OC/EC Analysis with Thermal-Optical Methods

Effects of temperature protocol and non-carbonaceous compounds

R SUBRAMANIAN[†], Andrey Khlystov[#], Allen Robinson*

Carnegie Mellon University, Pittsburgh, PA

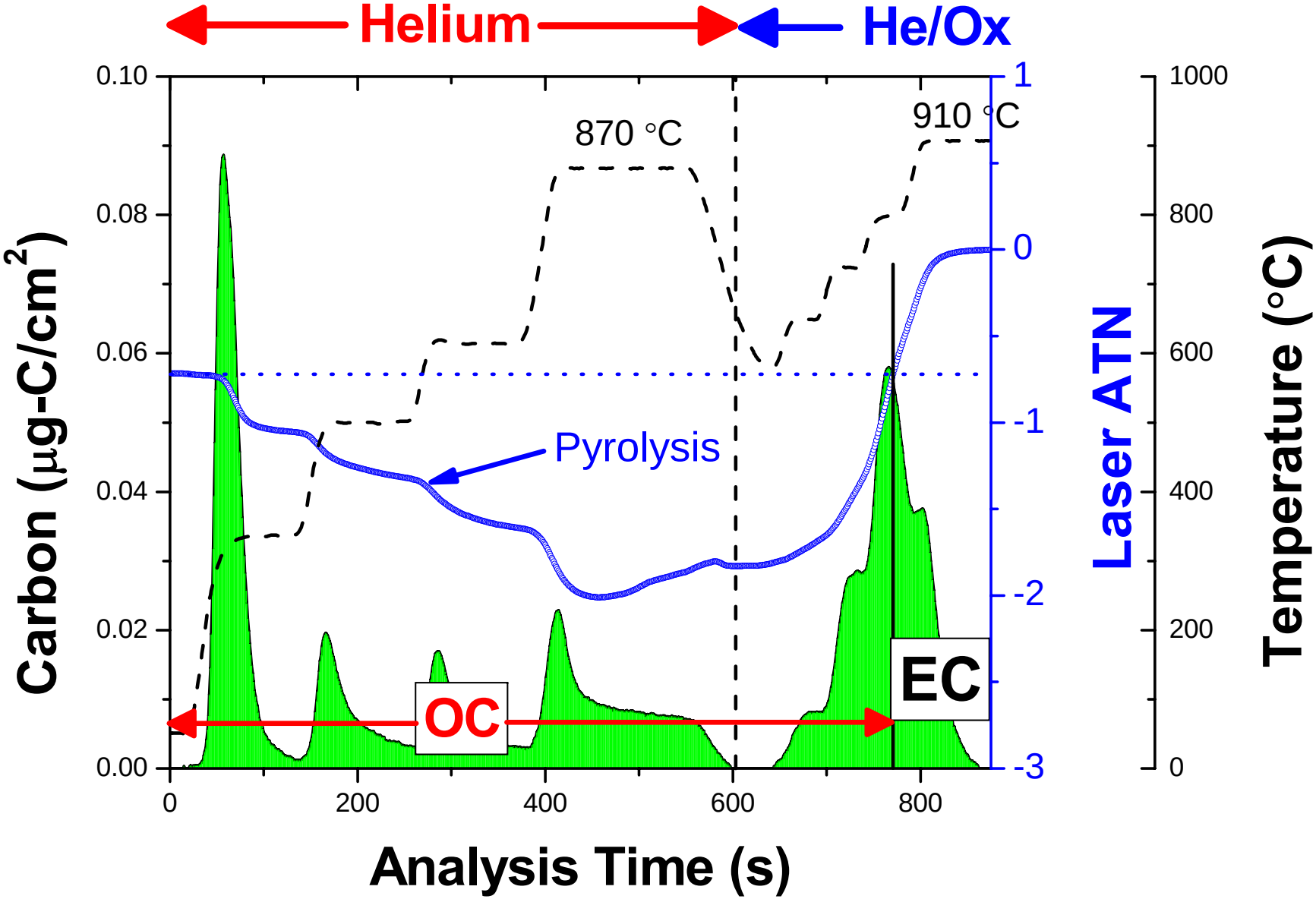
† now at the University of Illinois, Urbana-Champaign, IL

now at Duke University, Raleigh, NC

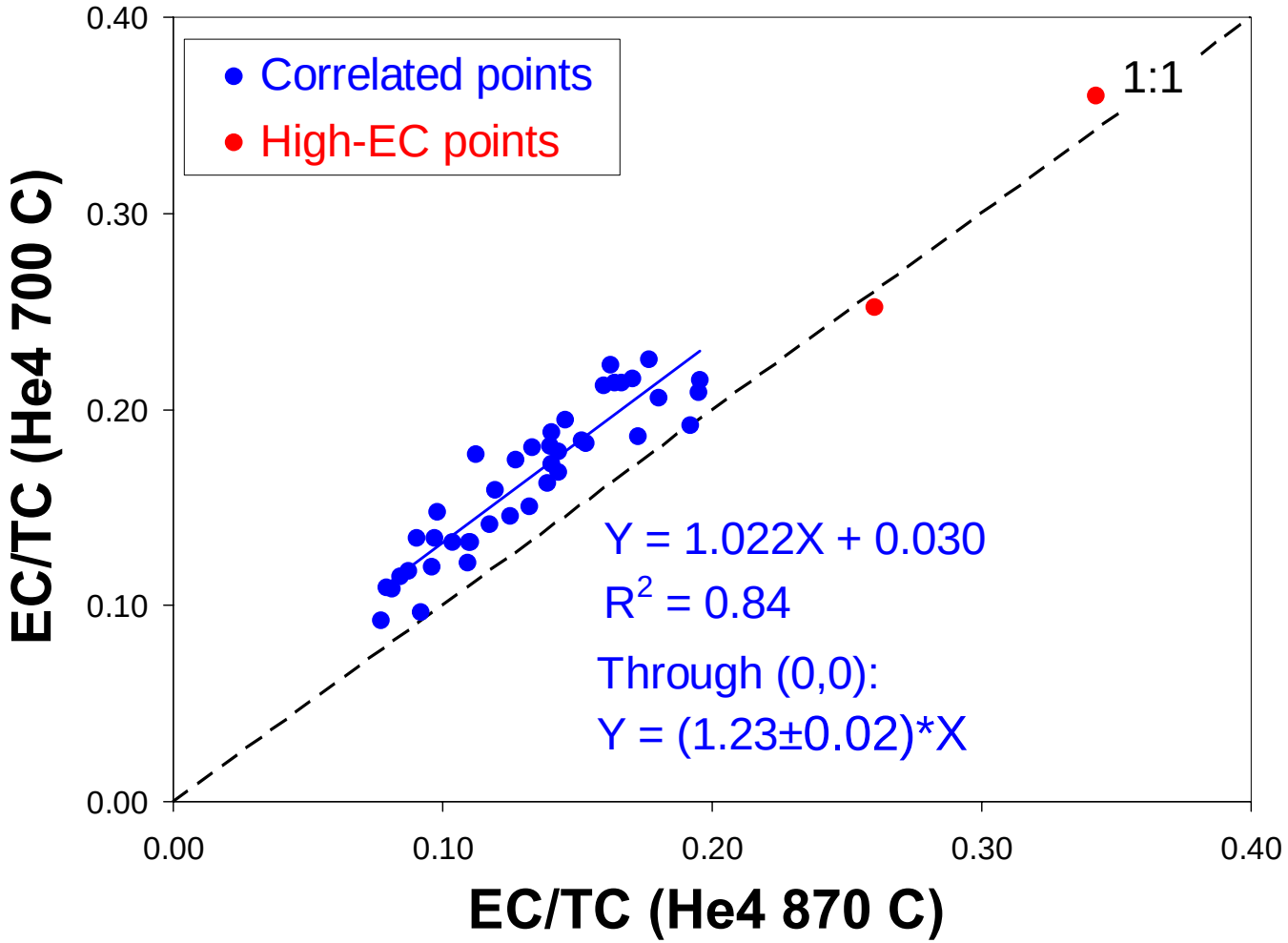
* alr@andrew.cmu.edu/ 412-268-3657

Platform 5C-1: AAAR Specialty Conference, February 2005

Thermal-Optical Analysis for OC/EC

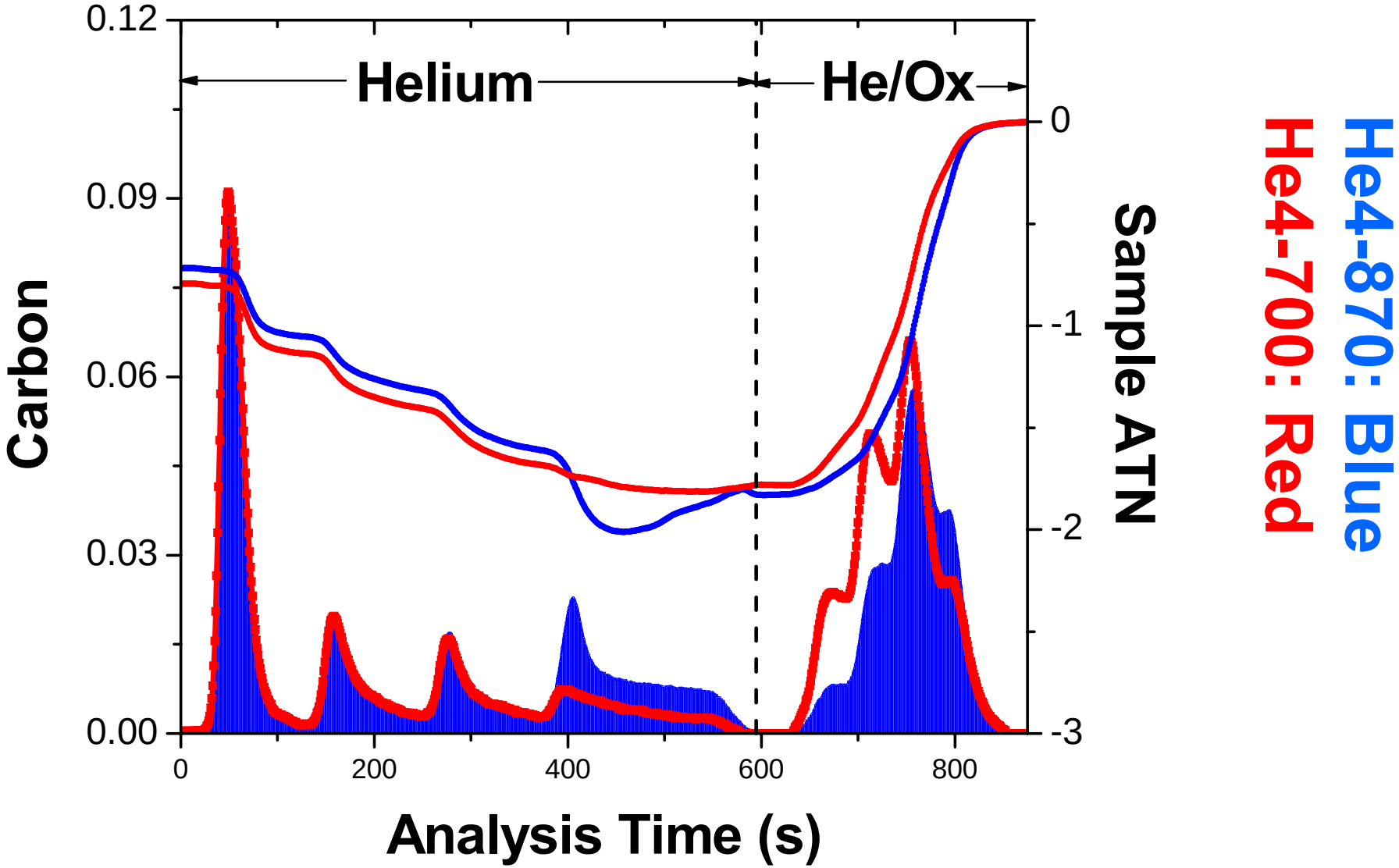


Temperature protocol affects EC



Also seen by Chow et al. (2001); Schauer et al. (2003); Conny et al. (2004)

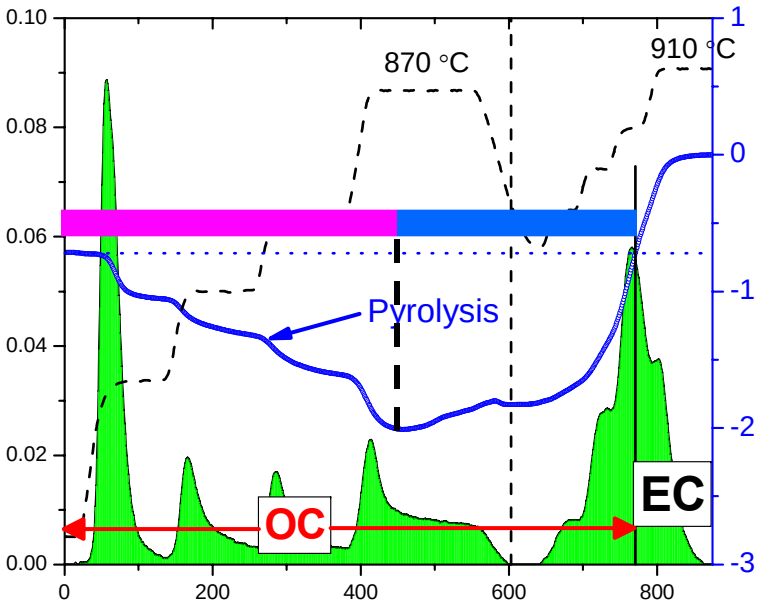
Differences: He4-870 v/s He4-700



Objectives of our research

- Develop a mechanistic understanding of the thermal/optical method:
  - Evaluate the assumptions
  - Carbon evolution pattern
  - Optical properties of evolving carbon
- Estimate the potential uncertainties
- Examine possible improvements to the EPA thermal/optical method

Method assumptions



$PC_{total} * k\_PC \sim PC_{pre\text{-}split} * k\_PC + EC_{pre\text{-}split} * k\_EC$

Assumption 1: $EC_{pre\text{-}split} = 0$

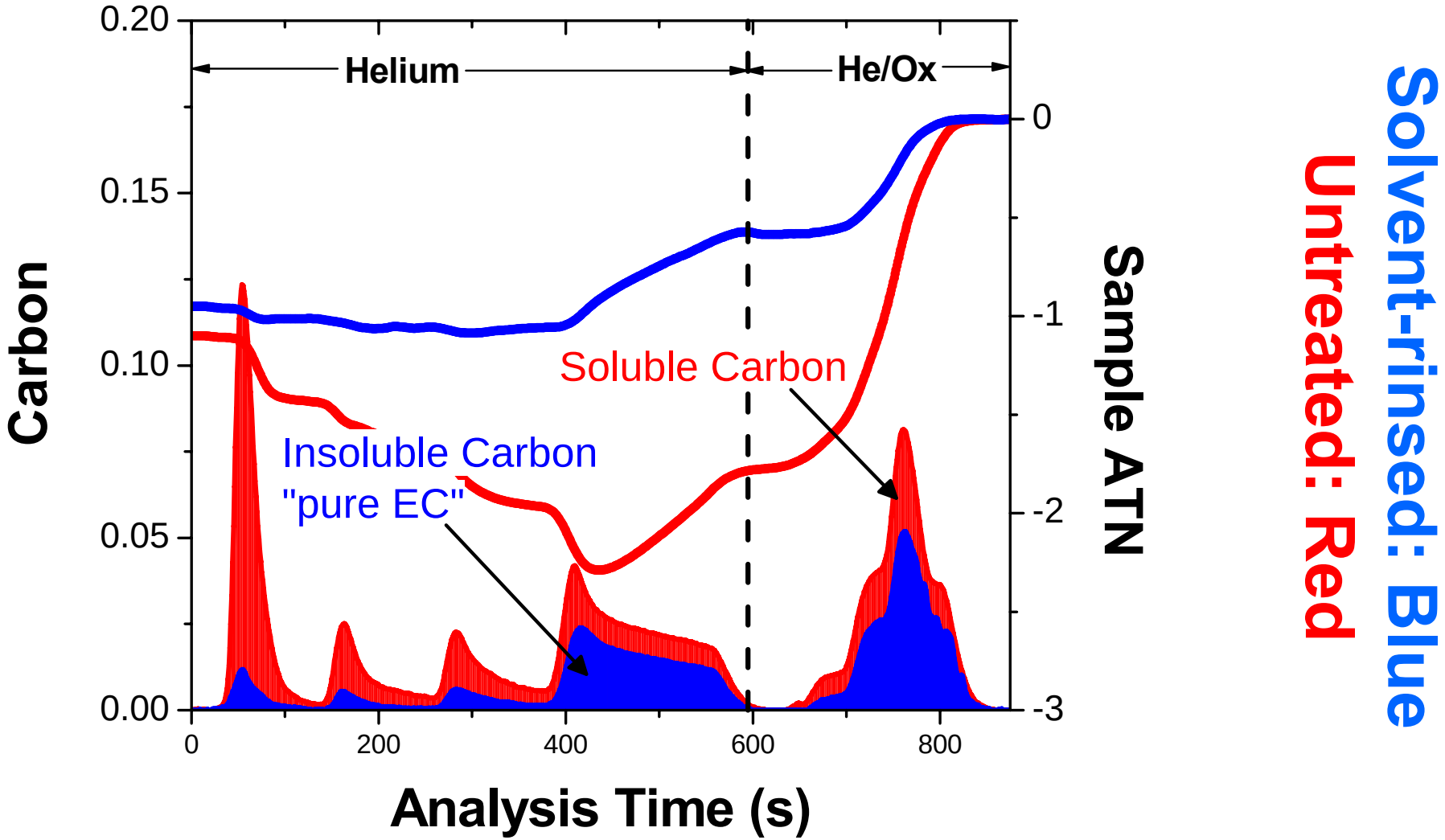
(PC evolves completely before EC)

or

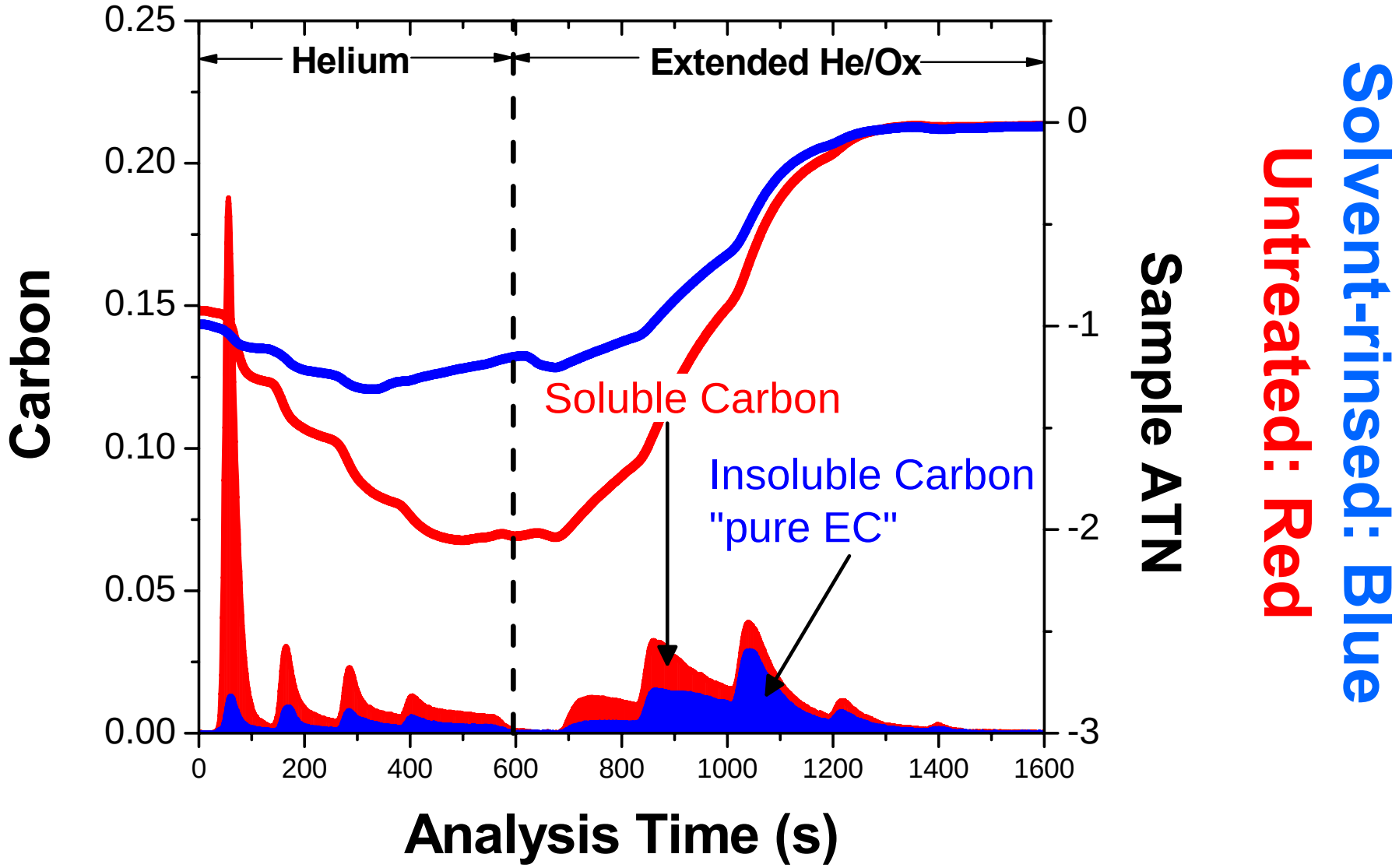
Assumption 2: k_PC = k_EC

(Optical properties of PC and EC are similar)

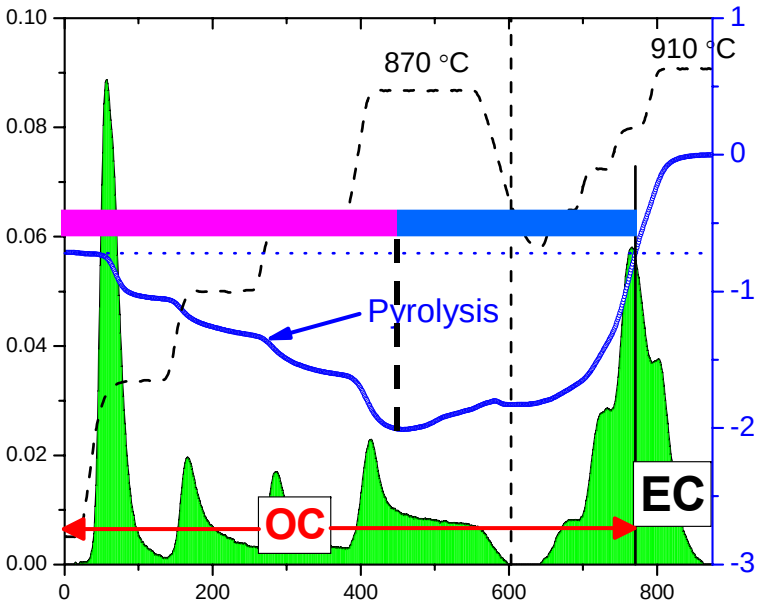
He4-870: Co-evolution of PC and EC



He4-700: Co-evolution of PC and EC



Assumption 1 not valid



$PC_{total} * k\_PC \sim PC_{pre\text{-}split} * k\_PC + EC_{pre\text{-}split} * k\_EC$

~~**Assumption 1: $EC_{pre\text{-}split} \neq 0$**~~

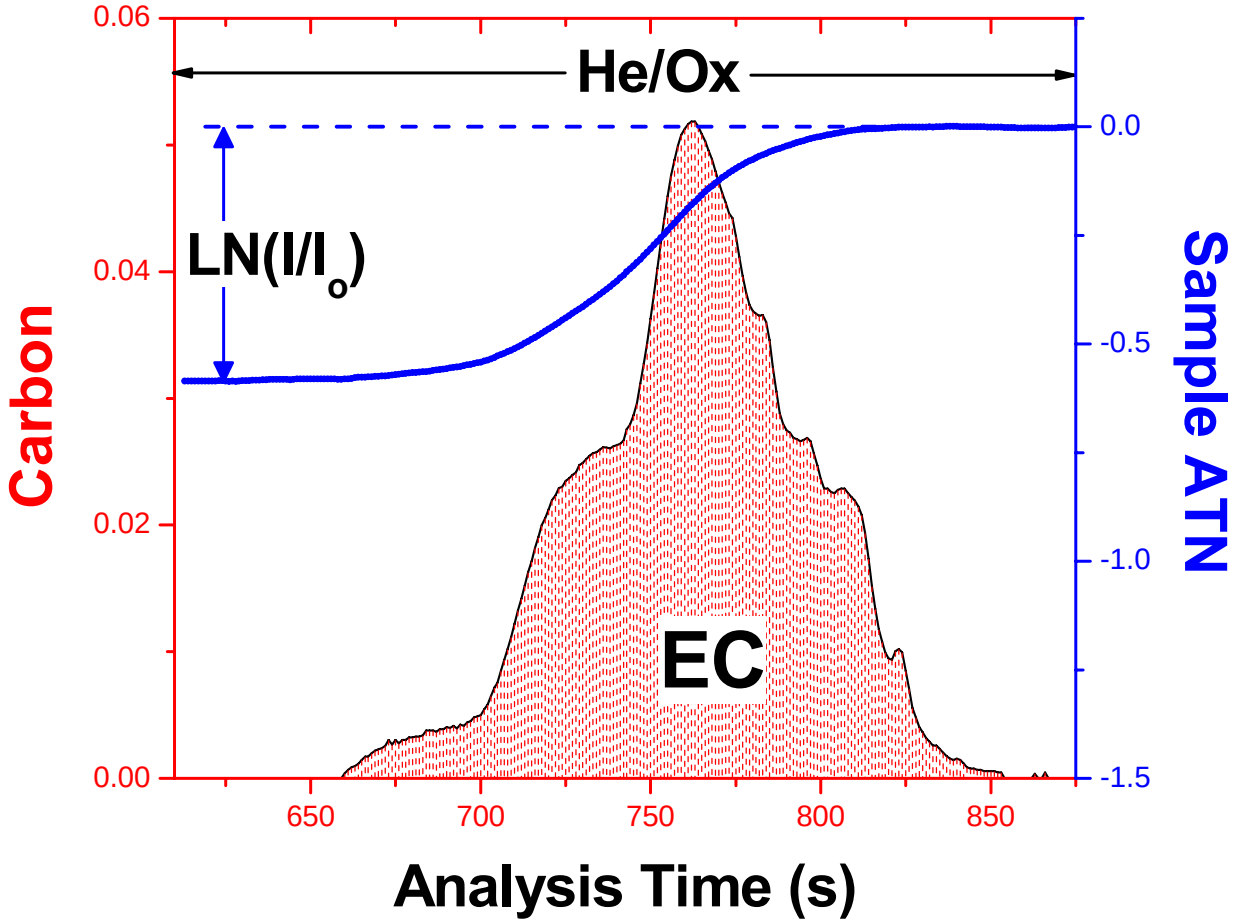
(PC co-evolves with EC)

or

Assumption 2: k_PC = k_EC

(Optical properties of PC and EC are similar)

Calculating k_EC with the solvent-rinsed filters

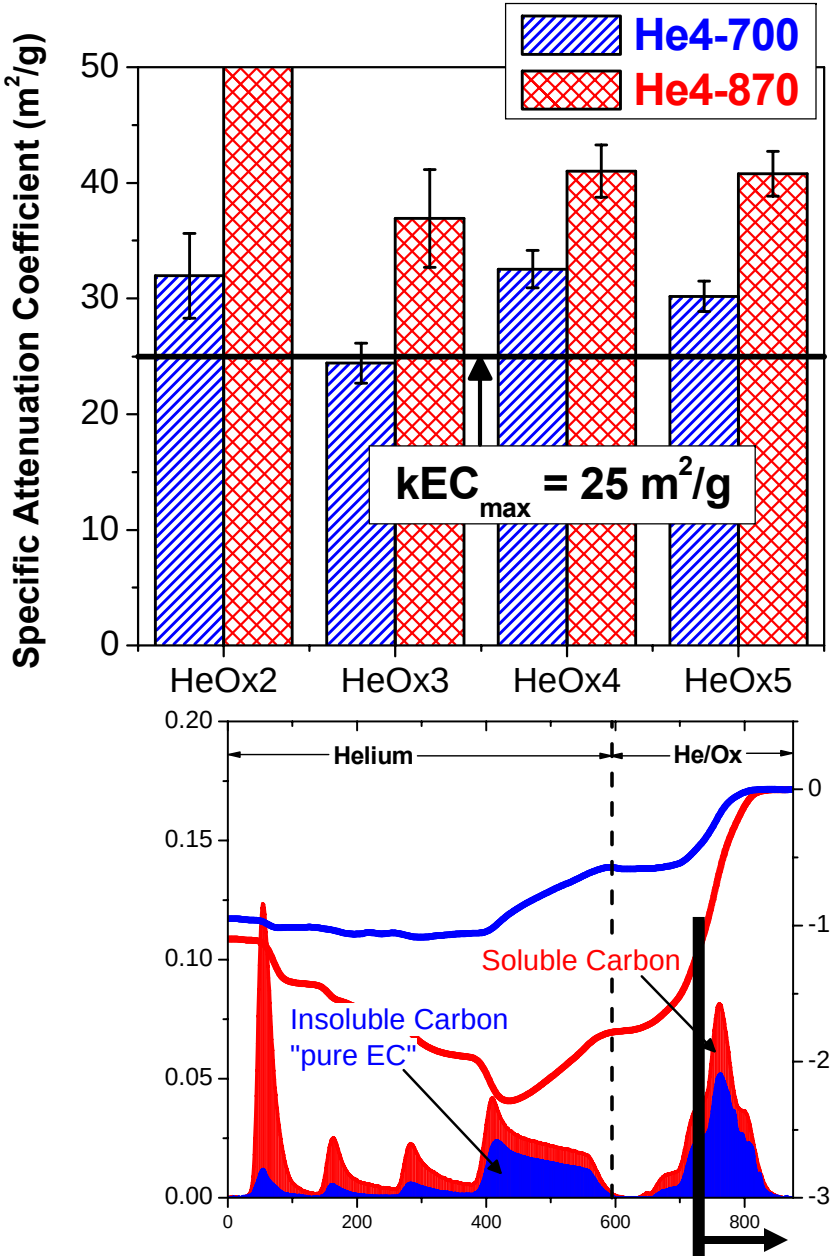


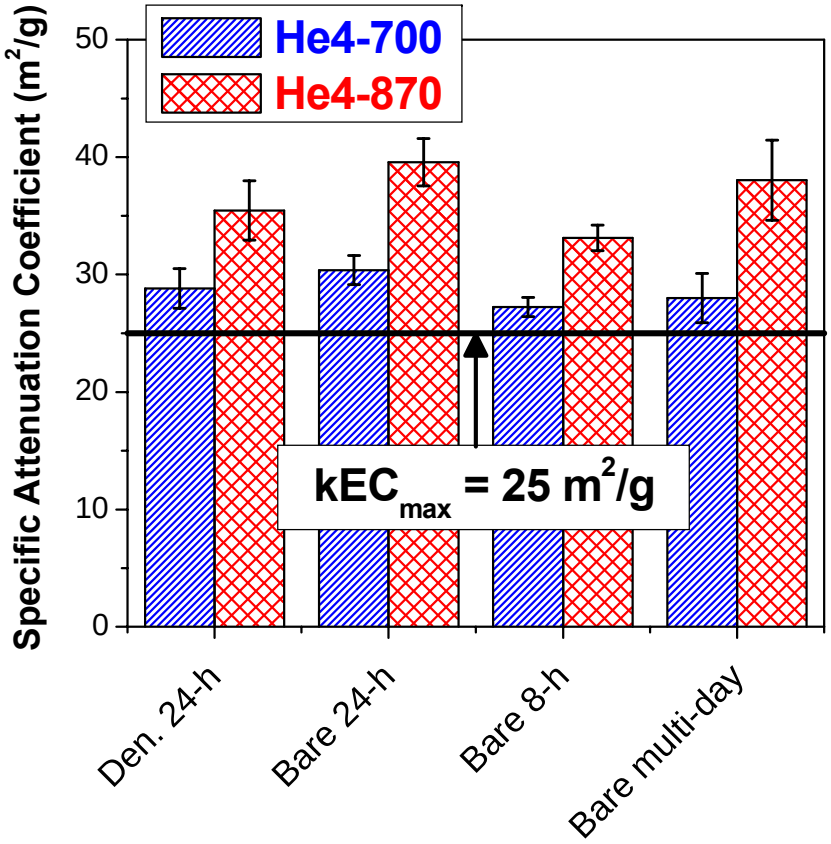
Lambert-Beer law:
LN(I/I$_o$) = EC * kEC

k_EC$_{rinsed}$
25.8 ± 2.8 m^2/g-C

k_EC similar to the findings of Gundel et al. (1984)
Squirrel Hill tunnel samples: k_EC ~ k_He/Ox = 20.6 ± 1.8 m^2/g

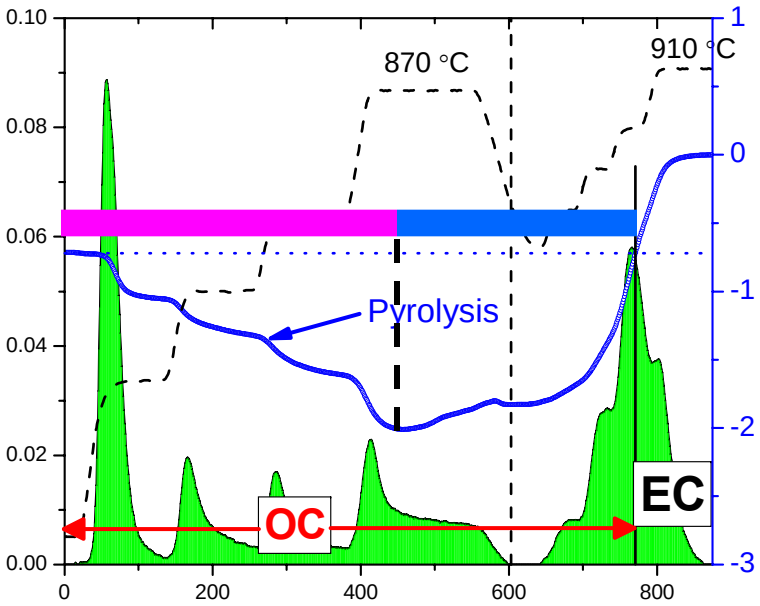
Specific attenuation of untreated carbon





Instrument-defined EC (k_"EC")

Assumption 2: also not valid!



$PC_{total} * k\_PC \sim PC_{pre\text{-}split} * k\_PC + EC_{pre\text{-}split} * k\_EC$

~~**Assumption 1: $EC_{pre\text{-}split} \neq 0$**~~

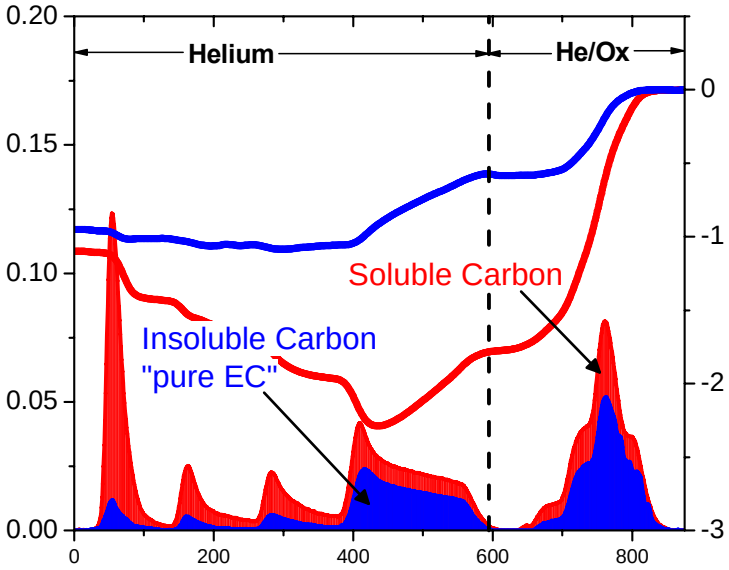
(PC co-evolves with EC)

or

~~**Assumption 2: k_PC >> k_EC**~~

(Optical attenuation by PC is much greater than that by EC)

Uncertainties due to different optical properties



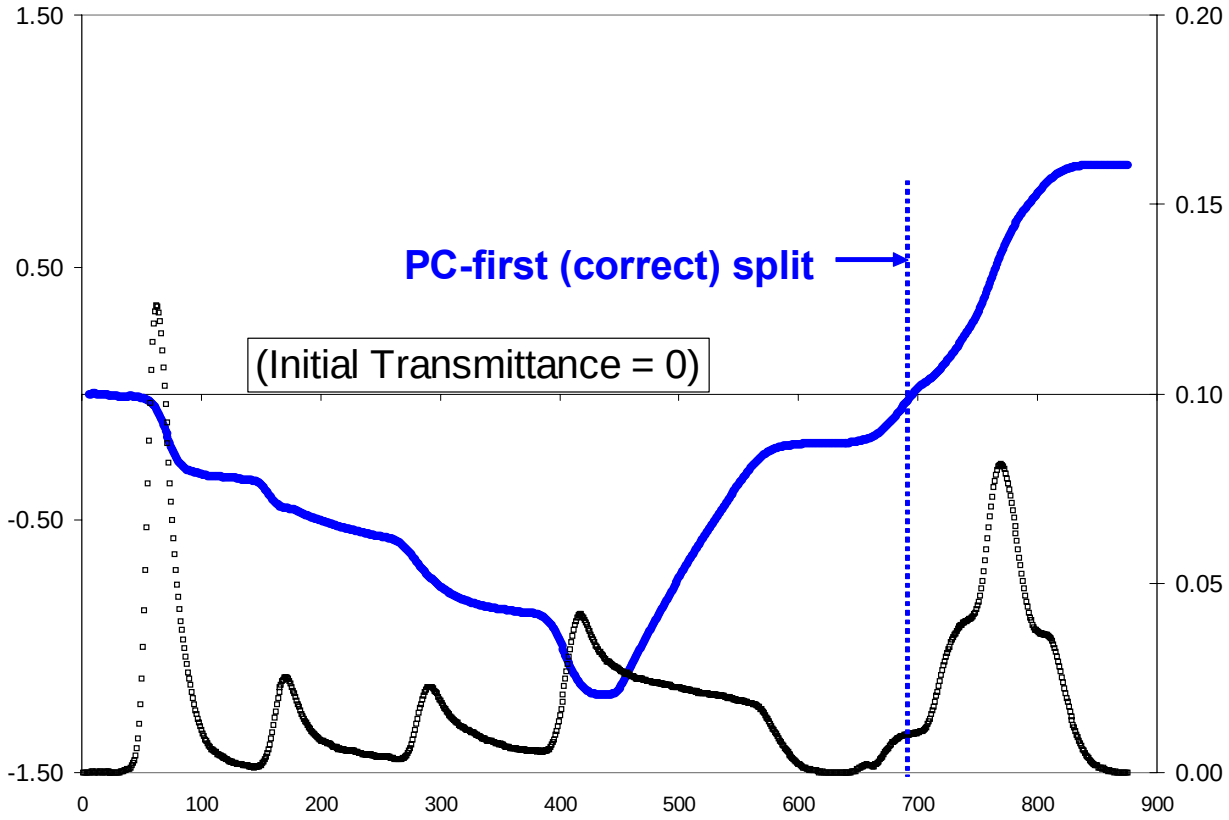
$$PC_{total} * 55.8 = PC_{pre\text{-}split} * 55.8 + EC_{pre\text{-}split} * 15.7$$

(a) Ideal: PC evolves completely before EC

(b) Worst case: EC evolves completely before PC

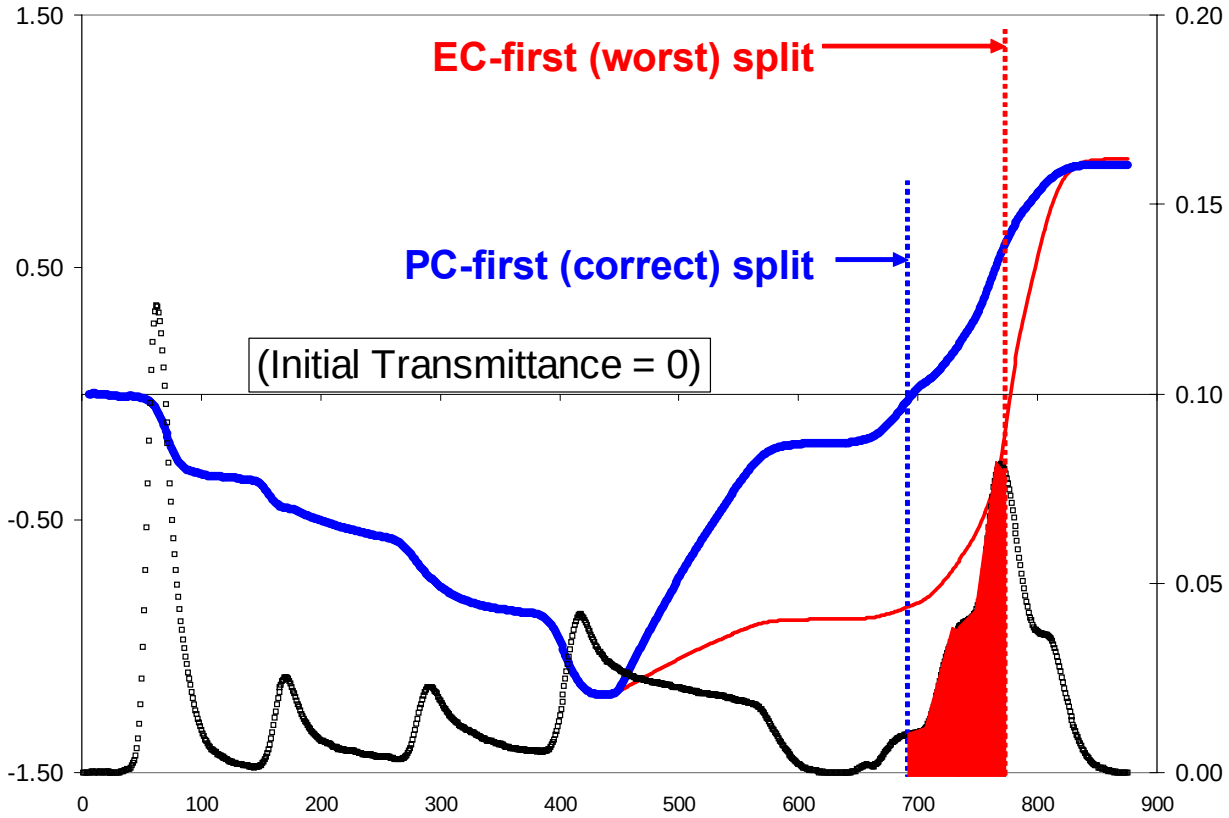
(c) Actual: Co-evolution of PC and EC

Ideal: PC evolves before EC



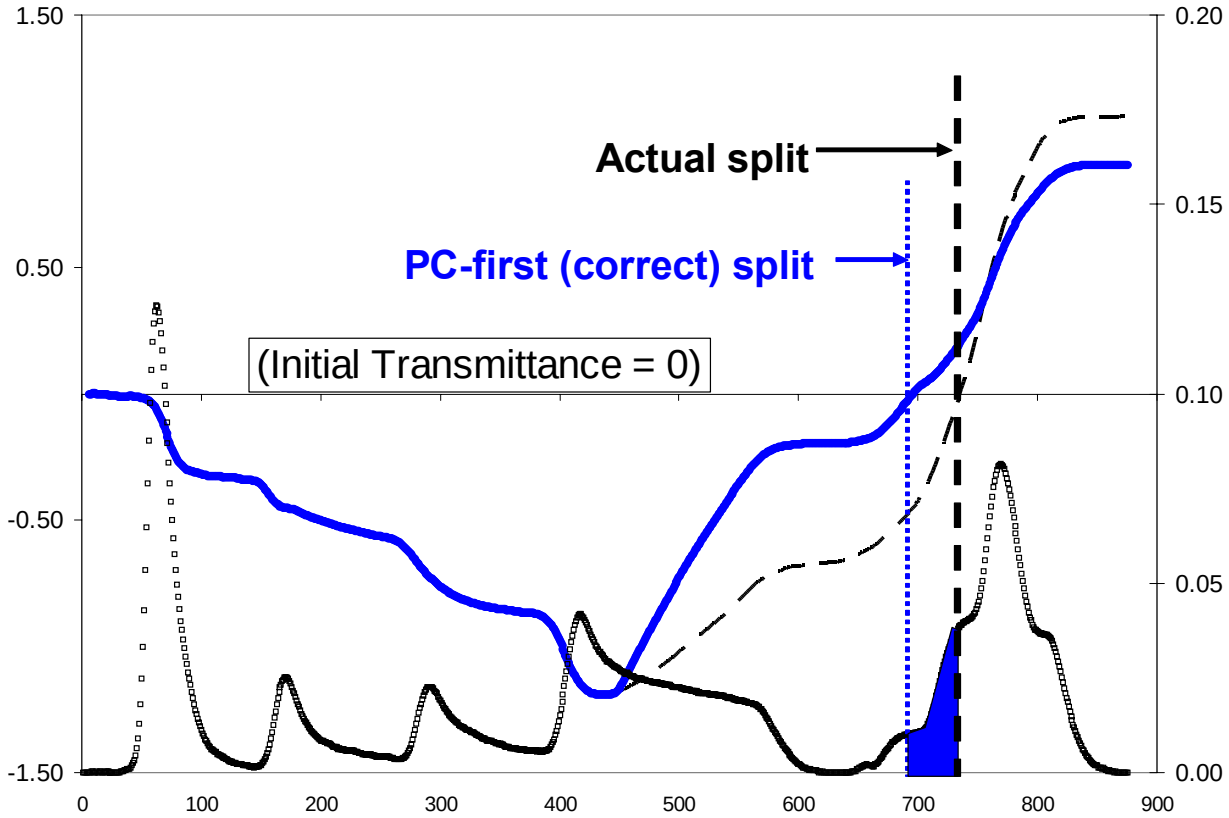
Actual EC = 5.5 µg-C/cm^2

Worst case: EC evolves completely before PC



Measured EC = 1.7 µg-C/cm^2
Error = - 68%

Actual under-estimation by He4-870 protocol



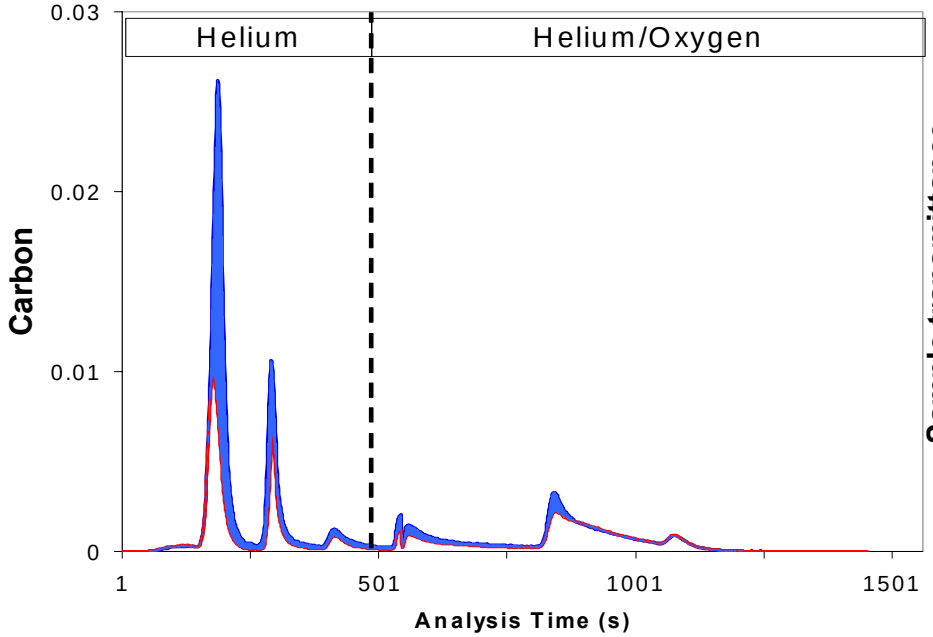
Measured EC = 4.4 µg-C/cm^2

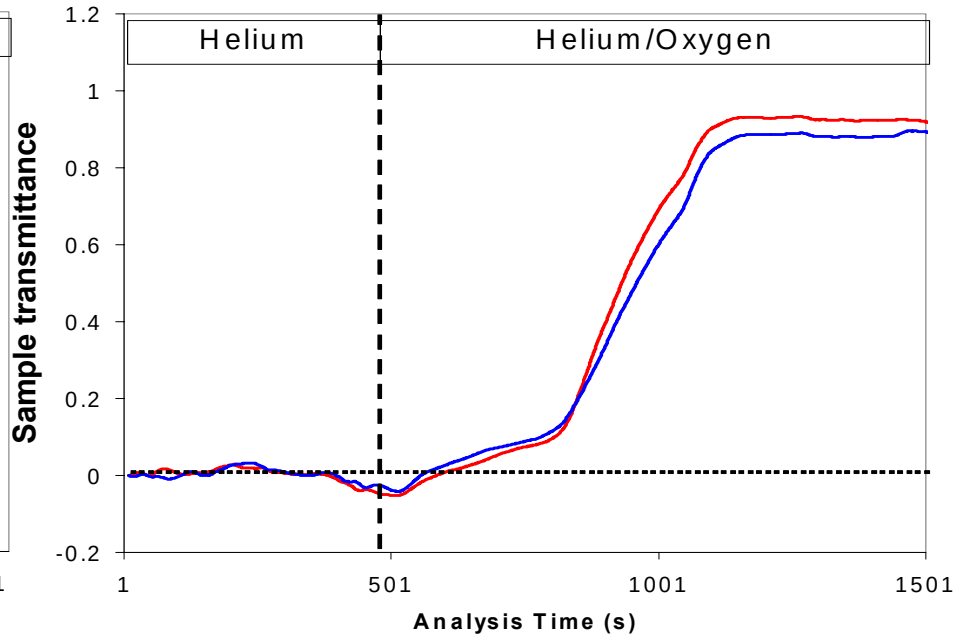
Error = - 20%

Improving the EPA thermal/optical method

- Reducing the peak Helium temperature reduces the negative bias
- He4-700 increases the EC compared to the He4-870
- What about reducing the peak Helium temperature further?
  - e.g. IMPROVE has a peak Helium temperature of 550 °C
  - Potential positive bias with unpyrolyzed organics?

Improving the EPA thermal/optical technique: He4-550?

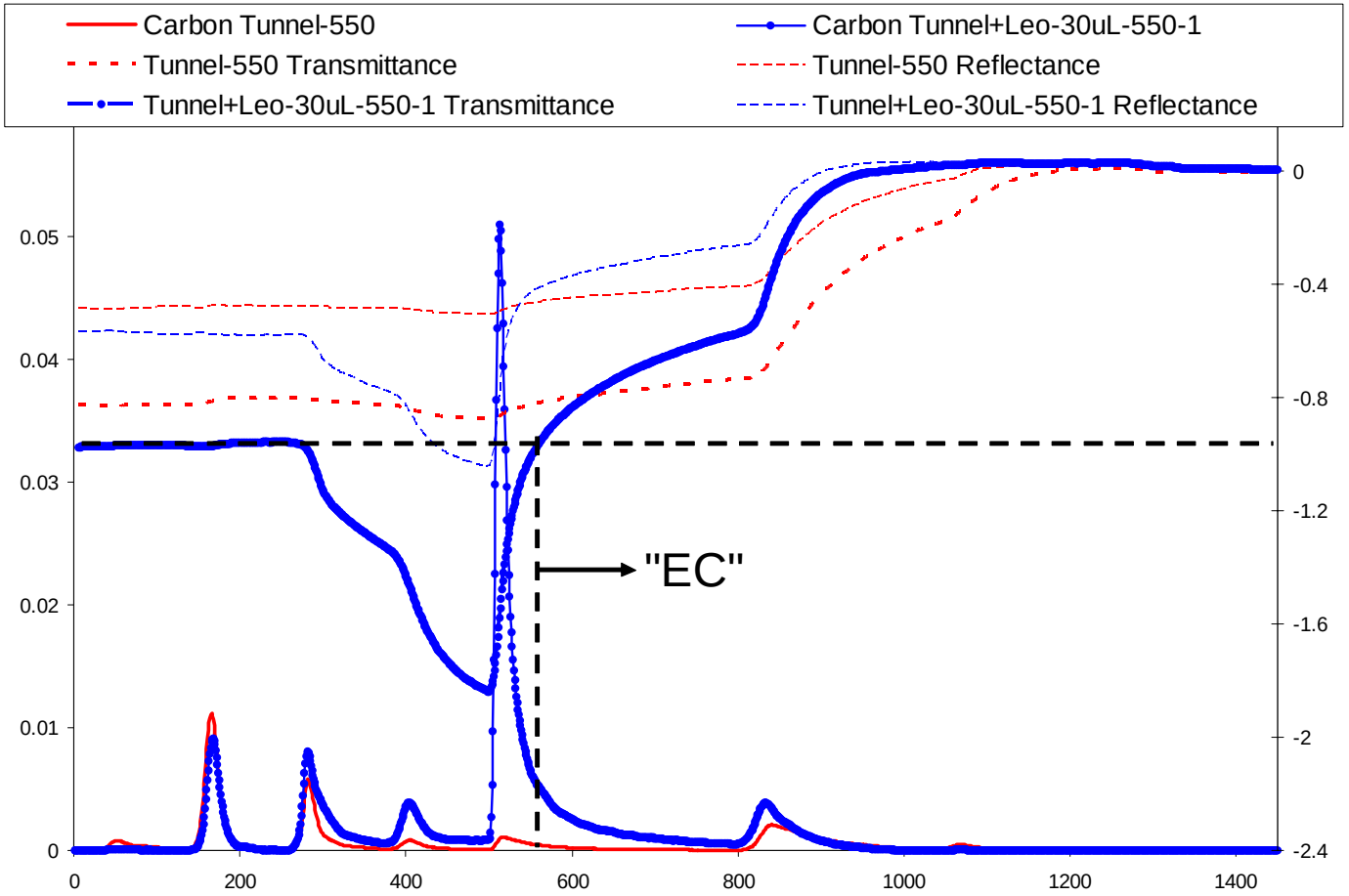




Vehicular exhaust:
TC 14.2 µg-C/cm^2
EC 5.4 µg-C/cm^2

Veh. exhaust + Levoglucosan:
TC 23.9 µg-C/cm^2
EC 7.4 µg-C/cm^2

He4-550: Positive bias with leonardite?



Vehicular exhaust:
TC 6.83 µg-C/punch
EC 2.28 µg-C/punch

Veh. exhaust + leonardite:
TC 22.2 µg-C/punch
EC 5.89 µg-C/punch

Conclusions

- The thermal/optical method assumptions are not valid
  - PC and EC co-evolve; k_PC >> k_EC for Pittsburgh samples
- He4-870 under-estimates EC
  - Premature EC evolution coupled with different k_EC and k_PC
- He4-700 EC is 23±2 % higher than He4-870 EC
  - Reduces premature EC loss
- He4-550 may be too low, possibly subject to positive bias
  - Need to investigate large polymeric and colored organic compounds

Acknowledgments

- US EPA
- US DOE/NETL

- AAAR travel grant for R.

- Spyros Pandis, Cliff Davidson
- Eric Lipsky, Sarah Rees, Juan Cabada, Charles Stanier
- Erin Casgren-Tindall, Prakash Rao, Leonard Lucas
- Barbara Turpin, David Smith, Robert Cary, Jeff Brook
- Paul Solomon
- Tami Bond