

Calculation of average molecular descriptions of heavy petroleum hydrocarbons by combined analysis by quantitative ^{13}C and DEPT-45 NMR experiments

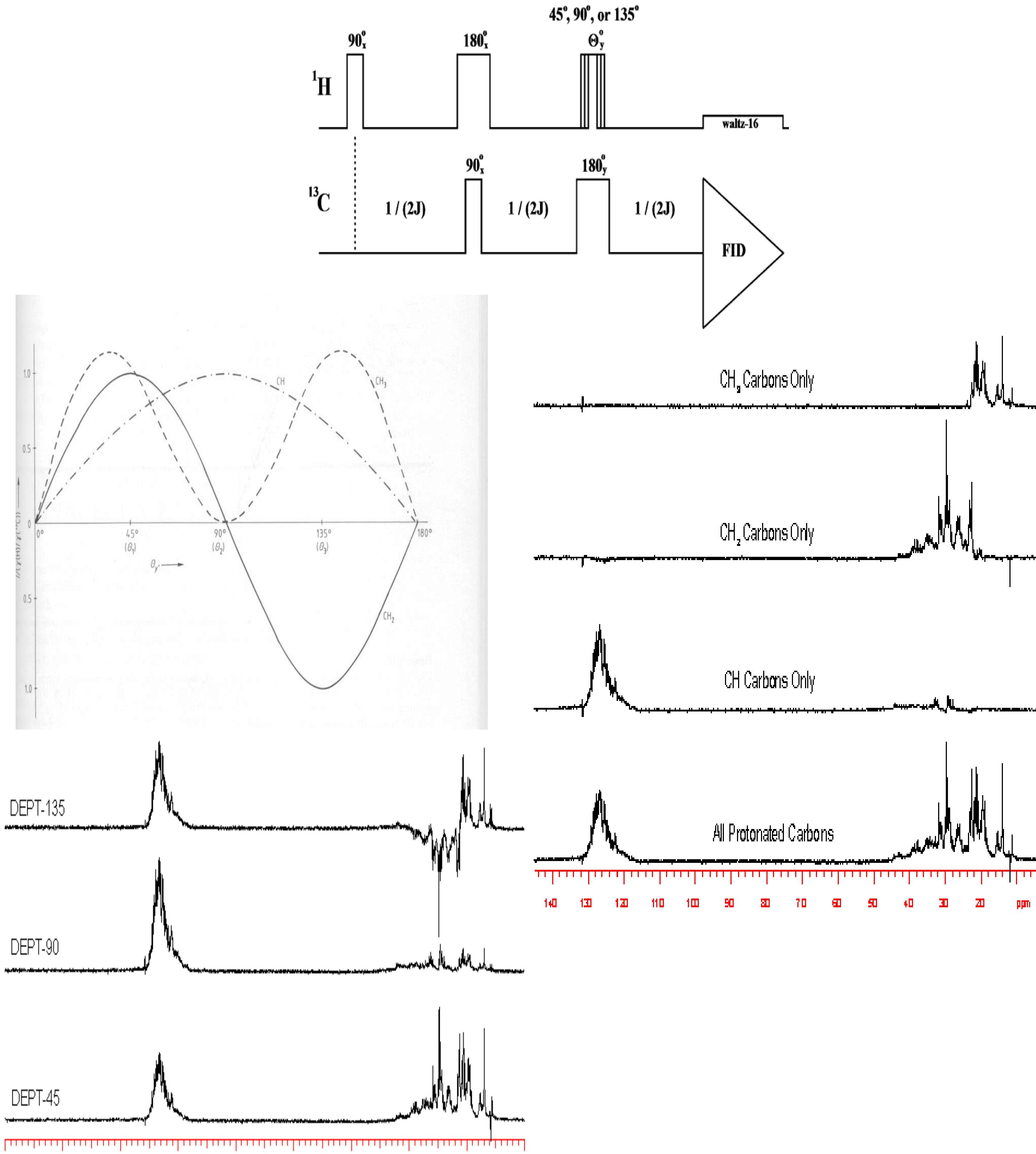
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Overview

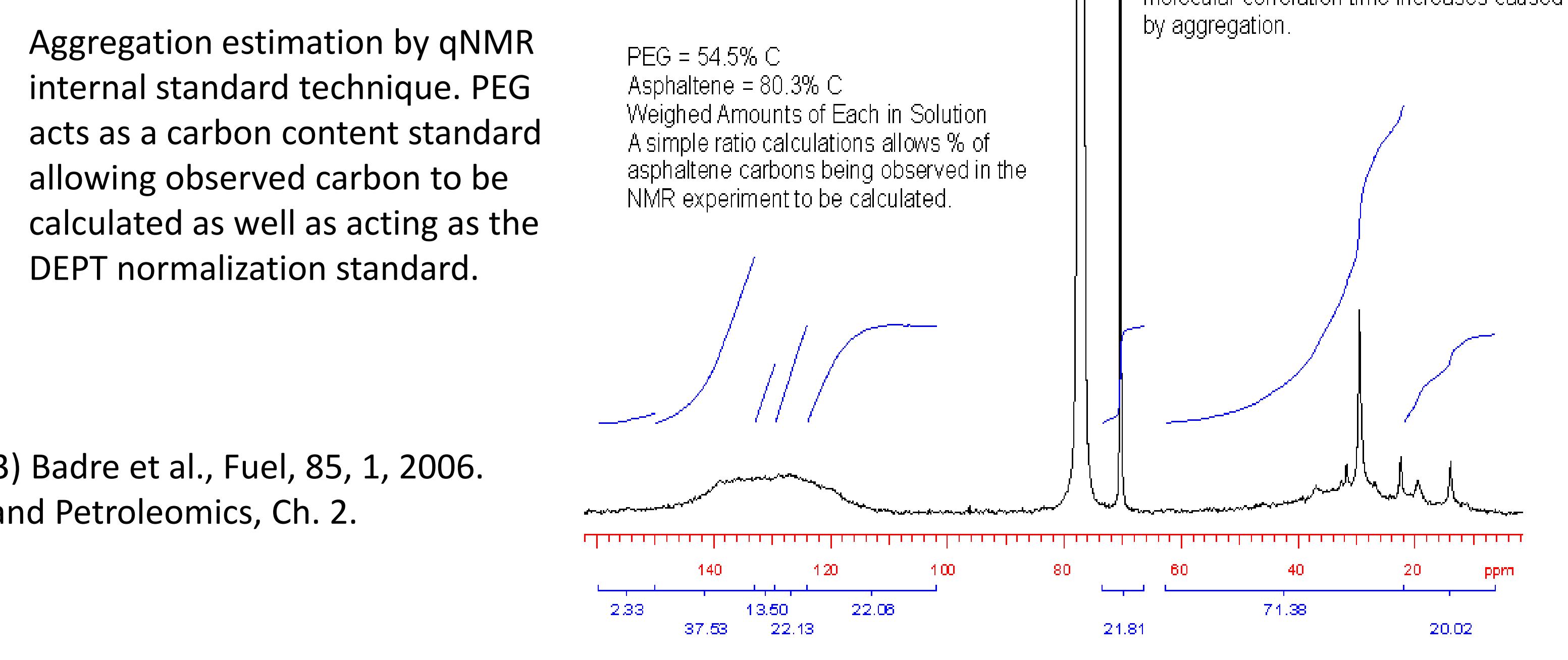
Over the years much debate has centered around the validity and accuracy of NMR measurements to accurately describe the sample chemistry of heavy petroleum materials. Of particular issue has been the calculated size of aromatic ring systems that in general seem to be underestimated in size by NMR methods. This underestimation is principally caused by variance in chemical shift ranges used by researchers to define the aromatic carbon types observed in the ^{13}C NMR spectrum, in particular the bridgehead aromatic carbons that can be shown to overlap strongly with the protonated aromatic carbons. The ability to discern between bridgehead aromatic carbons and protonated carbons in the 108-129.5 ppm region of the spectrum is key in the derivation of molecular parameters that properly describe the "molecular average" carbon structure present in the sample. Utilizing methodologies developed by Pugmire and Solum¹ for the solid-state ^{13}C NMR analysis of coals and other carbonaceous solids we have developed a liquid-state ^{13}C NMR methodology that allows the relative quantification of overlapping protonated and bridgehead aromatic carbon signals to be determined. The NMR experiments involve the combined analysis of both quantitative ^{13}C single pulse excitation which observes "all carbons in the observes only the protonated carbons in the sample. Though the DEPT-45 results are not quantitative across all carbon types (CH , CH_2 , and CH_3) due to polarization transfer differences, the technique is well enough understood that simple multiplication factors allow the relative absolute intensities of the different carbons to be determined. An additional aspect of the experiments is the addition of a standard material (Polyethyleneglycol (PEG) polymer) that allows the calculation of the absolute percentage of the carbons that are observed by the ^{13}C NMR technique. This allows the relative amount of bridgehead carbon to be calculated by direct comparison of the aromatic region with the standard signal intensity. The average ring system sizes derived from these NMR experiments tend to be several ring systems larger than has been calculated in previous studies. In asphaltenes for example the ring systems are 5-7 rings in size rather than the 3-4 rings reported previously². The ring sizes determined by this new combined NMR method are in agreement with FTICR-MS and fluorescence measurements³⁻⁶.

DEPT Experiment



	Scans	CH peak intensity	CH_2 peak intensity	CH_3 peak intensity	Relative noise level
Θ° ^1H pulse:		$\sin\Theta$	$2\sin\Theta\cos\Theta$	$3\sin\Theta\cos^2\Theta$	
s1, 45° ^1H pulse:	n	0.707	1.0	1.060	1.0
s2, 90° ^1H pulse:	$2n$	2.0	0	0	1.414
s3, 135° ^1H pulse:	n	0.707	-1.0	1.060	1.0

Aggregation estimation by qNMR internal standard technique. PEG acts as a carbon content standard allowing observed carbon to be calculated as well as acting as the DEPT normalization standard.

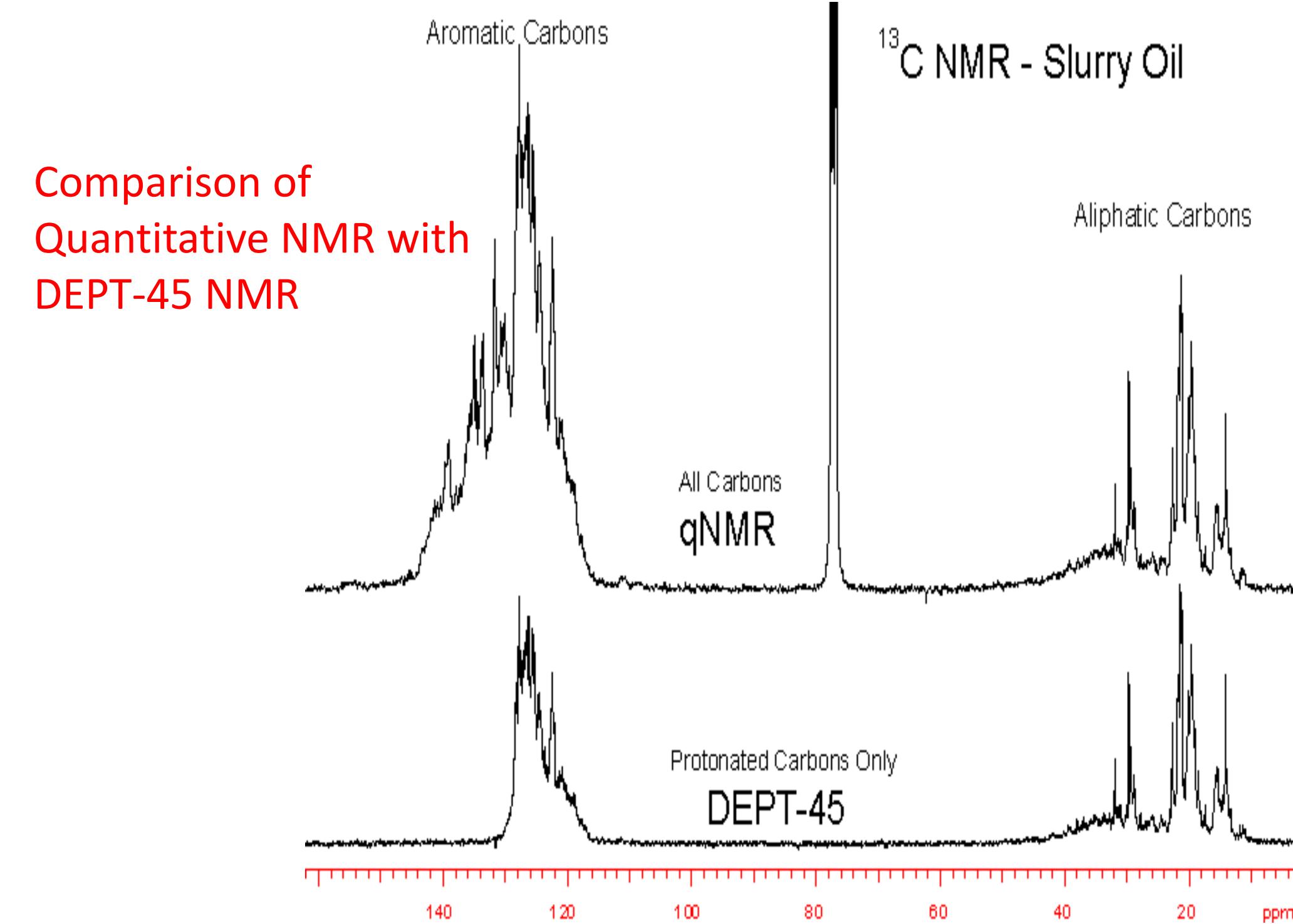


1) Pugmire et al., Energy & Fuels, 3, 187, 1989. 2) Sheremata et al., Energy & Fuels, 6, 414, 2004. 3) Badre et al., Fuel, 85, 1, 2006.

4) Sharman et al., Energy & Fuels 16, 490, 2002. 5) Groenin and Mullins, "Asphaltenes, Heavy Oils and Petroleomics, Ch. 2.

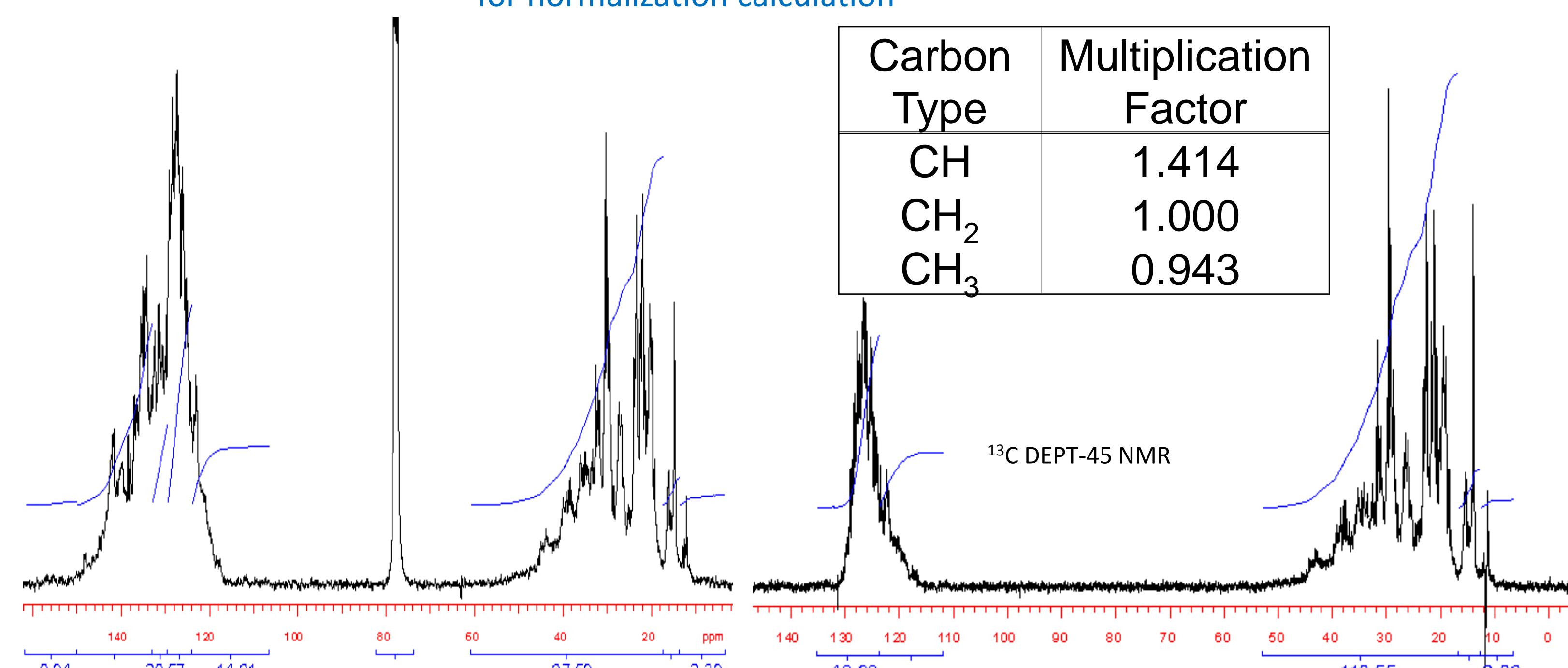
6) Rodgers and Marshall, "Asphaltenes, Heavy Oils and Petroleomics, Ch. 3.

^{13}C NMR Analysis

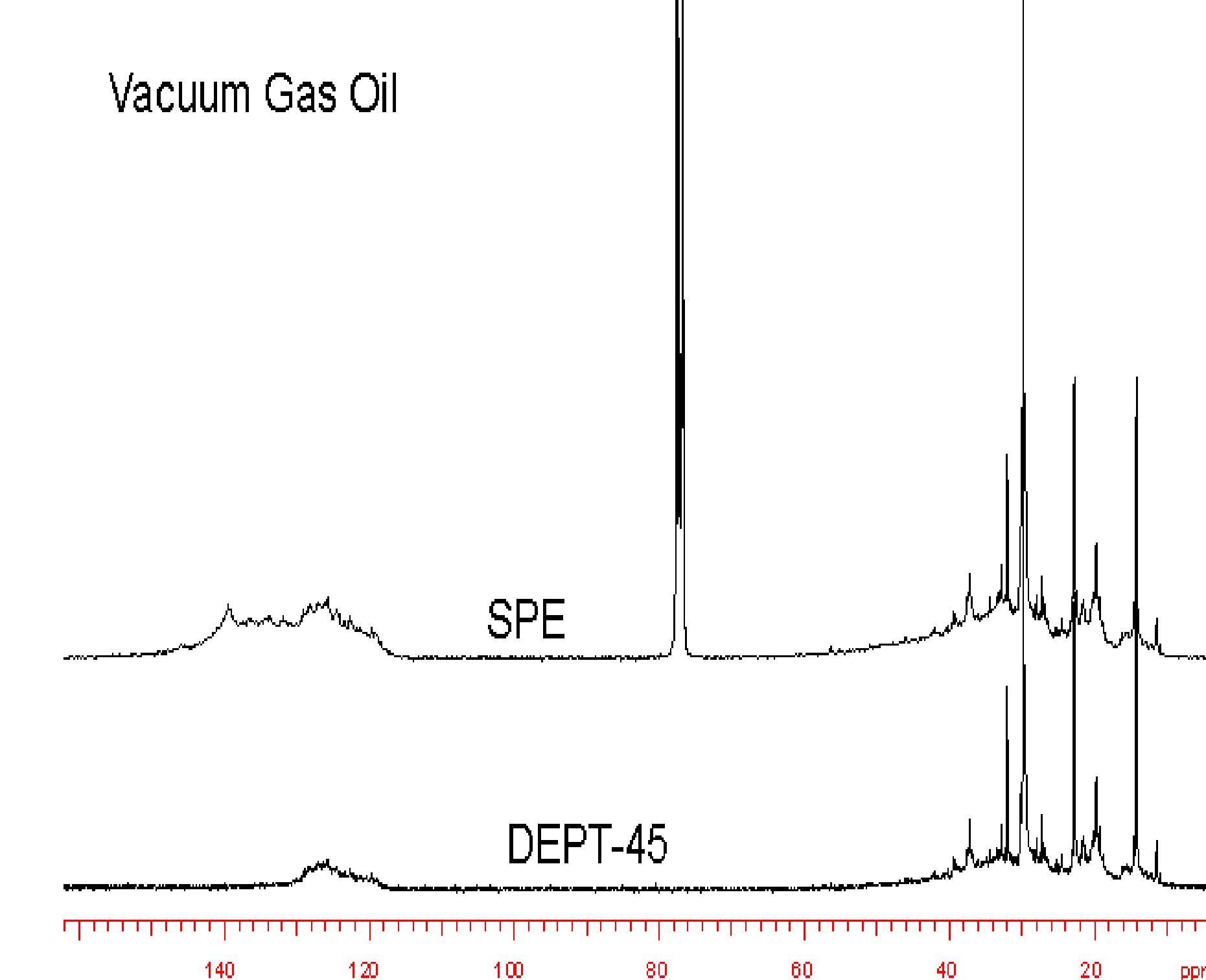
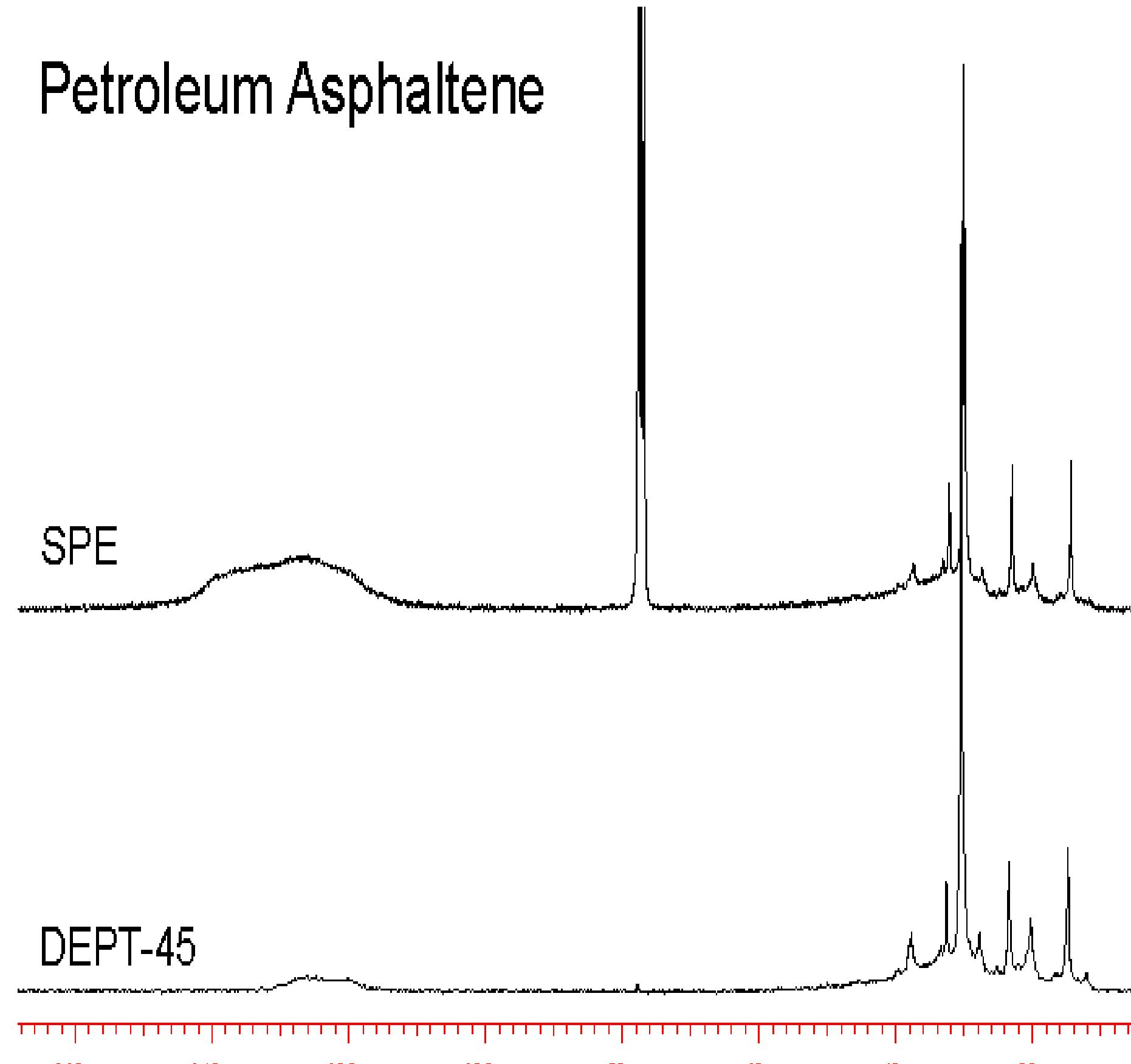
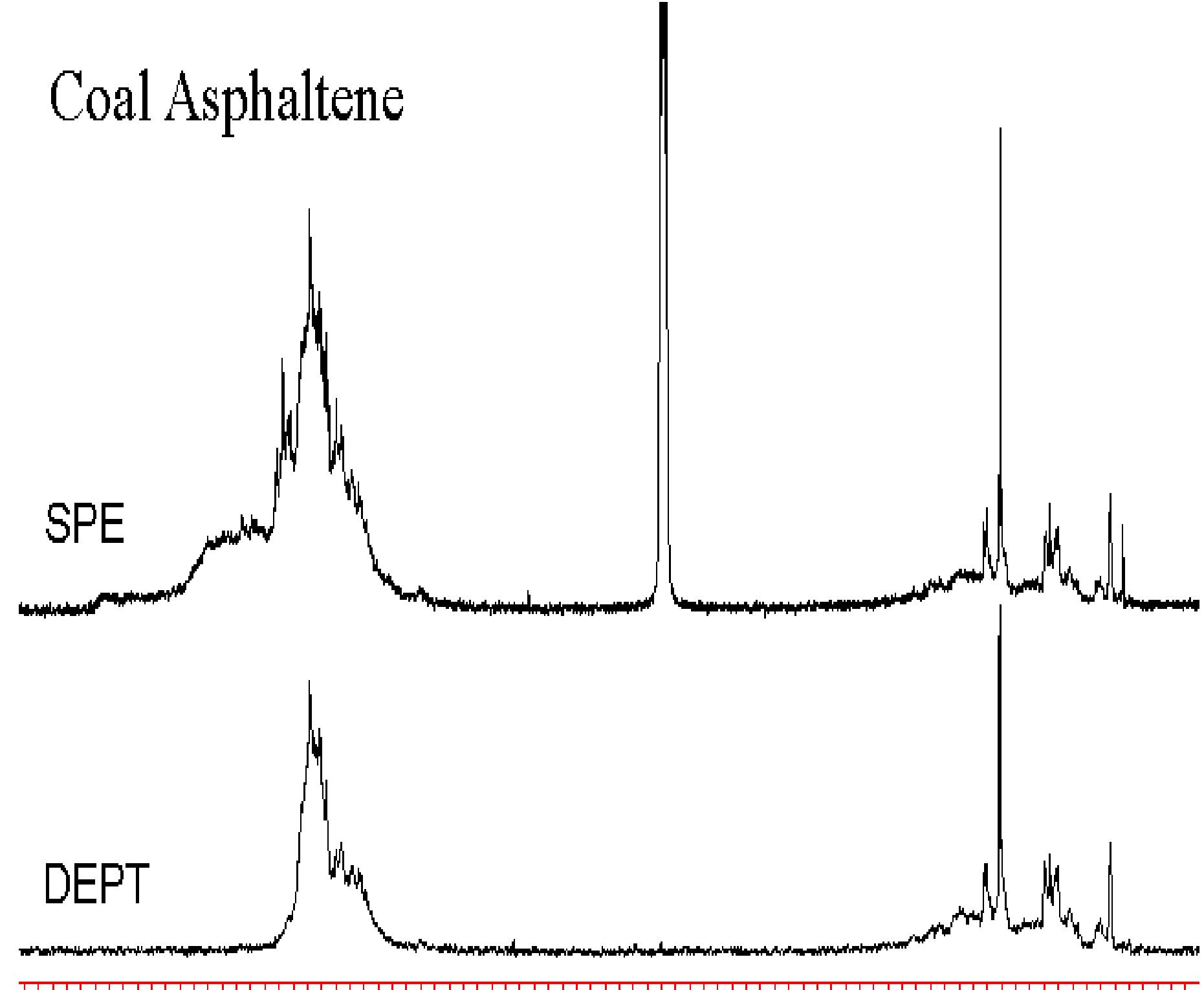


Integration of respective aliphatic carbon zones for normalization calculation

Carbon Type	Multiplication Factor
CH	1.414
CH_2	1.000
CH_3	0.943

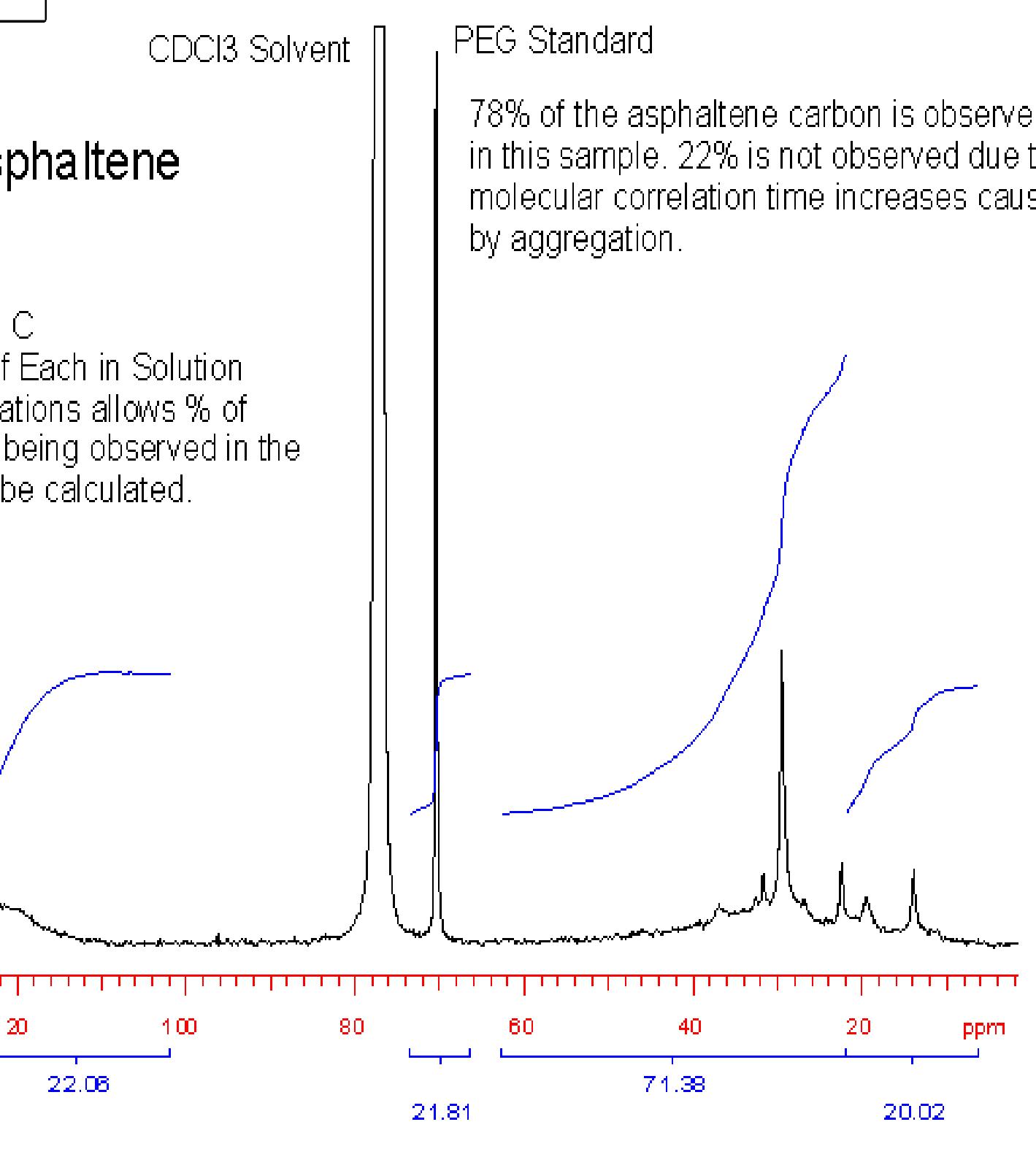
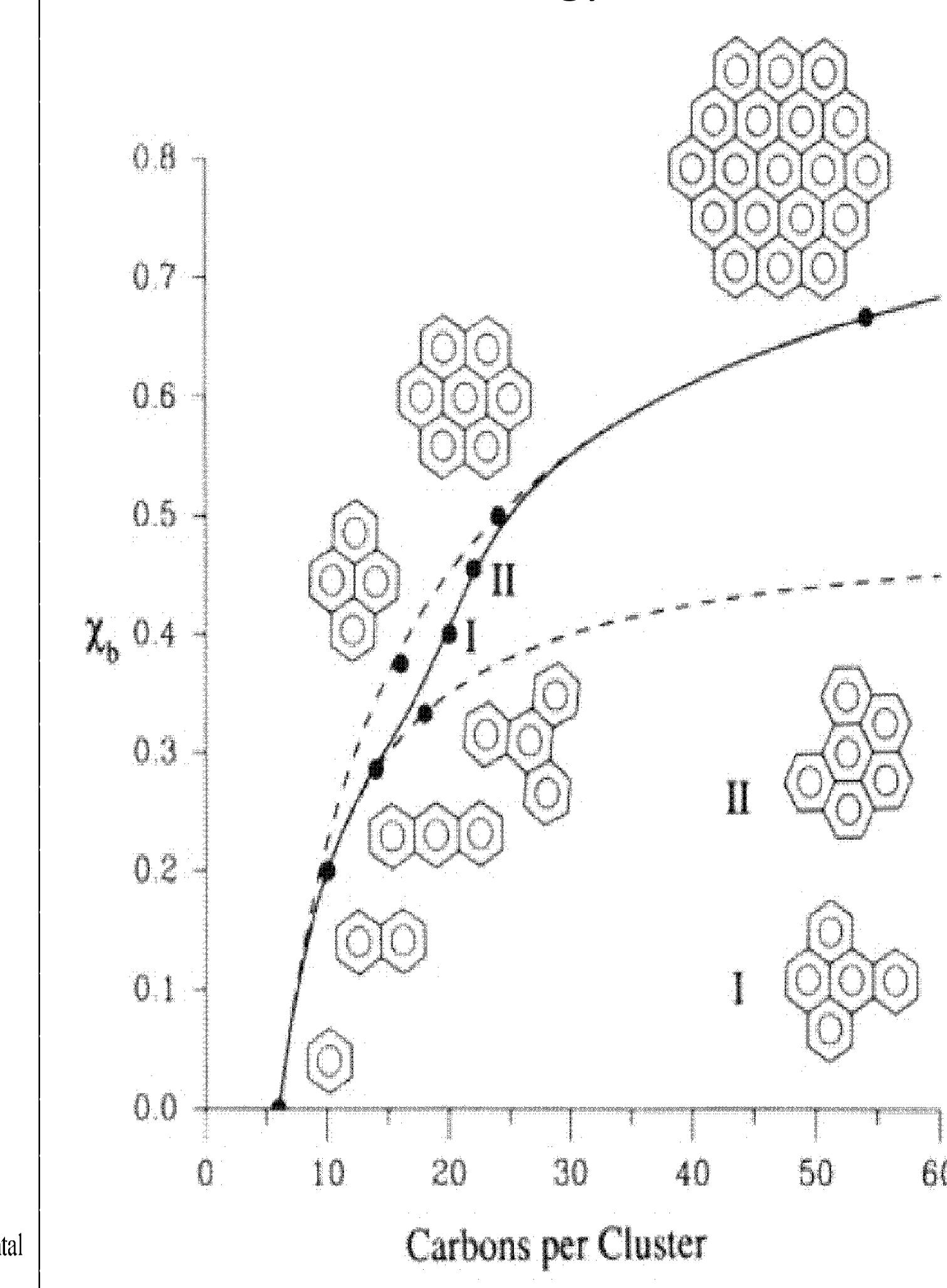


Examples



Parameter	Shift Range (ppm)	Description	Calculation
F_a	90-240	Carbon Aromatic	
F_a'	90-165	Aromaticity - not including Carboxyl/Carbonyl	$F_a' = F_a + F_a^{\text{C}}$
F_a^{C}	165-240	Carboxylic and Carbonyl Carbon	
F_a^{CO}	185-240	Carboxyl - Ketone, Aldehyde	
F_a^{COO}	165-185	Carboxylic - Acid, Ester, Amide	
F_a^P	150-165	Phenolic Aromatic Carbon	
F_a^S	135-150	Alkyl-Substituted Aromatic Carbons	
F_a^H	90-165	Protonated Aromatic Carbon	$\text{DD Aromatic} - F_a^H = F_a^{\text{H}} M_{\text{DG}}$
F_a^N	90-165	Non-Protonated Aromatic Carbon	$F_a^N = F_a^{\text{H}} - F_a^{\text{H}}$
F_a^B	90-165	Bridgehead Aromatic Carbon	$F_a^B = F_a^N + F_a^P + F_a^S$
F_{al}	0-50	Total Aliphatic Carbon	
F_{al}^O	50-90	Oxygenated Aliphatic Carbon	
F_{al}^H	22-50	Protonated Aliphatic Methylene and Methine	$\text{DD Aliphatic} - F_{\text{al}}^H = F_{\text{al}}^{\text{H}} M_{\text{DG}}$
F_{al}^*	0-22	Methyl Carbons	$F_{\text{al}}^* = F_{\text{al}}^{\text{H}} - F_{\text{al}}^{\text{H}}$
X_b		Mole fraction of Bridgehead Carbons	$X_b = F_a^B / F_a^{\text{H}}$
C		Carbons per Aromatic Cluster	See Figure 24-C is calculated from X_b
$\sigma + 1$		Average Number of Alkyl Attachments	$\sigma + 1 = F_a^P + F_a^S \times C/F_a^{\text{H}}$
P_0		Fraction of Intact Bridges and Loops	$P_0 = (F_a^P + F_a^S - F_{\text{al}}^*) / (F_a^P + F_a^S)$
$B.L.$		Bridge and Loop Alkyl Attachments	$B.L. = P_0(\sigma + 1) - B.L.$
$S.C.$		Terminal Alkyl Side Chains	$S.C. = 12.01 C / (F_a^{\text{H}} \times \% \text{C}/100) \% \text{C from Elemental}$
M_w		Average Molecular Weight of a Cluster	$M_w = 12.01 C / (F_a^{\text{H}} \times \% \text{C}/100) \% \text{C from Elemental}$
M_f		Average Molecular Weight of Attachments	$M_f = (M_w - 13M_{\text{DG}}) / (\sigma + 1)$

Relationship between mole fraction of bridgehead carbons X_b and aromatic cluster size (C). From Solum, et al. Energy & Fuels, 3, 187, 1989.



Carbon NMR Parameter	Slurry Oil	VGO	Petroleum Asphaltene	Coal Asphaltene	Pyrolyzed Coal Extract
Carboxyl Carbon % (F_a^{C})	0.00	0.00	0.00	0.00	1.13
Carbon Aromaticity % (F_a)	57.76	37.48	53.49	51.86	87.23
Carbon Aromaticity (No CO) % (F_a')	57.76	37.48	53.49	51.86	87.23
Carbon Aliphaticity % (F_a^{A})	42.24	62.52	46.51	48.14	11.64
Phenolic Aromatic C % (F_a^P)	0.41	0.67	1.03	0.71	6.43
Substituted Aromatic C % (F_a^S)	19.94	15.22	19.29	19.89	22.55
Bridgehead Aromatic C % (F_a^B)	23.17	12.14	30.77	28.34	44.95
Protonated/Hetero Aromatic C % (F_a^{H})	14.24	9.46	2.41	2.92	13.30
Non-Protonated Aromatic C % (F_a^N)	43.52	28.02	51.08	48.93	73.93
Methyl Aliphatic C % (F_a^{M})	13.31	13.18	9.37	9.27	5.25
Methylene/Methine C % (F_a^{H})	28.92	49.34	37.15	38.87	6.39
X_b	0.401	0.324	0.575	0.546	0.515
C - Carbons per Aromatic Cluster	19.7	16.5	31.9	28.4	25.7
No. Aromatic Rings per Cluster (linear-cata)	4.4	3.6	7.5	6.6	5.9
No. Aromatic Rings per Cluster (globular-pen)	5.3	4.2	9.6	8.4	7.5
No. Aromatic Rings per Cluster (Average 50/50 per/cata)	4.9	3.9	8.5	7.5	6.7
Clusters per 100C	2.93	2.28	1.68	1.83	3.39
Total Substitutions per Cluster (Alkyl + Phenolic)	6.94	6.98	12.11	11.28	8.55
Carboxyls per Cluster	0.00	0.00	0.00	0.00	0.33
Phenols per Cluster	0.14	0.29	0.61	0.39	1.90
Alkyl-Substitutions per Cluster	6.80	6.68	11.50	10.89	6.65
Average Length of Substitutions	2.08	3.94	2.29	2.34	1.55
Po - Fraction of Intact Bridges and Loops	0.35	0.17	0.54	0.55	0.82
B.L. Intact Bridges and Loops per Cluster	2.40	1.19	6.53	6.20	7.00
S.C. Terminal Side Chains per Cluster	4.54	5.79	5.58	5.08	1.55
Mw - Mw of Average Aromatic Cluster	410.6	558.7	681.1	619.6	386.89
Md - Average Mw B.L. and S.C.	25.1	51.8	25.7	24.3	10.8