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# **Nuclear Magnetic Resonance Analysis On-line**

Overview of the technology, benefits, solutions  
and applications to the Refinery



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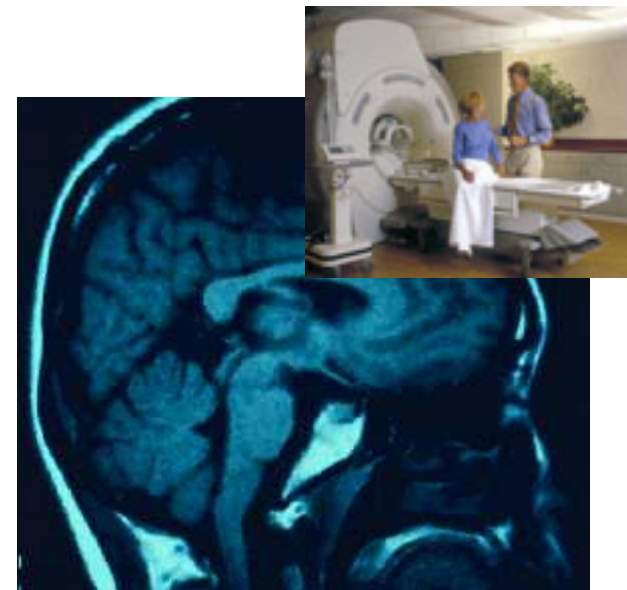
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# The NMR Technology

The analytical  
measurement principle

# What is $^1\text{H}$ NMR in general ?

- **H**ydrogen **N**uclear **M**agnetic **R**esonance
- Provides picture of the *hydrocarbon structure*. From this we determine physical and chemical information
- It is *non invasive* like MRI\*, therefore all samples can be returned back to the process.
- Heavy opaque or dark materials easily analyzed
- Technology developed from 1950's



MRI Picture

\* Magnetic Resonance Imaging



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# What is $^1\text{H}$ NMR Analysis?

- NMR = Nuclear Magnetic Resonance
- “Nuclear” because NMR looks at the nuclei of molecules (protons-neutrons)
- More specific at their “nuclear spin”
- Some nuclei have a “magnetic moment” due to that spin (behave like a small magnet)
- Most important nuclei are  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$
- $^1\text{H-NMR}$  is looking at  $^1\text{H}$ -protons in molecules, excellent for hydrocarbon analysis



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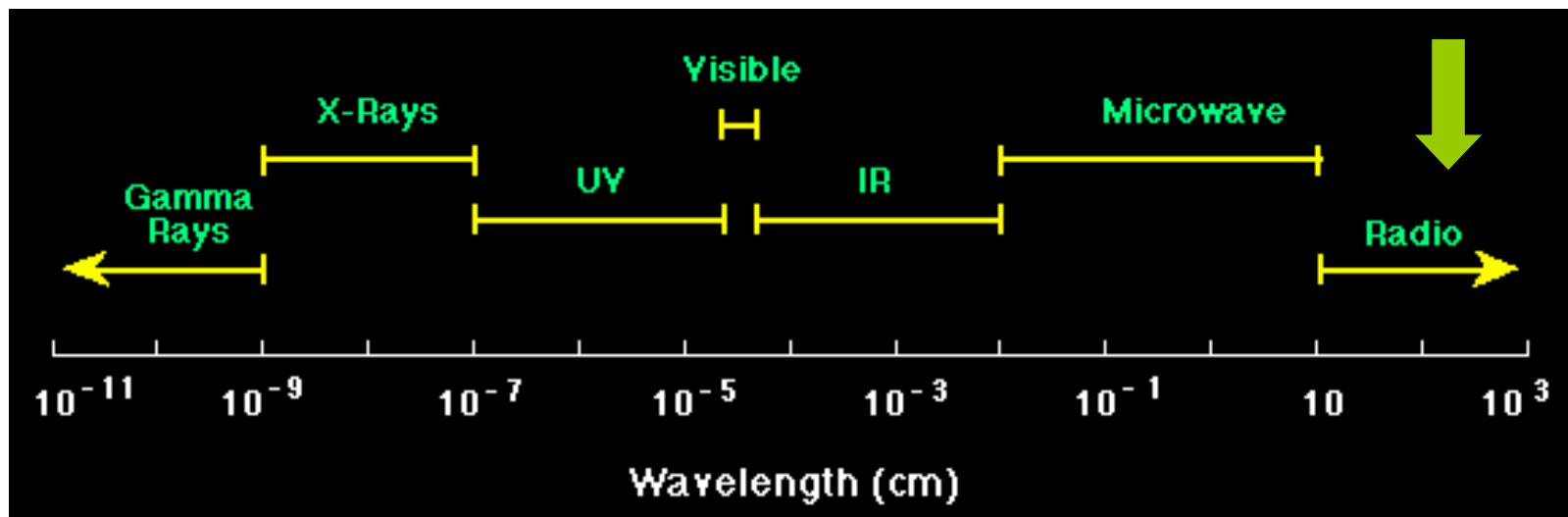
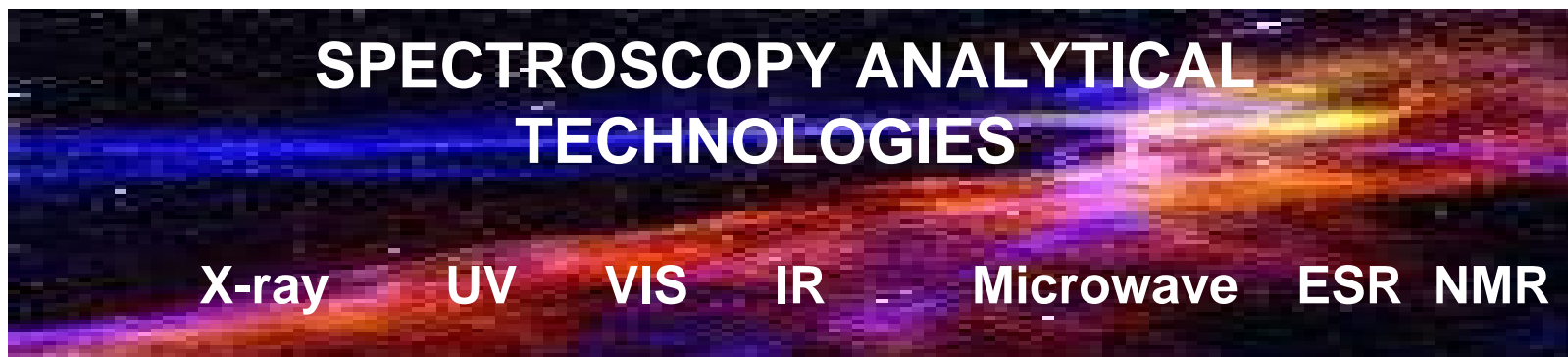
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# The Electromagnetic Spectrum



**NMR spectroscopy uses radio-waves to interact with samples**



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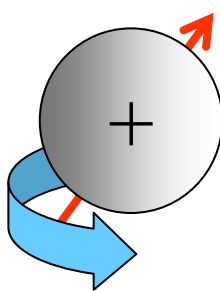


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# $^1\text{H}$ Proton – Magnetic Moment (**M**)

Hydrogen Atom  
(Proton)



**M**

Proton is spinning

Magnetic moment (**M**) generated



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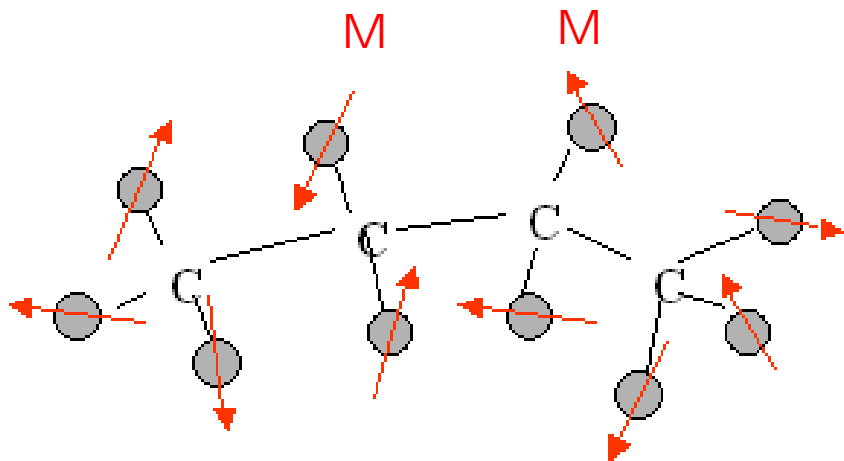
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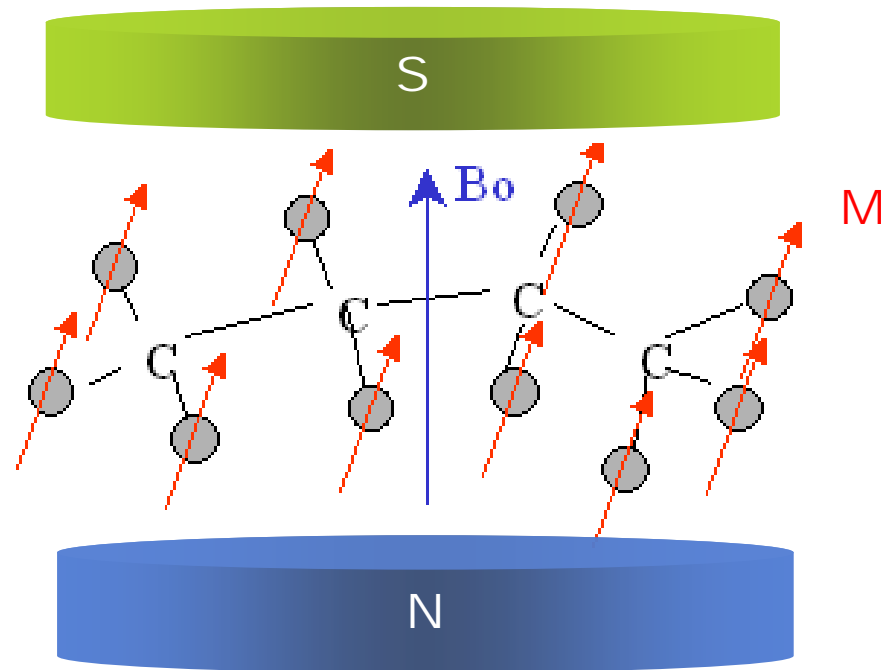
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# Nuclear Spins and Magnetic Fields

With no magnetic field, magnetic moments  $M$  are **random** oriented



In strong magnetic field ( $B_0$ ), magnetic moments  $M$  **align** along  $B_0$





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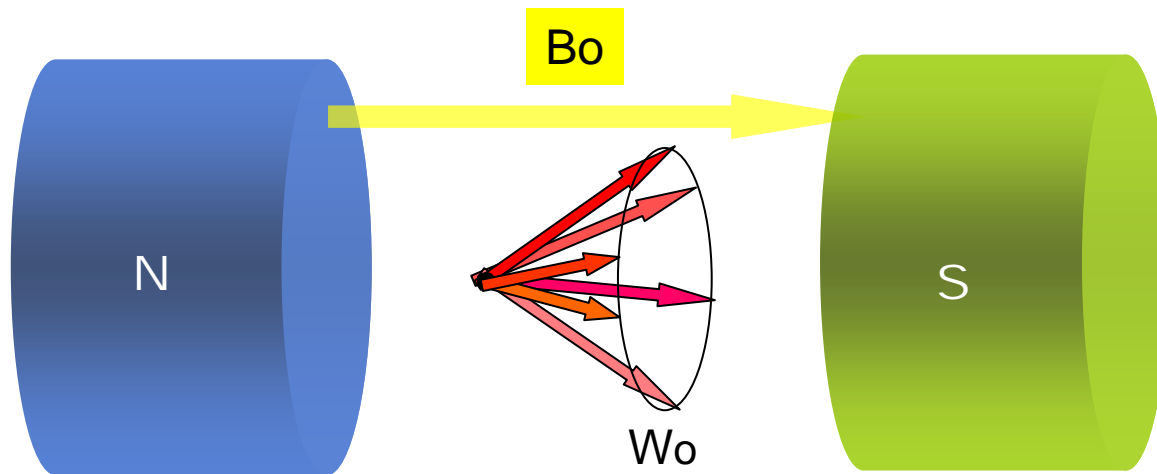
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# Alignment and precessing of M

Magnetic Moments Align and Precess  
at a Frequency  $\omega_0$



$\omega_0$  is proportional to size of  $B_0$

e.g.  $B_0 = 1.35$  Tesla  $\rightarrow$   $\omega_0 = 57$  MHz



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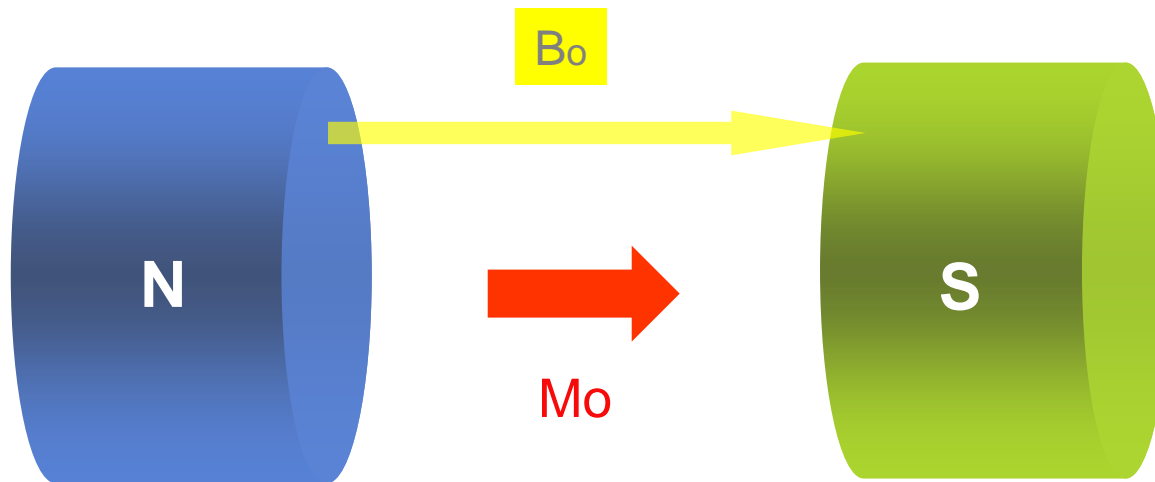
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# Bulk Magnetic Moment – $M_0$

Precessing spins can be described as  
a **bulk magnetic moment  $M_0^*$**



**\* $M_0$**  = Summation of individual magnetic moments  
of all protons in the sample



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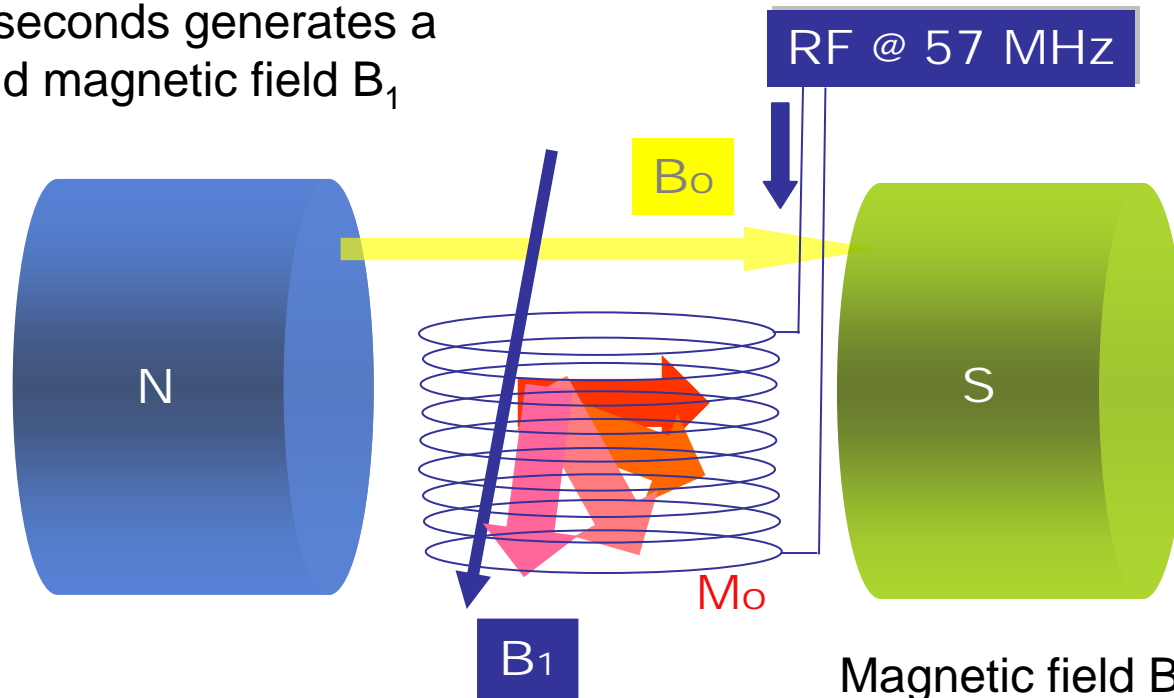
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# Re-align to second magnetic axis

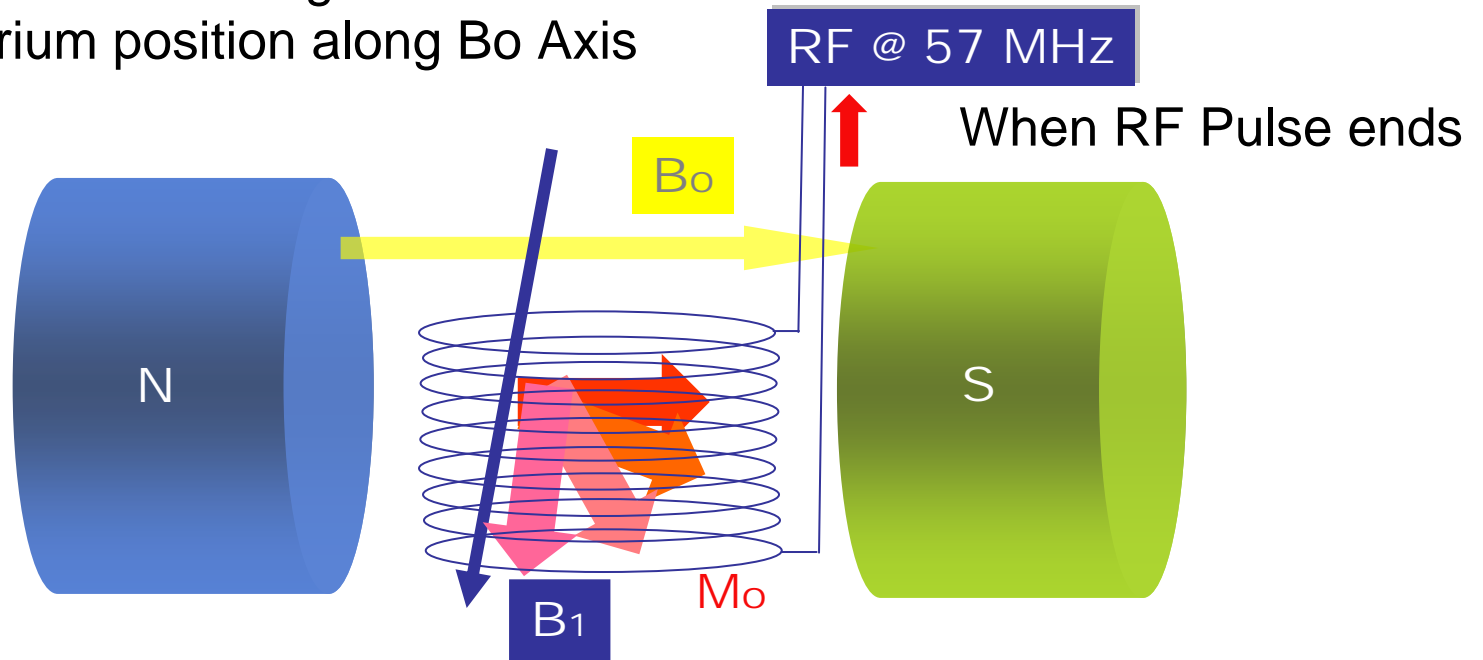
RF pulse turned on for 4-20 microseconds generates a second magnetic field  $B_1$



Magnetic field  $B_1$  causes  $M_0$  to move and re-align to second magnetic axis

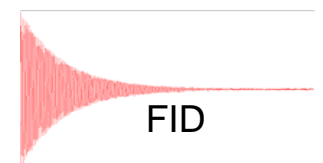
# Re-align to original magnetic axis

The protons relax and re-align to their original equilibrium position along  $B_0$  Axis



“Relaxation” of  $M_0$  generates a RF Current that is picked in the irradiation coil : A decay signal is generated called

**Free Induction Decay signal (FID)**





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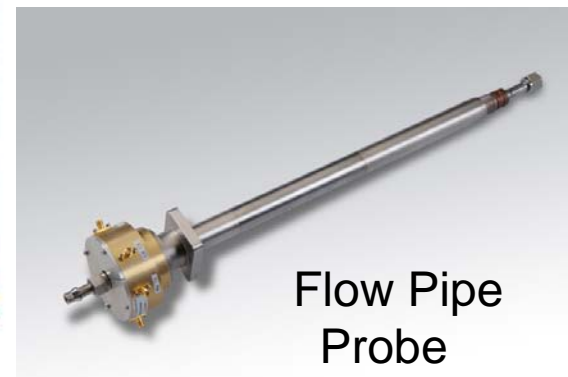
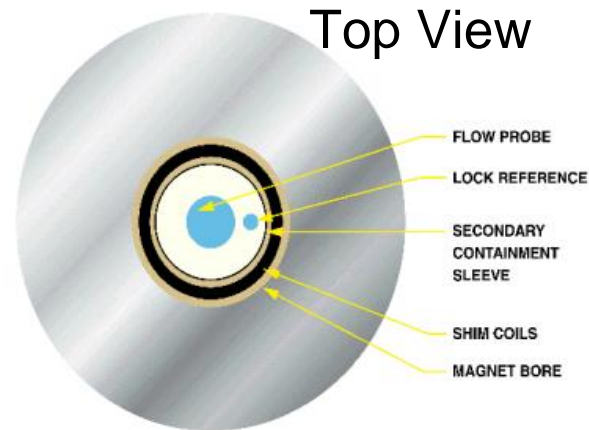
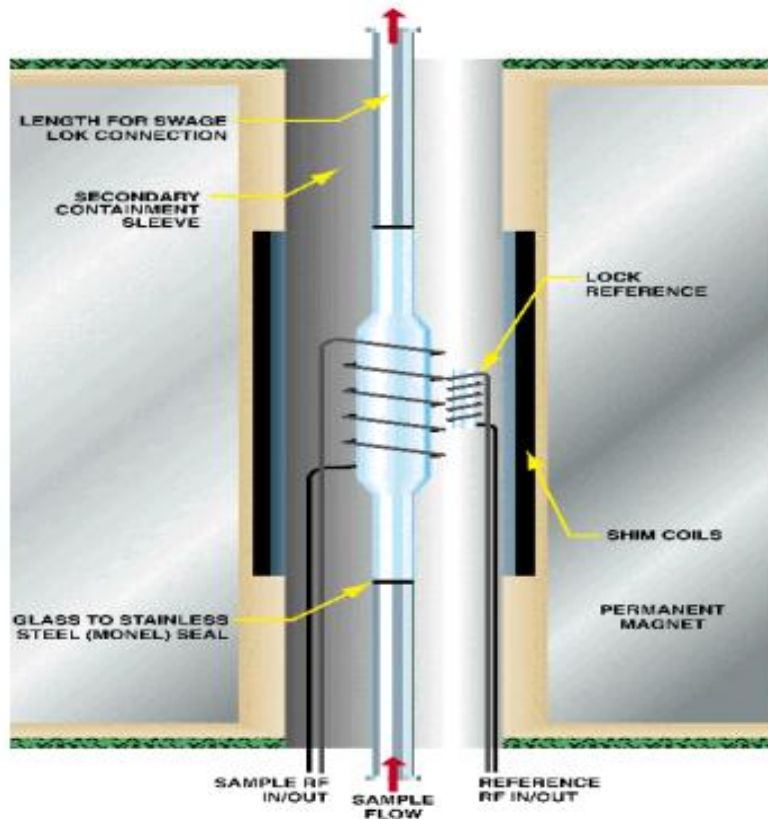


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# Measurement in a NMR Process analyser



Magnet

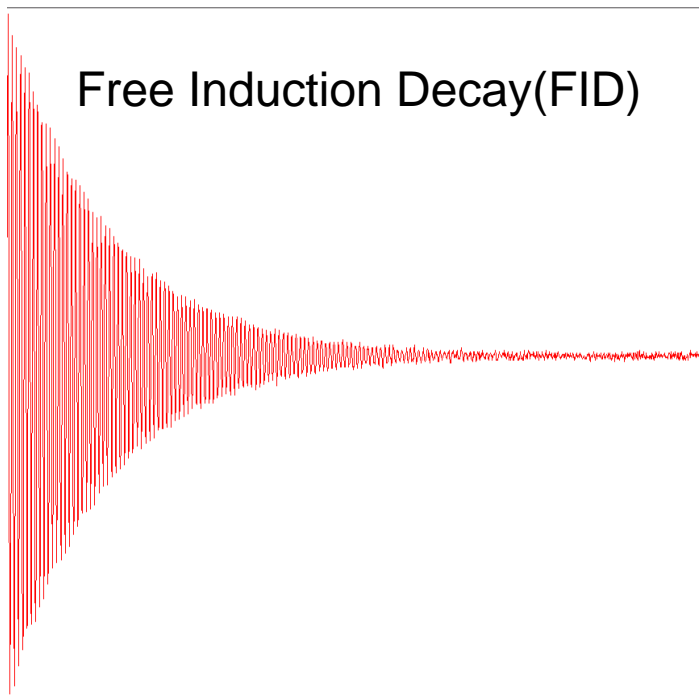


# Fast Fourier Transform- FFT

Time domain signal

Frequency domain signal

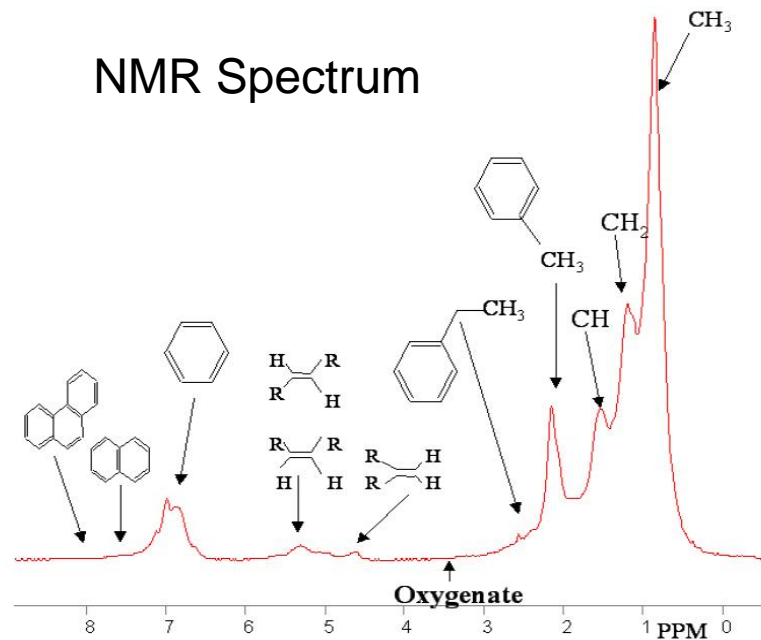
Free Induction Decay(FID)



F.F.T.



NMR Spectrum



H-Types Observed in a Gasoline <sup>1</sup>H NMR Spectrum

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



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# Chemical Shift in NMR spectra

- How does the NMR resolve the different protons in the spectra ?
- Each proton in a different chemical environment (bond) “senses” a different magnetic field  $B_x$  due to the *shielding* created by surrounding electrons
- More electrons = more *shielding*



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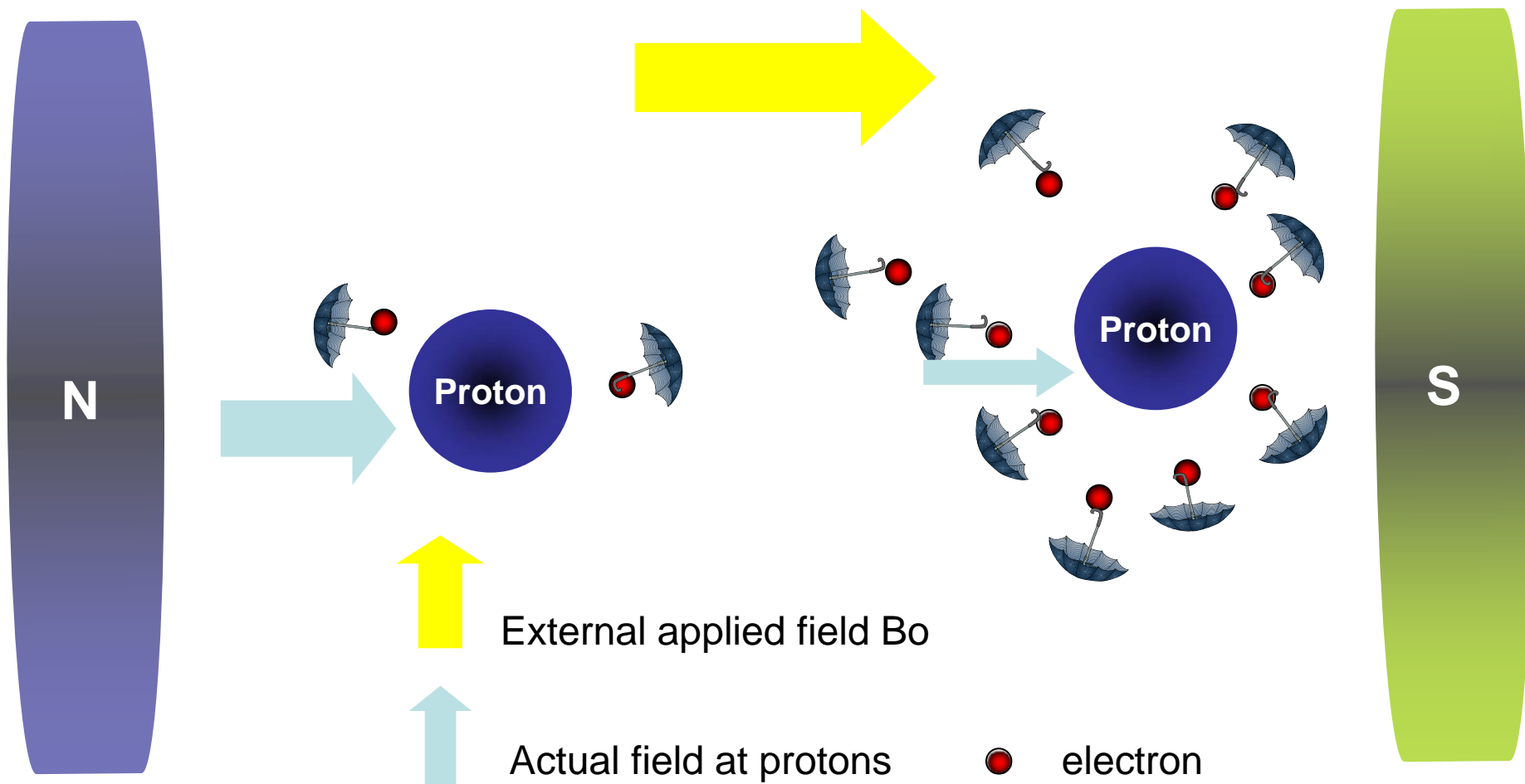
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# Protons in different chemical environment





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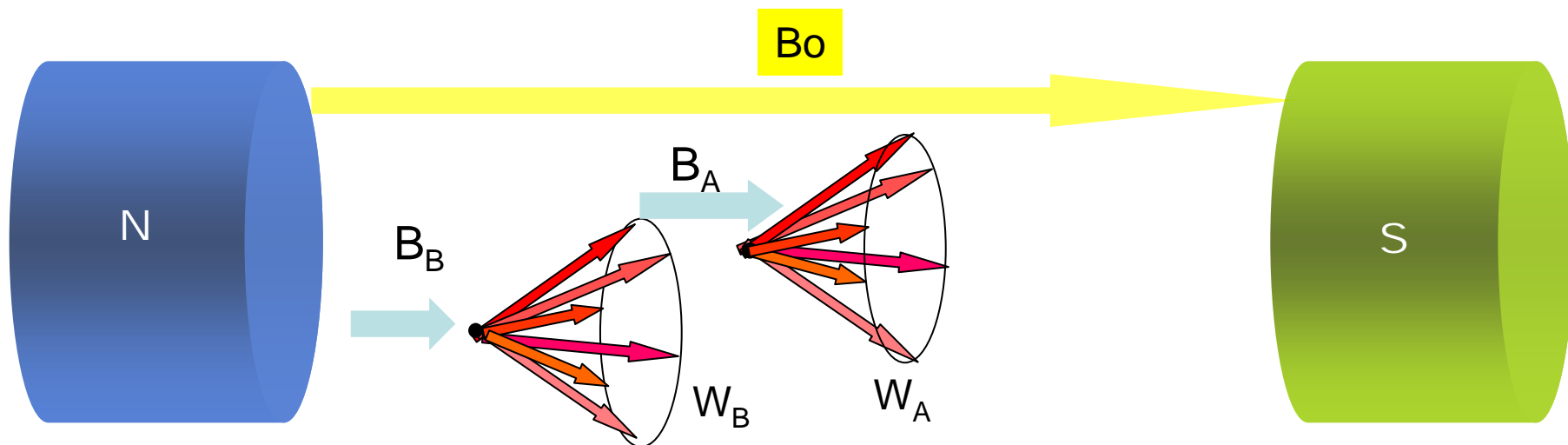
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# Difference in “sensed” magnetic field

Due to difference in “sensed” magnetic field protons A and B precess at a different frequency  $\omega_A$  and  $\omega_B$

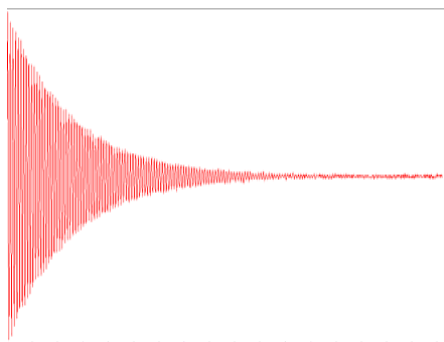


$\omega_A$  and  $\omega_B$  are proportional to size of  $B_A$  and  $B_B$

The precessing frequency becomes the fingerprint of the chemical environment of the different protons

# From FID to results

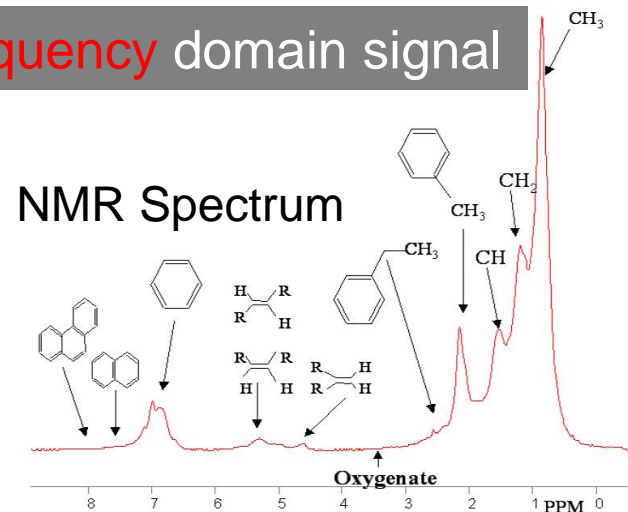
Time domain signal



Fast Fourier  
transform

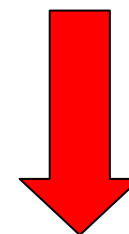


Frequency domain signal



H-Types Observed in a Gasoline <sup>1</sup>H NMR Spectrum

Chemometric  
calibration models



Results

Free Induction Decay(FID)

## WHAT IS CHEMOMETRICS?

- *“Chemometrics is the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods”.*

Definition by the International Chemometrics Society (ICS)

***Application and development of mathematical and statistical methods to extract information from chemical or process data***



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## **STATISTICAL METHOD USED**

- **Multivariate statistical analysis:**  
*is that branch of statistical analysis which is concerned with the simultaneous investigation of two or more variable characteristics which are measured over a set of objects.*



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# TYPES OF MULTIVARIATE DATA

- Sensory data
- Chemical data
- Spectral data
  - **Near- infrared (NIR)**
  - Excitation-emission matrix ( EEM) fluorescence
  - **Nuclear Magnetic Resonance (NMR)**



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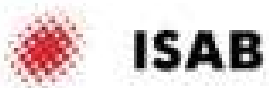


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# MULTIVARIATE REGRESSION

- **Near- infrared (NIR)**
- Excitation-emission matrix ( EEM) fluorescence
- **Nuclear Magnetic Resonance (NMR)**

*Regression is a generic term for all methods attempting to fit a model to observed data, in order to quantify the relationship between two groups of variables. The fitted model may then be used either to merely describe the relationship between the two groups of variables, or to predict new values*



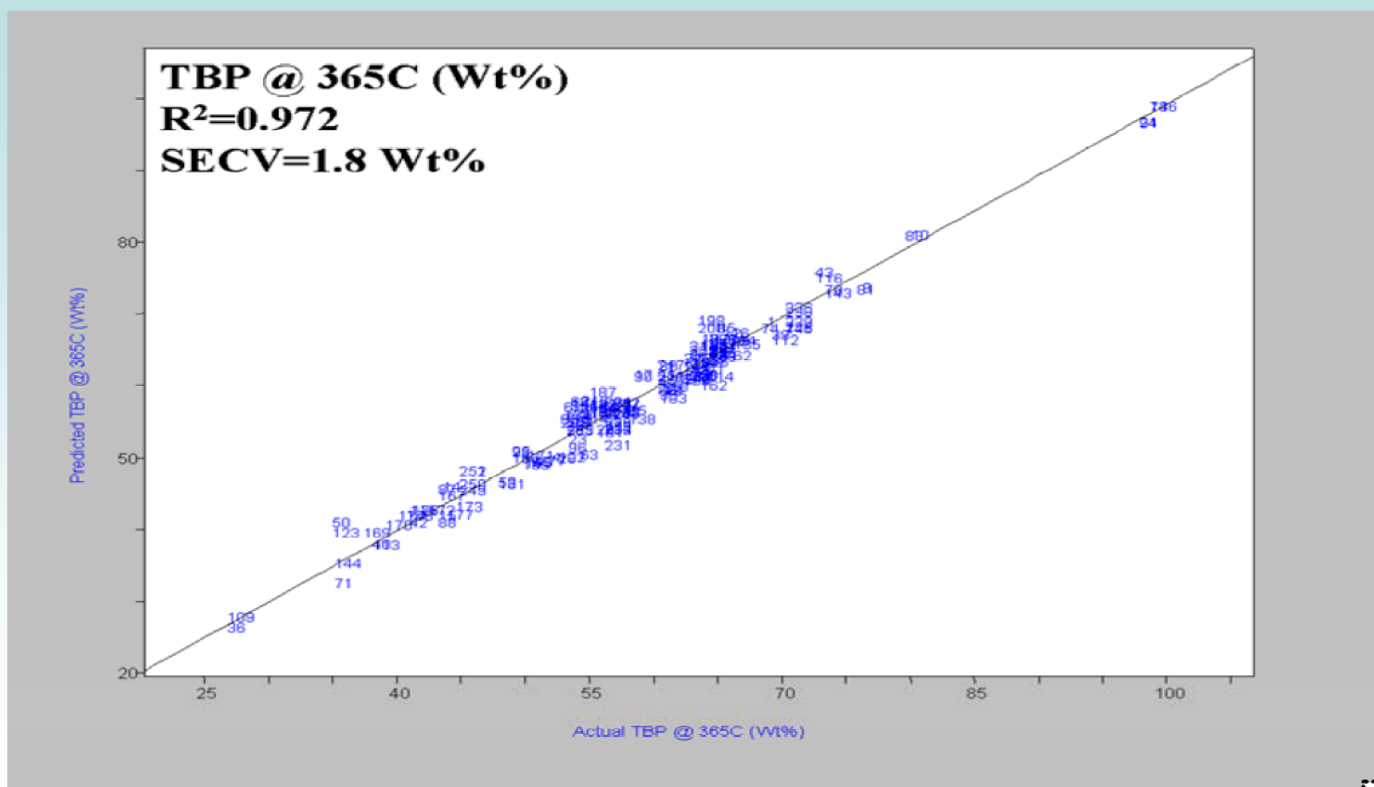
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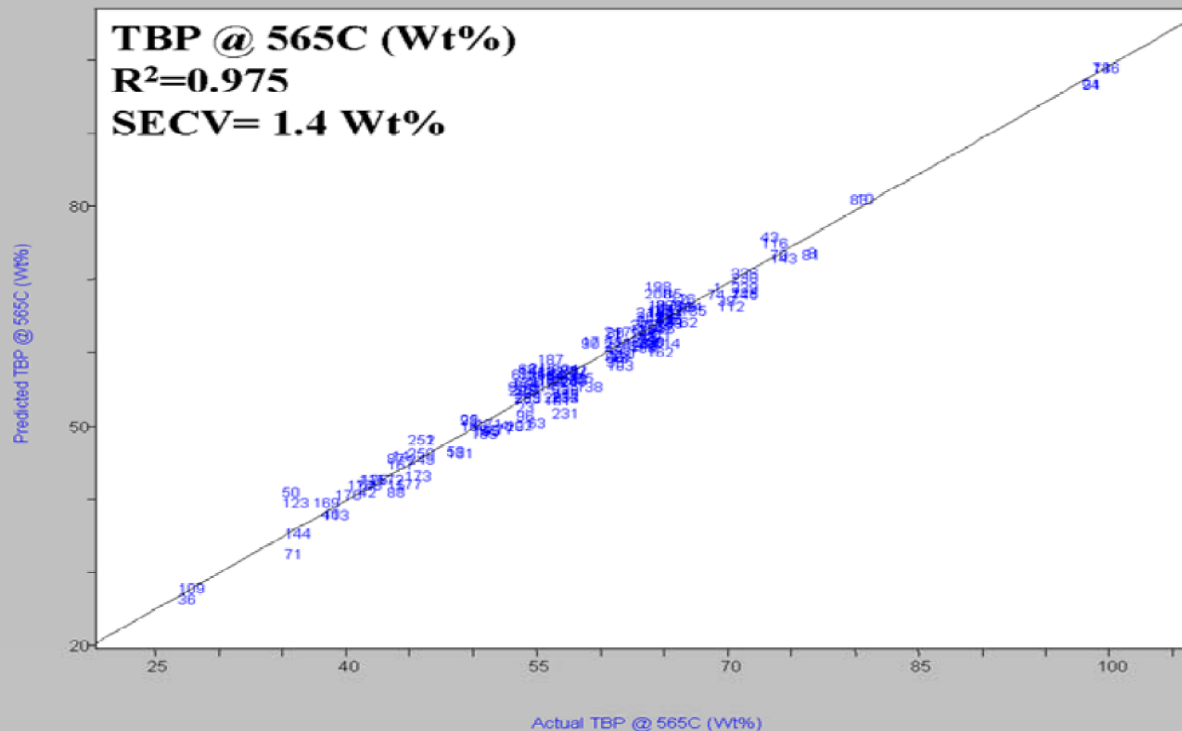


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# TBP of Crude predictions



# TBP of Crude predictions





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## **NMR benefits**

What advantages can the NMR spectrum offer?



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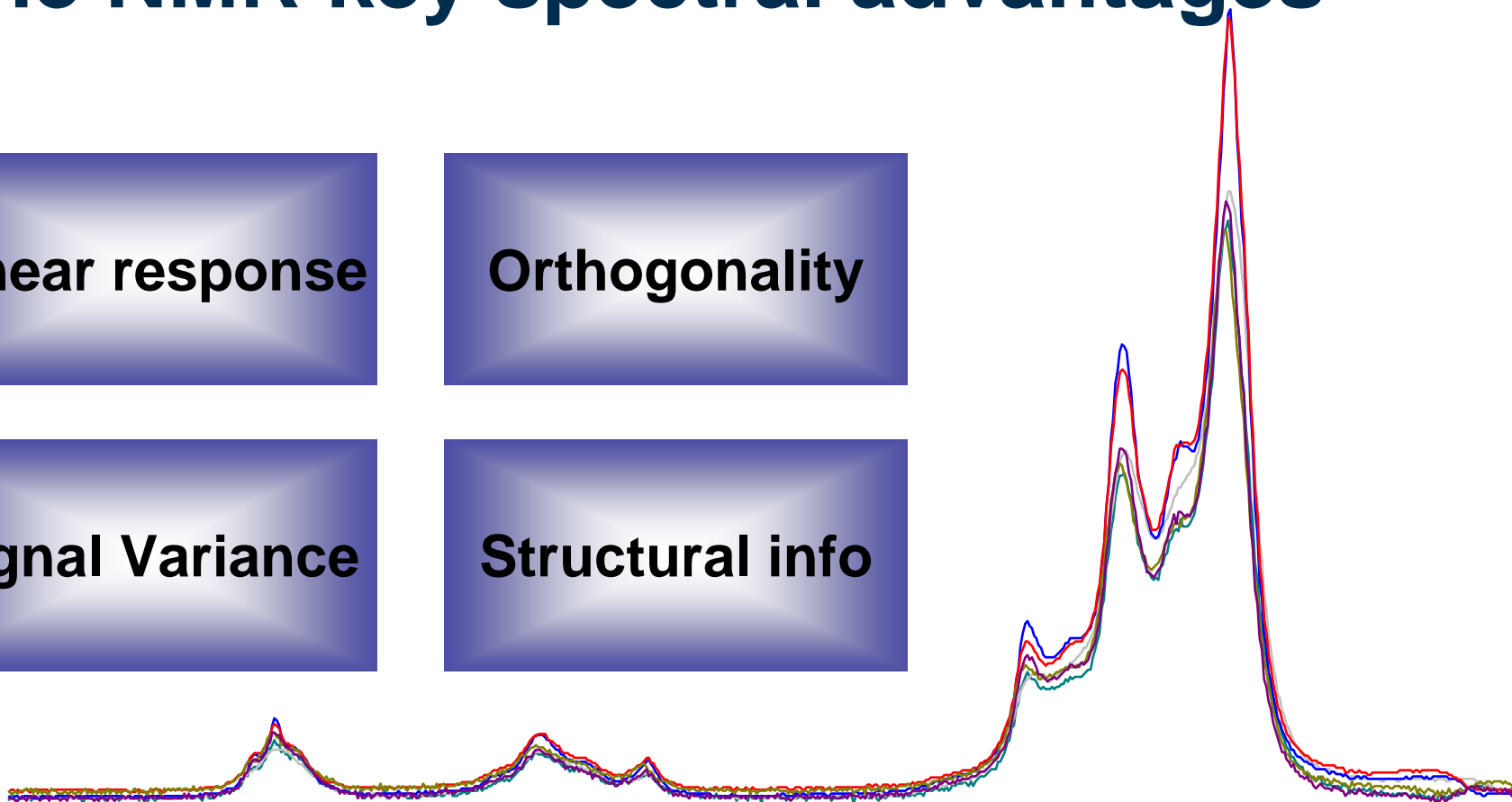
# The NMR key spectral advantages

**Linear response**

**Orthogonality**

**Signal Variance**

**Structural info**





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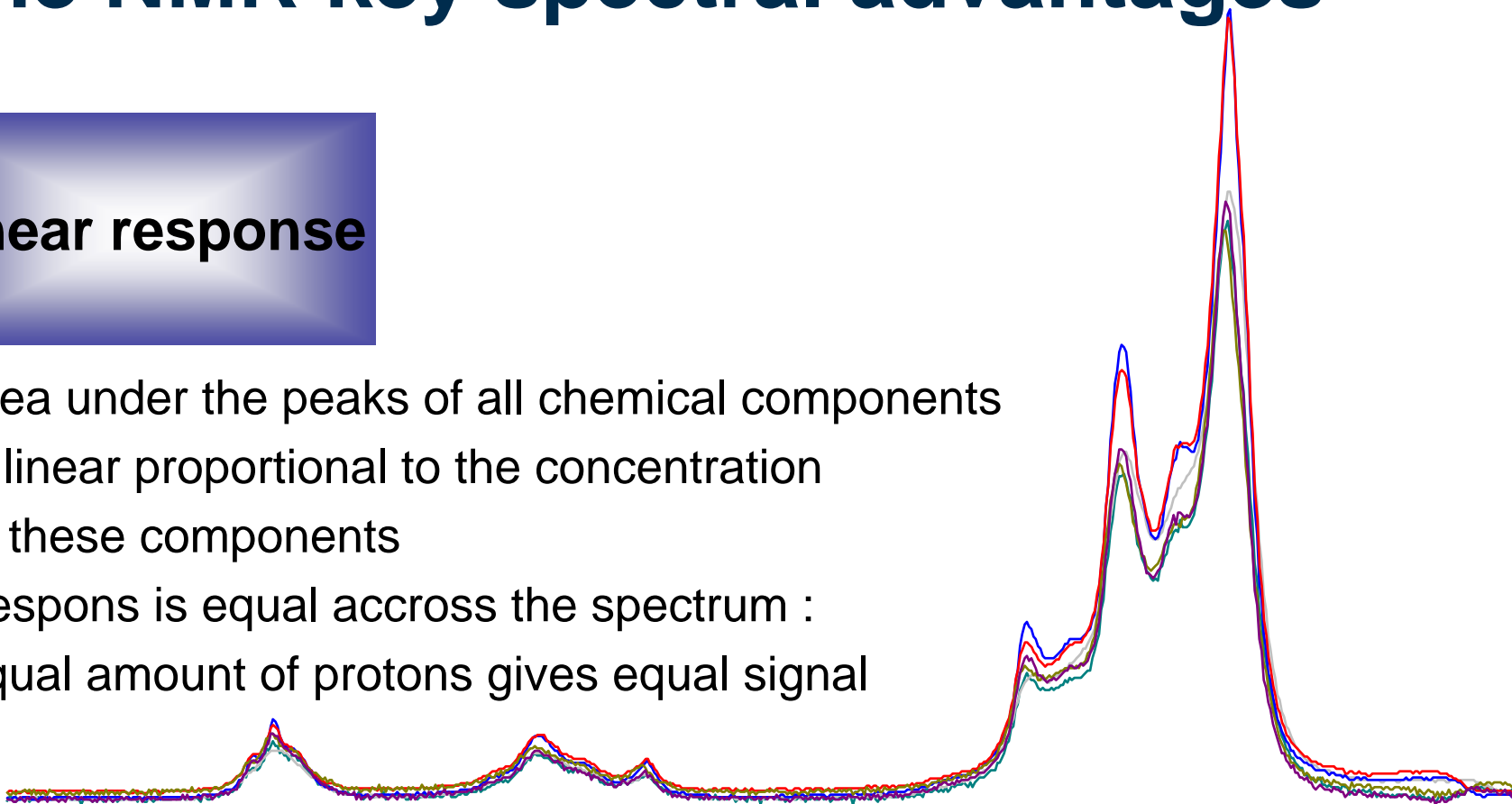
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# The NMR key spectral advantages

## Linear response

- Area under the peaks of all chemical components is linear proportional to the concentration of these components
- Response is equal across the spectrum : equal amount of protons gives equal signal





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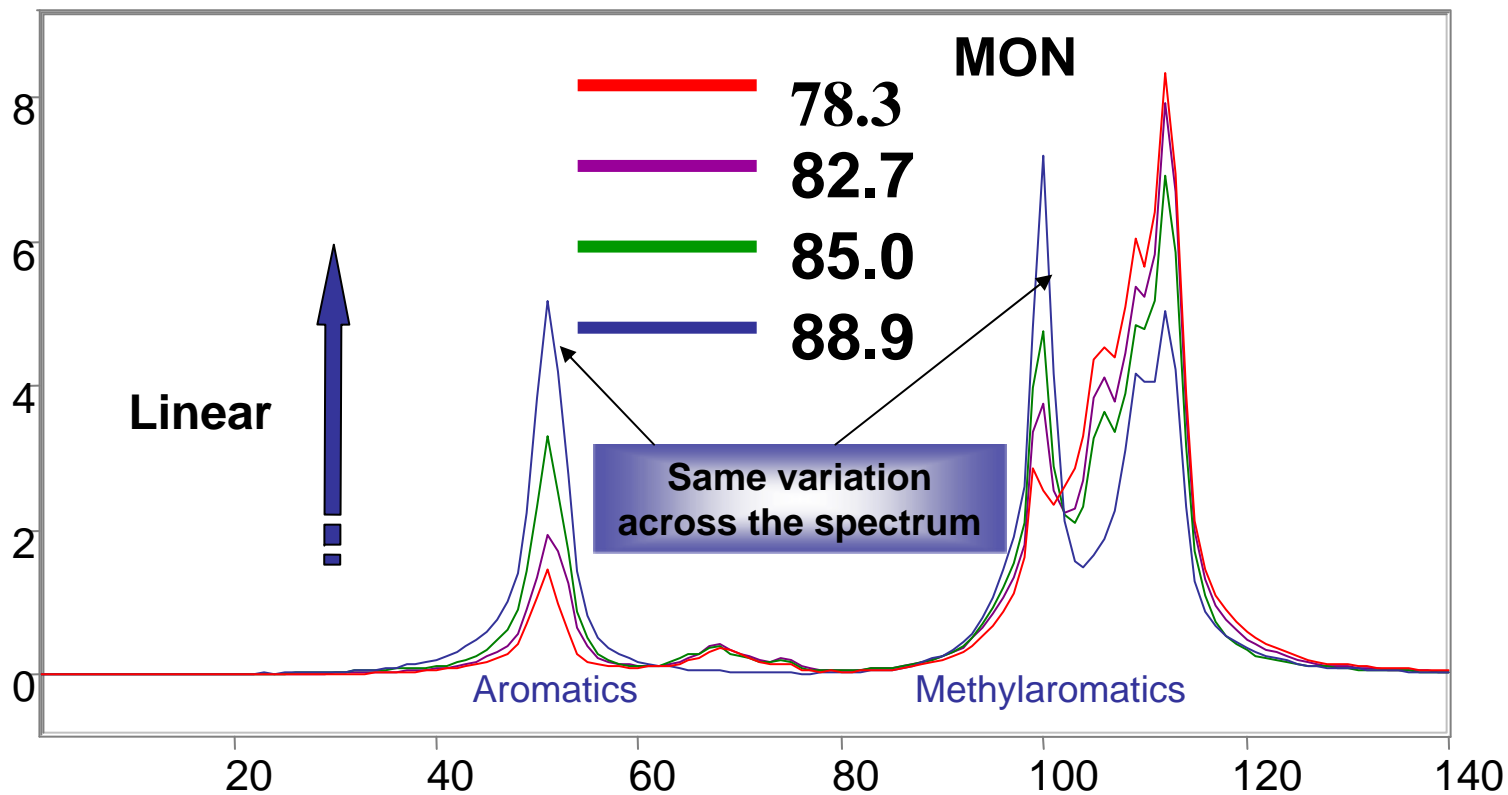
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# Linear response in gasoline NMR spectra



Superimposed  $^1\text{H}$  NMR spectra for samples spanning the entire MON range



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# Linearity in gasoline NMR spectra

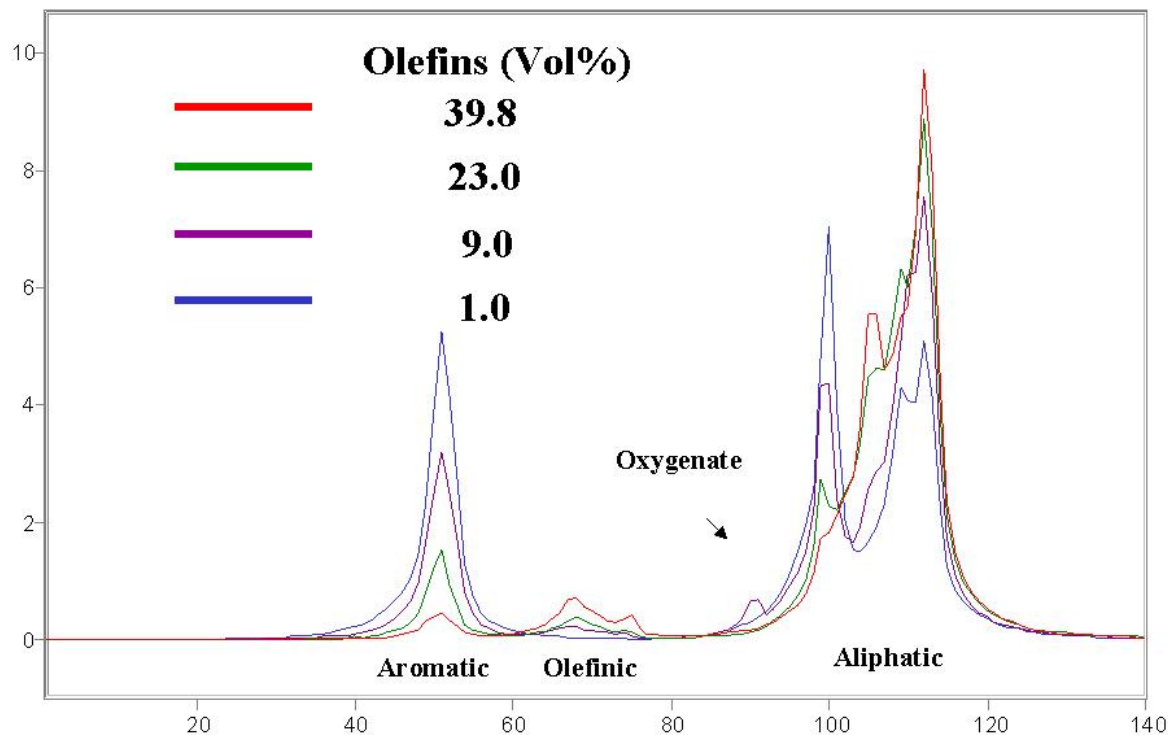


Fig 3: Empirical Olefins Quantification in Gasoline



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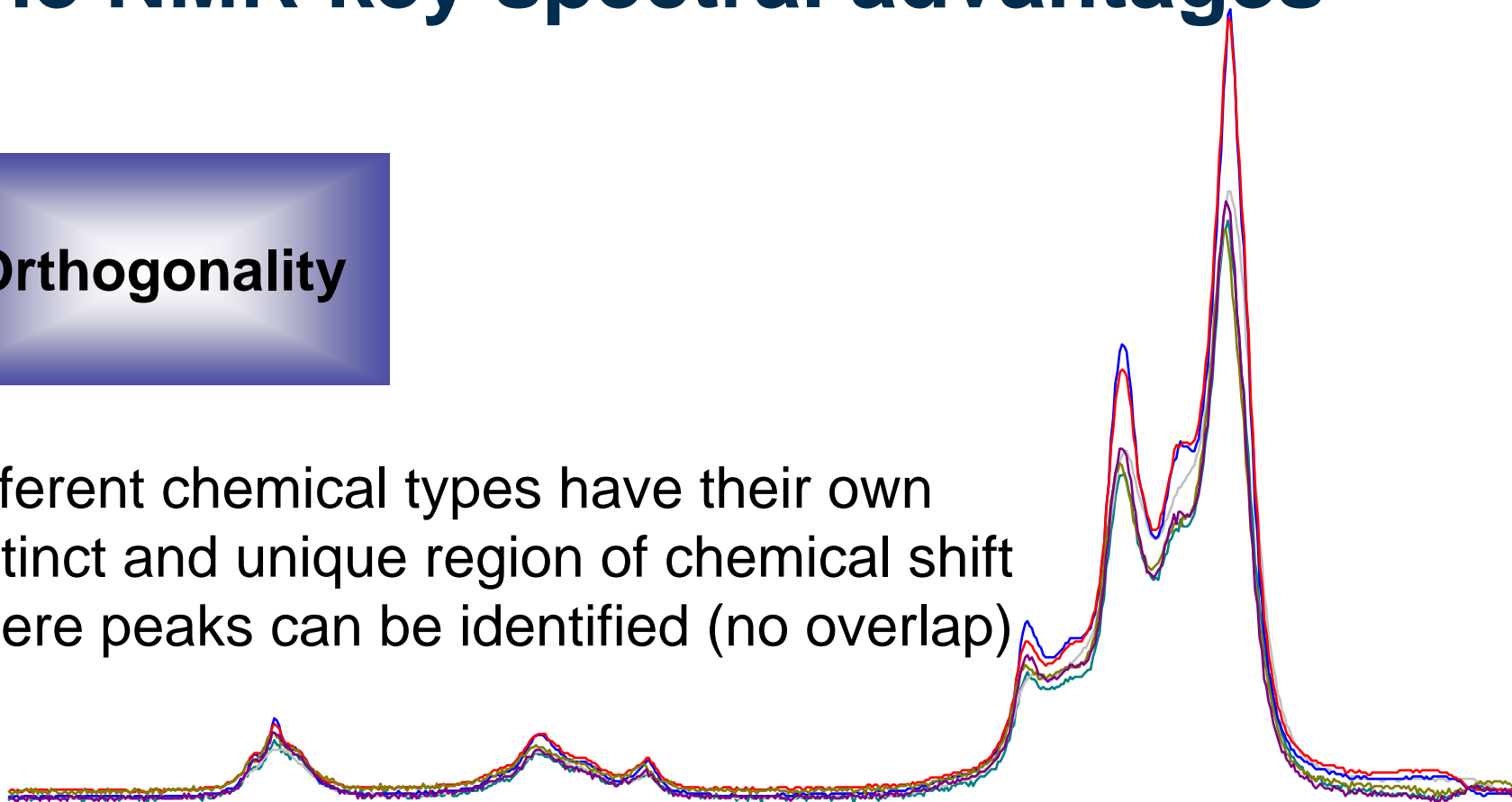
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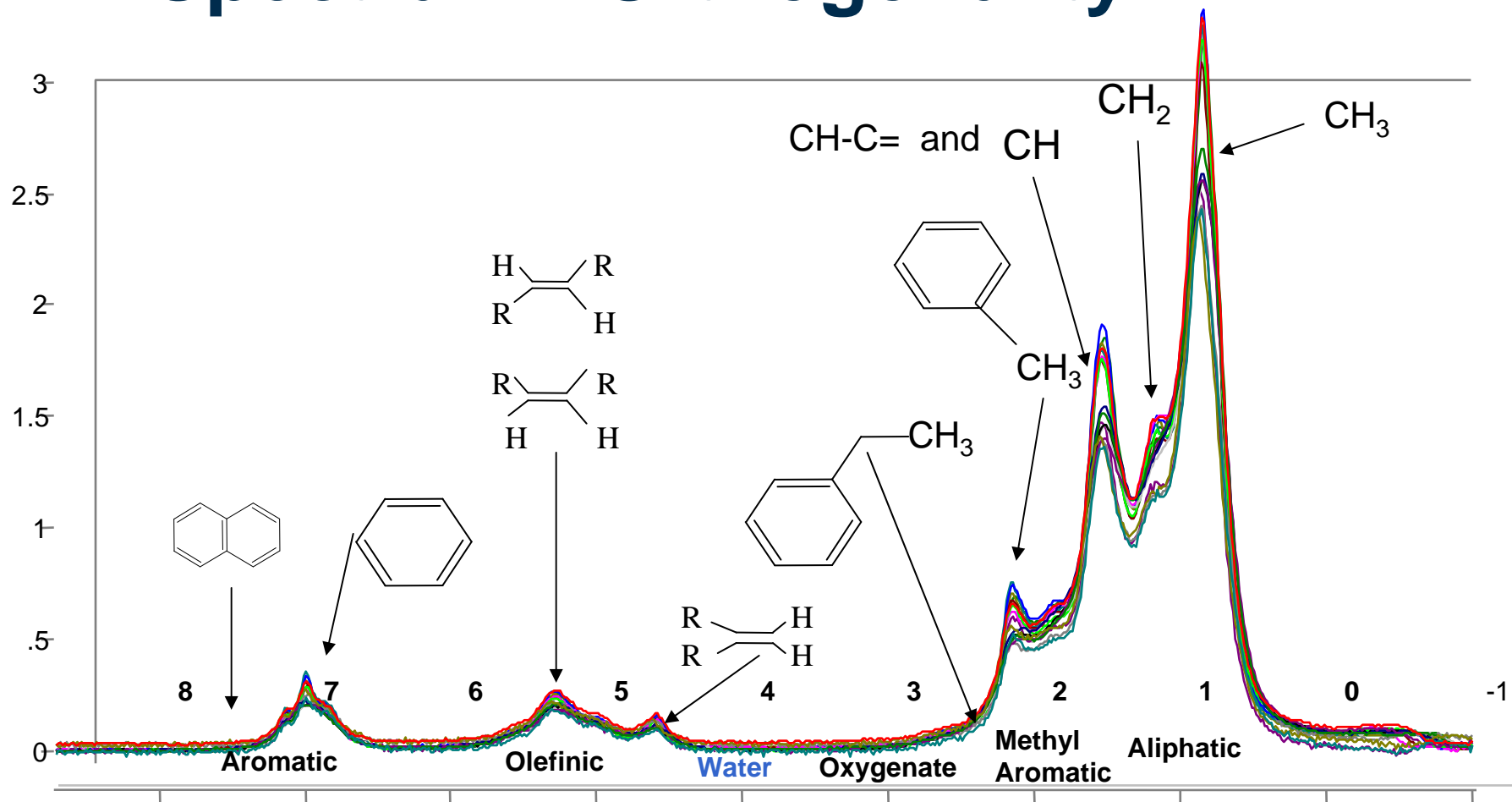
# The NMR key spectral advantages

## Orthogonality

Different chemical types have their own distinct and unique region of chemical shift where peaks can be identified (no overlap)



# NMR Spectrum : Orthogonality



All functional groups are clearly resolved and have unique and documented location



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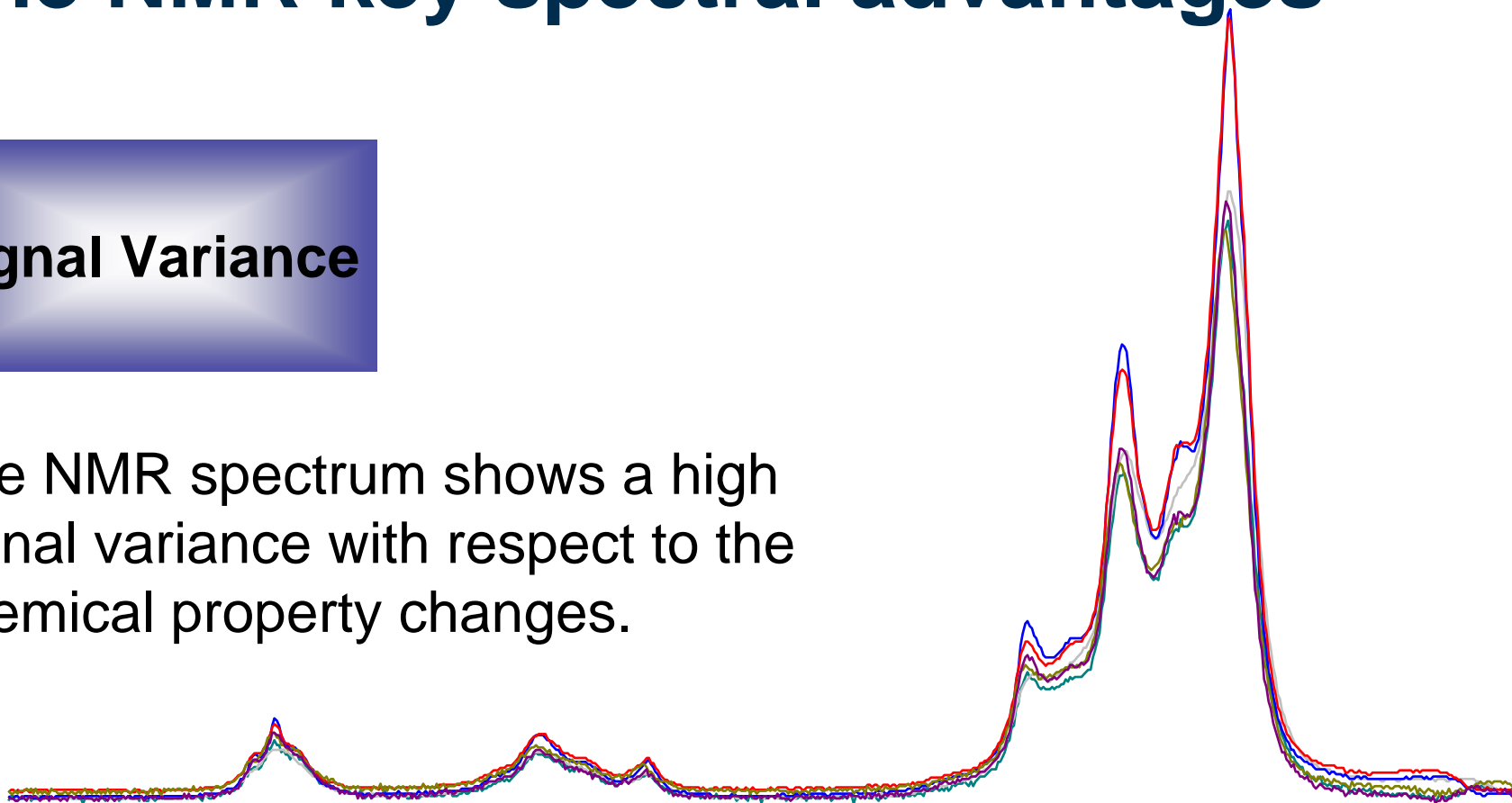
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# The NMR key spectral advantages

## Signal Variance

The NMR spectrum shows a high signal variance with respect to the chemical property changes.





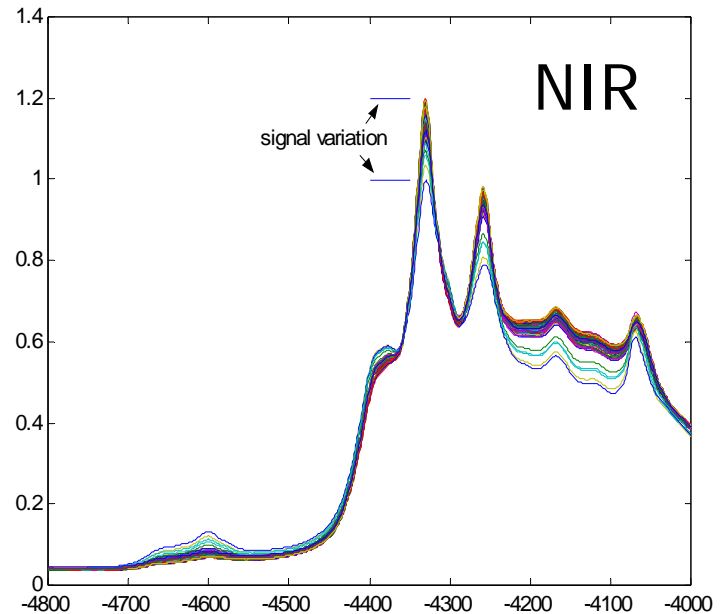
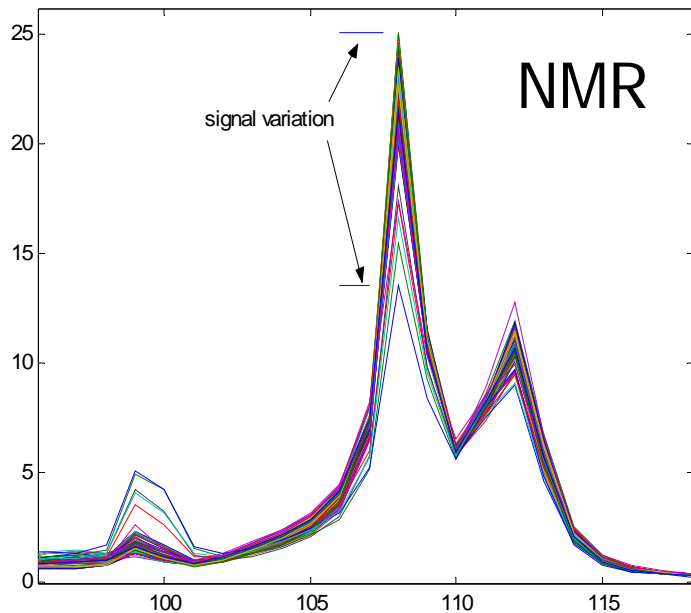
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# NMR signal variance



Identical 90 sample Gasoil data-set

High *Signal -Variance - to - Noise Ratio* provides high reliability in determining the precision and accuracy of the property predictions



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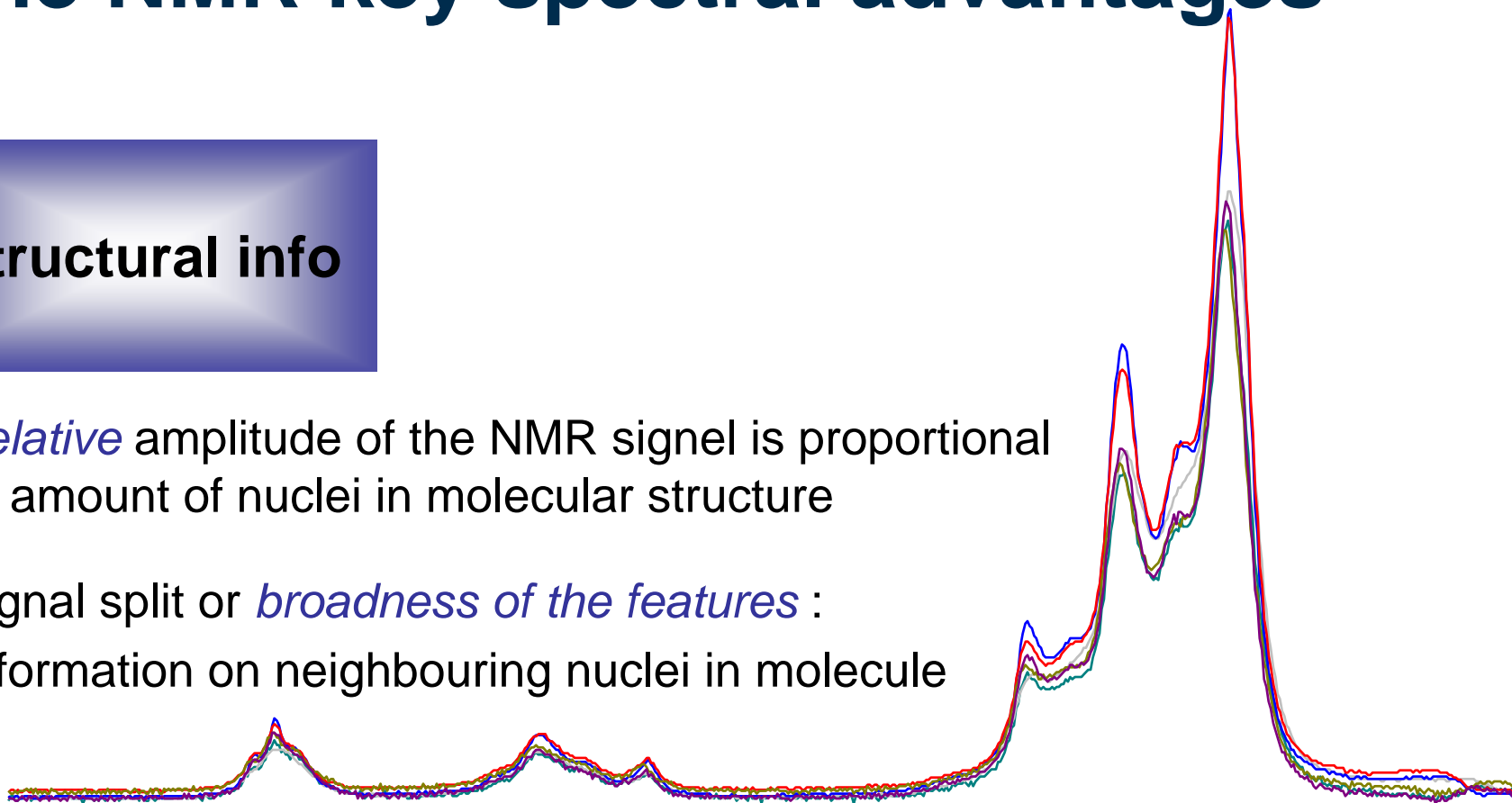
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# The NMR key spectral advantages

## Structural info

- *Relative* amplitude of the NMR signal is proportional to amount of nuclei in molecular structure
- Signal split or *broadness of the features* : information on neighbouring nuclei in molecule





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# Benefits offered by NMR spectra

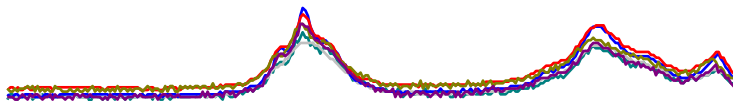
Linear response

Orthog

Benefits

Signal Variance

Structu



Simpler models and easy to maintain

Extrapolation for “out-of-range” samples : robust

Low running maintenance cost of model (cost of ownership)

Fewer data points required to build model



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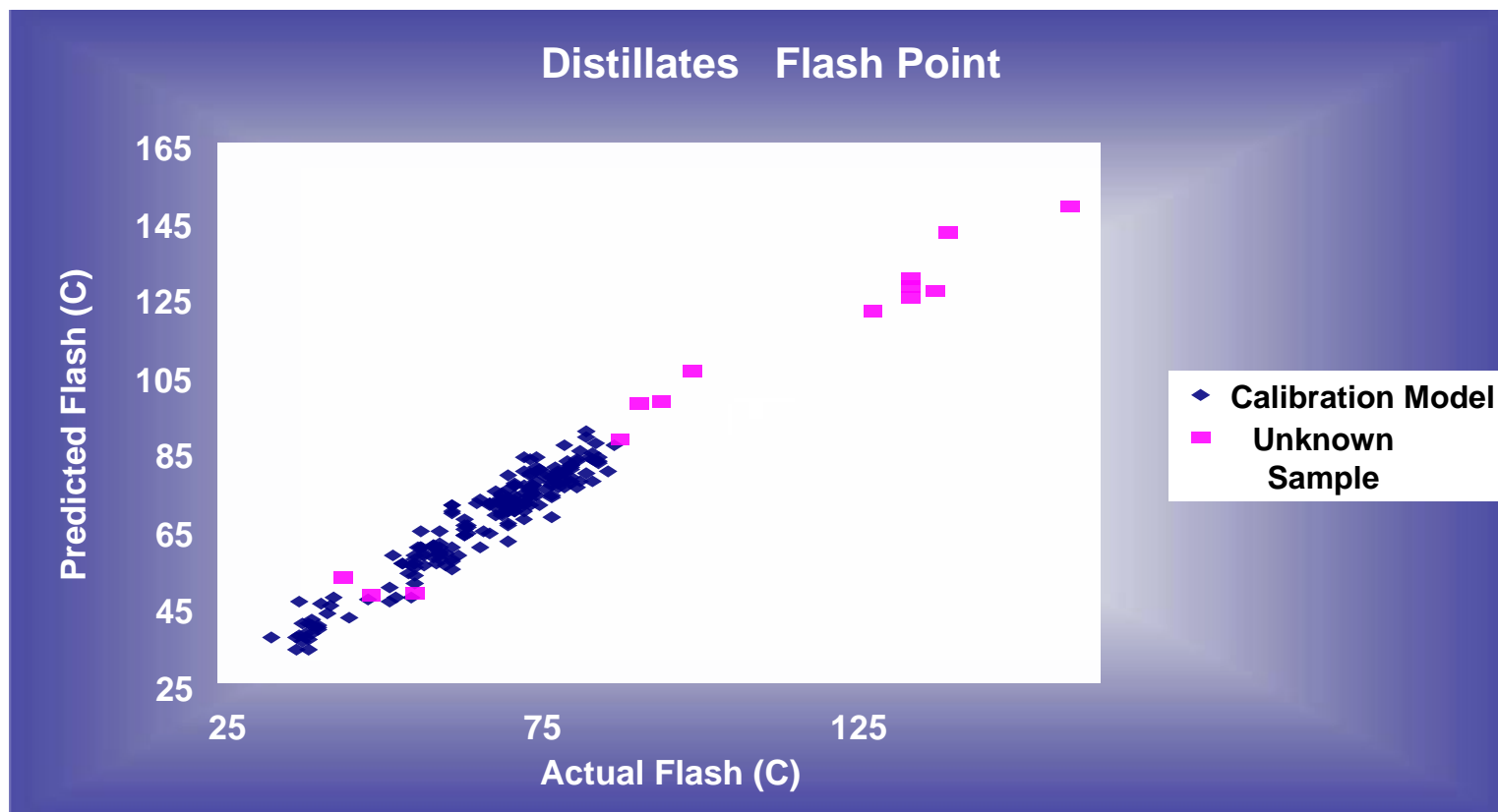
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# Models – advantage of extrapolation



NMR spectral quality allows extrapolate outside the calibration set



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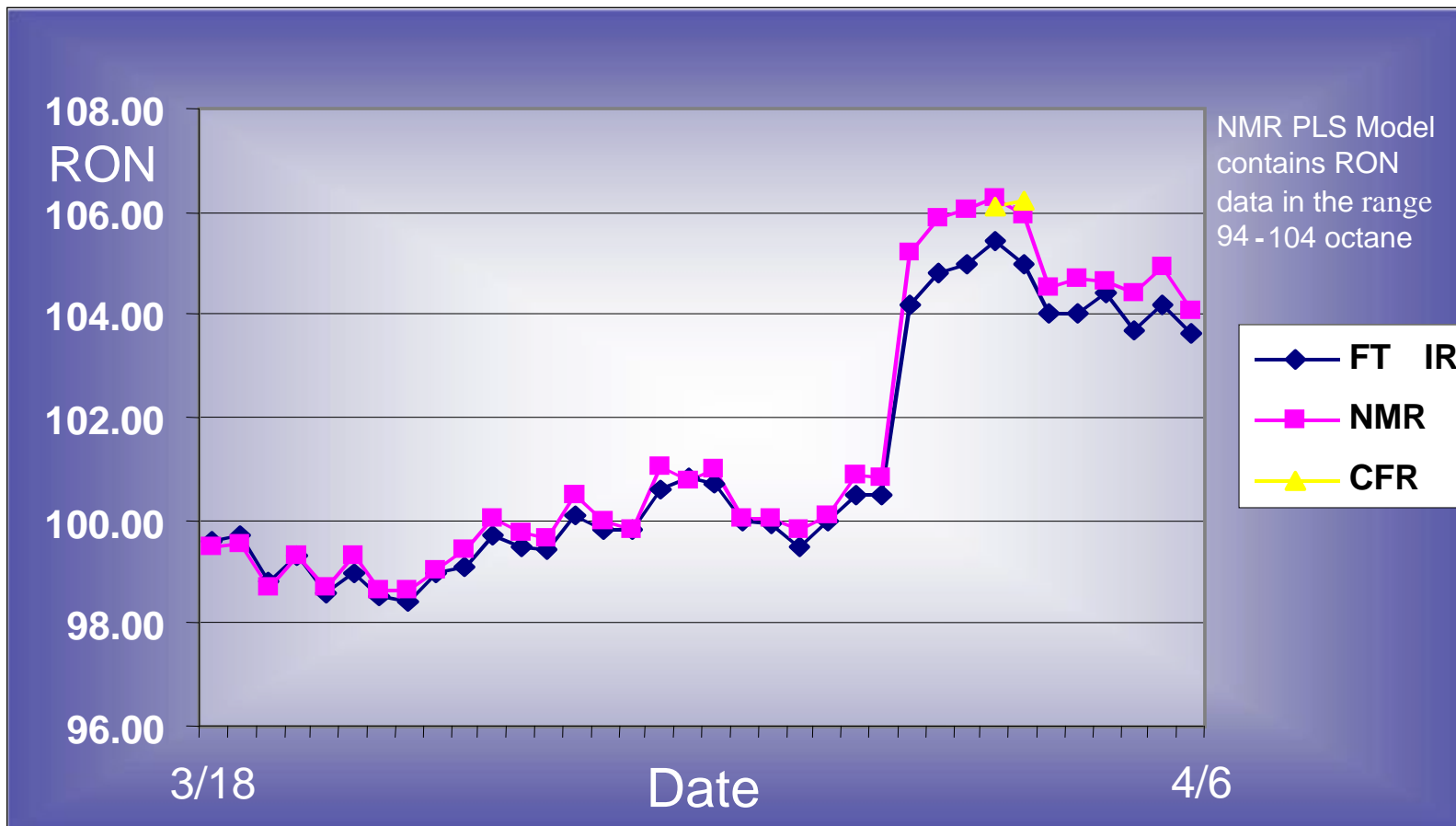
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# Extrapolation outside calibration set





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# Process NMR applications



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# Applications : distinct NMR analyser features

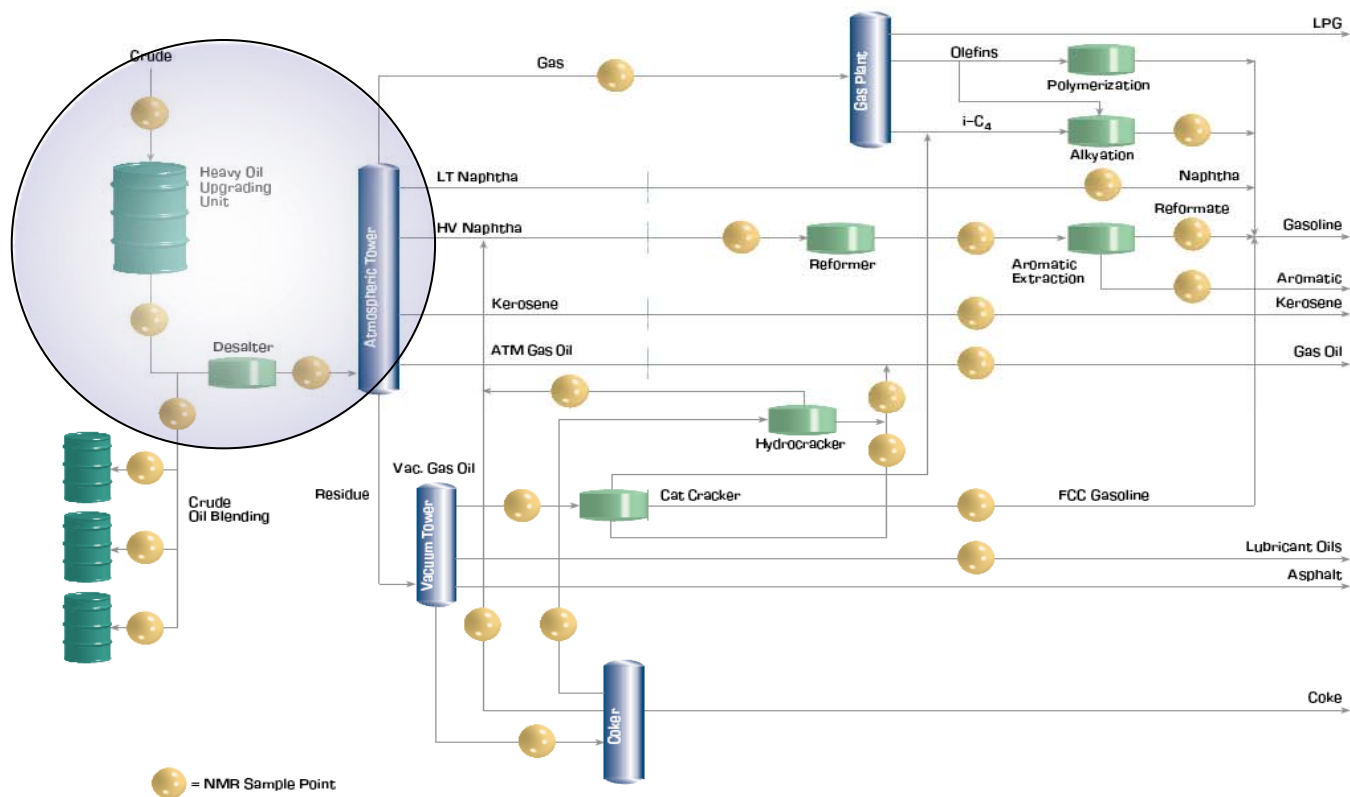
Some distinct features have oriented NMR in certain application fields :

- Non-invasive analytical technology
- Electronic , not optical

- Ability to analyse dark and opaque samples
- High temperature/wide flow-through probe for highly viscous samples
- Limited filtering of sample required

- Robust models due to highly resolved quality spectra , structural information
- Limited calibration data : short time-to-profit
- No moving parts inside – reduced maintenance

# Key application: Crude feed & distillation



# Why measure crude ?

## In the past...

- Little variation , constant supply of same crude
- Refineries were constructed for this stable feed
- Advance Control mainly on the CDU run-down products :  
feed-back control only

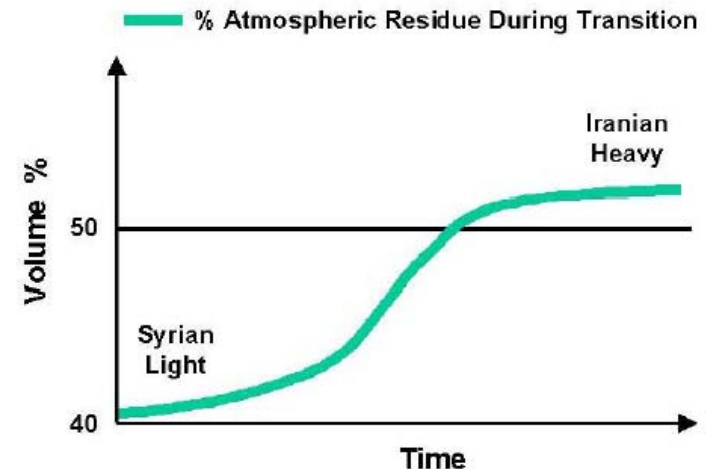
## The market today...

- Increased competition & drive to maximise profits
  - Buying of low-cost crudes (heavier types)
  - Buying on spot markets
  - High variability in crude quality offered
- The refiner today must cope with this variation in order to ensure profitability

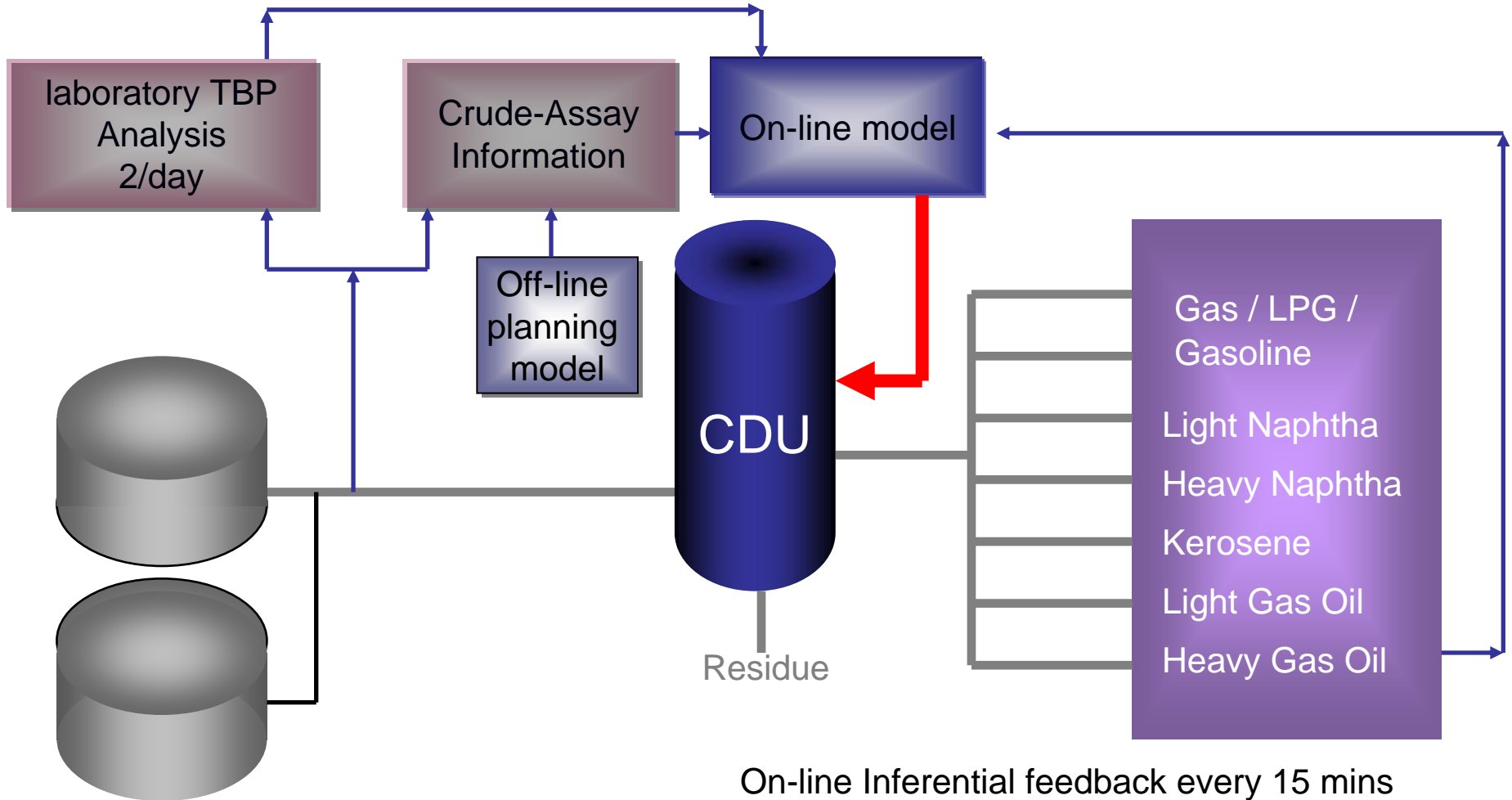
# Effect of crude quality variation on CDU

- Cut point optimisation affected
- Product quality control risks
- Feed rate is not maximised
- Energy consumption not optimal
- Risk of violating the process equipments constraints

- Unit operating conditions are upset by changing feed composition
- Product slate is not maintained at optimum
- User incurs significant financial penalties



# Traditional Crude CDU control





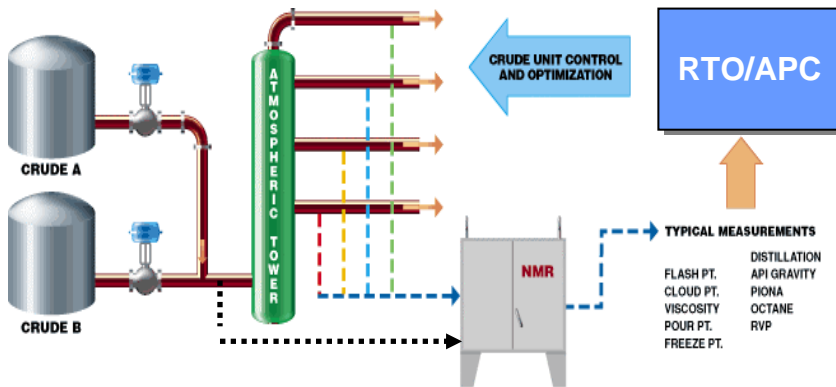
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# Problem with Crude Assay data?

- The crude assay data may be old
- Every crude tank has a heel of mixed crudes received earlier
- Crude in a tank will settle
  - Compatibility
  - Solubility
  - Stratification
- A crude switch (normally 7 to 8 hours) results in an unknown blend of the old and new crude in the pipeline

# CDU feed/distillation real time NMR data



## Feed

API Gravity  
 TBP  
 Sulfur Content  
 Water  
 TAN  
 Aromaticity  
 API Pred.Yields

## Run down

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

## Technology and Quality

**The following table is a description of the data upon which the design of the NMR Analyser application is based. The stream to be measured (Topping feed) includes the parameters, the ranges to be measured, the acceptance criteria of the different parameters and Reference Method.**

- Density API
- Sulphur % Wt
- Cuts TBP in % Wt

1. C5 – 71°C
2. 71-100
3. 100-125
4. 125-149
5. 149-165
6. 165-182
7. 182-200
8. 200-230
9. 230-250
10. 250-275
11. 275-300
12. 300-315
13. 315-340
14. 340-355
15. 355-371
16. 371-400
17. 400-525
18. 525-560
19. Over 560

Parameter	Range Min	Range Max	Reference Method	Acceptance Criteria
TBP atmospheric	NR	NR	ASTM D 2892	1.4 %wt
TBP vacuum	NR	NR	ASTM D 5236	1.7 %wt
Api density	33	27	ASTM D 1298 calculated	0.75
Density	860	900	ASTM D 1298	0.01 x measured lab value (Kg/m <sup>3</sup> )
Sulphur % Wt	1,5	2,8	ASTM D 1552	Average 0.40%wt

**NR: not relevant**



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**COMPARISON LAB vs PREDICTED VALUES TBP TO TOPPING FEED  
SAMPLE WITHDRAWN ON LINE 20.1.11 AT 2:49 PM**

<b>RANGE (°C)</b>	<b>Delta (NMR - Lab)</b>	<b>% Wt Lab</b>	<b>Prediction value</b>
<b>IBP-71</b>	-0,69	5,28	4,59
<b>71-100</b>	-0,53	2,91	2,38
<b>100-125</b>	-0,23	2,65	2,4
<b>125-149</b>	0,04	2,66	2,7
<b>149-165</b>	0,36	1,84	2,2
<b>165 - 182</b>	0,23	2,02	2,3
<b>182 - 200</b>	0,50	2,20	2,7
<b>200 - 230</b>	0,10	3,81	3,9
<b>230 - 250</b>	0,57	2,65	3,2
<b>250 - 275</b>	0,73	3,42	4,2
<b>275 - 300</b>	0,28	3,55	3,8
<b>300 - 315</b>	0,04	2,19	2,2
<b>315 - 340</b>	0,31	3,76	4,07
<b>340 - 355</b>	0,25	2,32	2,57
<b>355 - 371</b>	0,71	2,52	3,23
<b>371 - 400</b>	-1,70	4,71	3,01
<b>400 - 525</b>	4,63	22,27	26,91
<b>525 - 560</b>	-1,23	6,81	5,58
<b>560+</b>	-4,39	22,43	18,05
<b>API</b>	1,6	30,4	31,96
<b>S % m/m</b>	0,7	1,33	2,02



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**COMPARISON LAB vs PREDICTED VALUES TBP TO TOPPING FEED  
SAMPLE WITHDRAWN ON LINE 28.1.11 AT 12:31 PM**

<b>RANGE (°C)</b>	<b>Delta (NMR - Lab)</b>	<b>% Wt Lab</b>	<b>Prediction value</b>
<b>IBP-71</b>	0,17	4,59	4,76
<b>71-100</b>	-0,92	3,28	2,36
<b>100-125</b>	-0,50	2,92	2,4
<b>125-149</b>	-0,57	2,89	2,3
<b>149-165</b>	0,27	1,97	2,2
<b>165 - 182</b>	-0,01	2,13	2,1
<b>182 - 200</b>	0,15	2,30	2,5
<b>200 - 230</b>	-0,11	3,94	3,8
<b>230 - 250</b>	0,43	2,70	3,1
<b>250 - 275</b>	0,46	3,45	3,9
<b>275 - 300</b>	-0,03	3,54	3,5
<b>300 - 315</b>	0,00	2,16	2,2
<b>315 - 340</b>	0,53	3,68	4,21
<b>340 - 355</b>	0,22	2,25	2,47
<b>355 - 371</b>	0,77	2,43	3,2
<b>371 - 400</b>	-1,44	4,50	3,06
<b>400 - 525</b>	5,96	20,75	26,71
<b>525 - 560</b>	-0,71	6,20	5,49
<b>560+</b>	-4,65	24,31	19,66
<b>API</b>	-0,3	<b>28,68</b>	<b>28,38</b>
<b>S % m/m</b>	0,5	1,72	2,23



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**COMPARISON LAB vs PREDICTED VALUES TBP TO TOPPING FEED  
SAMPLE WITHDRAWN ON LINE 20.1.11 AT 2:49 PM**

<b>RANGE (°C)</b>	<b>Delta (NMR - Lab)</b>	<b>% Wt Lab</b>	<b>Prediction value</b>
<b>IBP-71</b>	0,23	4,88	5,11
<b>71-100</b>	-1,37	3,58	2,21
<b>100-125</b>	-0,82	3,15	2,3
<b>125-149</b>	-0,46	3,09	2,6
<b>149-165</b>	0,22	2,09	2,3
<b>165 - 182</b>	0,12	2,25	2,4
<b>182 - 200</b>	0,14	2,41	2,6
<b>200 - 230</b>	-0,14	4,09	4,0
<b>230 - 250</b>	0,59	2,78	3,4
<b>250 - 275</b>	0,28	3,53	3,8
<b>275 - 300</b>	0,21	3,59	3,8
<b>300 - 315</b>	0,01	2,18	2,2
<b>315 - 340</b>	0,69	3,69	4,38
<b>340 - 355</b>	0,30	2,24	2,54
<b>355 - 371</b>	0,88	2,42	3,3
<b>371 - 400</b>	-1,08	4,45	3,37
<b>400 - 525</b>	4,19	20,14	24,33
<b>525 - 560</b>	-0,50	5,92	5,42
<b>560+</b>	-3,37	23,52	20,15
<b>API</b>	2,2	29,59	31,81
<b>S % m/m</b>	0,4	1,73	2,09



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NMR ANALYZERS

# Nuclear Magnetic Resonance Analysis On-line

Conclusion



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# The NMR Analyzer Advantage - Control

- Real time, accurate stream analysis
  - Reduction in response time from Lab allows tighter control
  - Multi-property analysis and increased information regarding stream matrix to allow better management decisions
- Avoid errors in stream analysis
  - Measurements are reliable and done online in real time
  - Eliminates data entry errors from Lab input



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# The NMR Analyzer advantage - analytical

- Simple sample conditioning required
  - No water removal
  - Coarse or limited filtering to protect valve seats
- Linear Spectral Response across broad range
  - Models can be extrapolated accurately
- Multi-property analysis replaces conventional analyzers and provide much faster results
- Minimal maintenance required
  - No moving parts in sensor



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**NMR ANALYZERS**

**Thanks for Your attention !!!**