Analysis of Bio Diesel and Gasoline in Diesel Fuel by NMR Spectroscopy

A quick and robust alternative to gas chromatography

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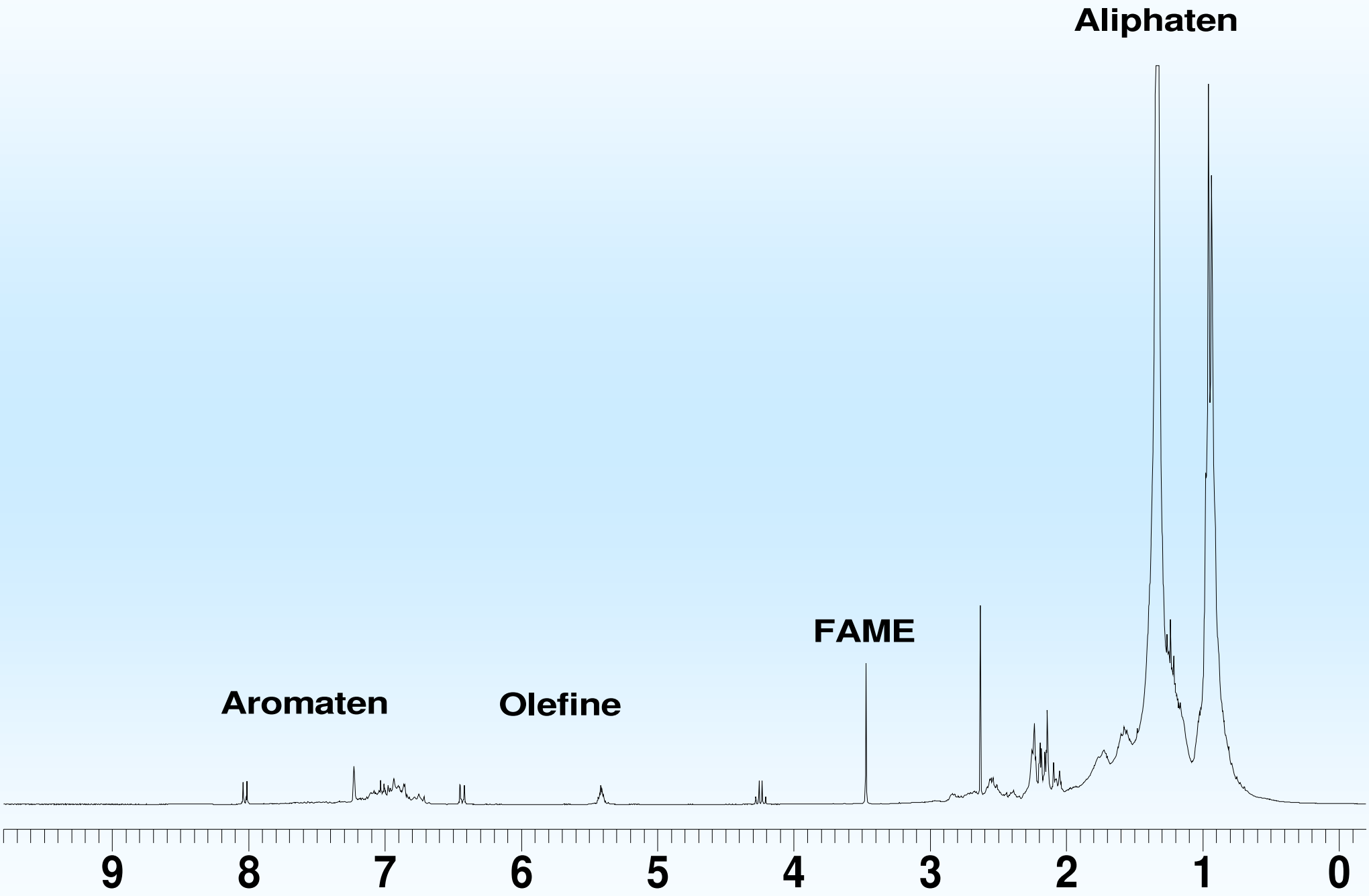
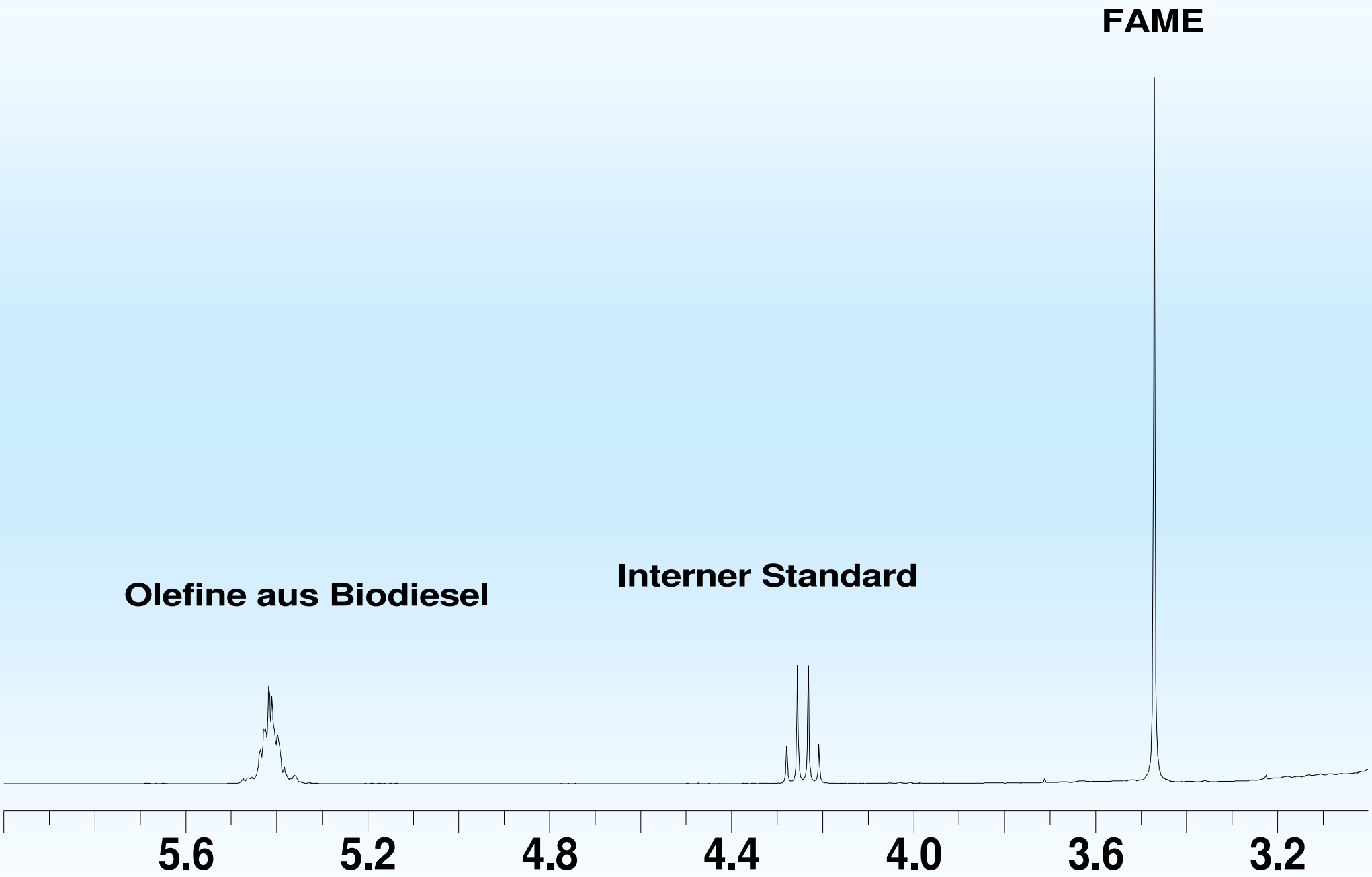
1. Using internal standards NMR spectroscopy is an absolute method.
2. Reproducibility of NMR Analysis
3. Comparison with Gas chromatography
4. Some additional features e.g.

   - analyses of vegetable oil
   - analyses of mixtures of Gasoline and Diesel
   - others by request

NMR spectrum of 5% bio Diesel in Diesel fuel



NMR spectrum of 5% bio Diesel in Diesel fuel (Detail)



Calculation and reproducibility of quantitative ^{1}H-NMR spectroscopy

For quantification 500 mg of test item and 10 mg of internal standard are exactly weighed, dissolved in 200µl Benzene-d_6 and measured. Integrated signals of test items methoxy group and of suitable internal standard group are compared.

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

Equation 1 $$MOL_{IS}\ [mMol] = \frac{IW_{IS}\ [mg] * C_{IS}\ [\%]}{MW_{IS}\ [g/Mol] * 100}$$

Equation 2 $$MOL_{TI}\ [mMol] = \frac{I_{TI} * NA_{IS} * MOL_{IS}\ [mMol]}{I_{IS} * NA_{TI}}$$

Equation 3 $$C_{TI}\ [\%\text{-by weight}] = \frac{MW_{TI}\ [g/Mol] * MOL_{TI}\ [mMol] * 100}{IW_{TI}\ [mg]}$$

	Test item (TI)	Internal Standard (IS)
Molecular weight [g/Mol]	MW_{TI}	MW_{IS}
Initial weight [mg]	IW_{TI}	IW_{IS}
Content [Gew.-%]	G_{TI}	G_{IS}
Mol [mMol]	MOL_{TI}	MOL_{IS}
Integral	I_{TI}	I_{IS}
Number of Atoms*)	NA_{TI}	NA_{IS}

*) atom refers to NMR active nucleus measured (e.g. 1H, 13C, 19F, 31P)

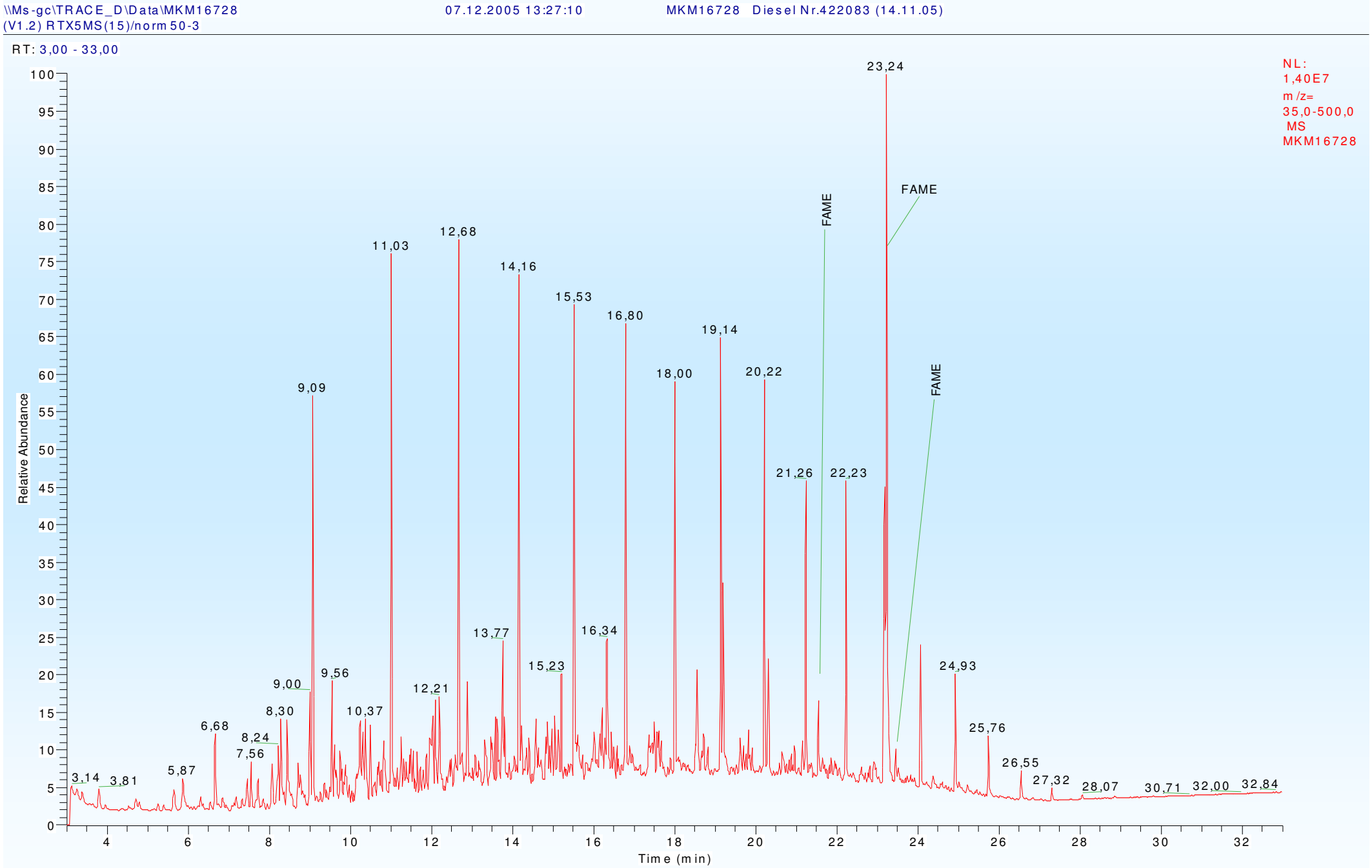
Reproducibility of FAME calculation by quantitative ^{1}H-NMR spectroscopy

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

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

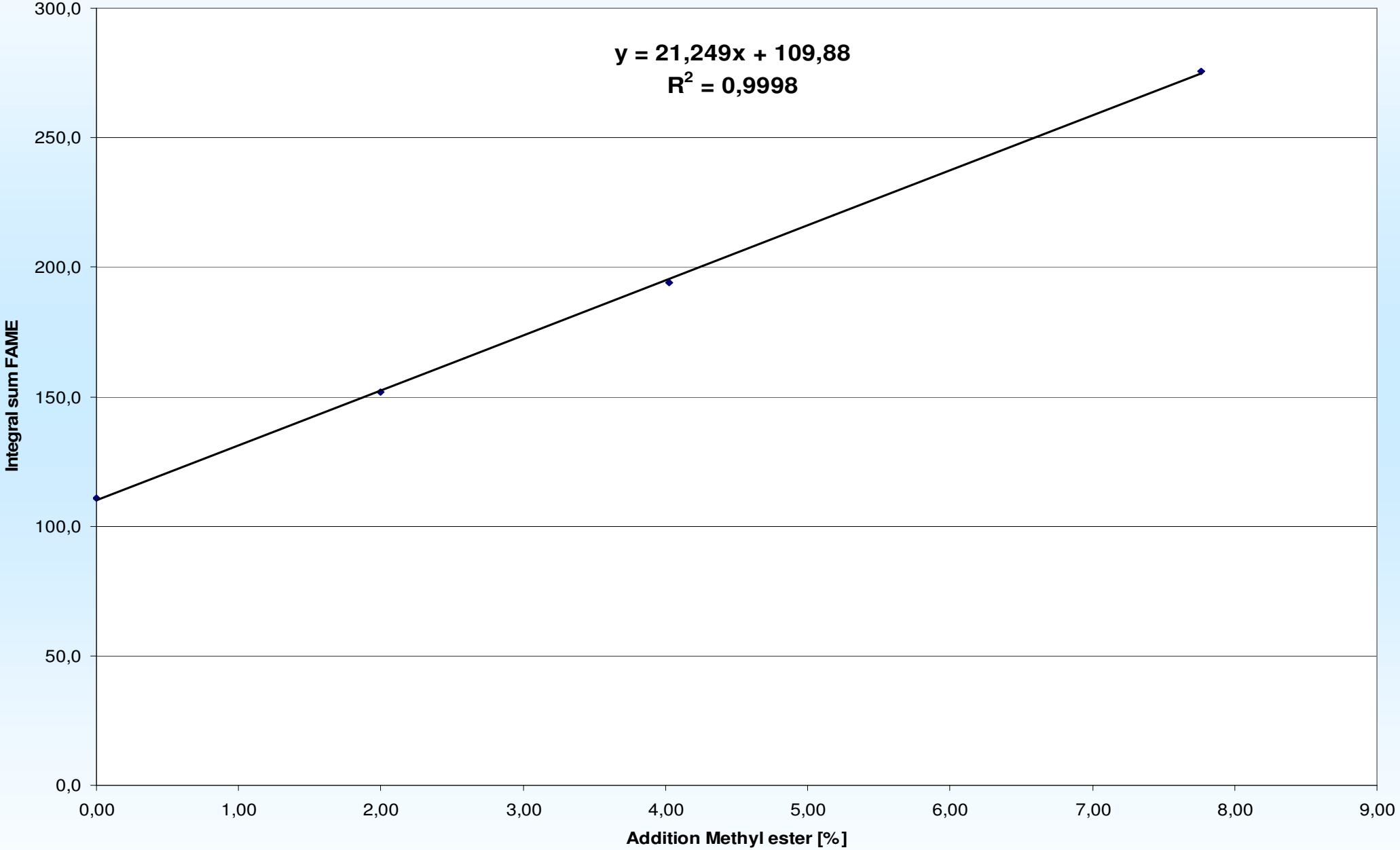


Standard addition as a tool for testing linearity and content of FAME

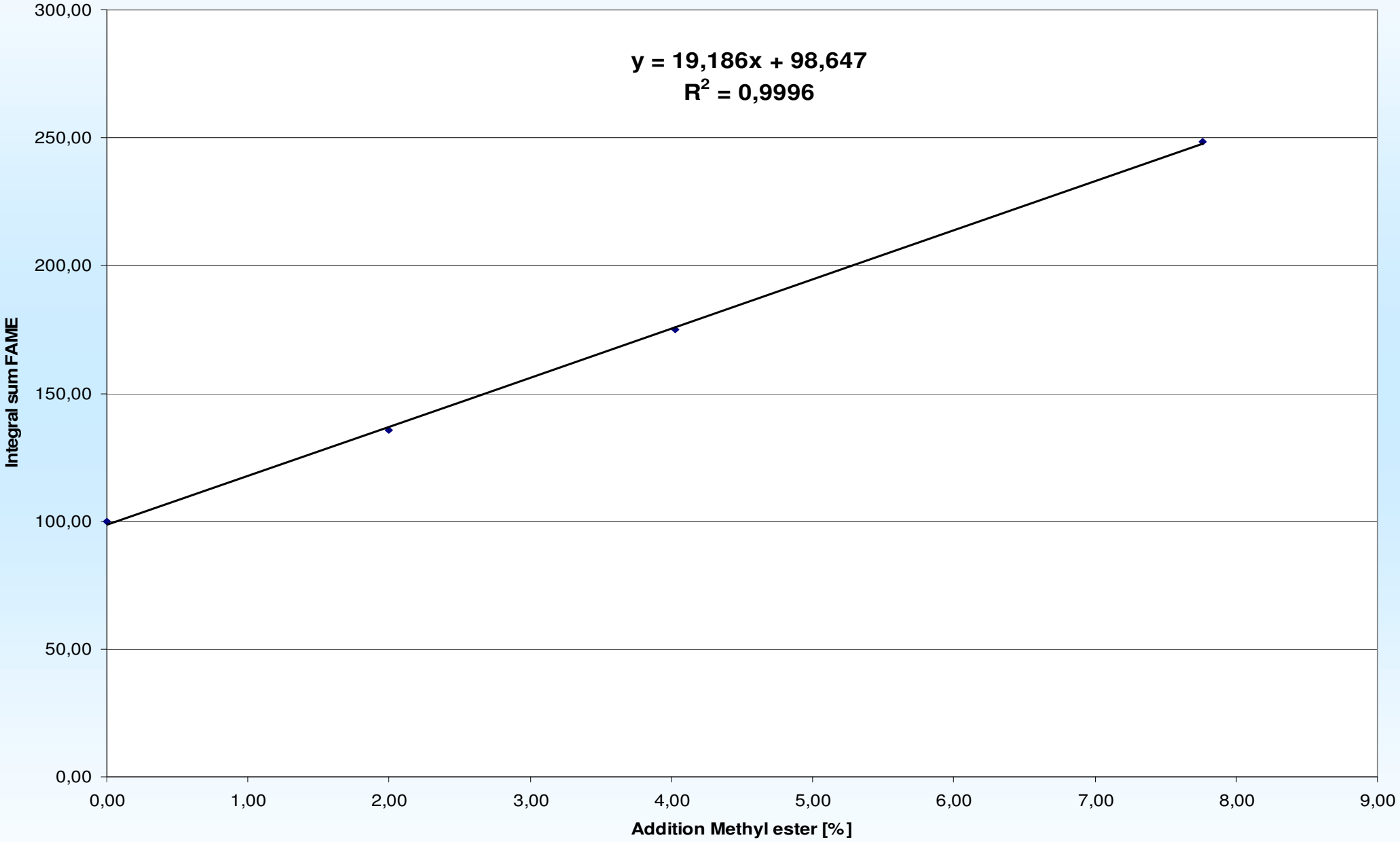
Comparison of analytical results by ^{1}H-NMR and GC/MS of identical samples

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	

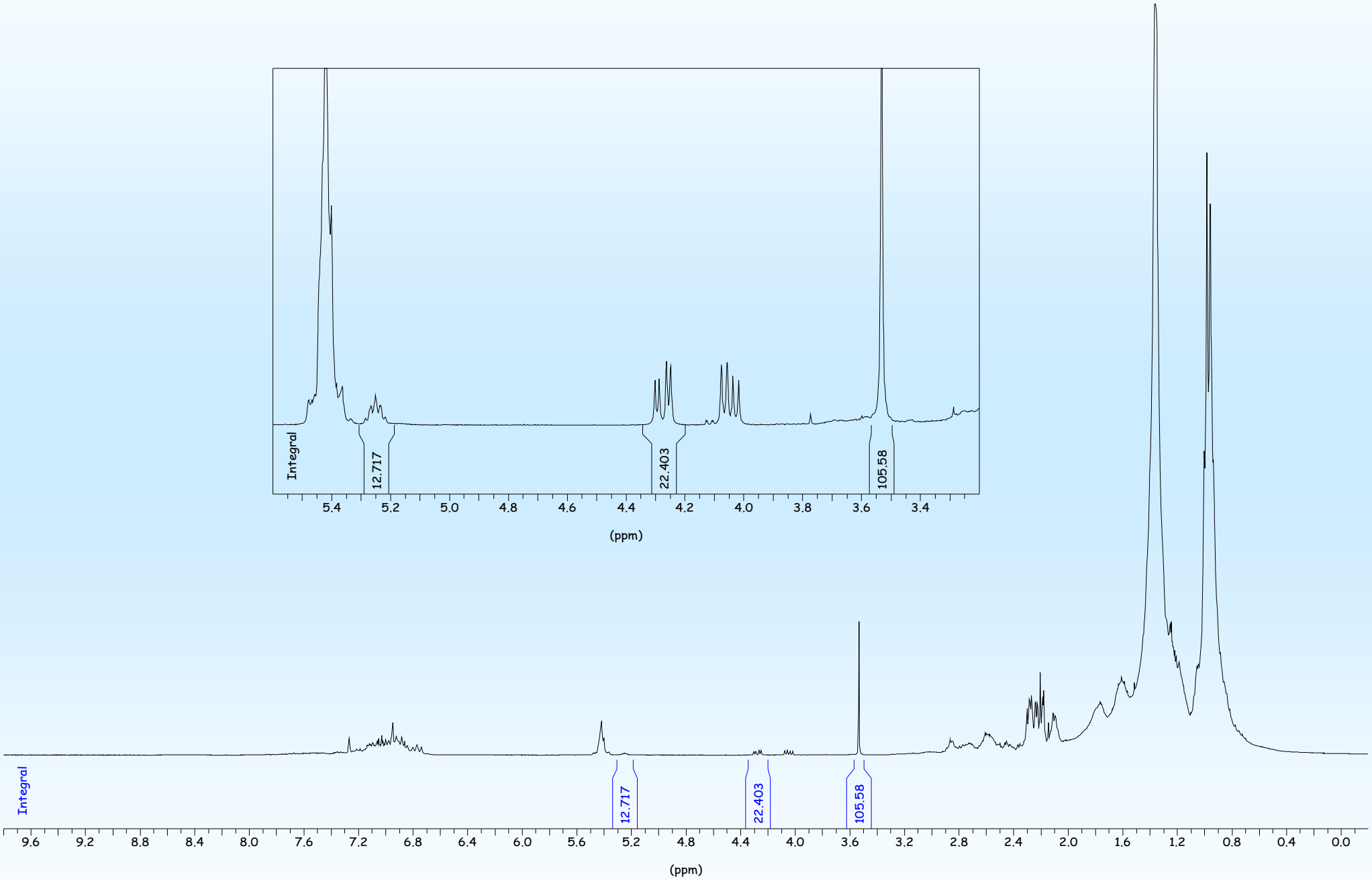
Standard addition as a tool for testing linearity and content of FAME by NMR



Standard addition as a tool for testing linearity and content of FAME by GC/MS



Analysis of rapeseed oil in Diesel by ^{1}H NMR



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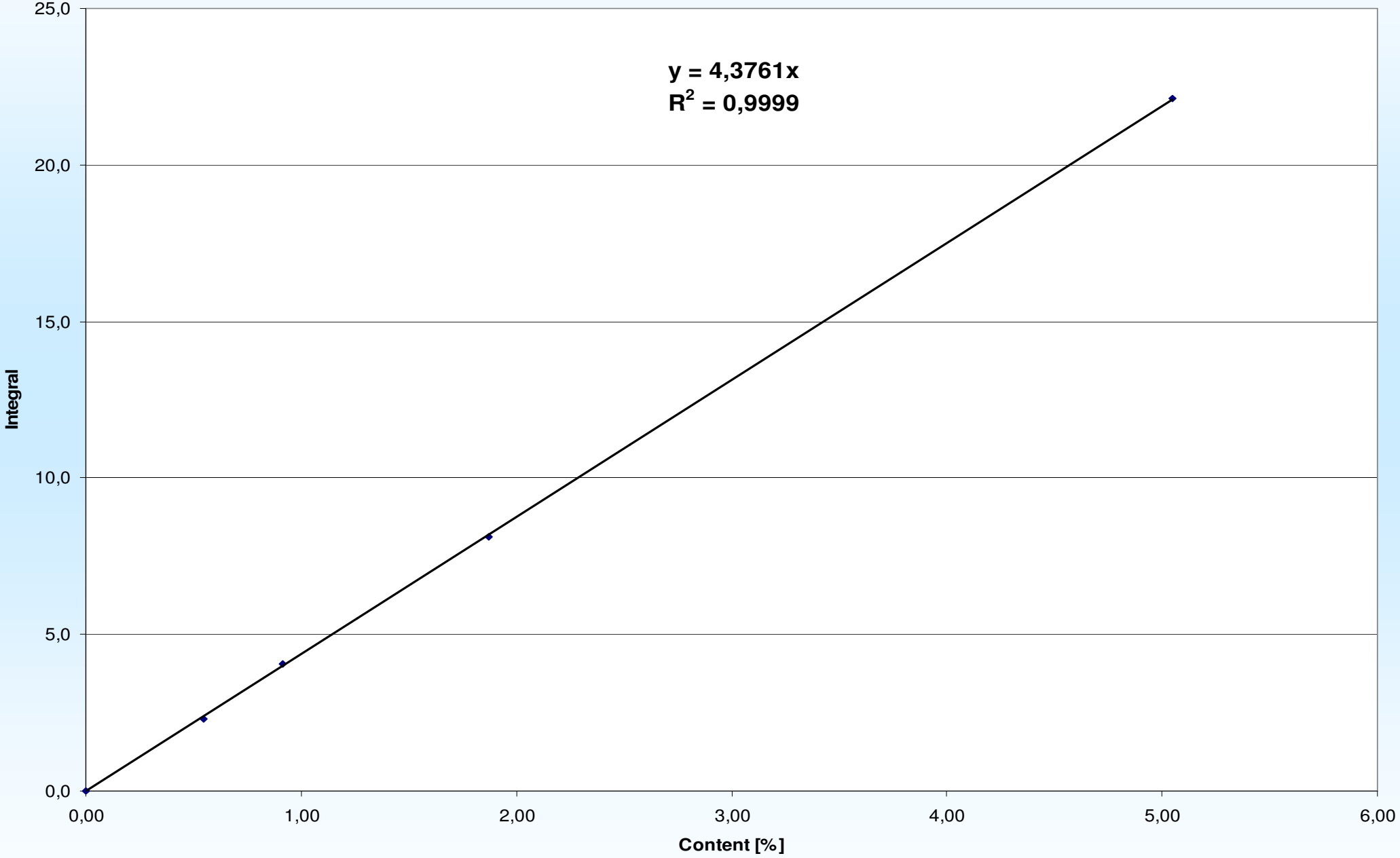
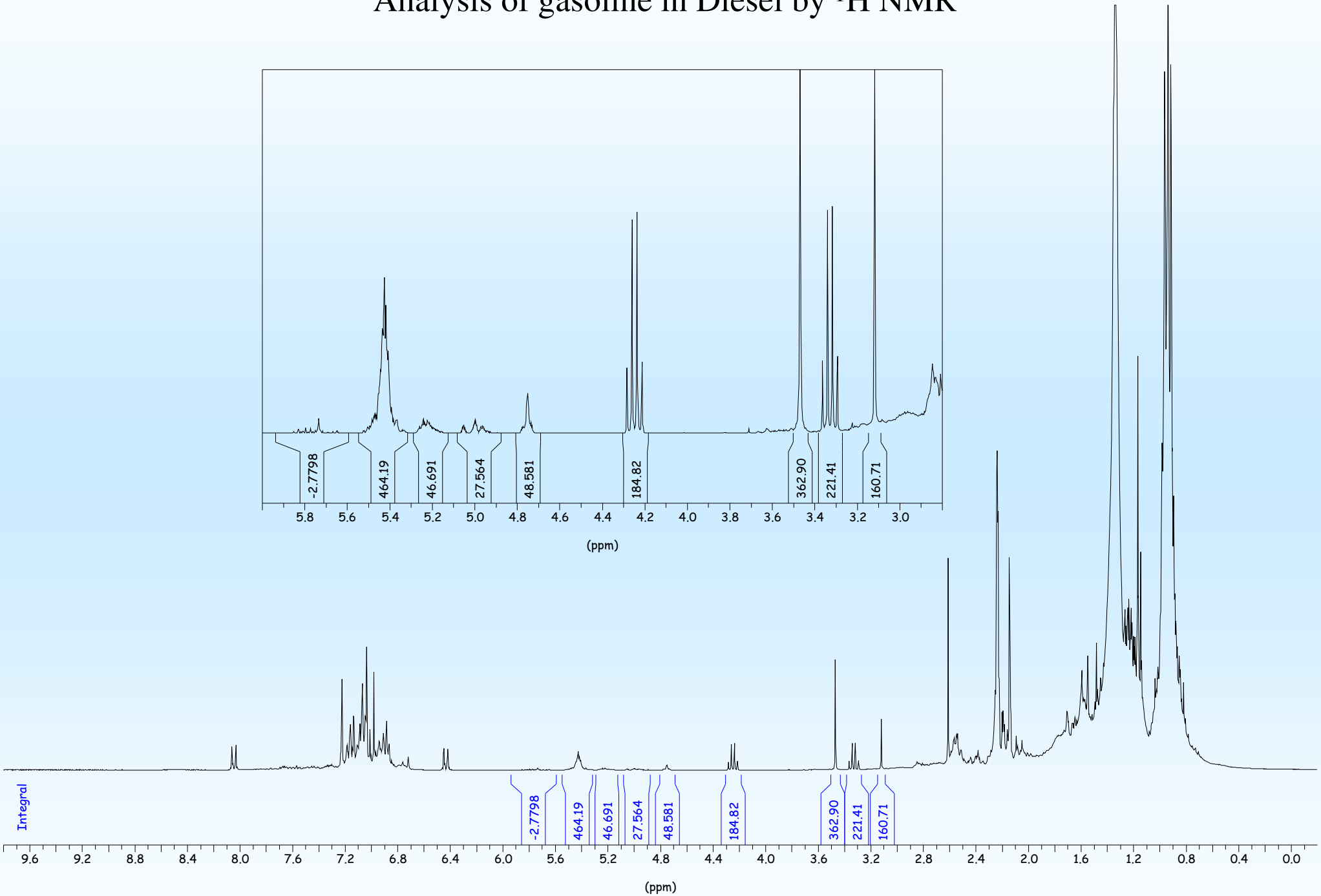
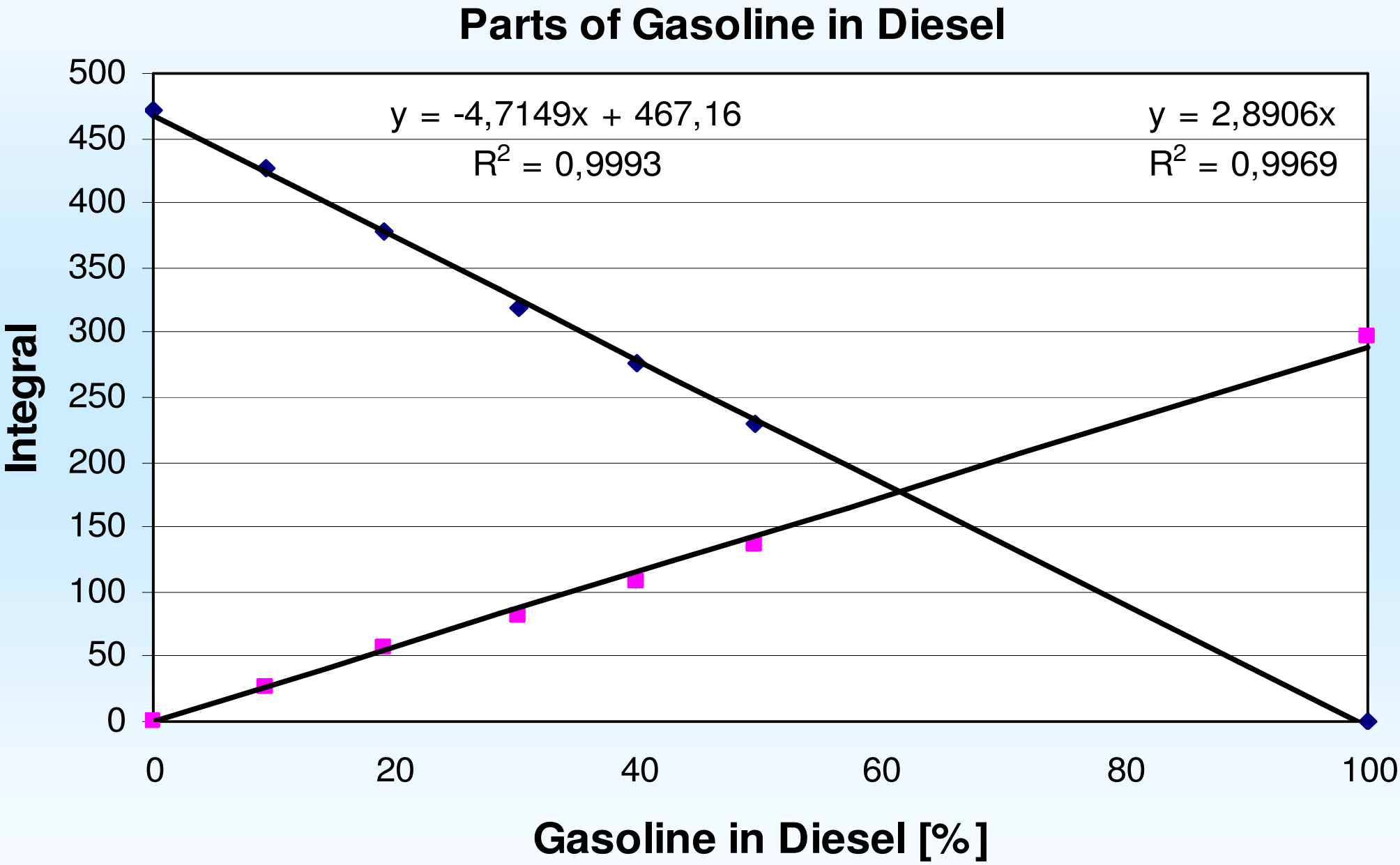


Analysis of gasoline in Diesel by ^{1}H NMR




Parts of Gasoline in Diesel
y = -4,7149x + 467,16
R2 = 0,9993
y = 2,8906x
R2 = 0,9969
Integral
500
450
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
Gasoline in Diesel [%]

Conclusion

It is shown that the results of bio Diesel calculation as a sum parameter by FAME (Fatty Acid Methyl Ester) as in Diesel fuel is identical for ^{1}H-NMR and GC/MS. In comparison the data evaluation of NMR spectra is easier, the method has a higher robustness.

The same results can be observed for analysis of low boiling additives like tert.-butyl ethyl ether, ethanol und MTBE in gasoline of different ROZ.

In many cases e.g. the analysis of the mixing ratio of gasoline and Diesel fuel only ^{1}H-NMR spectroscopy is a useful method.

NMR safes time. One run of a ^{1}H-NMR spectrum needs approx. 5 minutes. Gas chromatography analysis of the same sample needs 45 minutes.

Test may show that other problems in analysis of bio Diesel and related complex mixtures can be dissolved by NMR.

Literature

1 **U. Holzgrabe, I. Wawer, B. Diehl,** NMR Spectroscopy in Drug Development and Analysis, Viley-VCH, **(1999)**, ISBN 3-527-30092-9.

2 **Diehl, B.W.K**., in „LIPID ANALYSIS in OILS and FATS, edited by Prof. R.J. Hamilton, Blackie Academic& Professional, London“, “London“, (**1997**), 87-135, ISBN 0-751-40414-4.

3 **H. Janke, F. Malz**, Qualitätsanforderungen an die quantitative NMR-Spektroskopie, GIT Labor-Fachzeitschrift 5/2004, 492 - 493.