School of Earth and Environment
INSTITUTE FOR CLIMATE AND ATMOSPHERIC SCIENCE

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Analysis of Soot Produced on Combustion of Biomass

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An introduction to my research

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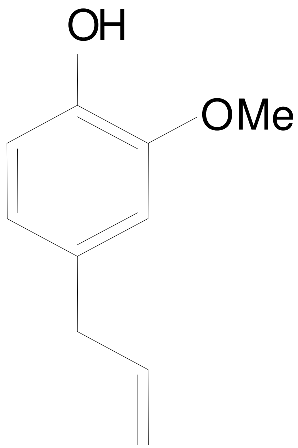
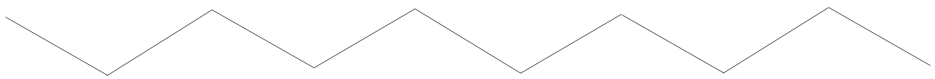
Objectives

- Determine composition of particles generated in the combustion of conventional fuels and biomass
- Determine composition of particles generated through oxidation of combustion products by ozone



Eugenol



Decane

Why investigate biomass soot?

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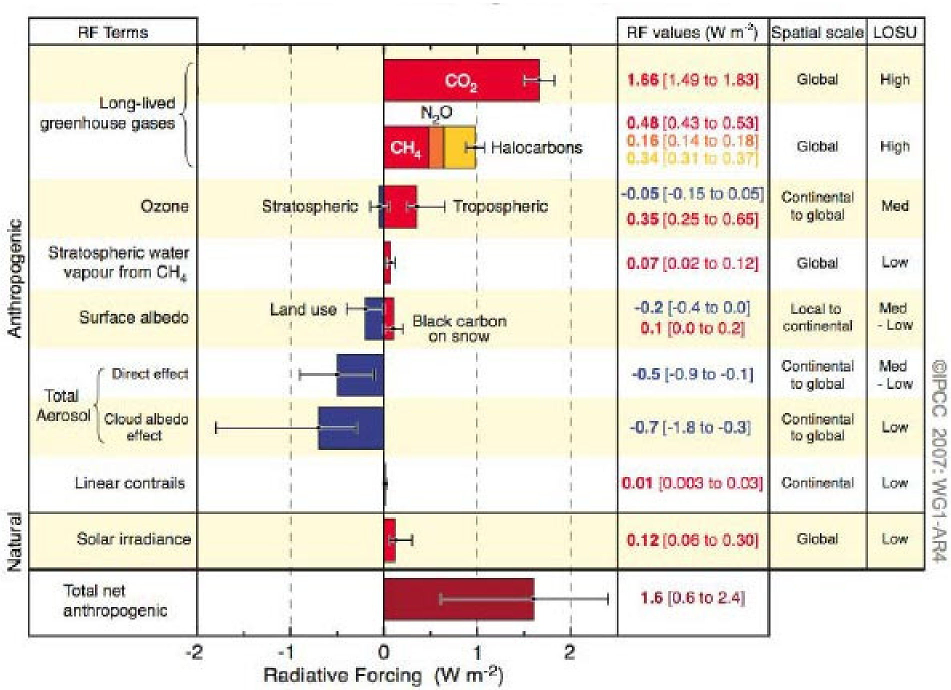
- Biomass smoke and associated black carbon has huge implications for atmospheric chemistry
- Climate effects



IPCC report 2007

- Conventional soot mechanisms do not fully describe soot formation from biomass.
- The role of oxygenates appears to be important according to previous off-line analysis.
- A new mechanism involving intermediates such as eugenol has been proposed and is to be investigated using an on-line technique - the ATOFMS (Aerosol Time of Flight Mass Spectrometer) (TSI inc).

Collaboration

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- Collaboration with a group from the Energy and Resources Research Institute (ERRI), University of Leeds.

Emma Fitzpatrick

Jenny Jones

Alan Williams

Previous work carried out by them has looked at:

- Pyrolysis GC-MS of pine wood and eugenol
- Surface analysis via Scanning Electron Microscopy (SEM) and X-ray Photoelectron Microscopy (XPS)

OFF-LINE TECHNIQUES

Mechanism from ERRI

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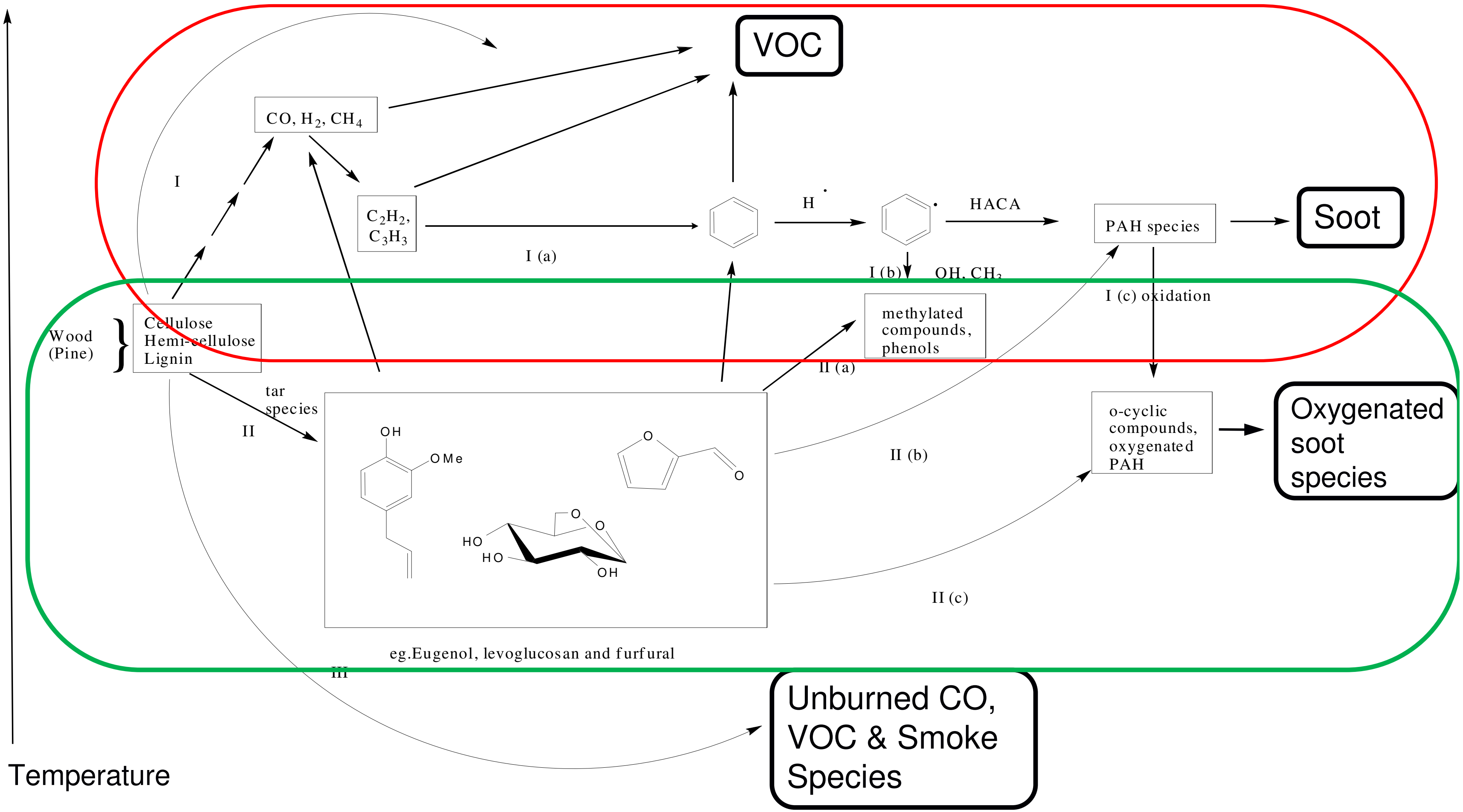

Fitzpatrick, E.M.,et al. 2007 IChemE

Why analyse on-line?

On-line vs. Offline analysis:

- Advantages of off-line analysis
  - Preparation of samples can give reproducible quantitative analysis
  - Electron microscopy techniques give information on particle morphology
- Limitations of off-line analysis
  - Volatile compounds can be lost
  - Chemical transformations due to time lapse between collection and analysis
- Advantages of on-line analysis
  - Minimal chemical modification of particles
  - High temporal resolution
  - Analysis of single particles
- Disadvantages of on-line analysis
  - Are there any ??

The experimental set-up

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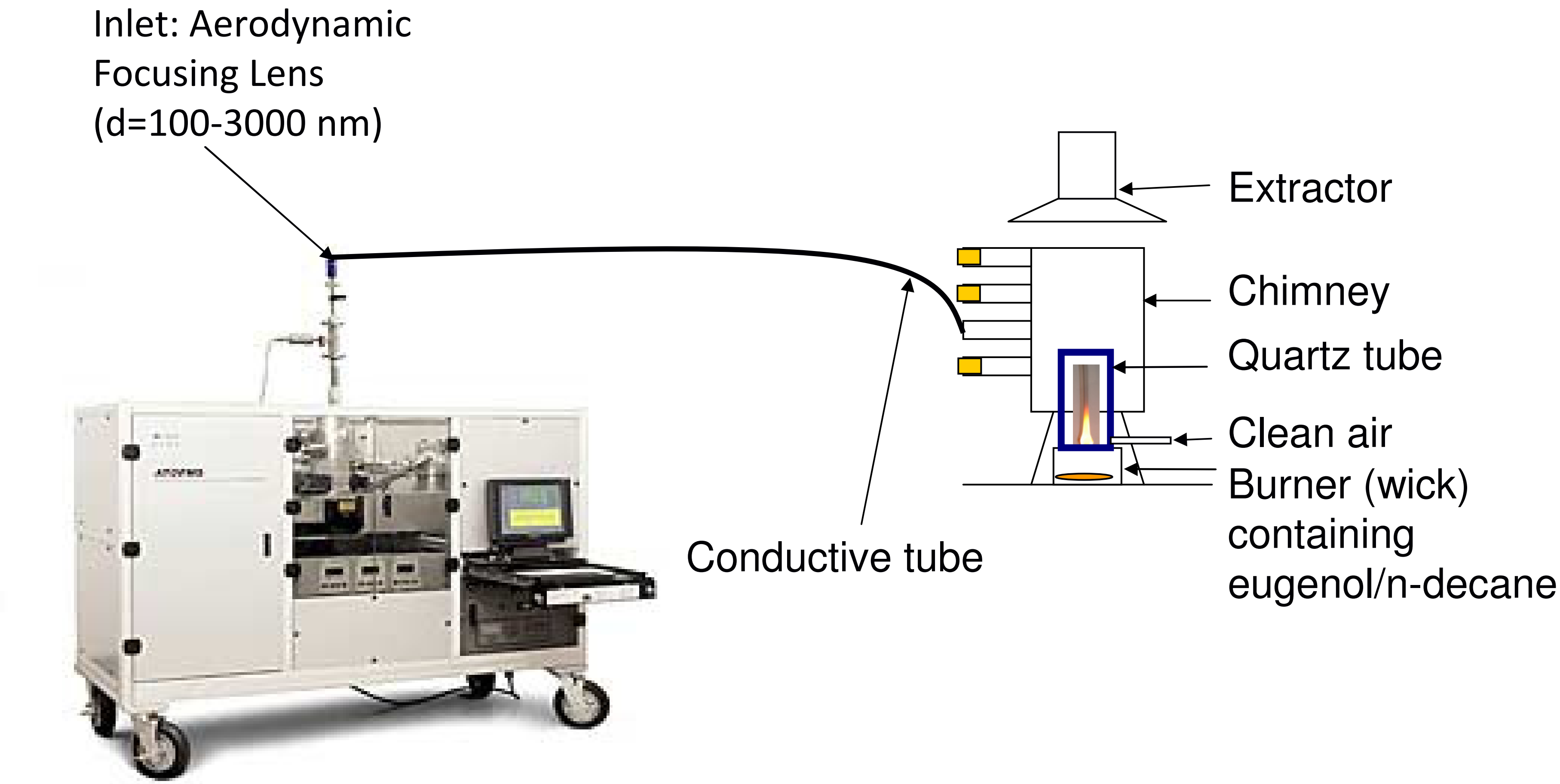

ATOFMS

http://www.tsi.com/Product.aspx?Pid=65

How does the ATOFMS work?

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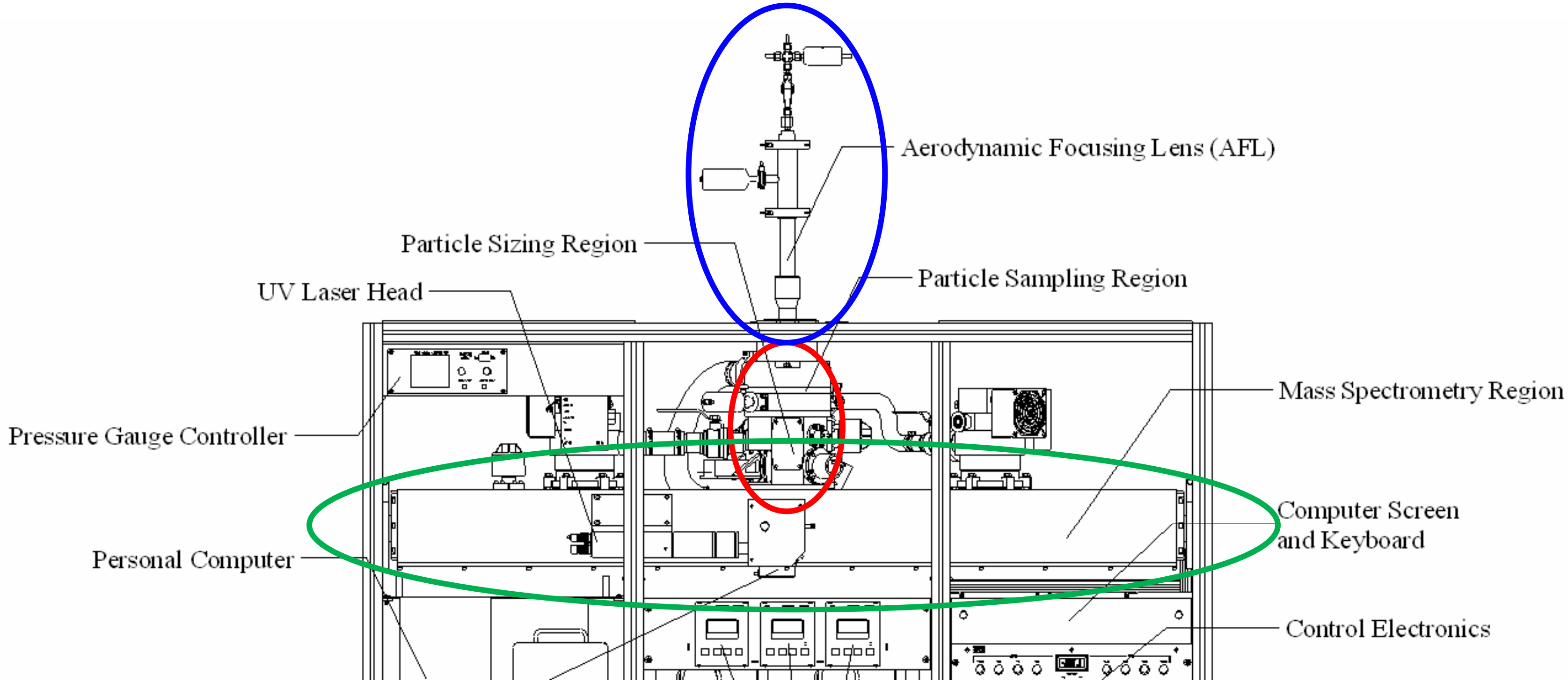
3 regions

- Sampling region
  - Particles introduced at atmospheric pressure then accelerated to terminal velocity
- Sizing region
  - Particle velocity measured by 2 continuous wave laser beams (532 nm)
  - Velocities compared with a calibration curve
- Mass spectrometry region
  - UV laser (266 nm) fired to hit particle at centre of ion source
  - Particle compounds desorbed and ionised
  - Bipolar time-of flight mass spectrometer analyses both positive and negative ions



Taken from Series 3800 Aerosol Time-of-Flight Mass Spectrometers (ATOFMS) with Aerodynamic Focusing Lens Operation and Service Manual *P/N 1930036, Revision C May 2007*

MS-Analyze – What comes out

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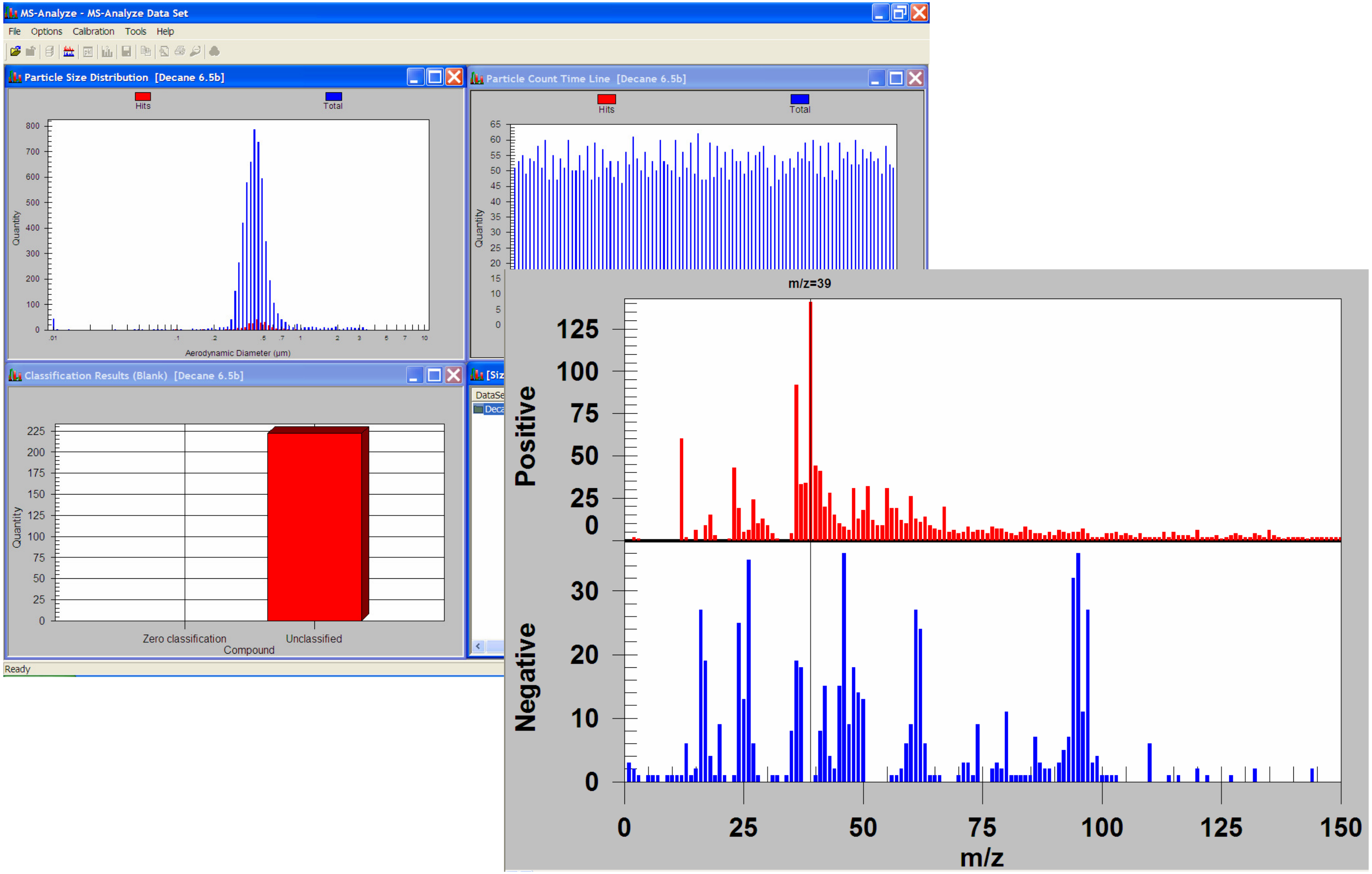
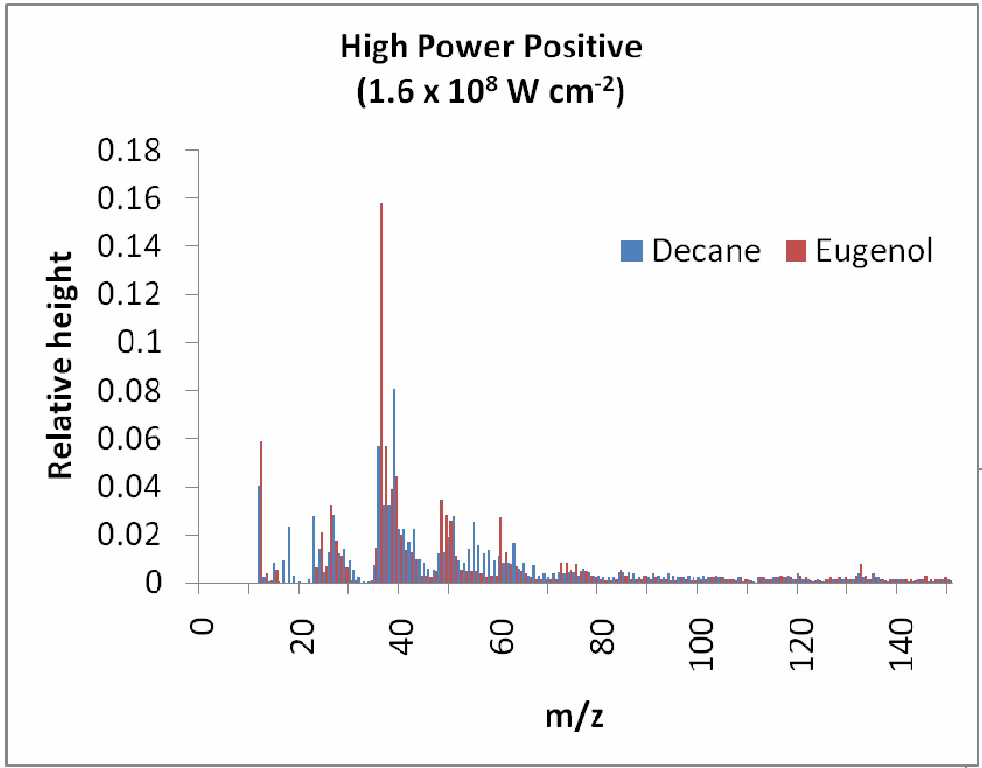
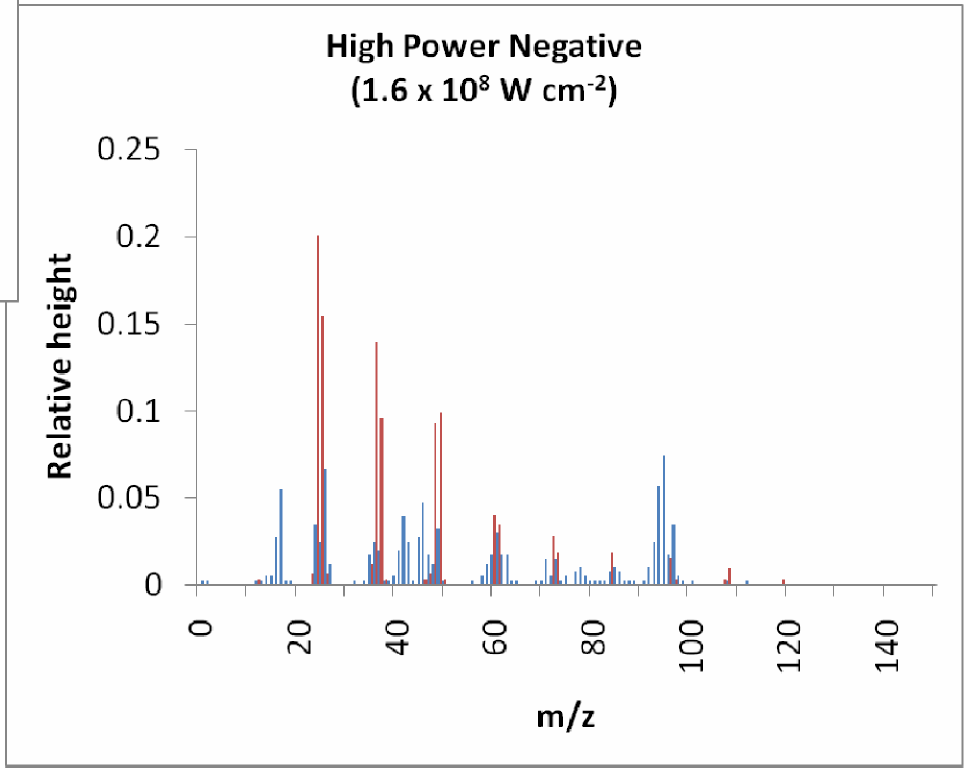


What can we do with this? (1)





What do we do with this? (2)

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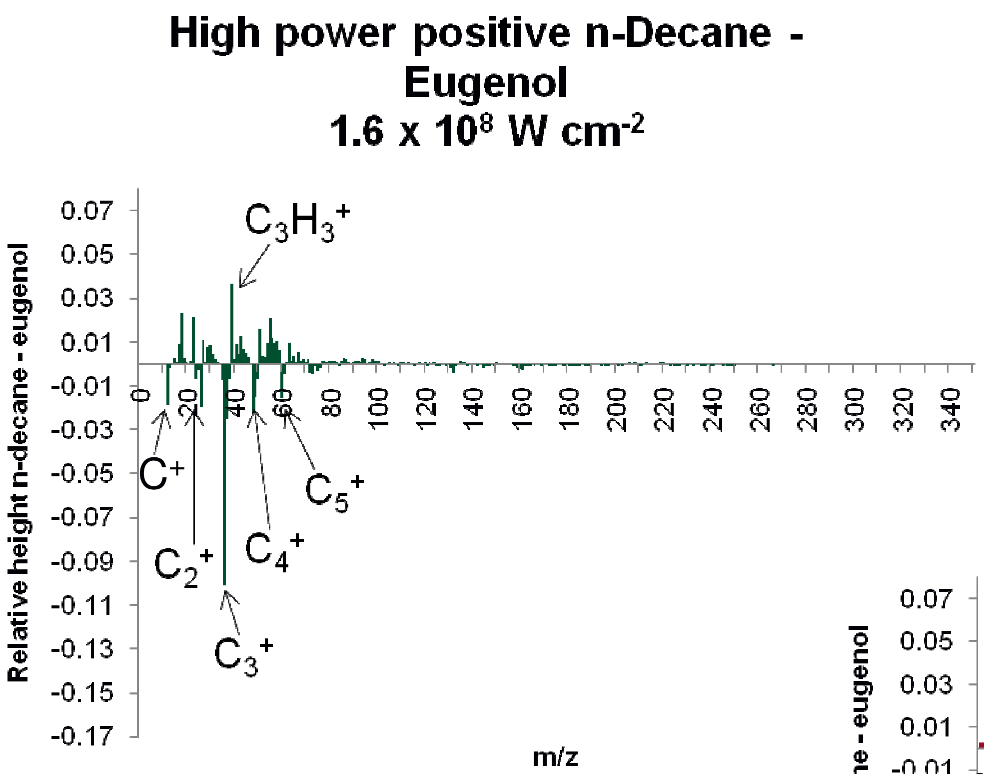

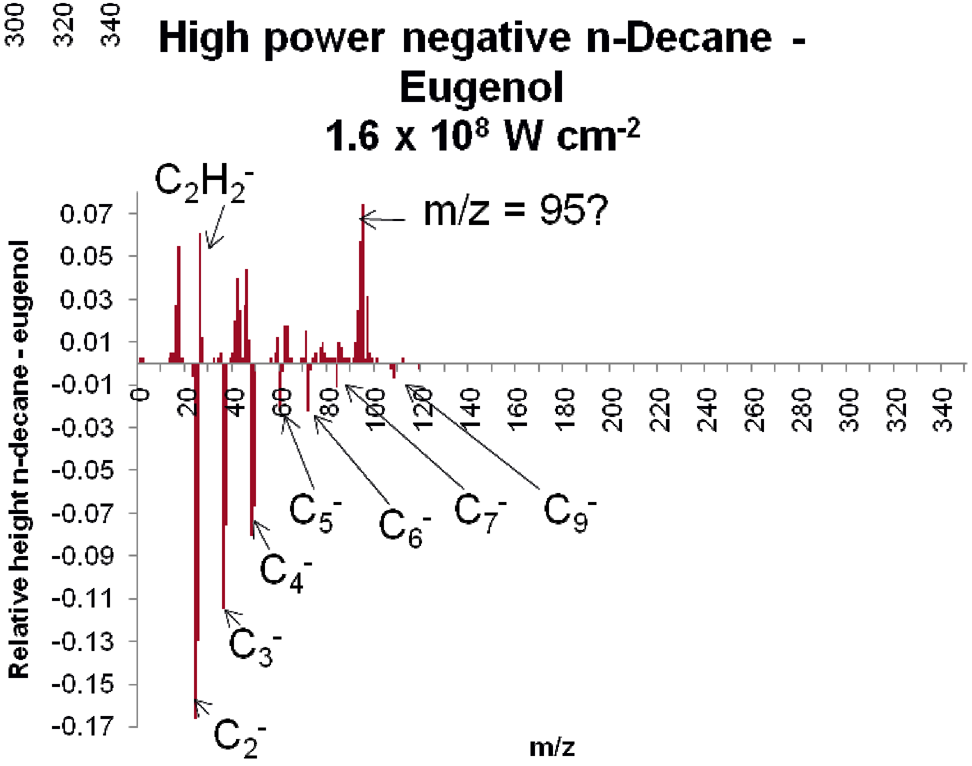

What do we do with this? (3)

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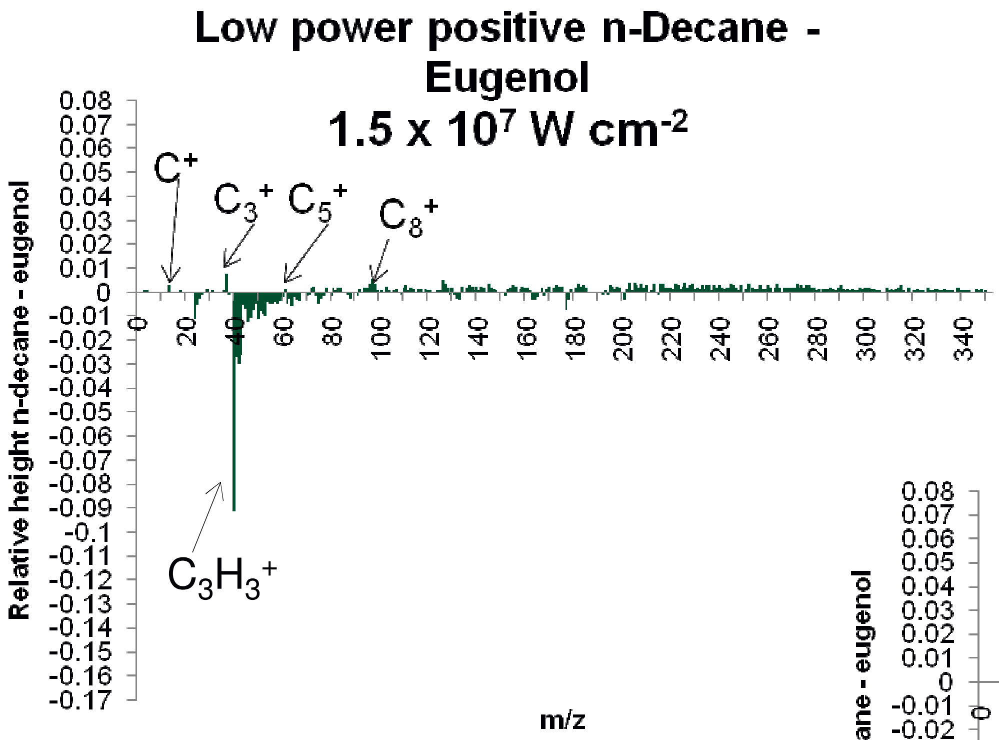

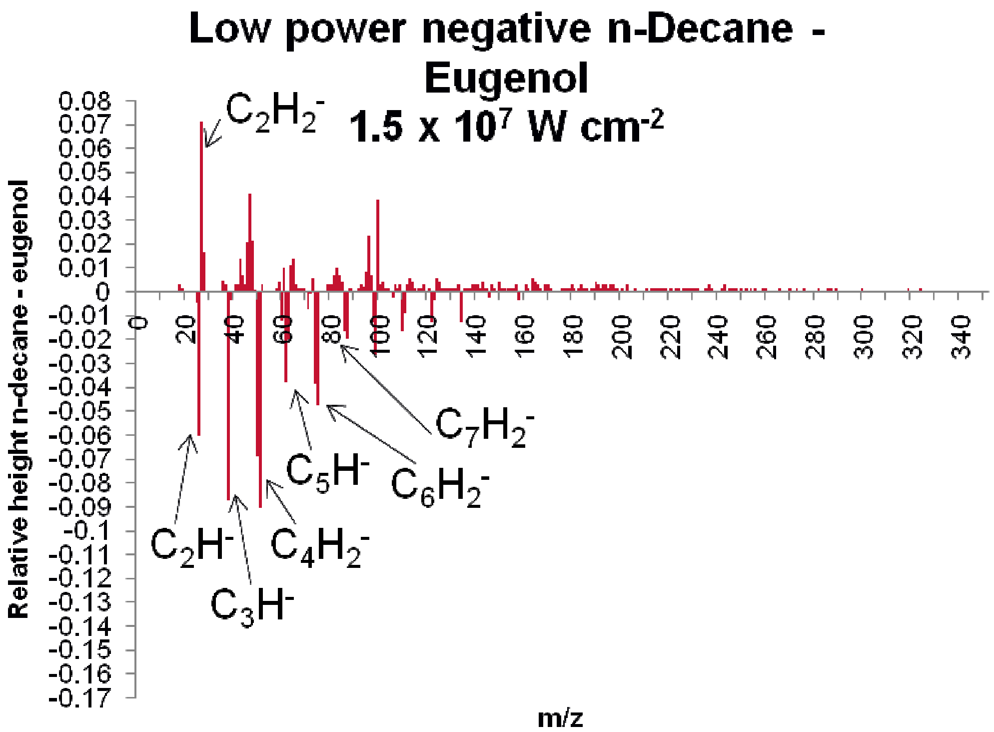

What else can we do?

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Average spectra only tell us about bulk properties. What about individual particles?

- Current problem with size analysis – too many eugenol particles
- CLUSTERING
  - Cannot analyse hundreds or thousands of spectra individually
  - Cannot categorise hundreds or thousands of spectra by eye
  - Need a computer programme to do it for us

Clustering programmes

Two analytical tools available:

- YAADA
  - http://www.yaada.org/
  - Developed by Jonathan Allen, Arizona State University
  - Runs in MatLab
  - Clusters using ART-2a algorithm

- Enchilada (Environmental Chemistry through Intelligent Atmospheric Data Analysis)
  - http://www.cs.carleton.edu/enchilada/
  - Open source, written in Java
  - Three clustering algorithms available
    - ART-2a
    - K-means
    - K-medians

Clustering with Enchilada

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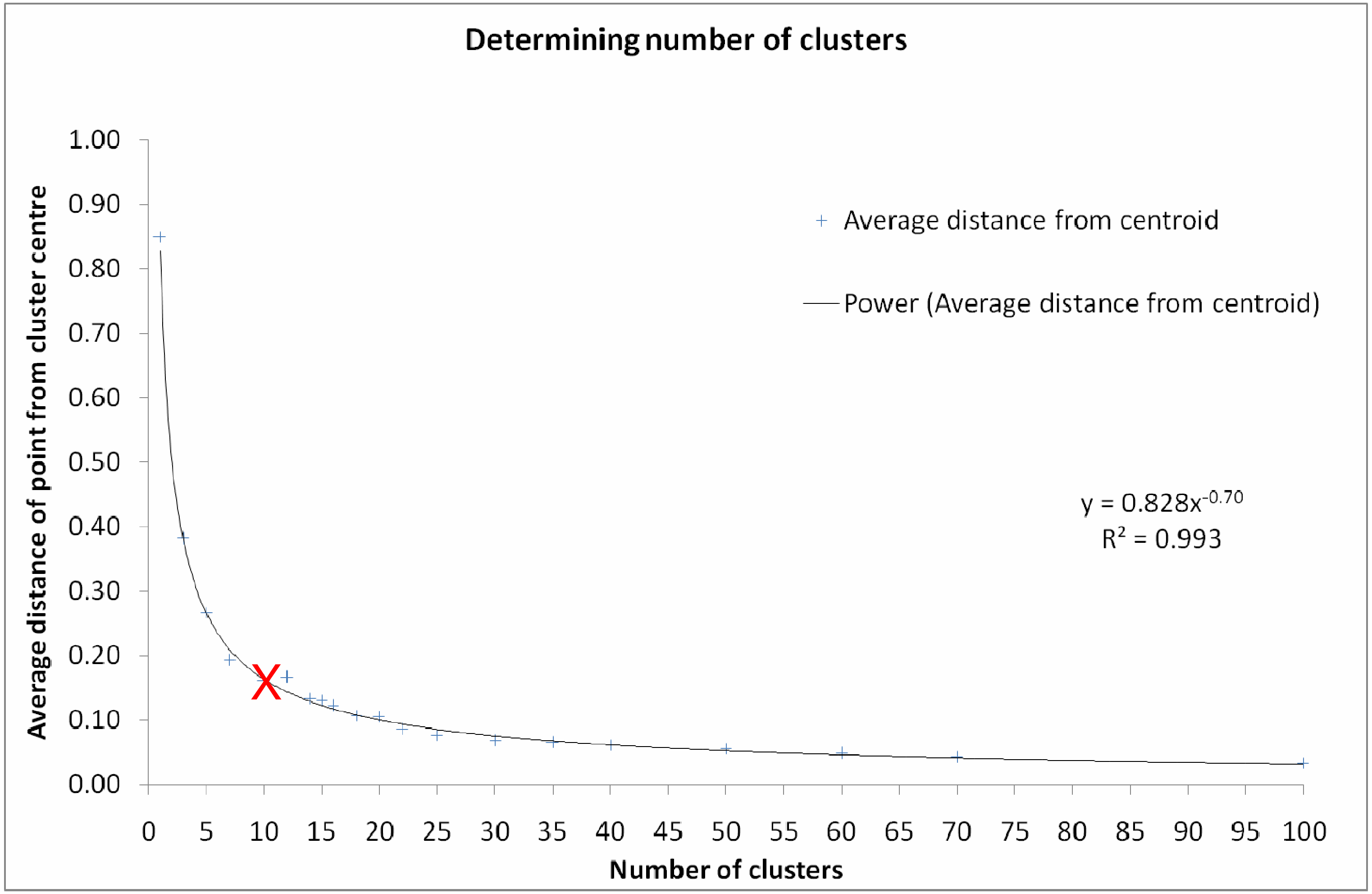
Clustering data using K-means needs:

- A user defined number of clusters

Method of finding number of clusters:

- Try clustering with different numbers of clusters
- Plot 'average distance of all points from their centers on final assignment' against number of clusters



Need to decide where the ‘elbow region’ is – when increasing the number of clusters no longer significantly improves the analysis

Decided on 10 clusters here

Cluster analysis

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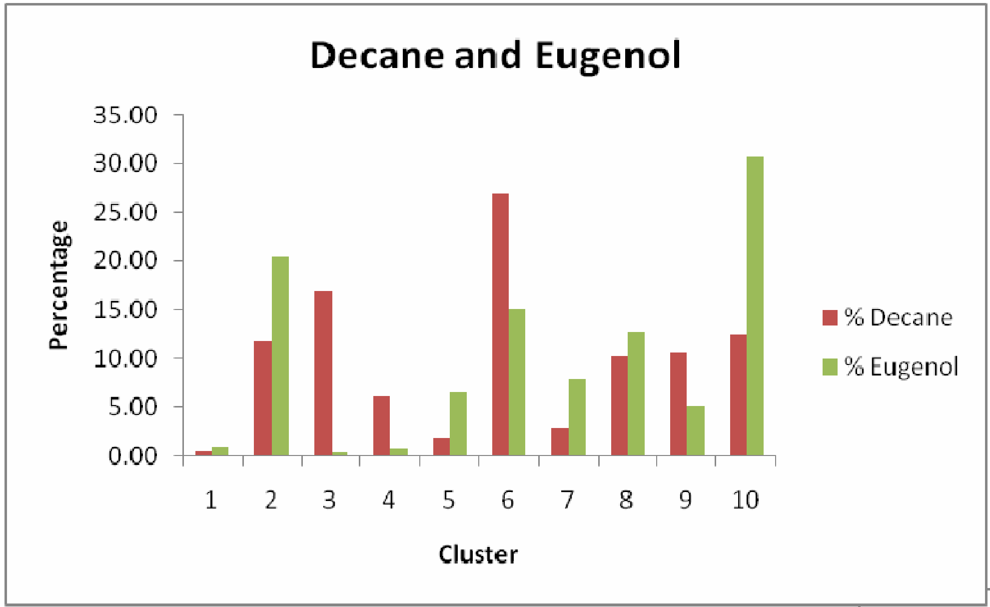


Clusters 3 and 4 mainly n-decane

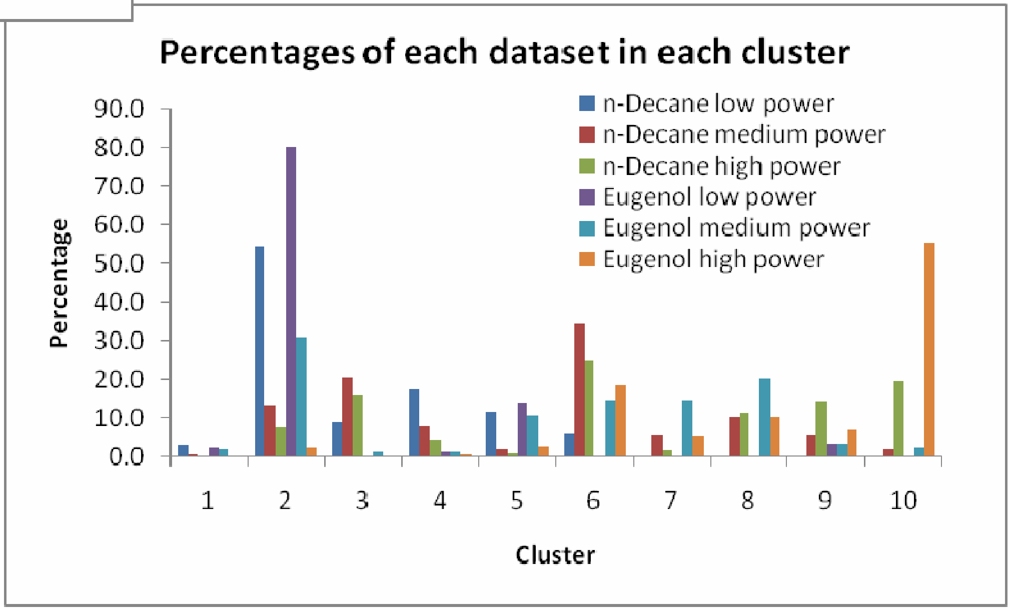
Clusters 5 and 10 mainly eugenol

Cluster 2 – low power

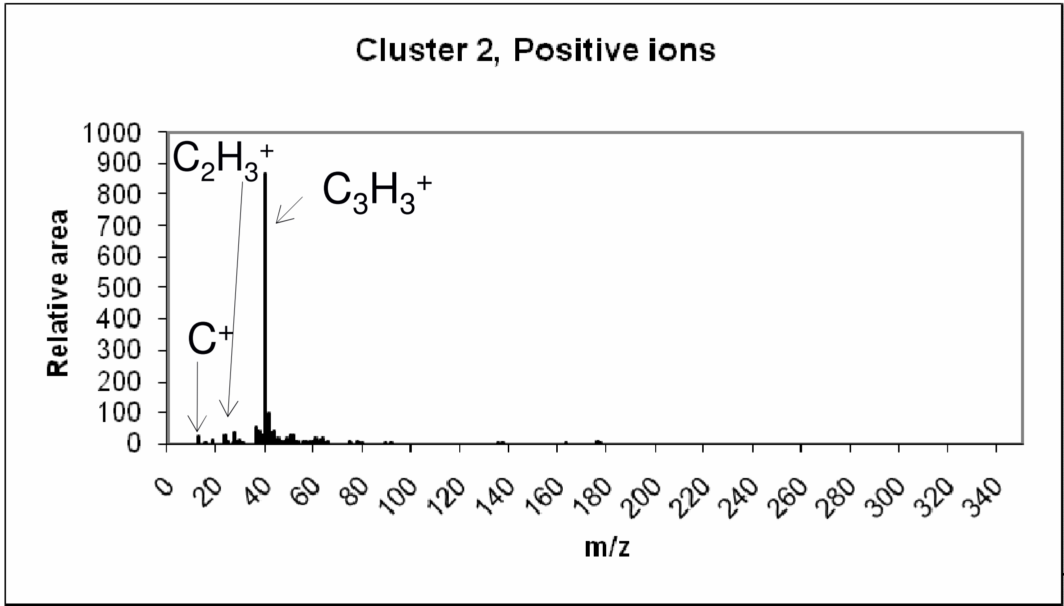
Cluster 7 – medium power

Cluster 8 – medium to high power

Cluster 10 – high power



Cluster 2 – low powers



Positive spectra more intense than negative

+39 $C_3H_3^+$

Building block of C_6H_6 and C_5 rings

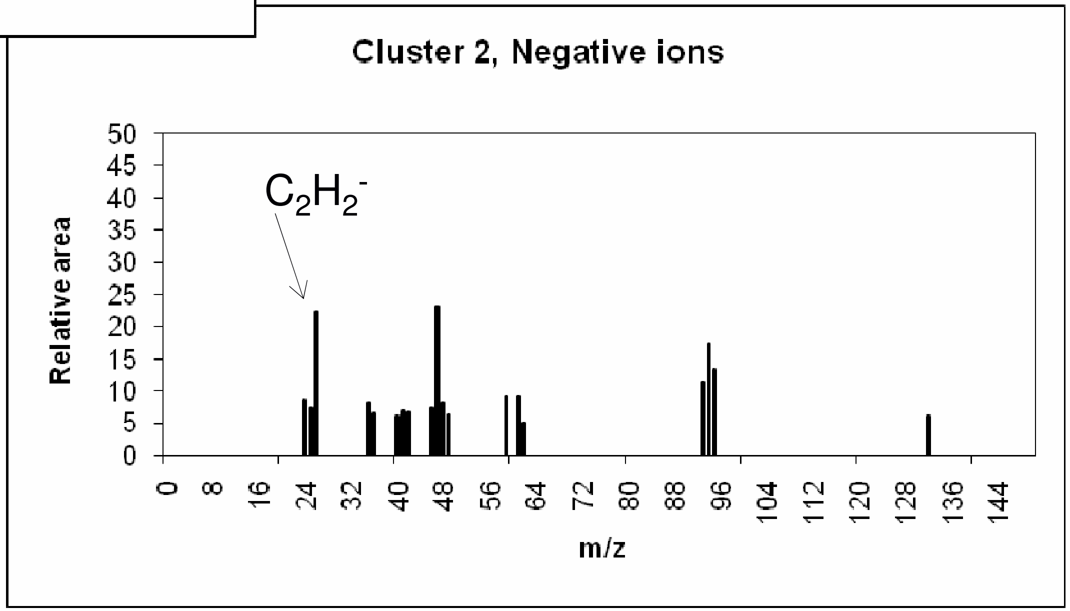
-26 $C_2H_2^-$

Building block of aromatic rings

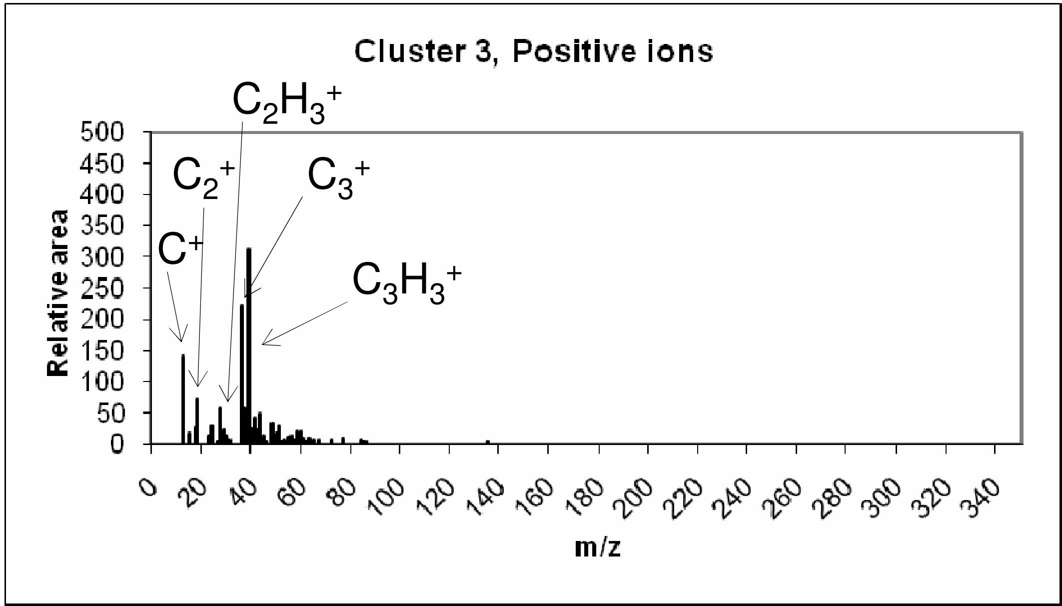
-47?

-94?

-132 C_{11}^-?



Cluster 3 – n-Decane



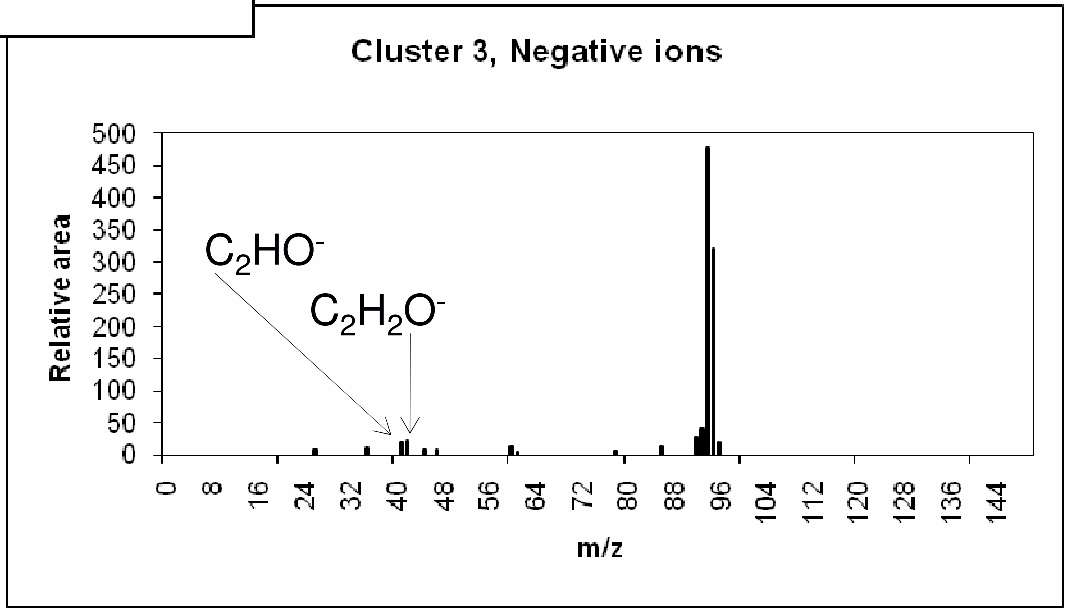
+39 $C_3H_3^+$

Building block of C_6H_6 and C_5 rings

$(-93\ C_6H_5O^-)$

-94?

-95?



Cluster 7 – medium power (mainly eugenol)

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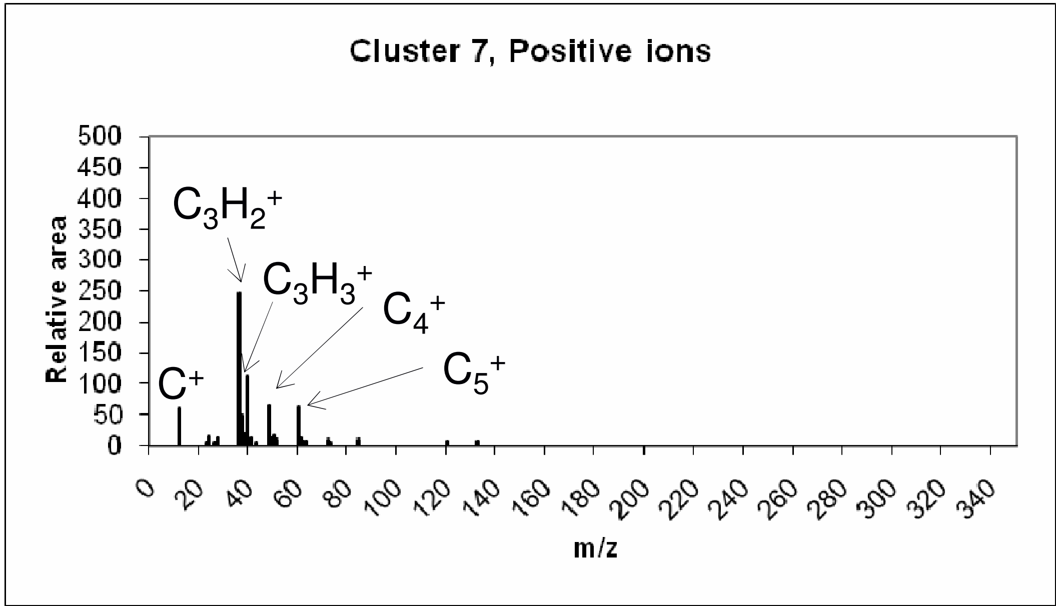
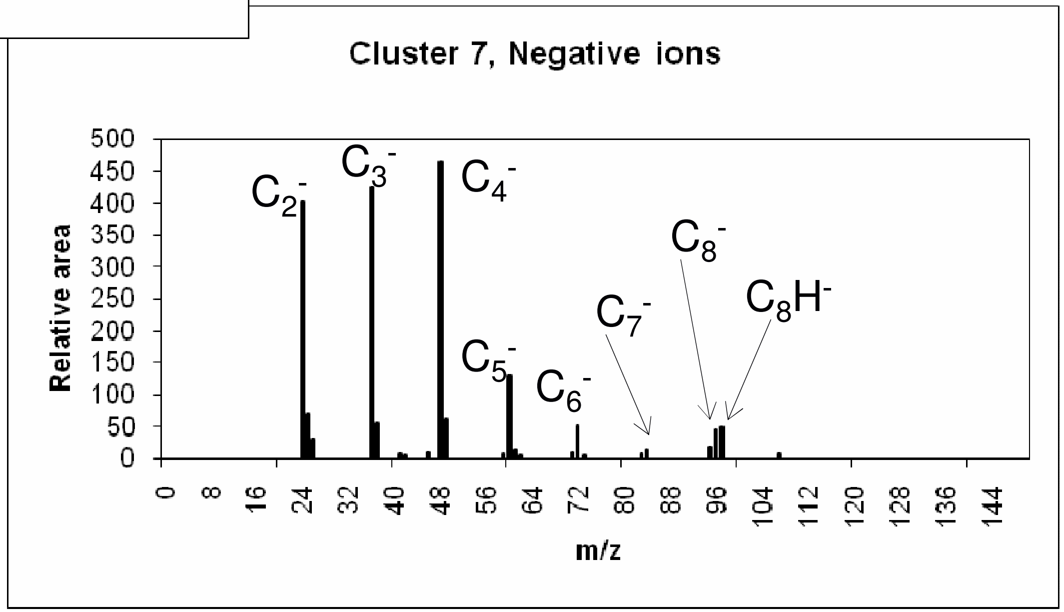
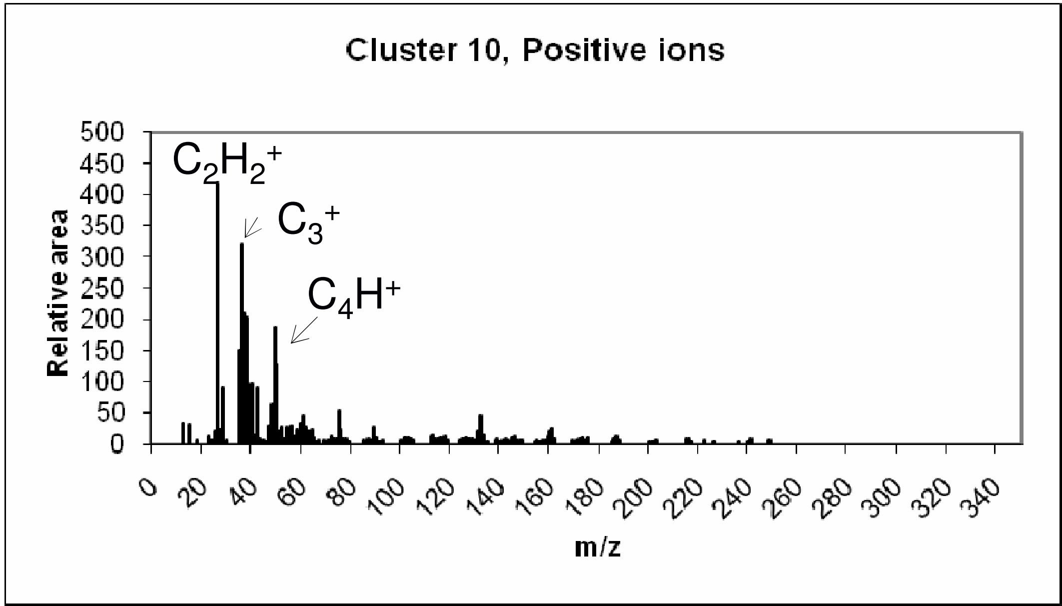


Principally C_n^+

C_n^-

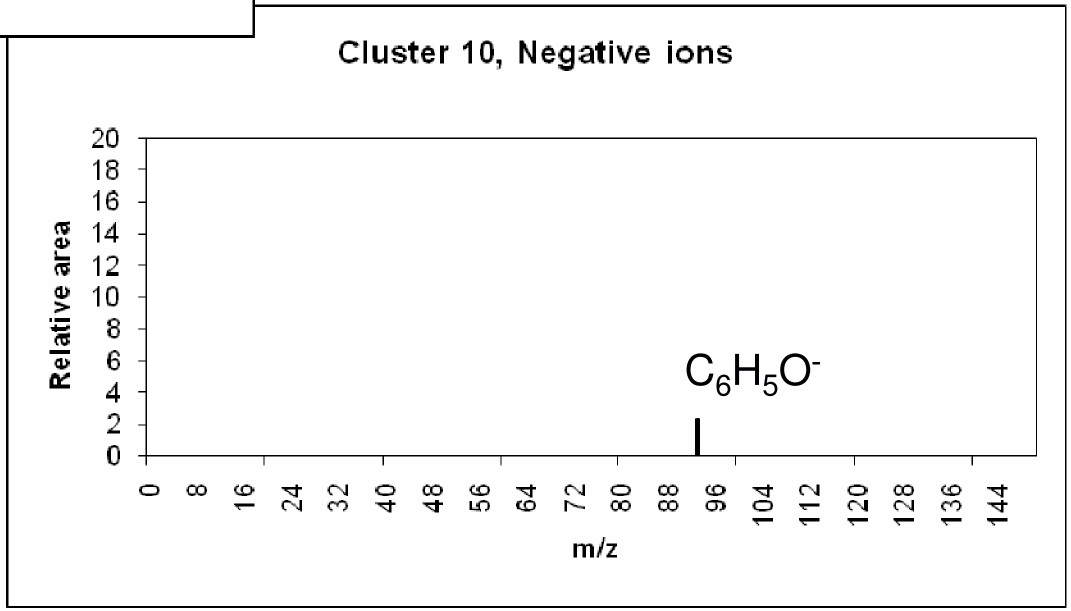


Cluster 10 – high power



Small intensity peaks at high values of m/z up to m/z = 249

-93 $C_6H_5O^-$
Very low intensity



Summary

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Experimental observations:

- More particles produced on combustion of eugenol

Data analysis:

- At high powers eugenol contains C_n^+ and C_n^-
- At high powers n-decane contains $C_3H_3^+$ and $C_2H_2^-$, the building blocks of aromatic rings
- At low powers eugenol appears to contain $C_3H_3^+$ while decane contains C_n^+
- At low powers n-decane still contains $C_2H_2^-$ but eugenol appears to contain C_nH^- and $C_nH_2^-$ (not $C_2H_2^-$)
- Low intensity peaks seen at much higher m/z values at low power but difficult to find peaks that stand out for analysis

Future improvements to experiments

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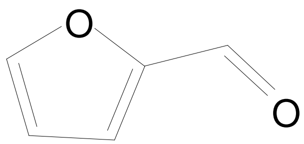
- Analysis of "clean" air – zero air generator vs. compressor and filters
- Better set-up of ATOFMS – alignment and calibration (User improvement!)

to improve sensitivity

- Use of other fuels in burners – both biomass based and traditional fuels
  - Octane/hexane
  - Furfural



- New inlet (30-300 nm)
- Reduce the number of particles to get better information on the relationship

between particle size and composition

- Repetition and further analysis – statistics!

Further future experiments

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- Once experiments to analyse particles produced on combustion of biomass and traditional fuels are completed satisfactorily I intend to move on to analysing the result when combustion products are oxidised by ozone

- This will utilise the environmental chamber at the University of Leeds
    - Temperature controllable from -60 to +40℃
    - Intend to set up a smog chamber inside using a Teflon reactor within which combustion particles can be resuspended
    - UV lamps to initiate reaction by forming O_3

3 take home messages

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1. Organic aerosols produced on combustion of fuels depend on many conditions e.g. temperature, fuel levels, air/fuel ratios

2. Differences in composition between fossil fuel and biomass combustion particles could mean important differences in their properties and effect on health

3. Analysis of ATOFMS data can release important information at the single particle level but is not necessarily easy to get out

THANK YOU

AND

ANY QUESTIONS?

EPSRC Engineering and Physical Sciences Research Council