

Biofuel

The Need for Hyphenation and the Possibility of a Green Solution for a Green Fuel

Dr John Langley (UoS) & Tom Lynch (BP)
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gjl@soton.ac.uk

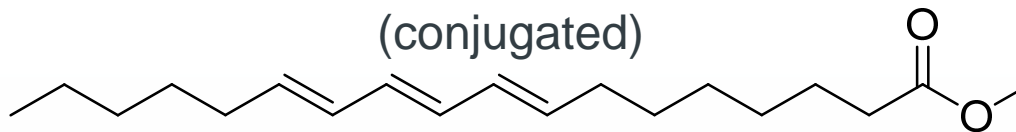
Outline

- Background
- Need for Hyphenated approaches
- Results and discussion
- Conclusions
- Acknowledgements

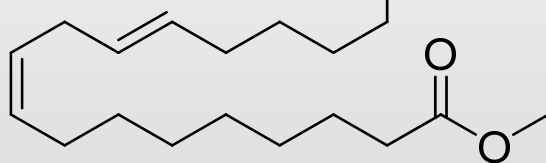
Biodiesel (G1) = FAMES

Varying chain length, saturated and unsaturated, fatty acid methyl esters

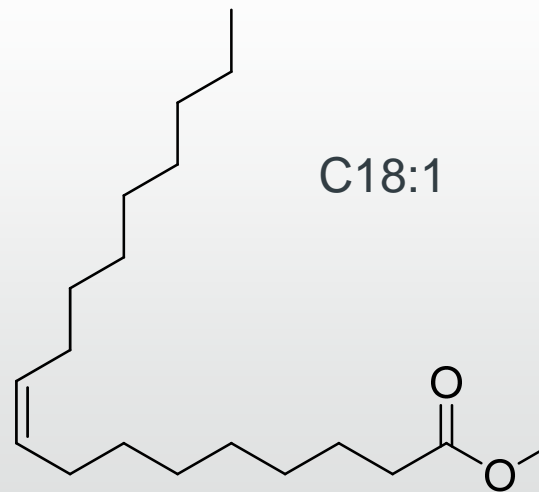
C18:3
(conjugated)



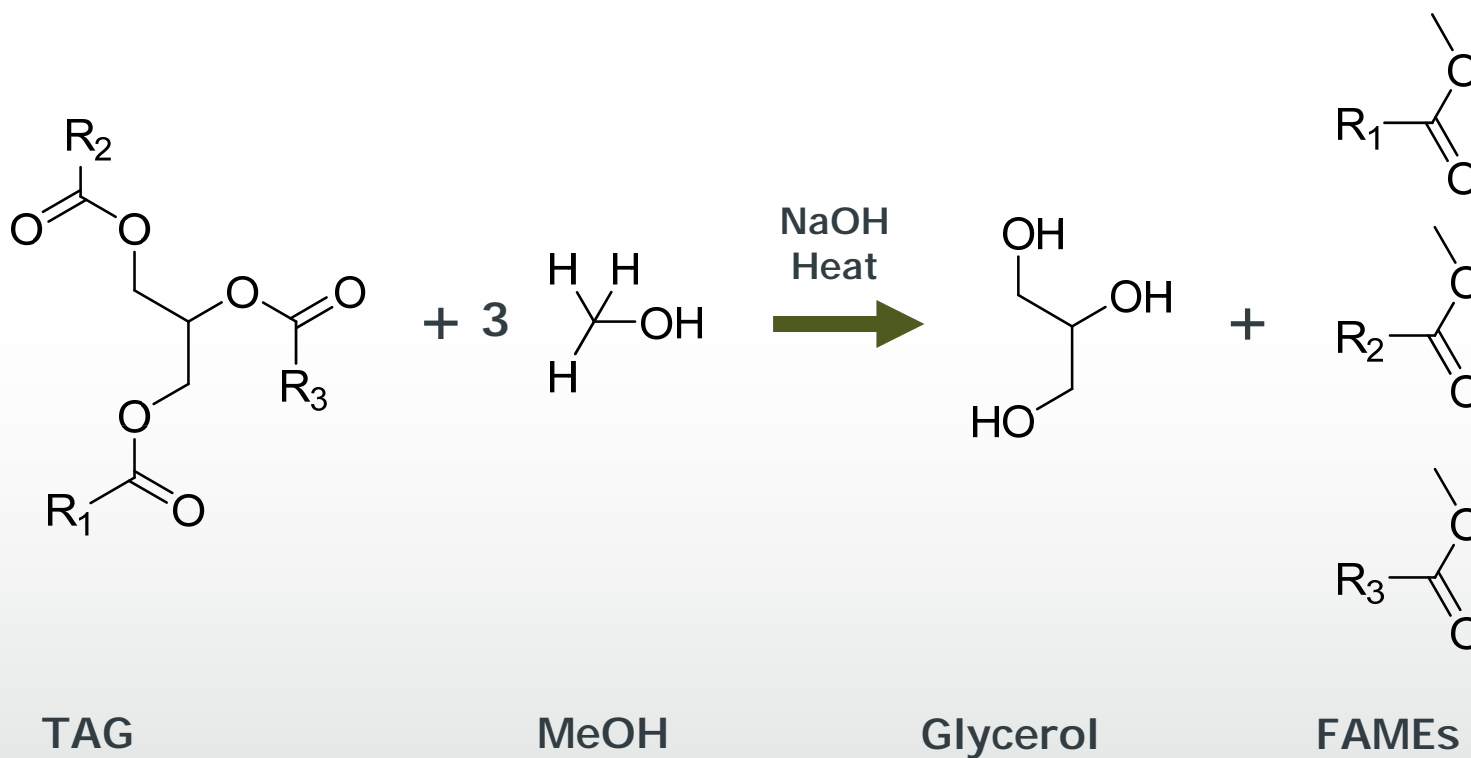
C18:2
(methylene interrupted)



C18:1



How do we make Biodiesel?



Sources of Biodiesel

Vegetable oils

Soybean

Rapeseed

Canola

Safflower

Sunflower

Yellow Mustard

Palm

Jatropha

Animal Fats

Lard

Tallow

Poultry Fat

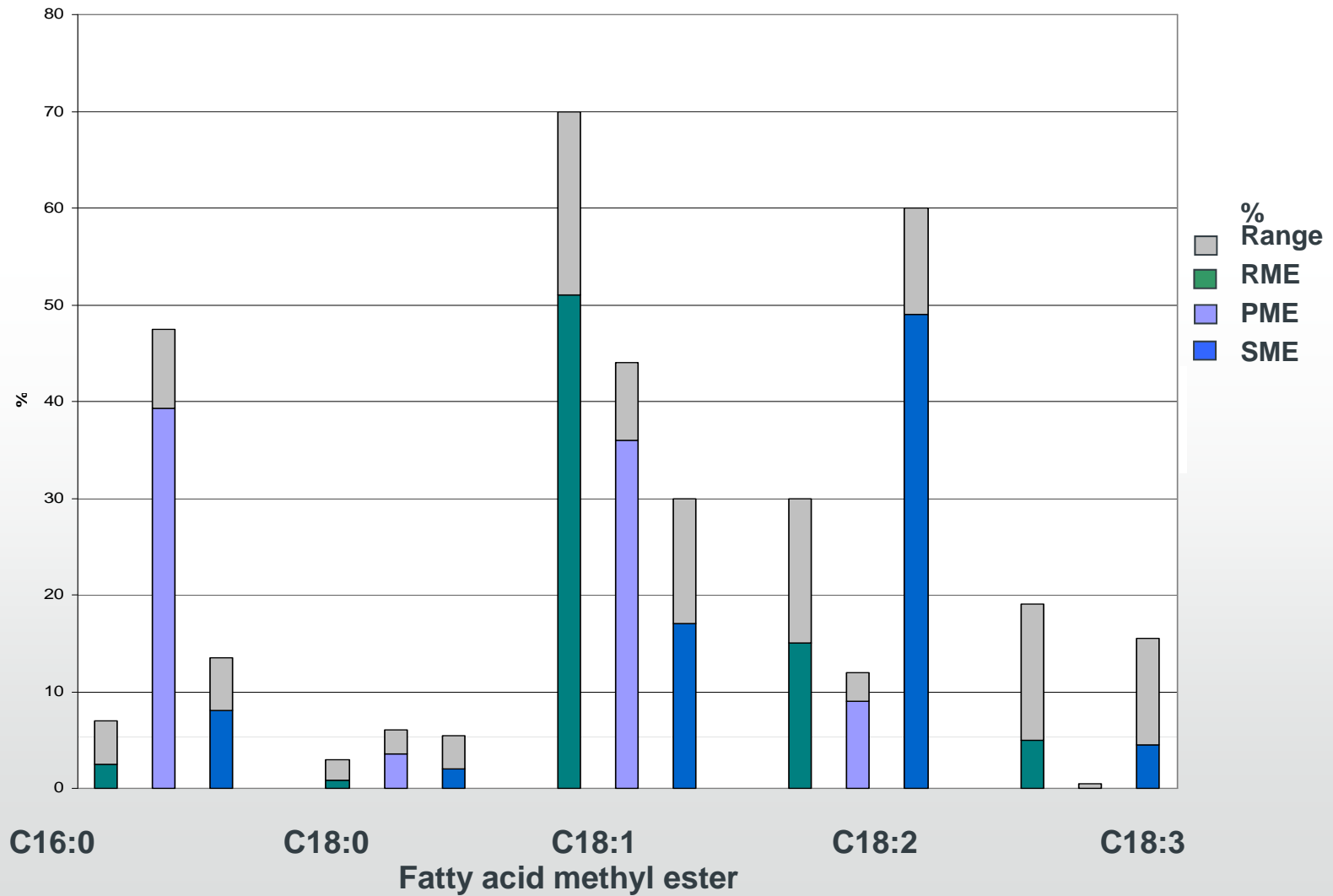
Other Sources

Recycled Cooking Oil

UFO

Plus many more...

Natural Variation



The Challenge

- Complex mixtures & matrices
- Sensitivity
- Speed
- Chemistries and changes in chemistries must drive the analytical approach
 - *e.g.* volatiles and involatiles

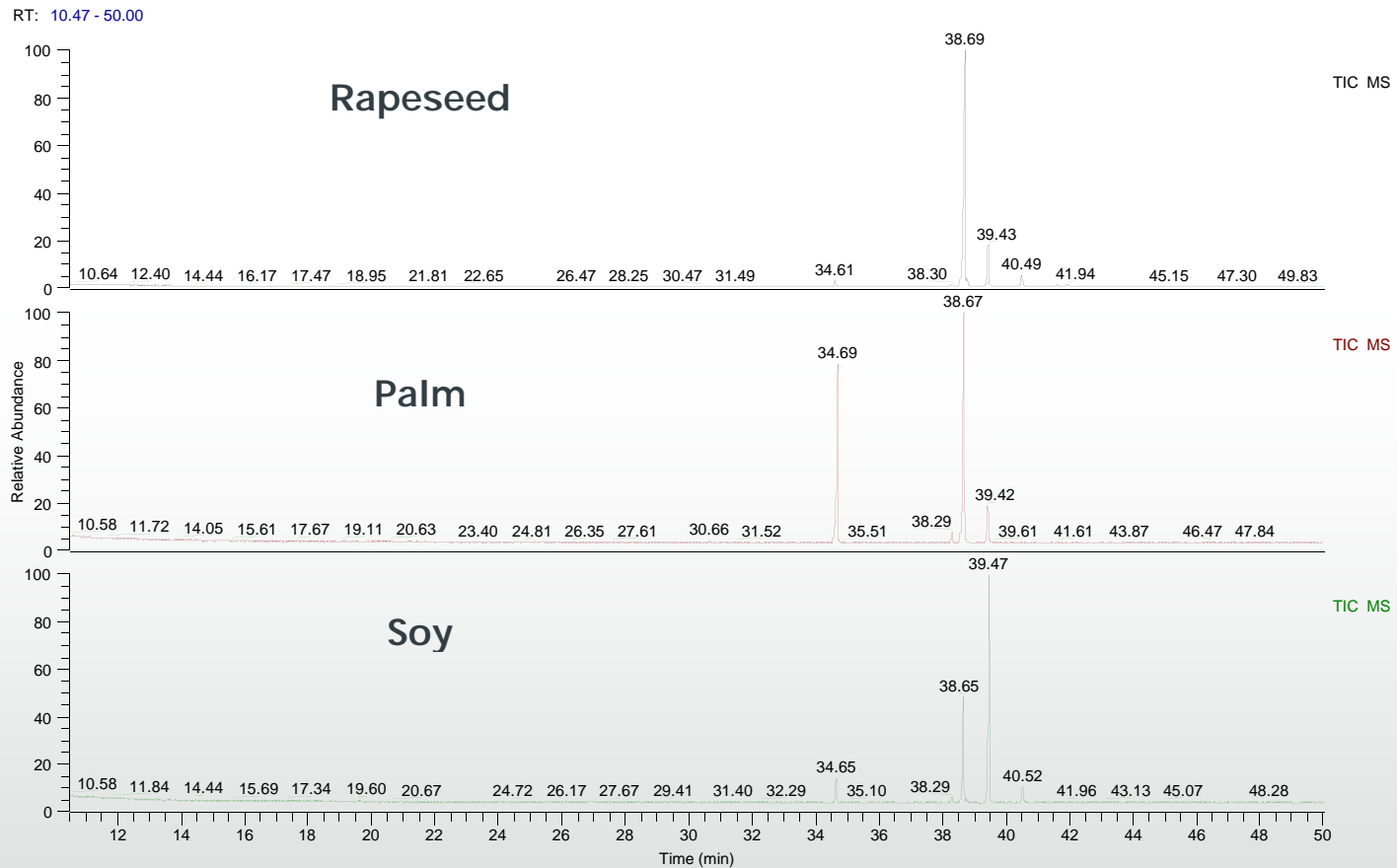
Typification of Biodiesel (I)

- FAME purity
 - no free acids *etc.*
- FAME source/origin
 - green, ethics, \$\$\$, *etc.*
- AVTUR (aviation fuel) must be B0
 - B0 defined as < 5 ppm biodiesel
- Legislation driven levels or renewable fuel source
 - diesel presently B5 UK, B7 Germany

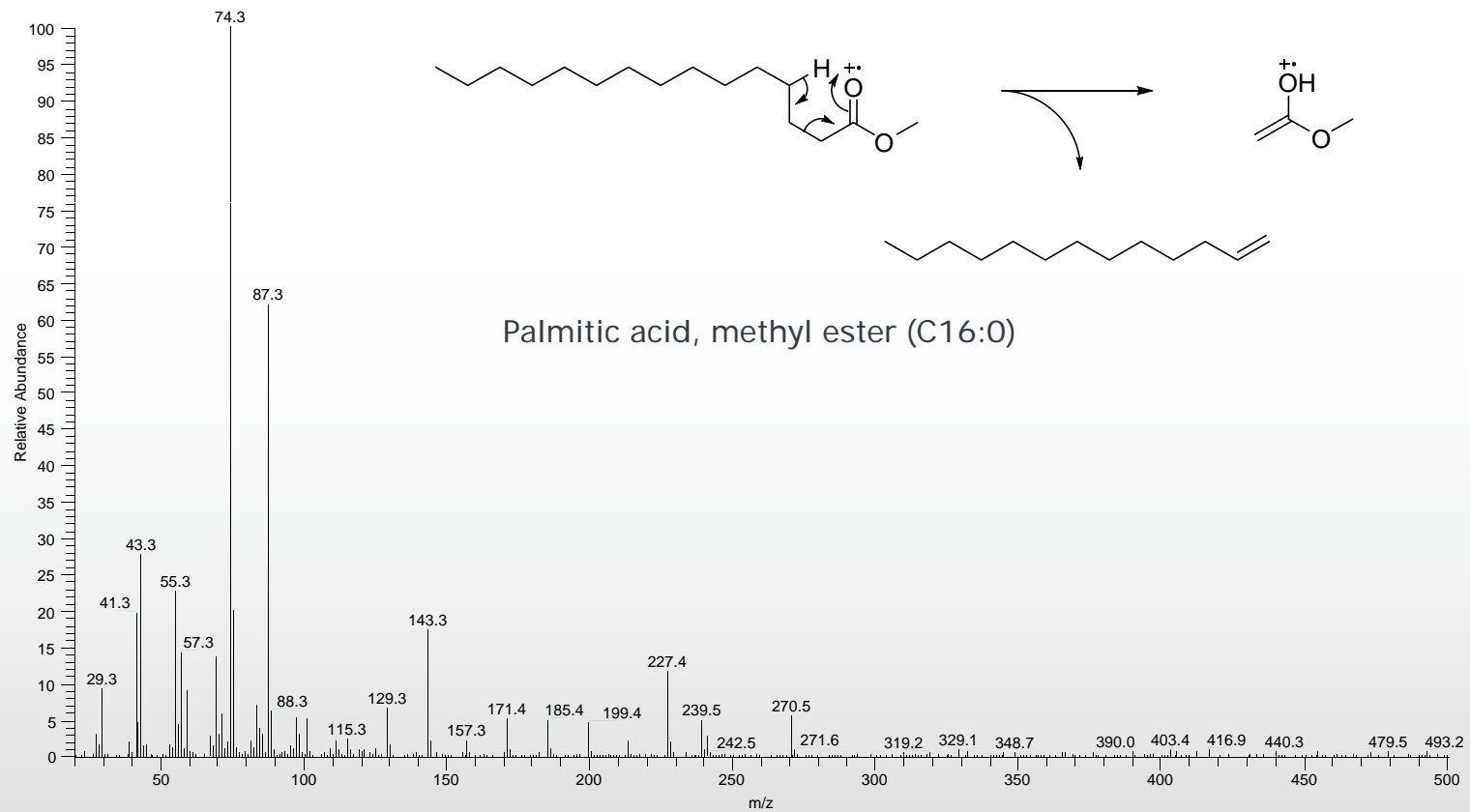
Typification of Biodiesel (II)

- 'Pure' FAME – one source ?
- FAME blends
- FAME storage
 - oxidation*, polymerisation, other....
- Biodiesel in complex matrices
 - biodiesel/petrodiesel
 - Biodiesel/lubricants (crankcase)
 - Biodiesel/AVTUR

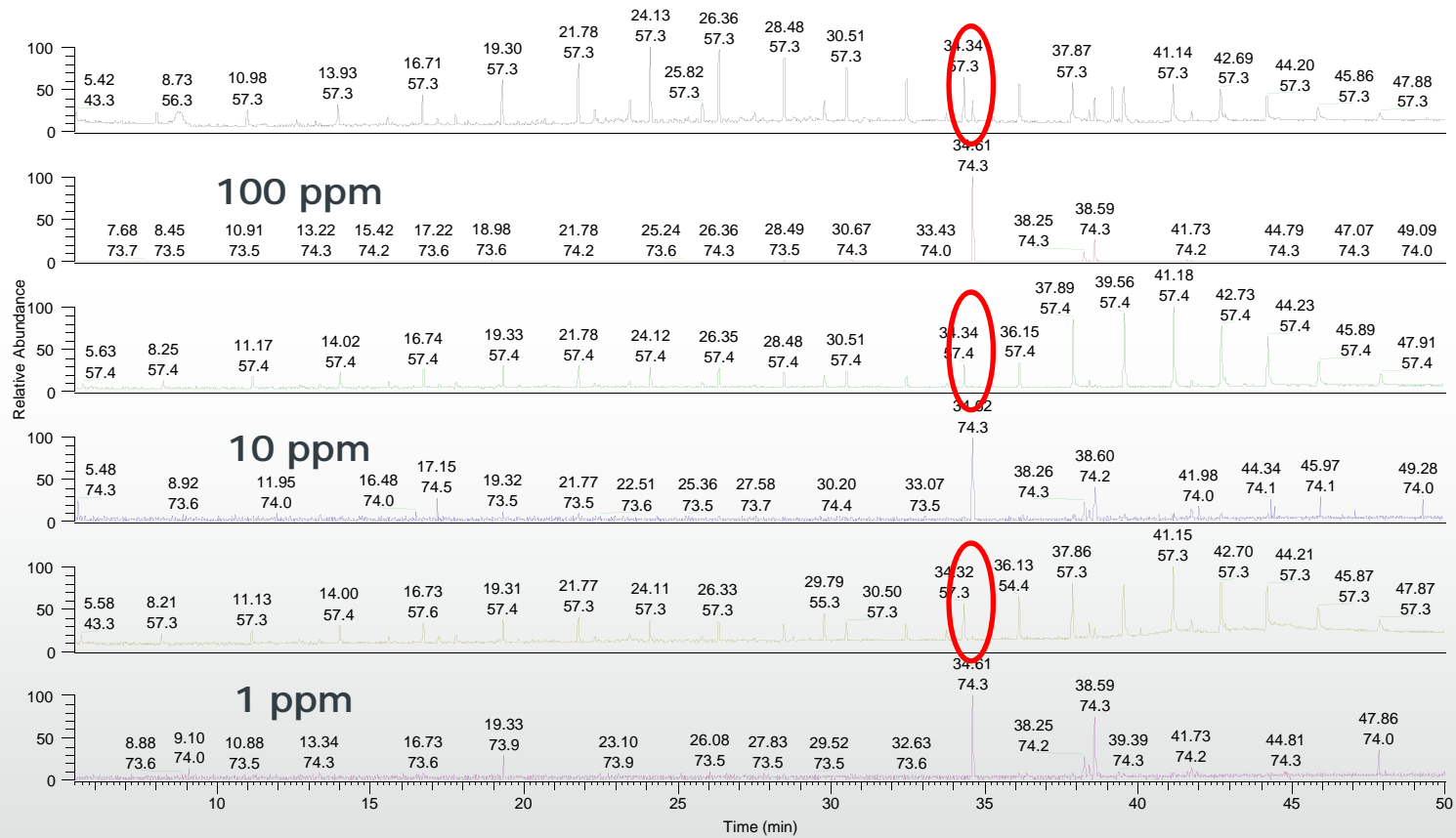
GC-MS of Different FAMES



EI-MS of a FAME



Diesel/Biodiesel



Standard EI (Energy Institute) method 2010. Lynch.

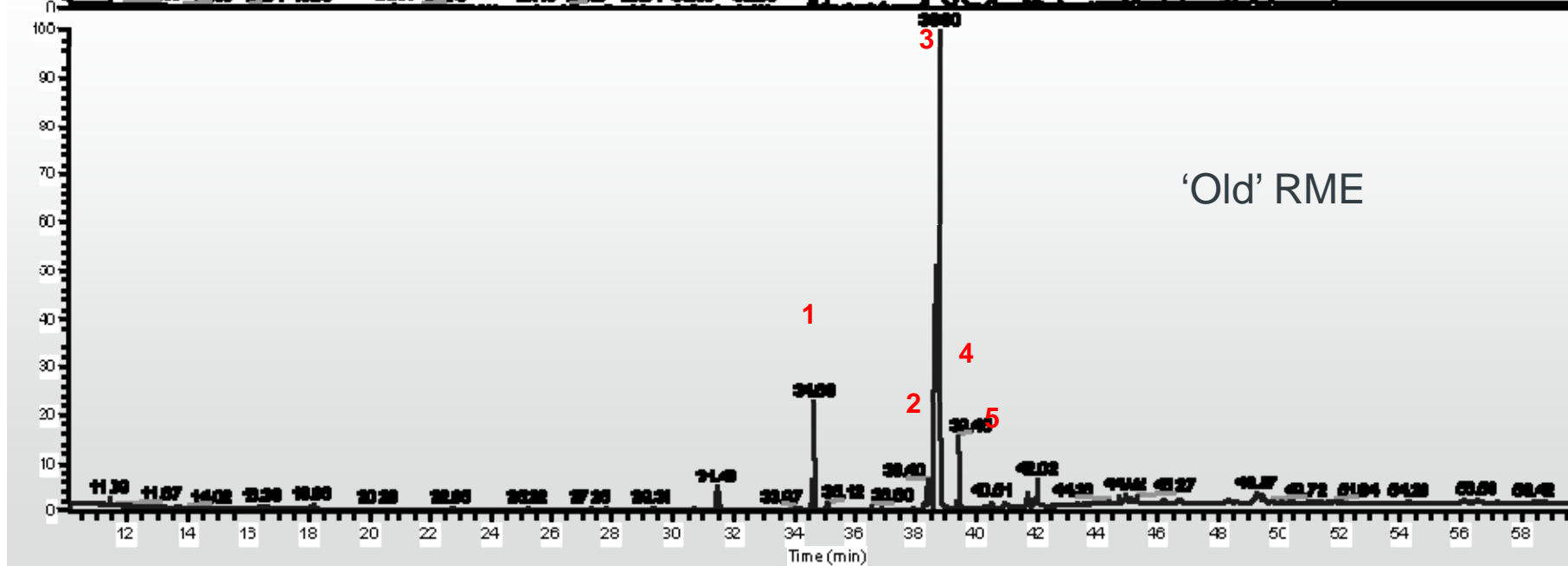
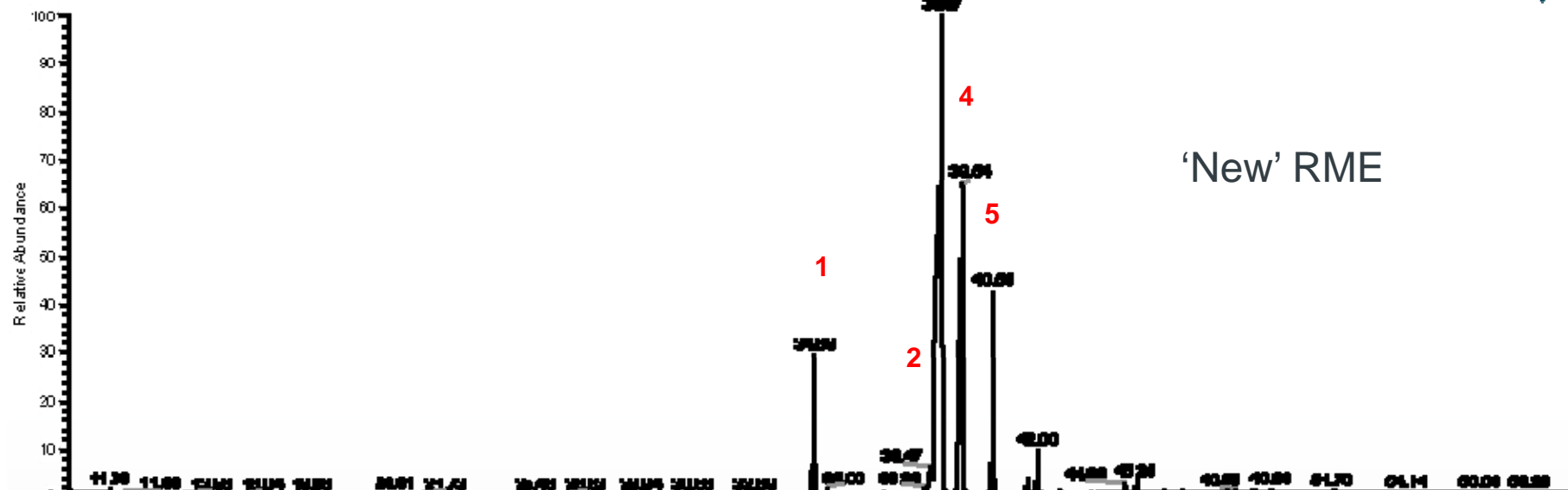
What about aged Biodiesel?

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Southampton

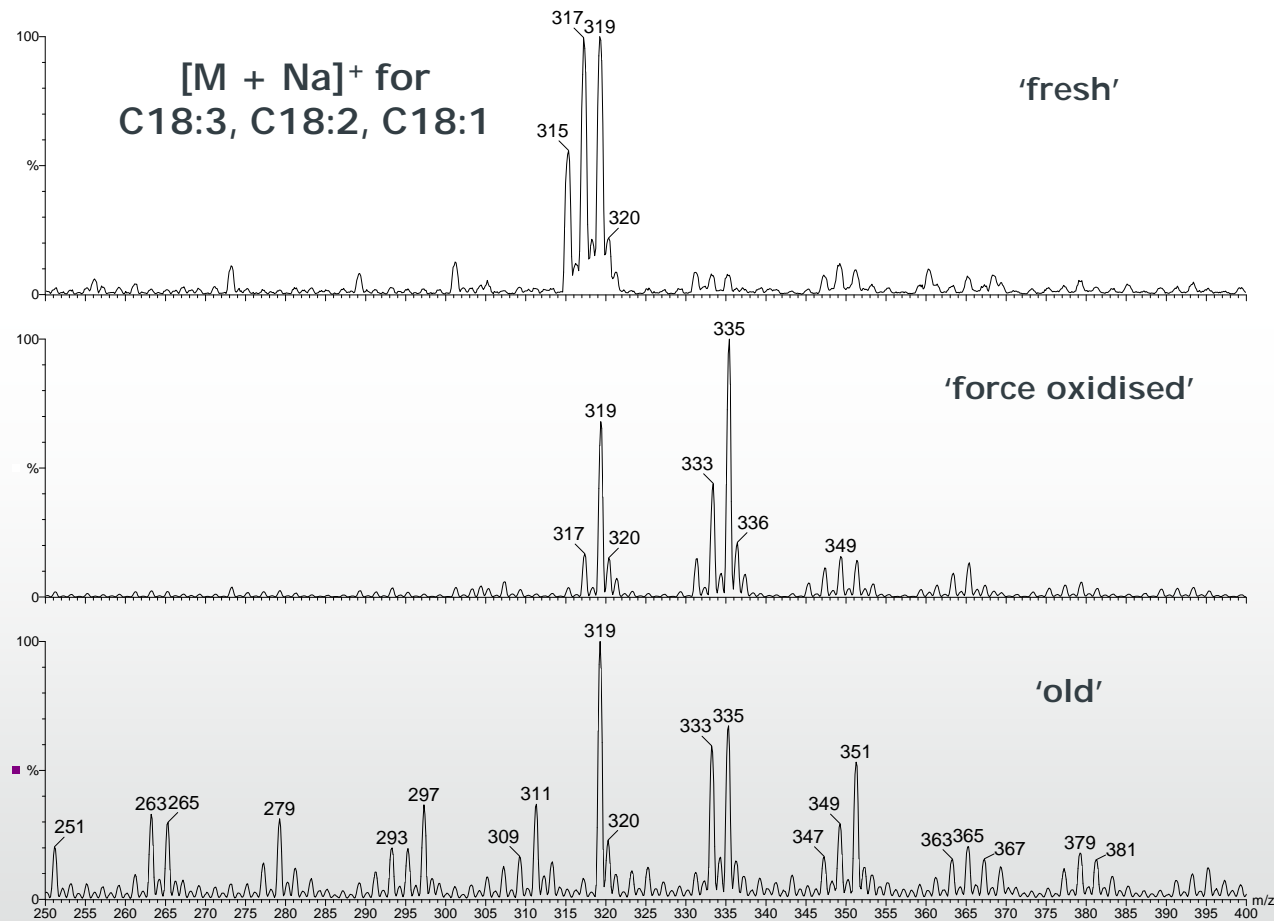
School of Chemistry

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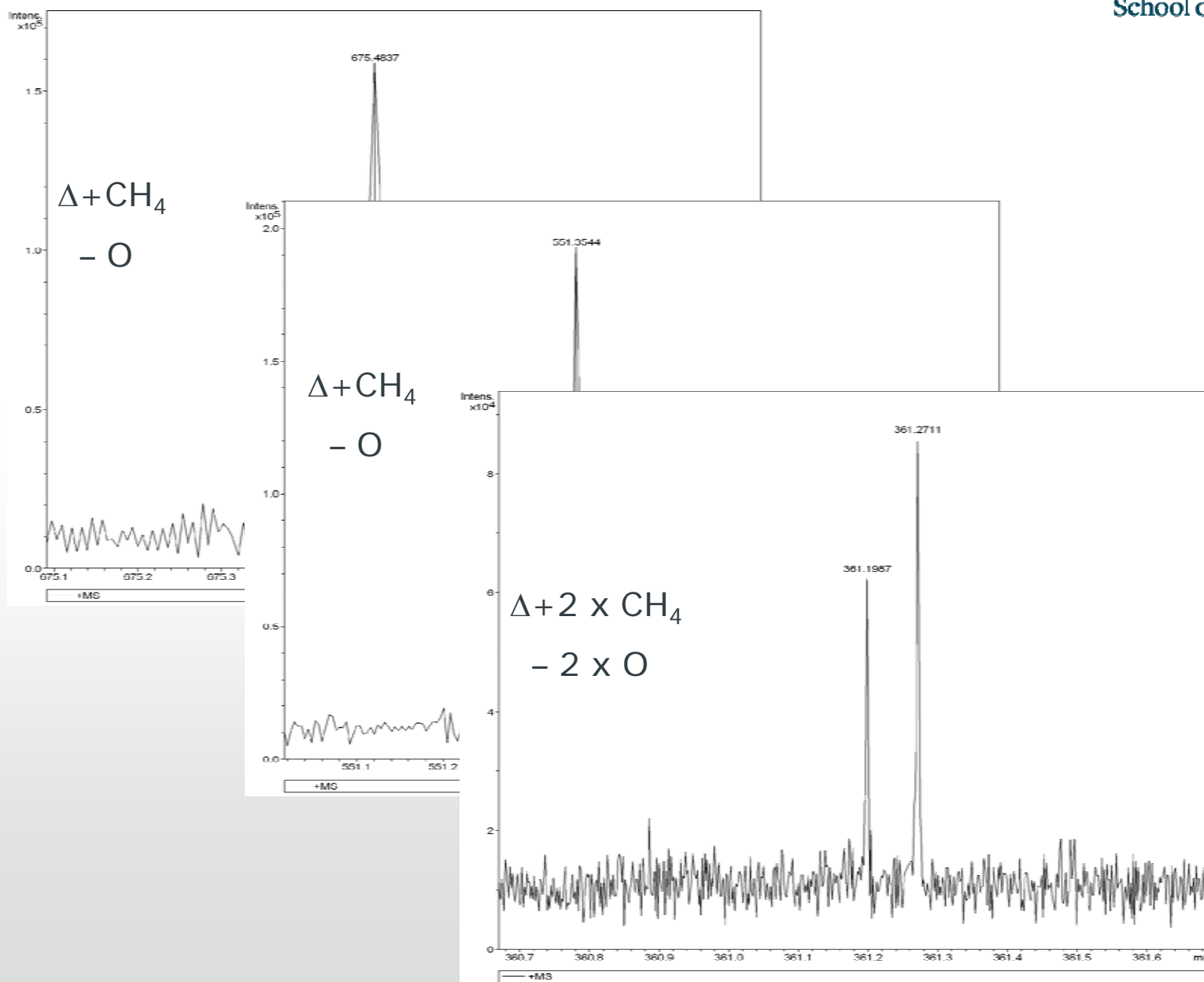
RT: 1073 - 5997



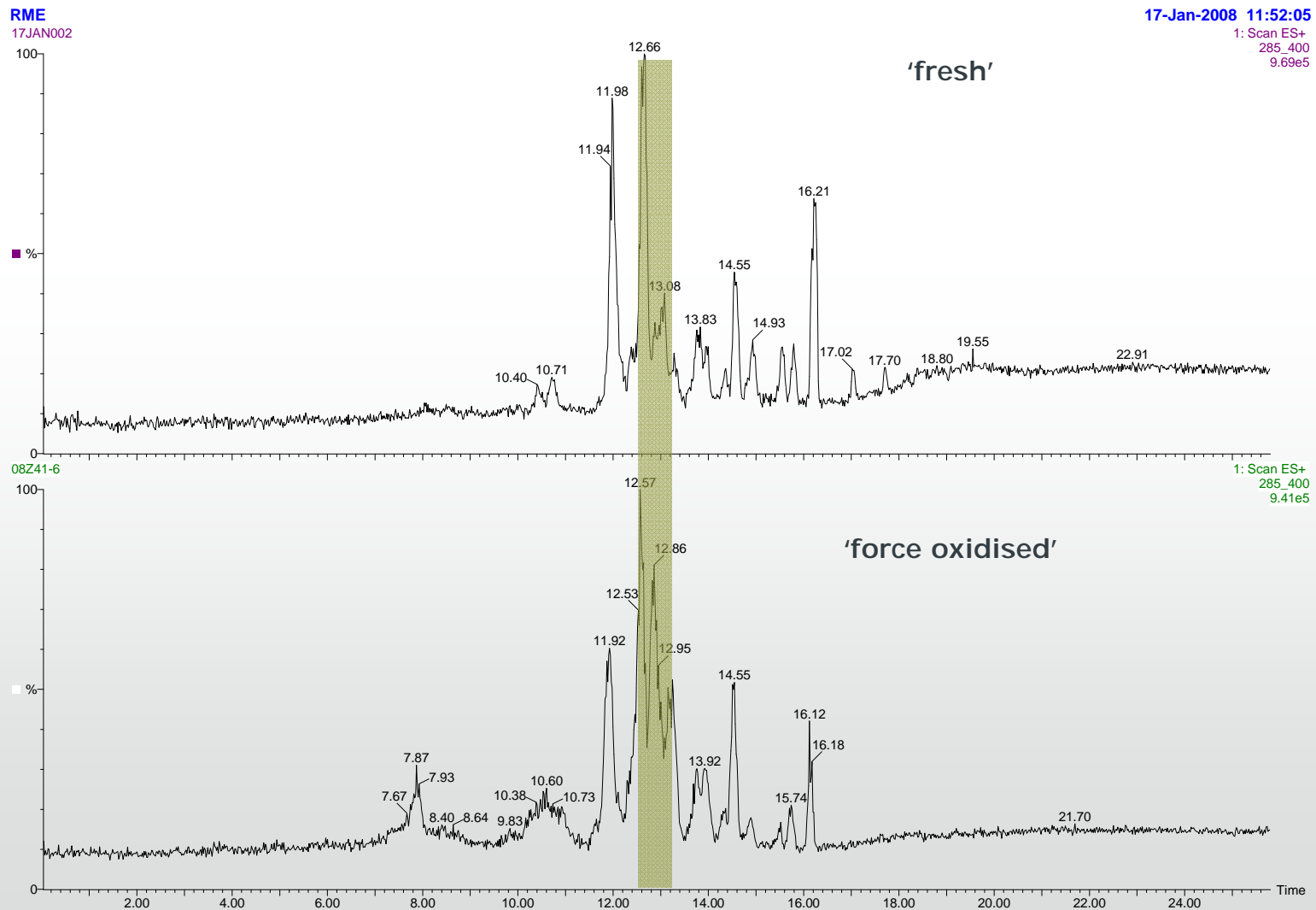
FIA ESI-MS of Oxidised RME



Nominal Isobars



HPLC-MS oxidised RME

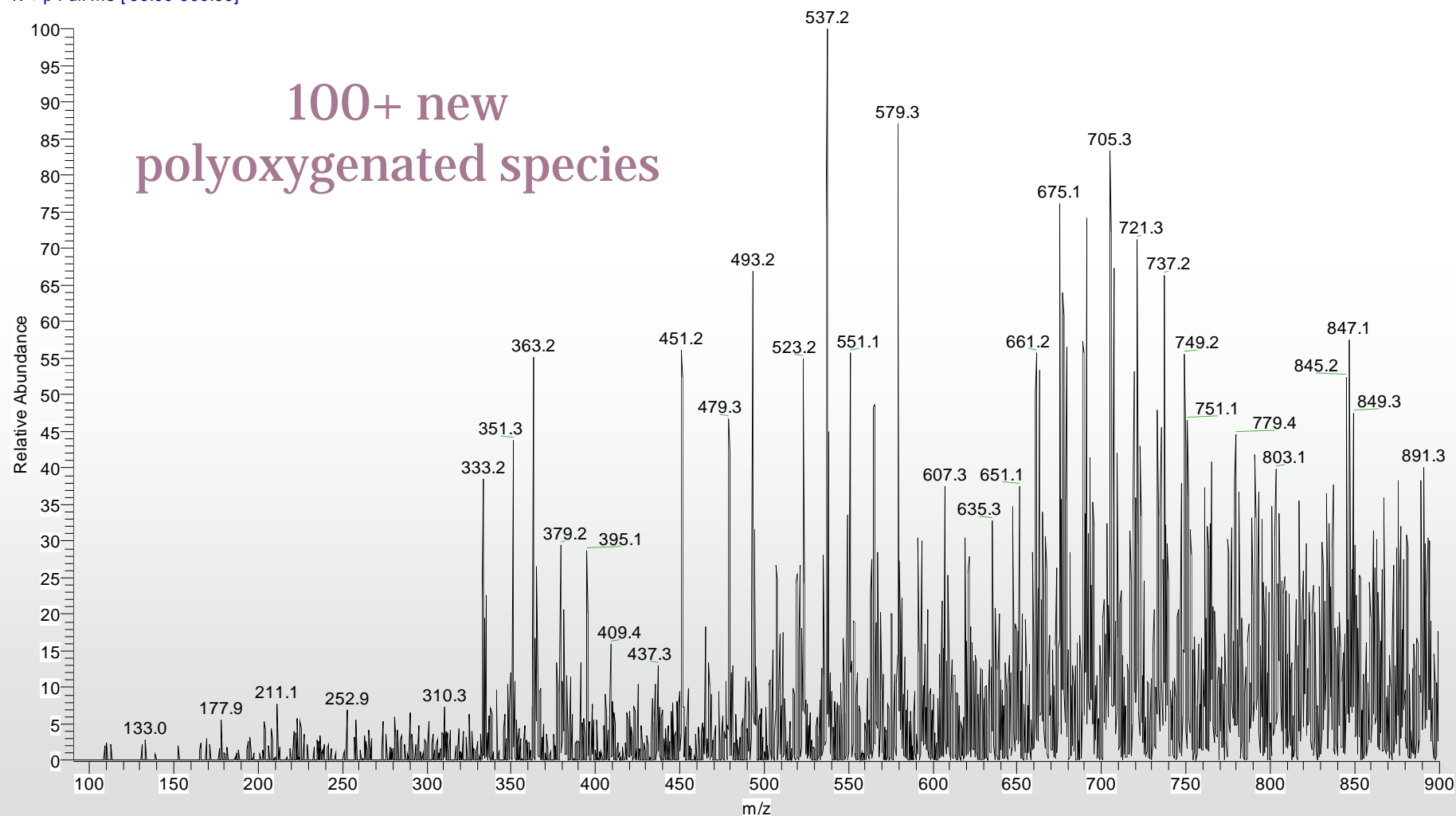


FT-ICR MS of Diesel/Biodiesel

Formula	<i>m/z</i>	Error (ppm)
C ₁₉ H ₃₂ O ₂ Na	315.2295	3.2
C ₁₉ H ₃₄ O ₂ Na	317.2451	0.2
C ₁₉ H ₃₆ O ₂ Na	319.2608	2.9
C ₁₉ H ₃₂ O ₃ Na	331.2244	3.6
C ₂₀ H ₃₈ O ₂ Na	333.2764	0.5
C ₁₉ H ₃₆ O ₃ Na	335.2557	0.6
C ₁₉ H ₃₂ O ₄ Na	347.2193	3.2
C ₂₁ H ₄₀ O ₂ Na	347.2921	4.6
C ₁₉ H ₃₄ O ₄ Na	349.2349	2.7
C ₂₁ H ₄₂ O ₂ Na	349.3077	4.4
C ₁₉ H ₃₆ O ₄ Na	351.2497	2.5
C ₁₉ H ₃₀ O ₅ Na	361.1981	1.1
C ₁₉ H ₃₂ O ₅ Na	363.2139	0.9
C ₁₉ H ₃₄ O ₅ Na	365.2296	0.7
C ₁₉ H ₃₂ O ₆ Na	379.2088	0.8
C ₁₉ H ₃₄ O ₆ Na	381.2245	0.8
C ₁₉ H ₃₂ O ₇ Na	395.2039	0.4
C ₁₉ H ₃₂ O ₇ Na	411.1986	0.8

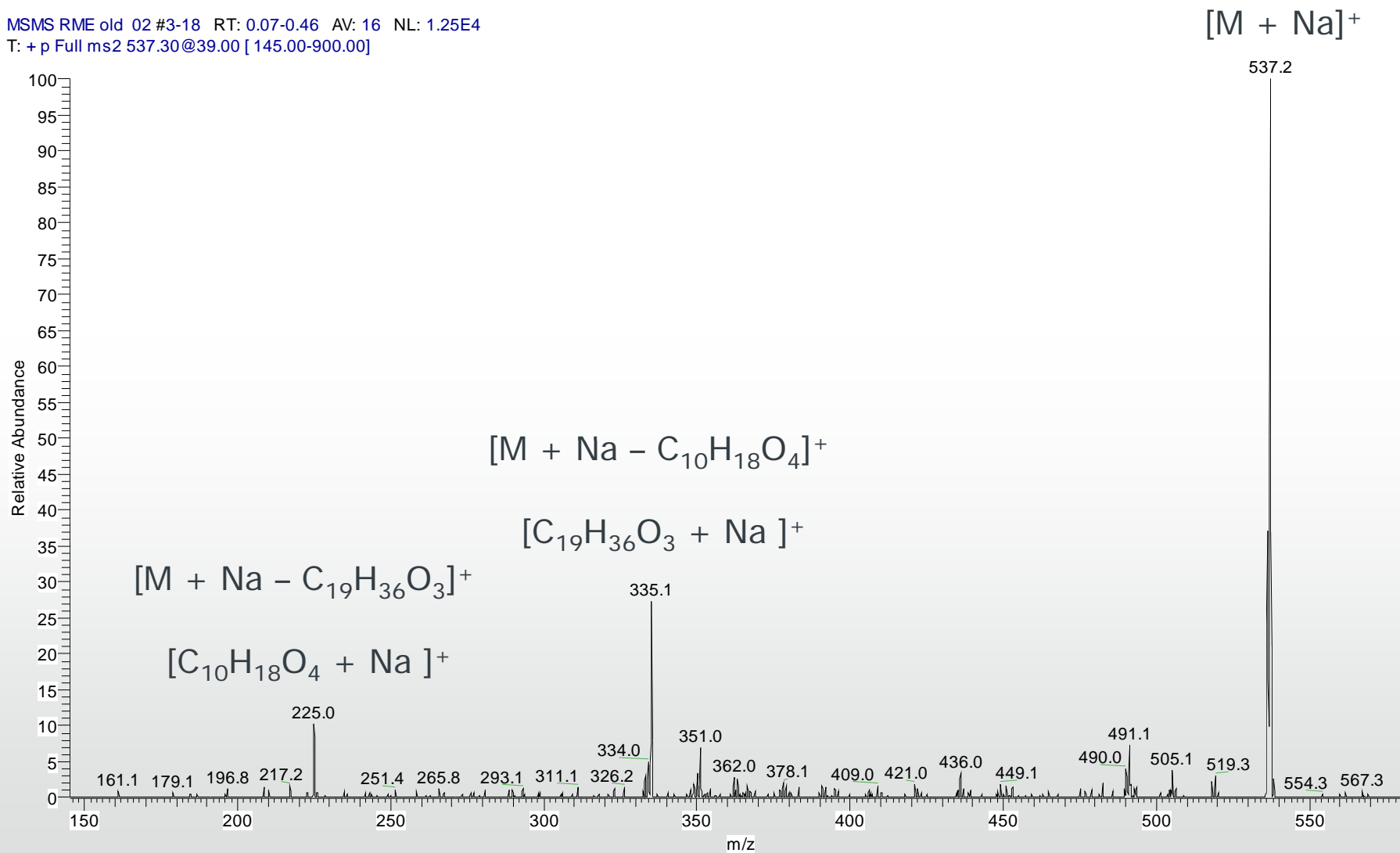
FIA ESI-MS of Oxidised RME

RME old 02 #10-16 RT: 0.21-0.31 AV: 7 NL: 7.23E5
T: + p Full ms [90.00-900.00]

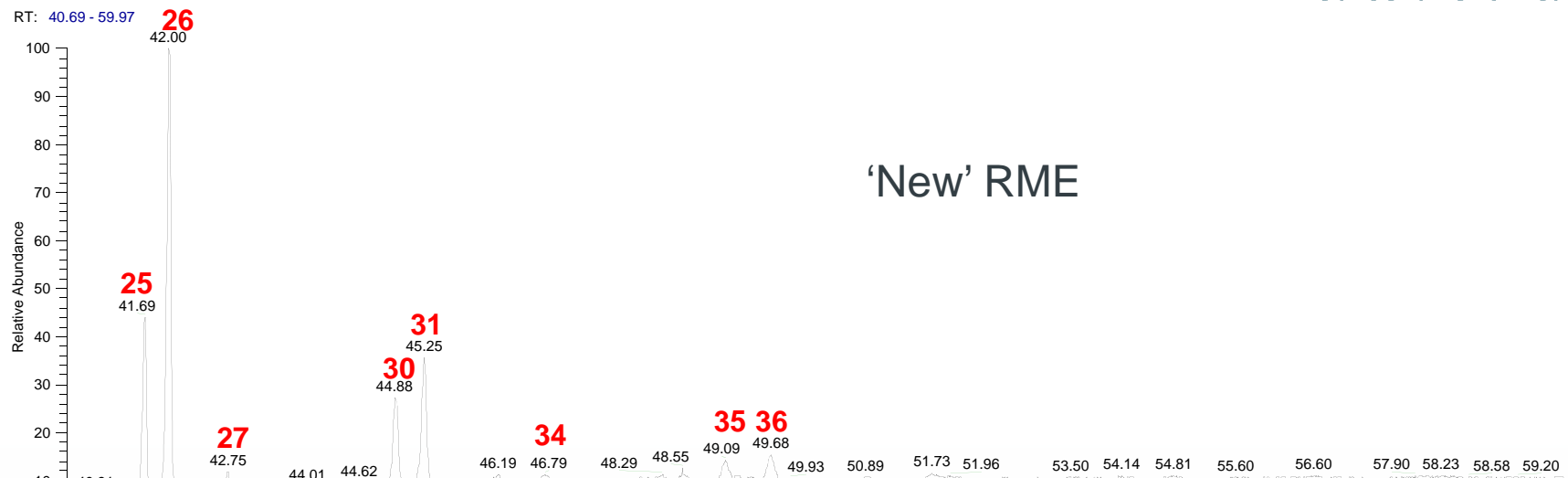


FIA ESI-MS/MS of m/z 537

MSMS RME old 02 #3-18 RT: 0.07-0.46 AV: 16 NL: 1.25E4
T: + p Full ms2 537.30@39.00 [145.00-900.00]

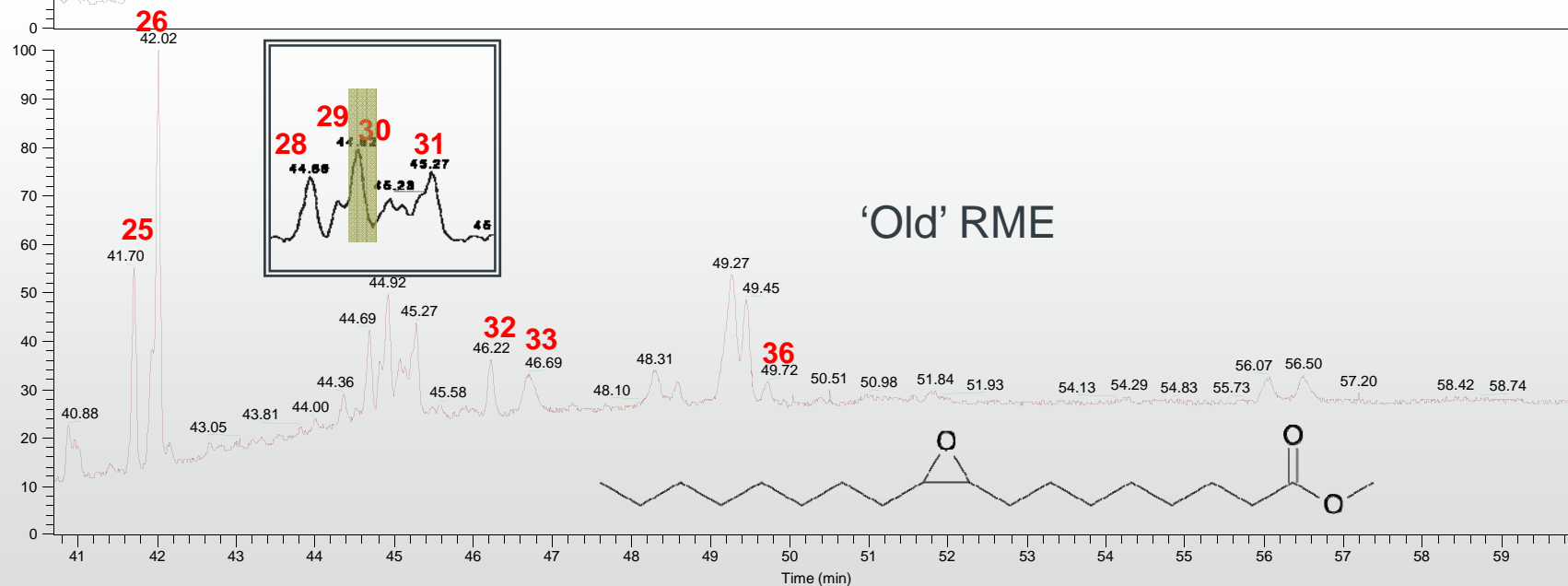


TICC 'new' RME vs 'old' RME



NL:
4.18E6
TIC MS
20090306
rme new

'New' RME



NL:
2.02E6
TIC MS
20090306
RME Old

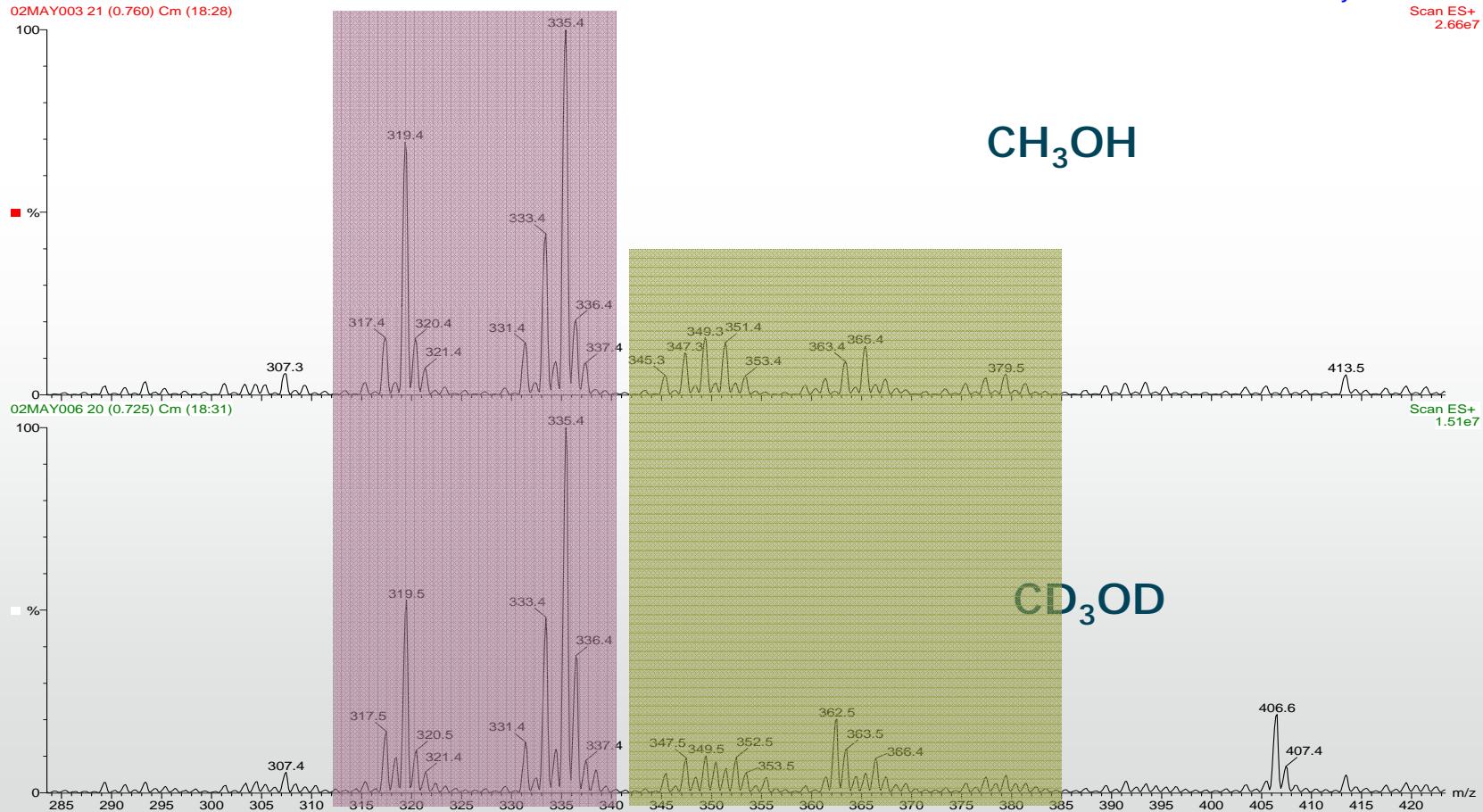
'Old' RME

HDX ESI of Oxidised RME

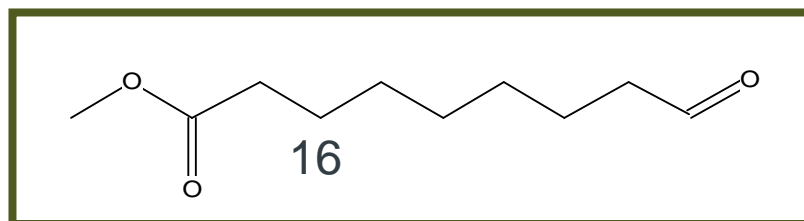
RME 180 24h dilute
02MAY003 21 (0.760) Cm (18:28)

CheMSoton

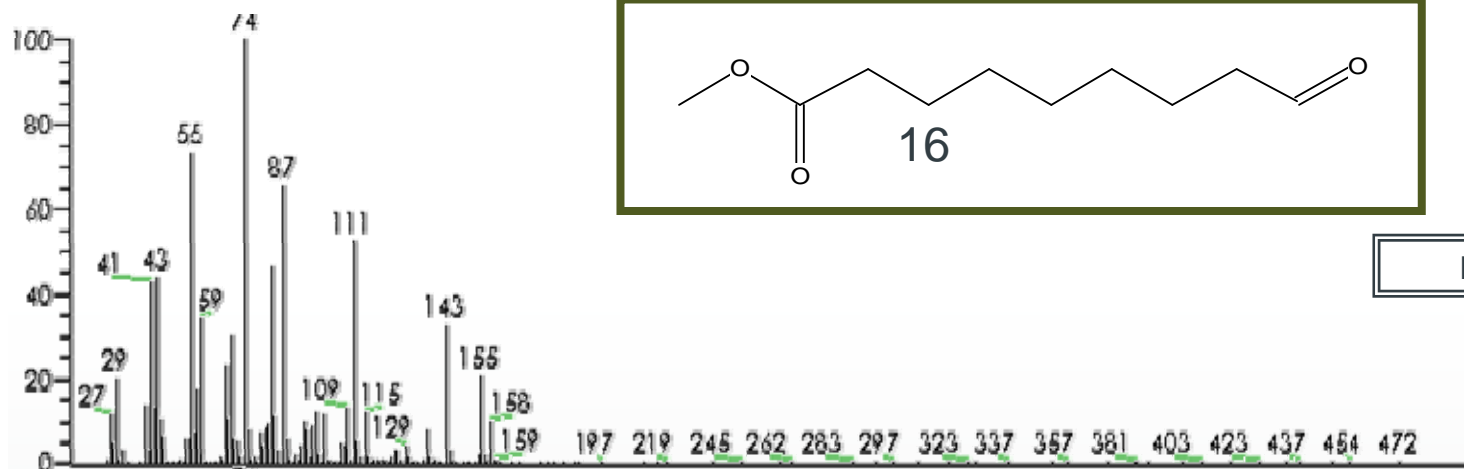
02-May-2008 11:15:31
Scan ES+
2.66e7



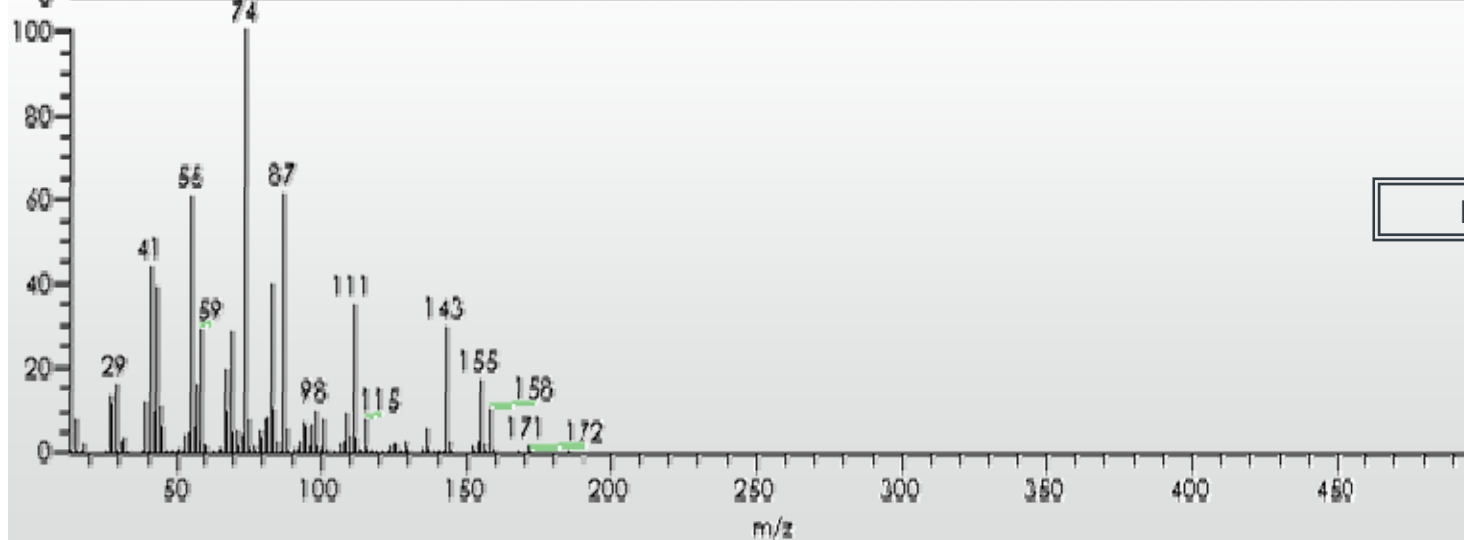
GC-EI-MS of methyl 9-oxononanoate



20070306 rme of#2549-2566 EI:
31.39-31.53 AV: 18 SB: 2 31.35 .
31.62 NL: 7.63E4 T: [0.0] +c EI
def=350.00 Full ms | 20.00-500.00



MS of peak no 16



31918, R31916, NISTMSmainlib, Entry#
35270, CAS# 1931-83-1, Nonanoic
acid, 9-oxo-, methyl ester

Library match MS

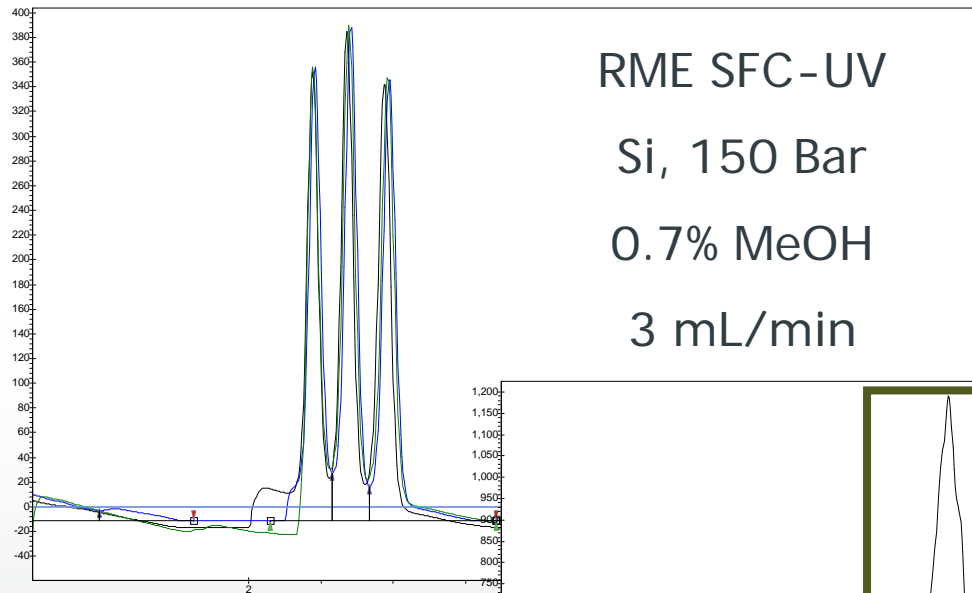
SFC-UV-MS

- Supercritical fluid chromatography (SFC) is considered a 'green' technique.
- Can analyse many compounds due to wide range of parameters.
- Run times are short.

SFC-UV-MS

- SFC instrumentation: Mettler-Toledo Bexger Thar Waters Minigram system run at a flow rate of 3 mL/min. Mobile phase: SFC Grade CO₂ Other parameters used as stated. Modifier: MeOH.
- 2 x 250 mm x 4.6 mm Si packed column
- UV detector: Knauer K-2501 UV Detector at 200 nm.
- ESI-MS instrumentation: Micromass Platform LCZ single quadrupole MS with Z-spray ESI

SFC-UV Biodiesel in Diesel



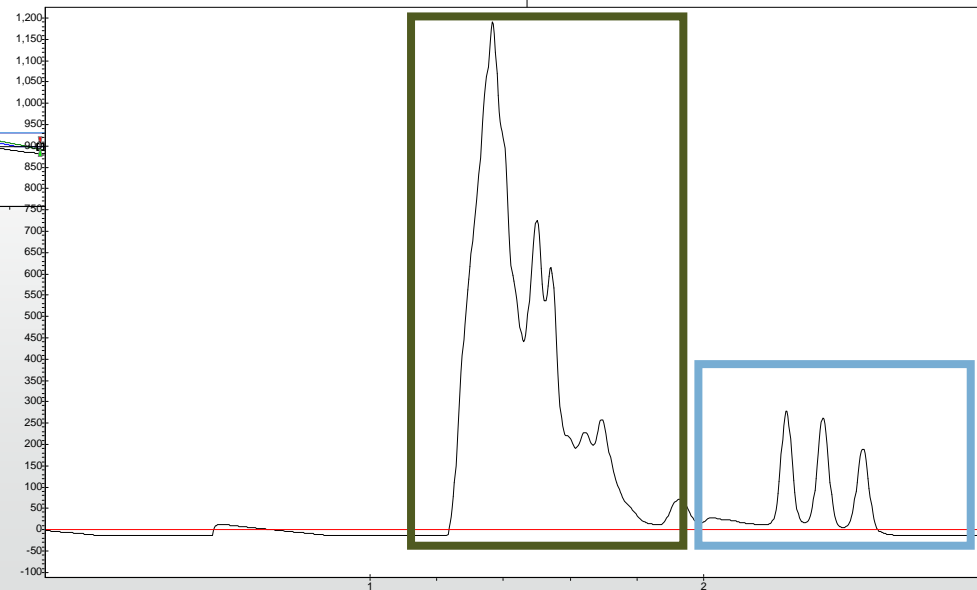
RME SFC-UV

Si, 150 Bar

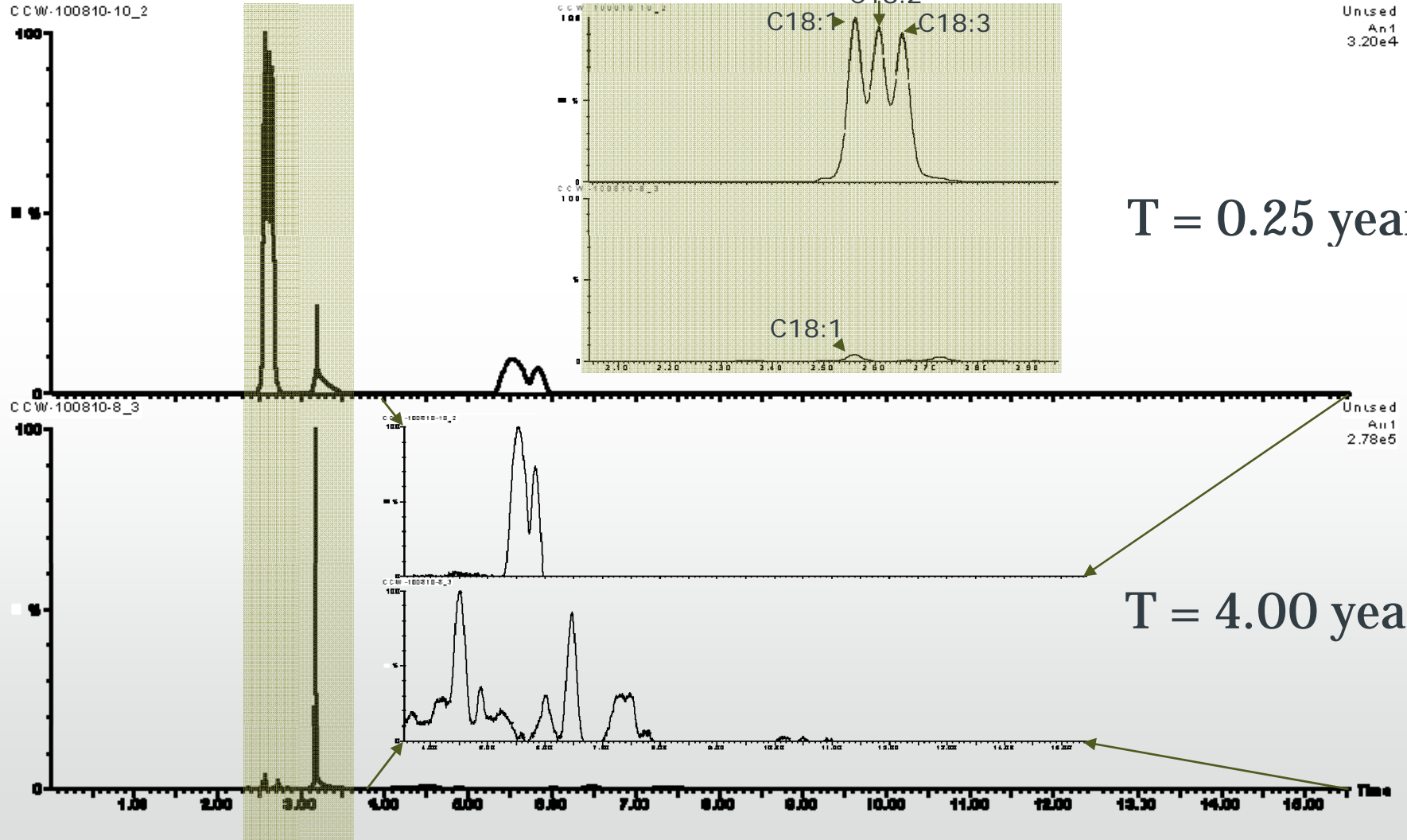
0.7% MeOH

3 mL/min

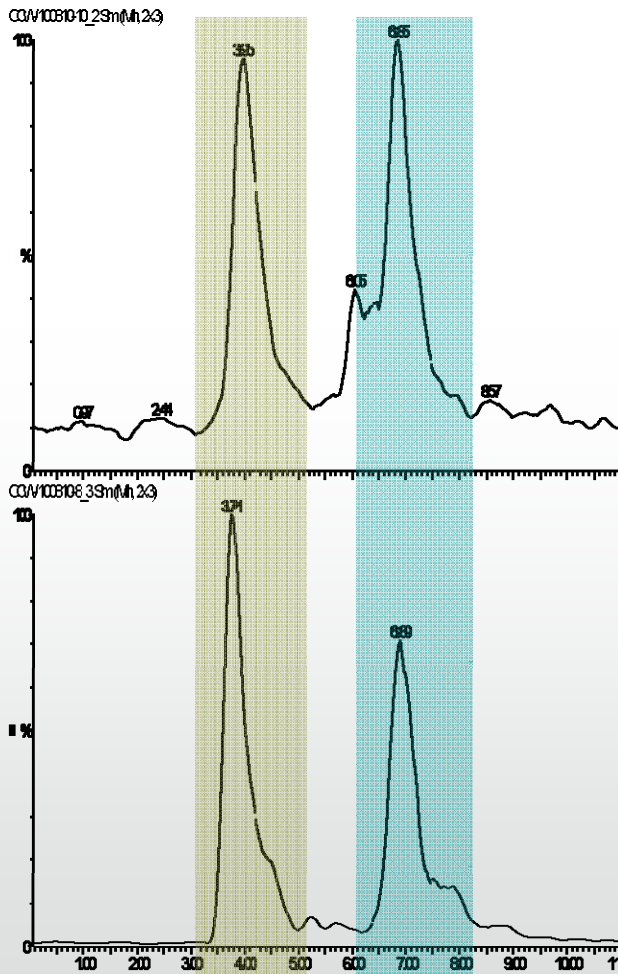
Total run time
3 minutes



UV chromatogram comparison



RIC m/z 335



- Consistent with auto-oxidation products of FAME
- Run times under 10 min.
 - To be improved

Conclusions

- Complex problem needs different hyphenation and detector approaches
- Early oxidised RME \Rightarrow little/no initial difference by GC-MS
- ESI & HPLC-ESI MS & MSⁿ
 - ☺ enhanced ionisation response
 - ☺ 100+ new oxygenated species
 - ☹ nominal isobars
- FT-ICR MS \Rightarrow elemental formulae
- Throughout, the different chemistries demand different approaches to sample introduction and analysis

Conclusions

- SFC-UV-MS a promising, effective tool for biodiesel analysis.
- Differences between different RME samples are clearly distinguished.
- SFC-UV-MS has the ability to separate:
 - Individual FAMES
 - Individual FAMES and other lube and fuel species.
 - Separations achieved within 8 min. *c.f.* ~60 min. (GC-MS) and 20 min (LC-MS)
 - Coupling of 2 columns increased the selectivity of the system, however this lengthens run times

Acknowledgements

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