.

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