Nutritional Supplement and Diesel Fuel Application Development for Benchtop NMR Systems Operating at 42, 60, and 80 MHz – Equivalency with Supercon NMR

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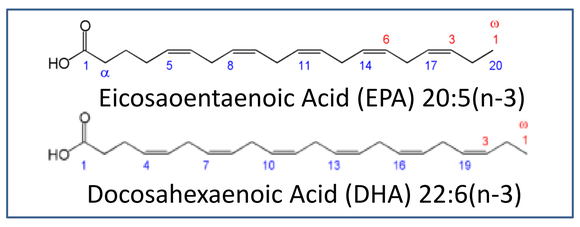
Benchtop high-resolution NMR systems are available at a number of field strengths and probe configurations. However beyond the obvious academic instruction market for these instruments very few applications have been demonstrated across all available platforms and thus proving the general applicability of benchtop NMR technology to industrial quality control. We will present two chemometric-based applications that have been developed at 4 different field strengths utilizing Varian Mercury 300 MHz, Magritek Spinsolve 42 MHz, Aspect AI 60 MHz, and Thermo Picospin 80 MHz NMR systems. Partial-least-squares (PLS) regression correlations were obtained on all 4 platforms relating to:

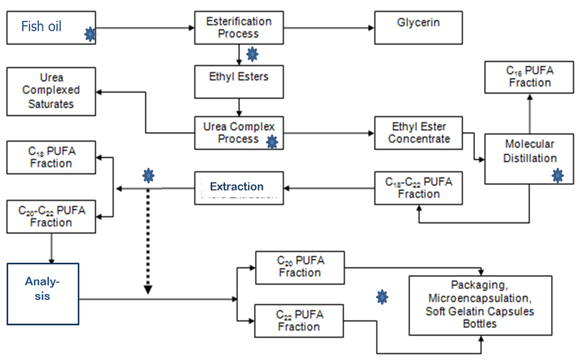
1) Omega-3 fatty acid composition of samples taken from various points in a nutritional supplement manufacturing process. Excellent correlations were obtained on all 4 NMR instruments proving that NMR technology is applicable to in-lab, at-line. or on-line analysis of fish oil derived omega-3 fatty acid supplements. The 40 second NMR analysis effectively replaces a 60+ minute GC analysis.

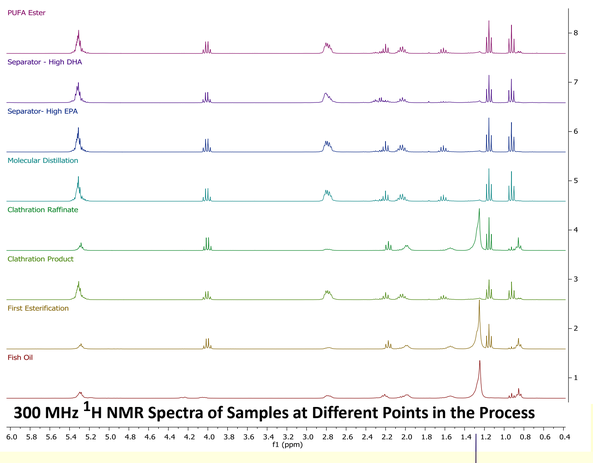
2) Physical and chemical property determination of diesel fuels where excellent correlations were obtained between ^{1}H NMR variability and parameters such as density, aromatic content by GC, hydrogen content by ^{1}H TD-NMR (ASTM D7171 method), and sulfur content. Many more physical and chemical properties can be correlated to the ^{1}H NMR spectrum allowing a single 40 second NMR experiment to predict 10-15 parameters that each require dedicated analyzers.

Finally, we will present the concept and initial results from an independent server-based NMR application software that can be utilized in conjunction with the NMR software of the current benchtop NMR systems, or alternatively as a stand-alone application platform. This software would effectively make chemometric and direct measurement NMR application ubiquitous across all NMR platforms.



Omega 3 Manufacturing Process Sampling Points





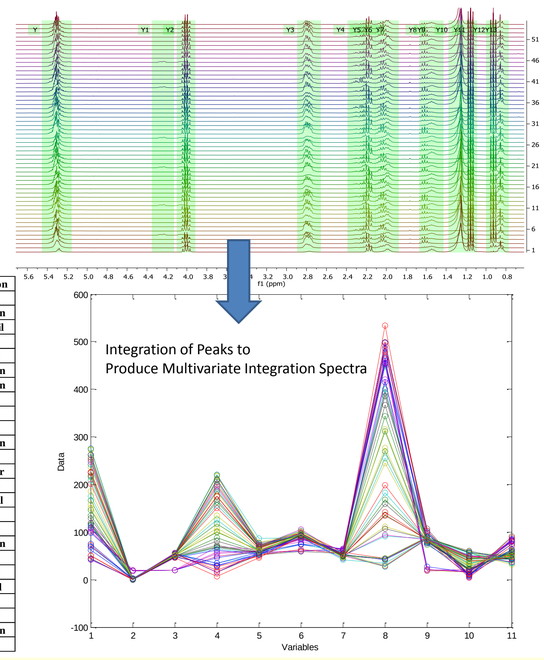
300 MHz ^{1}H NMR Spectra of Samples at Different Points in the Process

NMR ID	EPA (Area %)	DHA (Area %)	Sample Description
FO3h001	0.64	0.01	First Esterification
FO3h002	21.55	13.34	First Esterification
FO3h003	62.97	15.66	Clathration
FO3h004	29.43	18.16	Mol Dist
FO3h005	14.21	9.54	Pollock Oil
FO3h006	52.74	28.90	Separator
FO3h007	15.21	10.51	PolyUnsat Ester
FO3h008	7.18	0.23	First Esterification
FO3h009	16.95	10.04	First Esterification
FO3h010	36.35	16.47	Clathration
FO3h011	61.09	21.26	Mol Dist
FO3h012	13.32	5.95	MSC Pollock Oil
FO3h013	71.78	7.43	Separator
FO3h014	41.40	25.91	PolyUnsat Ester
FO3h015	1.19	0.06	First Esterification
FO3h016	11.73	12.23	First Esterification
FO3h017	43.38	19.30	Clathration
FO3h018	6.07	2.78	Cloth Raffinate
FO3h019	9.77	0.72	First Esterification
FO3h020	58.93	23.41	Mol Dist
FO3h021	10.62	5.18	MSC Pollock Oil
FO3h022	43.91	21.52	Separator
FO3h023	54.05	28.18	PolyUnsat Ester
FO3h024	0.00	0.00	First Esterification
FO3h025	26.97	12.82	First Esterification
FO3h026	44.55	19.30	Clathration
FO3h027	16.69	9.89	First Esterification
FO3h028	6.87	4.53	Crude Pollock Oil
FO3h029	62.79	19.43	Separator
FO3h030	37.29	22.03	PolyUnsat Ester
FO3h031	9.71	0.38	First Esterification
FO3h032	32.00	15.10	First Esterification
FO3h033	38.79	26.75	Clathration
FO3h034	41.87	23.25	Mol Dist
FO3h035	35.49	43.99	Separator
FO3h036	0.30	0.00	First Esterification
FO3h037	34.09	8.09	Clathration
FO3h038	15.44	9.82	MonoUnsat Ester
FO3h039	60.08	24.52	PolyUnsat Ester
FO3h040	8.77	5.75	Crude Salmon Oil
FO3h041	12.41	57.59	Separator
FO3h042	36.36	21.49	PolyUnsat Ester
FO3h043	3.79	0.15	First Esterification
FO3h044	29.23	13.78	Cloth Raffinate
FO3h045	45.99	33.51	PolyUnsat Ester
FO3h046	12.10	5.69	MSC Pollock Oil
FO3h047	24.57	14.32	Separator
FO3h048	45.86	33.61	PolyUnsat Ester
FO3h049	6.39	3.68	First Esterification
FO3h050	58.13	24.66	Clathration

50 sample initial data set from all points in manufacturing process. 40 Samples used for 80 MHz dataset

First round of PLS regression analysis revealed concentration outliers that were linked to limitations in the GC method. This study was performed on improved GC data values.

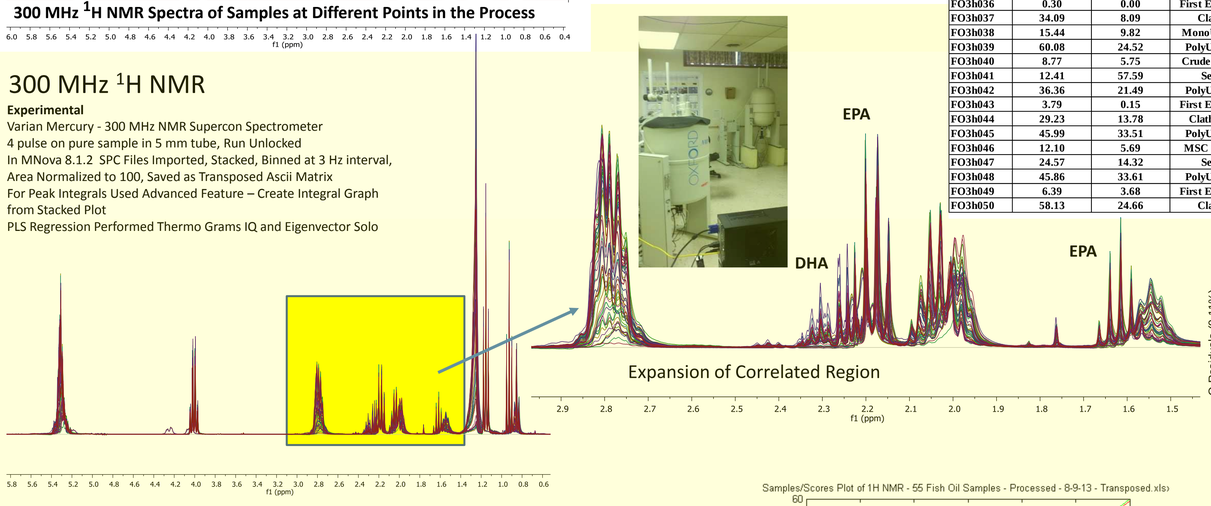
Final 80 Sample models were utilized to validate the calibrations on a 24 sample validation set (below).

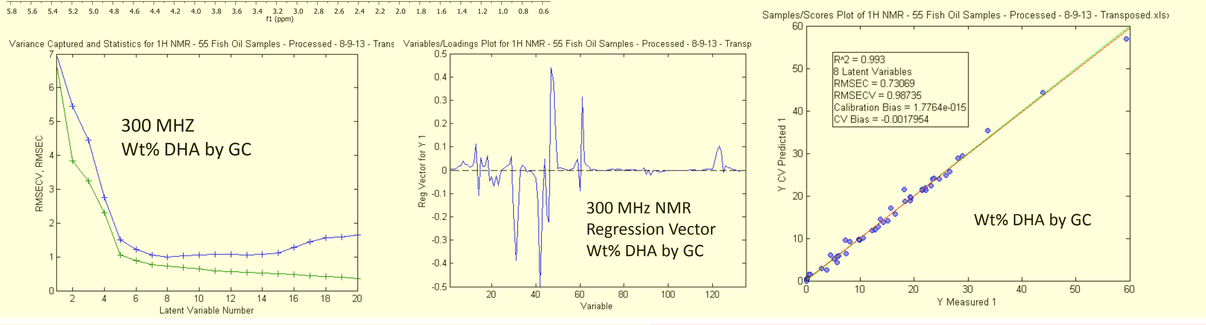


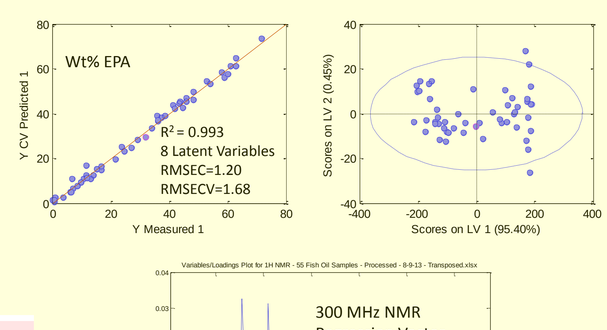
300 MHz ^{1}H NMR

Experimental

Varian Mercury - 300 MHz NMR Supercon Spectrometer
4 pulse on pure sample in 5 mm tube, Run Unlocked
In MNova 8.1.2 SPC Files Imported, Stacked, Binned at 3 Hz interval,
Area Normalized to 100, Saved as Transposed Ascii Matrix
For Peak Integrals Used Advanced Feature – Create Integral Graph from Stacked Plot
PLS Regression Performed Thermo Grams IQ and Eigenvector Solo

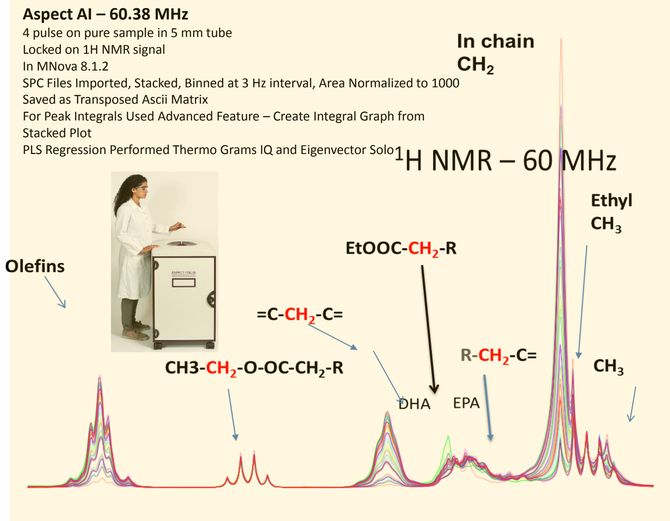


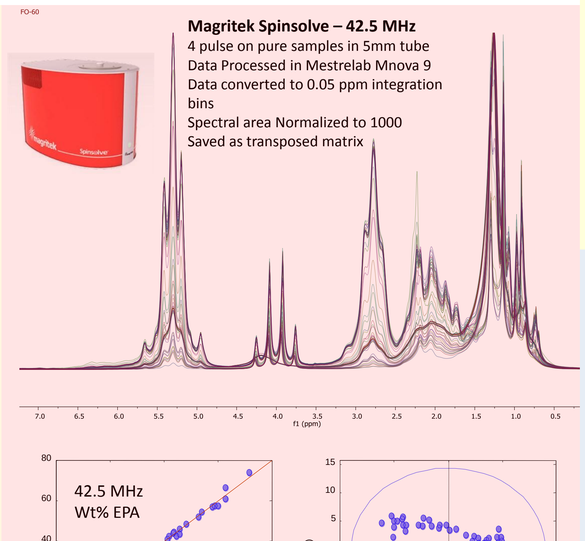




Aspect AI – 60.38 MHz

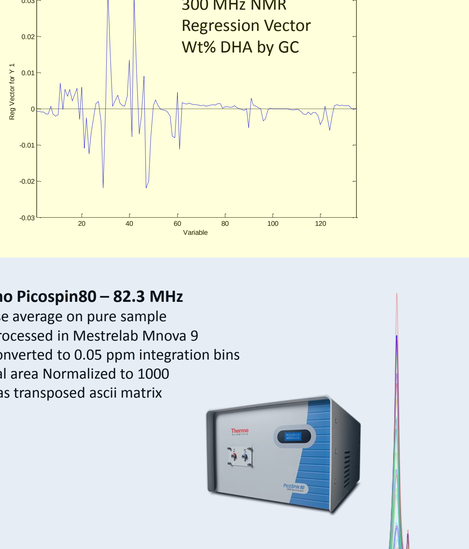
4 pulse on pure sample in 5 mm tube
Locked on 1H NMR signal
In MNova 8.1.2
SPC Files Imported, Stacked, Binned at 3 Hz interval, Area Normalized to 1000
Saved as Transposed Ascii Matrix
For Peak Integrals Used Advanced Feature – Create Integral Graph from Stacked Plot
PLS Regression Performed Thermo Grams IQ and Eigenvector Solo

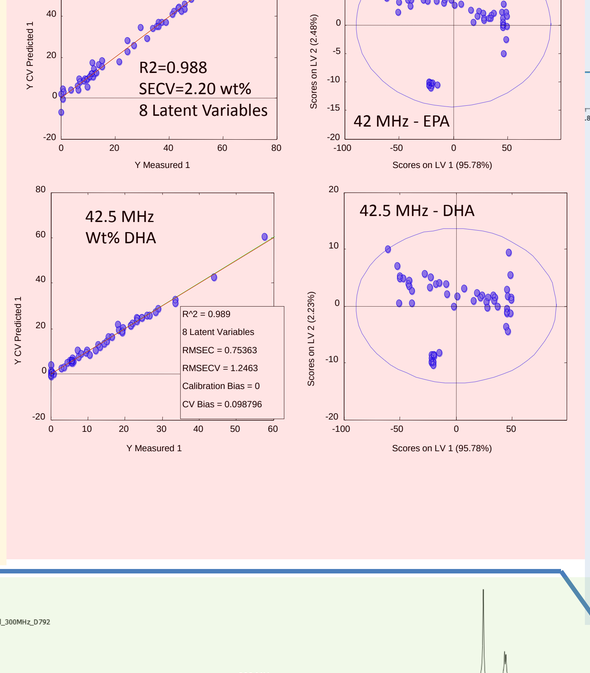




Magritek Spinsolve – 42.5 MHz

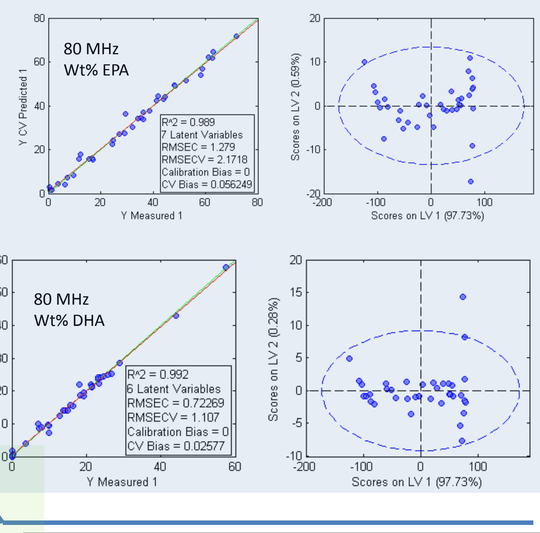
4 pulse on pure samples in 5mm tube
Data Processed in Mestrelab Mnova 9
Data converted to 0.05 ppm integration bins
Spectral area Normalized to 1000
Saved as transposed matrix

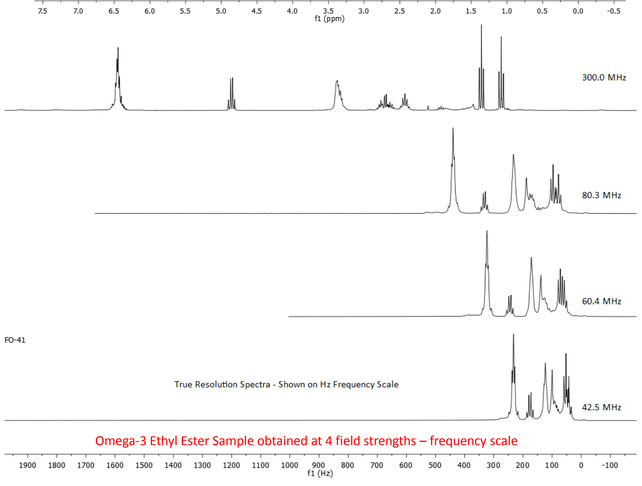




Thermo Picospin80 – 82.3 MHz

32 pulse average on pure sample
Data Processed in Mestrelab Mnova 9
Data converted to 0.05 ppm integration bins
Spectral area Normalized to 1000
Saved as transposed ascii matrix





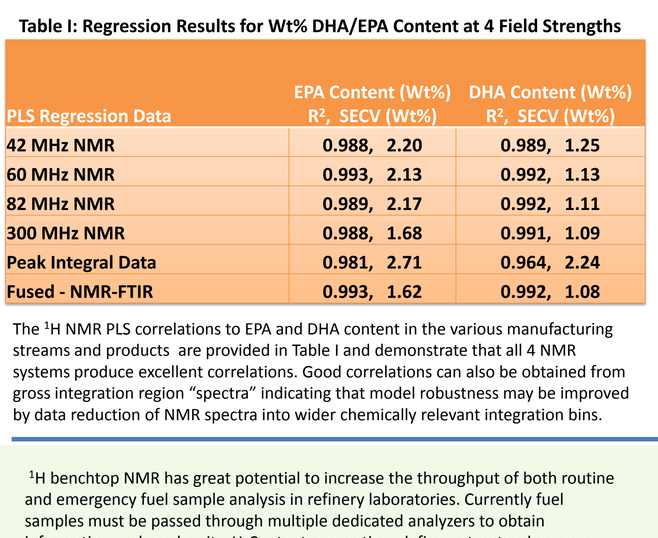
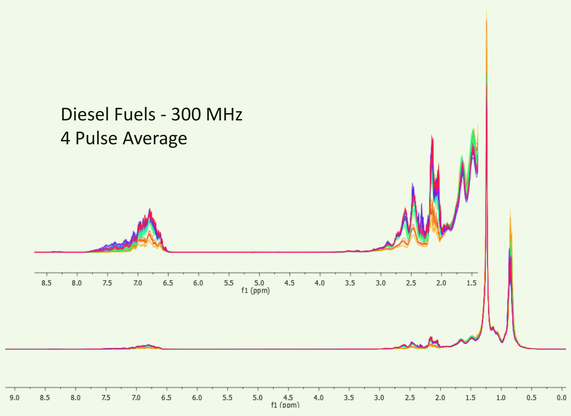
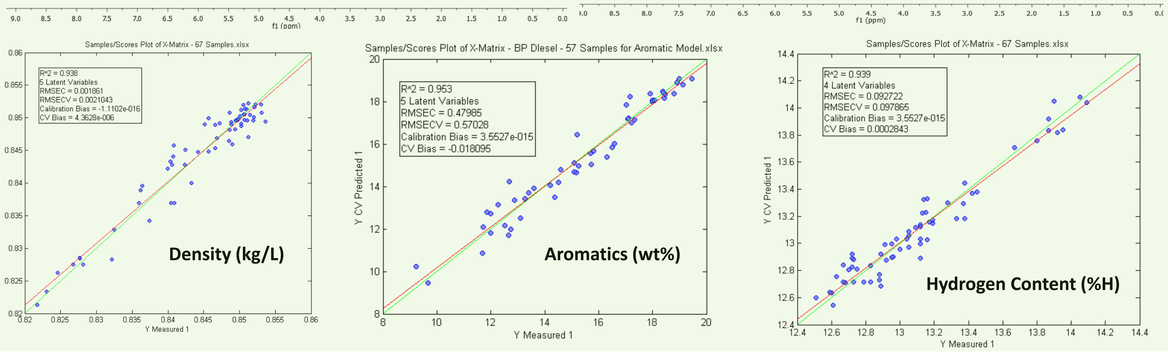


Table I: Regression Results for Wt% DHA/EPA Content at 4 Field Strengths

PLS Regression Data	EPA Content (Wt%) R^2, SECV (Wt%)	DHA Content (Wt%) R^2, SECV (Wt%)
42 MHz NMR	0.988, 2.20	0.989, 1.25
60 MHz NMR	0.993, 2.13	0.992, 1.13
82 MHz NMR	0.989, 2.17	0.992, 1.11
300 MHz NMR	0.988, 1.68	0.991, 1.09
Peak Integral Data	0.981, 2.71	0.964, 2.24
Fused - NMR-FTIR	0.993, 1.62	0.992, 1.08

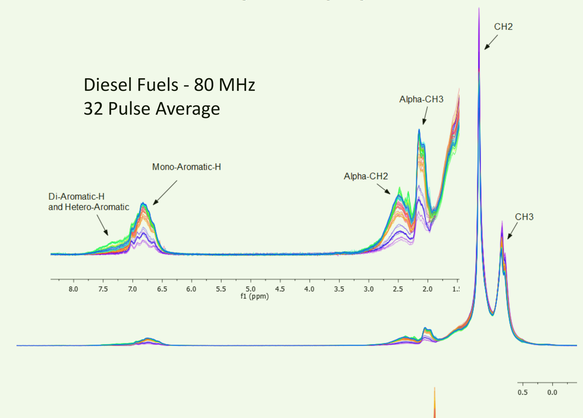
The ^{1}H NMR PLS correlations to EPA and DHA content in the various manufacturing streams and products are provided in Table I and demonstrate that all 4 NMR systems produce excellent correlations. Good correlations can also be obtained from gross integration region "spectra" indicating that model robustness may be improved by data reduction of NMR spectra into wider chemically relevant integration bins.

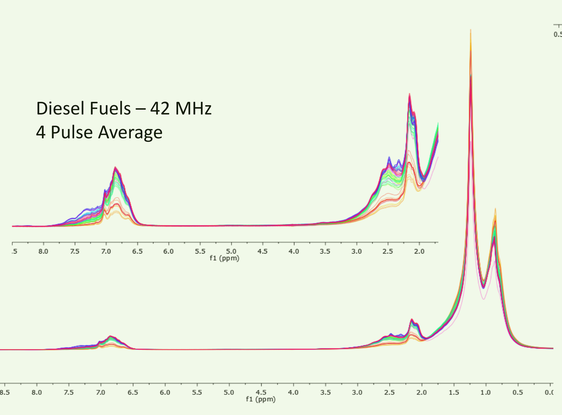




Diesel Fuel - Chemical/Physical Property Correlation

^{1}H benchtop NMR has great potential to increase the throughput of both routine and emergency fuel sample analysis in refinery laboratories. Currently fuel samples must be passed through multiple dedicated analyzers to obtain information such as density, H-Content, aromatics, olefins, saturates, benzene, Octane numbers, cetane index, cetane number, distillation curves, vapor pressure, flash point, pour point, freeze point, cloud point, etc. Correlation of the ^{1}H NMR spectra of these refinery fuel samples to these primary test results will allow all parameters to be predicted in about 40 seconds from the 4 pulse spectrum of the pure fuel. Here we have a few examples obtained on some diesel fuels that were submitted to our lab for ASTM D7171 – Hydrogen Content by TD-NMR. We had density, H-content, and aromatics wt% by GC. Below are three example correlation obtained on the Picospin 80 system (that requires 32 pulses per sample due to the capillary sample size). The results were very similar for the 300, 60, and 42 MHz data obtained on the three other NMR system in our laboratory. The comparative results are shown in Table II. The results are very similar independent of the field strength of the NMR system. The data from all 4 NMR systems is provided in this section.





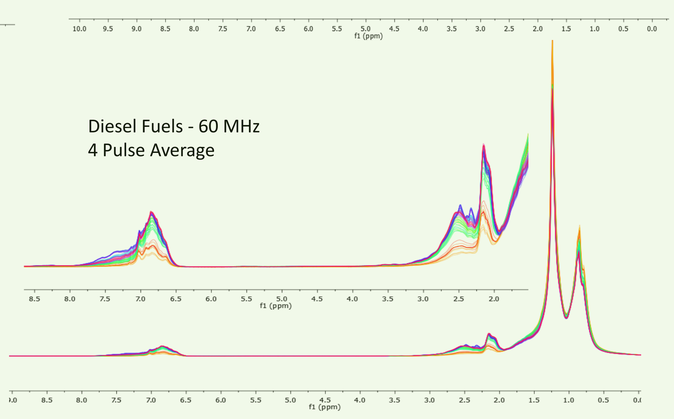
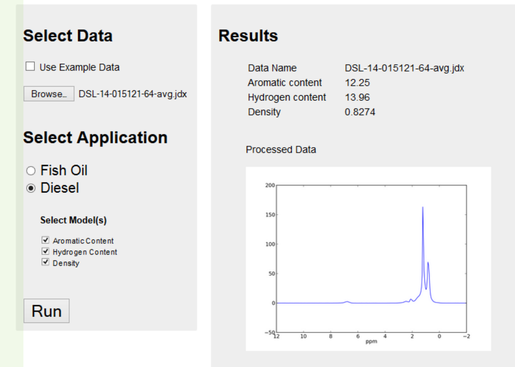


Table II: PLS Regression Results for Diesel Quality Parameters at 4 Field Strengths

^{1}H NMR and Diesel Parameter Correlation – PLS Regression									
	Hydrogen Content (%H) ASTM D7171 TD-NMR			Aromatic Content (Wt% GC)			Density (Kg/L)		
NMR Freq	R2	SECV	LV	R2	SECV	LV	R2	SECV	LV
42 MHz	0.951	0.10	3	0.959	0.54	4	0.944	0.0021	5
60 MHz	0.952	0.09	3	0.962	0.53	2	0.951	0.0020	2
80 MHz	0.934	0.10	3	0.953	0.57	3	0.937	0.0022	3
300 MHz	0.974	0.07	3	0.953	0.57	5	0.937	0.0021	5

Chemometric NMR Models



SpinMetrix is a joint venture company between Process NMR Associates and VisMagnetica developing an independent NMR application implementation software for full spectral processing automation, pre-processing for chemometric applications , chemometric model prediction, and results reporting. Here is an example webpage where NMR FID data obtained on Varian 300, Magritek Spinsolve, Picospin-80, and Aspect-60 can be uploaded pre-processed and passed through server based PLS models for multiple parameter prediction. Models can be accessed on-line or locally on the spectrometer computer.

Conclusion

A wide range of PLS correlation models can be readily built based on NMR data obtained on both superconducting and benchtop permanent magnet NMR systems. Currently models require that data be obtained on each individual spectrometer system but it may be possible that various spectral 'de-resolution' techniques may make models obtained on one system transferable between NMR systems at varying magnetic field strengths.

At-line and in-line permanent magnet NMR systems can yield the same high quality correlations as data obtained on much higher field superconducting NMR systems. Very little difference is observed in the quality of the correlations and errors of prediction on models developed on the 4 systems in our laboratory.