Analysis of Biodiesel and Gasoline in Diesel Fuel by NMR Spectroscopy

A quick and robust alternative to chromatography

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Introduction

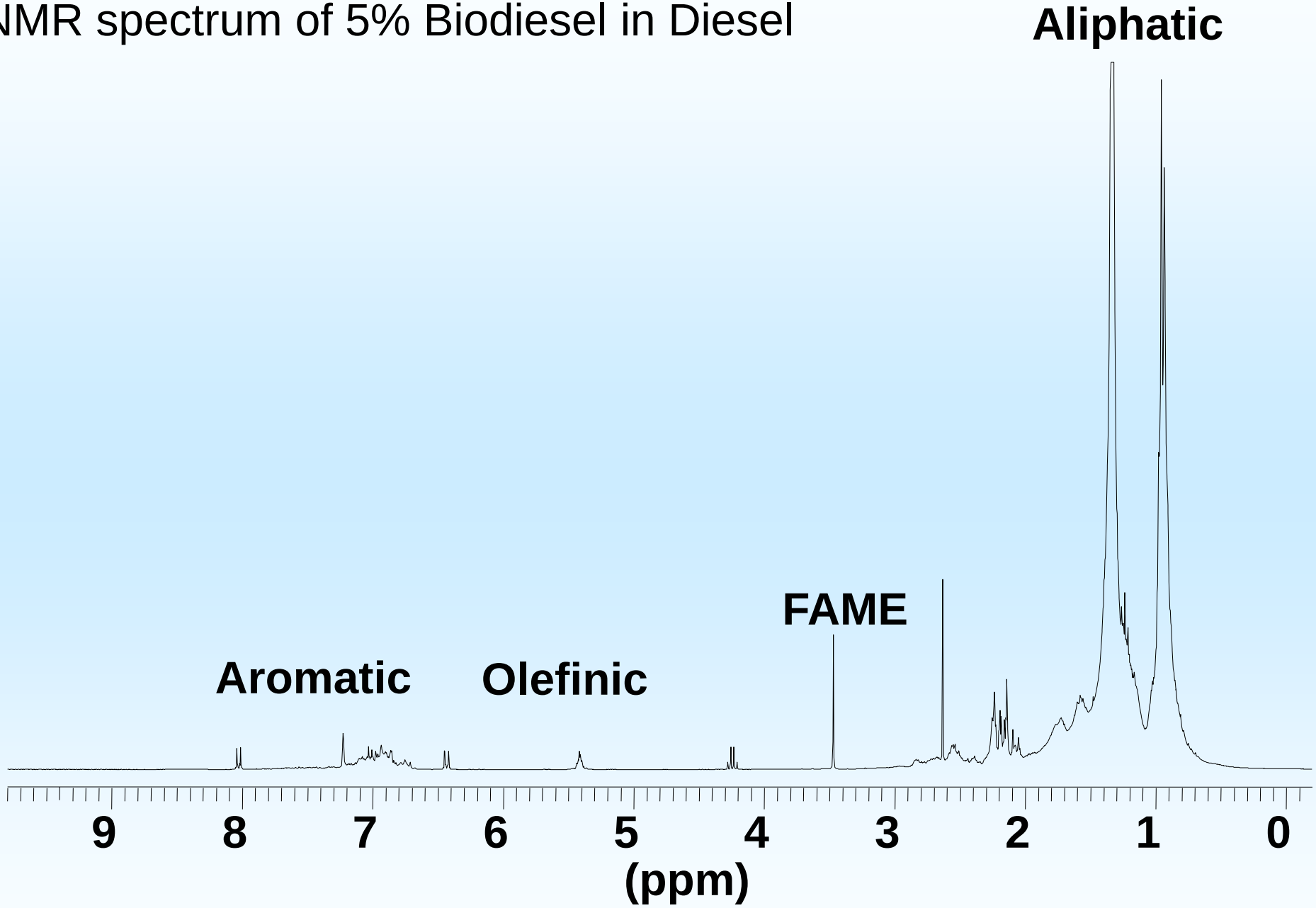
1. Using internal standards NMR spectroscopy is an absolute method.
2. Reproducibility of NMR Analysis
3. Comparison with Gas Chromatography
4. Some additional features

   - analyses of vegetable oil in Diesel

   - analyses of mixtures of Gasoline and Diesel

   - analysis of AdBlue

NMR spectrum of 5% Biodiesel in Diesel



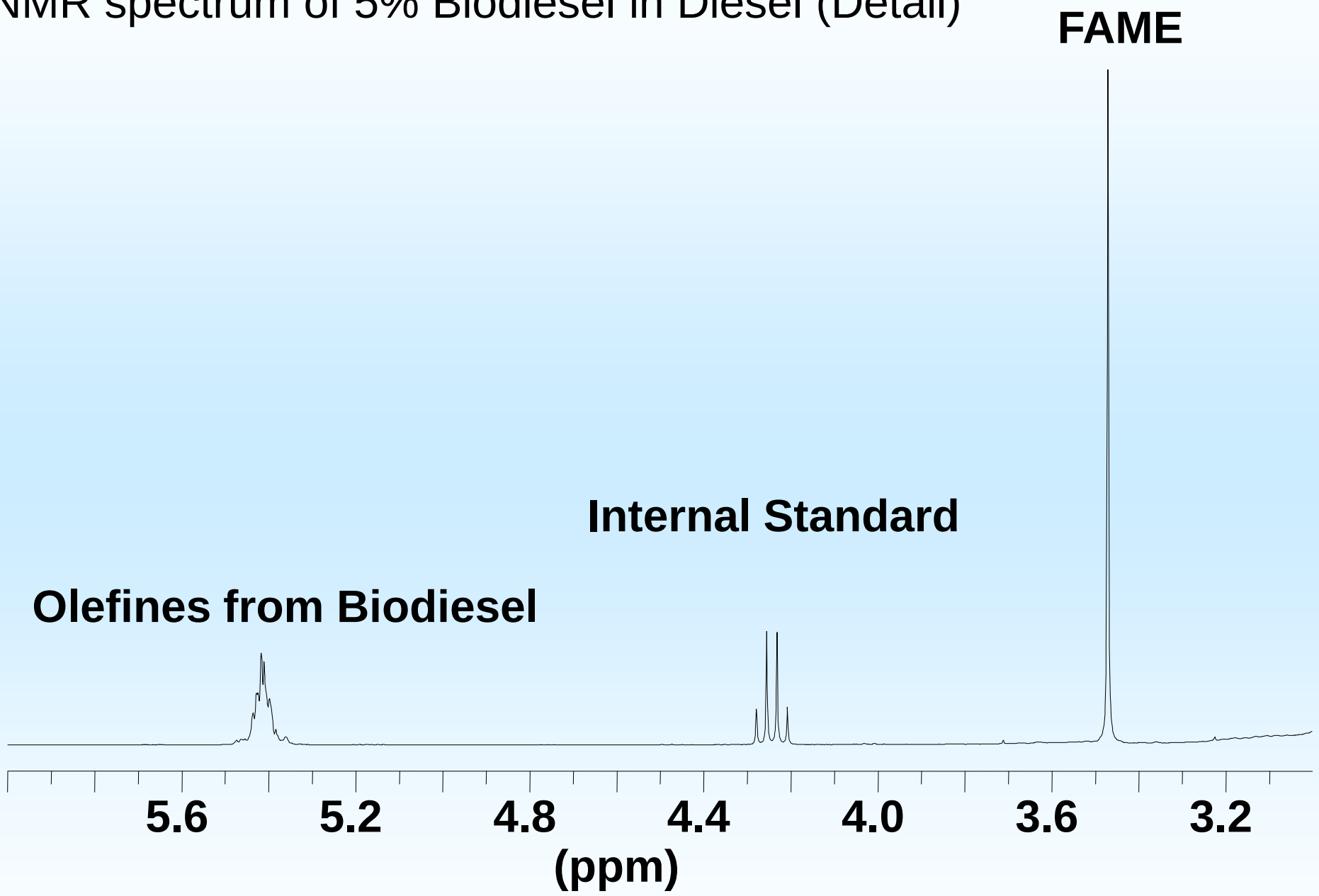
Standard Operation Procedure (SOP)

- 500 mg of test item and 10 mg of internal standard are exactly weighed,
- dissolved in 200µl Benzene-d_6
- measured by ^{1}H-NMR (NS = 16, D1 = 10s)
- overall measuring time approx. 6 min.

The integrated signal of the methoxy group is compared with the internal standard.

The ratio of integrals per atom corresponds to the molar ratio of the compared substances.

NMR spectrum of 5% Biodiesel in Diesel (Detail)



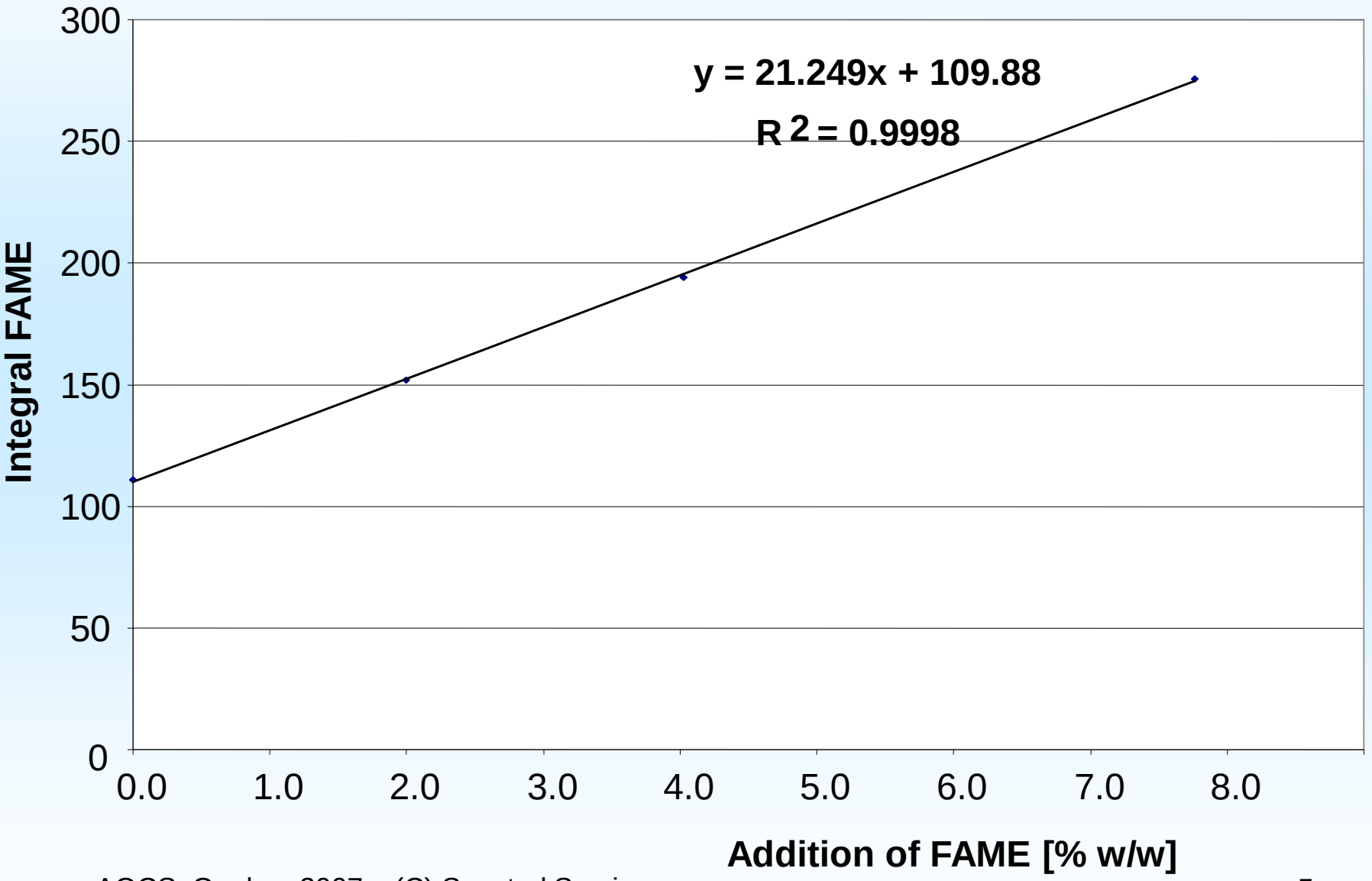
Reproducibility of quantitative ^{1}H-NMR

	Integral	MW	mMol	Content [mg]	NA	Content [%]	Initial weight [mg	
Test 1	370,00	298,51	0,0658	19,64	3	4,82	10,35	407,67
Test 2	485,00	298,51	0,0822	24,55	3	4,88	9,87	502,60
Test 3	452,67	298,51	0,0841	25,12	3	4,97	10,82	505,20
Test 4	477,90	298,51	0,0829	24,75	3	4,98	10,10	496,99
Test 5	453,50	298,51	0,0831	24,79	3	5,00	10,66	495,87
Test 6	487,27	298,51	0,0812	24,24	3	4,88	9,70	496,52
					Average	**4,92**		
					Std. Dev. [%]	**0,07**		

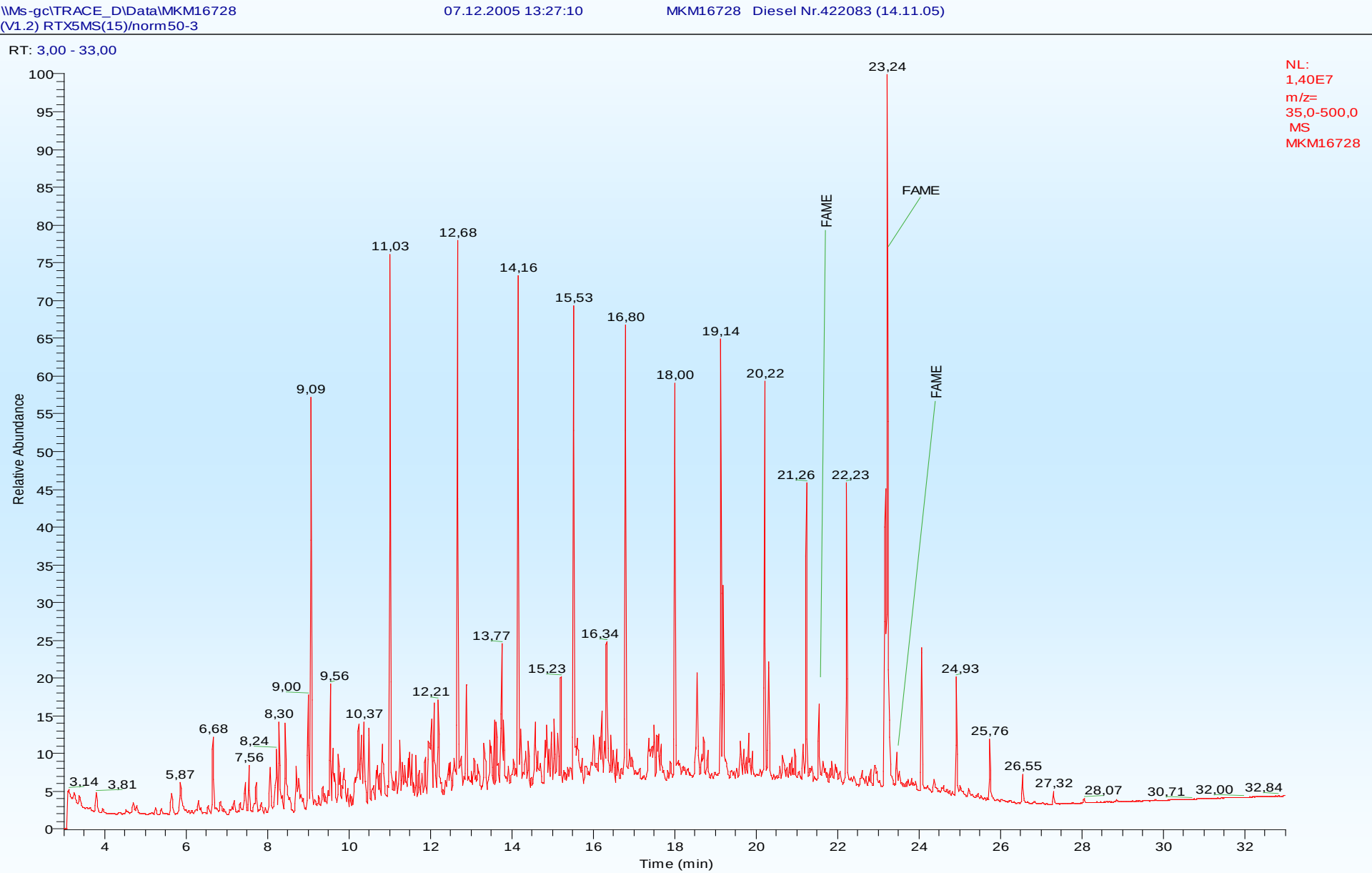
Calculated as methyl stearate using MW 298.51 g/mol.

If the fatty acid composition changes it is easy to recalculate the total amount of FAME using the mean molecular weight taken from other analytical methods.

Standard addition of FAME



GC/MS analysis of bio Diesel (FAME) in Diesel



Standard addition of FAME

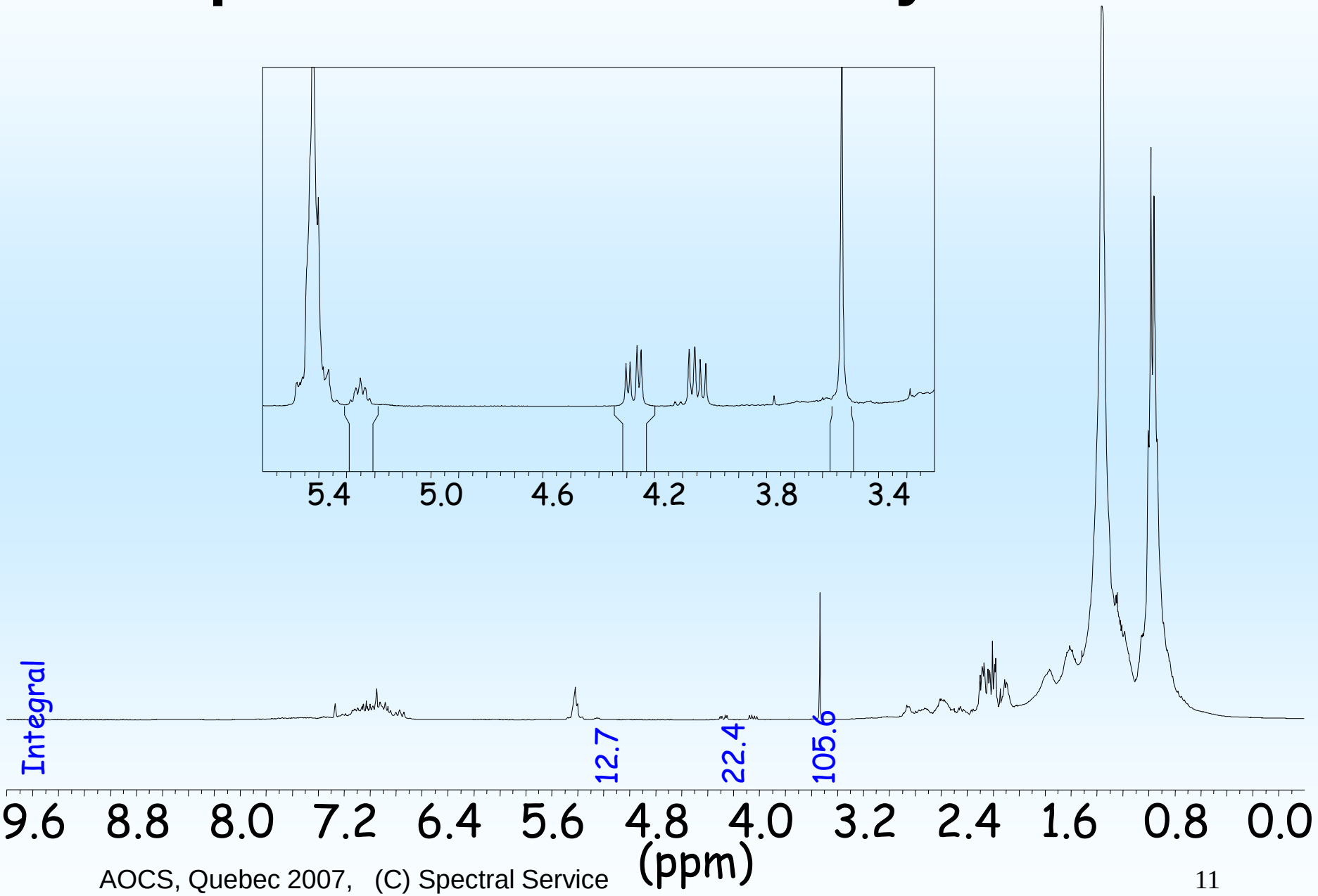
Comparison of ^{1}H-NMR and GC/MS results of identical samples

FAME [%]	NMR Integral	GC Integral	Sample [mg]	FAME [mg]
0,00	110,8	100,0	1054,8	0,0
2,00	152,0	135,6	1054,2	21,1
4,02	194,0	175,1	1001,8	40,3
7,77	275,7	248,3	1051,9	81,7
		NMR	GC/MS	
	gradient	21,25	19,19	
	ordinate	109,88	98,65	
	content	5,17	5,14	
calculated as stearate		**4,94**	**4,91**	

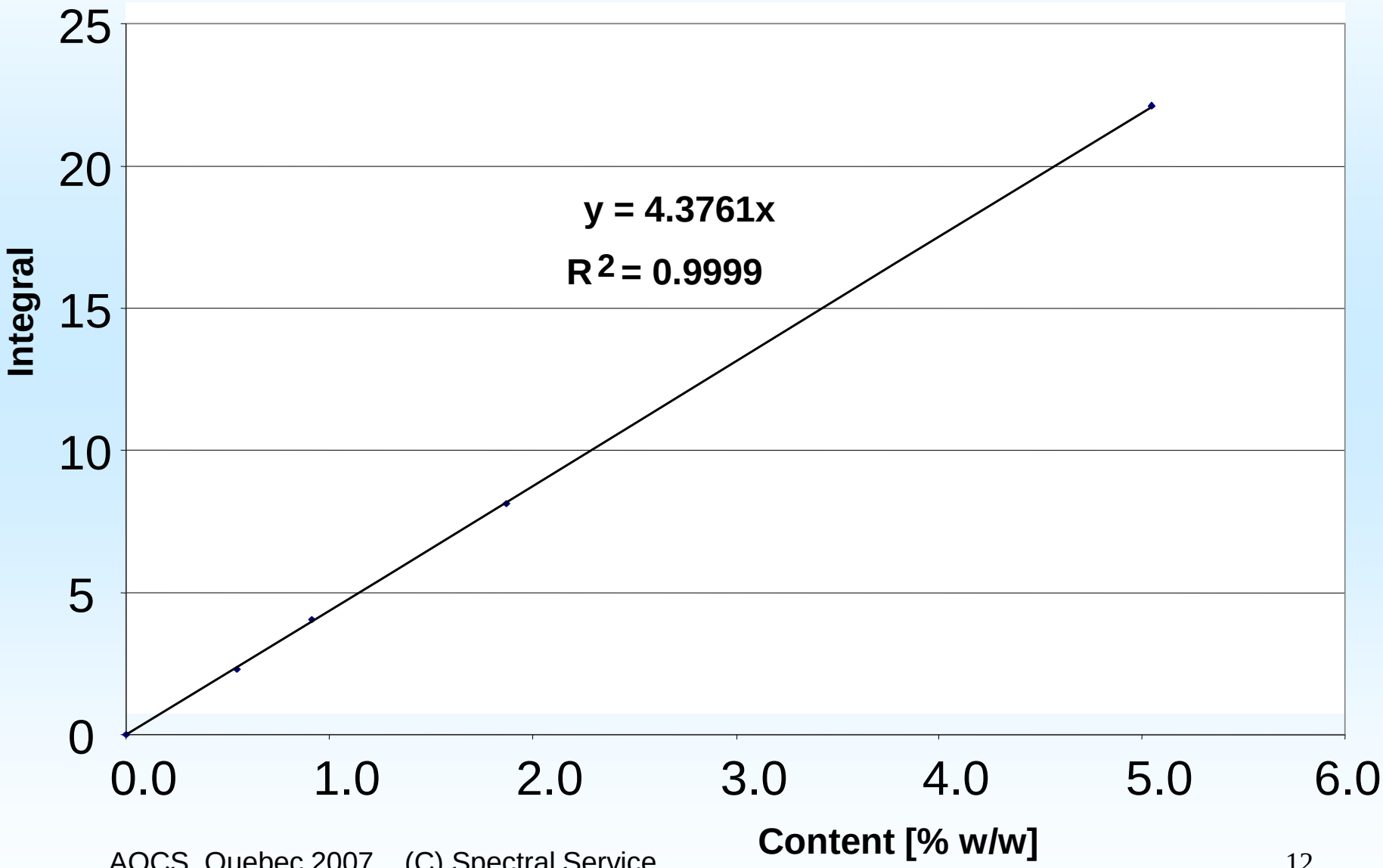
Some additional features

by qNMR

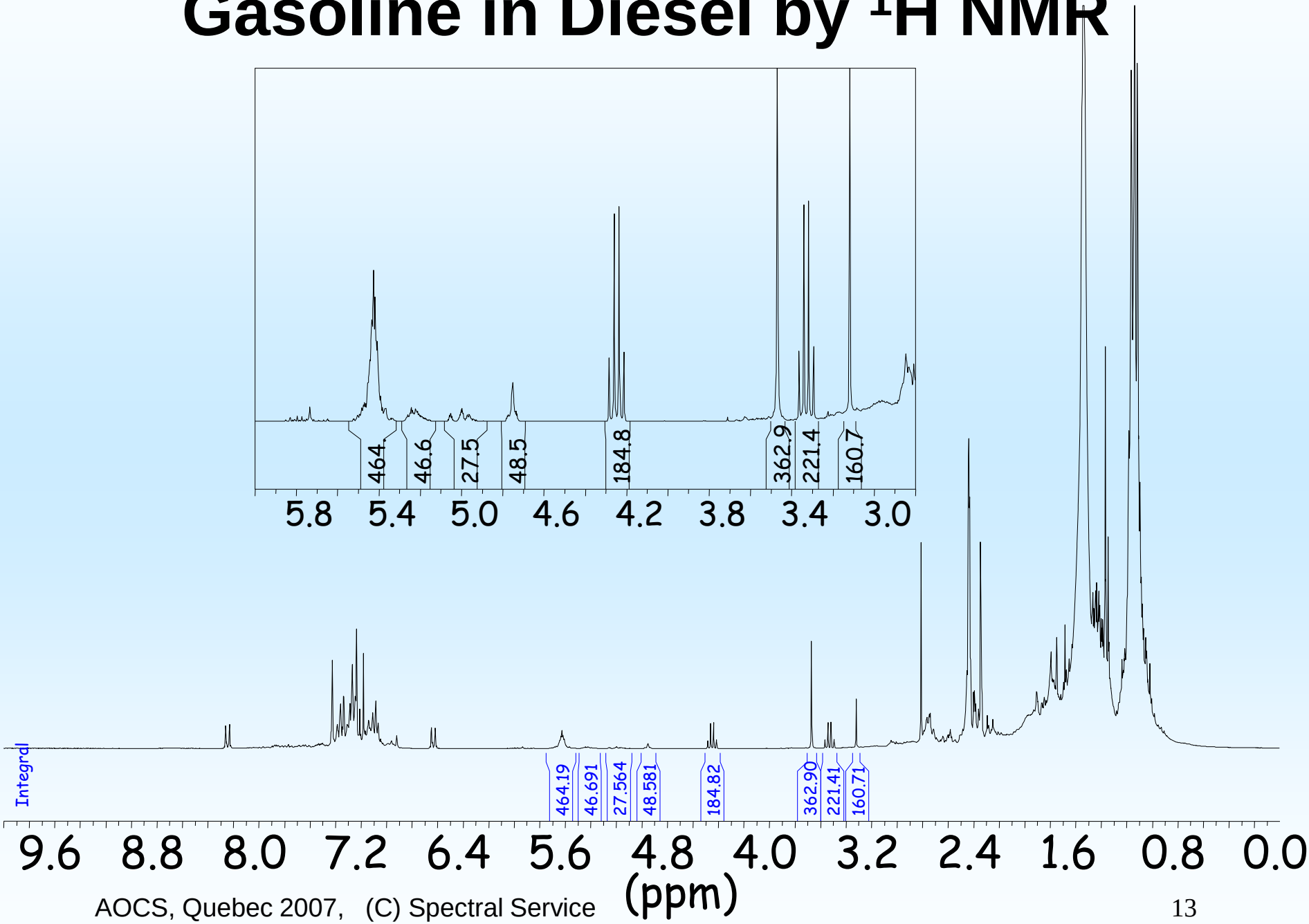
Rapeseed oil in Diesel by ^{1}H NMR



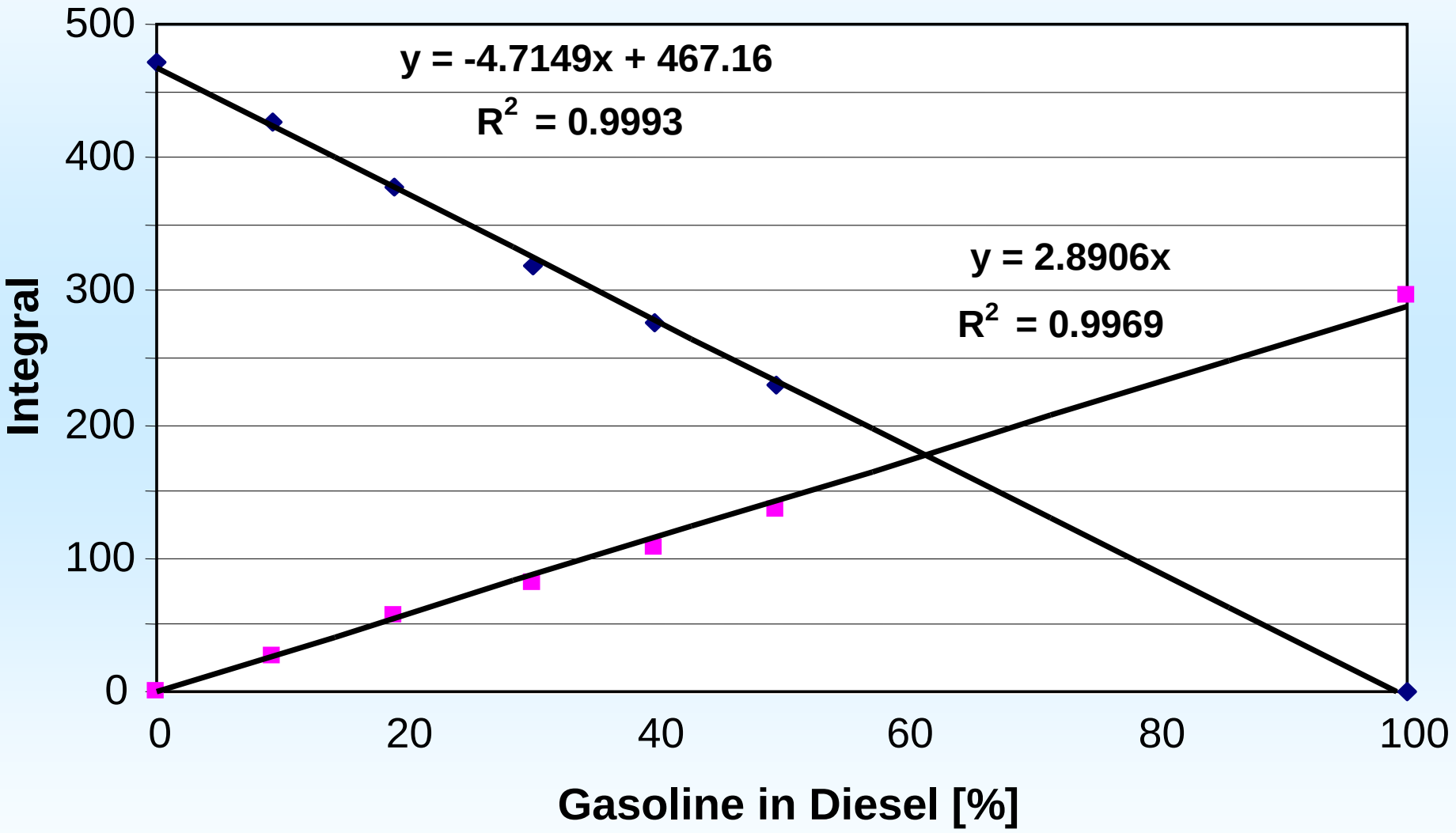
Rapeseed oil in Diesel by ^{1}H NMR



Gasoline in Diesel by ^{1}H NMR



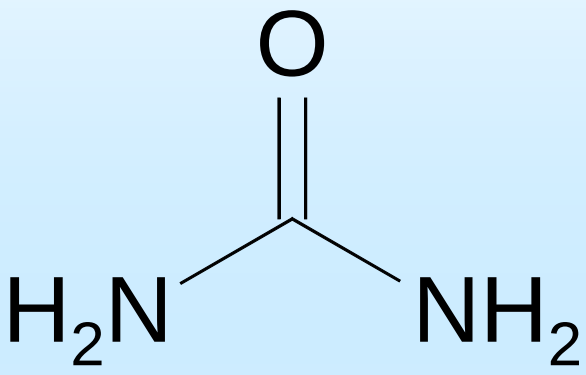
Gasoline in Diesel by ^{1}H NMR



AdBlue by ^{1}H NMR

D1 [sec]	Urea	H2O
1	18,03	81,98
5	18,11	81,90
10	18,06	81,94
20	18,10	81,91
40	17,97	82,03
60	18,06	81,94
Pure	18,11	81,89
Mean	18,06	81,94
STDDEV	0,05	0,05
STDDEV %	0,28	0,06

Urea solution in DMSO-d_6



Initial Weight	**26.9 %**
Analyzed	**26.7 %**

Conclusion

1. Cross validation between ^{1}H-NMR and GC/MS leads to identical results in Biodiesel quantification.

2. However, ^{1}H-NMR is faster, data evaluation is easier, the method is of higher robustness.

3. Analysing the mixing ratio of gasoline and Diesel only ^{1}H-NMR spectroscopy is an useful method.

4. Furthermore, problems in Biodiesel analysis and fuels in general can be solved by NMR.

Thank you for your patience