Finding a Sustainable Replacement for Peat in Scotch Whisky Production

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Peated Scotch Whisky

- Project focus - whiskies with smoky flavour and aroma.

- Imparted by burning peat when drying malt.

- Organic material composed mostly of large biopolymers: cellulose, hemicellulose and lignin.

- Thermal decomposition leads to release of phenols and carbonyls.

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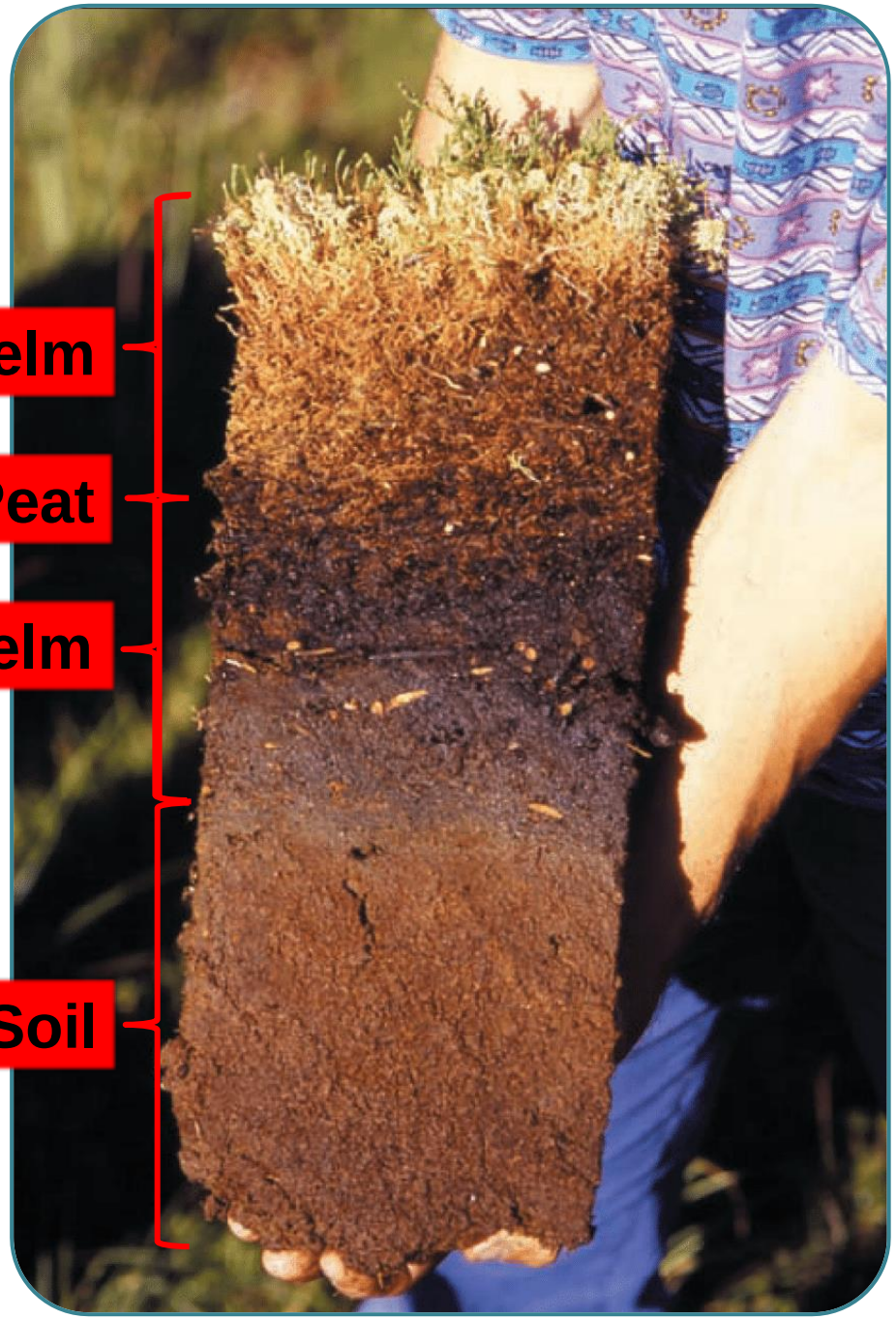

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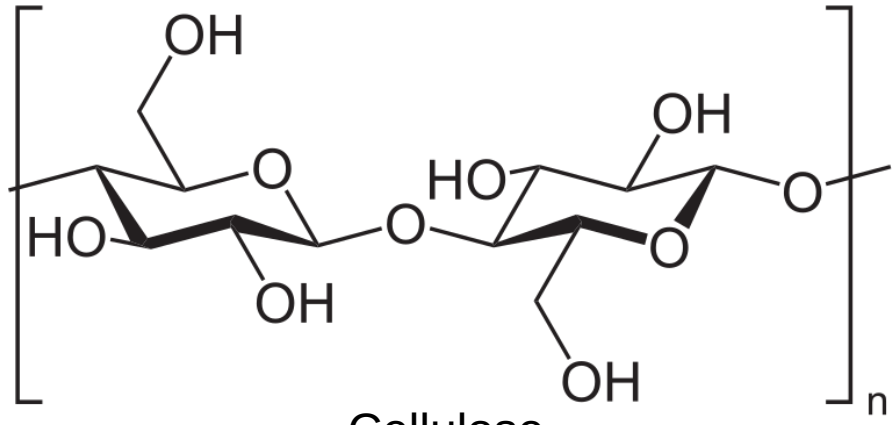
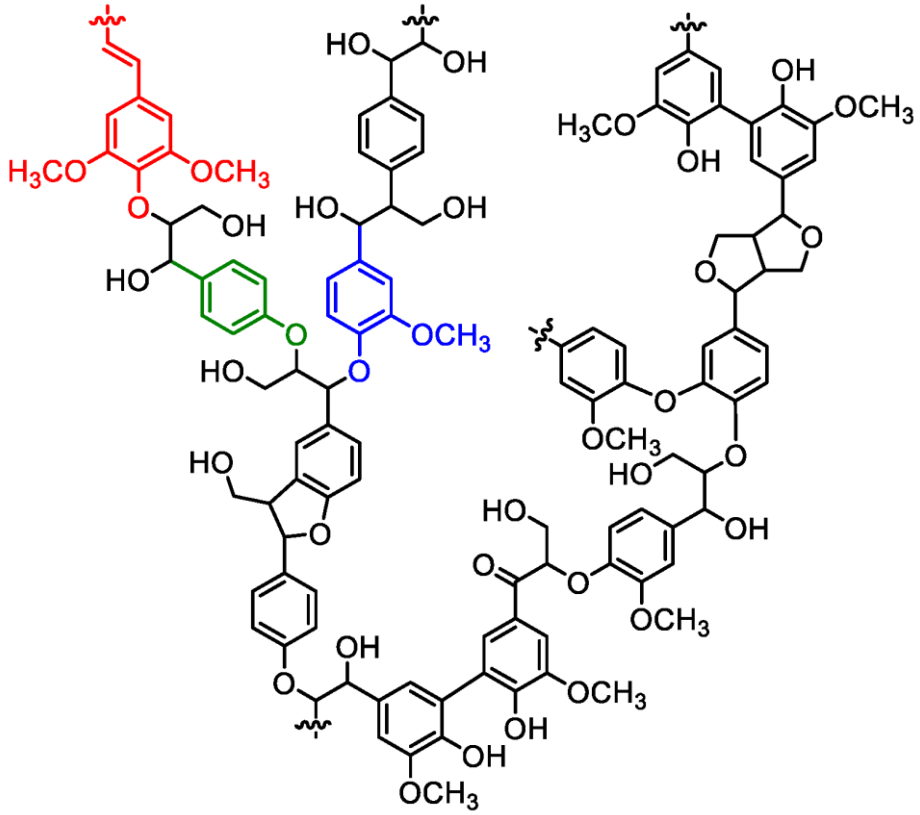


Cellulose



Lignin

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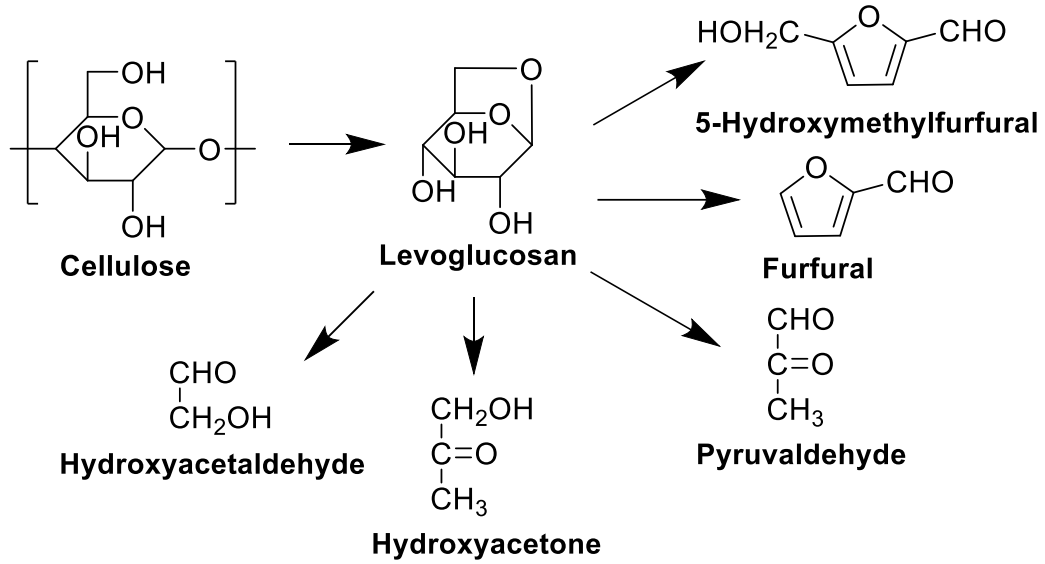

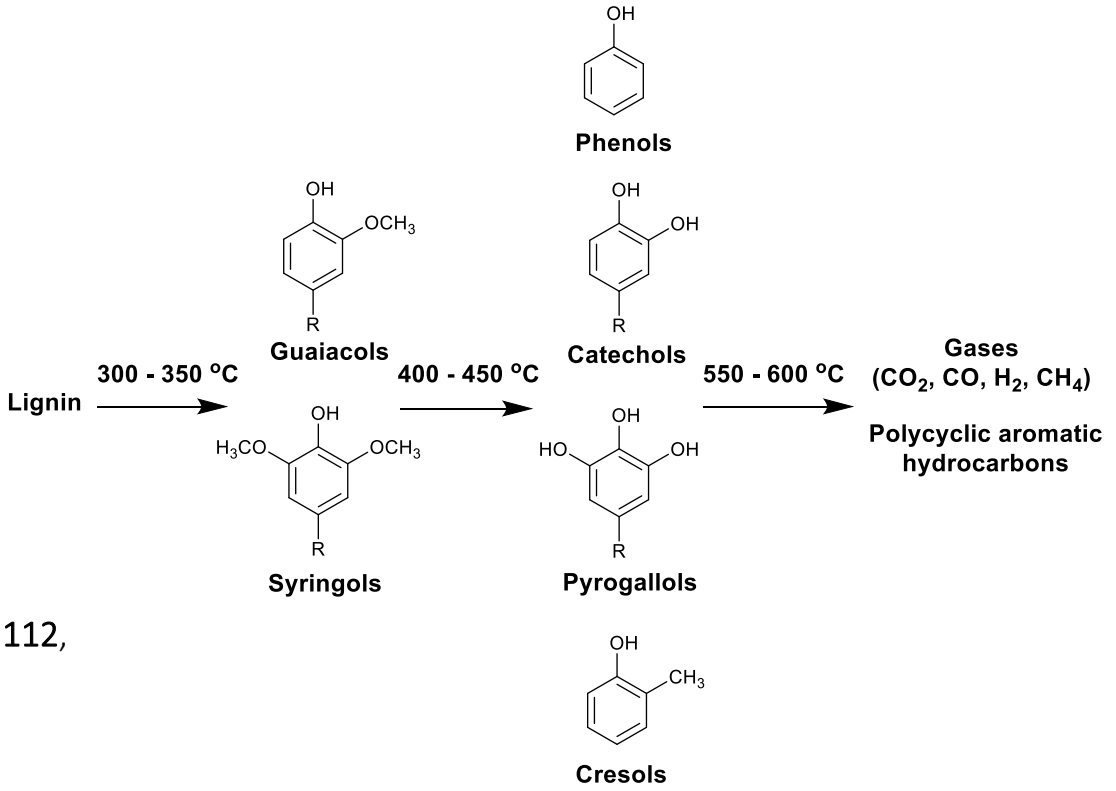

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Peat exploitation and restoration

- Peat is a limited resource.
- Peatlands act as carbon sink and habitat for a variety of plant and wildlife.
- Use of peat as fuel and fertiliser over hundreds of years lead to degradation of peatlands.
- Considerable restoration efforts made by the government and variety of environmental organisations.

Finding an alternative to peat

- Material composed primarily of the same biopolymers as peat.

- Thermal degradation products should be the same or similar.

- Should be available in large quantities and not be in widespread use for another purpose.

- Potential candidates include spent coffee grounds (SCG) and wood chips.

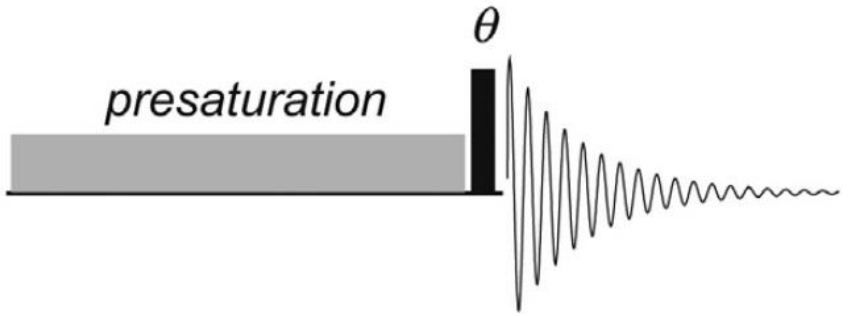
NMR Solvent Suppression

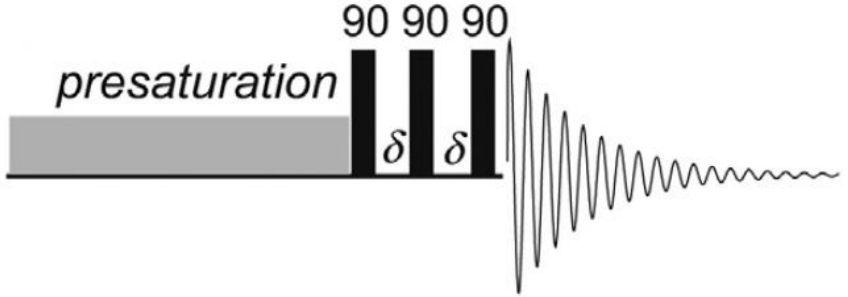
- Samples with protonated solvents require solvent suppression.

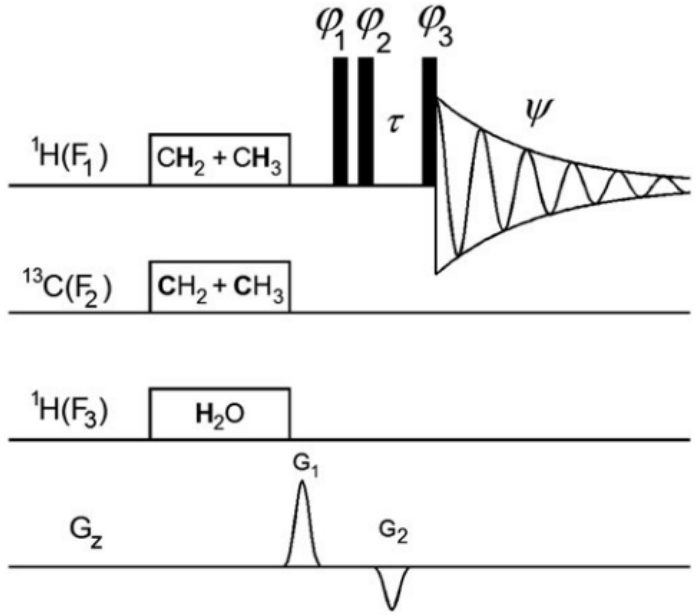
- Strong solvent signals mask weaker resonances and cause baseline distortions and radiation damping.

- Presaturation commonly used – application of a continuous weak pulse at the solvent frequency, leading to spin saturation.

- Suppression of multiple signals involves use of frequency modulated shaped pulses.

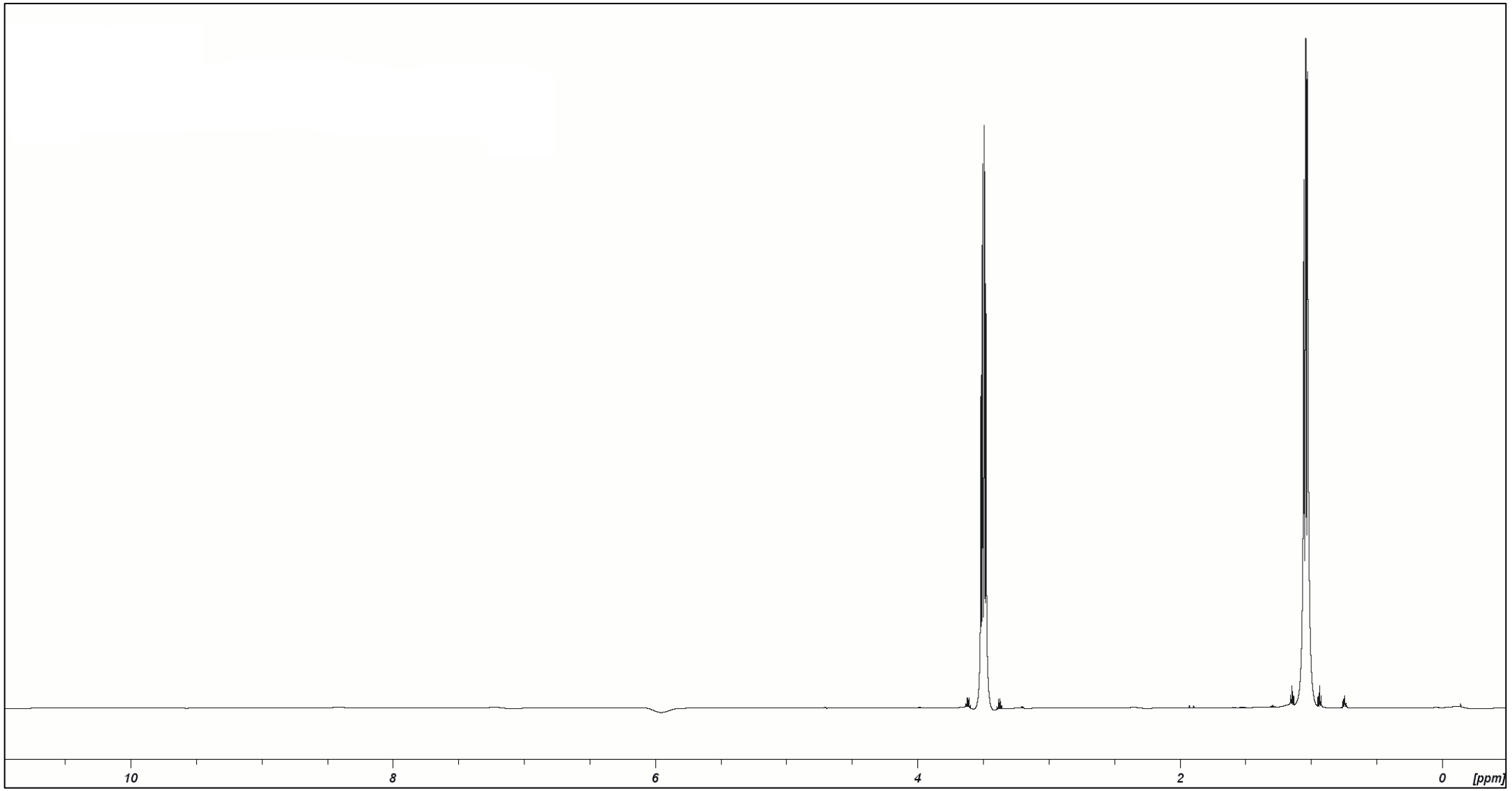




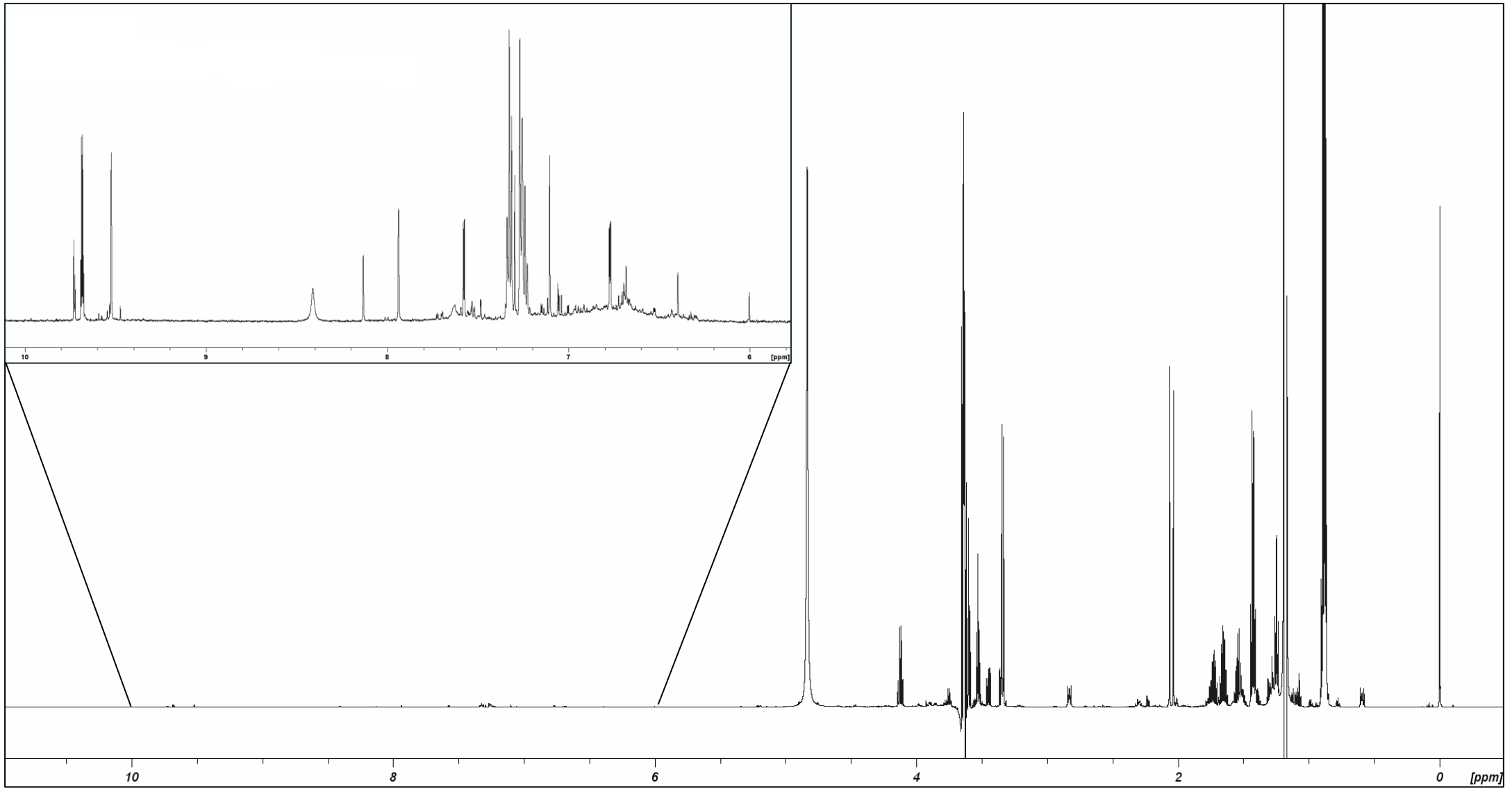


T. D. W. Claridge, Elsevier Ltd, Third Edition edn., 2016, DOI: 10.1016/B978-0-08-099986-9.00012-9, pp. 457-498.
W. Kew, N. G. A. Bell, I. Goodall and D. Uhrín, *Magn. Reson. Chem.*, 2017, **55**, 785-796.

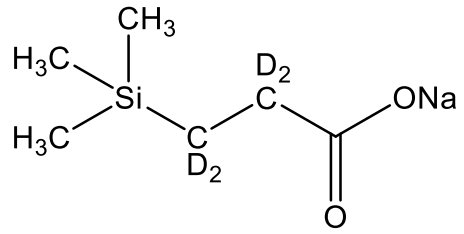
Solvent suppression – unsuppressed whisky ^{1}H NMR spectrum



Solvent suppression – suppressed whisky ^{1}H NMR spectrum



^{1}H NMR of methanol extract of peat



TSP
(Trimethylsilylpropionate)

Aromatic region (6-10 ppm)

Ferulic acid

Phenol, cresols, ethylphenol

Fatty acids, alkanes, alcohols etc.

Methanol

Ketones, cresols, ethylphenol, organic acids

Ferulic acid

Esters, guaiacols, syringols

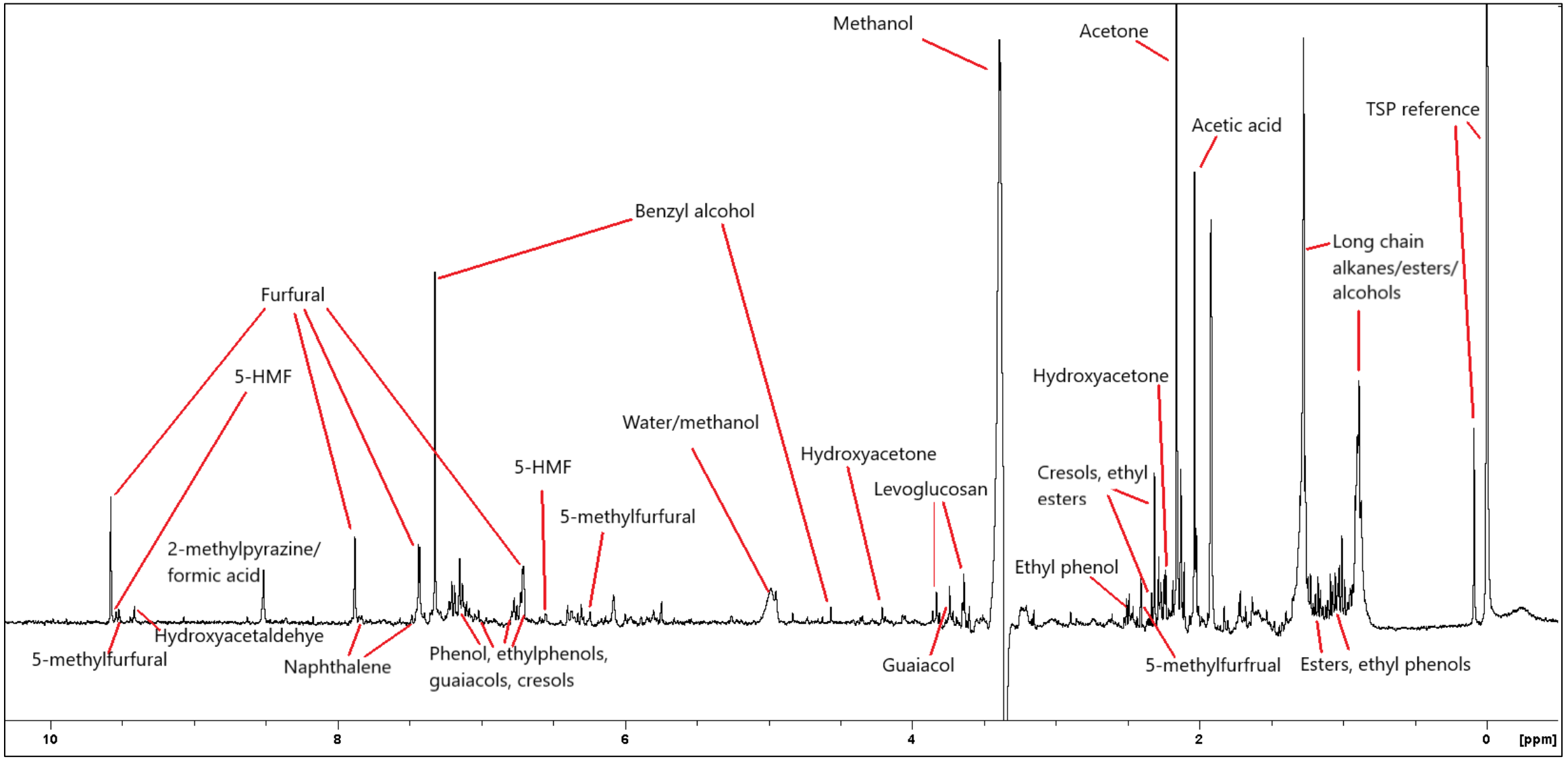
10 9 8 7 6 [ppm]

10 8 6 4 2 0 [ppm]

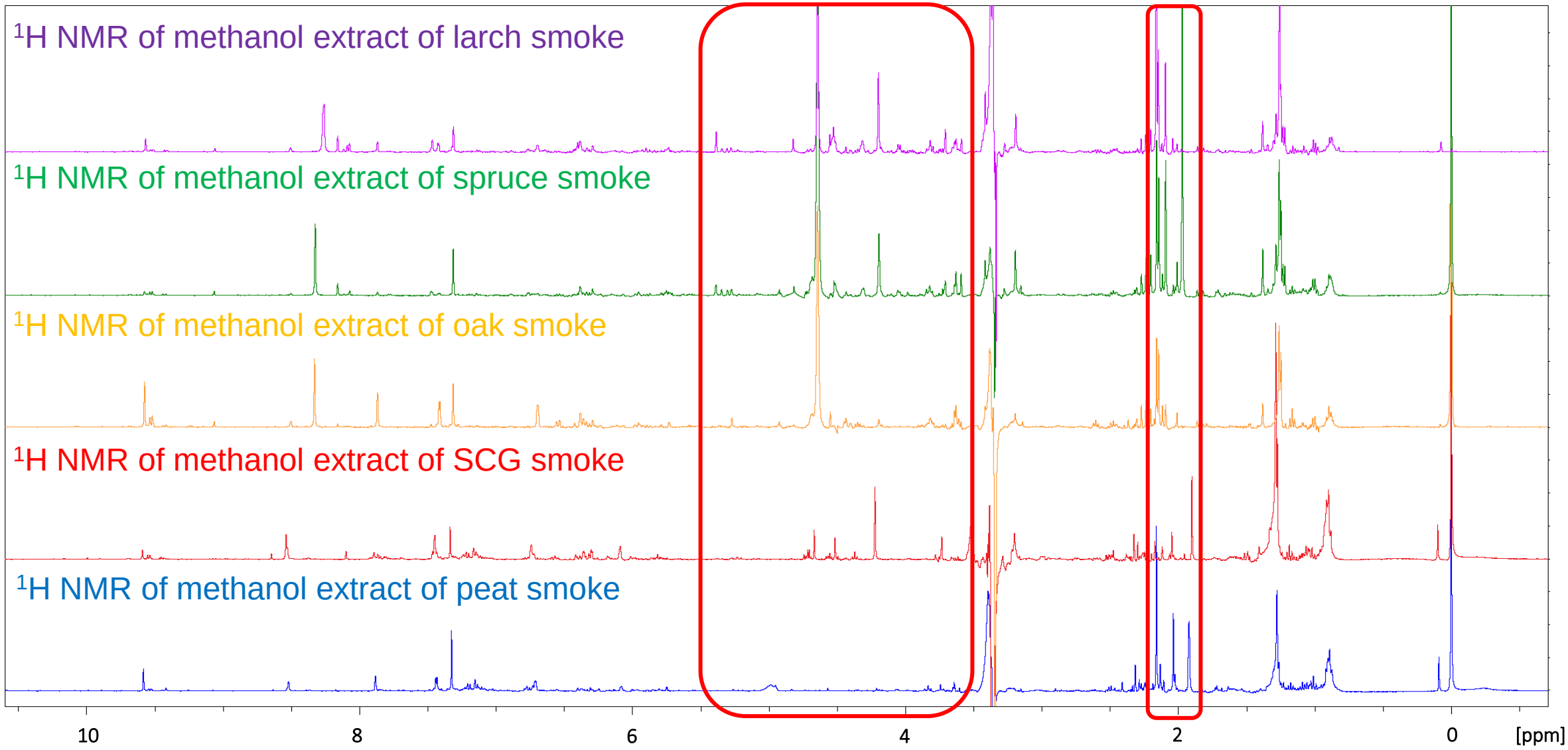
Smoke NMR spectra acquisition

- Smoke produced using commercially available smoker
- Approximately 0.5 g of material burnt
- Fan directs resulting smoke into a vial containing solvent
- Methanol used for majority of samples
- Solution with dissolved smoke components analysed using NMR

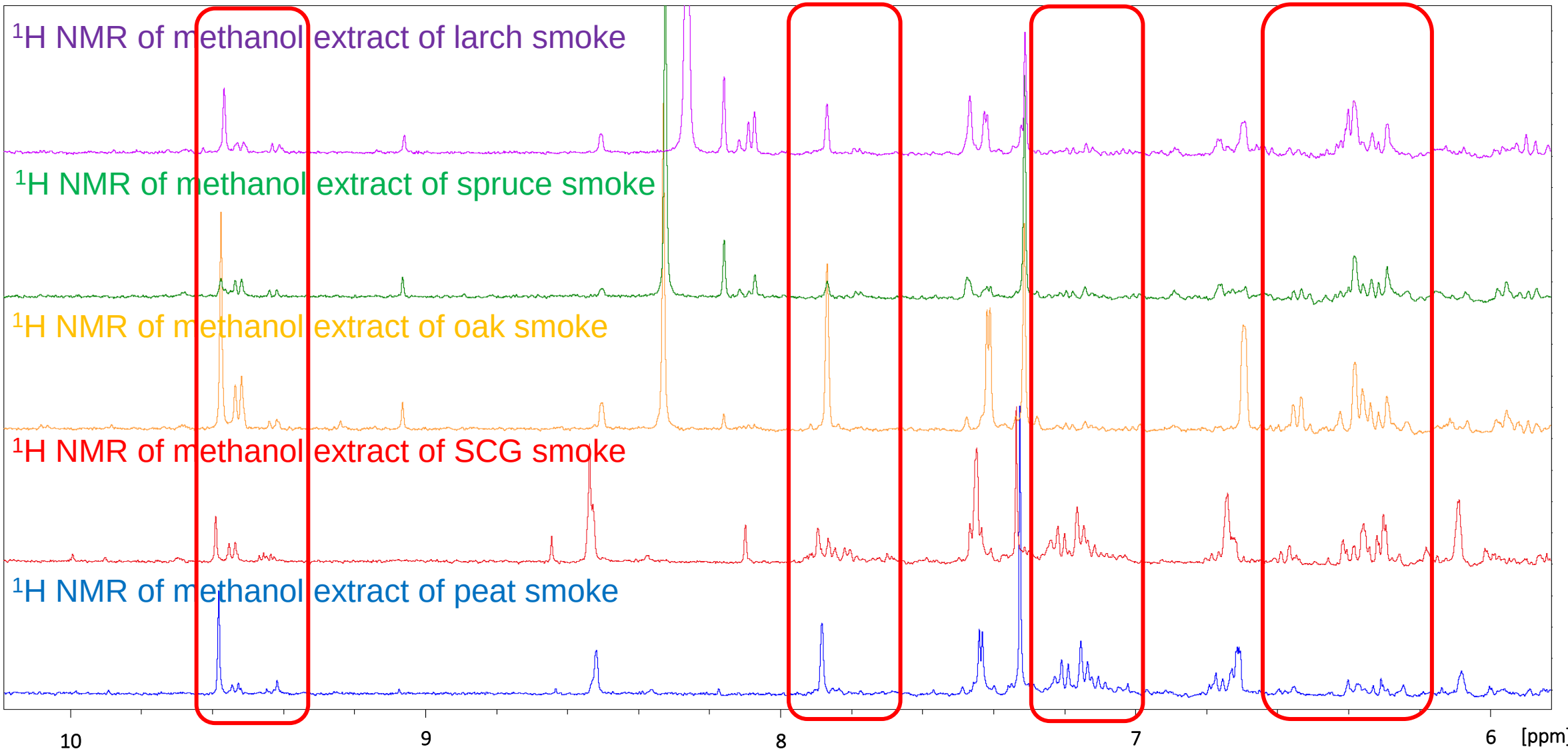
^{1}H NMR of peat smoke



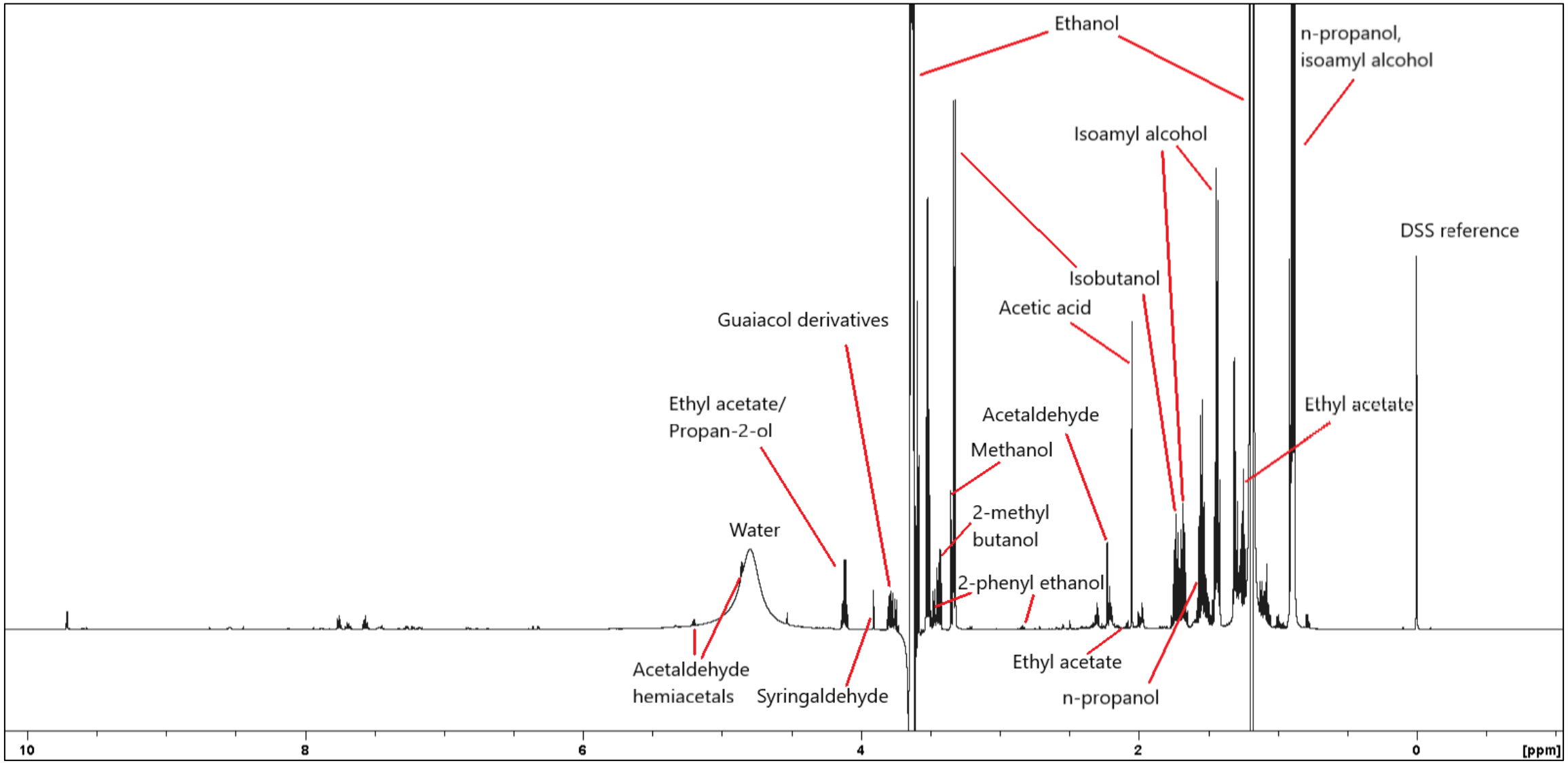
Smoke comparison – ^{1}H NMR



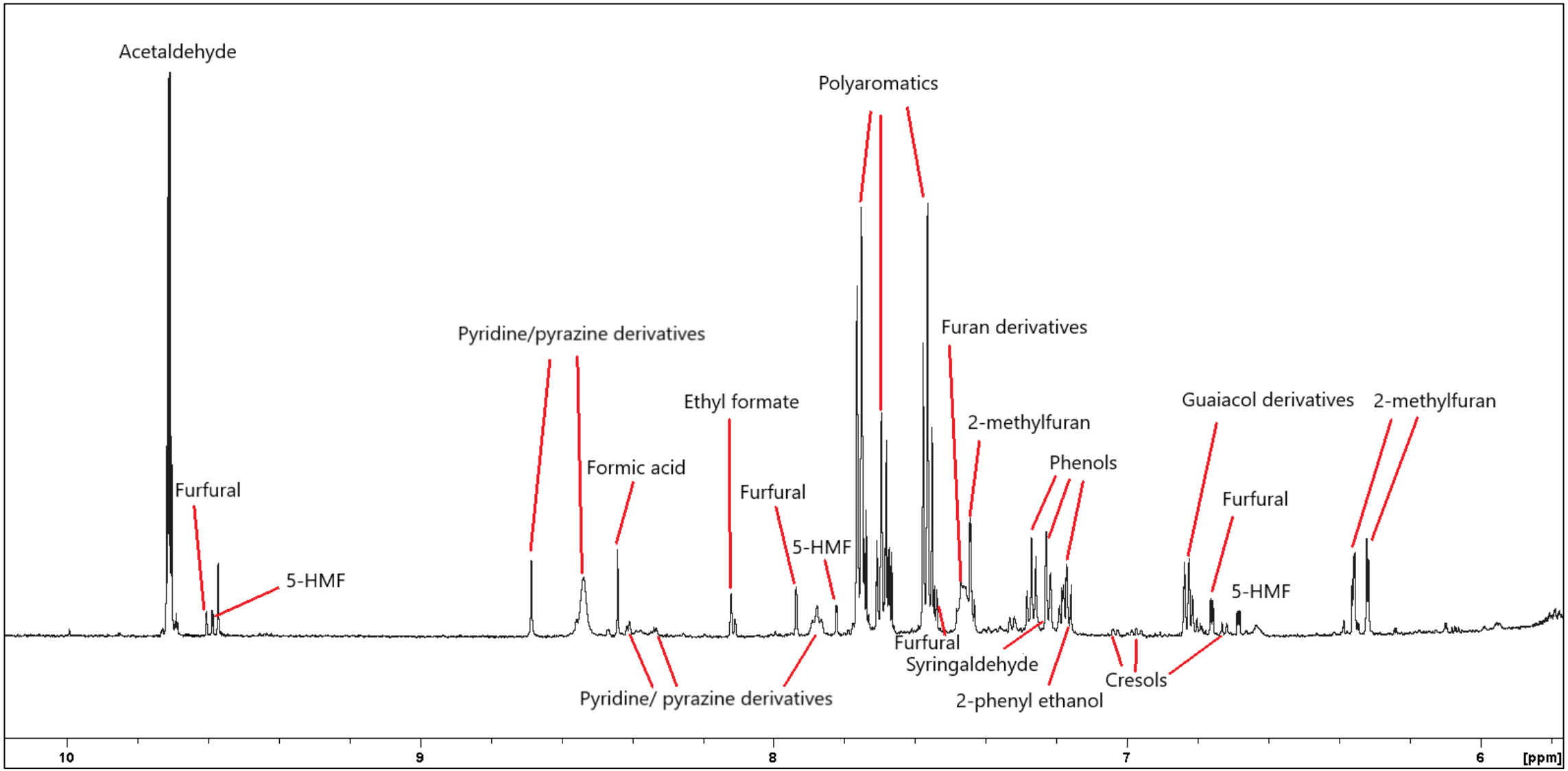
Smoke comparison – aromatic region



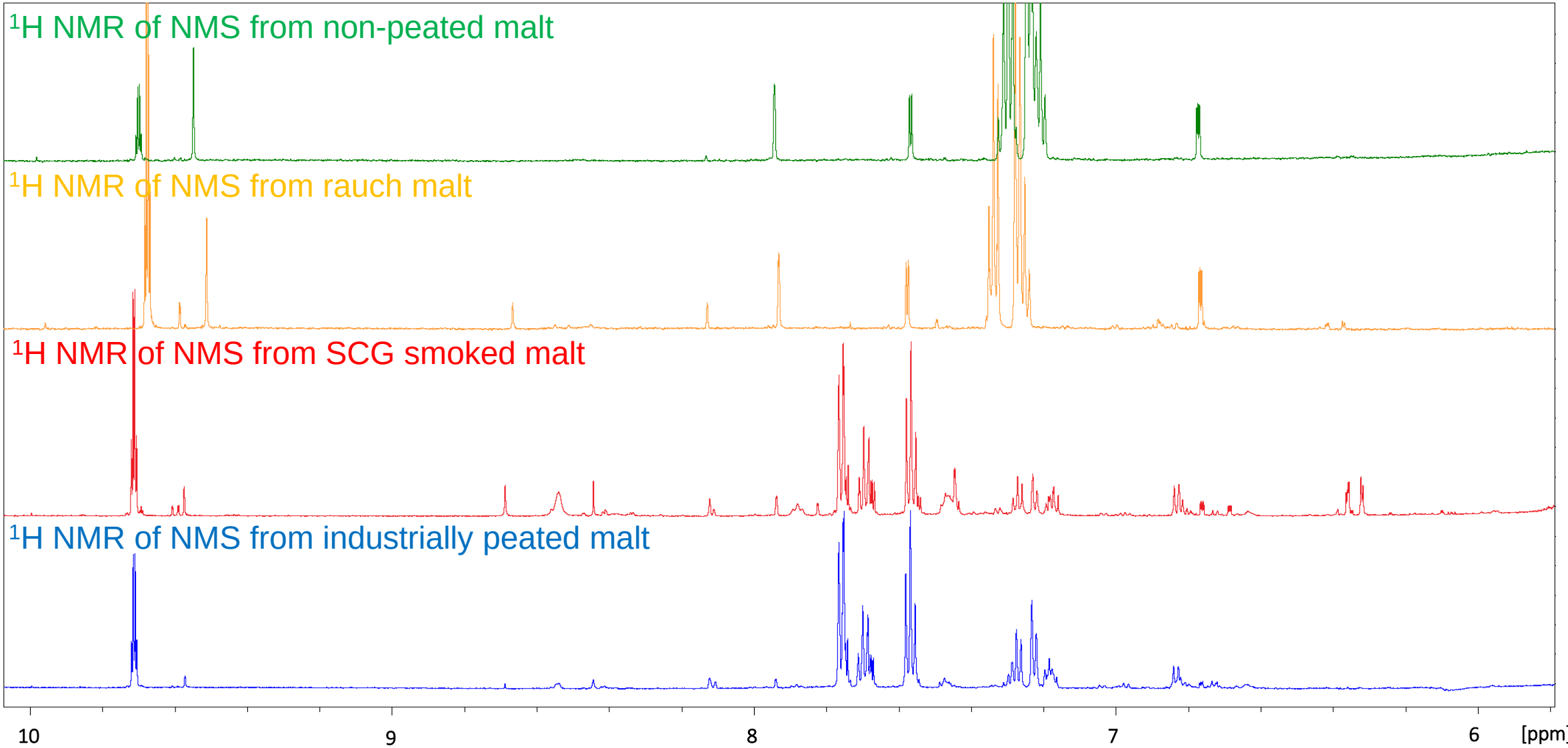
SCG New make spirit - ^{1}H NMR



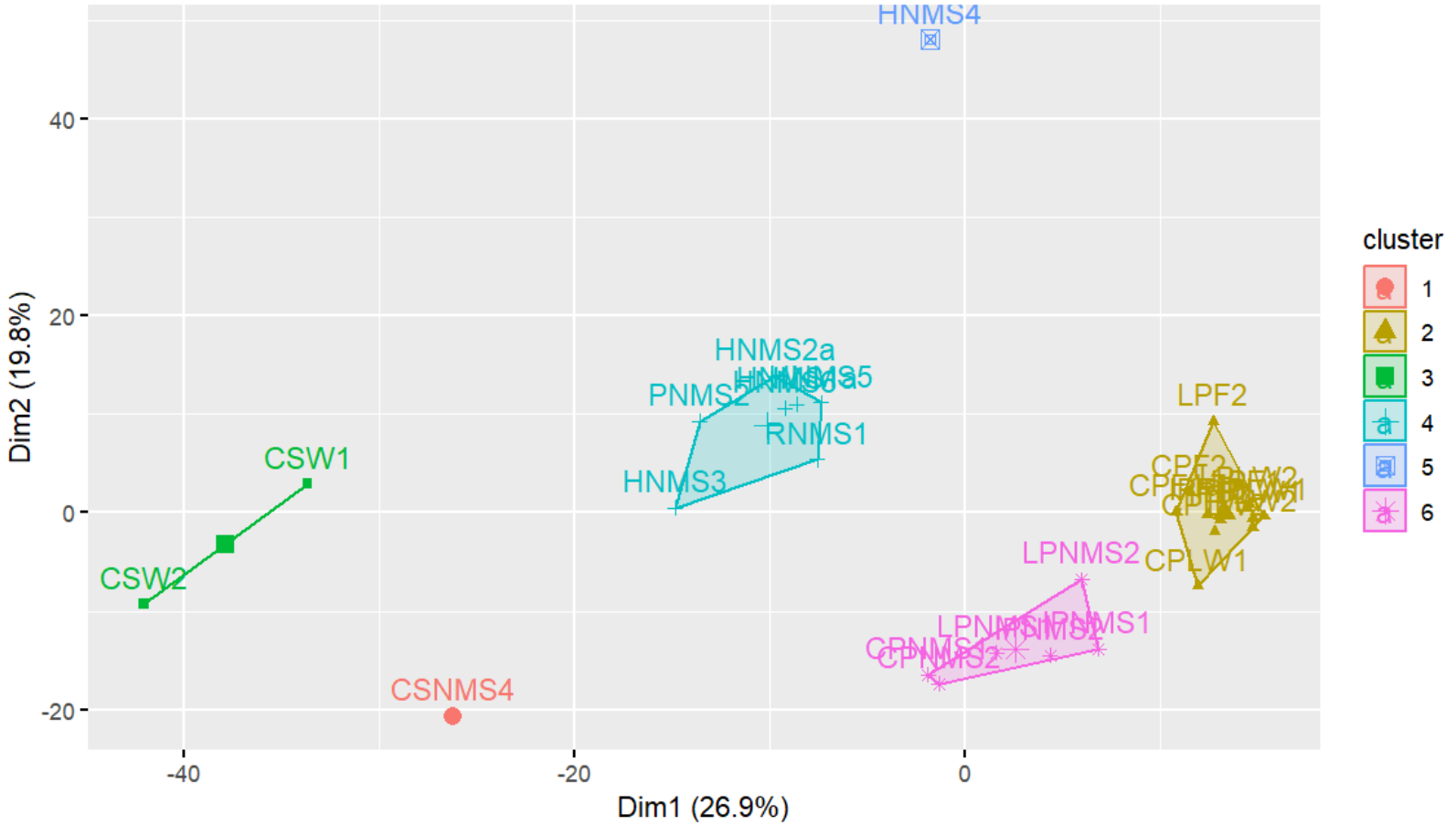
SCG New make spirit aromatic region - ^{1}H NMR



New make spirit comparison – ^{1}H NMR, aromatic region

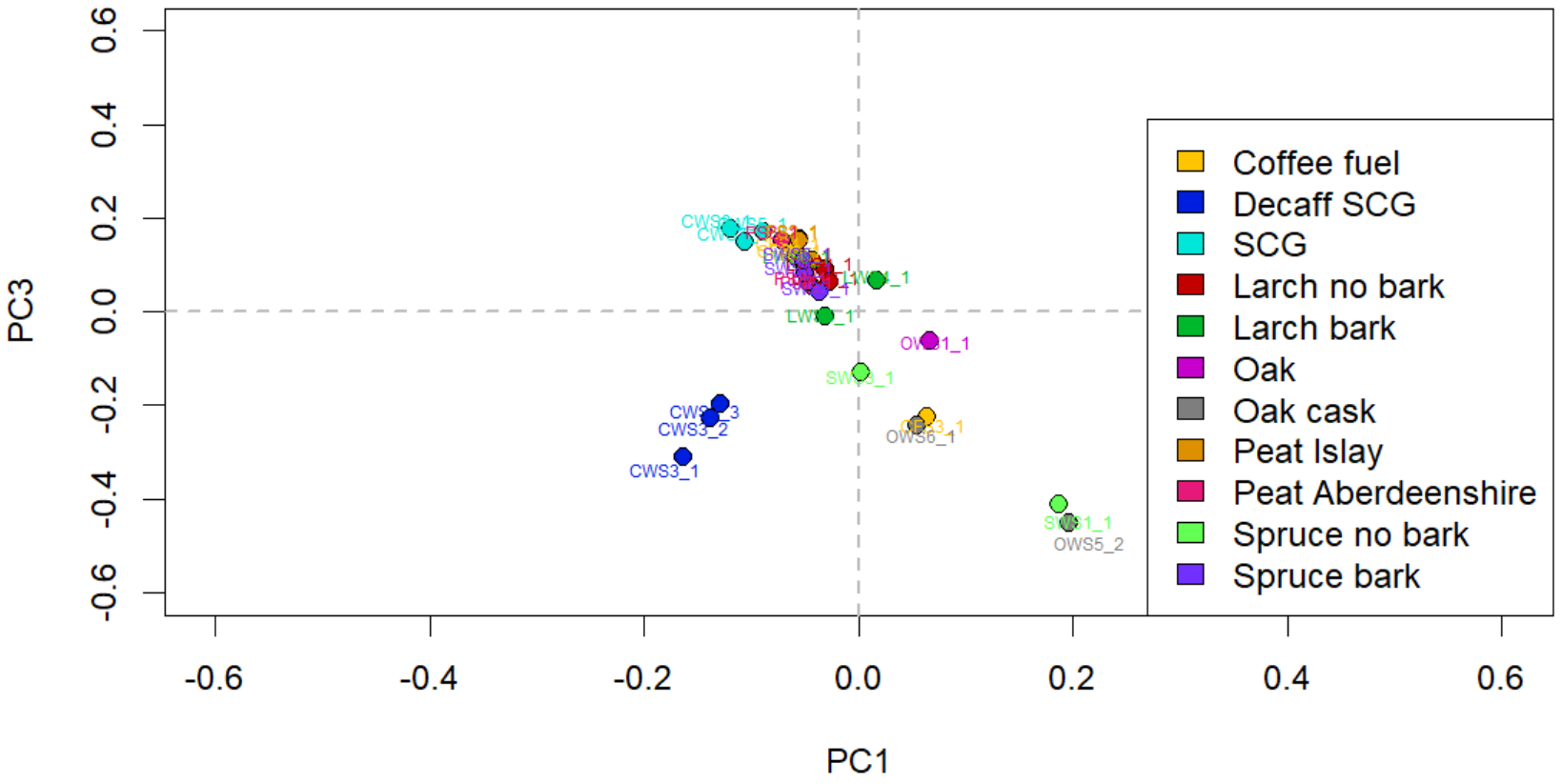


New make spirit comparison – Cluster Analysis



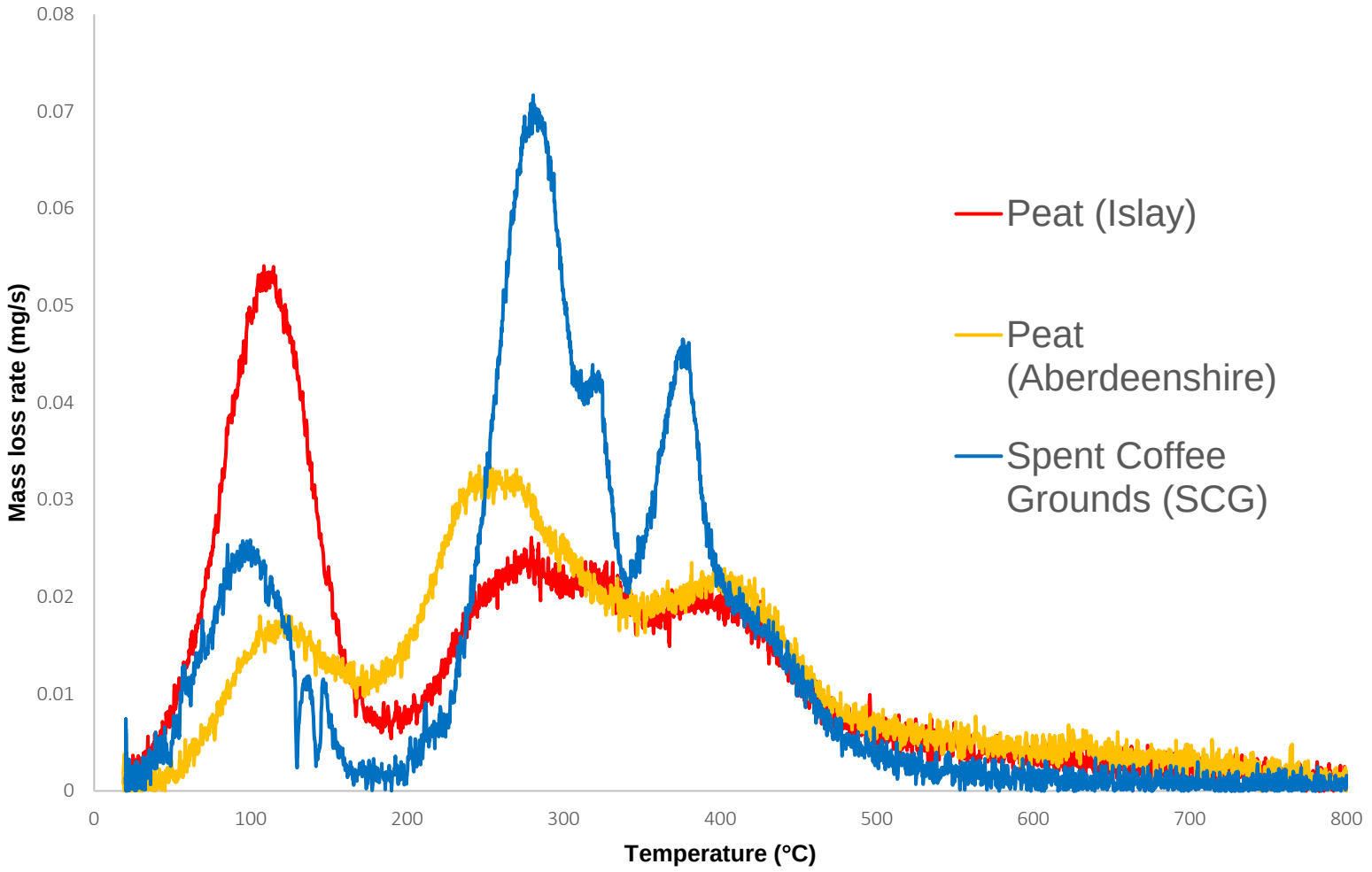
- 29 samples of new make spirits, low wines, feints and whiskies.
- Samples from one distillery grouped into cluster 4.
- New makes spirits smoked in the lab using peat and SCG grouped together in cluster 6.
- All low wines and feints samples grouped together in cluster 2.
- Source of smoke appears to have less effect on the composition than stage of distillation or distillery.
- Whisky samples clearly separated.
- Two samples (CSNMS4, HNMS4) are clear outliers.

Smoke comparison – Principal Component Analysis



- 29 samples of methanol smoke solutions.
- Difference between samples of peat from different locations is small.
- Several materials produce smoke with composition remarkably similar to that of peat.
- Some materials show large variation within a set of three samples, including oak cask wood and spruce heartwood.
- SCG smoke samples show little difference from peat smoke, while decaffeinated SCG smoke appears notably different, which may suggest that origin of the coffee grounds is an important consideration.

Thermogravimetric Analysis



Peak	Temp. (°C)	Mass loss (%)	Compound
PI 1	285	17.0	Hemicellulose (225-325 °C)
PI 2	325	11.3	Cellulose (290-350 °C)
PI 3	400	28.3	Lignin (200-400 °C)
PA 1	265	26.3	Hemicellulose, cellulose
PA 2	400	24.3	Lignin
SCG 1	285	32.7	Hemicellulose
SCG 2	325	7.1	Cellulose
SCG 3	380	23.9	Lignin

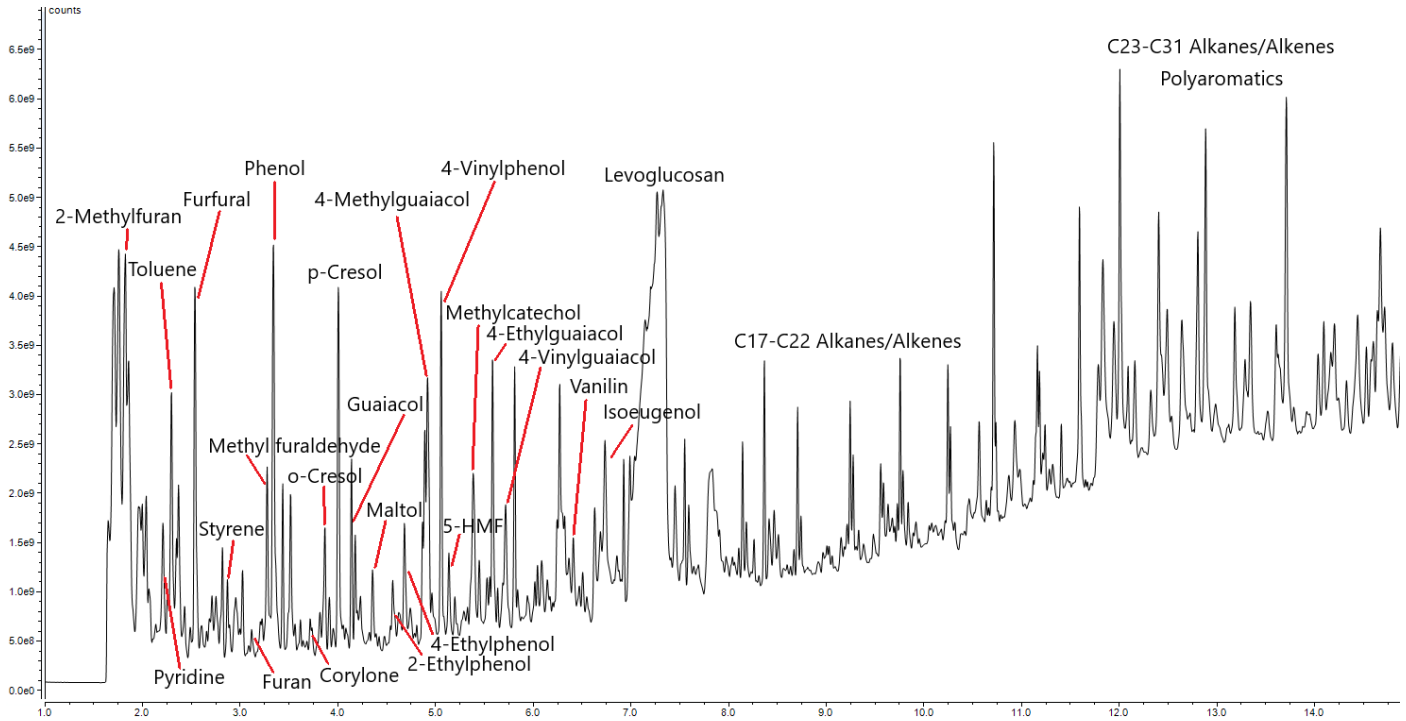
C. Di Blasi, *Prog, Energy Combust, Sci.*, 2008, **34**, 47-90.
D. K. Shen and S. Gu, *Bioresour. Technol.*, 2009, **100**, 6496-6504.
M. Asmadi, H. Kawamoto and S. Saka, *J. Anal. and Appl. Pyrolysis*, 2011, **92**, 417-425.

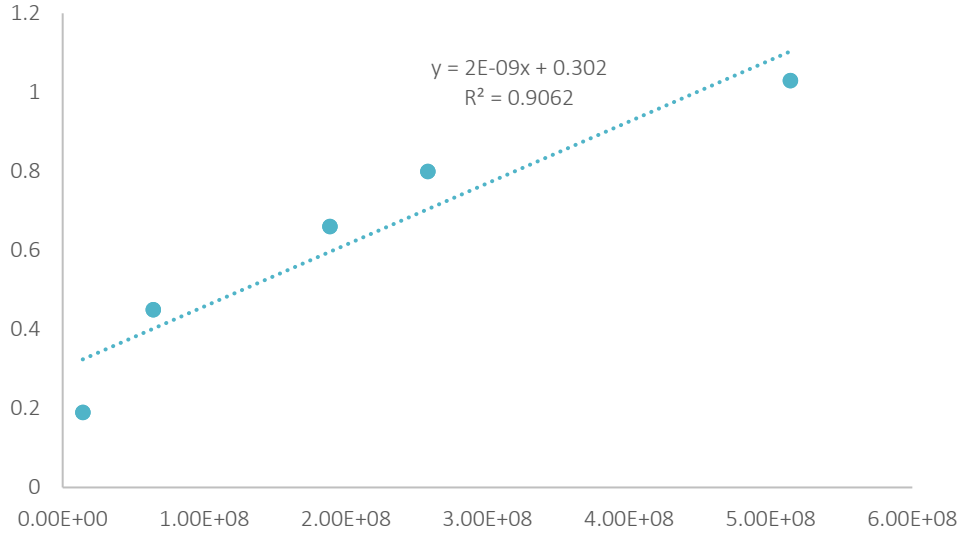
Pyrolysis – Gas Chromatography – Mass Spectrometry

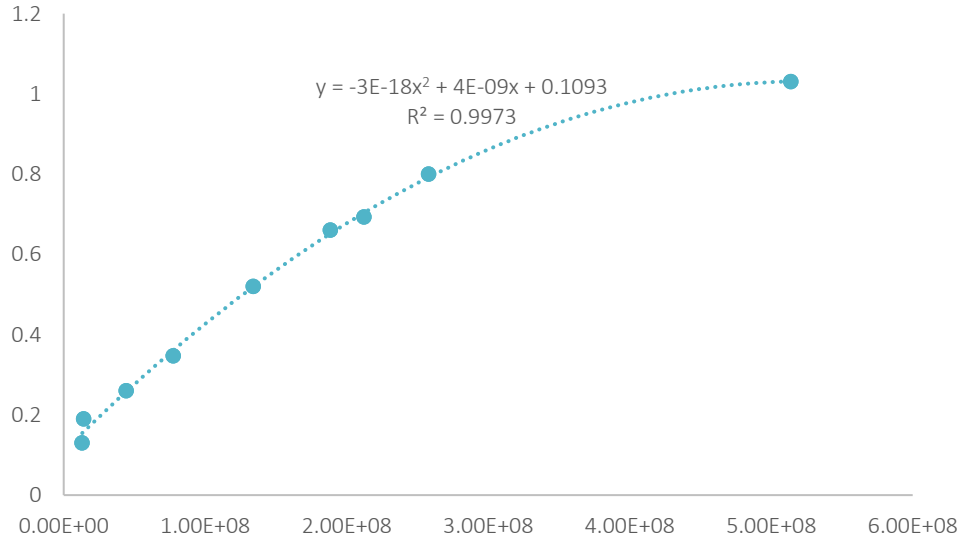
- Samples heated to 650 °C under N_2 atmosphere.

- 9 points calibration curve constructed using trans-Ferulic Acid as reference compound.

- Successful quantitation of 18 phenolic products of peat pyrolysis.







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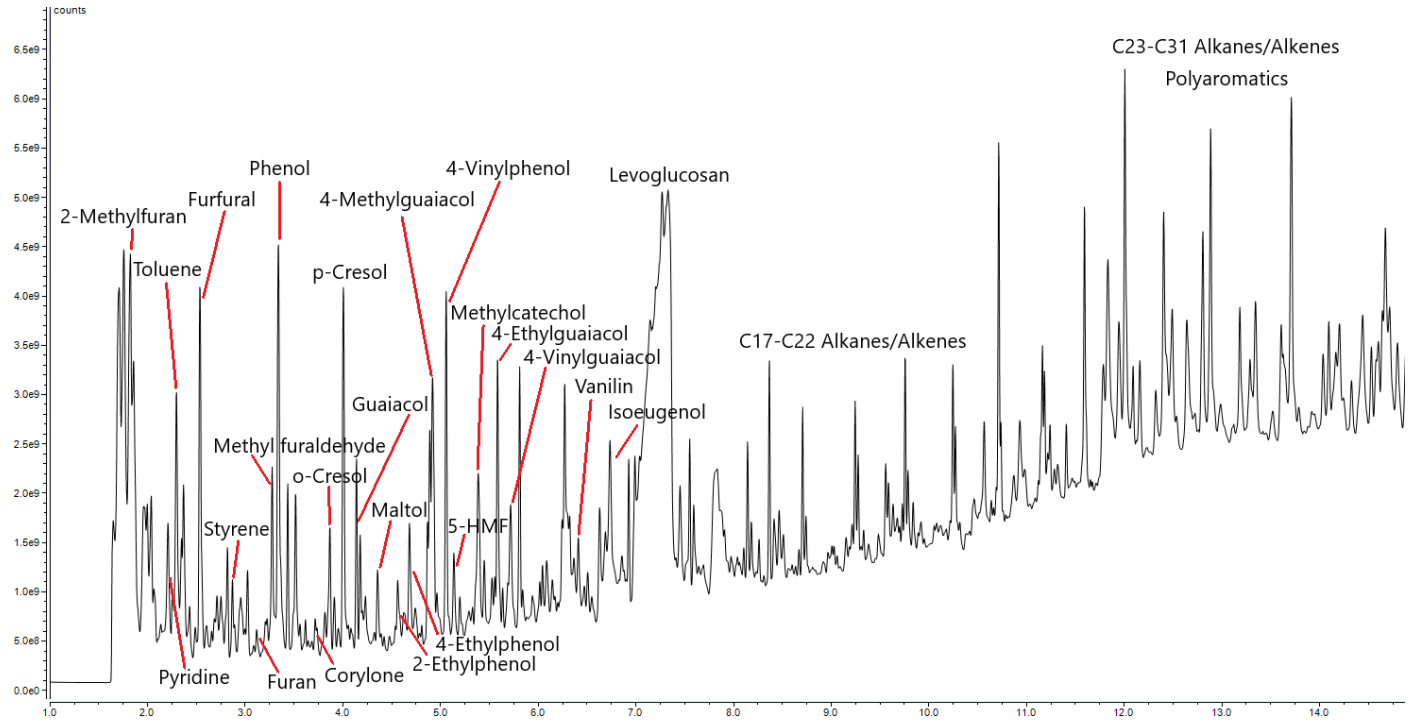

Compound	µg compound/mg peat
trans-Ferulic Acid	0.202 ± 0.016
Toluene	0.309 ± 0.009
Styrene	0.168 ± 0.004
Phenol	0.464 ± 0.017
o-Cresol	0.213 ± 0.004
p-Cresol	0.354 ± 0.015
Guaiacol	0.187 ± 0.002
2-Ethylphenol	0.175 ± 0.041
2,4-Xylenol	0.204 ± 0.011
4-Ethylphenol	0.235 ± 0.031
4-Methylguaiacol	0.316 ± 0.031
4-Vinylphenol	0.350 ± 0.033
4-Methylcatechol	0.338 ± 0.005
4-Ethylguaiacol	0.156 ± 0.004
4-Vinylguiacol	0.297 ± 0.006
Vanillin	0.233 ± 0.006

Conclusions

- Same biopolymers in SCG, wood and peat, different proportions.

- SCG smoke contains flavour congeners but also undesirable pyridine compounds.

- Higher levels of phenolics in peat, compared to alternative materials, which have more furans and carbonyls.

Future work

- Extend Py-GC-MS quantitation.

- Produce and analyse new make spirits using malt smoked using alternative materials.

- Acquire more NMR spectra to improve the statistical models.

- Search for other alternative materials.

Thank you for listening

Acknowledgements:

Dr David Ellis, Dr Ruaraidh McIntosh

Carnegie Trust for Universities of Scotland

Scotch Whisky Research Institute

Dr Clayton Magill

NMR group at University of Edinburgh

EPSRC

Everyone in lab WP3.23