Introduction to High Resolution NMR in Process Control

Presented By

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Presentation Overview

- NMR Basics – Briefly

- Process NMR / Benchtop NMR Technology

- Advantages/Disadvantages as a Process Spectroscopy for Real-Time Analysis

- Timeline of NMR Application Development

- Process NMR Applications

- Conclusions
Superconducting NMR Systems
High Resolution FT-NMR – Online / in Process
**Nuclear Magnetic Resonance Spectroscopy - The Basics**

**Involves Magnetic Energy of Nuclei**

- **m** (Magnetic Moment)
- Hydrogen Atom (Proton)
- Proton is spinning - magnetic moment generated

**With no magnetic field, magnetic moments are random**

**In Strong Magnetic Field (Bo), magnetic moments align along Bo**

**Magnetic Moments Align and Precess at a Frequency \( w_0 \)**

- \( w_0 \) is Proportional to size of Bo
- \( Bo = 1.35 \) Tesla  \( w_0 = 58 \) MHz

**Precessing Spins can be Described as a Bulk Magnetic Moment \( Mo \)**

- \( Mo = \) Summation of Individual Magnetic Moments
NMR Experiment

5. RF Pulse Turned On for 4-20 microseconds
   Generates a Second Magnetic Field B₁

6. Magnetic Field B₁ Causes M₀ to Move

7. Relaxation
   RF Signal Detected
   RF Pulse Turned Off
   M₀ Realigns With B₀
   Generating and RF Current In the Coil

8. The RF Current Generated by “Relaxation”
   of M₀ is Picked Up in the Irradiation Coil.

   Signal Generated is a Free Induction Decay
   (FID) Fourier Transform of FID Yields Spectrum
Permanent Magnet Technology
Halbach Magnet Designs

Multiple Matched Magnet Segments. Physically Brought Together to Form Condensed Magnetic Field of 1.35 Tesla

Mechanical Shims Obtain Rough B, Homogeneity

Current Passed Through Wire Gradients Creates Shaped Magnetic Fields That are Used to "Straighten" Field Lines

Electrical Shim Gradients
NMR Spectroscopy

Eg. H$_2$O in NMR Tube

Bad Shim
Inhomogeneous Field

H$_2$O Should Give One Resonance if Shim is Good

Why Shim?

NMR Imaging (MRI)

Eg. H$_2$O in Human Body

Head

Field Lines With Different Bo

FT

In MRI Large Shims are Utilized to Distort the Magnetic Field in a Known Manner in Order to Make the H$_2$O Peak Position Spatially Dependent

Computer Obtains Spatial Location of H$_2$O in Head

Computer Generates Image Based on Water Location
NMR Lock - External $^7$Li Lock @ 22.5 MHz

Matrix Shimming Performed by Optimizing FID RMS

Shim DACs Built into the Magnet Enclosure
## 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) magnet with integral field gradient (shim) coils and 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 enclosure of magnet</td>
</tr>
<tr>
<td>Dimensions</td>
<td>145 cm H x 106 cm W x 65 cm D (57 in H x 42 in W x 26 in D) 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 444 kg (980 lb) gross shipping weight</td>
</tr>
<tr>
<td>Power Requirement</td>
<td>220-240 Vac, 3500W maximum 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: Temperature controlled environment</td>
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<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>
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</table>
60 MHz NMR of Alcoholic Beverages
Whiskeys, Vodkas, Gin, Rum

Schnapps

Port

Beers

Non Alcoholic Beer

Zoomed CH₃ Spectral Region
Showing Increasing Alcohol Content
$^1$H NMR of Essential Oils
NMR Spectral Differences Between Various Edible Oils
Jumping on the Biodiesel Bandwagon

[Graph showing chemical spectrums for Glycerol, Vegetable oil, and Biodiesel]
Biodiesel – Diesel Blends – B0, B5, B15, B20, B100
H-Types Observed in a Gasoline $^1$H NMR Spectrum
Typical Variability Observed in Gasoline Blending
64 Superimposed Diesel Spectra from an on-line Diesel blending application – 3 Hour Stability Test
NMR Innovations Developed to Bring NMR On-Line

- Permanent Magnet Stability and Design
- Shimming Protocols
- Flow-Through Probe Technology
- Post Processing Developments

  Robust auto-phasing routines

  Frequency Domain Averaging

Post-processing monitoring of each constituent spectrum for heavy stream analyses where sediment/rust may be present.
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)
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
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 n-paraffin, i-paraffin, aromatics, naphthenes

Spectral Variability Observed in Naphtha Samples
Process NMR Associates

Application: Closed Loop Reformer Control
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
Application: Crude Distillation Unit Optimization and Control   Installed 2001
Crude Unit Capacity: 180,000 Barrels per Day
Control Strategy: Control on Kero Freeze Point and Crude Tower Optimization
NMR Analysis: 15 Minute Cycle - NMR Results into ROMEO CDU Optimization
NMR PLS Outputs: Naphtha – T10, T50, T90, EP - D86 Distillation
Kero – Freeze, Flash
Crude – API, Sulfur, TBP (38, 105, 165, 365, 565°C)
Units Problem Faced by NMR Spectroscopy for Process Control

NMR Spectrum Reveals: Orthogonal Distinction of Proton Chemical Types

Quantified in Units that are: Atomic% Hydrogen

Reaction Monitoring – Chemical Shift Resolved Peaks or Peak Ratios Can be Monitored

What the Engineer Wants: Historically Derived Analysis Units for Chemical Properties….. GC or MS - Wt % or Vol % - (Which are Molecularly Incorrect Numbers)

Chemometrics is Required to Produce Values for Chemical Properties in the Units Desired by the Control Community. Long term many chemical property control variables could be controlled directly from the NMR spectral variance in the appropriate chemical shift area.

Long Term Direction is to Control Directly from the NMR Spectrum

Base Oil Manufacturing Process – An Example of Using NMR and PCA Based Control
Area under aromatic peaks corresponds to carbon aromaticity

$^{13}$C NMR Spectrum

Correlate to 60 MHz
Process $^1$H NMR Using PLS Regression

Actual Aromaticity ($^{13}$C) vs Predicted Aromaticity ($^1$H)
Empirical Relationship Between Carbon and Proton Aromaticity

$R^2 = 0.99490707$  $DF\ Adj\ R^2 = 0.9947354$  $FitStdErr = 0.86059792$  $Fstat = 8790.7782$

$y = a + bx + cx^2$

$a = -0.23878276$  $b = 4.581846$
Dearomatization and De-Waxing

Base Oil Manufacturing Process

Key Parameters: Carbon Aromaticity, Paraffinicity, Naphthenicity

Typical Spectra
PCA Analysis Performed on Base Oil Samples

Dearomatization

Dewaxing

Process NMR Associates
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