

ASPECT Magnet Technologies Ltd.

Process NMR Systems

March 2011

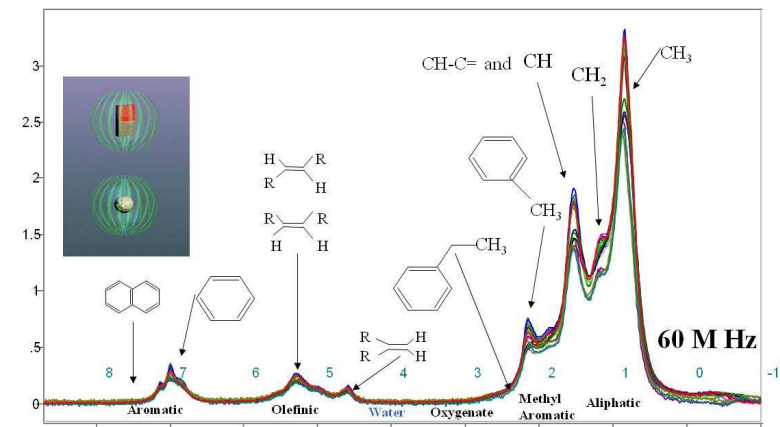


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The Technology :What is NMR?

- Nuclear Magnetic Resonance - is an effect whereby magnetic nuclei in a magnetic field absorb and re-emit electromagnetic (EM) energy at a specific resonance frequency. The resonance frequency depends mainly on the strength of the magnetic field.
- This physical phenomena can provides picture or spectra of the *hydrocarbon structure*, which enable to determine *physical and chemical information*.
- A major benefit of this analyzer is the capability to provides continuous flow-through and accurate chemical and physical analysis of multiple components in *dense and opaque materials*.
- Additional key advantage is a *linear spectral* response across a broad range which enables models to be extrapolated accurately. NMR technology *does not* have the continual *model maintenance* issue which caused by spectral changes seen with *crude composition changes*.



Typical Hydrocarbon Spectrum

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Evolution of the Process NMR Systems

- **1997 - 1st Generation of On-line Process NMR System**

- Magnet – 18mm bore size (medium homogeneity; high temperature susceptibility; inadequate repeatability)
- 7 Electronic units (Shim controller; RF unit; PS unit; 19" rack PC; Heater controller; ADC PCB; Timing PCB)
- Shim coils – manually wrap around coils (inferior performance; inadequate repeatability)
- Software – DOS based software (awfully limited; no remote diagnostic; lacking major process requirements; imperfect signal processing algorithms; imperfect communication ability)
- Probe – Low Q (low SNR- Signal to Noise Ratio); defective temperature insulation
- Huge overall foot print of the entire enclosure



- **2000 – 2nd Generation of On-line Process NMR System**

- Magnet – 24mm bore size (high homogeneity; high temperature susceptibility)
- 6 Electronic units (Shim-Heater controller; RF unit; PS unit; 19" rack PC; ADC PCB; Timing PCB)
- Shim Coils – manually wrap around coils (inferior performance; inadequate repeatability)
- Software – Windows NT based software
- Probe – Low Q (low SNR- Signal to Noise Ratio); imperfect temperature insulation
- Large overall foot print of the entire enclosure



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2010- 3rd Generation of Process NMR System

New magnet design – 30mm bore size

Better long term and short term stability
Improve temperature susceptibility

State of the Art electronics (Only 2 units)

Smaller foot-print
40 Shim coils on 2 single PCB
Complete integrated PCB for
Shim & Heater Control
Digital RF & Acquisition Boards
Panel mount touch screen PC
(ATEX certified)

New concept of Process Probe

An entire pipe go through without contact
with the system
Much better temperature insulation
Higher Q (better SNR)

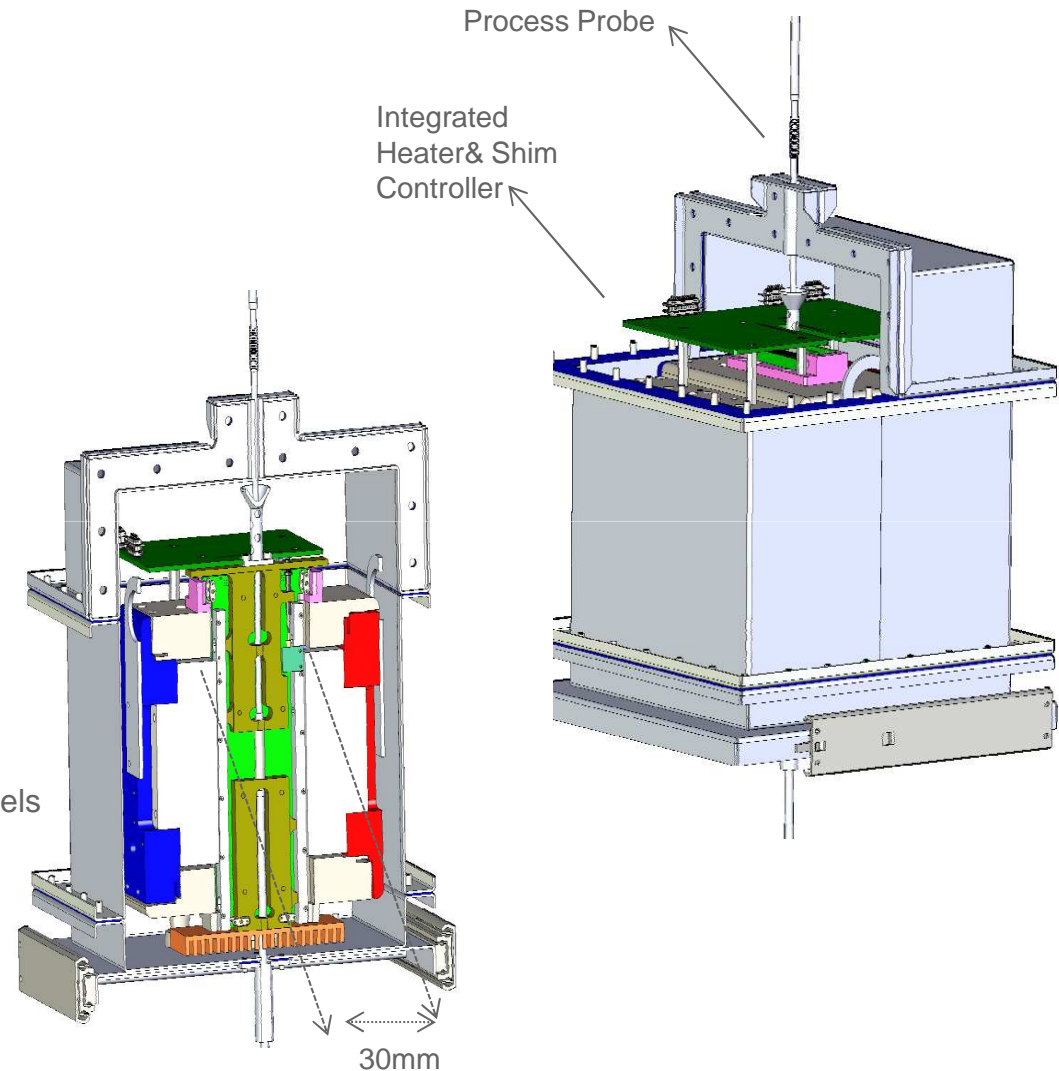
Windows XP or 7 based Software

Includes new algorithm for standard and global Models
Fully automated process capacity
Extensive remote diagnostic capabilities

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Aspect NMR Complete Solution

- 3rd generation Process NMR Analyzer
- Sample Switching and Conditioning System
- Engineering Services
 - Models
 - Systems validation
 - Models maintained for one year after validation
 - Round the clock remote support
 - All hardware under warranty for one year after start-up

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Operation Conditions

ATEX II 2G Eex pdem [ib] IIC T4 Certificate
Housing

Operational to 38° C, IP 54

Sample Cell Design

Flow through cell

Up to 120° c

Up to 24 Bar g

Alarming

Digital inputs for Alarms

Built in user configurable alarm logic

Communications

Modbus (RS485 or TCP/IP)

Ethernet to remote interface

Stream Switching

8 Solenoid outputs

Built in user configurable stream switching logic



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Sample Handling System

- Sample must be Homogeneous
- Filtering
 - 100 μ to protect valve seats
- Temperature Control
 - Analyzer sample inlet (+/- 10 ° C)
 - Hot enough for the heaviest stream
 - Cool enough for the lightest stream
- Stream Switching
 - Double Block and bleed
- No water removal necessary



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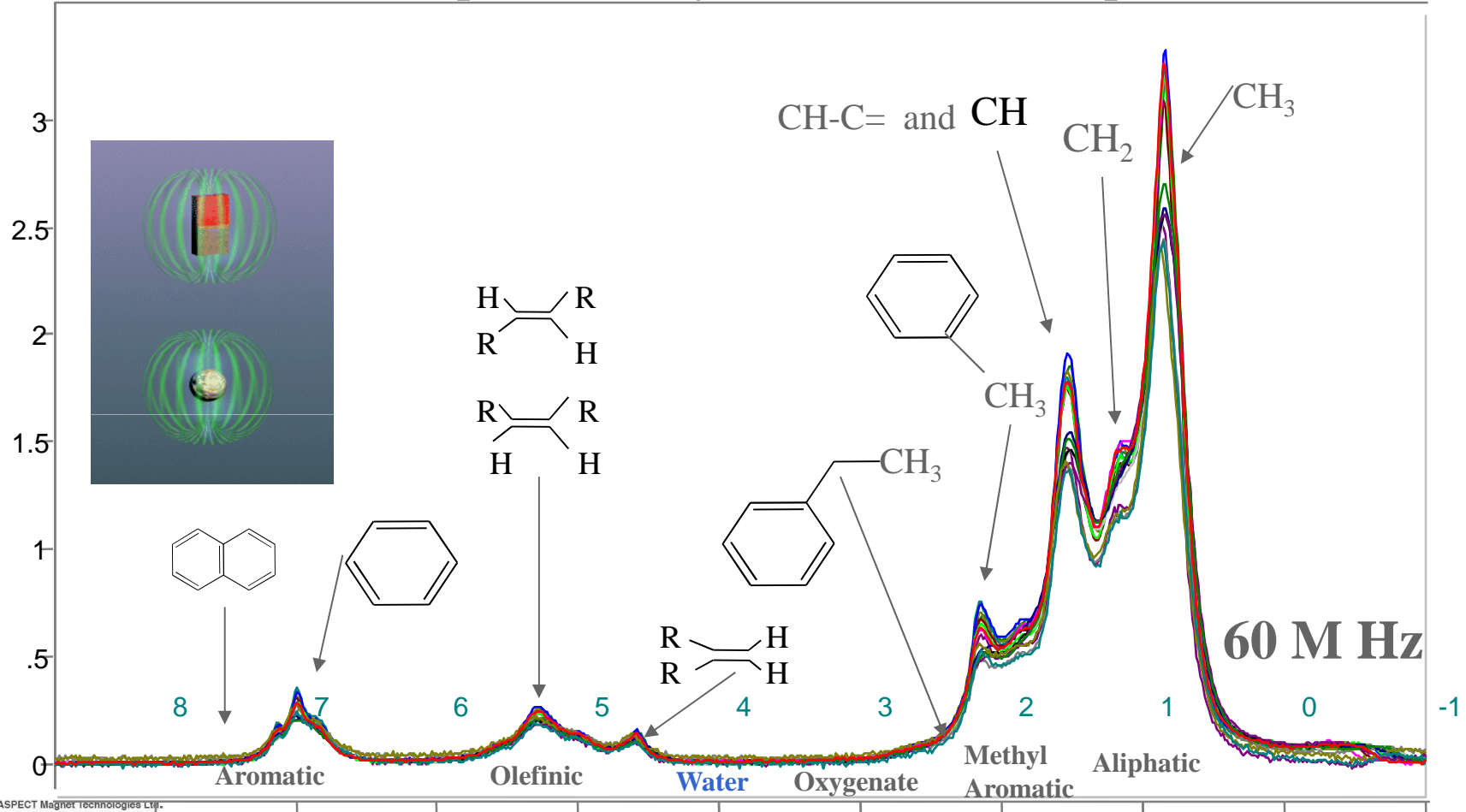
NMR Spectroscopy Spectra and Modelling

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Typical Hydrocarbon Spectrum

All Functional Groups are clearly Resolved & the response is Linear

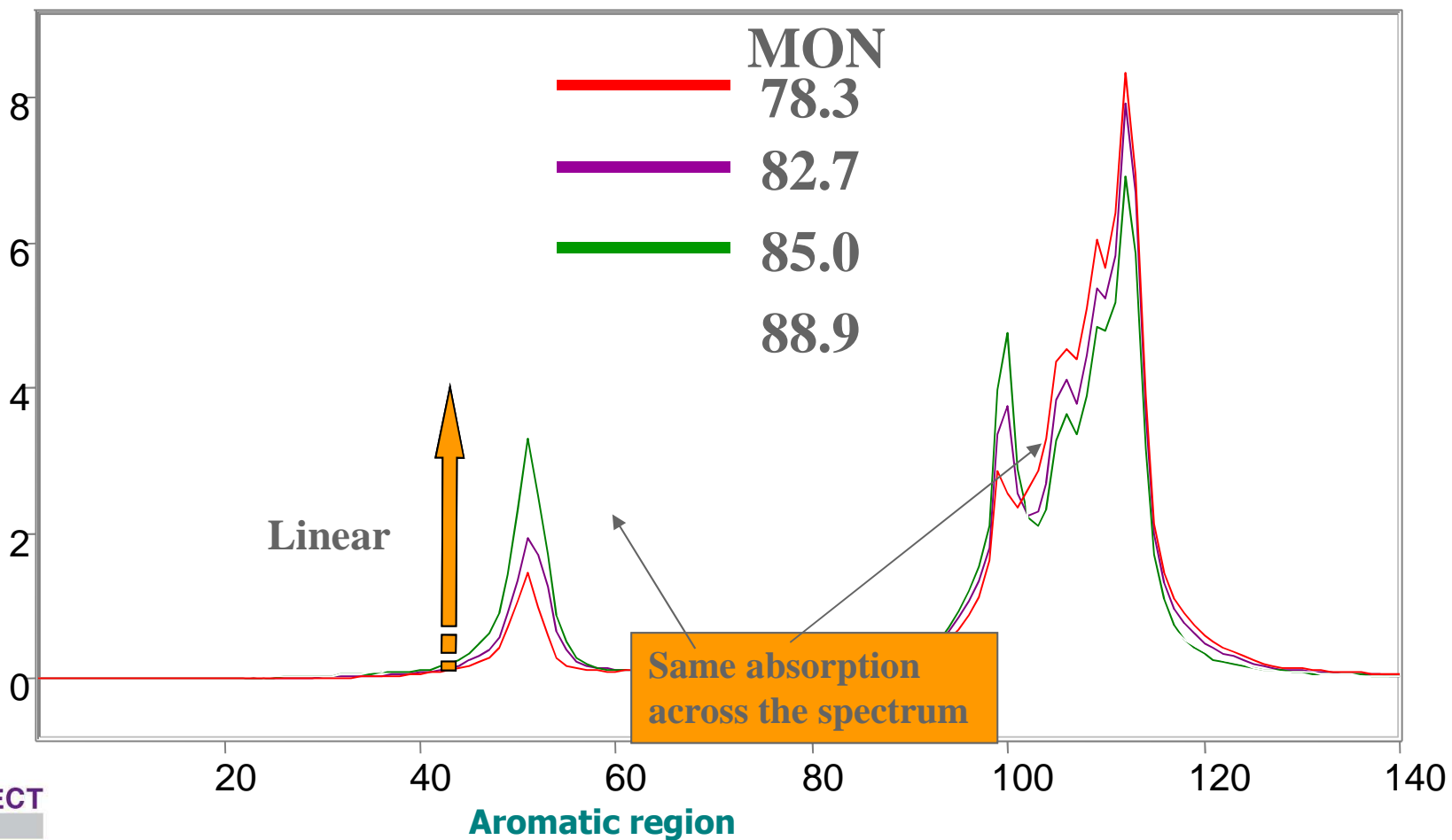


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Variability of Gasoline NMR Spectra



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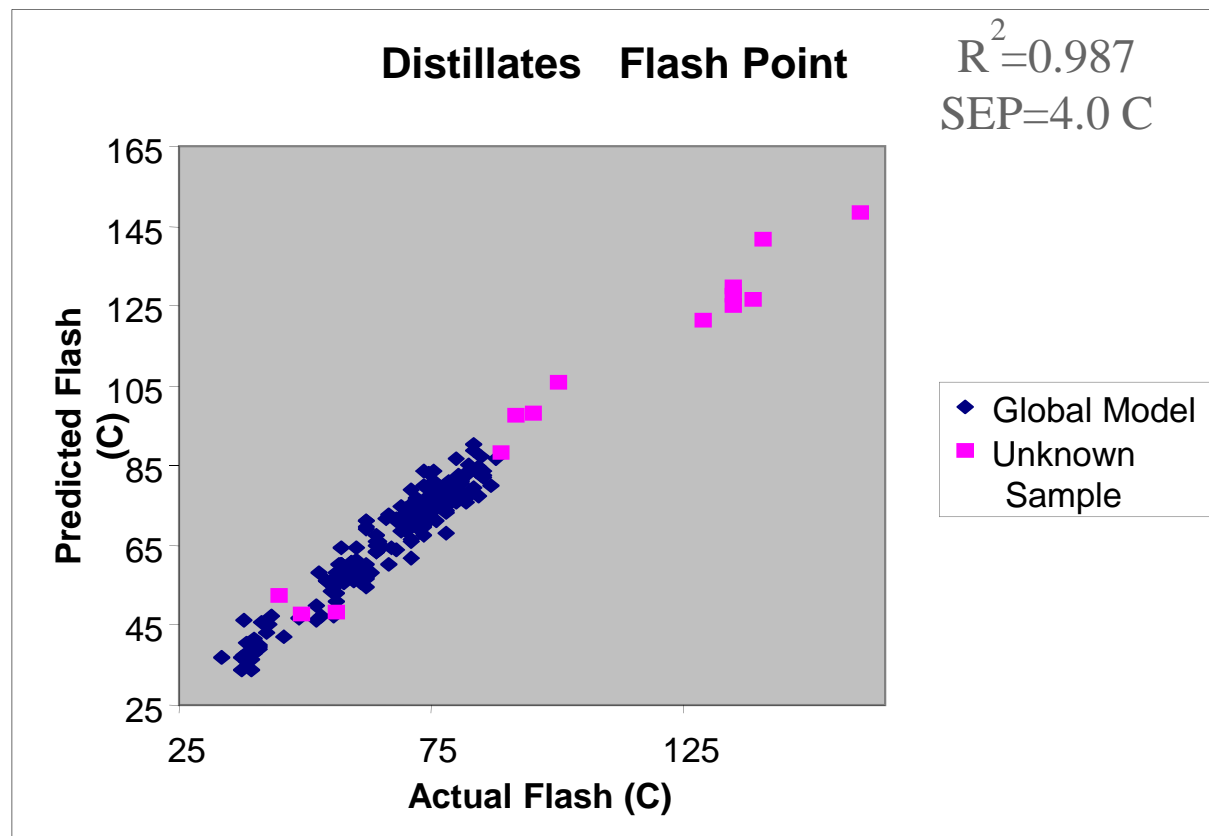
Superimposed ^1H NMR spectra for samples spanning the entire MON range

The Linear Modelling - Advantage

Fewer Data Points required to build model

Extrapolation for “out-of-range” feeds benefits :

- Faster start up
- Low maintenance of model



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Where is NMR Technology Used?

- Refineries
- Olefins plants
- Biotech
- Bio-Chemical
- Ag/Food
- R&D - Both Academia and Industrial
- Polymer

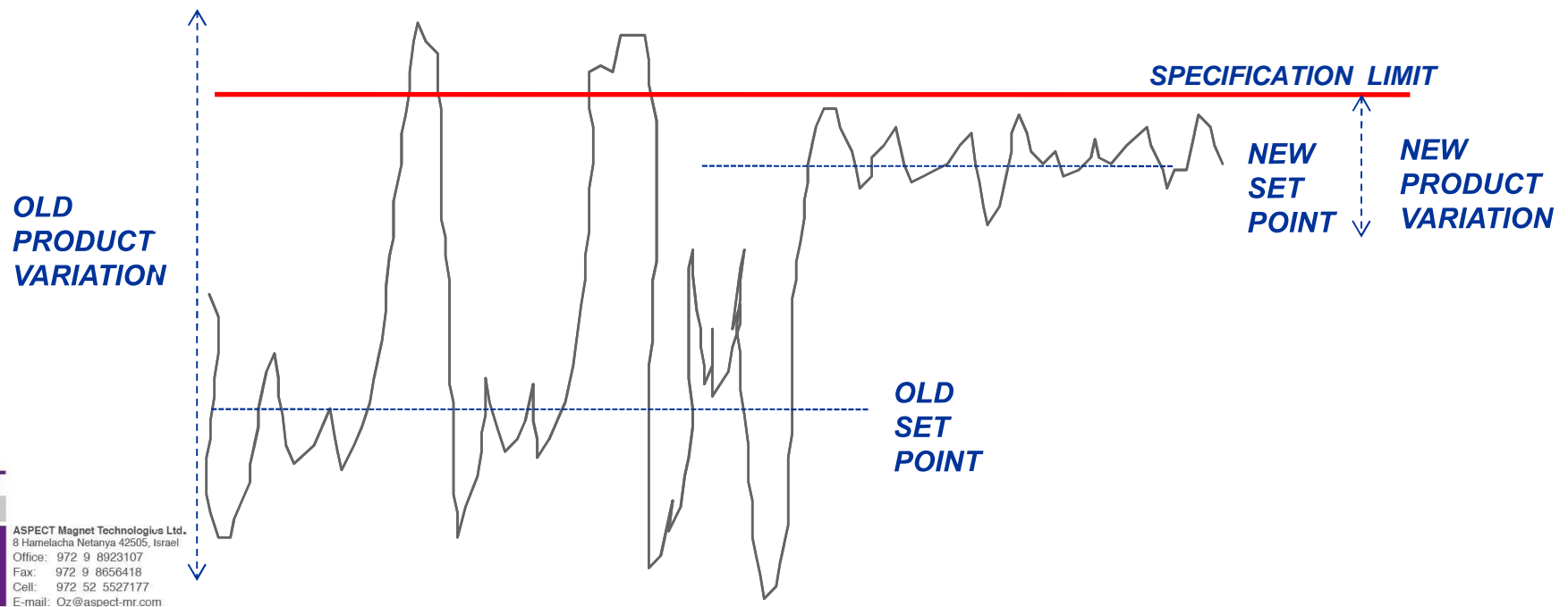
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Automation Objectives

- Stabilize Operation
- Minimize Content of More Valuable Products
- Maintain Product Quality Within Specs
- Optimize Unit (Production, Energy, Raw Materials)
- Integration with offline systems
- Provide Operational Tool



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NMR Analyzers Advantages

- **Real time**, continuous **flow-through stream** analysis
 - Reduction in response time from Lab allows tighter control
- Provides analysis in **dense** and **opaque** materials
- **Direct Molecular Measurement**
 - No indirect predictions on critical measurements
- **Linear Spectral Response** across broad range
 - Models can be extrapolated accurately
- **Direct and Multi-property** analysis
 - Replaces conventional analyzers and provide faster results
 - Provides high accuracy data for precise control
 - High repeatability and reproducibility
- **Simple Sample Conditioning** required
 - No water removal, limited filtering to protect valve seats
- **Minimal maintenance** required
 - No moving parts in sensor

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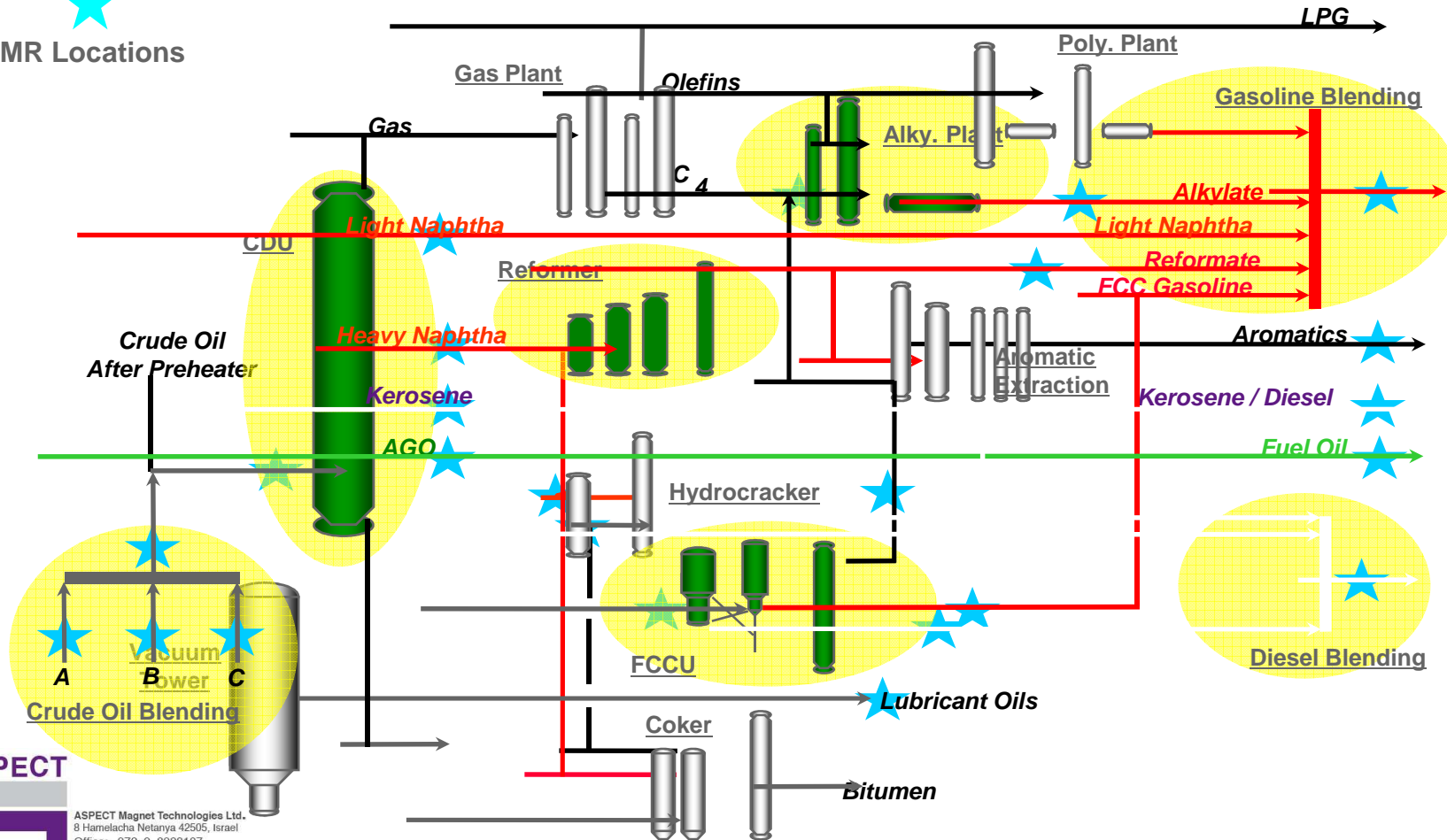


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NMR Refinery Applications



NMR Locations

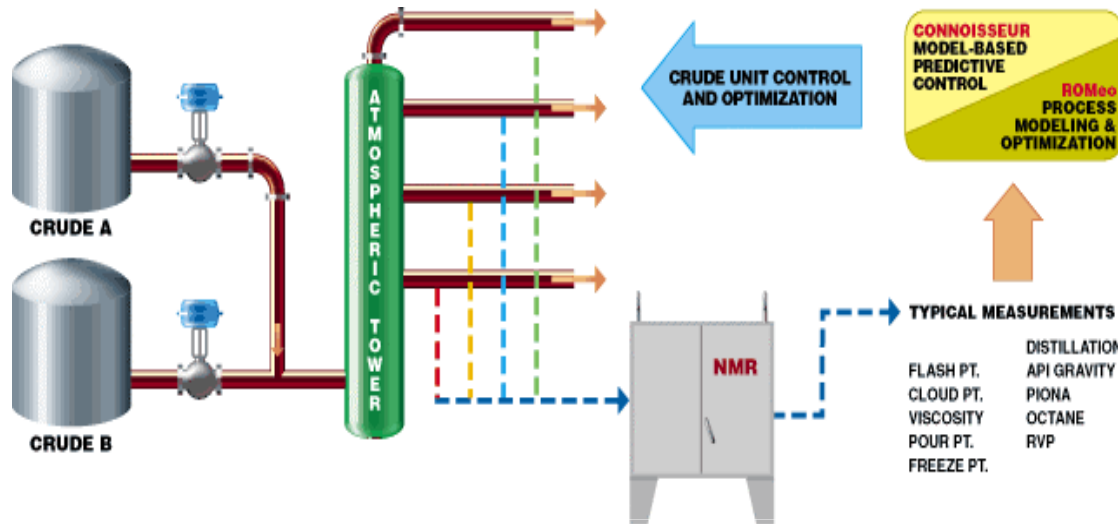


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Case Study – Crude/FCC Rundown



Measurements

- Cetane Index
- API Gravity
- Distillation
- Flash Point
- Cloud Point
- Sulfur Content
- Freeze Point
- Octane (RON,MON)
- Specific Gravity @ 15C
- Density
- RVP
- Naphthalene Content
- PIONA
- Viscosity
- Pour Point

Offering

- Process NMR Analyzer
- Sample System for multi-stream analysis
- Engineering Services

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Case Study - CDU Feed (1)

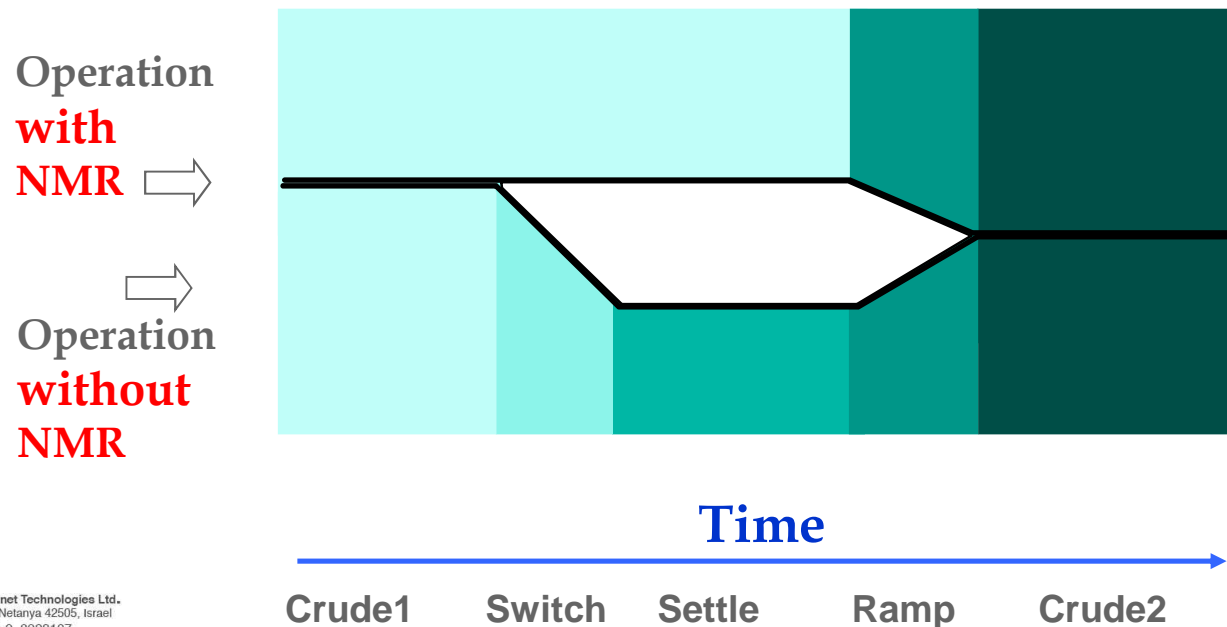
■ Today's situation

Loose throughput during crude slate changes

Crude transition times

However, refiners need to be flexible with feed stocks

CDU influences on downstream performance - increases (constraints)

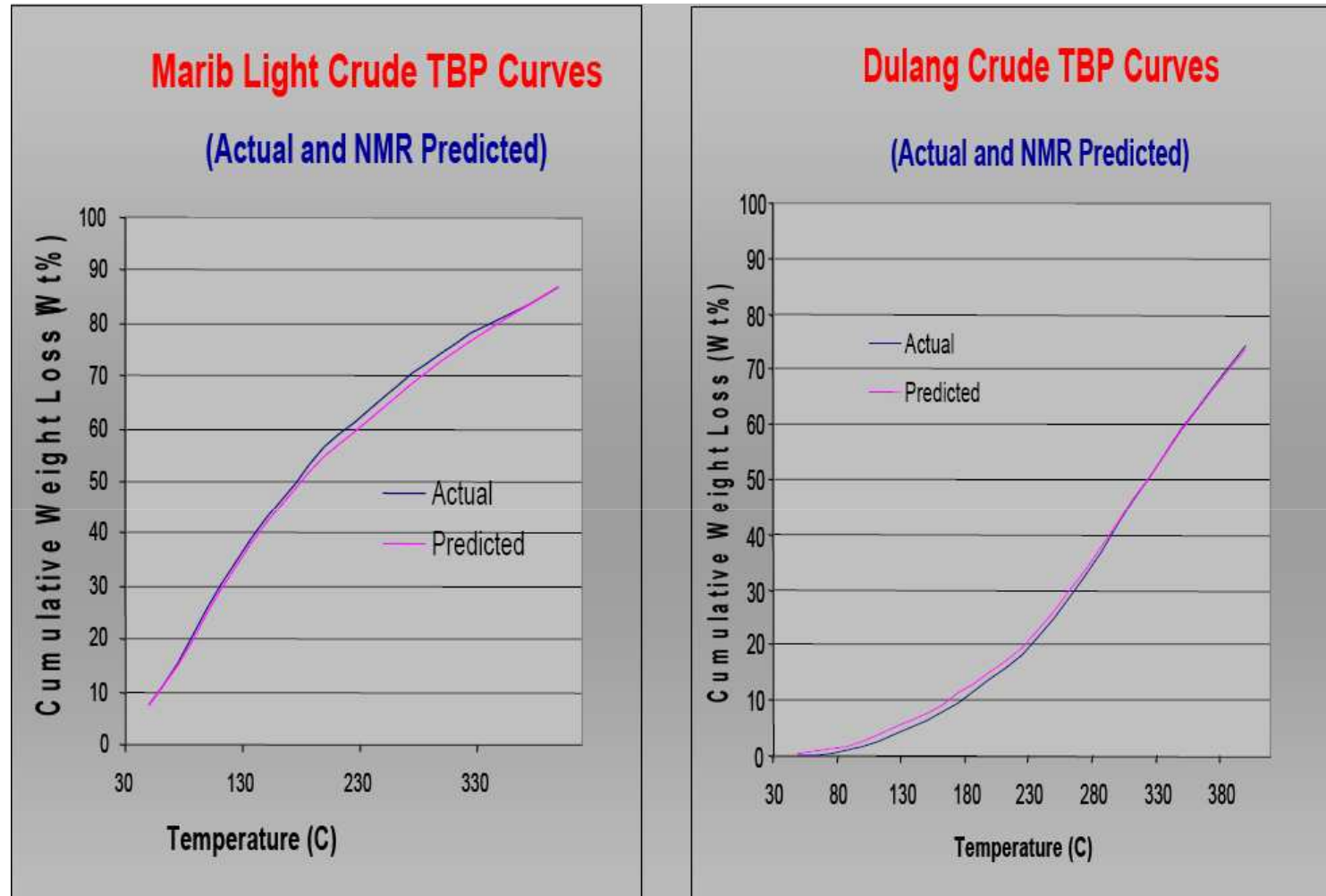


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Case Study – CDU Feed (2)



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Crude TBP

Case Study - FCC Feed Application (1)

Yesterdays situation

- Refiners need to be flexible with feed stocks
 - Can the VDU provide enough feed ?
 - Is it more economical to buy feed on the open market ?
- Lost throughput during feed tank changes
- Feed transition times
- If controlled the FCCU is the biggest money maker

And ...

- On line measurement on FCC feed was traditionally not available !

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Case Study - FCC Feed Application (2)

Today:

- NMR Analyzer can provide ability to run combined feed stock (Both from the VAC unit and Tank Park)
- Increase unit feed variability
- Shift closer to constraint of process unit
- Eliminate lab sampling
- Biggest money generating unit on the refinery
- Feed forward control into cat cracker (RTO)
- Feedstock is variable and needs analysis

Measurements

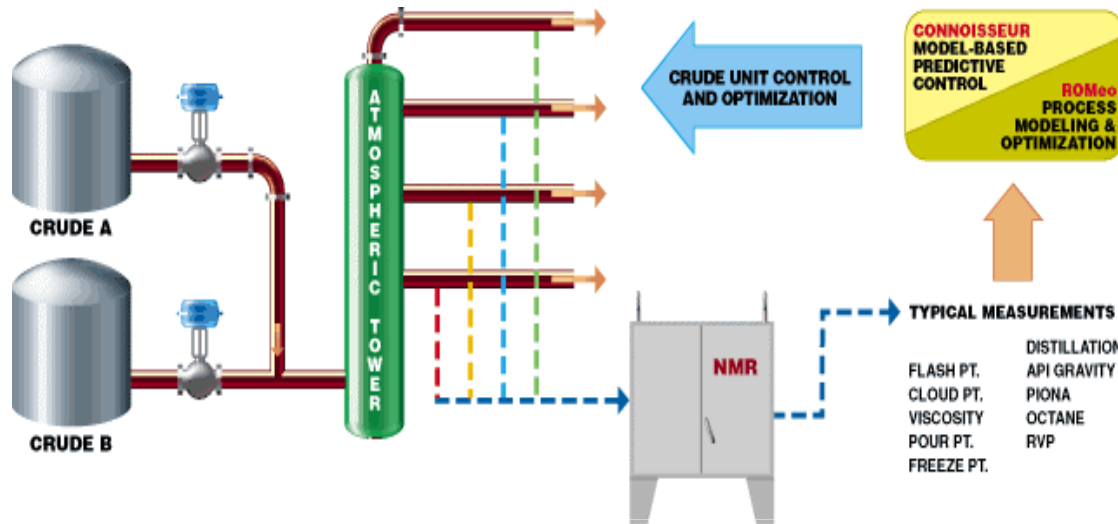
Distillation
API Gravity
Water
Viscosity
Sulfur
Aromaticity
Concarbons
Basic Nitrogen
Asphaltenes
Refractive Index
Parafins
Naphtalenes
Carbon Aromaticity
Carbon Naphthenicity
Carbon Parafinicity

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Case Study – Crude/FCC Rundown



Offering

- Process NMR Analyzer
- Sample System for multi-stream analysis
- Engineering Services

Measurements

- Cetane Index
- API Gravity
- Distillation
- Flash Point
- Cloud Point
- Sulfur Content
- Freeze Point
- Octane (RON,MON)
- Specific Gravity @ 15C
- Density
- RVP
- Naphthalene Content
- PIONA
- Viscosity
- Pour Point

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Case Study – CCR Application

Features:

- One analyzer for feed and product stream analysis
- Online measurements historically not available
- Increase unit yield capabilities
- Shift closer to constraint of process unit
- Eliminate lab sampling

Benefits:

- Reduce number of analyzers
- Reduce maintenance costs
- Reduce product giveaways

Measurements

RON

MON

Benzene

Aromatics

Distillation

API Gravity

PIONA

Detailed Hydrocarbons

S.G.

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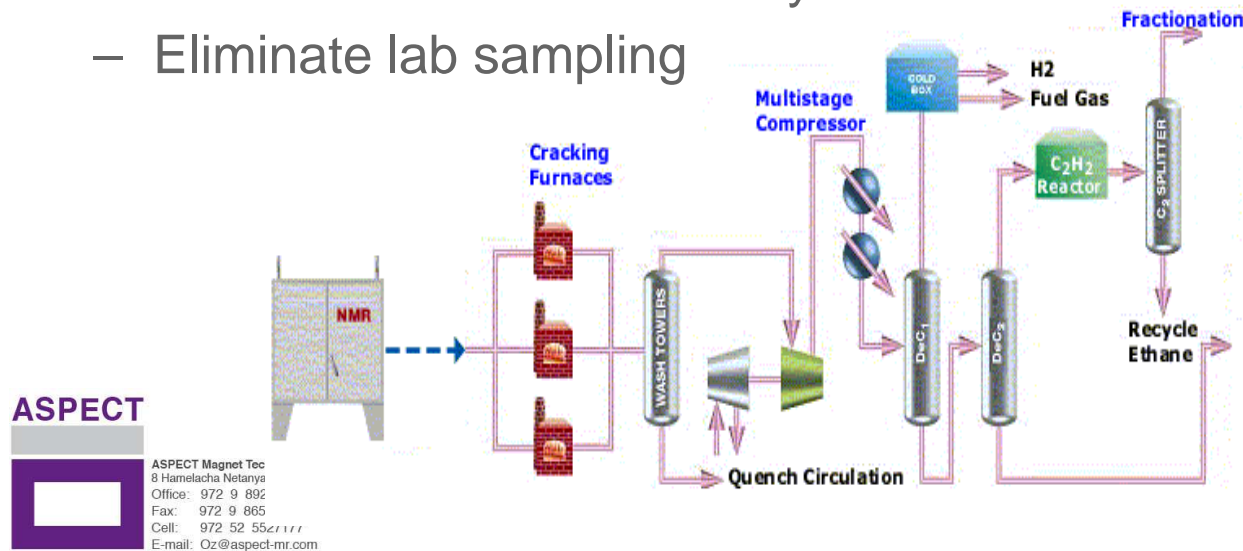
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Case Study– Naphtha Cracker Application

- Features:
 - Only NMR can provide all liquid feed Compositions in *minutes*
 - Real time analysis of critical compositional data allowing tighter control
 - Increase unit feed variability
 - Eliminate lab sampling

Measurements

- PIONA
- Distillation
- Sulfur
- API Gravity
- Specific Gravity
- Density
- Detailed Hydrocarbons
- Cyclopentane
- Cyclohexane
- me-cyclopentane
- Methylcyclohexane
- Benzene
- Toluene
- Ethylbenzene
- Xylenes
- Hydrogen
- Viscosity

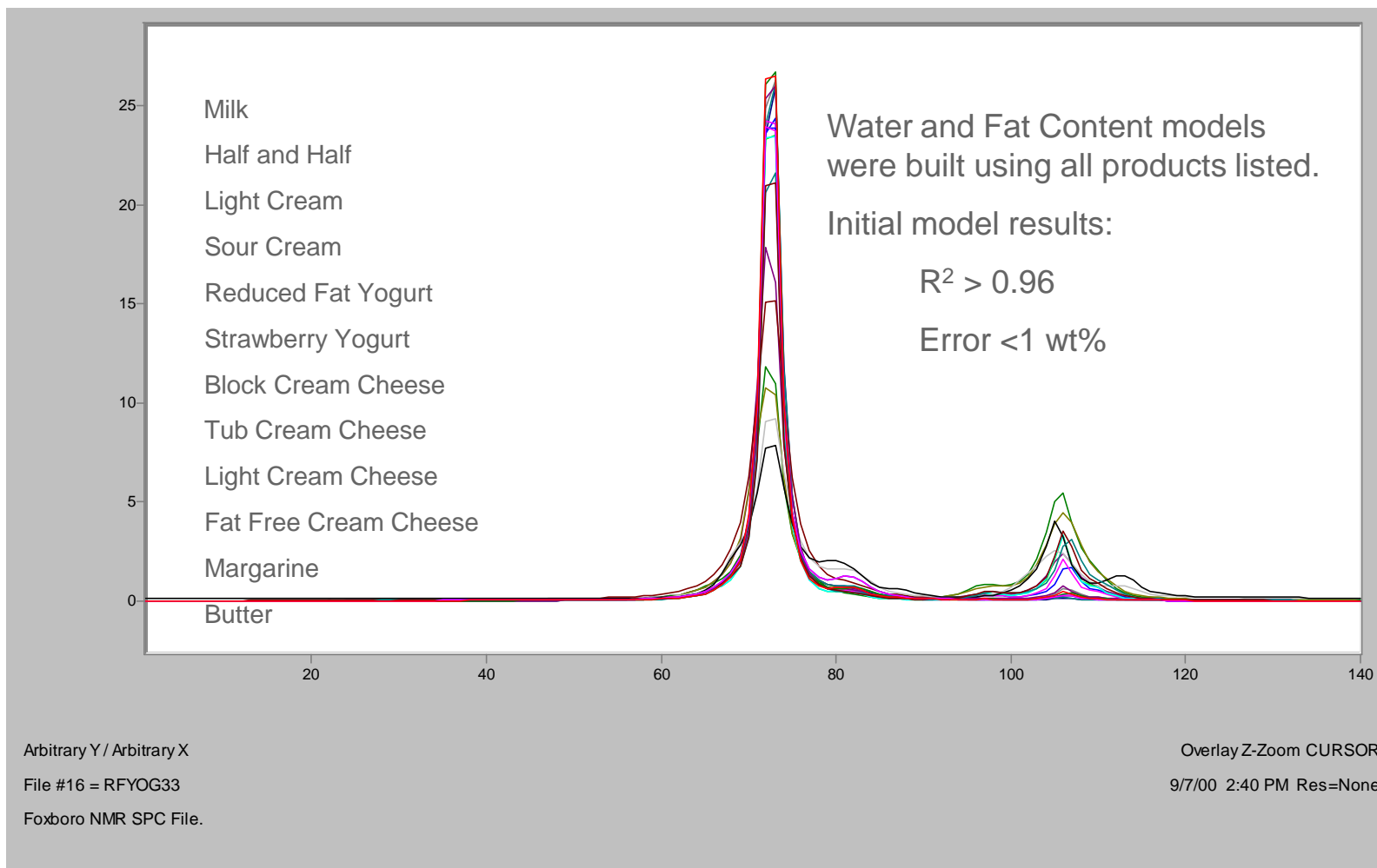


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Case Study - Dairy Products



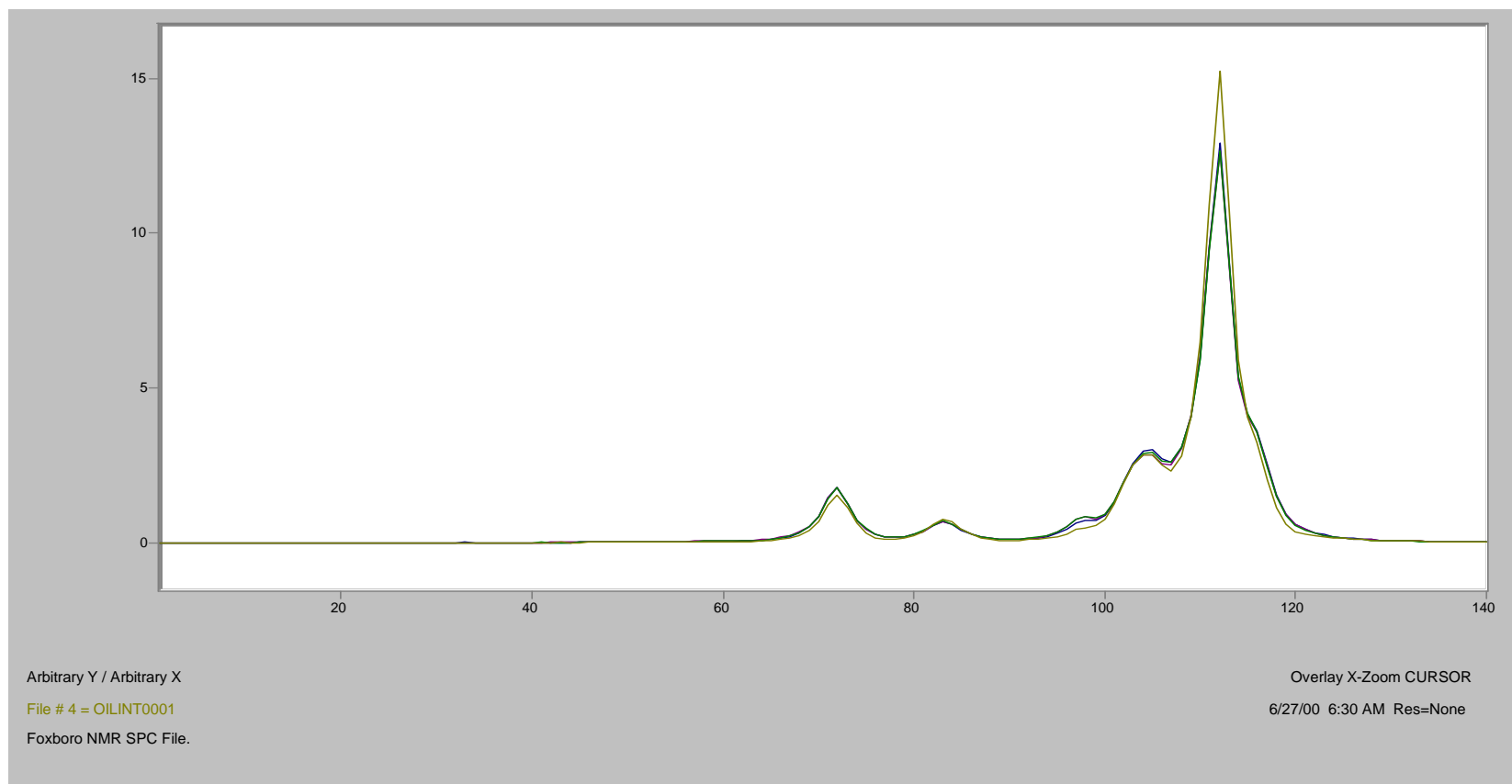
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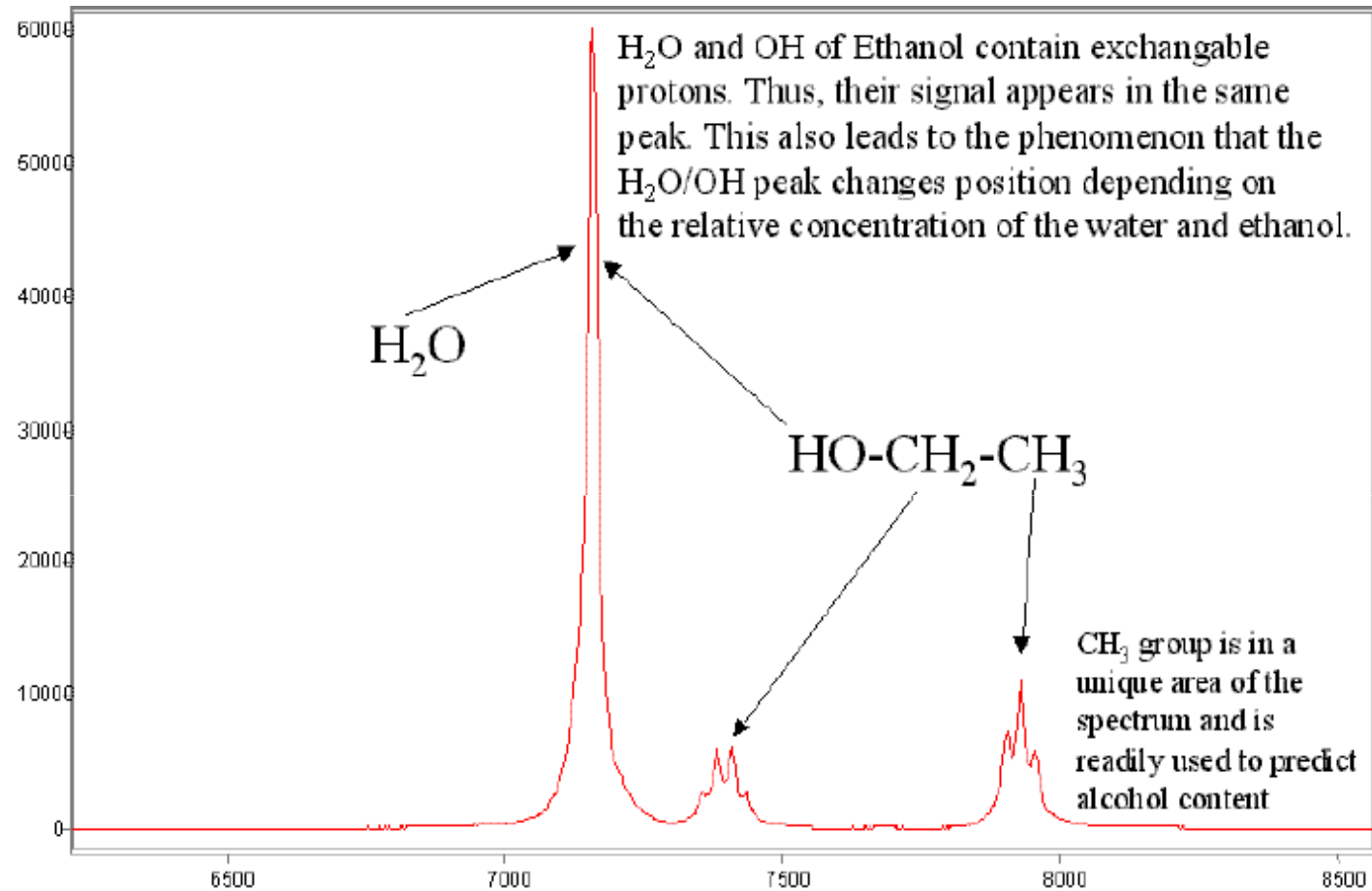
Case Study - Food Oil Analysis

Oils and fats are key elements in the taste, melting properties, shelf life, and appearance of foods



Composite Spectra of 4 Oils (Olive, Sesame, Canola and Caesar Salad Dressing) Showing Differences Observed by NMR

Case Study - Liquors Analysis (I)



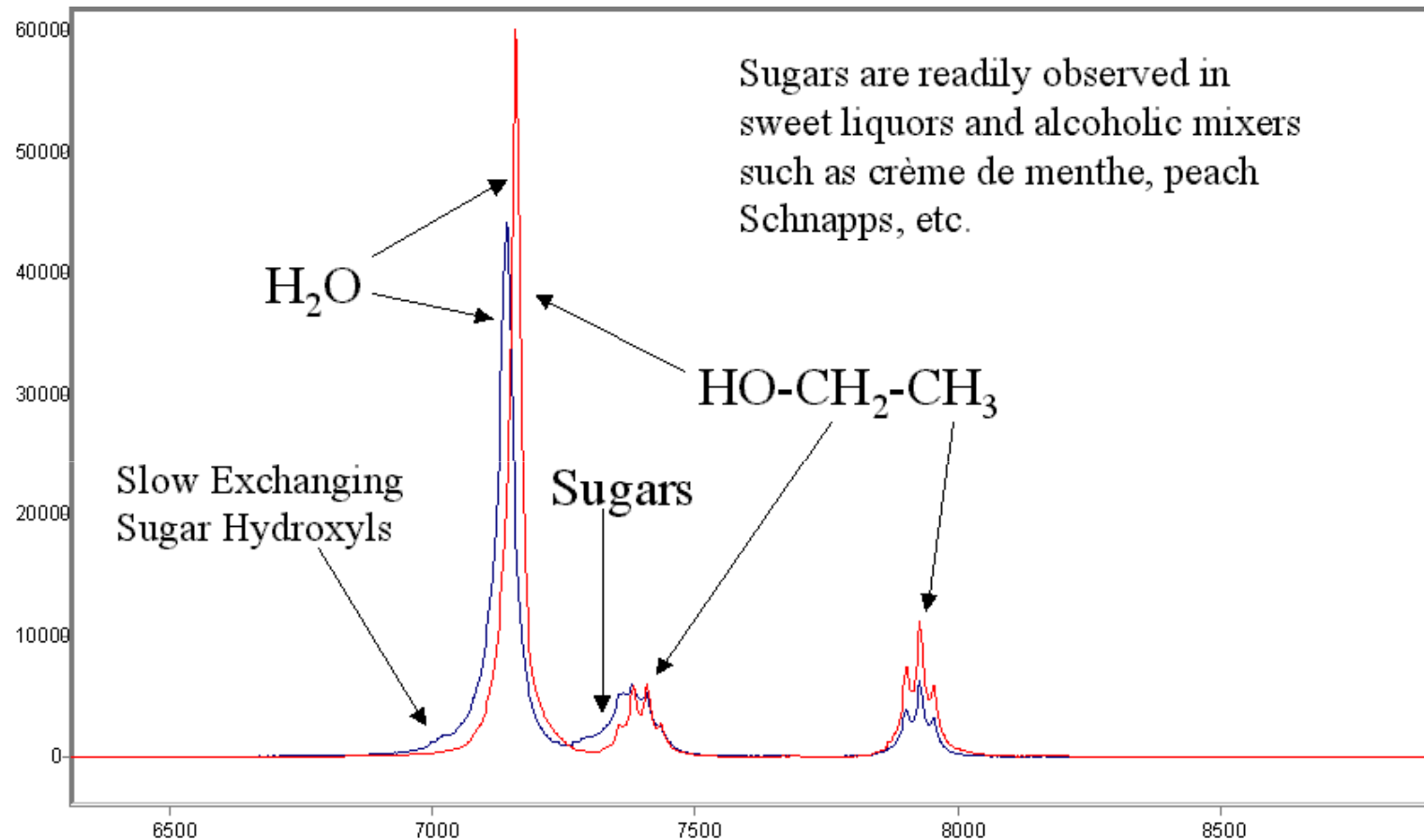
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Chemistry Observed in Whiskey
“Hard” Liquors, Port, Wine, and Beer

Case Study - Liquors Analysis (II)



**Comparison of Whiskey (Red) and
A Sweet Whiskey Based Liquor (Blue)**

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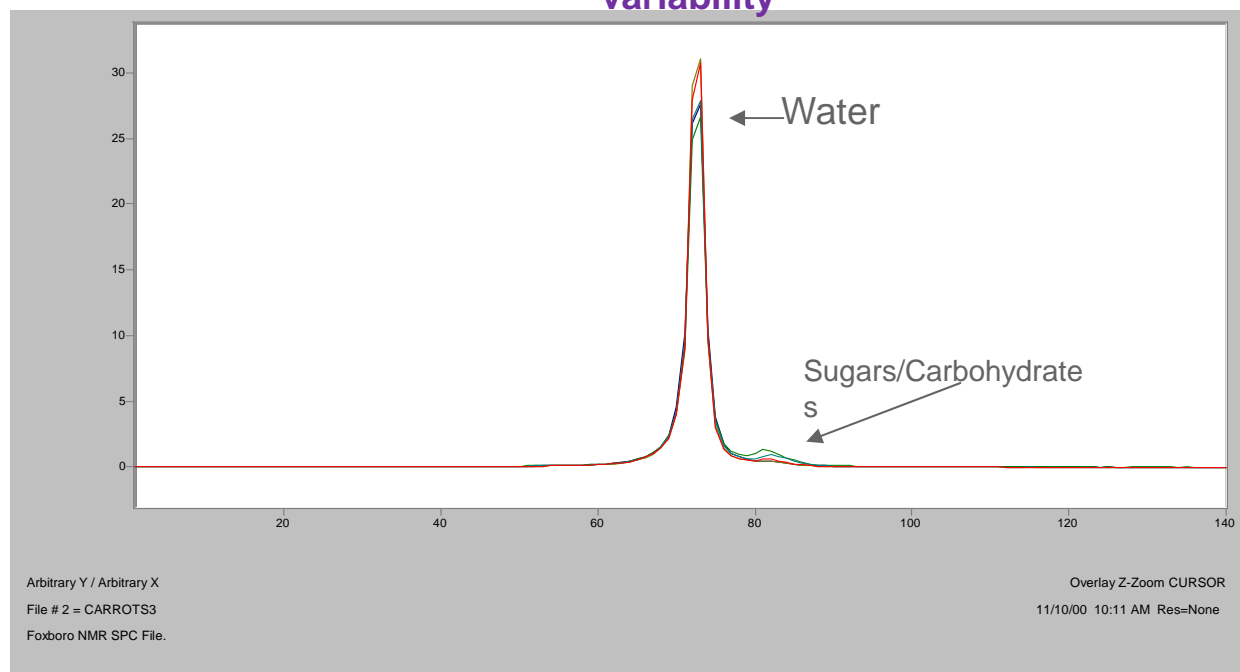


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Case Study - Baby Food

<u>Package Description</u>	<u>Serving Size</u>	<u>Total Fat</u>	<u>Total Carbohydrate</u>	<u>Protein</u>	<u>Water (by diff)</u>
Bananas	71g	0g	17g	1g	52.8g
Sweet potatoes	71g	0g	10g	1g	59.8g
Squash	71g	0g	5g	1g	64.8g
Carrots	113g	0g	7g	1g	104.7g
Peas	71g	0g	5g	2g	63.9g

Overlay of all 5 baby food products showing NMR variability



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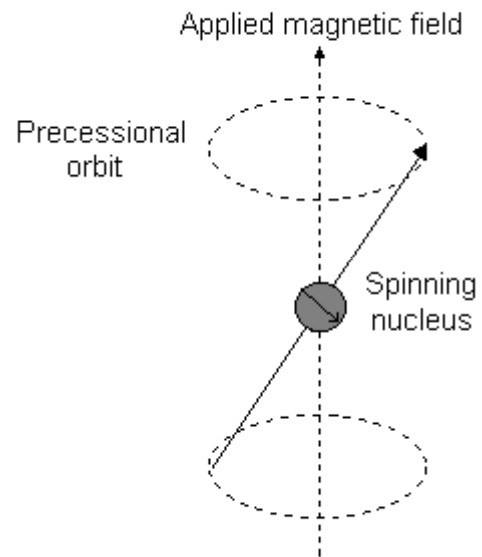
The NMR Technology

Fundamental background

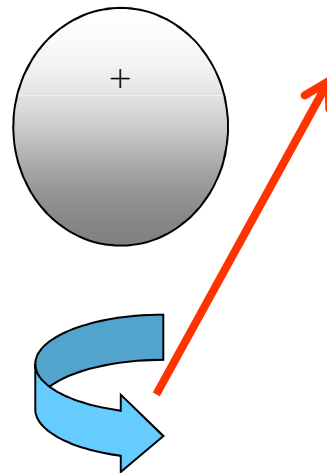
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Proton – Magnetic Moment (M)



Hydrogen Atom (Proton)



**Proton is spinning -
Magnetic moment generated**

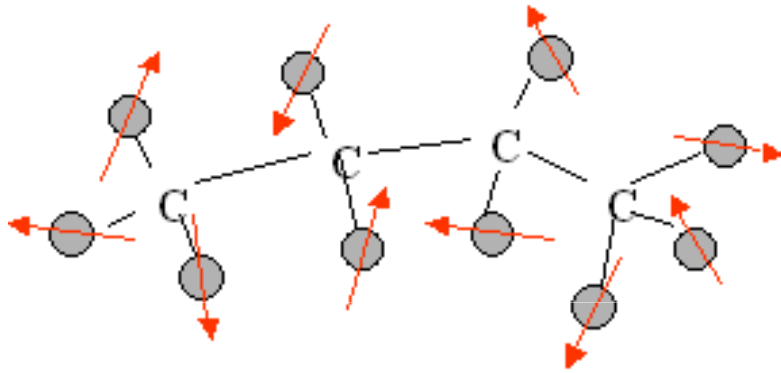
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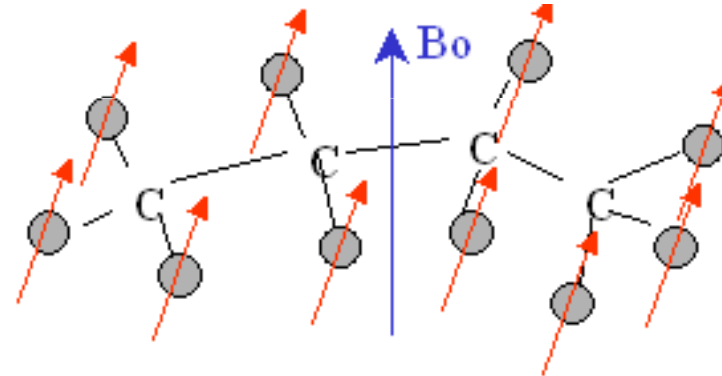
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Spins

With no magnetic field,
magnetic moments are random



In Strong magnetic moments
align along B_0



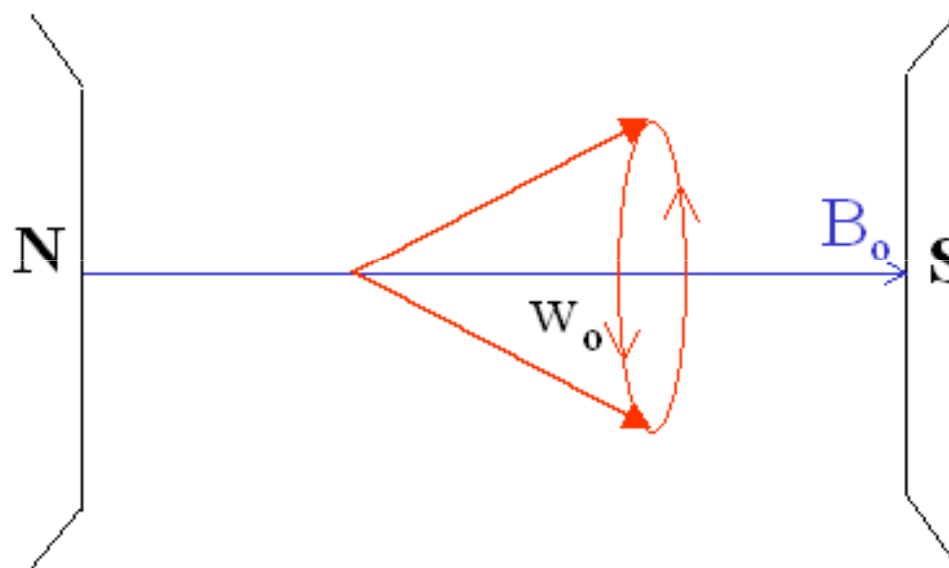
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Align and Precess

Magnetic Moments Align and Precess
at a Frequency ω_0



ω_0 is Proportional to size of B_0

$B_0 = 1.4$ Tesla $\omega_0 = 60$ MHz

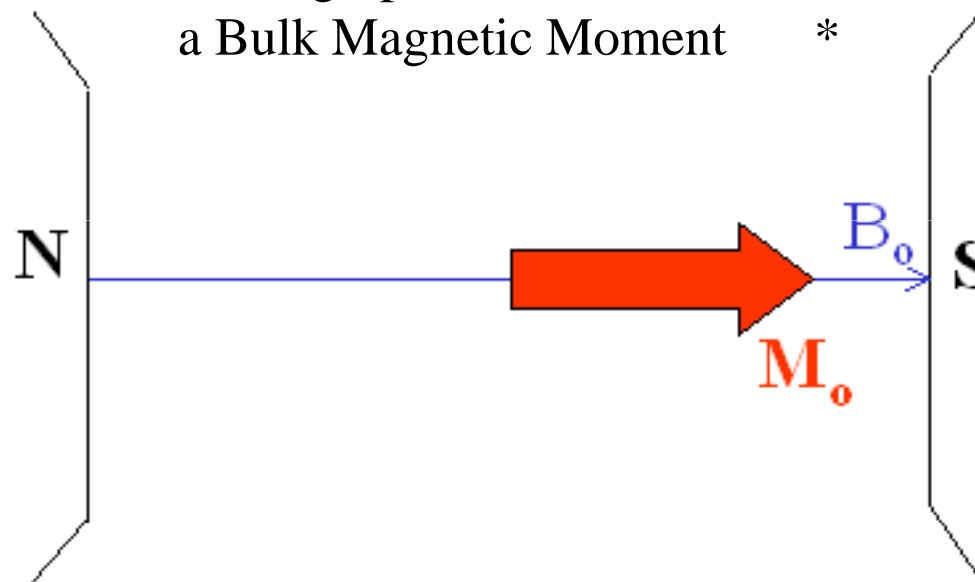
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Magnetic Moment

Precessing Spins can be described as
a Bulk Magnetic Moment *



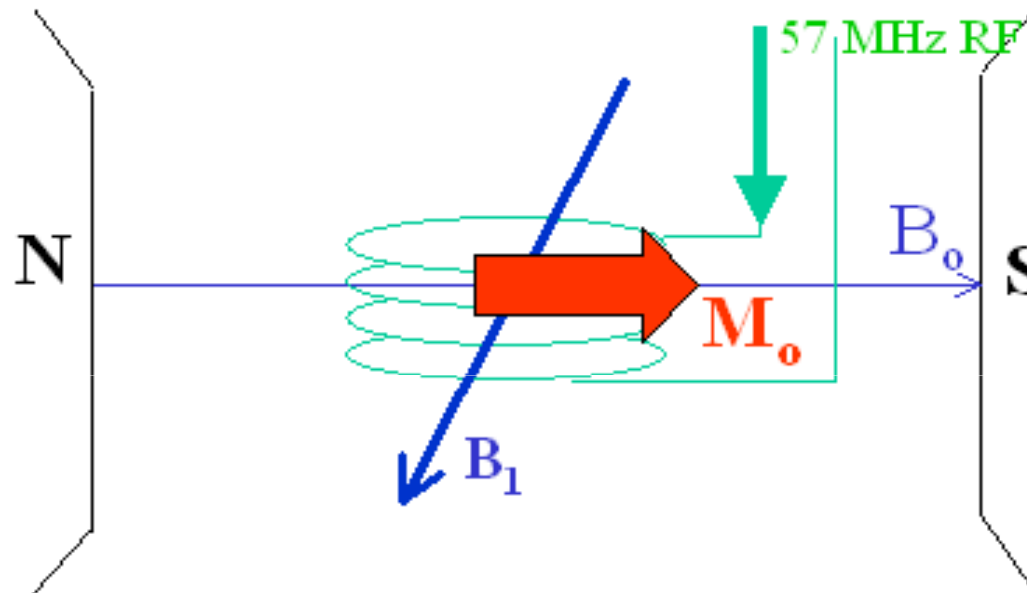
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= Summation of Individual Magnetic Moments

Radio Frequency Pulse



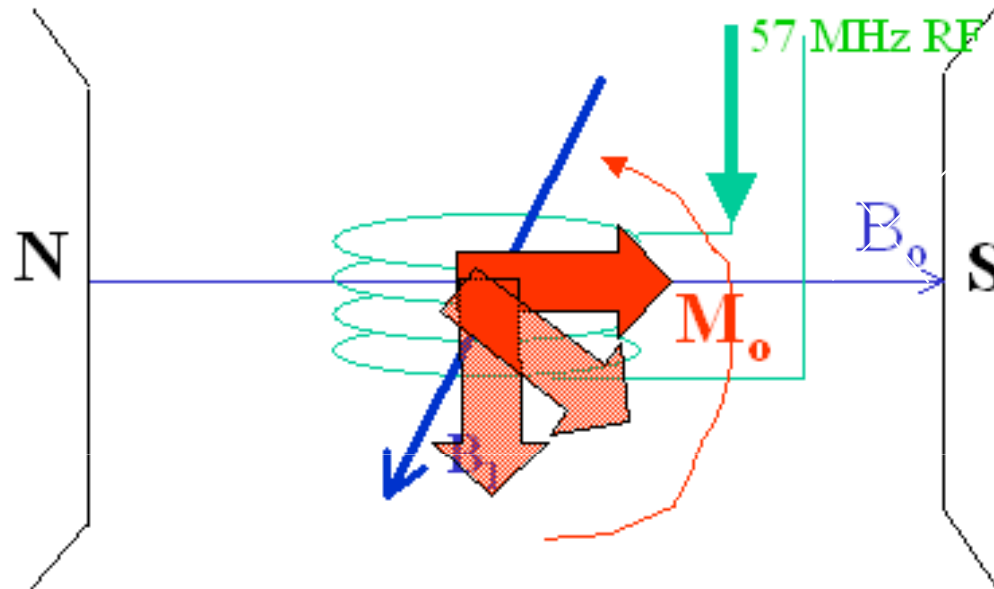
RF Pulse turned on for 4-20 microseconds
Generates a

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Re-Align to Original Magnetic Axis



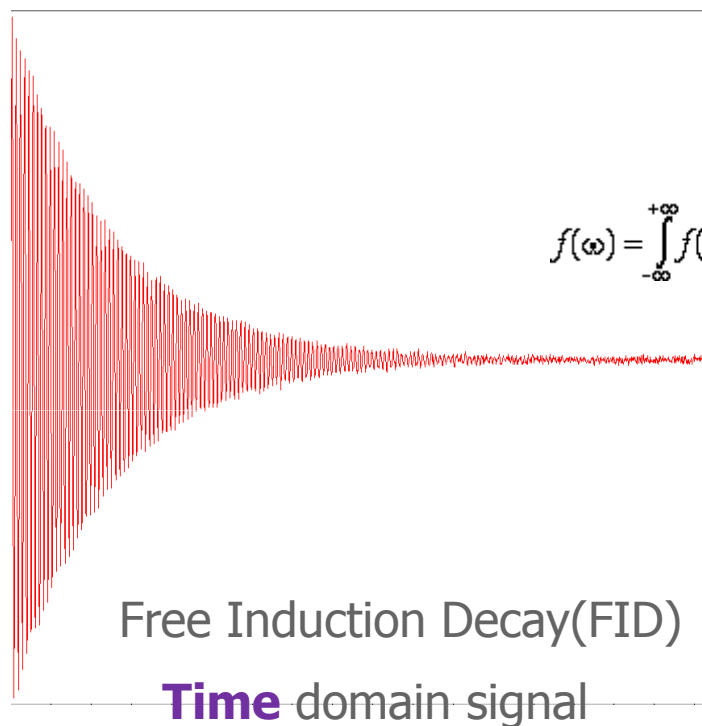
When RF Pulse ends protons relax and align to their original equilibrium position along B_0 Axis
A decay signal is generated : free induction decay signal (FID)

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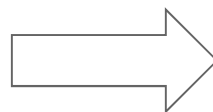


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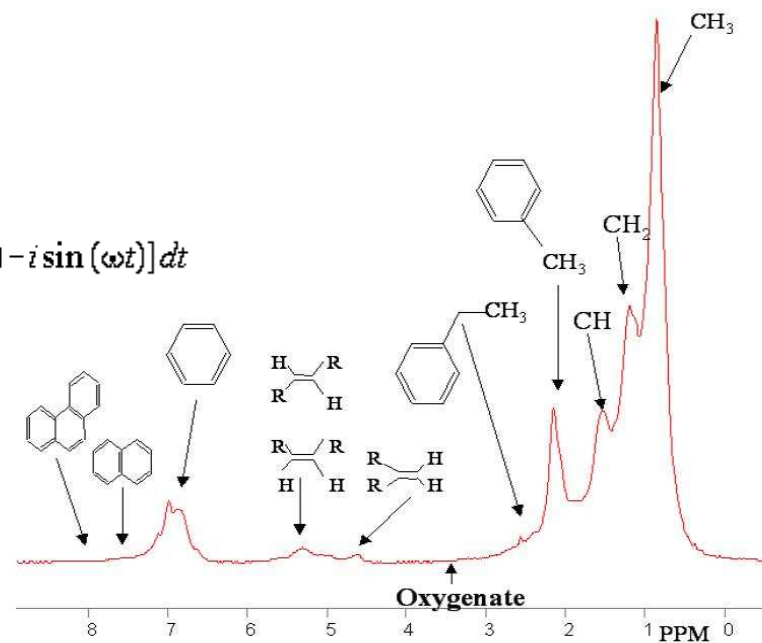
Fourier Transform



$$f(\omega) = \int_{-\infty}^{+\infty} f(t)e^{-i\omega t} dt = \int_{-\infty}^{+\infty} f(t)[\cos(\omega t) - i \sin(\omega t)] dt$$



F.F.T.



NMR Spectrum

Frequency domain

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