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

Presented By

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Process NMR Associates, LLC
Danbury, Connecticut

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PROCESS NMR ASSOCIATES

250+ Analytical NMR Customers

TTC Labs, Inc.
Process Engineering Excellence

TopNIR Systems

TTC Labs, Inc.
Process Engineering Excellence

Triangle Analytical, Inc.
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>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nuclei Observed</strong></td>
<td>H+ (primary)</td>
</tr>
<tr>
<td><strong>Operating Frequency</strong></td>
<td>58±1.0 MHz for H+</td>
</tr>
<tr>
<td><strong>Sample Tube</strong></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>
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<tr>
<td><strong>Sample Temperature</strong></td>
<td>Controlled between 30°C – 80°C</td>
</tr>
<tr>
<td></td>
<td>(86°F to 176°F)</td>
</tr>
<tr>
<td><strong>Magnet System</strong></td>
<td>Temperature stabilized, self-condensed field, permanent (neodymium) magnet with integral field gradient (shim) coils and automatic shim control</td>
</tr>
<tr>
<td><strong>Field Strength</strong></td>
<td>1.35 Tesla at 45°C</td>
</tr>
<tr>
<td><strong>Fringe Field</strong></td>
<td>Less than 1 gauss on external enclosure of magnet</td>
</tr>
<tr>
<td><strong>Dimensions</strong></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><strong>Enclosure</strong></td>
<td>Self standing, wheel driven carriage</td>
</tr>
<tr>
<td><strong>Weight</strong></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><strong>Power Requirement</strong></td>
<td>220-240 Vac, 3500W maximum</td>
</tr>
<tr>
<td></td>
<td>110-120 Vac, 3500W maximum</td>
</tr>
<tr>
<td><strong>Other Utilities</strong></td>
<td>Internal Air condition system for higher stability</td>
</tr>
<tr>
<td><strong>Operating temperature</strong></td>
<td>Ambient Range:</td>
</tr>
<tr>
<td></td>
<td>Temperature controlled environment</td>
</tr>
<tr>
<td><strong>Relative humidity</strong></td>
<td>Min / Max 30%-50%</td>
</tr>
<tr>
<td><strong>Vibration</strong></td>
<td>Max: 0.3 mm/s² on the 3 axes</td>
</tr>
<tr>
<td><strong>Communication</strong></td>
<td>Local Ethernet Base - 10/100.</td>
</tr>
<tr>
<td></td>
<td>Remote connection via modem.</td>
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</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
60 MHz $^1$H NMR of Gasoline

300 MHz $^1$H NMR of Gasoline
Typical Variability Observed in Gasoline Blending

Gasoline Parameters:

- Octane Numbers
- Distillation Properties (T10, T50, T90)
- Benzene Content (wt%)
- Total Aromatics (Wt%)
- Total Olefins (Wt%)
- Total Saturates (Wt%)
- Oxygenates (Wt%)
- Reid Vapor Pressure
Diesel Fuels

Biodiesels

Ethyl-benzene
Diethyl-benzene

Vinegar an Alcohol Fermentation
Advantages and Disadvantages of NMR Applied to Process Control

**Advantages:**
- Non-Optical Spectroscopy
- No Spectral Temperature Dependence
- Minimal Sampling Requirements
- Spectral Response to Sample Chemistry is Linear
- Chemical Regions of NMR Spectra are Orthogonal
- Entire Volume is Sampled by the RF Experiment
- Water is in Distinct Region and can be digitally removed
- Detailed Hydrocarbon information is readily observed.
- Fundamental Chemical Information Can be Derived Directly from Spectrum.
- Colored/Black Samples Readily Observed Without Impact

**Disadvantages:**
- Solids Cannot be Observed in a Liquid Stream
- Individual Molecular Component Sensitivity Not Observed Directly in the Spectrum.
- Low Sensitivity to Impurities – Quantitative > 500 ppm.
- Sensitive to Ferromagnetics.
- Sample Viscosity Causes Decrease in Resolution
- Non-Hydrogen Containing Species are Not Observed (Exceptions Na, P, F, Al)
Application: Closed Loop Reformer Control - Installed 1998
Reformer Capacity: 34,000 Barrels per Day
Control Strategy: Control on MON and Benzene Content
NMR Analysis: 2 Minute Analysis
NMR PLS Outputs: RON, MON, Benzene (Wt%) Total Aromatics (Wt%)

Variation of Reformate Processed $^1$H NMR Data Observed with Changing Research Octane Number

$R^2=0.984$
SECV=0.21 octane
8 Factors
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
Spectral Variability in Aromatic and Aliphatic Regions
Cyclopentane

Wt% vs Date

- GC
- NMR
96 Hours of NMR Process Output – iso-Paraffin Components
96 Hours of NMR Process Output – Aromatic 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
Acetic Anhydride + Methanol
Acid Catalyzed
With Shake Before Insertion
Methyl Ester CH$_3$

Acetic Anhydride CH$_3$

Acetic Acid/Ester CH$_3$

-O-CH$_3$

Acetic Acid and Acetic Acid Ester - CH$_3$-CO

Acetic Anhydride

H$_2$O
Acetic Anhydride + Methanol
Acid Catalyzed
No Shaking

Methyl Ester CH₃
Acetic Anhydride CH₃
Acetic Acid/Ester CH₃

Acid Methanol
Acetic Acid OH

Methyl Ester Methyl
Acetic anhydride Methyl
Acetic Acid and Acetic Ester Methyl
Microreactor Hydrogenation Reaction
Cyclohexene to Cyclohexane

Methanol
Chloroform
Cyclohexene
13C Satellites do not interfere
Cyclohexane
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.
Acknowledgements

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