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Post Processing Methodology to Calculate the Carbon Aromaticity (Fa), Paraffinicity (Fp), and Naphthenicity (Fn) from ^{13}C NMR Data

NMR Experimental Details:

^{13}C NMR spectra were obtained on a Varian 300S NMR spectrometer under the following conditions:

- 10 mm probe
- Pure Sample
- 45° pulse angle, with gated decoupling, 10 second delay
- 368 pulses (S/N ~3500)
- 90°C temperature

Aromaticity Calculation:

Acquired FID must be weighted Fourier transformed with appropriate zero filling (128k). Spectrum must be carefully phased and base line corrected. Integrals should be cleared and the integral scale set at 1000 (the integral scale can be set to any number the operator wishes but must be maintained at that value throughout the following procedures).

Integrals are defined as follows:

Aromatic Region (165-100 ppm)	integral value = Ar
Aliphatic Region (75 to -5 ppm)	integral value = Al

$$\text{Carbon Aromaticity (Fa)} = \text{Ar}/\text{Ar}+\text{Al}$$

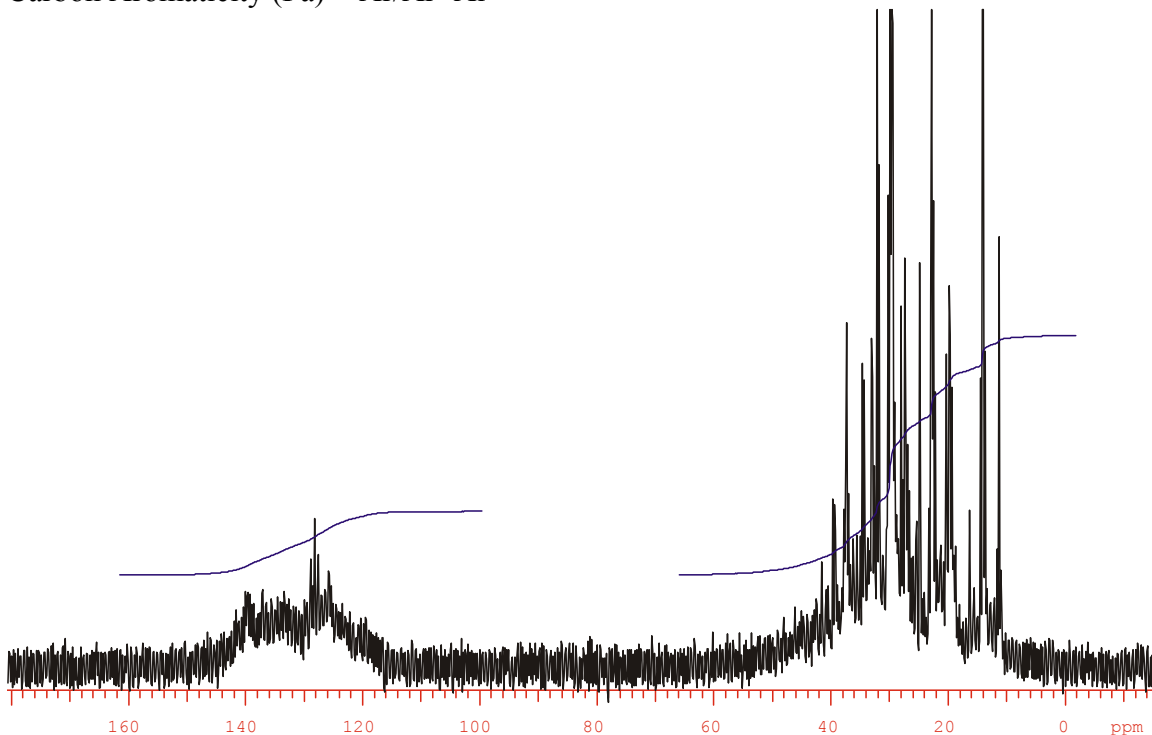


Figure 1: Example of integral regions used to determine aromatic/aliphatic content.

Paraffinicity and Naphthenicity Calculation:

The next step is to zoom into the 80 to -5 ppm region of the spectrum and define integrals wherever a paraffin resonance is found. It is assumed that all narrow resonances are paraffinic, and that any obvious broader NMR peak groups that represent a superposition of narrow paraffinic resonances are 100% paraffinic. There is some error in this assumption but it cannot be avoided. Due to these assumptions and the natural variance observed in oils with different chemistries the definition of the integral positions must be left to the judgment of the NMR operator. Here are two examples of oils processed to remove the naphthenic “hump”. Figure 2 shows the definition of the paraffinic integrals and Figure 3 shows the same integrals after a bc command is executed. The integrals are then cleared and a new single integral obtained to define the paraffinic carbon (see Figure 4). The scale value of this integral must be identical to that used for the aromatic/aliphatic definition.

The integral found in Figure 4 represents the paraffinic carbon only (I_p). The difference between the original “Total Aliphatic” integral and this new paraffinic integral is the naphthenic carbon content.

$$\text{Carbon Paraffinicity (Fp)} = I_p / (A_r + A_l)$$

$$\text{Carbon Naphthenicity (Fn)} = (A_l - I_p) / (A_r + A_l)$$

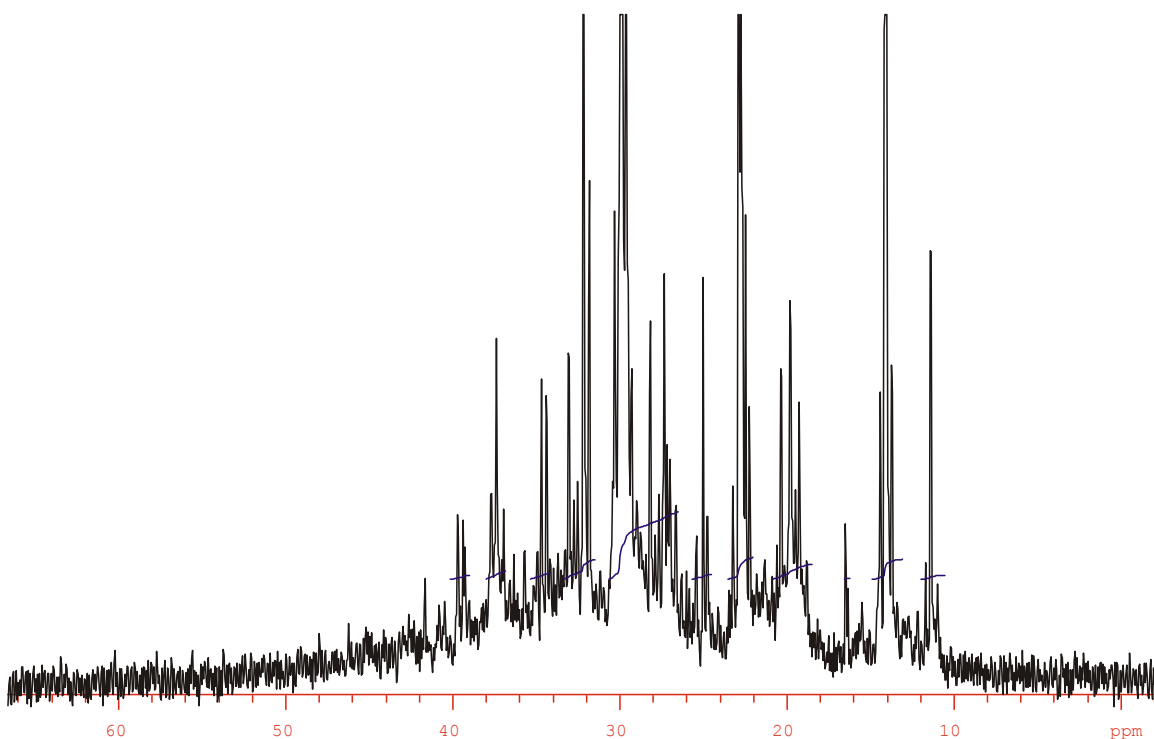


Figure 2: Integral Definition

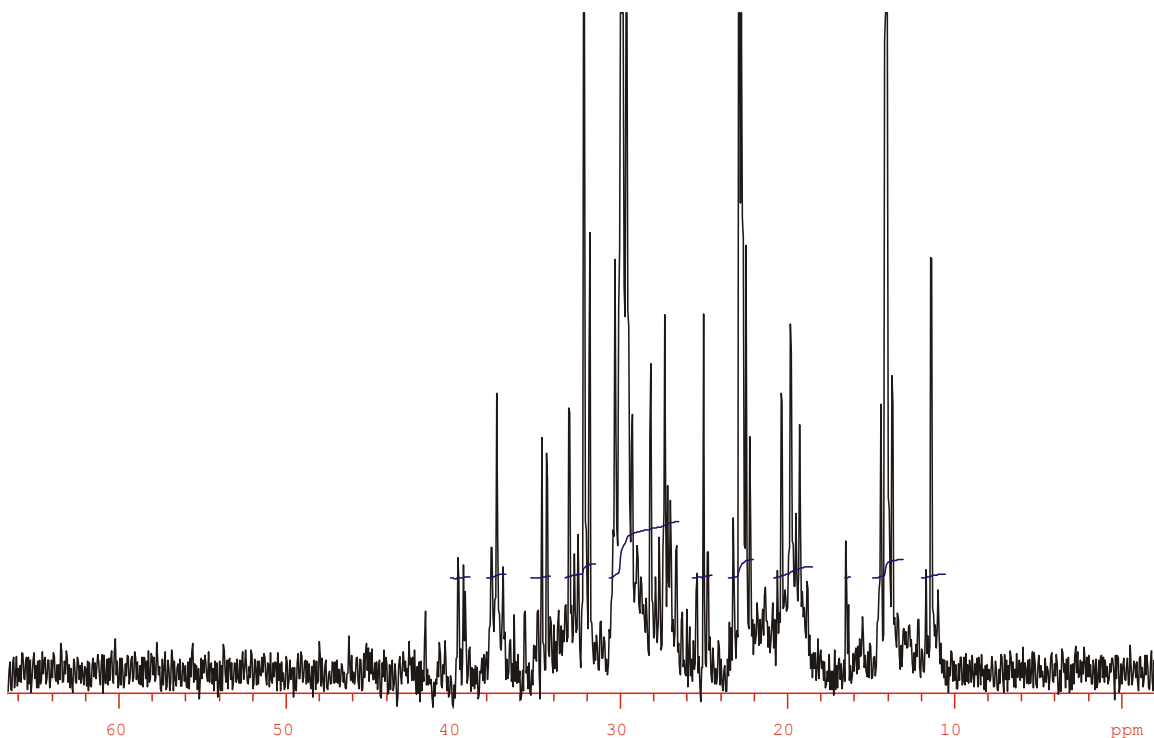


Figure 3: Effect of baseline correction routine after integral definition (note flat baseline and no dispersion in spectral features).

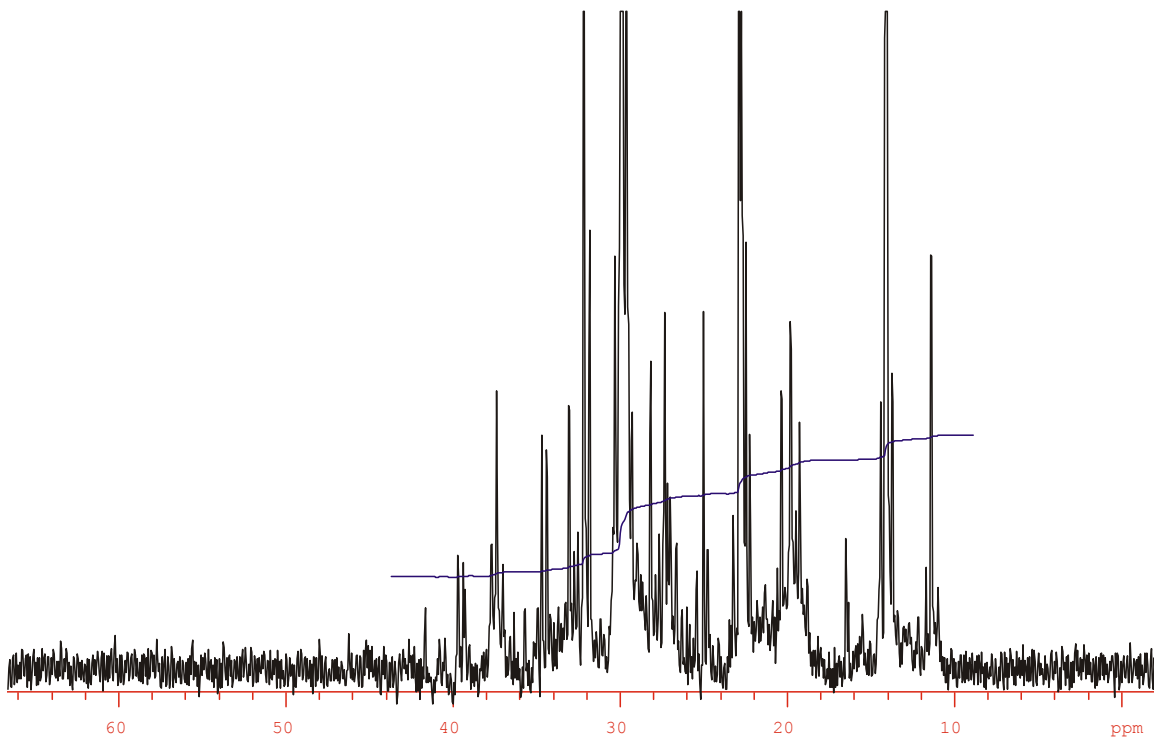


Figure 4: Integral value (I_p) equivalent to paraffinic carbon content.

The table below represents the integral cut points used for this sample. Note that the exact number of integrals and the exact cut positions will vary slightly from one sample to another.

Table I – Integral Cut Points

Integral	Start (ppm)	End (ppm)
1	47.17	46.02
2	41.93	39.35
3	38.97	36.97
4	35.54	31.91
5	31.25	26.58
6	25.81	24.57
7	23.81	19.33
8	15.13	13.80
9	11.99	11.13

The figures below show another base oil sample which required slightly different integral definition and is an example of a spectrum that had to be processed several times in order to avoid having the baseline correction cause serious spectral distortion (“baseline negative” or dispersive regions of the spectrum).

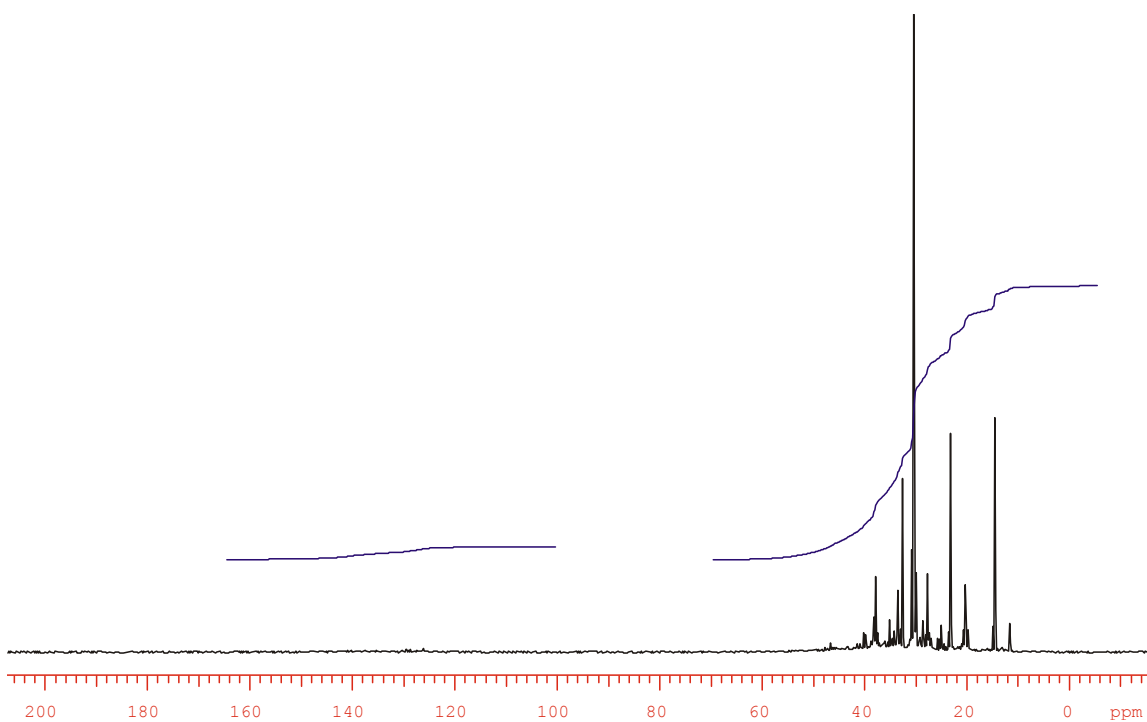


Figure 5: Aliphatic/Aromatic Integral Definition.

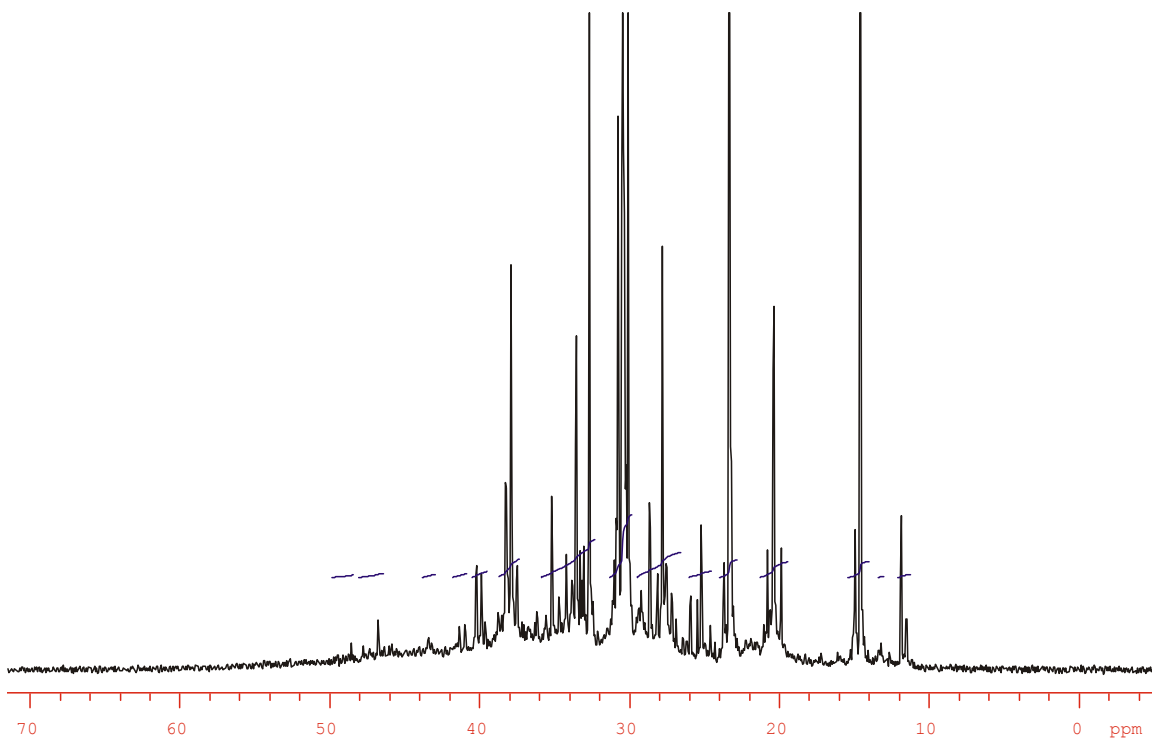


Figure 6: Aliphatic Region Integral Definition.

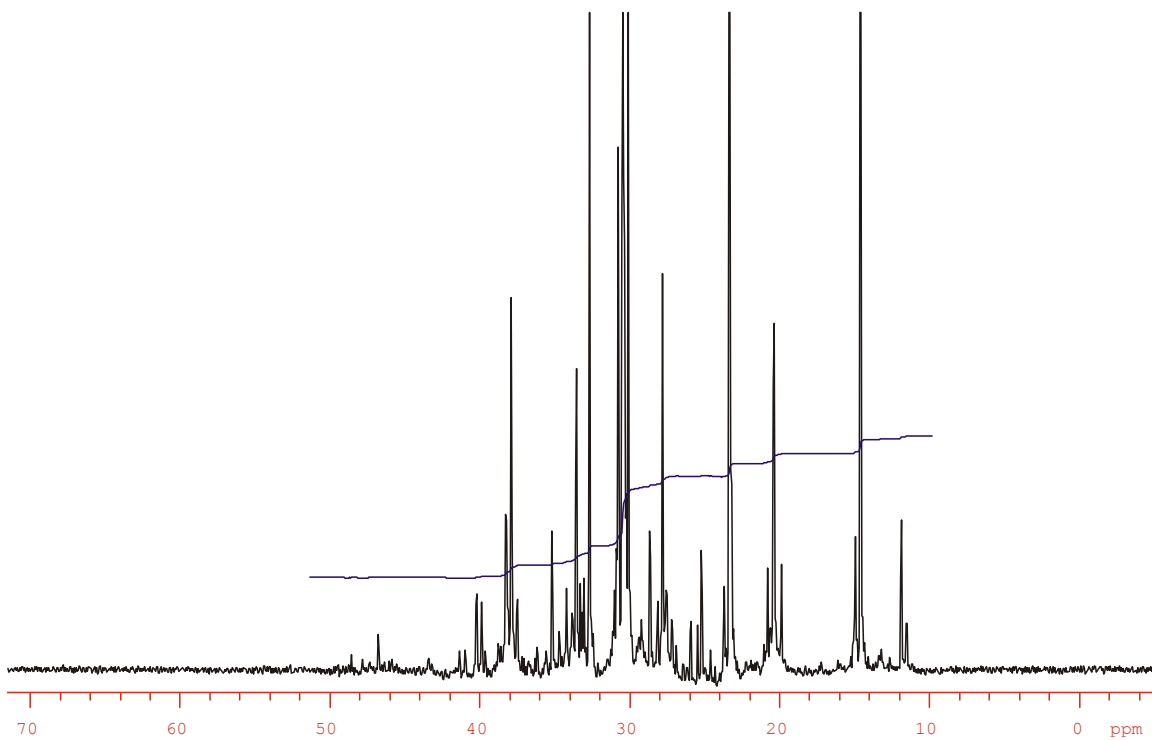


Figure 7: Integral of paraffinic intensity (I_p) obtained after baseline correction. Note baseline negative region at 24-26 ppm, and 40-42 ppm.

Figure 7 demonstrates an example of a poor naphthenic “hump” removal by the baseline correction. When this occurs it will impact the quantitation of the paraffinic/naphthenic carbon. When this occurs the spectrum should be Fourier transformed again and the procedure performed again with slight changes to the integral cut points in order to prevent the phenomenon shown in Figure 7.

Unfortunately a single methodology can be defined where cut points for integrals are strictly definable. In all cases the NMR operator must use his best judgment to define the integrals and decide when the baseline corrected spectrum is free from distortions such as peak dispersions and/or “baseline-negative” regions.

Model Validation

Case A: ^{13}C NMR Analysis is Unavailable to Customer

In order to ensure that the ^{13}C carbon aromaticity predicted output is correct we can utilize the empirical relationship between ^1H proton aromaticity (a number that can be derived directly from the FoxboroNMR ^1H spectrum) and ^{13}C carbon aromaticity.

The proton aromaticity is a value that is readily obtained from a ^1H NMR spectrum. In the case of the normalized integral data that is generated by the FoxboroNMR analyzer it is simply a matter of adding the integral values represented by points 30 to 60 to generate the proton aromaticity value. Figure 1 shows the area of the spectrum used to generate the proton aromaticity value. There is a well-known non-linear correlation between ^1H NMR derived aromaticity and ^{13}C NMR derived aromaticity (see “A Novel Semi-Empirical Relationship Between Aromaticities Measured from ^1H and ^{13}C NMR Spectra”, David J. Cookson, C. Paul Lloyd, and Brian E. Smith, **Fuel**, 65, p 1247-1253, 1986.). Figure 2 shows the relationship usually observed.

Thus, while the NMR is operational the proton aromaticity number can be determined and outputted into the DCS where an “estimated carbon aromaticity” value can be calculated. This value can be used to confirm the “true carbon aromaticity” value being outputted by the on-line PLS models. When the two values disagree by more than X atomic%C (X to be agreed upon between parties) then the predicted values shall be considered invalid. In the initial model building stage the relationship between ^{13}C aromaticity and the on-line proton aromaticity will be developed in parallel with the PLS models.

Spot checks on this system can be made by performing the actual ^{13}C NMR analysis at the PNA facility on a pre-determined schedule.

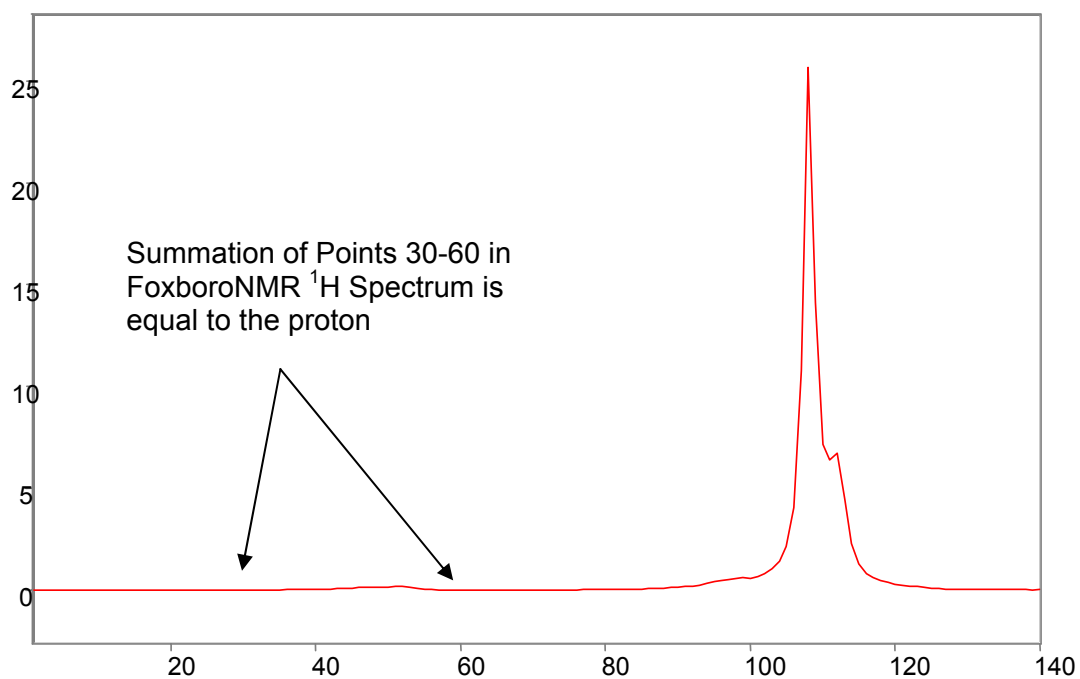


Figure 1: Region of NMR Spectrum to be summed to yield proton aromaticity.

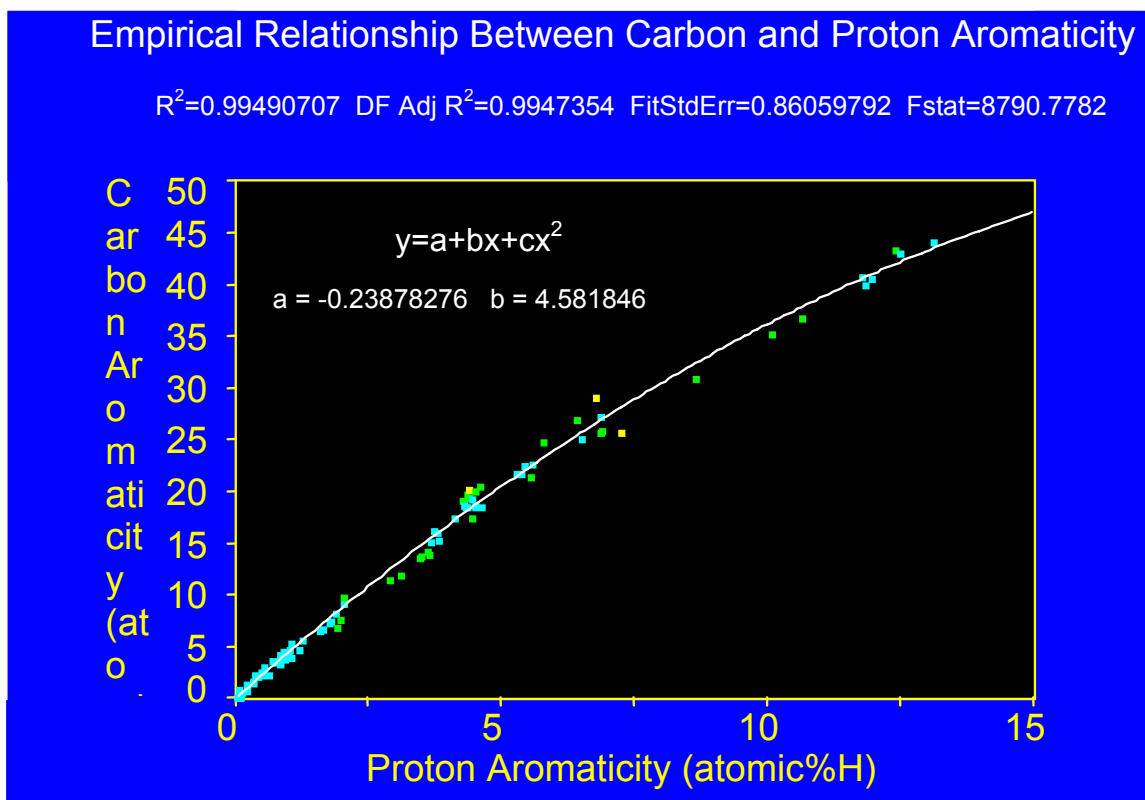


Figure 2: Empirical Relationship Between Proton and Carbon Aromaticity

Case B: ^{13}C NMR is Available to Customer

Carbon Aromaticity parameter will be validated as per standard Foxboro NMR standard validation protocols.

Contact information for this standard:

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