Energy

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Determining Hydrogen Content in Crude Oils Using Nanalysis Benchtop ^{1}H NMR Spectroscopy

The hydrogen content of a sample, put simply, is a measure of its hydrogen content, by weight. The determination of this parameter in various oil samples is crucial, whether before or after refining, as it is closely related to the product's combustion properties. In many cases, more efficient combustion can be achieved with a sample bearing a larger hydrogen content.[1]

While several methods exist for the determination of hydrogen content in crude oils, fuels and additives, ASTM D5291 remains one of the most widely used.[2] This method allows for testing in a concentration range of 9-16 wt% for hydrogen, while analyses outside of this range would require an alternative approach. Importantly, this specific method is not recommended for the analysis of volatile materials (*e.g.*, gasoline). The use of ASTM D5291 requires an elemental analyzer, which in turn necessitates compressed gases and routine maintenance and calibration.

Nuclear magnetic resonance (NMR) spectroscopy has emerged as an elegant solution to hydrogen content determination in oils. Specifically, the acquisition of a ^{1}H NMR spectrum affords information on all the relevant constituents of these oils, such as paraffins, naphthenes and aromatics.[3] NMR is an inherently quantitative technique, as the area under the curve of the various signals in a spectrum is directly related to the number of atoms in the sample. As such, quantitative NMR (qNMR) is a powerful tool that has been steadily increasing in popularity.[4]

The use of an internal calibrant, in this case hexamethyldisiloxane (HMDSO), provides a quick and simple way of determining hydrogen content by integrating the various regions and making use of the following equation:

$$H\ (wt\%\ Sample) = \frac{I\ (Sample)}{I\ (HMDSO)} \times \frac{W\ (HMDSO)}{W\ (Sample)} \times H\ (wt\%\ HMDSO) \qquad \textbf{(1)}$$

Where I (Sample) is the sum of the sample's integration areas,
I (HMDSO) is the integration area of HMDSO,
W (HMDSO) is the mass of HMDSO,
W (Sample) is the mass of sample
H (wt% HMDSO) is the hydrogen content of HMDSO.

Note that it is extremely important that the masses for both the sample and HMDSO be accurately recorded, as these have a very big impact on the results of these calculations. Likewise, it is crucial that the ^{1}H NMR wspectrum is properly processed in order to obtain accurate integration values.

Table 1. Comparison of running 3000 samples between elemental analysis (EA) (following ASTM D5291 for hydrogen content analysis in oils), and benchtop nuclear magnetic resonance (NMR) spectroscopy.

			Elemental Analyzer	Benchtop NMR
Capital Cost (k USD)	**Equipment**		60	45
	Balance		40	10
	TOTAL		**100**	**55**
Operating Cost (k USD)	**Standards**		2	n/a
	Consumables		1	1
	Oxidation Tubes	*Replace every 1000 samples*	3	n/a
	Reduction Tubes	*Replace every 300 samples*	4	n/a
	Compressed Gases	*Oxygen (99.998%); 100 kPa;* *20 cm^3/min* *Helium (99.995%); 200 kPa;* *40 cm^3/min – reference detector;* *80 cm^3/min – measure detector;* *60 cm^3/min – sample purge;* *Air; 500 kPa*	0.2	n/a
	TOTAL		**10.2**	**1**
Time (min)	**Maintenance**	*Assume 60 min per tube replacement*	13 hours	n/a
	Calibration	*Performed every 10 samples*	150 hours	n/a
	Operating Time		350 hours (7 min/sample)	200 (4 min/sample)
	TOTAL		**513 hours**	**200 hours**

**Gas flow rates as described in ASTM D5291*

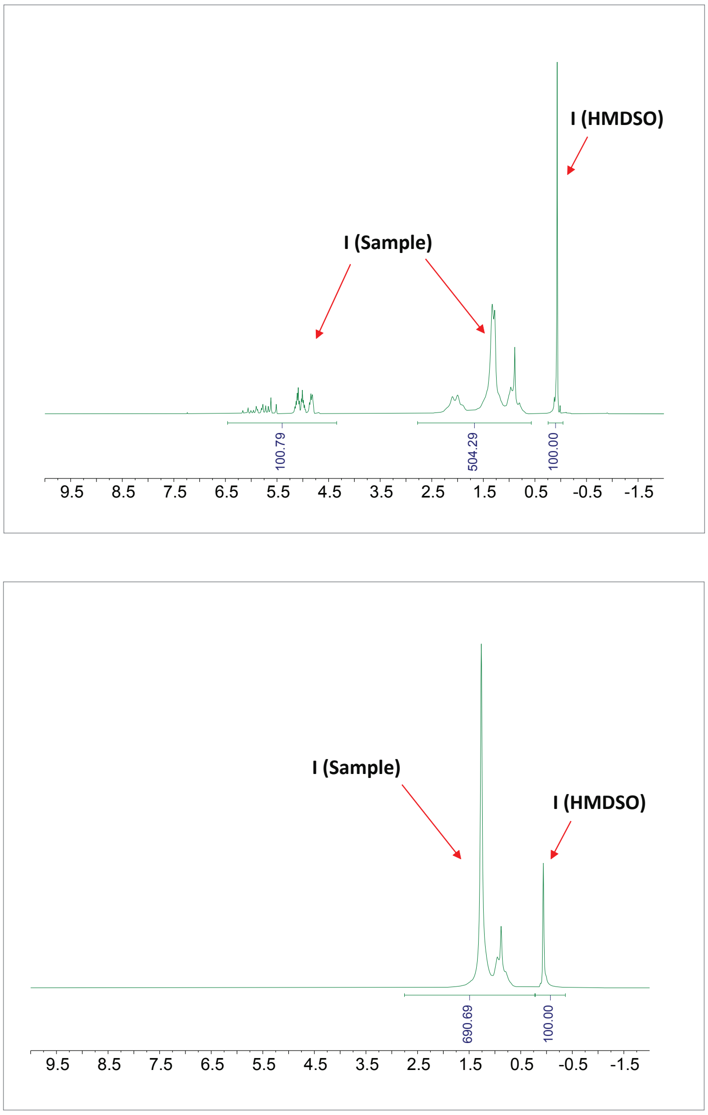

Figure 1. Representative ^{1}H NMR spectrum of 1-octene (top) and undecane (bottom) in $CDCl_3$. The integration regions used in the equation above, namely I (Sample) and I (HMDSO), are highlighted.

The ^{1}H NMR spectra for 1-octene and undecane were acquired in triplicate at 32 °C using a Nanalysis 60PRO instrument at 60.73 MHz proton frequency with the following parameters: spectral width, 40 ppm; spectral center, 10 ppm; number of points, 16384; scans, 8; dummy scans, 0; interscan delay, 23 seconds; pulse angle, 90.00°.

Using Equation (1) and the integration regions for I (Sample) highlighted in **Figure 1**, the hydrogen content in 1-octene and undecane was determined and compared to their theoretical values. The results are summarized in **Table 2**. While 1-octene and undecane were chosen for this study, this method can be applied to a variety of crude oils. Once the region for I (Sample) has been determined and the T_1 values are known, this approach can be expanded to include new types of samples.

Table 2. Results of hydrogen content determination using the 60 MHz benchtop NMR for 1-octene and undecane.

	Hydrogen Content (%)	
	1-Octene	Undecane
Run 1	14.39	15.81
Run 2	14.38	15.93
Run 3	14.23	15.78
Average (A)	**14.33**	**15.84**
Theoretical (B)	14.37	15.47
Difference (A-B)	-0.04	0.37
RSD	0.6	0.5

As evidenced by these results, qNMR is a very useful technique for the determination of hydrogen content in various oils. In addition, benchtop NMR is especially convenient as this allows the analyses to be performed in-house, instead of outsourcing to a third party or having to send these to another laboratory within the company, minimizing both the costs and waiting times associated with these approaches.

References

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