What is Elemental Carbon and How Do Definitions Differ for Different Applications?

Bob Cary and David Smith

Speciation of Carbon Aerosol

- **Organic – Elemental – Inorganic**
- **Sources**: OC – Many
  EC – Pyrolysis of OC's

Analysis of Ambient Carbon Aerosols

- HOW
  - -???
- WHAT
  - -Elemental Carbon
  - -Organic Carbon
  - -Inorganic Carbonate Carbon
- WHY
  - -Health
  - -Visibility
  - -Source Tracer
  - -Climate Effects

Carbonate and Organic Carbon

- **Inorganic Carbonate Carbon**

  -e.g. CaCO3 (limestone dust – most common)

- **Organic Carbon**

  -Nearly all remaining carbon

  -Primary-Secondary-Condensed Vapor

  -Wide Range of Chemical and Physical Characteristics

EC Aerosol Species
(BC, Graphitic Carbon; NOT Soot)

- **Elemental Carbon**

  -Extended Aromatic Rings of Carbon Atoms

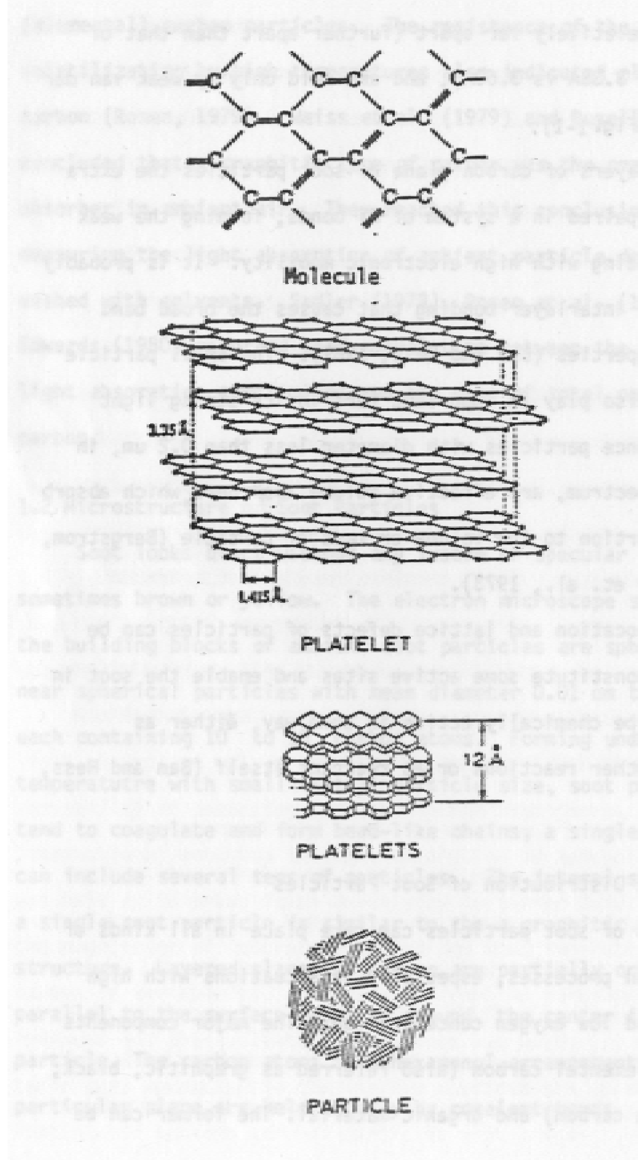
  -Black (absorbs all visible light radiation)

  (Degenerate Resonance Pi-bond electrons in conductance bands; Metal-like)

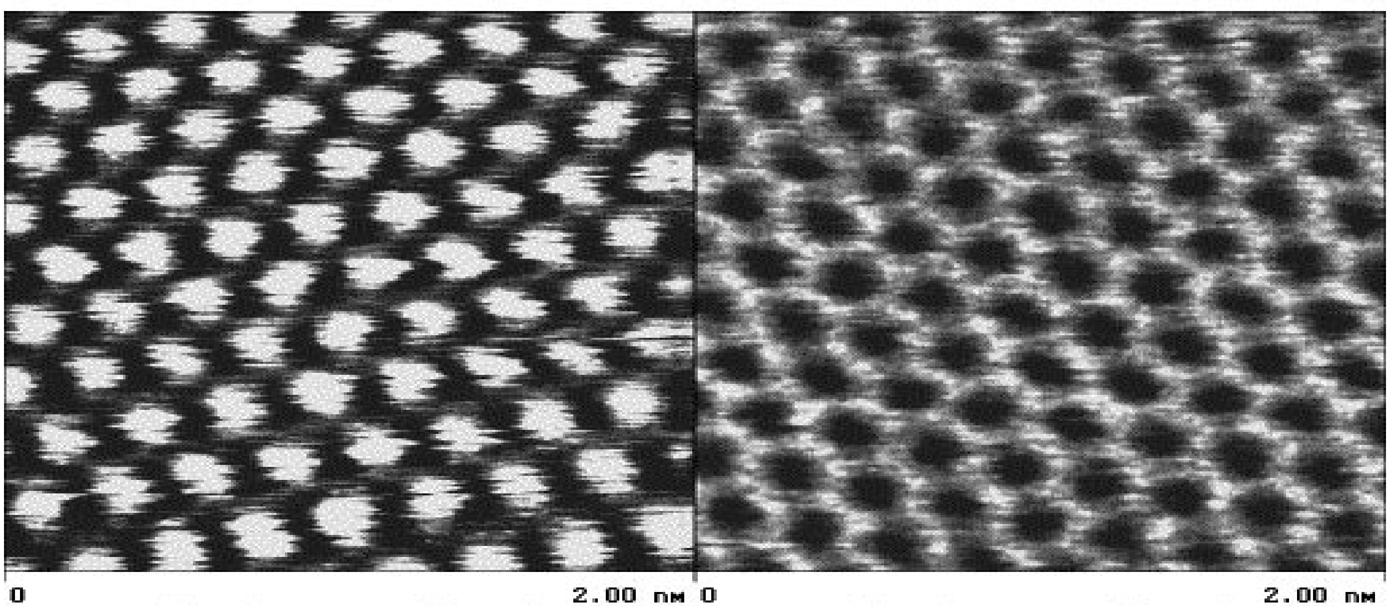
  -Refractory (does not melt or sublime, even at high temperatures; >2000 C)

  - Insoluble and Chemically inert at normal temperatures

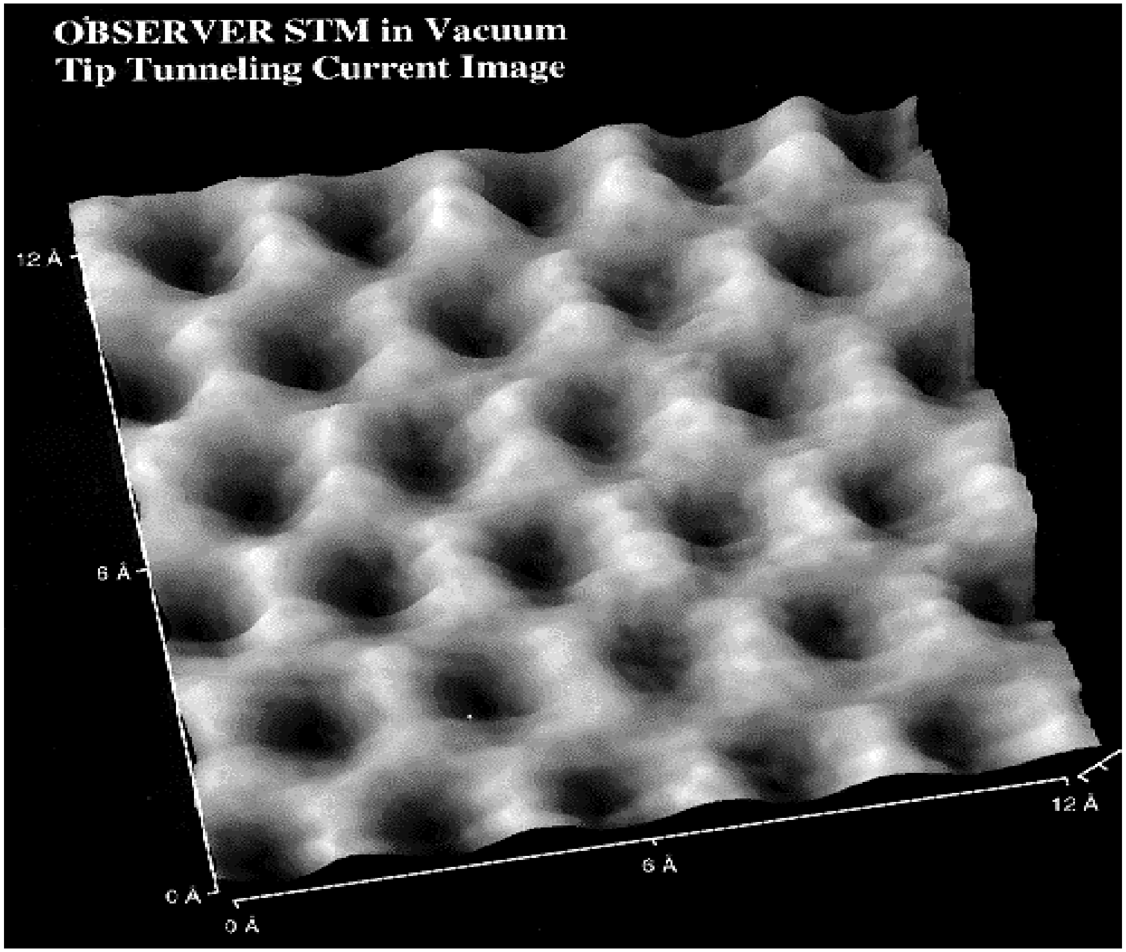
Idealized EC Structure



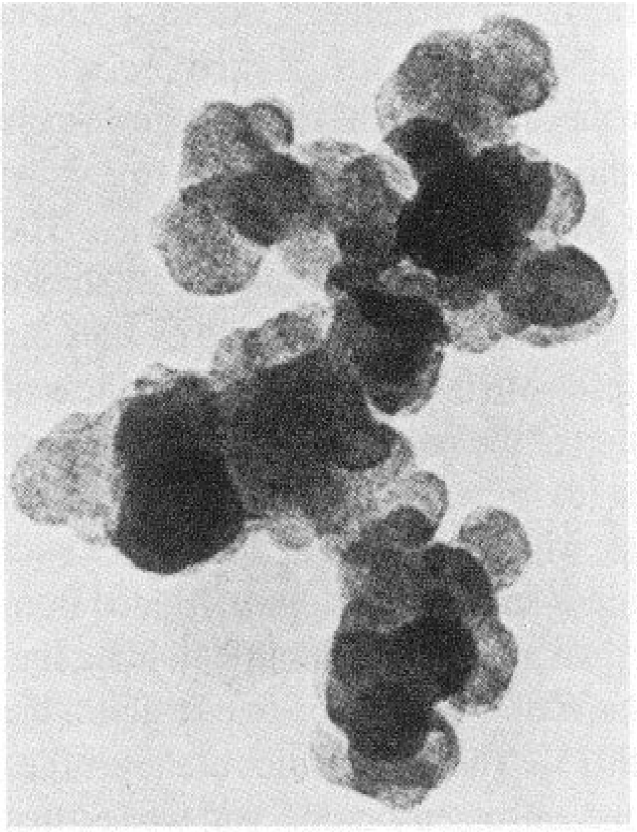
STM of Graphitic Carbon



STM of Graphitic Carbon

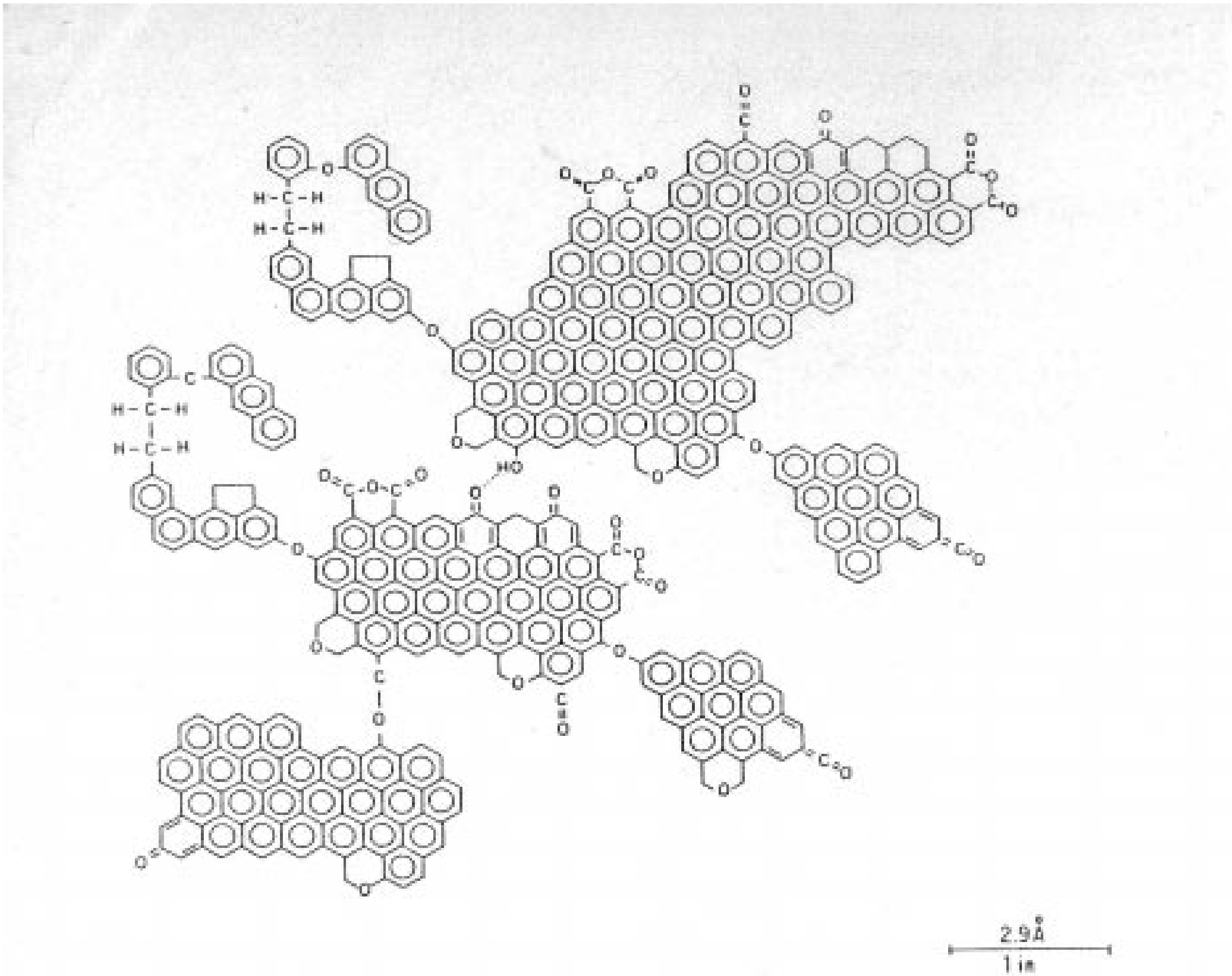


Fractal Structure of EC



Soot Representation

from Akhter, Chughtal and Smith, Applied Spectroscopy, 1985



Formation of EC

- EC created by Pyrolysis of OC
- Thermal Energy breaks bonds creating atoms and molecule fragments
- Usually exist as Radicals
- Subsequent collisions can cause recombination to form new bonds
- Extended C-C bonds build aromatics
- Small atoms or fragments diffuse away quickly; e.g., H_2 or H-radicals

Quantitative Measurement of EC

- DIRECT
- DIFFERENCE

Direct Measure of EC

- Using Optical Properties and Spectroscopic Techniques

  i.e., Absorbance of Electromagnetic Radiation

Abs. Coeff. Vs. Size

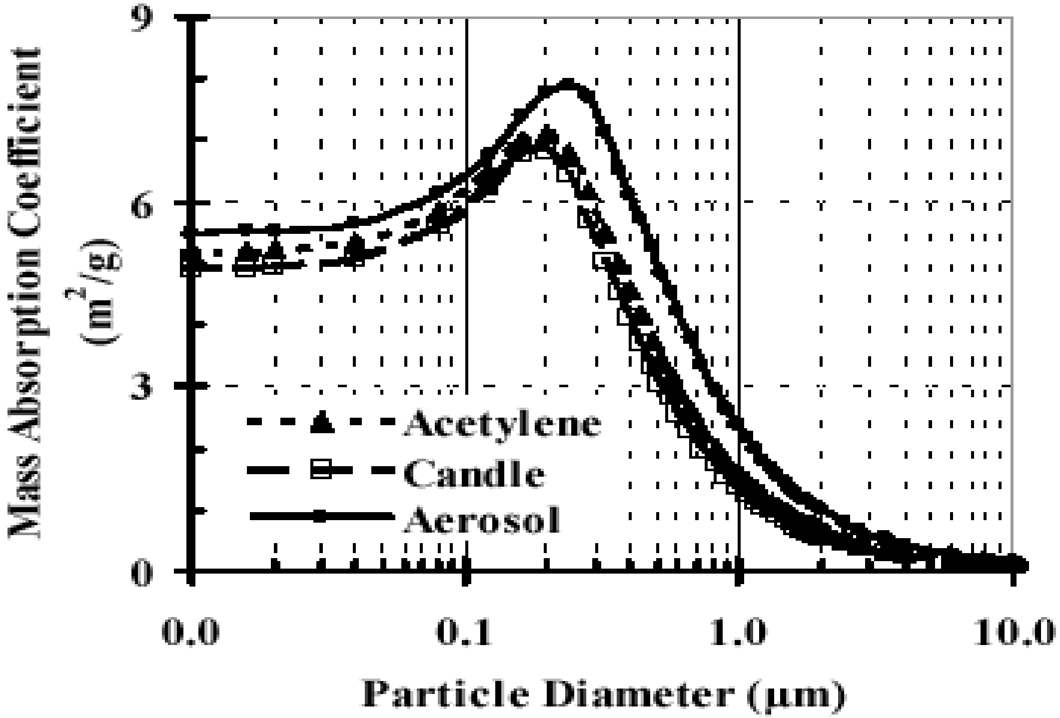


Fig.2. Calculated mass absorption coefficients for candle smoke, acetylene and atmospheric aerosols versus particle aerodynamic diameter for 633nm wavelength He/Ne laser light.

e.g., from Horvath, Fuller, Taha

Absorbance by EC

- Depends on wavelength
- Depends on size of particle
- Depends on morphology of particle (e.g., small monomeric clusters or fractals or agglomerated fractals)

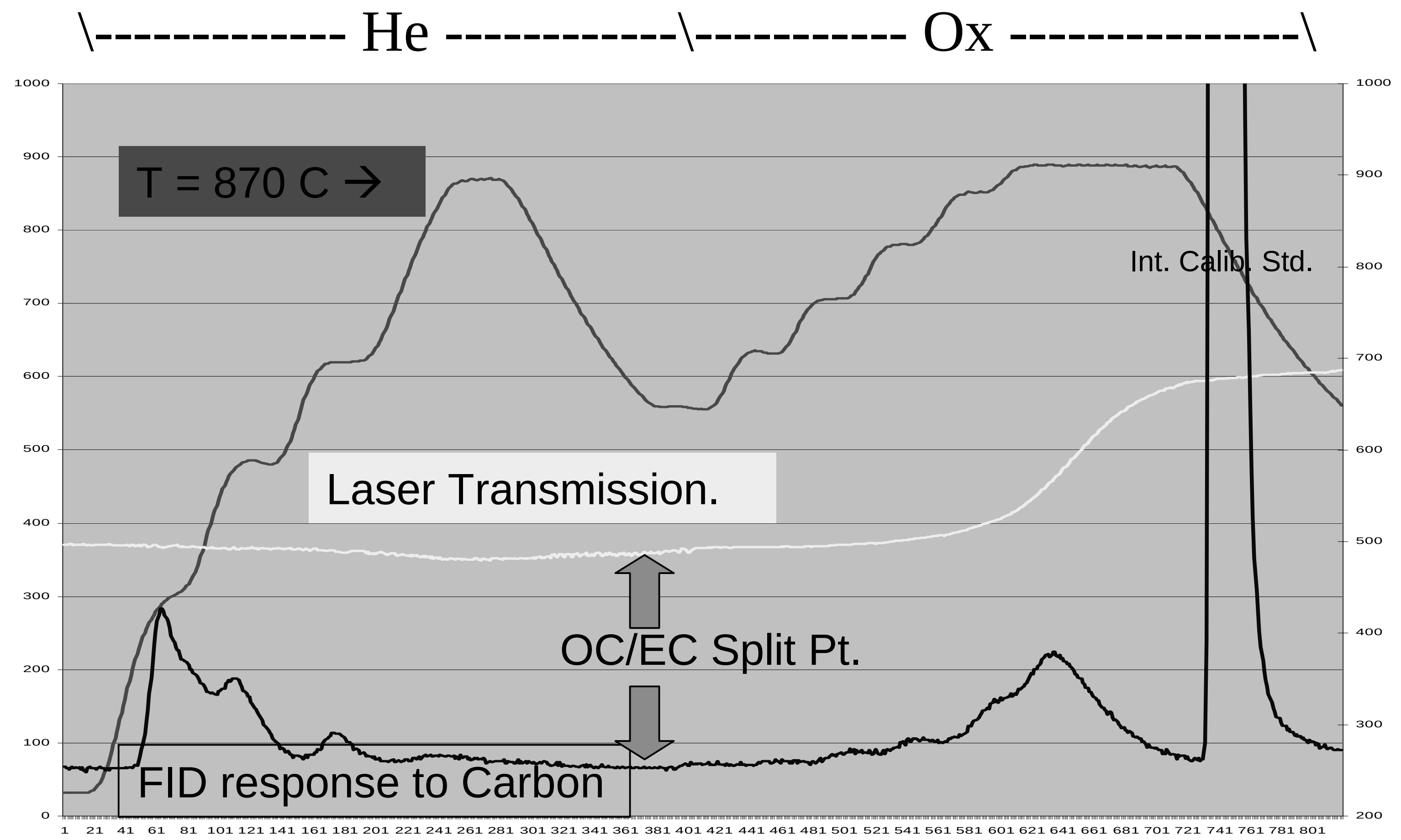
Difference Measure of EC by Removal of OC from TC

- Remove OC by Solvent of Chemical Means
- Remove OC by Thermal Methods
- Combinations of Above

  e.g., heat in oxygen atmosphere

Finally Do some Type of Direct Measurement

T/O Analysis of Diesel



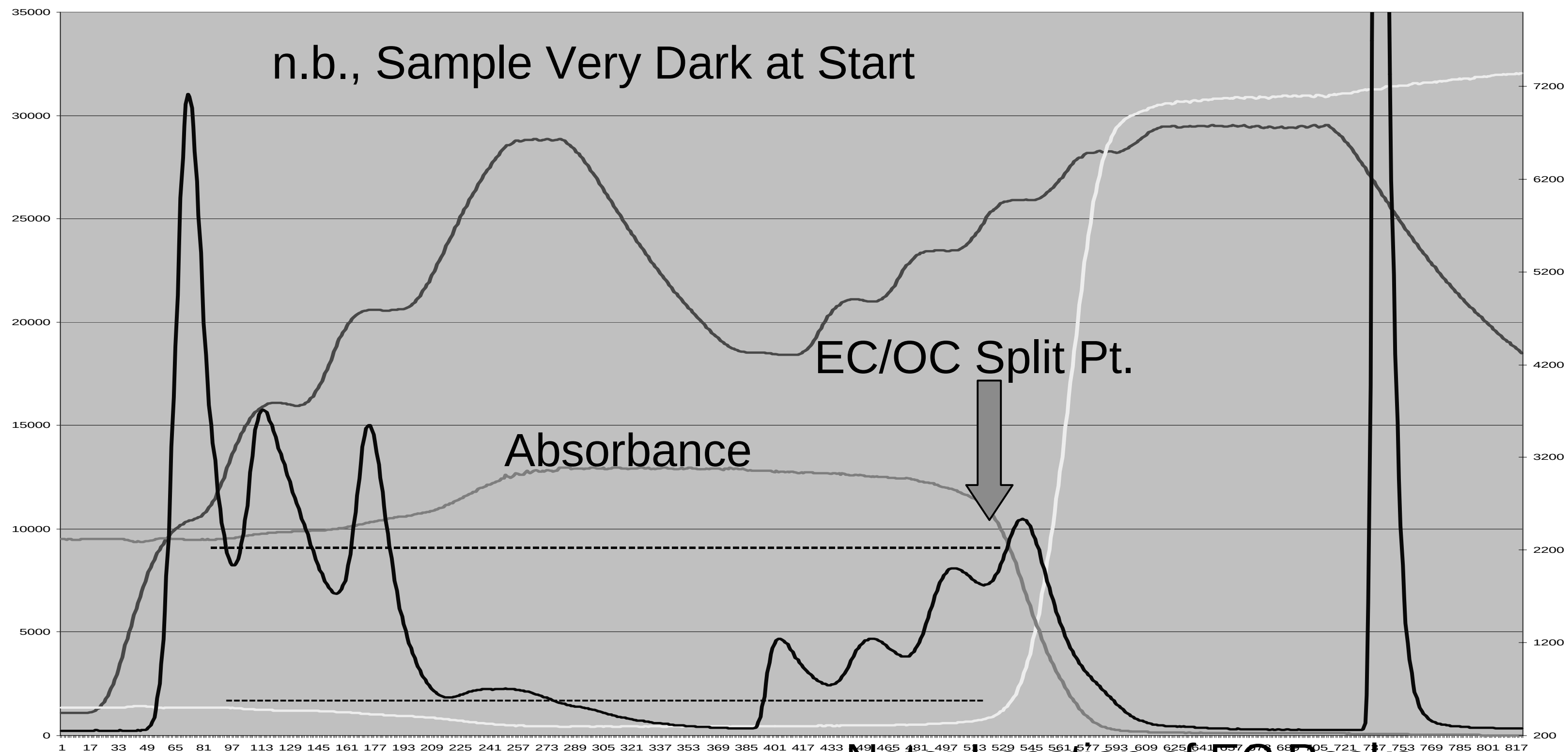
Note: Very Little Pyrolysis

Note: Small OC4 Peak

Note: EC Peak Location

T/O Analysis of Ambient
(wood smoke and metal oxides)

\------------- He ---------------------\-------------- Ox --------------------------\



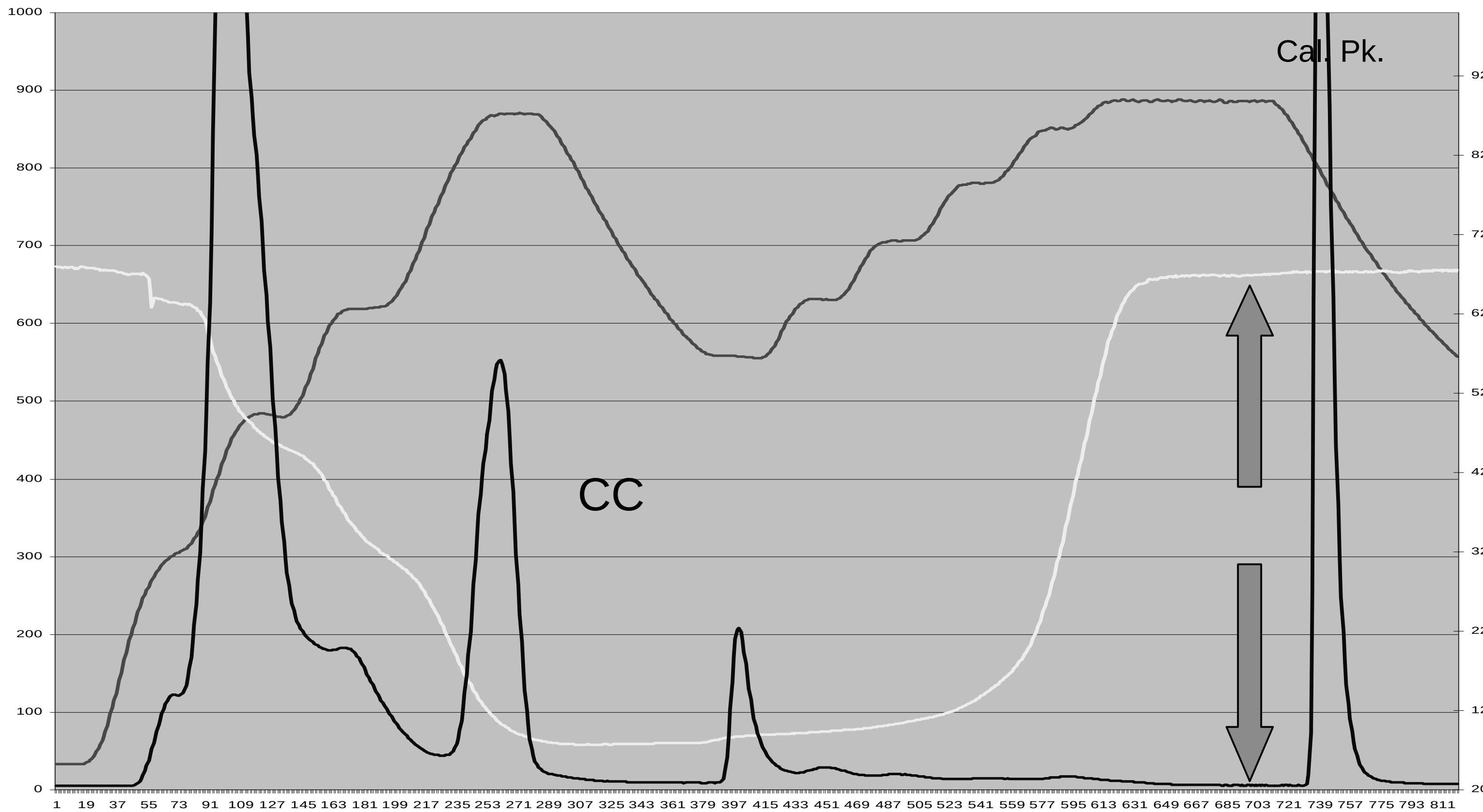
Note: Abs Increase at OC4

Note: Location of EC Peaks

[Fe] = 7.8 ug/sq cm

Sample with OC and Carbonate Carbon

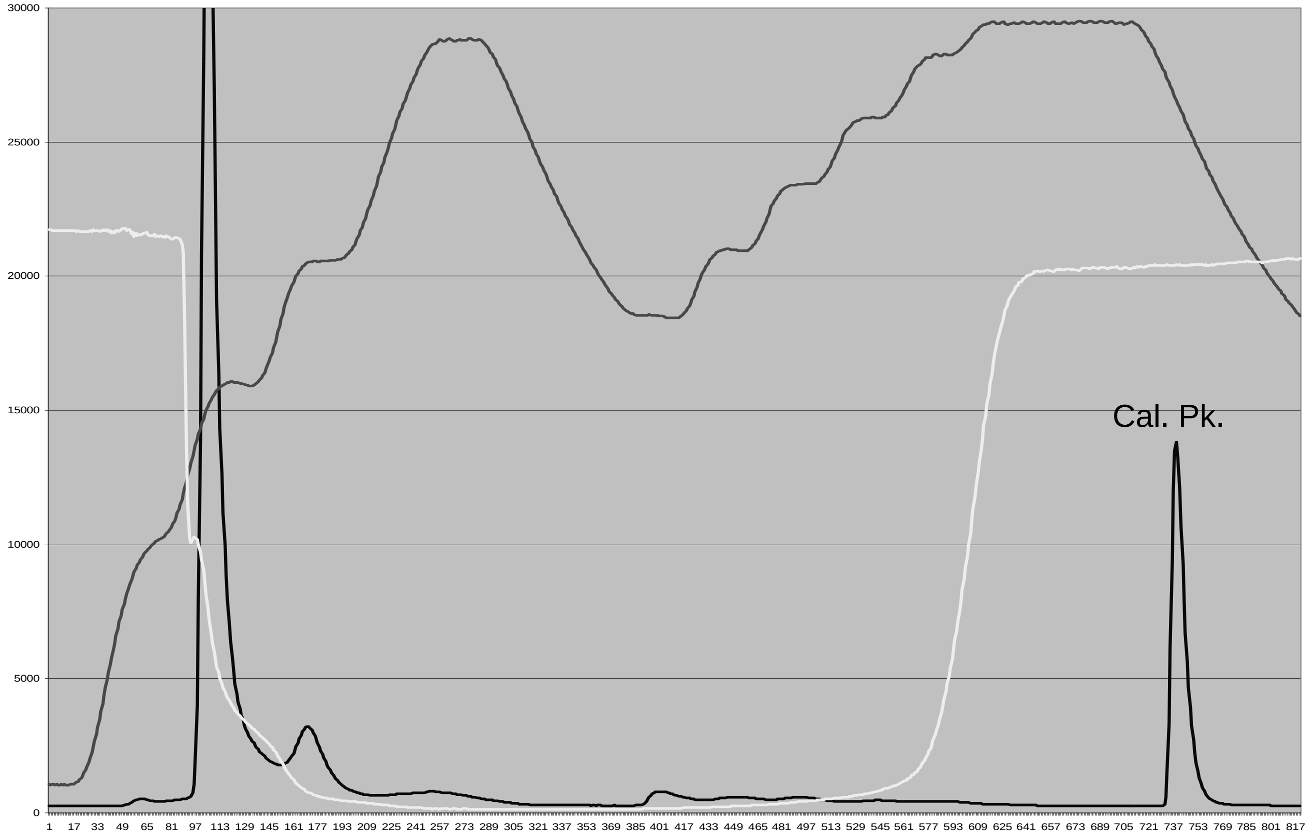
\\----------------- He -----------------\\-------------------- Ox --------------------\\



Note: Sharp OC4 Peak

T/O of Pure Organic EDTA

\------------------ He -------------\---------------- Ox ----------------\



Further Pre-Treatments

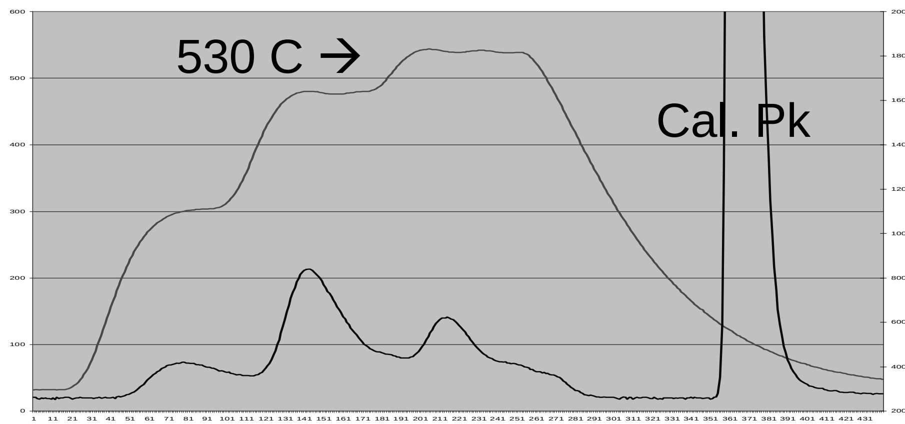
- Solvent Extractions (organic or water)
- Chemical Pre-Treatments
- Other Thermal-Treatments

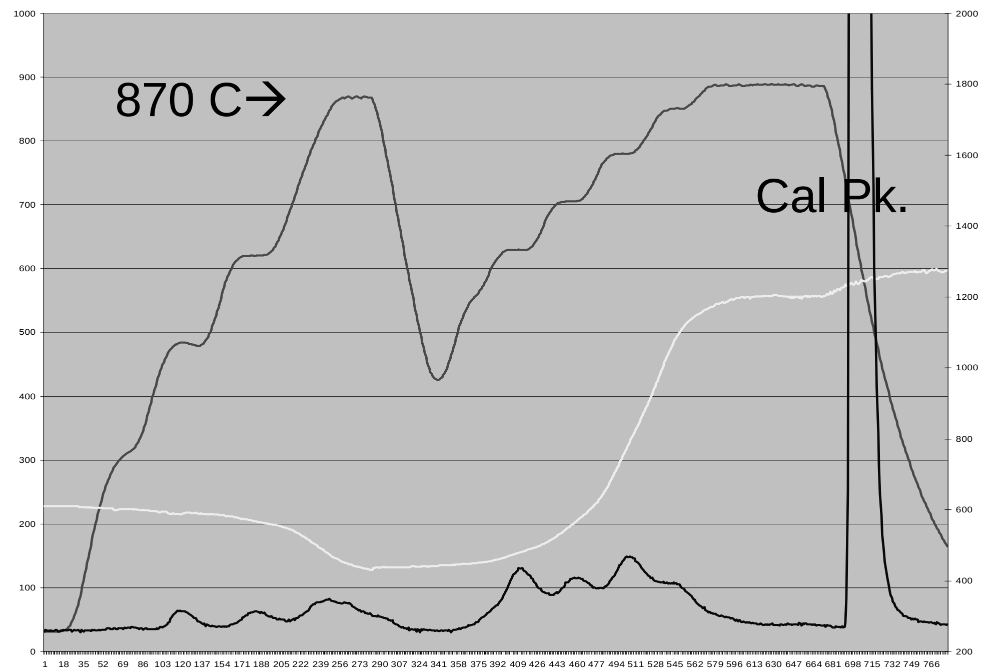
Pre-Treatment with Oxygen followed by Full Thermal-Optical Analysis

Residual then Analyzed with TOA

\------- He -----------\---------- Ox --------------\

\-----------------He and Oxygen -------------\





SUMMARY

- There are Chemical and Physical Definitions of EC
- These Properties may differ for small particles compared with bulk material
- Analytical Methods should try to be consistent with these definitions

Further Research on EC

- Can Additional Pre-treatments Help?
- Do the Physical or Chemical Properties Change?

  - From Source to final Collection or Measurement?

  - During Analysis itself?