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Application of Low-Resolution Pulsed Nuclear Magnetic Resonance Spectroscopy (TD-NMR) for the measurement of Hydrogen Content in Middle Distillate Petroleum Products with the new compact, modular, fixed magnet TD-NMR Spectrometer; the SpinPulse Model CX-20.

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ASTM D7171 is the standard test method for determining the hydrogen content in petroleum distillates and fuels such as kerosene, aviation fuels, and diesel. It is based on low-resolution, time domain pulsed nuclear magnetic resonance (NMR) spectroscopy.

Overview of Method

1. Test samples and reference standard materials are non-destructively analyzed in a pulsed NMR spectrometer.
2. The total NMR signal obtained from the hydrogen atoms in the reference materials and test samples are normalized by the corresponding sample mass.
3. Signal per gram ratios are used to compare “known” hydrogen content from the reference materials to that of the test samples.

Cosa Xentaur SpinPulse CX-20 Series NMR

Dimensions (L,W,H), not more than:

- Spectrometer: 18" x 15" x 6"
- 40mm Magnets: 12" x 9.5" x 11"





10 mm

Dimensions (L,W,H), not more than:

- Spectrometer: 18" x 15" x 6"
- 20mm and 40mm Magnets: 12" x 9.5" x 11"
- 10mm Magnet: 7" x 7" x 7"

Spectrometer Frequency Range: 2 – 60 MHz

Magnet Frequencies: 10 mm 25 MHz, 20 mm 18.5 MHz, 40 mm 14.4 MHz

Simple cable switch between spectrometer and magnets.



Sample Chamber Temperature Control

Ambient to 38° C +/- 0.1° C

Optional Variable Temperature Probe

No extraneous magnetic field.

RELAXENT Software

- Windows 7™ Based
- User Defined - Open and/or “Closed” access.
- Performance Optimization
 - On Resonance
 - Pulse Calibration
- Multi-functional:
 - FID
 - Relaxation (T1, T2)
 - Echo (Hahn, CPMG)
- Application Oriented
 - “Standard” (Total Hydrogen, Seed Oil Content, etc)
 - Custom

User Defined

Basic settings | Standard applications | Advanced | Relax 8 Settings

Analog block

RX Gain [0..100%]: 32.00

TX Gain [0..100%]: 98.00

Frequency, MHz: 23.60800

LP Filter, MHz: 0.50

Digital block and processing

dwell time, us: 0.07

Relaxation period, ms: 100

Amount of scans: 64

Dummy Shots: 0

Phase cycling:

Incoherent accumulating:

Pulses

90° pulse, us: 2.1 Tune

180° pulse, us: 4.3

Processing

Remove points from start: 0

Remove points from end: 0

Fourier Transformation

Adding zero in FFT: 2000

Lower Frequency, MHz: 0.300

Higher Frequency, MHz: 0.300

Fitting options

Save application with data:

Ini - file: experiment_ini

Update Ini File | Apply | Close

Basic settings | Standard applications | Advanced | Relax 8 Settings

Intervals of magnitude measurements (FID, SFC, T1)

Initial measur. of short, us: 40.0

Final measur. of short, us: 48.0

Initial measur. of long, us: 80.0

Final measur. of long, us: 90.0

Echo sequences

Echo time, us: 800.0

Number of Echo: 300

Multi-Step Experiments

Time of observation, us: 2000000.0

Initial step, us: 10000.0

Number of points: 16

Spin Track Validation

Limiting values for check

90° max, us: 5.0

180° max, us: 10.0

Frequency min, MHz: 18.80000

Frequency max, MHz: 19.50000

S/N min: 50.0

Grad. B0 max, kHz/cm: 5.0

Daily Tuning

Echo Shift, us: -1.2

Point per Echo: 20

Auto bases CPMG:

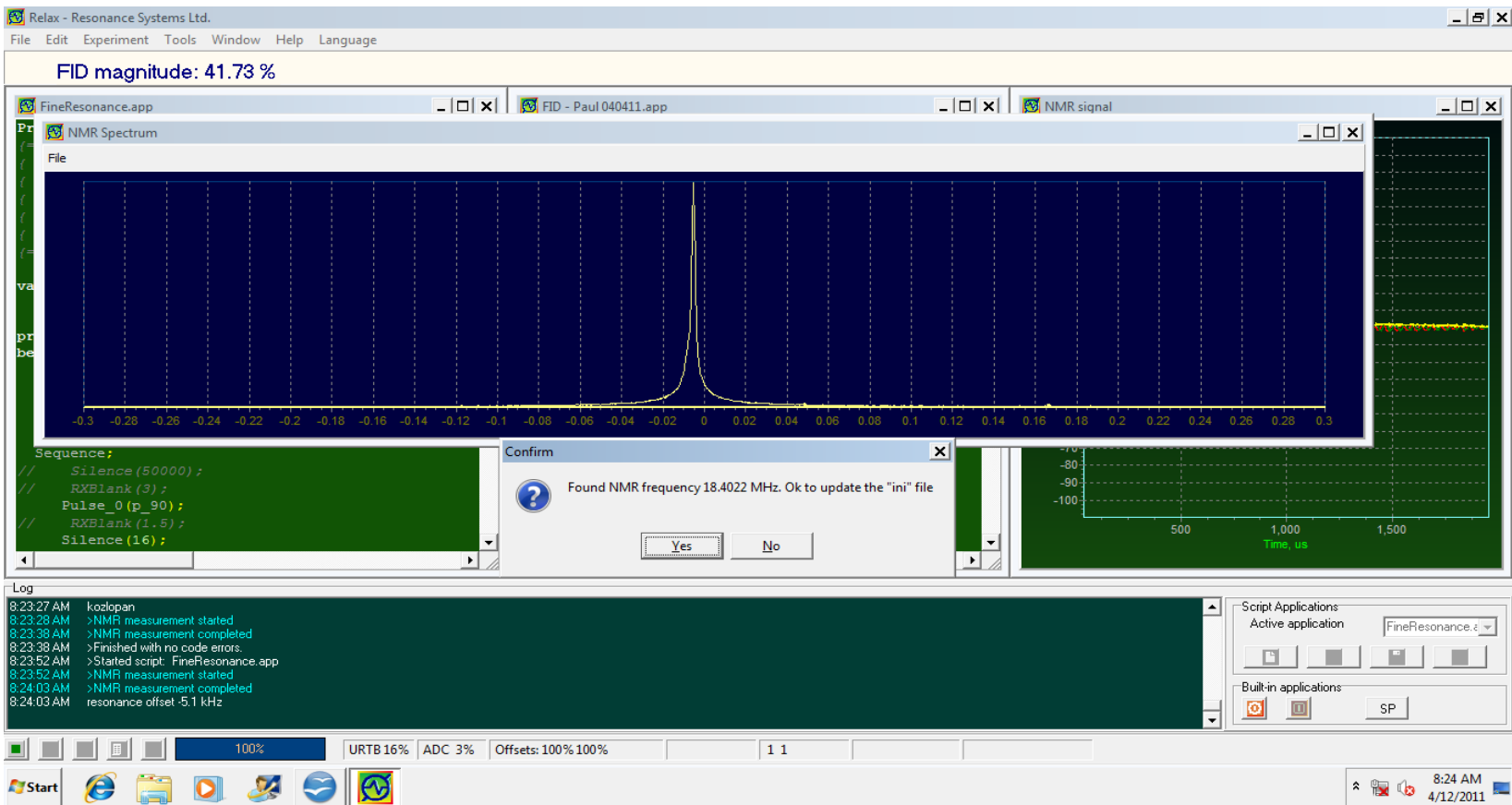
Ini - file: experiment_ini

Update Ini File | Apply | Close

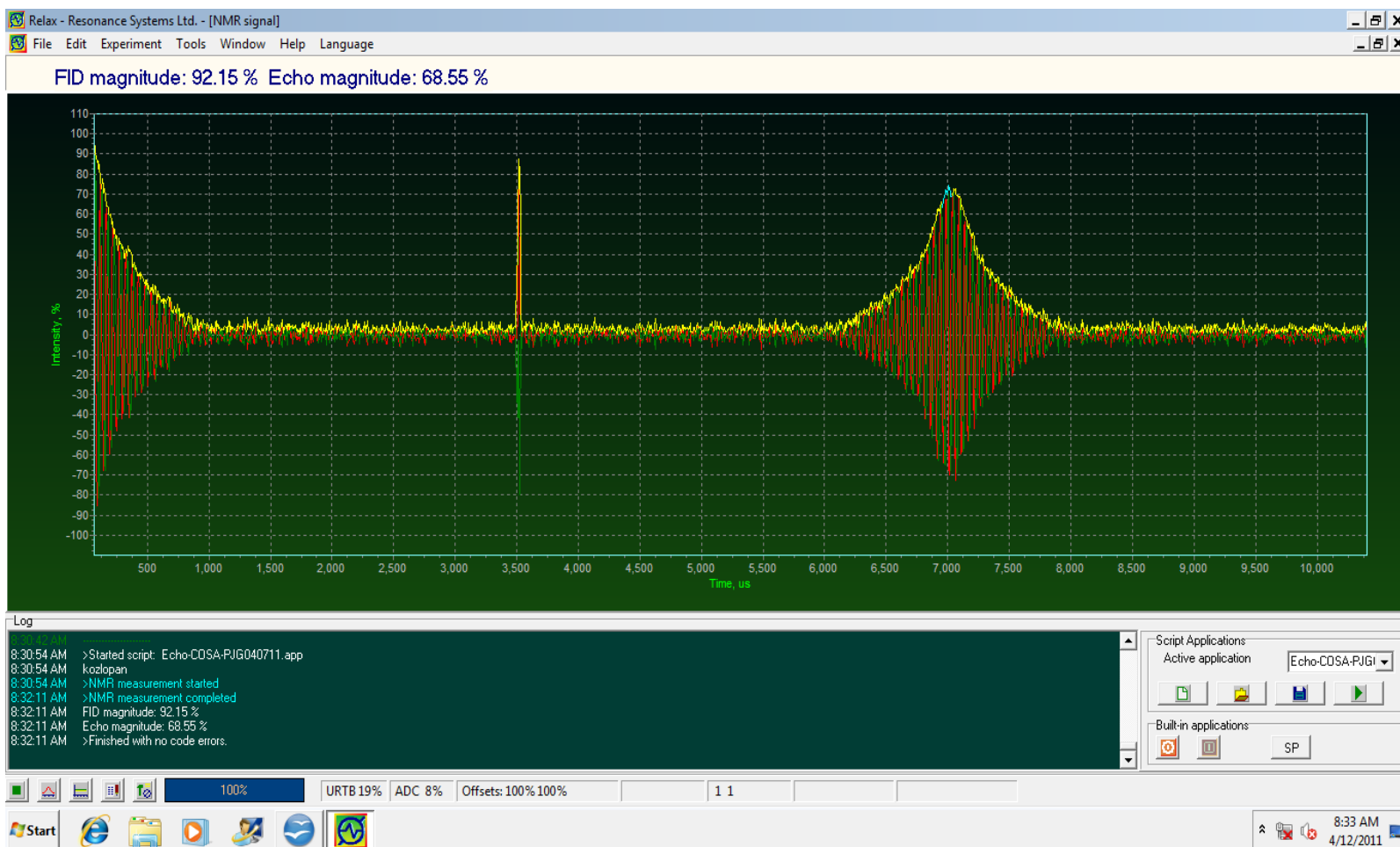
•Performance Optimization

•On Resonance

•Pulse Calibration



Multi-functional: Example – Hahn Echo



Application Oriented

The screenshot displays the Relax software interface for configuring an NMR experiment. The main window is titled "NMR Experiment: Hahn Echo Decay".

Parameters:

- Initial Step: 1200.0 us
- Points: 8
- Observation Time: 2400.0 us

Plots: Two identical plots are shown, both with a y-axis labeled "Intensity, %" ranging from 0 to 100 and an x-axis labeled "0". Each plot has a data point at (0, 100).

Controls:

- Buttons: Experiment, Script, Sequence, RUN/STOP
- Checkboxes: Apply Variables, Show Parameters
- Experiment type selection:
 - FID
 - Hahn Echo
 - Echo Decay
 - T1 Experiment
 - CPMG

Log:

- 9:34:23 AM 10/10/2011. The software Relax
- 9:34:40 AM
- 9:35:00 AM
- 9:35:27 AM

Script Applications: Active application dropdown menu.

Built-in applications: SP, Seeds

NMR Experiment: Hahn Echo Decay

Initial Step: us Points:

Observation Time: us

Hahn Echo Decay

This is a multi-step experiment to measure Spin-Spin Relaxation decay

'TAU' value varies from 'Initial Step' to 'Observation Time'.

On each step the value of Hahn Echo magnitude is recorded to get the NMR relaxation curves to have amount of 'Points' experimental values.

Experiment | Script | Sequence

Apply Variables

Show Parameters

Experiment type

- FID
- Hahn Echo
- Echo Decay
- T1 Experiment
- CPMG

NMR Experiment: FID

Observation Time: us

Free Induction Decay

Experiment | Script | Sequence

Apply Variables

Show Parameters

Experiment type

- FID
- Hahn Echo
- Echo Decay
- T1 Experiment
- CPMG

Empty	Full	Samp Wt	Sample	Samp Wt	NMR 1	NMR 2	NMR 3	Avg NMR Signal	Actual H Wt%	Standard/Reference Calculation					
21.3797	25.7978	4.4181	Dodecane	4.4181	49.42	49.54	49.04	49.33	15.39	Standard	Dodecane				
21.5211	26.2335	4.7124	oXylene	4.7124	33.16	32.45	32.76	32.79	9.49	carbon	12	144.13	C AMU		
15.6420	20.6289	4.9869	Sample A	4.9869	47.98	47.01	47.08	47.36		hydrogen	26	26.21	H AMU		
15.6683	20.9181	5.2498	Sample B	5.2498	49.04	49.28	48.66	48.99		wt%H	15.386	170.34	MW		
15.6293	20.7064	5.0771	Sample C	5.0771	52.01	51.44	51.09	51.51		lower limit	15.14				
15.5559	20.6384	5.0825	Sample D	5.0825	53.37	53.63	53.20	53.40		Upper limit	15.60				
										Purity	0.999				
21.3797	25.7978	4.4181	Dodecane Rpt	4.4181	49.52	49.34	48.95	49.27		Reference Unkn	oXylene				
										carbon	8	96.09	C AMU		
			Sample		Wt%H					hydrogen	10	10.08	H AMU		
			Dodecane		15.39		oXylene	Acceptance		wt%H	9.494	106.168	MW		
			oXylene		9.59	Pass	9.34	9.63		lower limit	9.34				
			Sample A		13.08					Upper limit	9.63				
			Sample B		12.86					Purity	0.999				
			Sample C		13.98										
			Sample D		14.48										
			Dodecane				Dodecane	Acceptance		Standard =	Is the known H content to which all calculations are based				
			Repeat		15.37	Pass	15.14	15.60		Reference Unkn =	Is a second standard of know H Content				
											This is calculated based on Standard H Content				
											The actual value must fall within the limits				
Freq	20.013500									Standard =	Is a second run of the Standard that is then				
Gain	30									Repeat	experimentally calculated as an unknown				

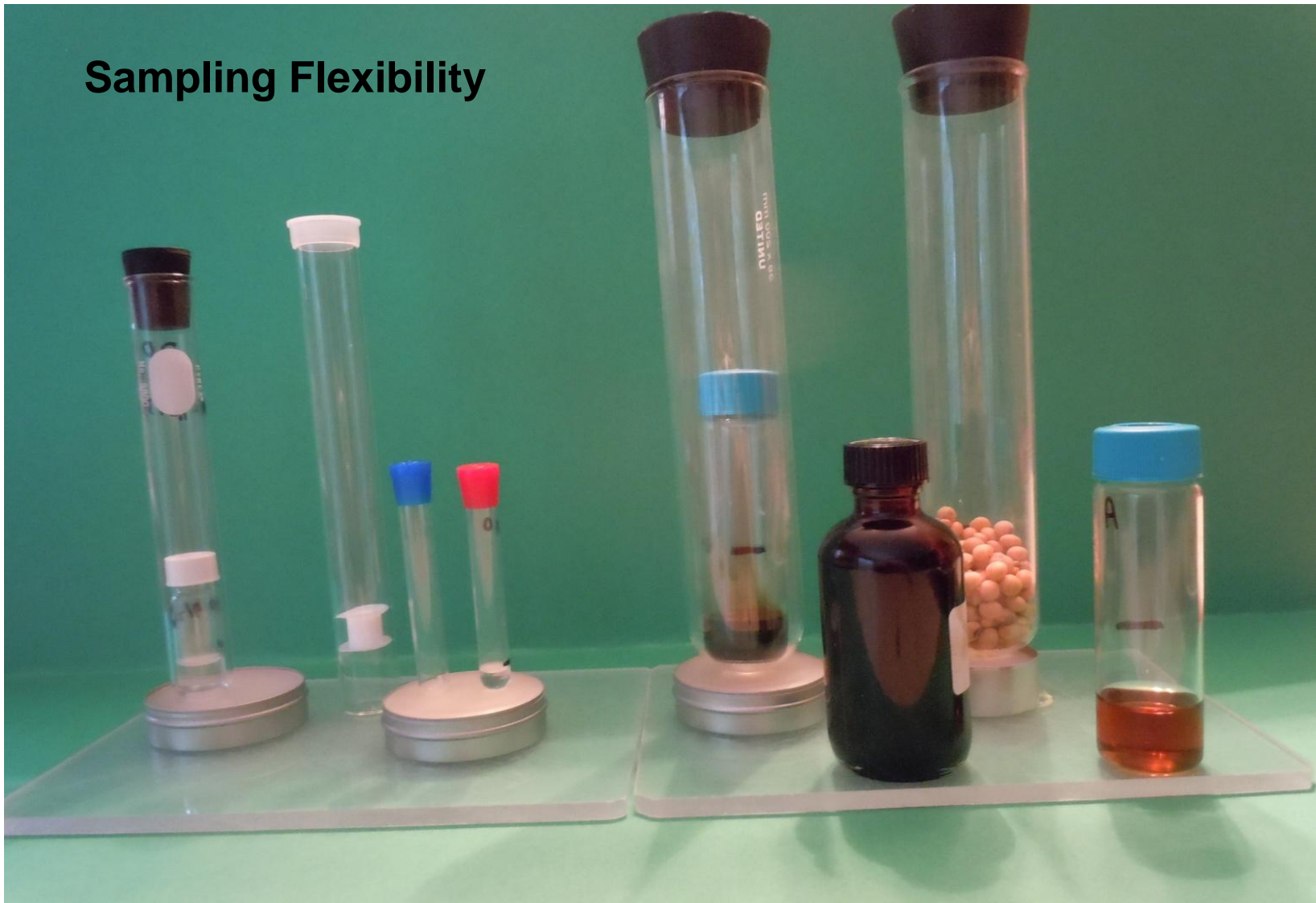
Sampling Technique:

1. Entire sample (mass/volume) must be completely within the NMR sample volume.
2. It is not necessary to always fill the entire sampling volume.
3. It is not necessary keep fill height consistent between samples.
4. Sample temperatures should be equilibrated with magnet/probe temperatures, but not required to be specifically at 35⁰ or 40⁰ C.
5. Sample Containers should have no background hydrogen intensity inside the NMR sample volume.

Instrumental Considerations for D7171:

1. NMR Probe sample volume/maximum fill height must be known.
2. NMR transmitter and receiver design should have wide ranging power settings to achieve good signal to noise for a wide range of sample volumes/weights.

Sampling Flexibility



Comparison of ASTM D7171 Results with Different Systems, Magnets and Sample Temperatures

- **Systems:** Oxford QP20 and Cosa Xentaur Spin Pulse CX-20
- **Magnets and Sample Temperatures:**
 - Oxford QP20 18 mm, 20.01 MHz, 35° C
 - Cosa Xentaur Spin Pulse CX-20-20, 20 mm, 18.36 MHz Ambient and 35° C
 - Cosa Xentaur Spin Pulse CX-20-40, 40 mm, 14.45 MHz Ambient
 - Cosa Xentaur Spin Pulse CX-20-10, 10 mm, 19.51 MHz Ambient
- **Samples:**
 - 4 Middle Distillates including store purchased K1 Kerosene
 - FCC Feed (high aromatic)
- **Sampling:** As per ASTM D7171 or modified

	Cosa CX SP20		Cosa CX SP10	Cosa CX SP40	Oxford				Cosa CX SP20	
	ASTM	Small Vial			OQP20			Actual	Previous Analyses	
Sample	Mass% H	Mass% H	Mass% H	Mass% H	Mass% H	Acceptance Range		H Mass%	Result	Date
Dodecane	15.39	15.39	15.39	15.39	15.39			15.39		
o-Xylene	9.47	9.56	9.50		9.59	9.34	9.63	9.49		
Sample A	13.09	13.02	12.95	12.95	13.08	12.84	13.23		13.02	02/07/11
Sample B	12.74	12.77	12.99	13.00	12.86	12.67	13.05		12.92	01/25/11
Sample C	13.94	13.80	13.70		13.98	13.77	14.19			
Sample D	14.67	14.43	14.36		14.48	14.26	14.69			
Dodec Rpt	15.39	15.44	15.44	15.58	15.37	15.14	15.60			
FCC Feed				10.78						
Sample	Samp Wt	Samp Wt	Samp Wt	Samp Wt	Samp Wt					
Dodecane	2.2947	0.9744	0.2194	6.0407	4.4181					
oXylene	2.8507	1.4987	0.2654		4.7124					
Sample A	2.4578	1.4156	0.2228	6.4107	4.9869					
Sample B	2.4143	1.4032	0.2260	6.3060	5.2498					
Sample C	2.6769	1.4716	0.2482		5.0771					
Sample D	2.6303	1.3699	0.2026		5.0825					
FCC Feed				5.4929						

Conclusions:

1. Varying sample weights/volumes are not a barrier to performing ASTM D7171. Most helpful in sample limited and/or viscous sample situations.
2. Sample and magnet/probe temperature matching is essential but specifically at 35° or 40° C is not required.
3. Sampling options can improve efficiency and lower cost by:
 - Improving filling procedures (long v short)
 - Reducing sample volumes (disposal)
 - Reducing “clean up” costs
4. Sampling options will be beneficial in expanding total hydrogen content measurements.