magritek
www.magritek.com

Spinsolve Carbon

Hydrogen Content in Fuels

Total and Aromatic Hydrogen Content Determination in Fuels Using Benchtop NMR Spectroscopy

The **total hydrogen content** is a very important parameter for many petroleum products such as gasoline, jet fuel and kerosene. A higher hydrogen content can result in superior ignition and combustion properties of fuels[1]. Comparing the hydrogen content of feedstocks and products in the catalytic cracking process can provide valuable information about catalyst performance. Another useful parameter for petroleum analysis is the **aromatic hydrogen content**. For example, the aromatic hydrogen content provides important information about the properties of the petroleum, such as the K factor[2].

ASTM method D7171-16[3] describes the determination of the total hydrogen content using time-domain NMR. However, time-domain NMR does not have the frequency resolution required to determine the aromatic hydrogen content, so is not suitable for this type of analysis. In contrast, ASTM method D5292-99[4] describes how high-resolution NMR can be used for the determination of aromatic hydrogen content, but does not provide a method for determining the total hydrogen content.

In this Application Note, a combined method for total and aromatic hydrogen content determination is described that uses the **Spinsolve benchtop NMR spectrometer**. The method is illustrated using gas oil samples but can be applied to a variety of other petroleum products. The method is accurate, fast, robust and requires minimal sample preparation, consumables and instrument calibration.

Instrument Calibration

The instrument is calibrated with a one-time procedure that is performed when setting the system up and is not required before every routine sample measurement. To perform the calibration, two or more of the reference standards listed in ASTM D7171-16 are pipetted into standard 5 mm NMR tubes and a single-scan ^{1}H spectrum of each is collected in 15 seconds. The total peak areas of the spectra are then used to generate a calibration line which is used to determine total hydrogen content in routine measurements. Figure 1 shows a calibration line constructed using five reference compounds, octyl acetate, cyclohexyl acetate, 2-nonanone, 2-phenylethyl acetate and dodecane. The data were recorded on a Spinsolve 43 proton benchtop NMR spectrometer. Note the excellent correlation coefficient of the calibration line, which easily exceeds the ≥ 0.98 criterion given in ASTM D7171-16.

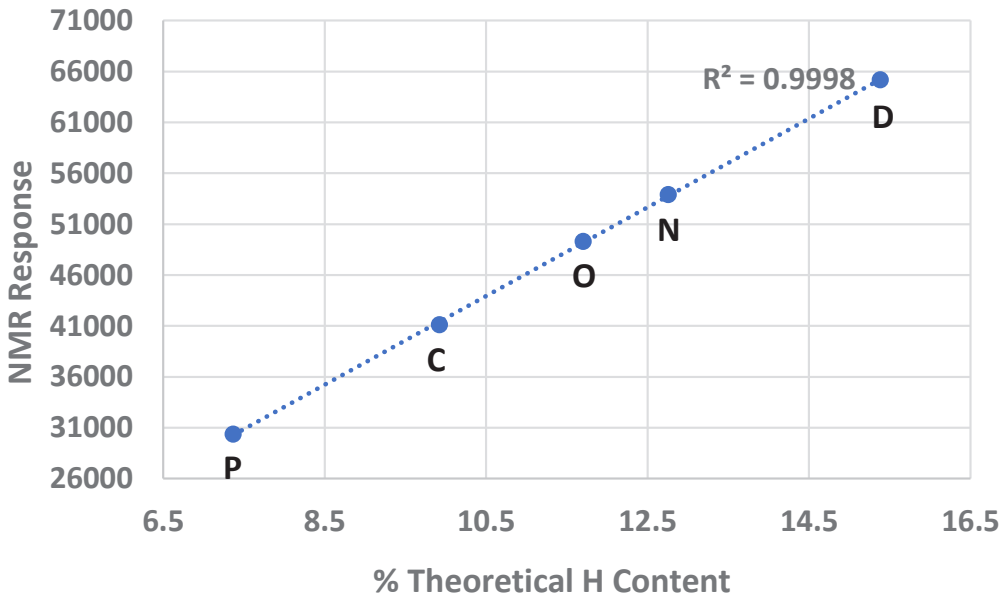

Figure 1. Calibration line for total hydrogen content determination constructed from NMR spectra of reference compounds dodecane (D), 2-nonanone (N), octyl acetate (O), cyclohexyl acetate (C) and 2-phenylethyl acetate (P).

Workflow

The workflow for routine sample measurements on fuel samples is summarized in Figure 2. To prepare the sample, 2.5 mL of fuel is accurately weighed out according to its specific gravity and then diluted with 3.75 g $CDCl_3$ to give a 50% v/v solution. 0.6 mL of the solution is then pipetted into a standard 5 mm NMR tube and inserted into the spectrometer. Prior to scanning the sample, the specific gravity of the neat fuel and the % v/v fuel in the sample are inputted into the spectrometer software interface. The rest of the operation is automated and requires only a single click in the software to start the process. Subsequent samples can be run by simply removing the first NMR tube, replacing it with the next sample, inputting the sample information and clicking the start button again. Multiple samples can be run quickly and easily this way and due to the linear nature of NMR, no re-calibration is required, even if a different petroleum product is measured.

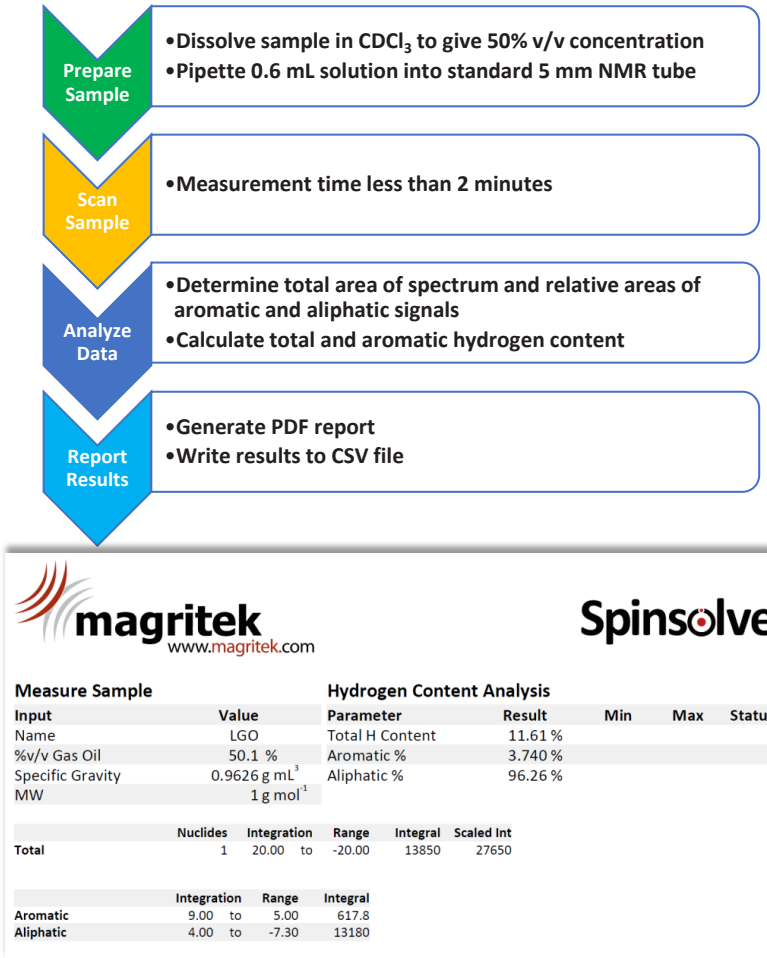

Figure 2. Workflow for hydrogen content measurements on petroleum samples.

The data processing and reporting of results are fully automated and require no NMR data processing expertise. Results are also outputted to a CSV file for importing into a LIMS or other data management system.

Reproducibility

Table 1 lists the results of 10 repeated measurements performed on a typical heavy gas oil (HGO) sample. Each measurement took less than 2 minutes to acquire. The results agreed with the known values for this sample.

Measurement	Mass % Total Hydrogen	Mass % Aromatic Hydrogen
1	11.90	4.95
2	11.74	4.91
3	11.89	4.89
4	11.52	4.90
5	11.68	4.87
6	11.79	4.92
7	11.76	4.97
8	11.62	5.03
9	11.65	5.09
10	11.71	5.14
Average	11.72 +/- 0.12	4.97 +/- 0.09

Table 1. Reproducibility of total and aromatic hydrogen measurements on Spinsolve.

As table 1 illustrates, the results for both the total and aromatic hydrogen content show excellent reproducibility, with standard deviations of 0.12% (1.0% RSD) and 0.09% (1.8% RSD), respectively.

Spinsolve

Conclusions

Accurate and precise measurement of the total and aromatic hydrogen content of gas oils and other fuel products can be performed using the Spinsolve benchtop NMR spectrometer. The sample preparation is straightforward and uses small quantities of solvents and analytes. The measurement time for each sample is short, and the processing and reporting of results are fully automated.

References

1. Ali, M.A. Basit, “Significance of hydrogen content in fuel combustion”, Int. J. Hydrogen Energy, Vol. 18, No. 12, pp. 1009-1011 (1993).

2. James G. Speight (2007). “The Chemistry And Technology of Petroleum (4th ed.)”. CRC Press.

3. ASTM Designation D7171-16, “Standard Test Method for Hydrogen Content of Middle Distillate Petroleum Products by Low-Resolution Pulsed Nuclear Magnetic Resonance Spectroscopy”.

4. ASTM Designation D5292-99, “Standard Test Method for Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy”.

Contact us now for a quote, to request a demo or to measure your samples

Email: sales@magritek.com

Website: www.magritek.com/contact-us

GERMANY	+49 241 9278 7270	**UNITED STATES**	+1 855 667 6835
UNITED KINGDOM	+44 7468 529 615	**NEW ZEALAND**	+64 4 477 7096

For a complete listing of our global offices and distributors visit: www.magritek.com/about-us/distributors/