Practical Applications of Compact High-Resolution
60 MHz Permanent Magnet NMR Systems
for Reaction Monitoring and Online Process Control

Presented By

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High Resolution FT-NMR – Online / in Process
NMR Sample System and Placement
NMR Lock - External $^7$Li Lock @ 22.5 MHz

Shim DACs Built into the Magnet Enclosure

Matrix Shimming Performed by Optimizing FID RMS
**SPECIFICATIONS**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclei Observed</td>
<td>H+ (primary)</td>
</tr>
<tr>
<td>Operating Frequency</td>
<td>58±1.0 MHz for H+</td>
</tr>
<tr>
<td>Sample Tube</td>
<td>Standard laboratory glass tube</td>
</tr>
<tr>
<td></td>
<td>L: 35.5 cm O.D 8 mm - I.D 7 mm</td>
</tr>
<tr>
<td></td>
<td>Other size optional</td>
</tr>
<tr>
<td>Sample Temperature Heating</td>
<td>Controlled between 30°C – 80°C (86°F to 176°F)</td>
</tr>
<tr>
<td>Magnet System</td>
<td>Temperature stabilized, self-condensed field, permanent (neodymium)</td>
</tr>
<tr>
<td></td>
<td>magnet with integral field gradient (shim) coils and</td>
</tr>
<tr>
<td></td>
<td>automatic shim control</td>
</tr>
<tr>
<td>Field Strength</td>
<td>1.35 Tesla at 45°C</td>
</tr>
<tr>
<td>Fringe Field</td>
<td>Less than 1 gauss on external</td>
</tr>
<tr>
<td></td>
<td>enclosure of magnet</td>
</tr>
<tr>
<td>Dimensions</td>
<td>145 cm H x 106 cm W x 65 cm D</td>
</tr>
<tr>
<td></td>
<td>(57 in H x 42 in W x 26 in D)</td>
</tr>
<tr>
<td></td>
<td>Add 15 cm (6 in) to height for shipping pallet</td>
</tr>
<tr>
<td>Enclosure</td>
<td>Self standing, wheel driven carriage</td>
</tr>
<tr>
<td>Weight</td>
<td>400 kg (882 lb) net weight</td>
</tr>
<tr>
<td></td>
<td>444 kg (980 lb) gross shipping weight</td>
</tr>
<tr>
<td>Power Requirement</td>
<td>220-240 Vac, 3500W maximum</td>
</tr>
<tr>
<td></td>
<td>110-120 Vac, 3500W maximum</td>
</tr>
<tr>
<td>Other Utilities</td>
<td>Internal Air condition system for higher stability</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>Ambient Range:</td>
</tr>
<tr>
<td></td>
<td>Temperature controlled environment</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Min / Max 30%-50%</td>
</tr>
<tr>
<td>Vibration</td>
<td>Max: 0.3 mm/s² on the 3 axes</td>
</tr>
<tr>
<td>Communication</td>
<td>Local Ethernet Base - 10/100. Remote connection via modem.</td>
</tr>
</tbody>
</table>
New magnet design solves the problem of:
Long term and short term Stability
Temperature sensitivity

State of the Art electronics:
Smaller foot-print
40 Shim coils on 2 single PCB
Integrated PCB for Shim & Heater Control
Digital RF & Acquisition – improve SNR

New concept of Process Probe:
Entire sample pipe through without contact with the system
Much better temperature insulation
Higher Q (better sensitivity)

New Software:
Includes new algorithm for standard and global Models
Fully automated process capacity
Extensive remote diagnostic capabilities
Advantages and Disadvantages of NMR Applied to Process Control

<table>
<thead>
<tr>
<th>Advantages:</th>
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<tbody>
<tr>
<td>Non-Optical Spectroscopy</td>
</tr>
<tr>
<td>No Spectral Temperature Dependence</td>
</tr>
<tr>
<td>Minimal Sampling Requirements</td>
</tr>
<tr>
<td>Spectral Response to Sample Chemistry is Linear</td>
</tr>
<tr>
<td>Chemical Regions of NMR Spectra are Orthogonal</td>
</tr>
<tr>
<td>Entire Volume is Sampled by the RF Experiment</td>
</tr>
<tr>
<td>Water is in Distinct Region and can be digitally removed</td>
</tr>
<tr>
<td>Detailed Hydrocarbon information is readily observed</td>
</tr>
<tr>
<td>Fundamental Chemical Information Can be Derived Directly from Spectrum.</td>
</tr>
<tr>
<td>Colored/Black Samples Readily Observed Without Impact</td>
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<table>
<thead>
<tr>
<th>Disadvantages:</th>
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<tbody>
<tr>
<td>Solids Cannot be Observed in a Liquid Stream</td>
</tr>
<tr>
<td>Individual Molecular Component Sensitivity Not Observed Directly in the Spectrum.</td>
</tr>
<tr>
<td>Low Sensitivity to Impurities – Quantitative &gt; 500 ppm.</td>
</tr>
<tr>
<td>Sensitive to Ferromagnetics.</td>
</tr>
<tr>
<td>Sample Viscosity Causes Decrease in Resolution</td>
</tr>
<tr>
<td>Non-Hydrogen Containing Species are Not Observed (Exceptions Na, P, F, Al)</td>
</tr>
</tbody>
</table>
**Application: Steam Cracking Optimization**  
**Installed 2000**  
Cracker Facility Capacity: 600,000 Tonnes per Year  
Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization  
NMR Analysis: 3-4 Minute Cycle (Single Stream)  
NMR PLS Outputs: Naphtha – Detailed PIONA  
C4-C10 normal-paraffin, iso-paraffin, aromatics, naphthenes
Predicted Cyclohexane (F9 C1)

Actual Cyclohexane (Wt%)

Beta Coefficients

Spectral Units ( )
Cyclopentane

Wt% over time from May to September.
96 Hours of NMR Process Output – iso-Paraffin Components
Online NMR Applications Timeline

1993 - Development of Laboratory Based process NMR Methodologies
1995 - BTU Analysis of Refinery Fuel Gas
1995 - Sulfuric Acid Strength in Emulsion Zone of Stratco Acid Alkylation Unit
1999 - Diesel Blending System
1999 - Reformer Control System
2000 - Naphtha Cracker Feed Analyzer – Full GC PIONA
2000 - Crude Unit Analyzer
2000 - Crude Blending System
2001 - Gasoline Blending System,
2001 - Base Oil Manufacturing Analyzer
2002 - FCC Unit Analyzer
Acid CH₃ Intensity
Anhydride CH₃ Intensity

Acetic Acid
Acetic Anhydride

Water
Acetic Anhydride + Methanol
Acid Catalyzed
With Shake Before Insertion
-O-CH₃

H₂O

Methyl Ester CH₃
Acetic Anhydride CH₃
Acetic Acid/Ester CH₃

Acetic Acid
Acetic Acid Ester - CH₃-CO

4  3.6  3.2  2.8  2.4  2 ppm
t-BuOH+AA
IPA+AA early in reaction before reference shift
EtOH+AA

Shifts caused by auto-referencing changes caused by intensity shifts in the methyl resonance area.
MeOH (m)
EtOH (e)
IPA (i)
t-BuOH (b)
+
AA

OH - pH shift
Acetic-ester
MeOH (m)
EtOH (e)
IPA (l)
t-BuOH (b)
+
AA
MeOH (m)
EtOH (e)
IPA (l)
t-BuOH (b)
+ AA

Acetic Acid
and Ester
Acetate CH3

OH
OH
i-ester

m ester

b ester

ppm
Methoxyketone + HO-NH₂ → 1,3-dihydro-2H-imidazol-2-one + H₂O
Microreactor Hydrogenation Reaction
Cyclohexene to Cyclohexane

Methanol
Chloroform
Cyclohexene
Cyclohexane

13C Satellites do not interfere
Continuous Flow (10 ml/min).
Starting Cyclohexane concentration 0.08 gm/18 ml MeOH.
Final Cyclohexane concentration 0.4 gm in 18 ml MeOH.
Cyclohexane was added in 0.01 gm increments every 12 seconds with no mixing.
Total run time: 9 minutes.
19F NMR at 54.6 MHZ
LWHH=3 Hz
Acknowledgements

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