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

OBSERVER STM in Vacuum
Tip Tunneling Current Image
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., H2 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

![Graph showing mass absorption coefficients for different particle diameters.](image)

**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

\[\text{He} \quad \text{Ox}\]

T = 870 C 

Laser Transmission.

OC/EC Split Pt.

FID response to Carbon

Note: Very Little Pyrolysis
Note: Small OC4 Peak
Note: EC Peak Location

3/18/2003
T/O Analysis of Ambient (wood smoke and metal oxides)

\[ \text{[Fe]} = 7.8 \text{ ug/sq cm} \]

n.b., Sample Very Dark at Start

Note: Abs Increase at OC4

Note: Location of EC Peaks

3/18/2003 Sunset Lab OCEC
Sample with OC and Carbonate Carbon

Note: Sharp OC4 Peak
T/O of Pure Organic EDTA

Cal. Pk.
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

\( \text{He and Oxygen} \)

\( 530 \text{ C} \rightarrow \text{Cal. Pk} \)

\( 870 \text{ C} \rightarrow \text{Cal. Pk.} \)
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?