Advances in Field-Deployable NMR Instrument for Laboratory and Process Applications in the Petroleum and Petrochemical Industries: Chemometrics, Direct Measurements, and Data Fusion

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PROCESS NMR ASSOCIATES

250+ Analytical NMR Customers

TTC Labs, Inc.
Process Engineering Excellence

Analytical Services And Consulting

TopNIR Systems

Analytical Services And Consulting
First Generation NMR – 1998
Elbit-ATI/Foxboro NMR

Second Generation NMR – 2003
Qualion
Third Generation NMR - 2013– Aspect AI NMR System

New magnet design – 30mm bore size

- The amount of magnetic pieces that assemble the magnet reduced from 34 to 10. Reduction in Mechanical Complexity

- Bore size of the magnet was increased to 30 mm - improved temperature susceptibility

- Improved temperature and shim stability.

New Digital Spectrometer Design - reduces footprint, improves signal processing capabilities

Probe - Improved Probe Q for Higher Sensitivity.

Software – Windows 7 – Improved Chemometric Capabilities
NMR Sample System and Placement
NMR Lock - External \(^7\)Li Lock @ 22.5 MHz
Spectrum \(^1\)H Frequency Lock

Shim DACs Built into the Magnet Enclosure

Matrix Shimming Performed by Optimizing FID RMS
60 MHz NMR of Essential Oils

13C NMR at 7 Tesla

60 MHz

300 MHz

Yatver Essential Oil

1H NMR

1H NMR

60 MHz

300 MHz

Ginger Essential Oil

13C NMR at 7 Tesla

1H NMR

60 MHz

300 MHz

Cinnamon Leaf Essential Oil

60 MHz

300 MHz

Eucalyptus Globulus Essential Oil
Fish Oil Nutritional Supplement - Manufacturing Process

Omega-3 Fatty Acid Concentration

Eicosapentanoic acid (EPA)
Docosahexanoic acid (DHA)

EPA PLS1 Model 5 Factors R2=0.984
Adhesive Pre-polymers

Polyurethane A

Polyurethane B

Polyurethane D

Polyurethane C
Processed Oil Shale Hydrocarbon

60 MHz

300 MHz
Gasoline $^1$H NMR

- **60 MHz**:
  - Aromatics
  - Alkenes
  - Ethanol
  - $\alpha$-CH$_2$
  - CH

- **300 MHz**:
  - Aromatics
  - Alkenes
  - Ethanol
  - $\alpha$-CH$_3$
  - CH$_3$
  - CH$_2$
NMR Data Processing for Input into Chemometrics

- 2K FID → ZERO FILL → 16K FID
- Binned Spectrum
- PLS, PCA, MLR
- INTEGRATION BINNING NORMALIZATION
- Unphased Spectrum
- FT
- Phased Spectrum
- AUTOPHASE
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
Superimposed $^1$H NMR spectra for samples spanning the entire density range.

- 0.691 g/ml
- 0.753 g/ml
- 0.791 g/ml
- 0.827 g/ml
Superimposed $^1$H NMR spectra for samples spanning the entire MON range.
$R^2 = 0.976$
$secv = 0.60$ Octane
9 Factors
346 Samples
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

RON Validation - April 2001 - April 2002
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 Observed in Naphtha Samples
Predicted Toluene (Wt%) ( F9 C1 )

Actual Toluene (Wt%)  |  Beta Coefficient ( F9 C1 )

Predicted Toluene (Wt%) ( F9 C1 )

Toluene
Predicted Cyclohexane (F9 C1)

Actual Cyclohexane (Wt%)

Beta Coefficient (F9 C1)

Spectral Units ( )

Cyclohexane
Iso-C5 Paraffin

Date


Wt%
96 Hours of NMR Process Output – iso-Paraffin Components
96 Hours of NMR Process Output – Aromatic Components
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, 565C)

Kero Freeze Lab Vs NMR

-65
-60
-55
-50
-45
-40
2002/05/01 2002/05/03 2002/05/05 2002/05/07 2002/05/09 2002/05/11 2002/05/13 2002/05/15 2002/05/17 2002/05/19
Lab Freeze (DegC)
NMR Freeze (DegC)
Online NMR Applications

1995 - BTU Analysis of Refinery Fuel Gas - Texaco
1995 - Sulfuric Acid Strength in Emulsion Zone of Stratco Acid Alkylation Unit - Texaco
1999 - Diesel Blending System - Motiva
1999 - Reformer Control System – BP, Pertamina
2000 - Naphtha Cracker Feed Analyzer – Full GC PIONA – BASF, Lyondell
2000 - Crude Unit Analyzer – PDVSA, BRC, ConocoPhillips
2000 - Crude Blending System - Reliance
2001 - Gasoline Blending System – Fina, Valero
2001 - Base Oil Manufacturing Analyzer - AGIP
2002 - FCC Unit Analyzer – BP
2002 - At-Line Bitumen and Vacuum Residue Analyzer – ERG
Process NMR Associates

**SpinSolve™**
- 42 MHz NMR
- 3-5 mm Samples
- Lab Only

**Oxford Instruments**
- Pulsar
- 60 MHz NMR
- 3-5 mm Samples
- Lab Only

**Bruker**
- Fourier 60
- 60 MHz NMR
- 3-5 mm Samples
- Lab Only

**MobiLab™ SPECTRA 2T**
- 85+ MHz NMR
- 3-5 mm Samples
- Lab Only

**nanalysis**
- NMReady 60
- 60 MHz NMR
- 3-5 mm Samples
- Lab Only

**Thermo Scientific**
- Picospin 45 and 80
- 45 MHz and 82 MHz NMR
- 300 micron capillary injection
- Lab Only

**Qualion**
- 60 MHz NMR
- 3-10 mm Samples
- Lab or On-Line

**aspect imaging**
- 60 MHz NMR
- 3-10 mm Samples
- Lab or On-Line

September 12, 2013
Why the Entrance of so many players into low field NMR analyzers?

Vindication of potential value and markets?

Petroleum, Petrochemical, Food, Pharmaceutical, Diagnostic Materials, Agriculture, Mining, Consumer Goods, Cosmetics
Direct Measurements

Integration of Particular Peaks in Spectrum to Obtain:

Quantitative Analysis

Monomer Ratios

Reaction Monitoring – Kinetic Modeling from Reactant Peak Intensity

Molecular Ratios and Mixture Analysis
$^1$H NMR Reaction Monitoring – Esterification of t-butanol with acetic anhydride
Acid Catalyzed Esterification of Iso-Butanol with Acetic Anhydride
Esterification of t-BuOH
Integral Graph
And Integration Plot

T-BuOH
T-Bu-Ester
Ac-Ester
Acetic Acid
AcAn
1H NMR – Sucrose Hydrolysis by Invertase Enzyme
Microreactor Process Monitoring – $^1$H NMR – Reaction: Cyclohexene $\rightarrow$ Cyclohexane

Microreactor Hydrogenation Reaction
Cyclohexene to Cyclohexane

13C Satellites do not interfere

Cyclohexene

Chloroform

Methanol

Cyclohexane
At-Line Analyzer - $^1$H NMR Observation of Alkene Saturation
31P NMR
Phosphoric Acid in Water
Concentration Range 21-85 Wt%

Linewidth = 2.5/8/23 Hz
at 50%/10%/0.5% peak height

24 Signal Averages (2 Minutes)
S/N 1800:1 for 1H
S/N  160:1 for 31P
31P NMR - Polyphosphoric Acid - Catalyst for Alkylation Process

Acid Strength Calculated from Ratio of Peaks

- Acid Strength: 106.37
- Fresh Acid

- Acid Strength: 113.60
- Process Acid

24.2 MHz at 1.4 Tesla
8 Pulses
2 Minute Analysis

Replaces 500 MHz NMR Test
No more emergency tests that bring research personnel in at night and weekends.

Immediate Answer
Data Fusion ..... ?

No Benefit Observed in Analyses Performed so Far ....
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For more information and applications visit www.process-nmr.com