X-Ray Photoelectron Spectroscopy (XPS) Applied to Soot & What It Can Do for You

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USRA **The U.S. EPA**

Acknowledgements:

1. Former funding through NASA NRA 99-HEDs-01 (RVW) and the U.S. EPA
2. Soot samples supplied by the U.S. EPA, Sandia National Labs
3. Vicki Bryg, Patrick Rodgers, Y.L.Chen, David R. Hull and Dr. Chuck Mueller, Sandia National Labs

Results Regarding Soot Nanostructure

Soot Nanostructure: (Definition)

* Soot Nanostructure refers to carbon lamella (layer plane) length, orientation, separation and tortuosity.

* Nanostructure is variable, dependent upon temperature, residence time and fuel identity.

Fringe Analysis Algorithm: (Quantification)

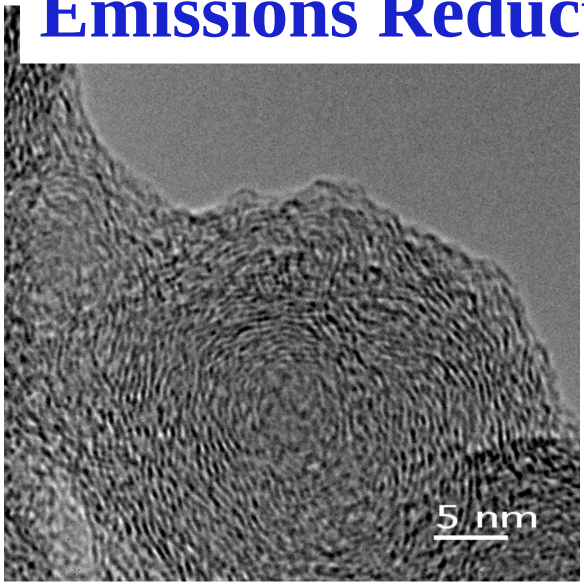
* Lattice fringe analysis can be used to analyze HRTEM image data and quantify carbon nanostructure through statistical analysis.

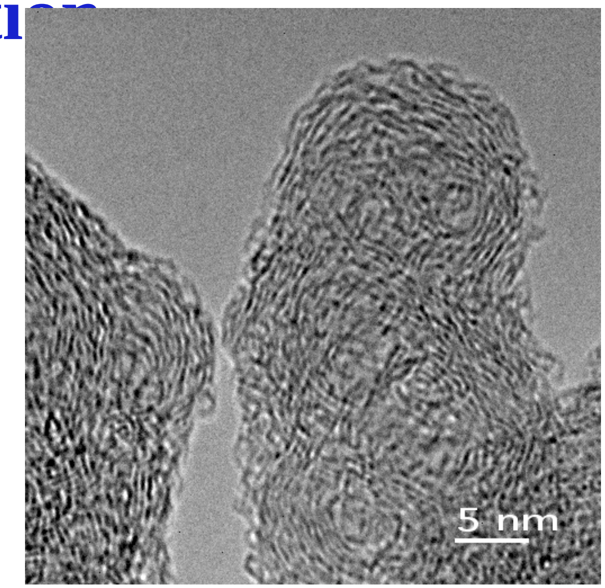
Oxidation Rates: (Implications)

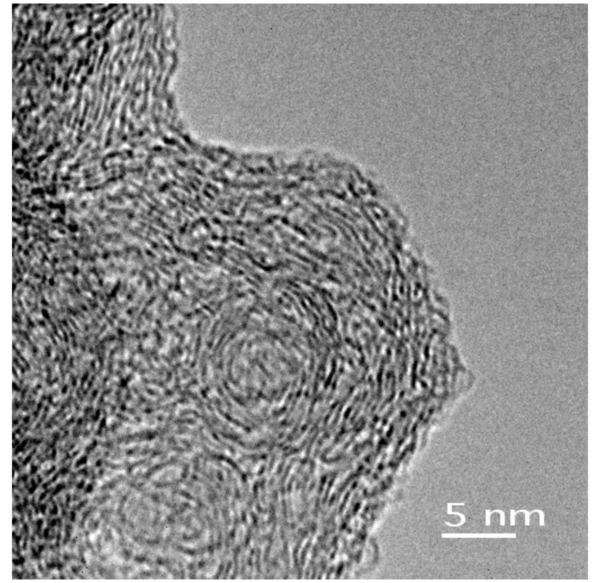
* Oxidation rates are dependent upon nanostructure - suggests using nanostructure to control (accelerate) oxidation.
* Source apportionment via analysis of nanostructure?
* Health consequences related to nanostructure?
* Environmental impact dependent upon nanostructure?

Application I: Emissions Reduction

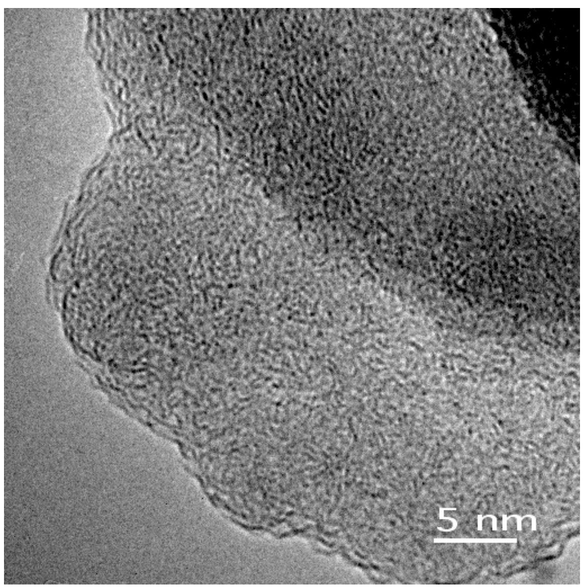
Pure Hydrocarbon

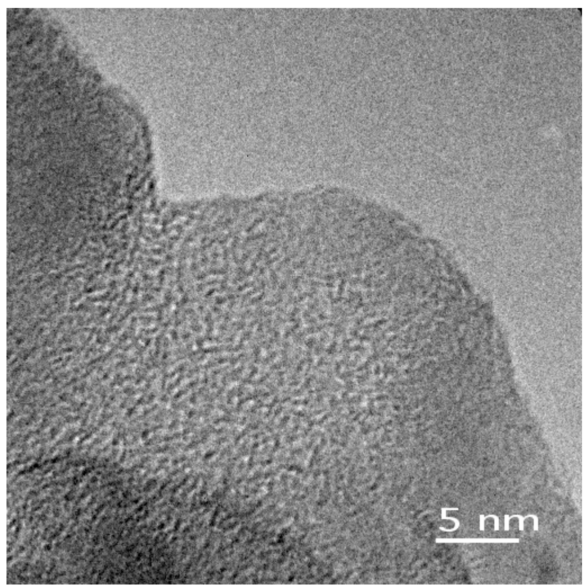


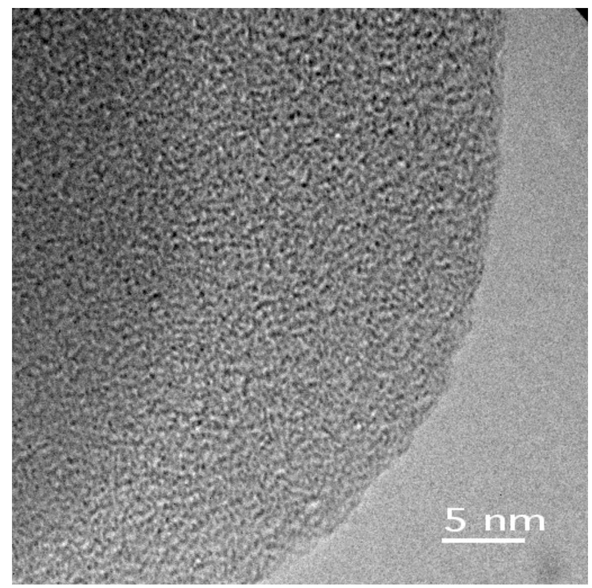




Oxygenated Additive

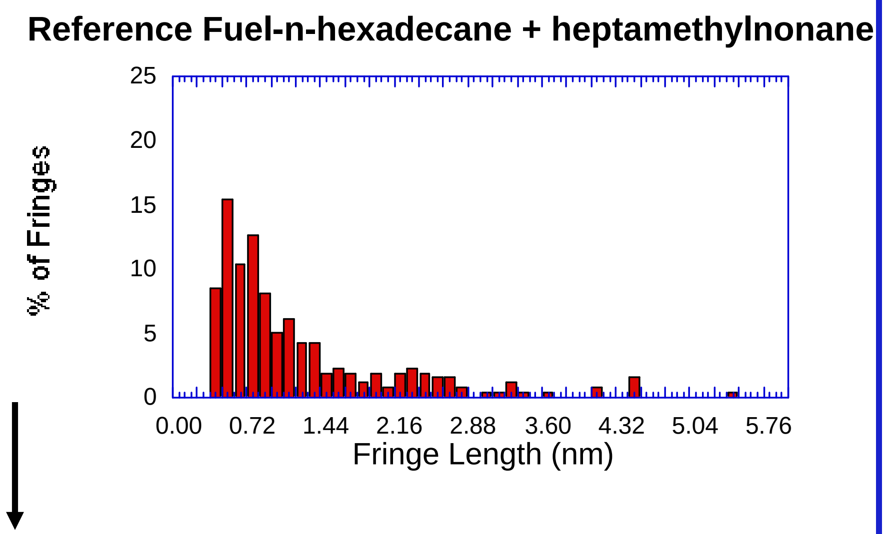


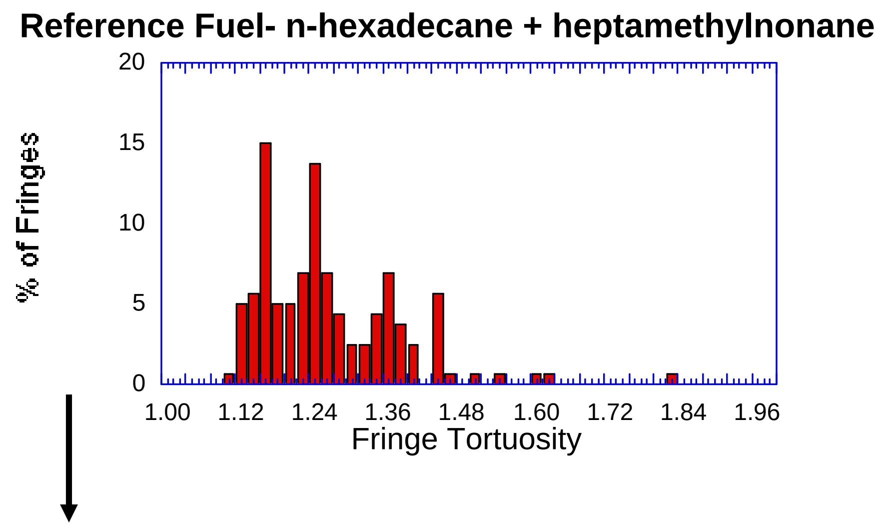


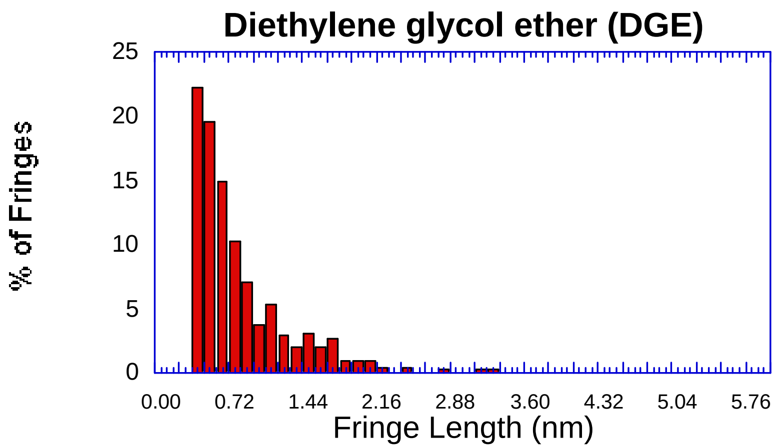


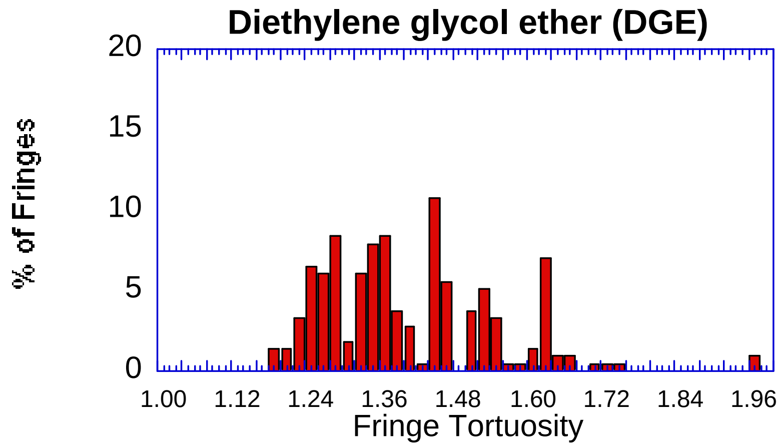
Fringe Length Analysis

Fringe Tortuosity Analysis

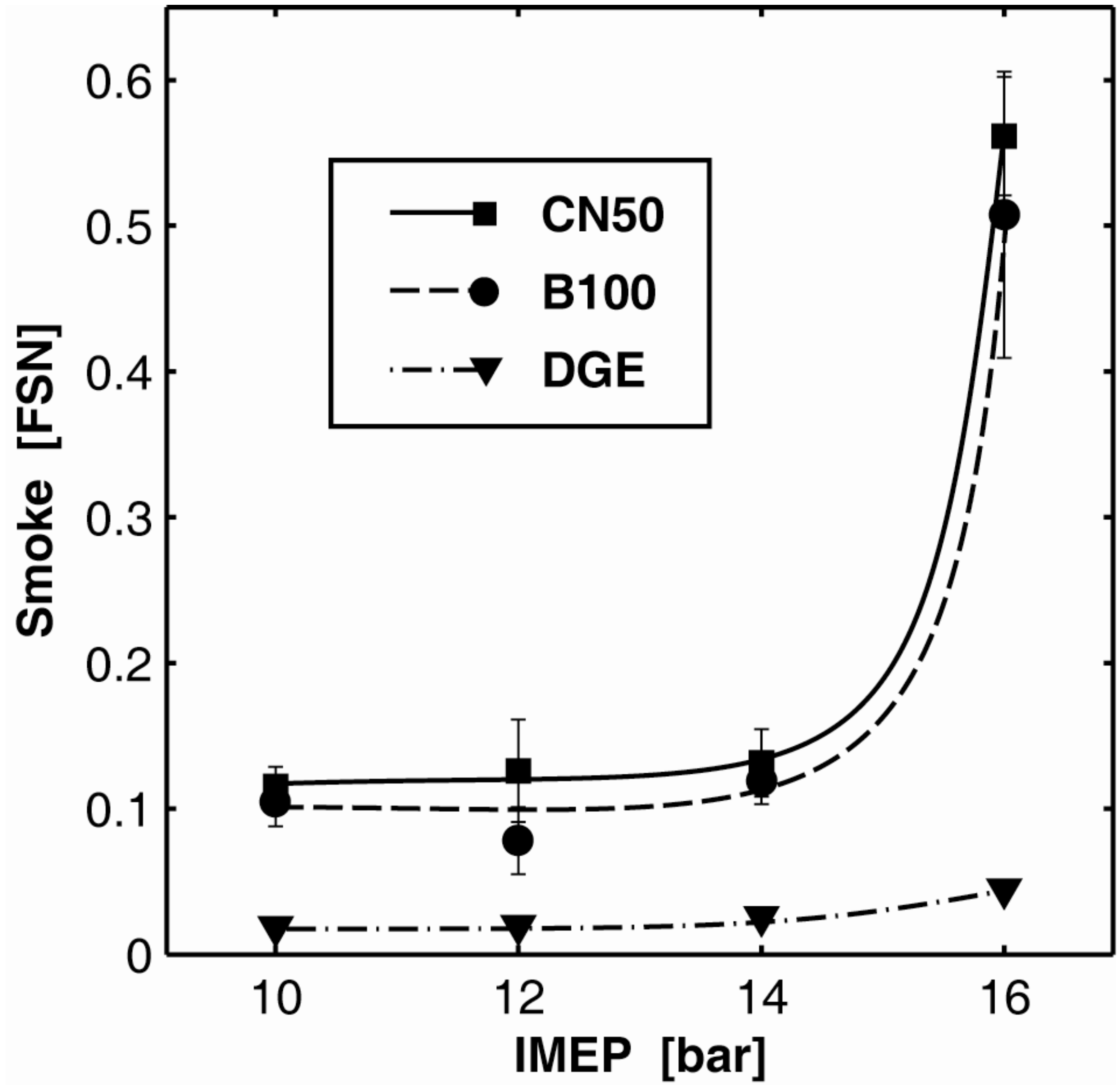








Smoke Meter (Engine Out)



Microscopic and Spectroscopic Analysis Techniques for Soot Characterization

HRTEM
(high resolution transmission electron microscopy)

Microscopy Technique

Physical Structure (nanostructure)

XPS
(X-ray photoelectron spectroscopy)

Spectroscopy Technique

Chemical Composition (& bonding states)

Outline - XPS

1. Motivation & Background
2. Introduction to XPS
3. Analytical capabilities:

    A. Elemental Composition (Identification of source; wear, etc.)

    B. Carbon Oxidation State - Oxygen Functional Groups
    (Oxidation conditions)
    * Consistency of samples within the same class
    * Distinctness between different classes of samples

    C. Carbon (nano)structure

4. Conclusions

Introduction to X-Ray Photoelectron Spectroscopy (XPS)

* XPS provides information about elemental composition
and
oxidation state of the surface.

* A monochromatic X-ray beam of known energy displaces an electron from a K-shell orbital.

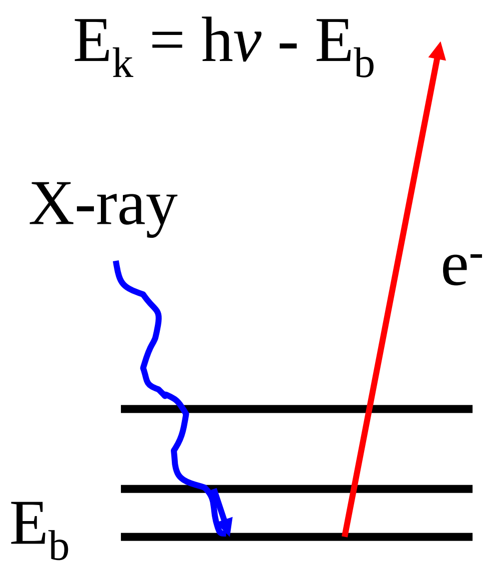
* The kinetic energy of the emitted electron is measured in an electron spectrometer.

* The binding energy $E_b = h\nu - E_k$
is characteristic of the atom and orbital from which the electron is emitted.

Introduction to XPS (continued)

* A low-resolution wide-scan (survey) spectrum serves as the basis for the determination of the elemental composition of samples.

* At higher resolution, chemical shifts are observed depending upon oxidation state.



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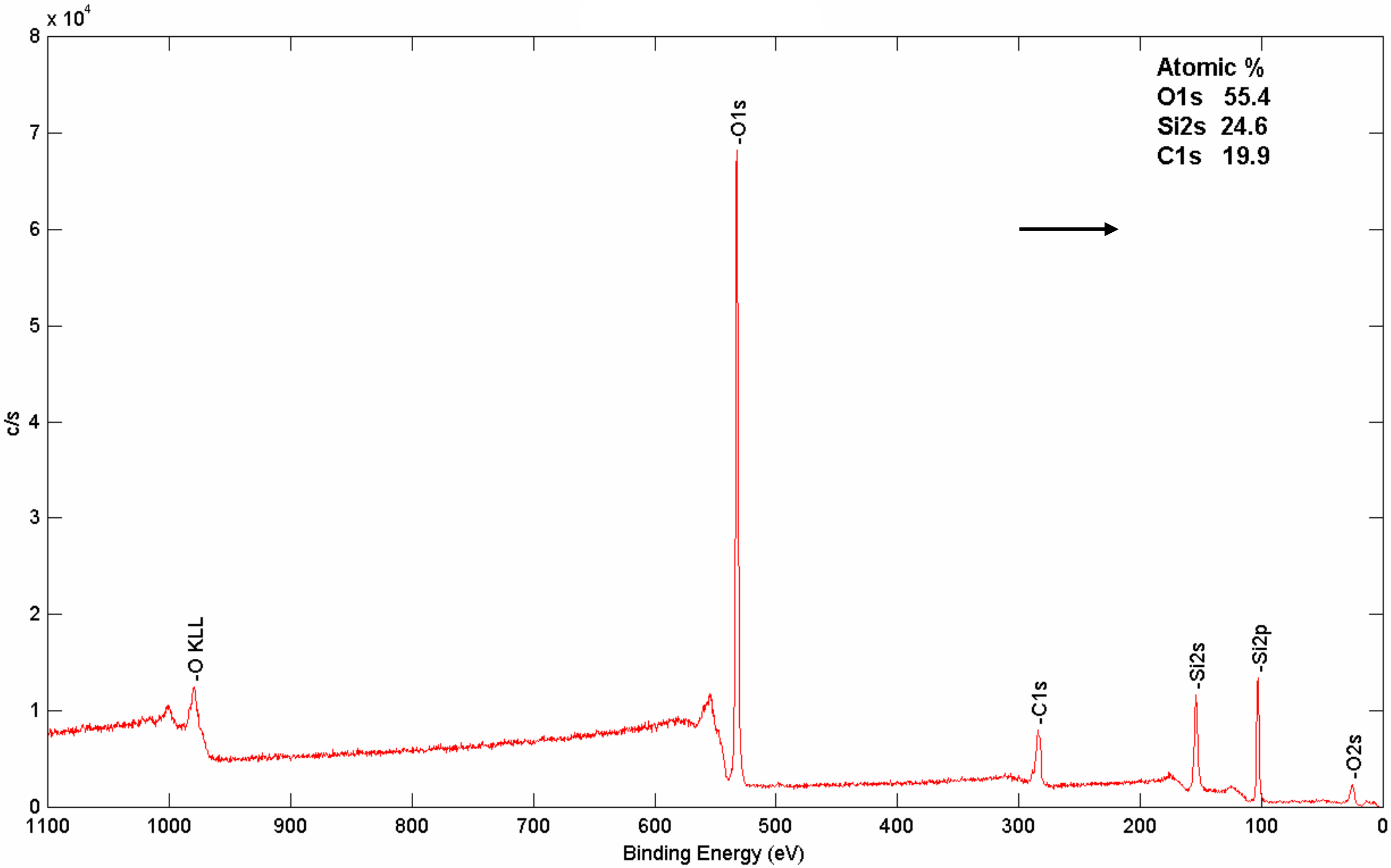
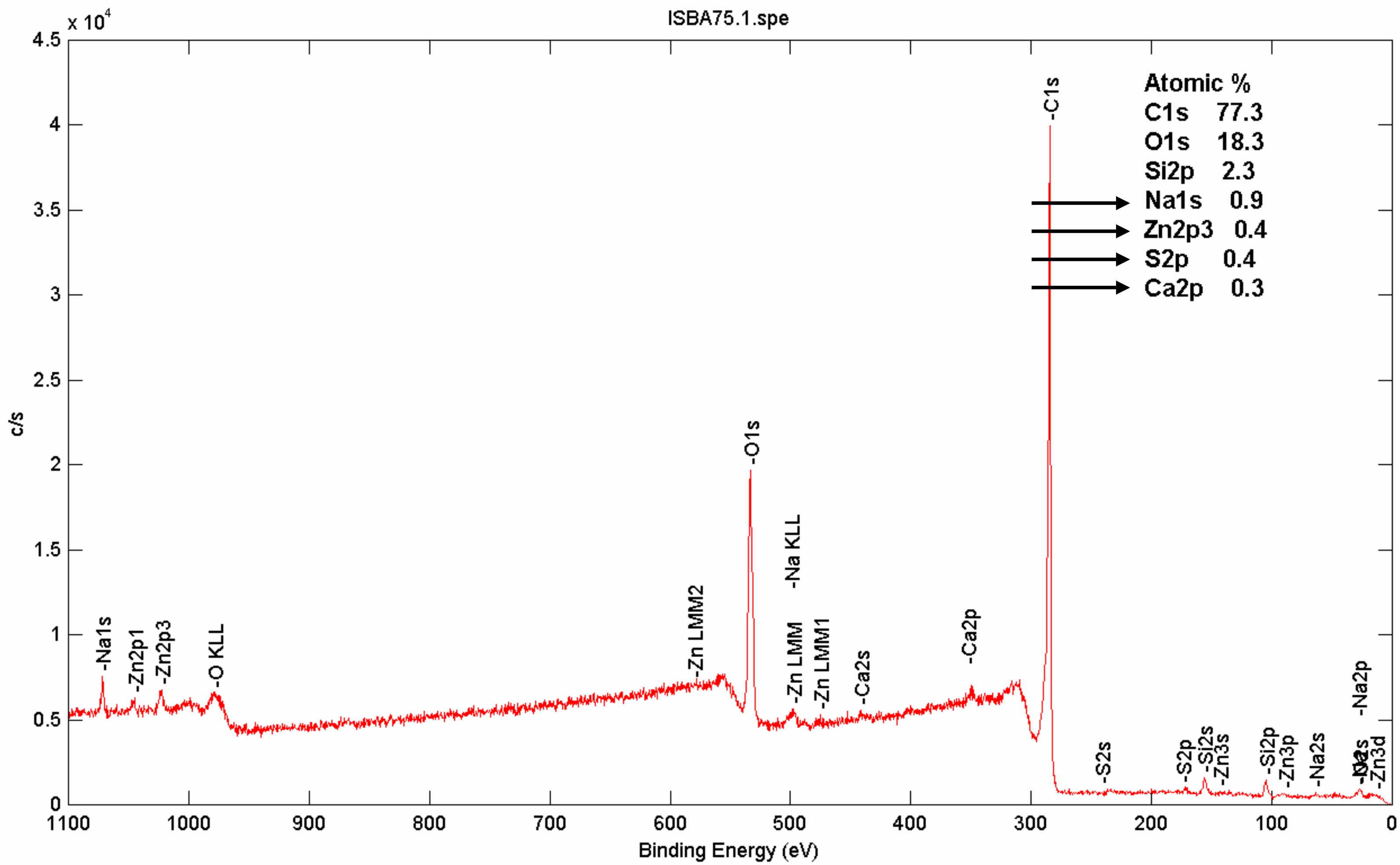
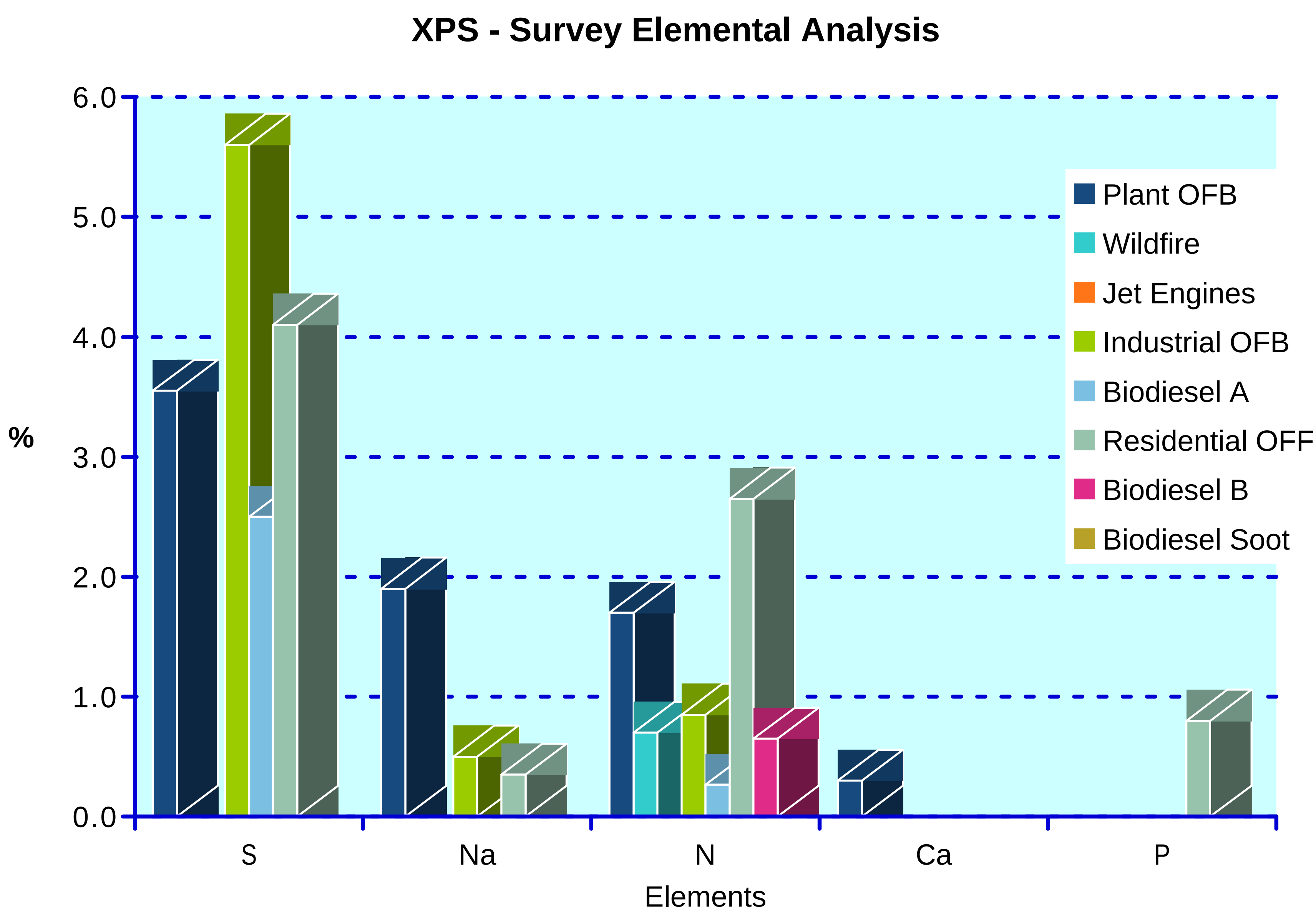
Low-Resolution Survey Scan - Jet Aircraft Emissions



Low-Resolution Survey Scan - Diesel Engine Soot




XPS - Survey Elemental Analysis
%
6.0
5.0
4.0
3.0
2.0
1.0
0.0
S
Na
N
Ca
P
Elements
Plant OFB
Wildfire
Jet Engines
Industrial OFB
Biodiesel A
Residential OFF
Biodiesel B
Biodiesel Soot

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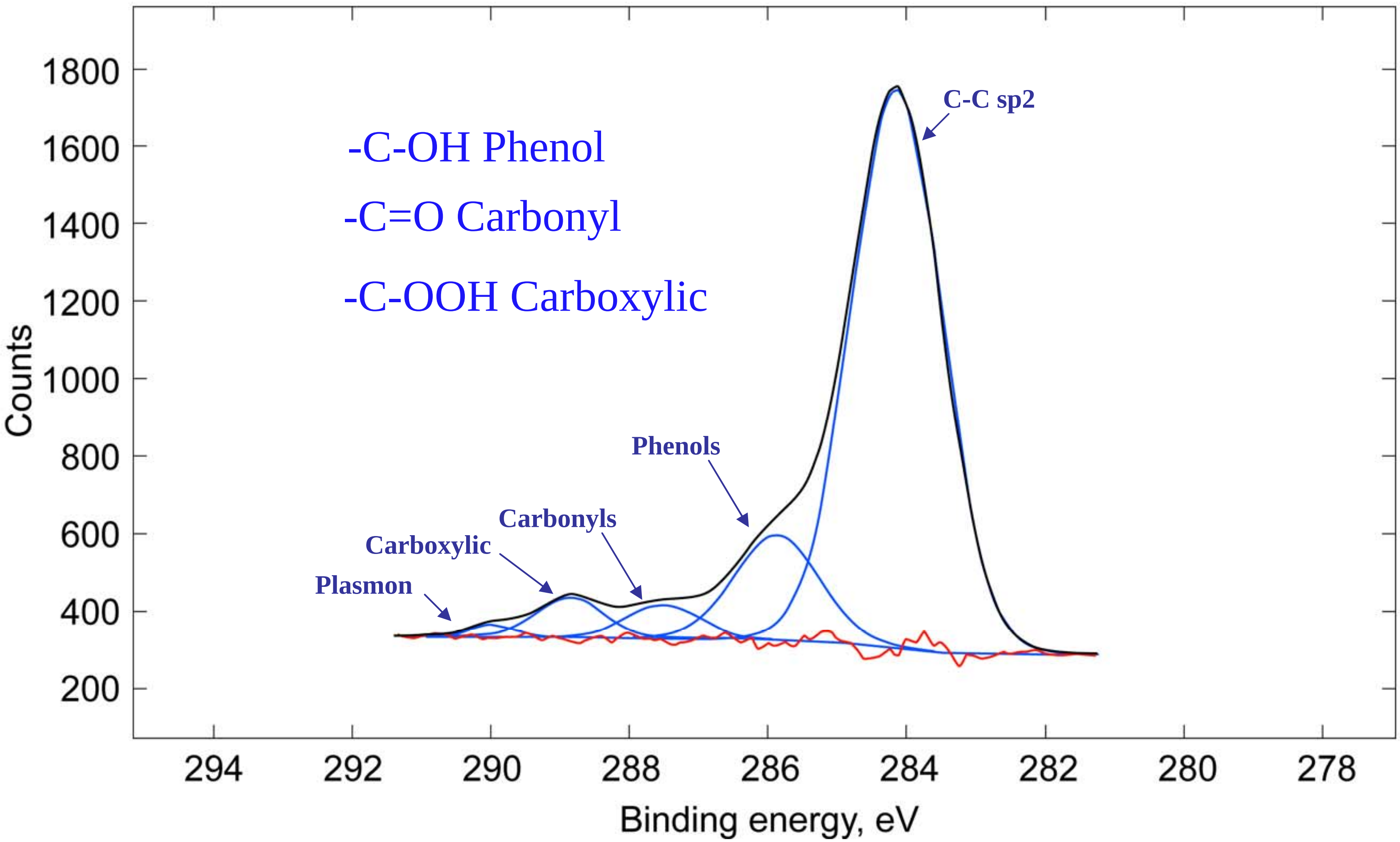
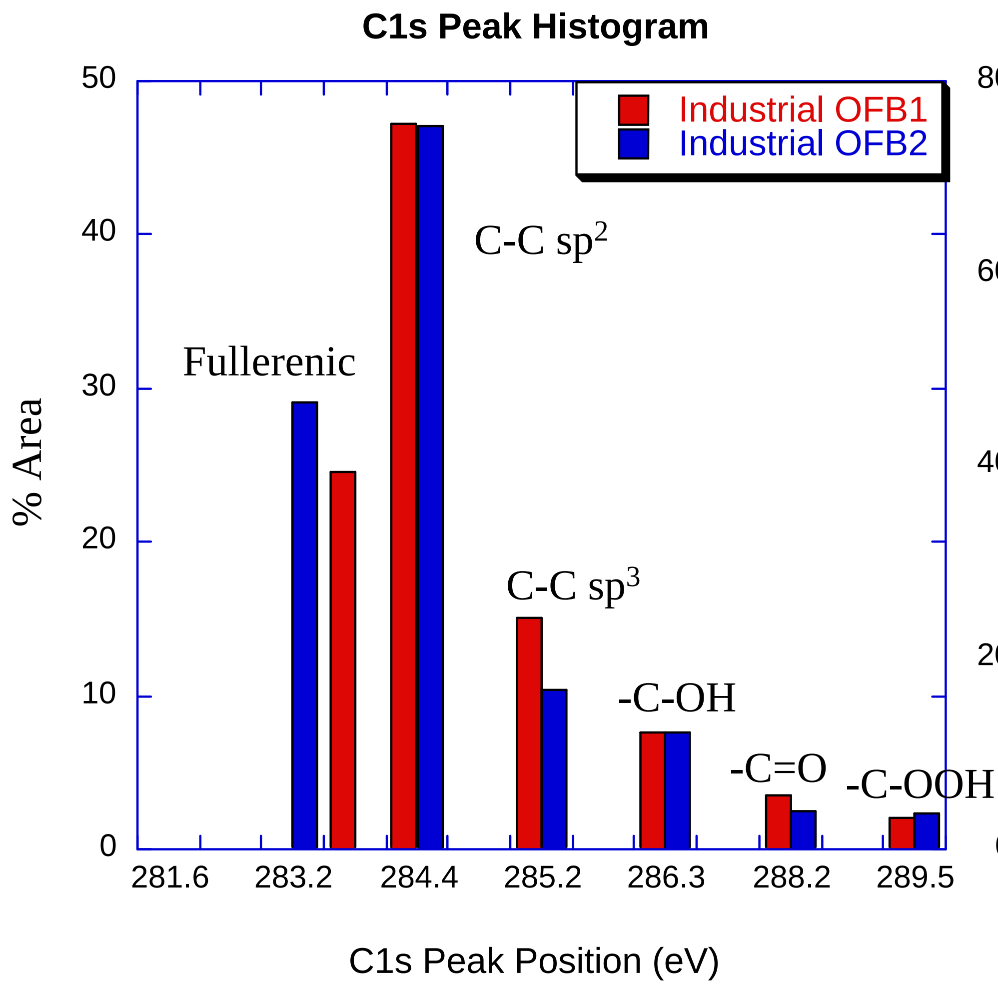
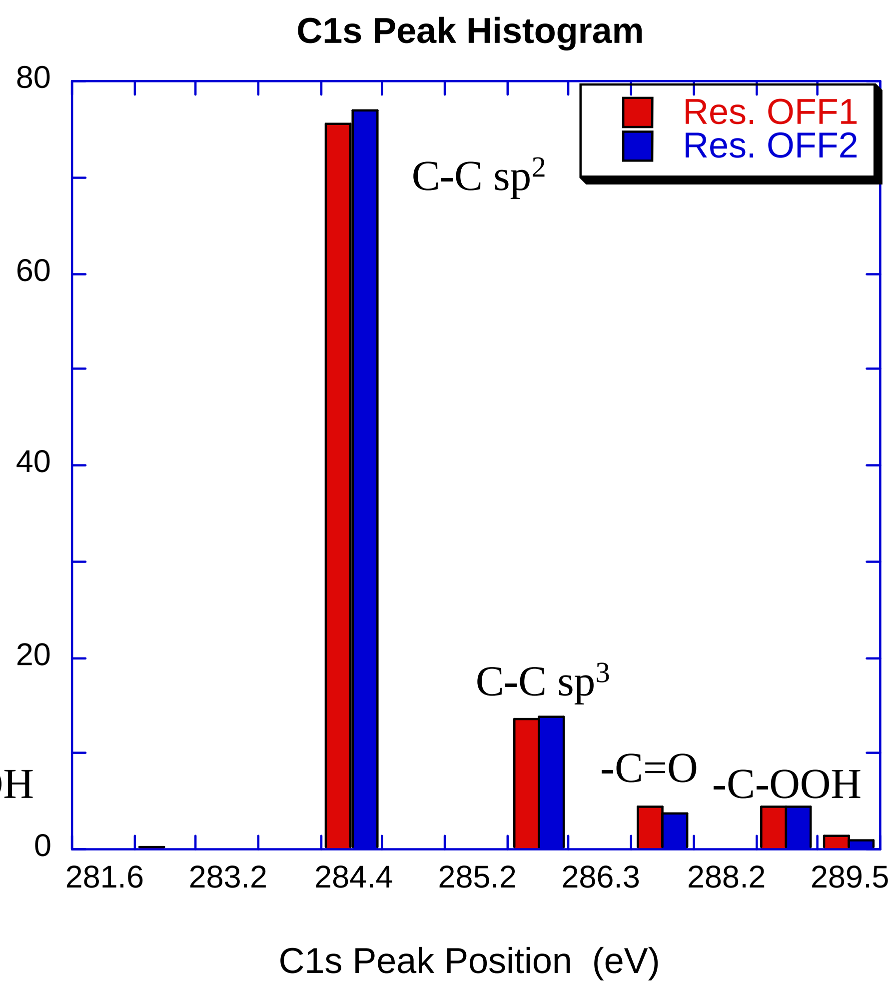
Identify Oxygen Functional Groups

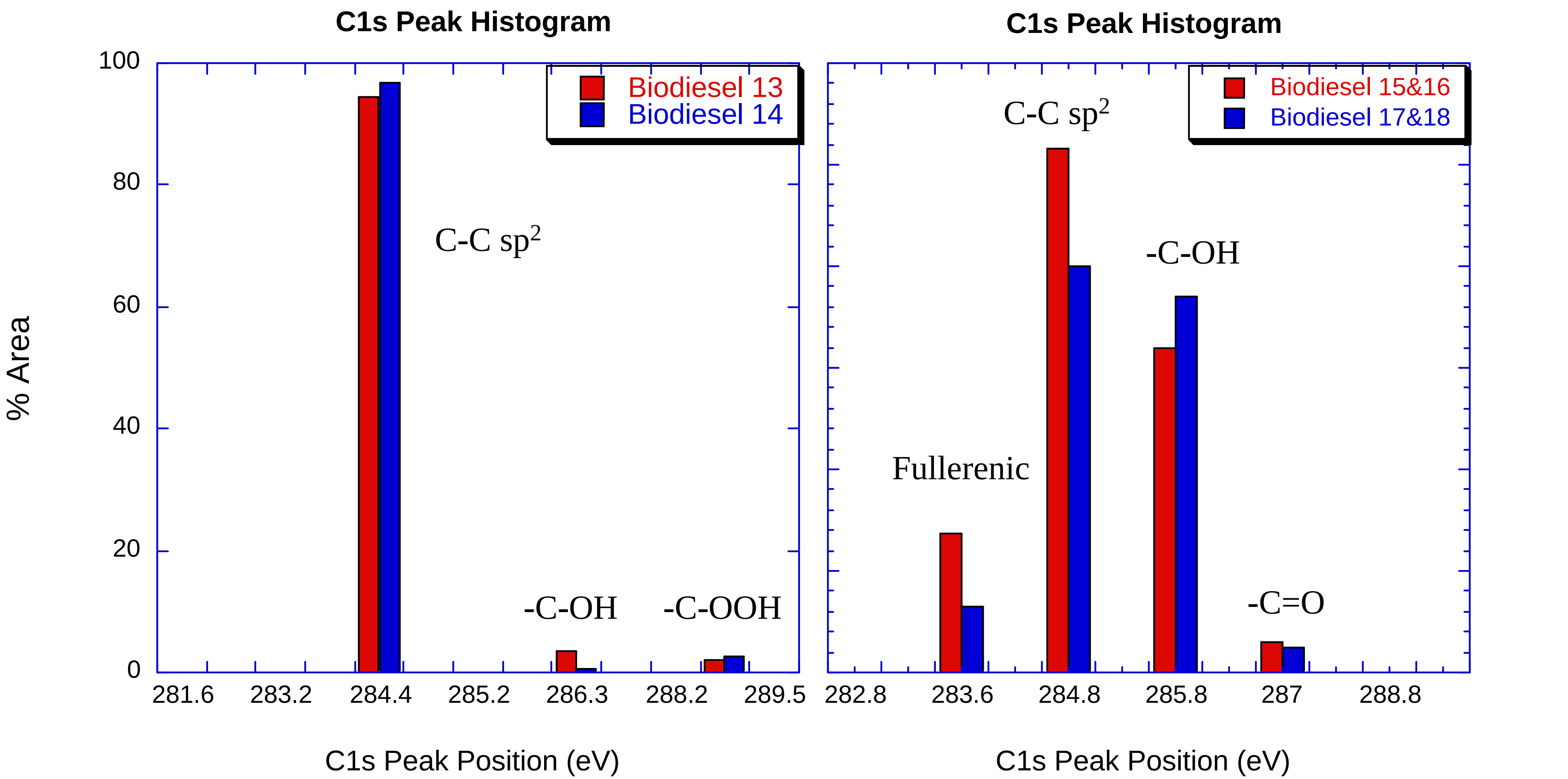


Oil Fired Boiler versus Residential Oil Fired Furnace

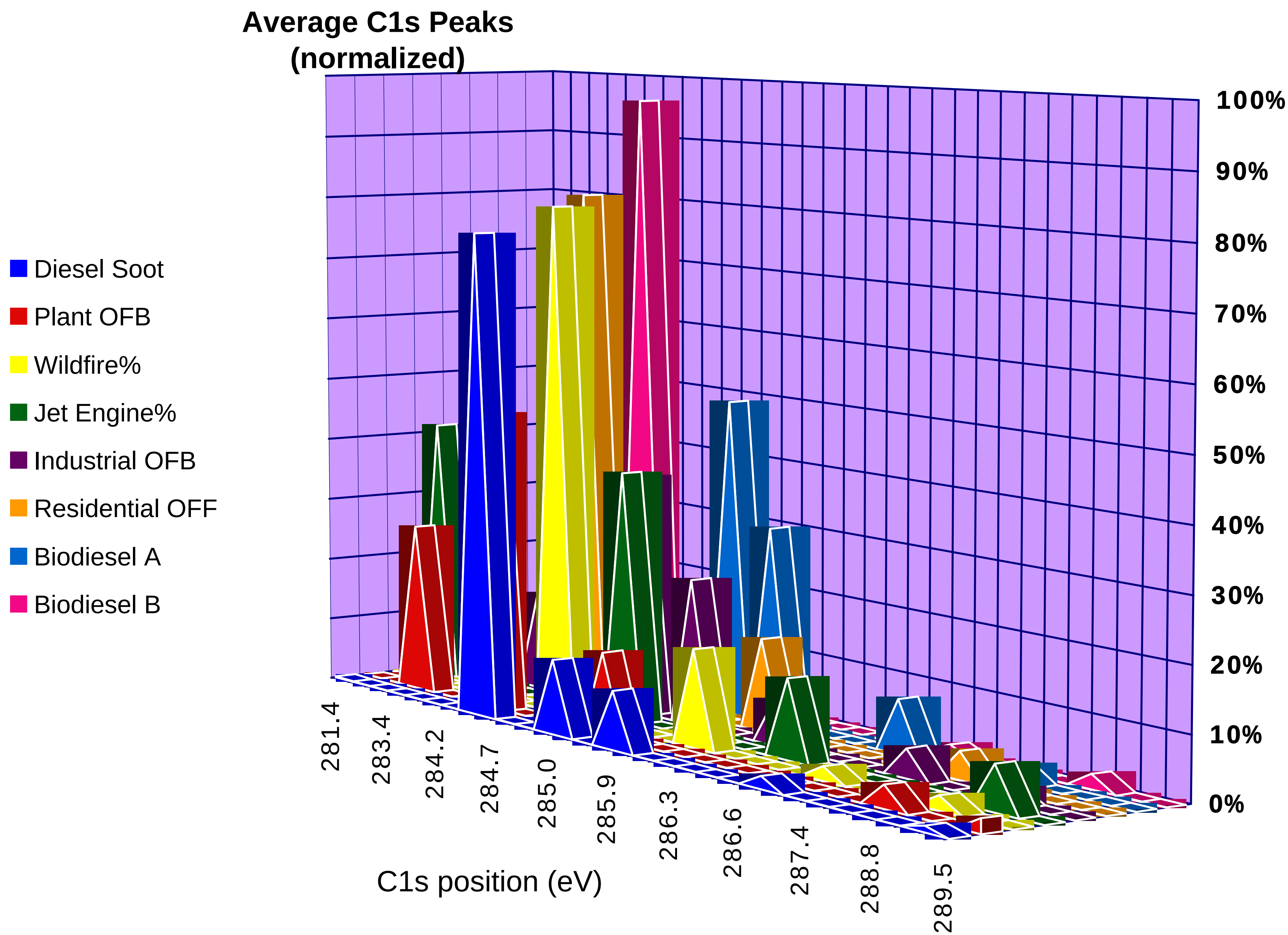




Comparison Between Biodiesel Soots



Comparative Peak Intensities - Oxygen Functional Groups



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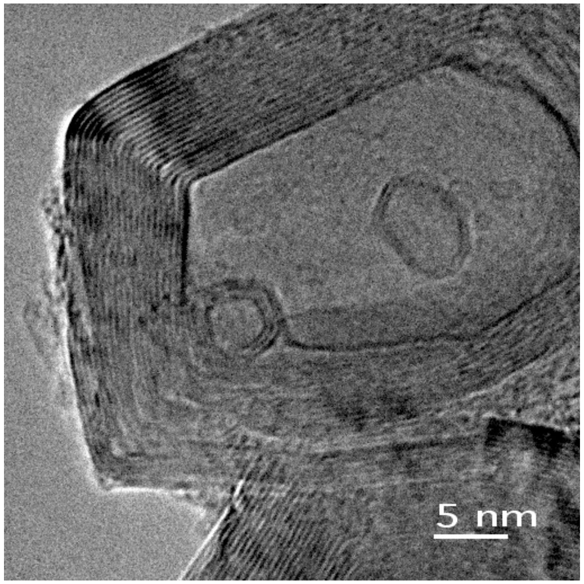
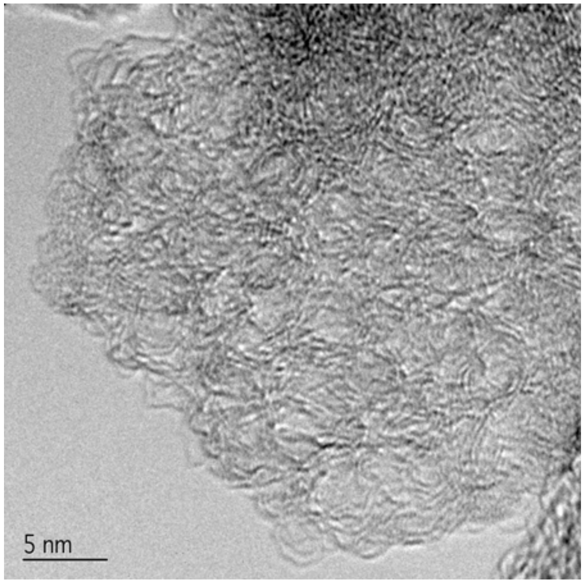
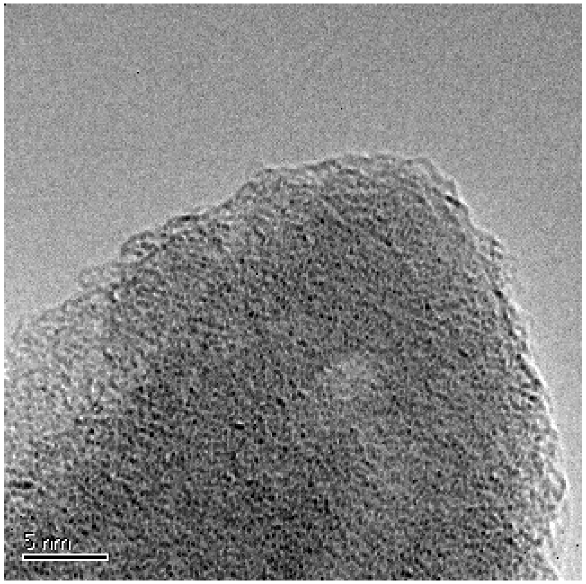
Motivation for Alternative Analysis Techniques

1. Lattice Fringe Analysis is time consuming

2. Analysis can be difficult to apply (in some cases)

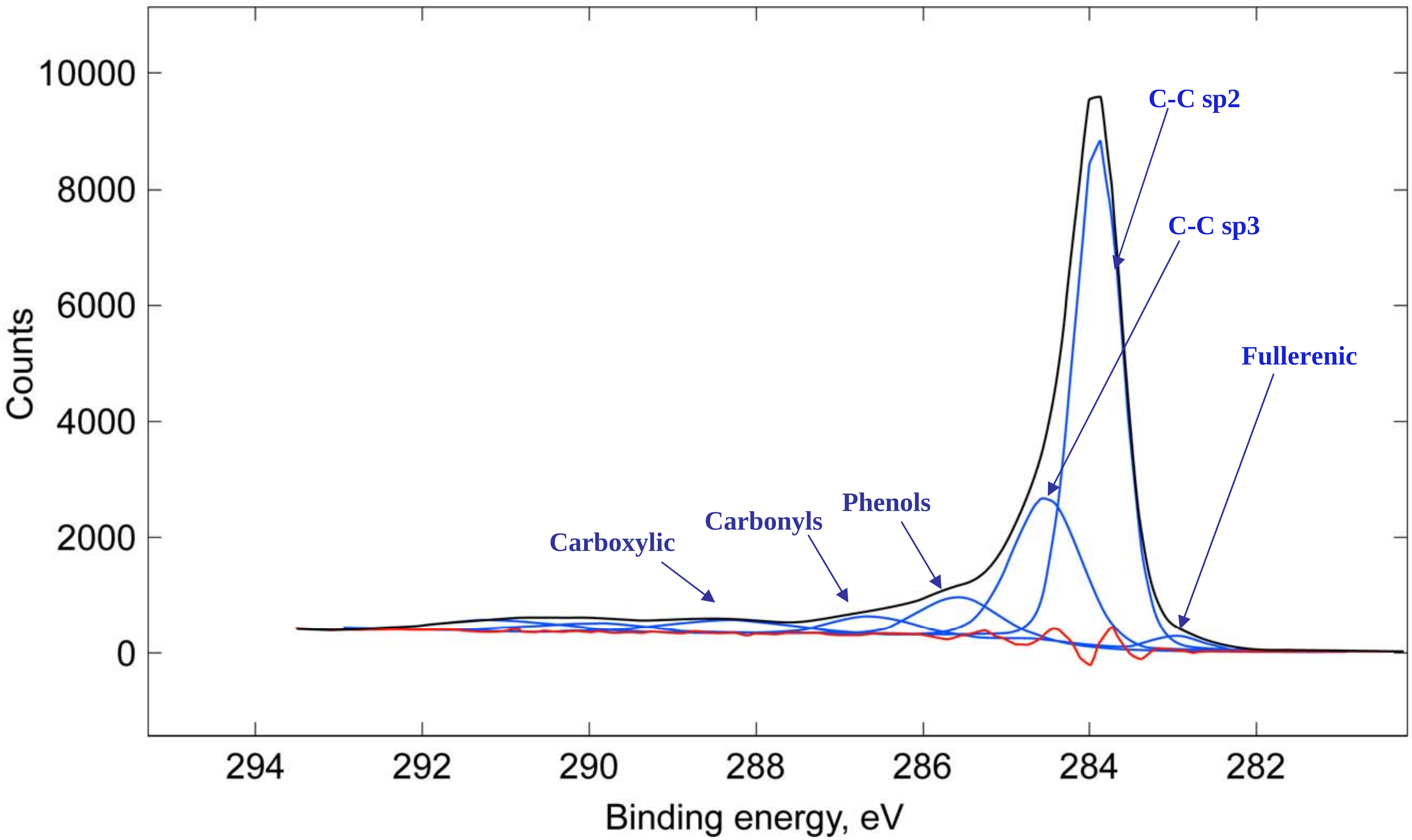






Hmmm….

Identify Types of Carbon Nanostructure



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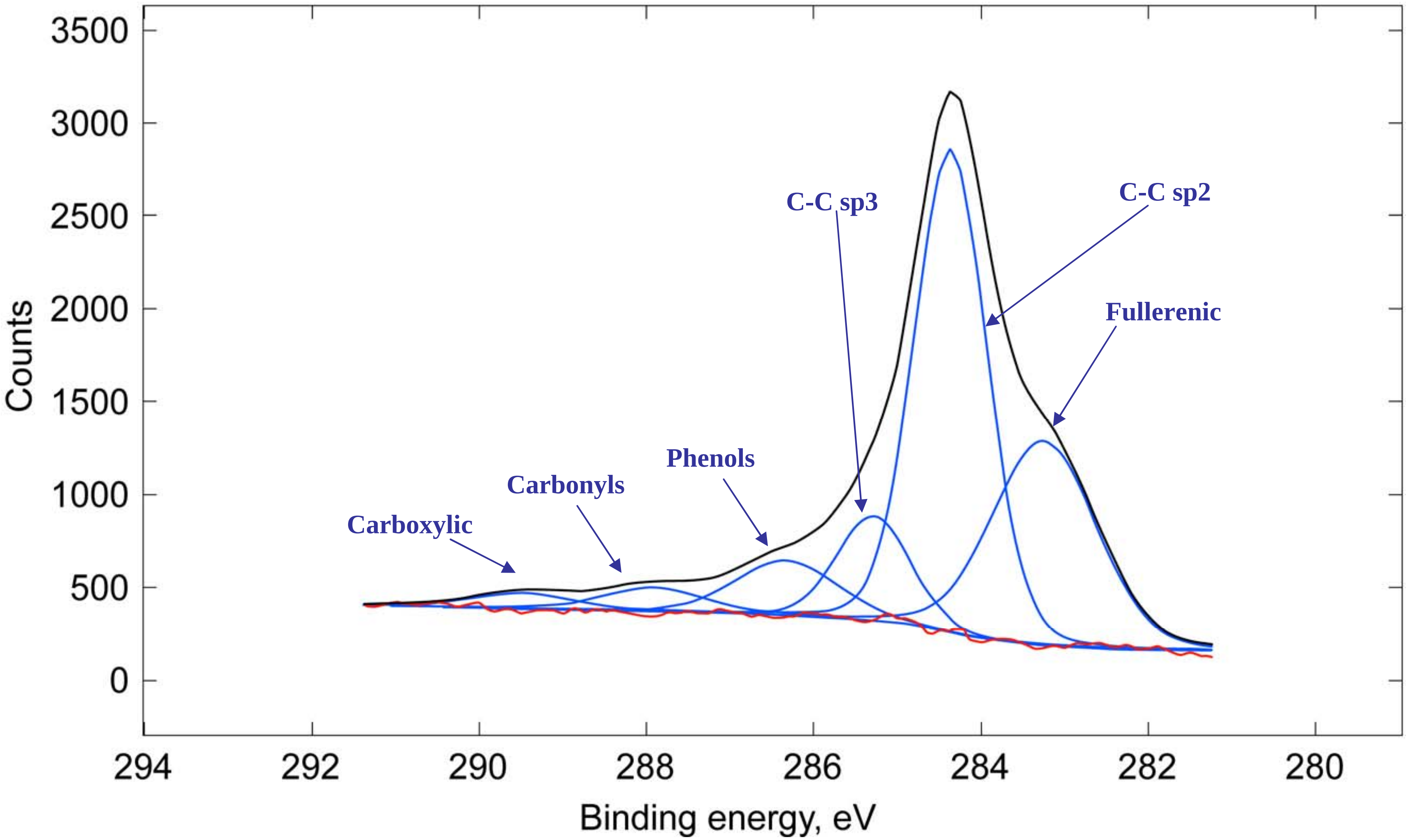

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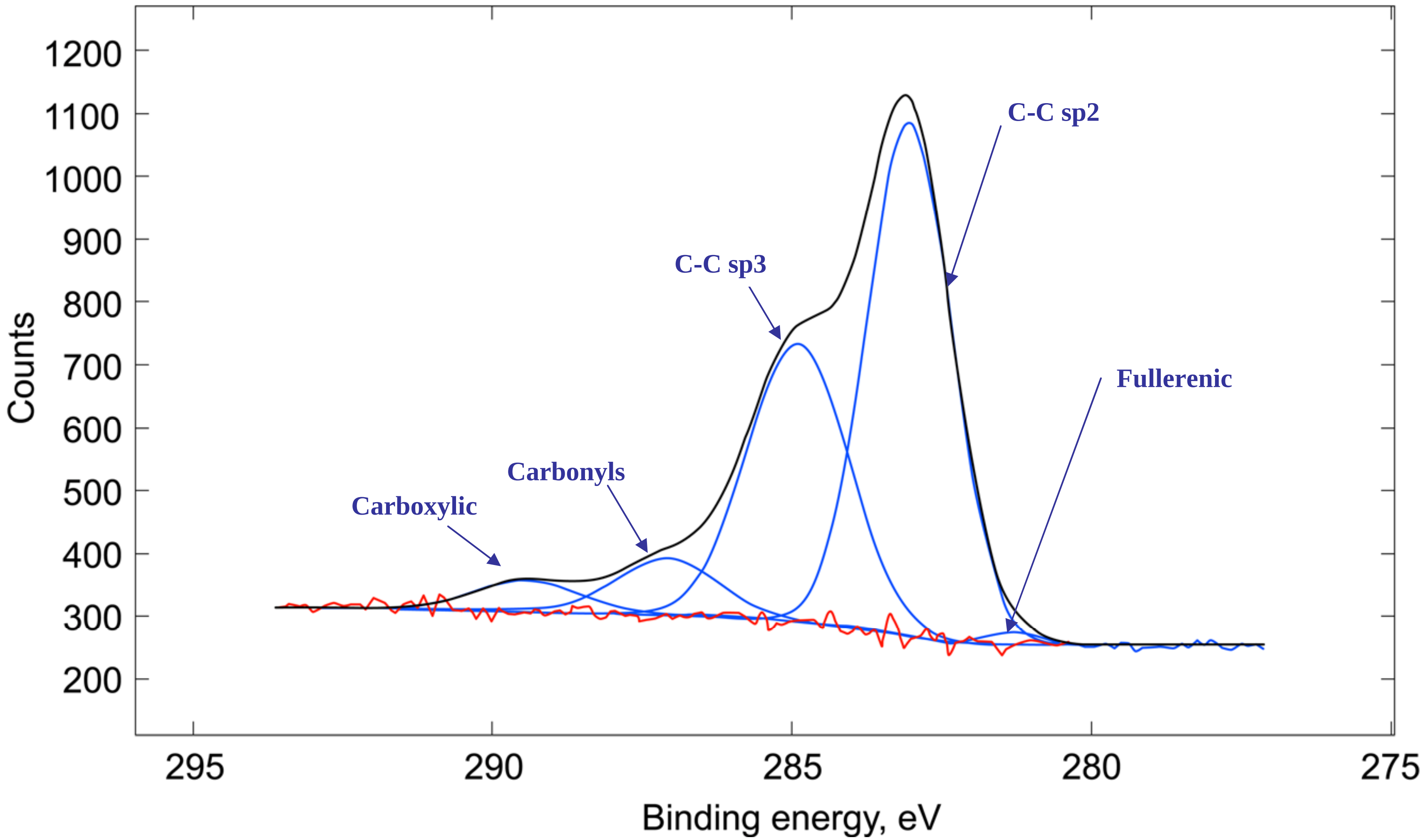

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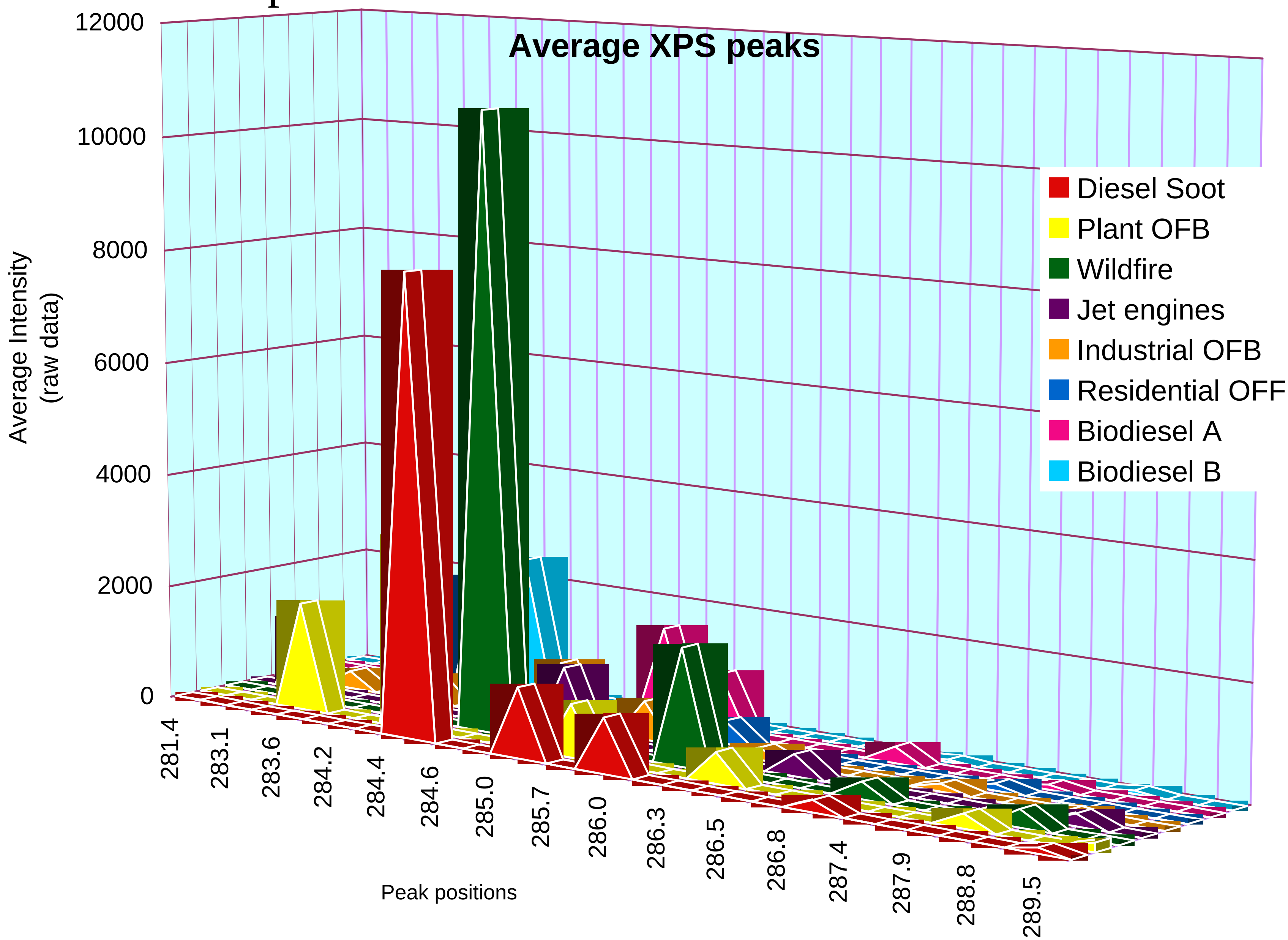
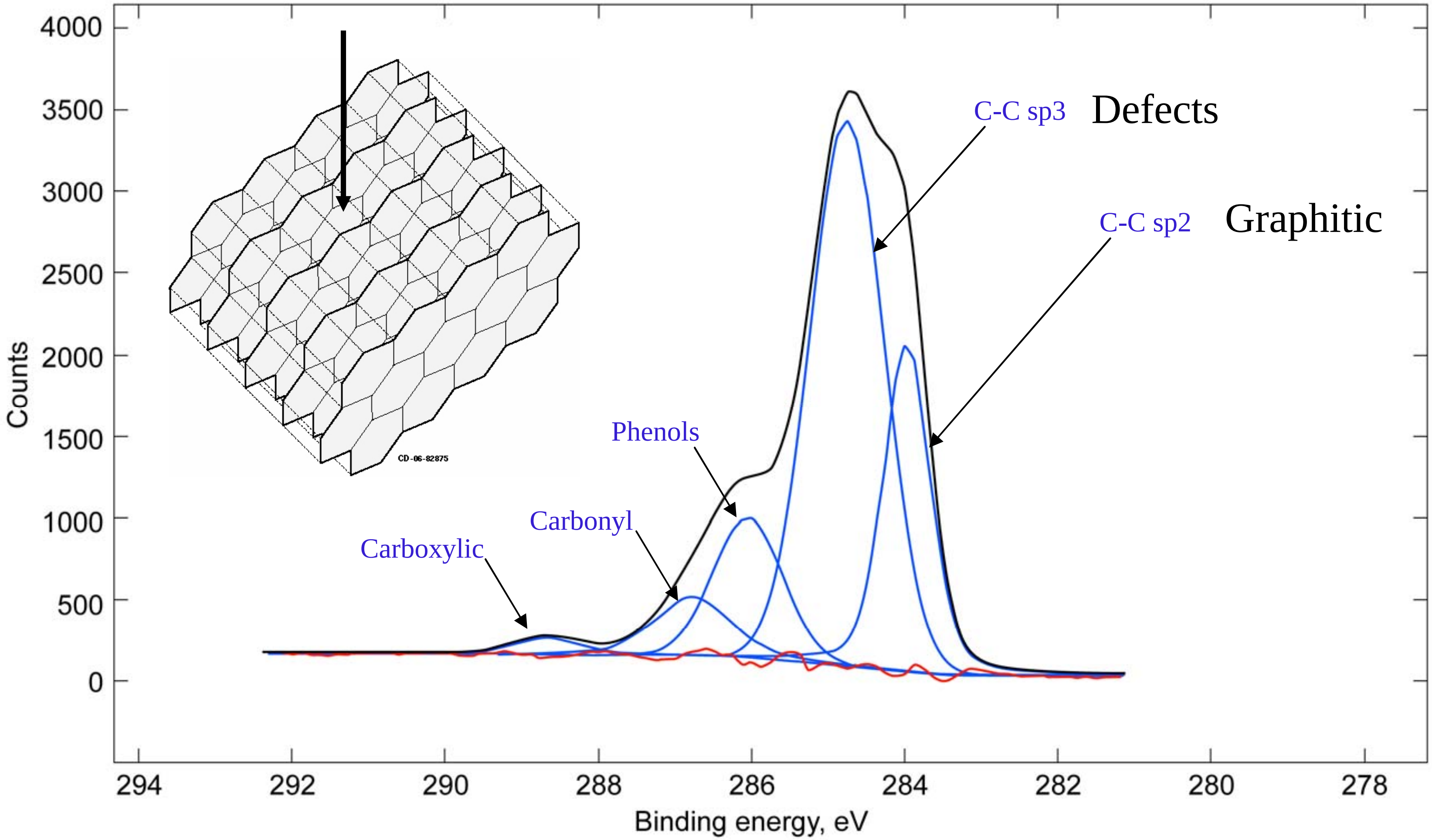
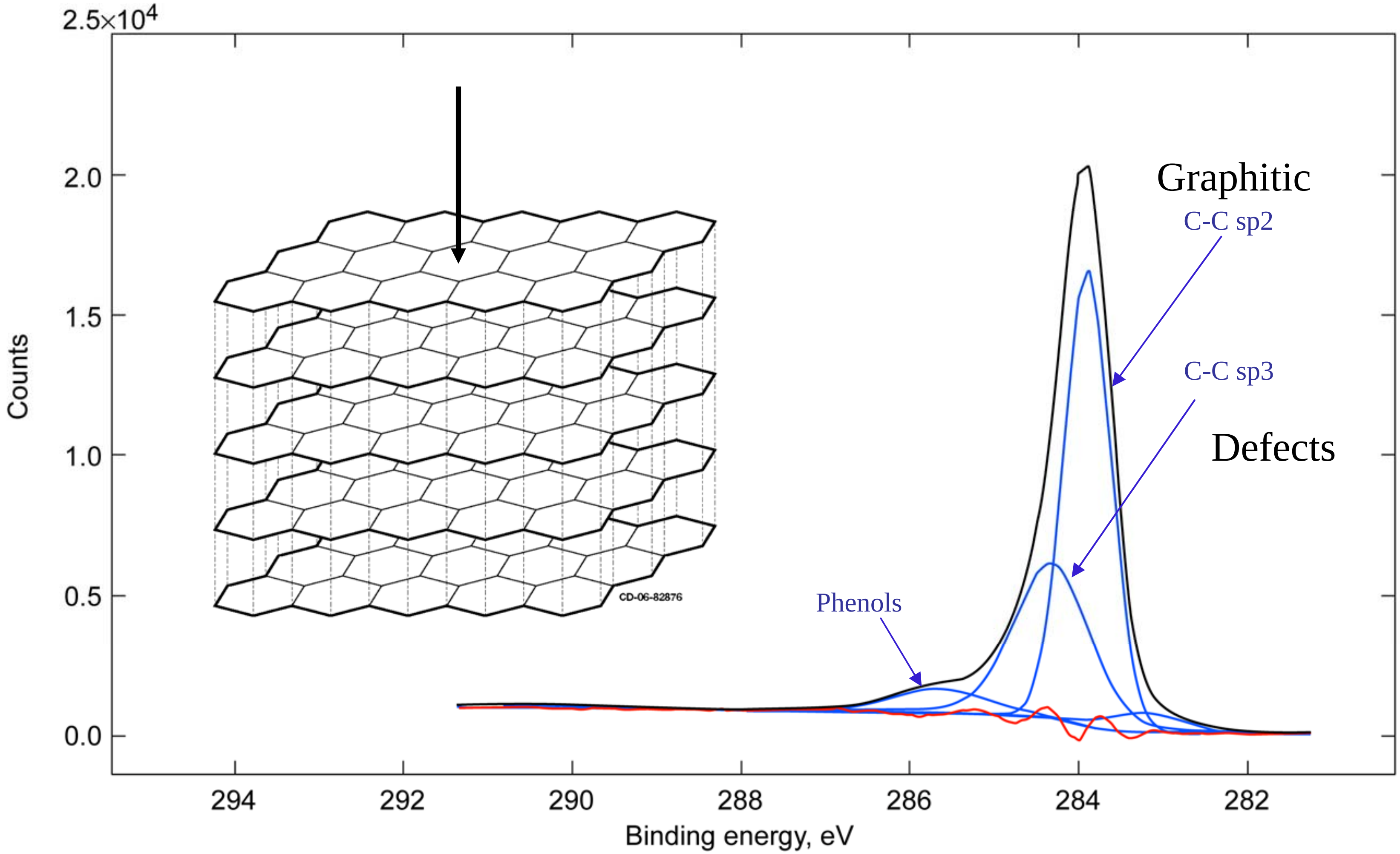


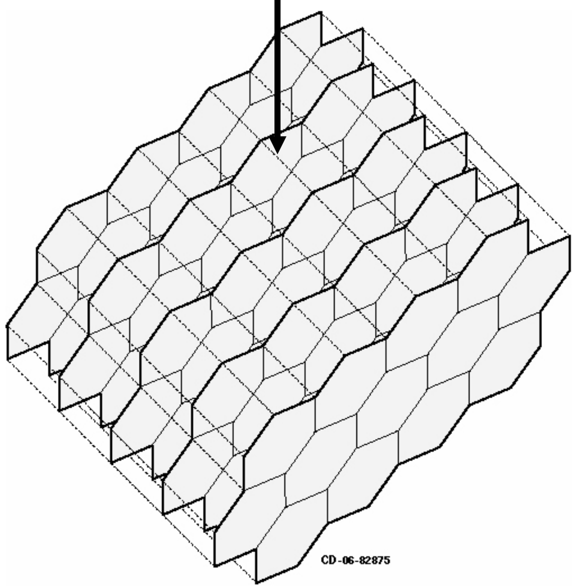
High Resolution Scan - C1s Region - HOPG Edge Planes

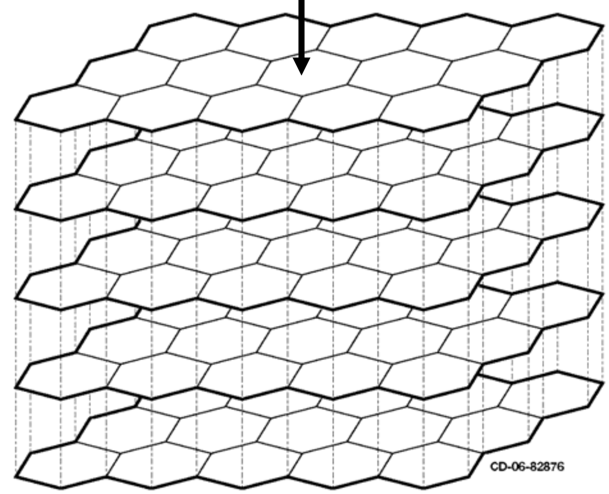


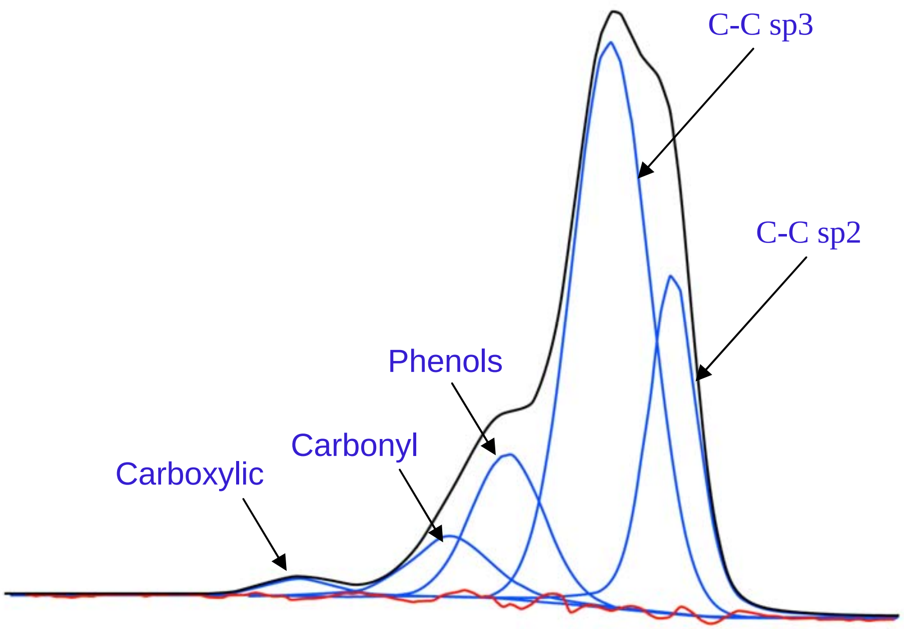
High Resolution Scan - C1s Region - HOPG Layer Planes

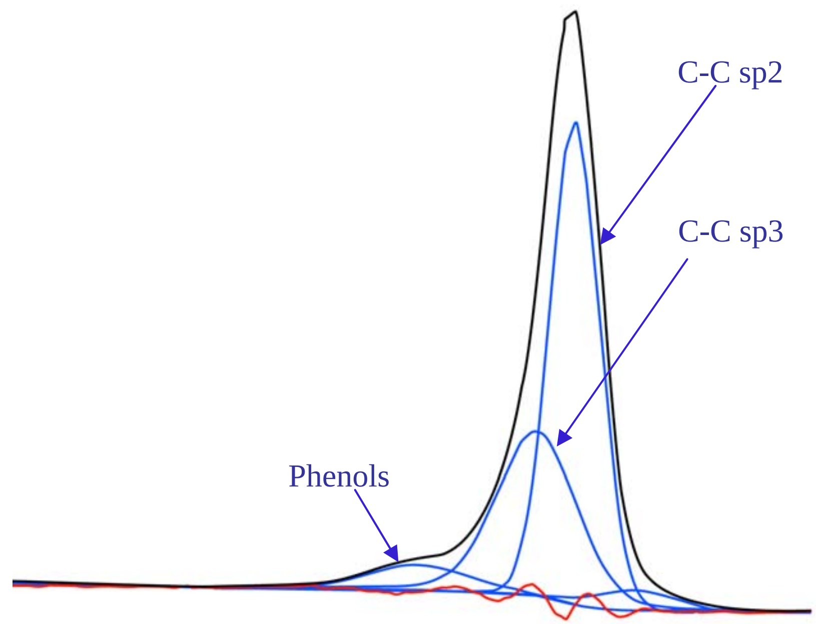


XPS Sensitivity to Carbon Nanostructure









*** Developing Correlations with Carbon Reactivity***

Sample:	Edge Sites Intensity Sum	Basal Plane Intensity Sum
Planar Graphite (~ 284 eV, sp^2)	1749 13%	11265 87%
Edge Graphite (~ 285 eV, sp^3)	4021 37%	6723 63%
Ratio (G/D)	0.35	1.38

Edge site carbons can be nearly 10-fold more reactive than basal plane sites

Goal & Result

HRTEM & Lattice Fringe Analysis

XPS → Carbon nanostructure → Oxidative Reactivity

Conclusions

1. XPS analysis can identify & quantify trace elements.

Utility: Can be used to identify source based on specific elements present and their distribution.

* Track fuel and/or oil elements
* Analysis of engine wear

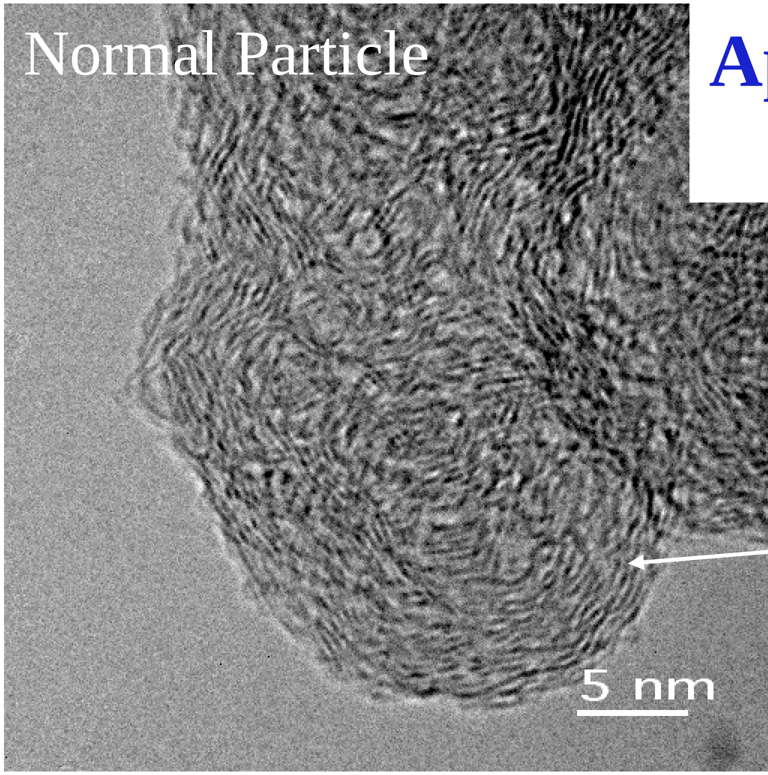
2. XPS can identify oxygen groups by bonding type; C-OH, C=O, and C-OOH. These reflect the soot oxidation history.

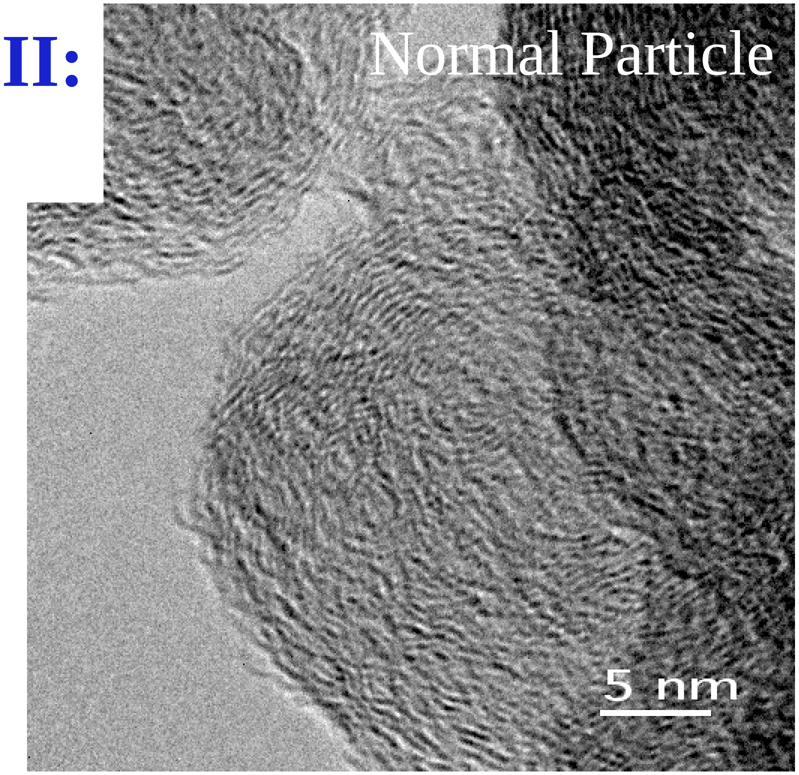
Utility: Identify the occurrence and degree of oxidation, such as the soot cake within a DPF

3. XPS can identify the types of carbon present, sp^2, sp^3 and fullerenic Therein it can provide a complimentary method to HRTEM and image analysis.

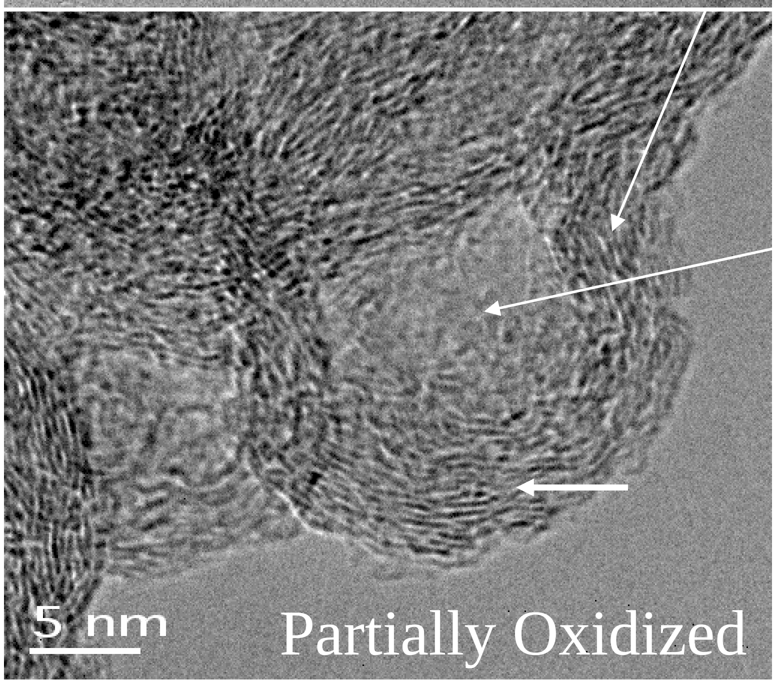
Utility: Correlate nanostructure with soot reactivity, and changes new fuels, e.g. biodiesel

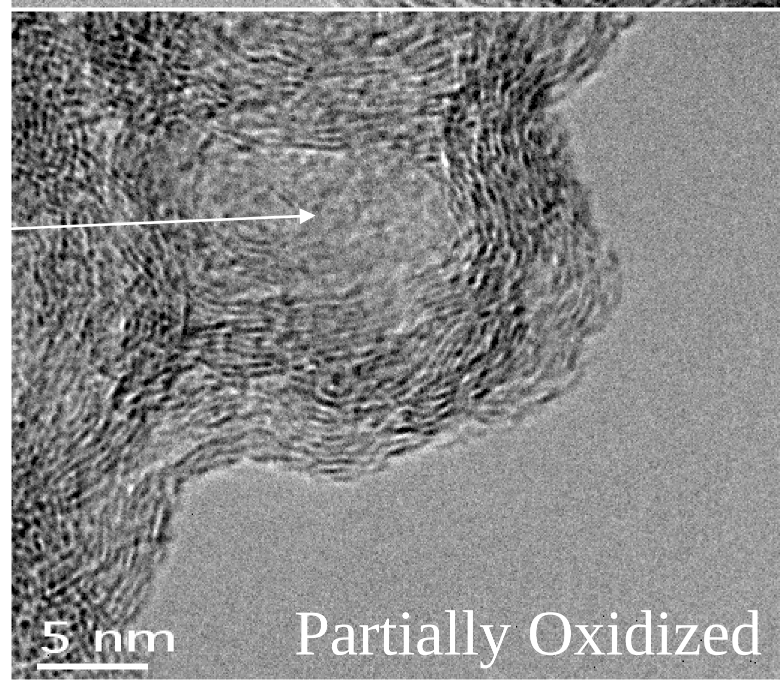
Application III: DPFs





DPF
Soot
Graphitic
outer shell

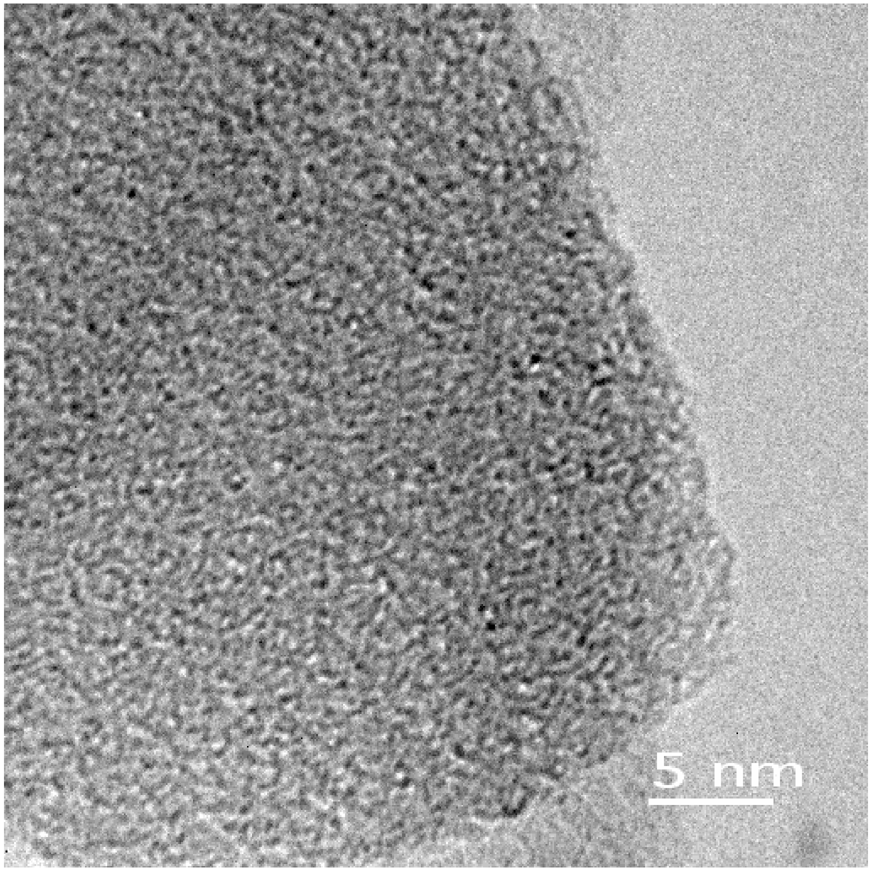


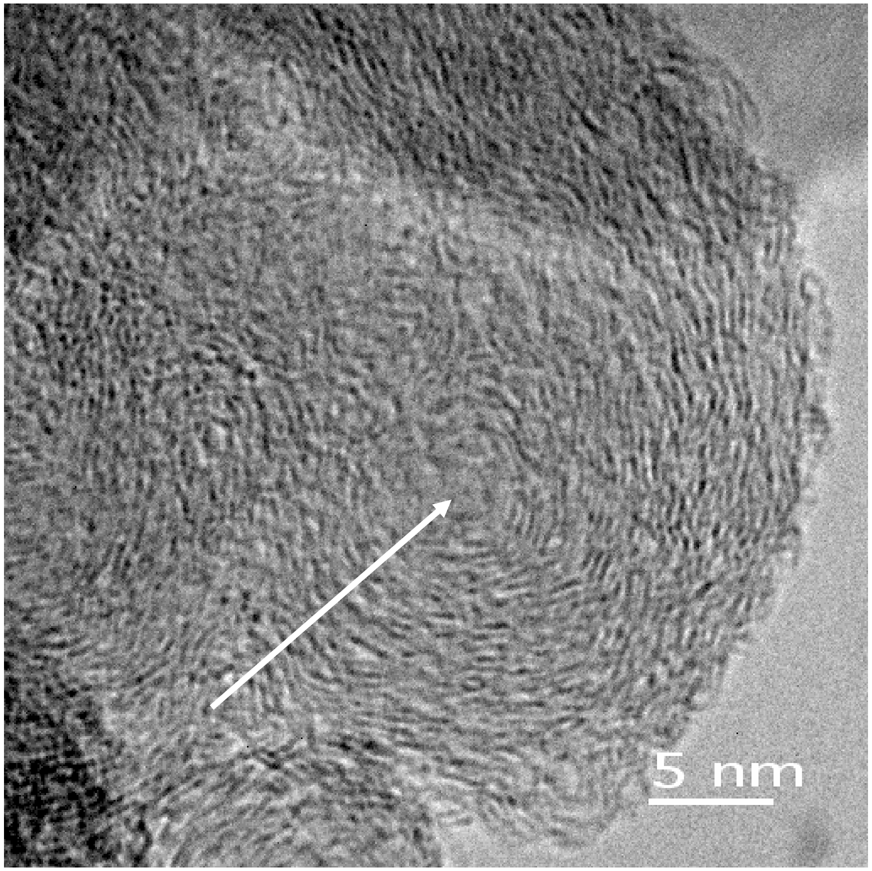


Hollow
Interiors

Application II: Source Specific Nanostructure

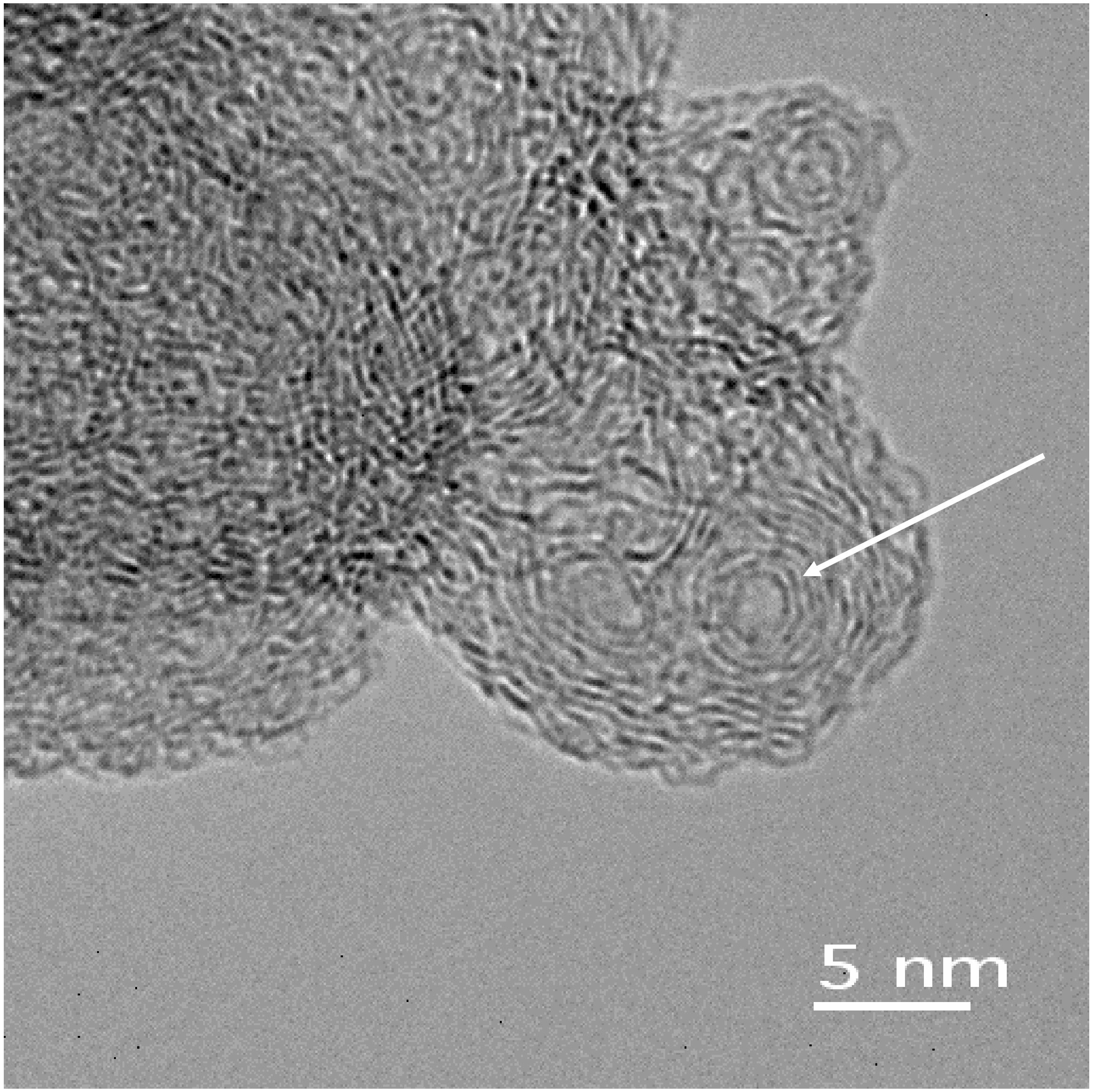
Wildfire Emissions | **Oil Fired Boiler**



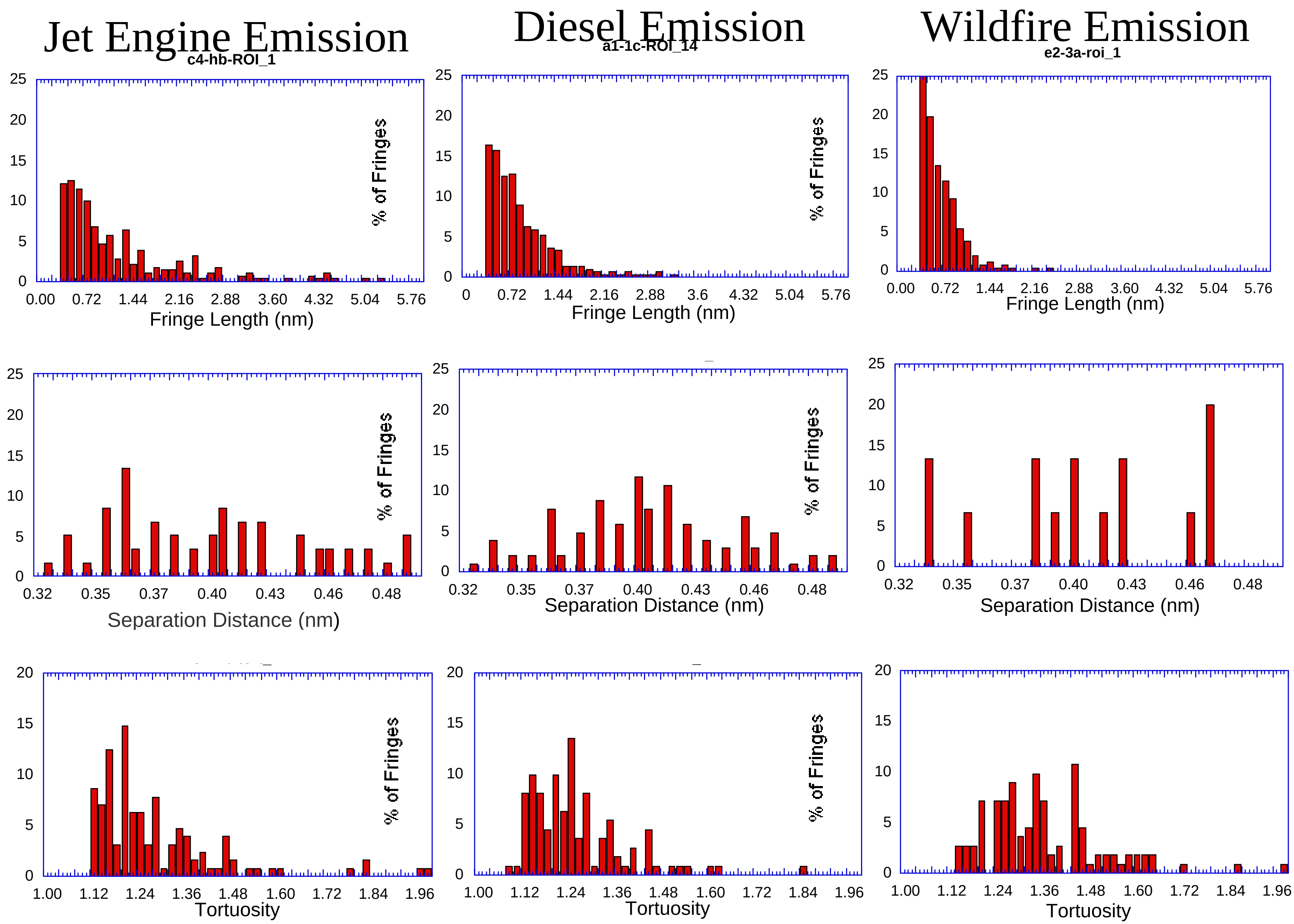


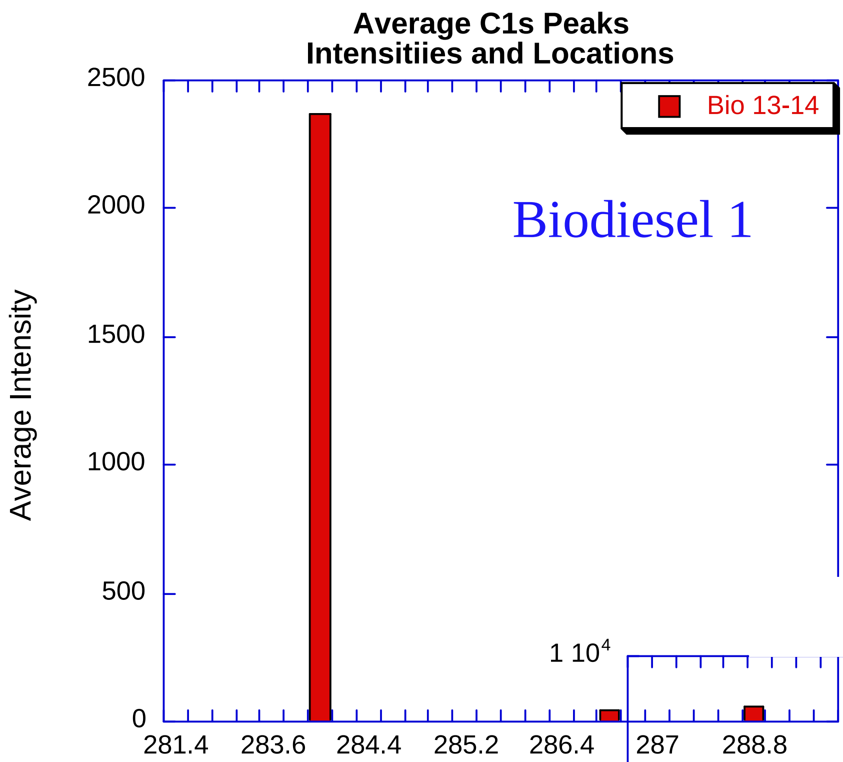
Comparison between carbon lamella;
short, disconnected versus longer range structure and order

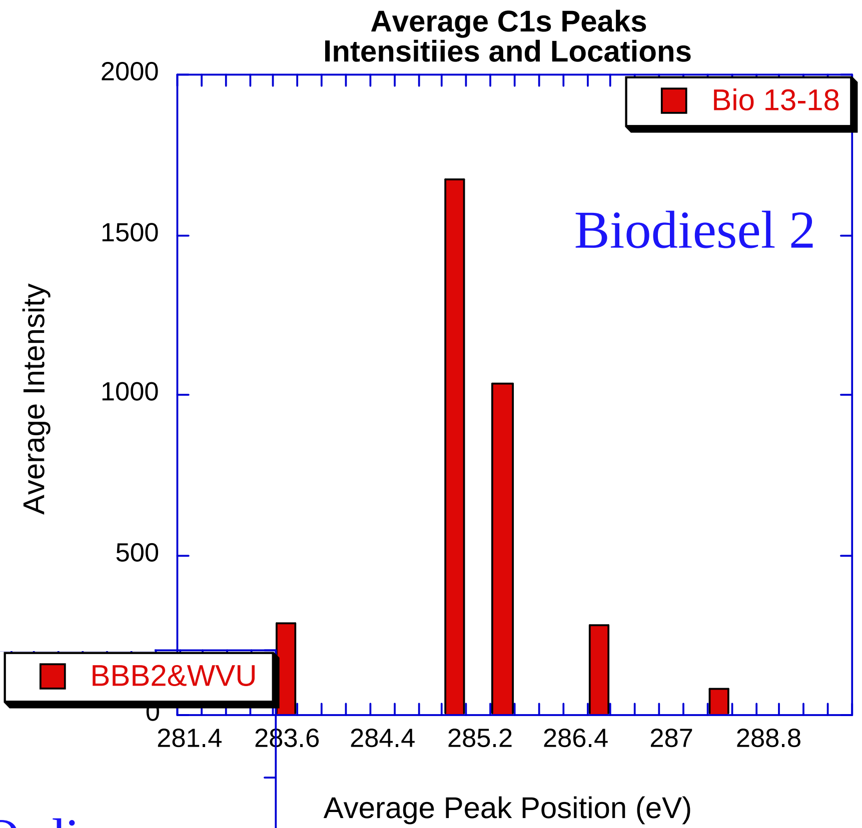
Jet Aircraft Engine Exhaust

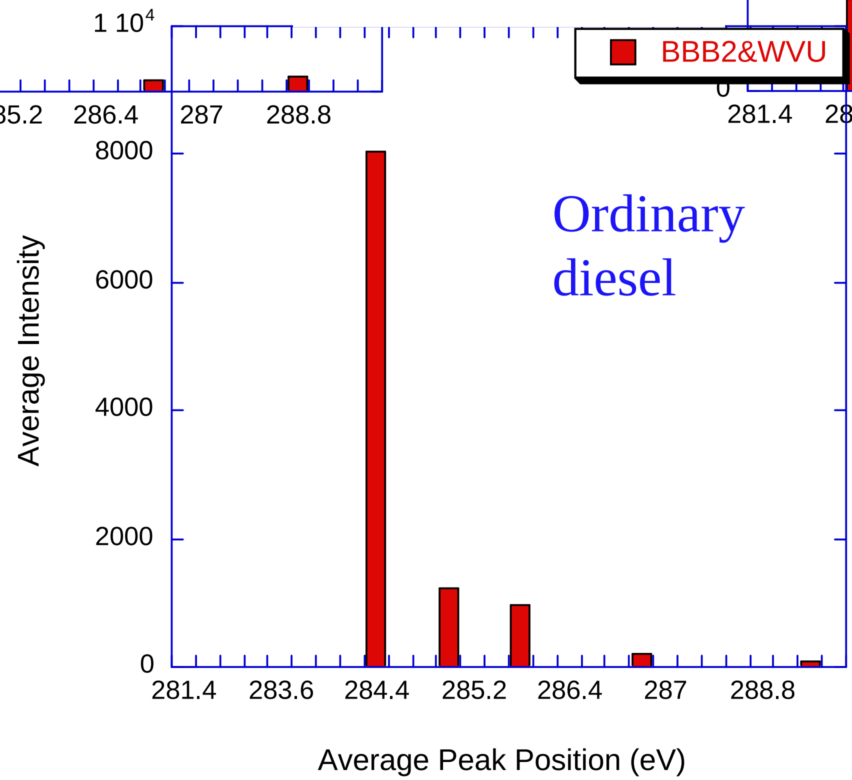


Fullerenic
Structure


Jet Engine Emission
c4-hb-ROI_1
Diesel Emission
a1-1c-ROI_14
Wildfire Emission
e2-3a-roi_1
% of Fringes
Fringe Length (nm)
Separation Distance (nm)
Tortuosity
0.00 0.72 1.44 2.16 2.88 3.60 4.32 5.04 5.76
0 0.72 1.44 2.16 2.88 3.6 4.32 5.04 5.76
0.32 0.35 0.37 0.40 0.43 0.46 0.48
1.00 1.12 1.24 1.36 1.48 1.60 1.72 1.84 1.96
0 5 10 15 20 25







Averaged by Intensity

Averaged by Position