

# **IMPROVE Carbon Analysis**

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# Objectives

- Report progress on IMPROVE carbon analysis
- Demonstrate OC/EC consistency between IMPROVE\_A (DRI Model 2001) and IMPROVE (DRI/OGC) protocols
- Evaluate differences in carbon fractions among various laboratory-generated carbon sources
- Examine the effects of mixtures on carbon fractions

# **IMPROVE Samples for Carbon Analysis using the IMPROVE\_A Protocol**

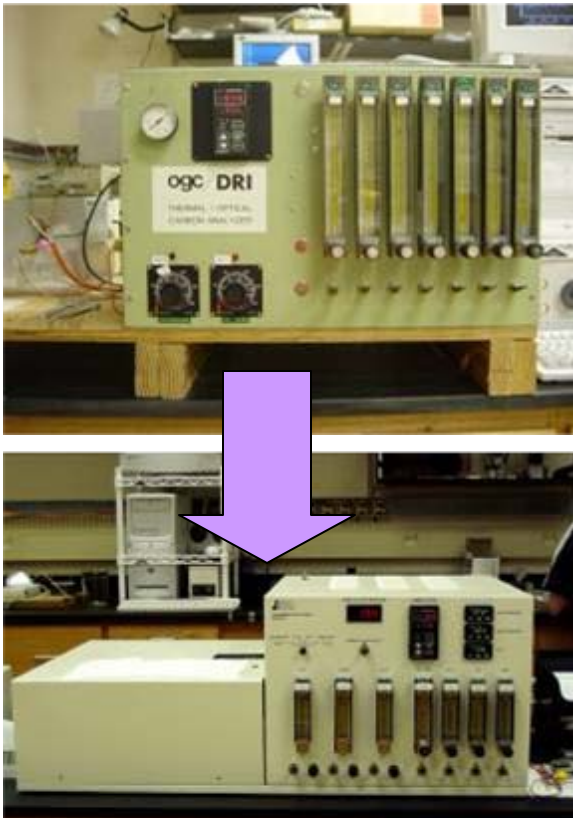
| <b>Sampling Period</b> | <b>Samples<br/>Received</b> | <b>Analysis Completion<br/>Date</b> |
|------------------------|-----------------------------|-------------------------------------|
| 1/1/05-12/31/05        | 22,460                      | 5/5/07                              |
| 1/1/06-12/31/06        | 22,443                      | 3/15/07                             |
| 1/1/07-6/30/07         | 10,604                      | 9/30/07*                            |

\* Expected completion date

# IMPROVE vs. IMPROVE\_A\*

## Thermal Protocols

Original OGC/DRI  
Thermal Optical  
Analyzer (1986)



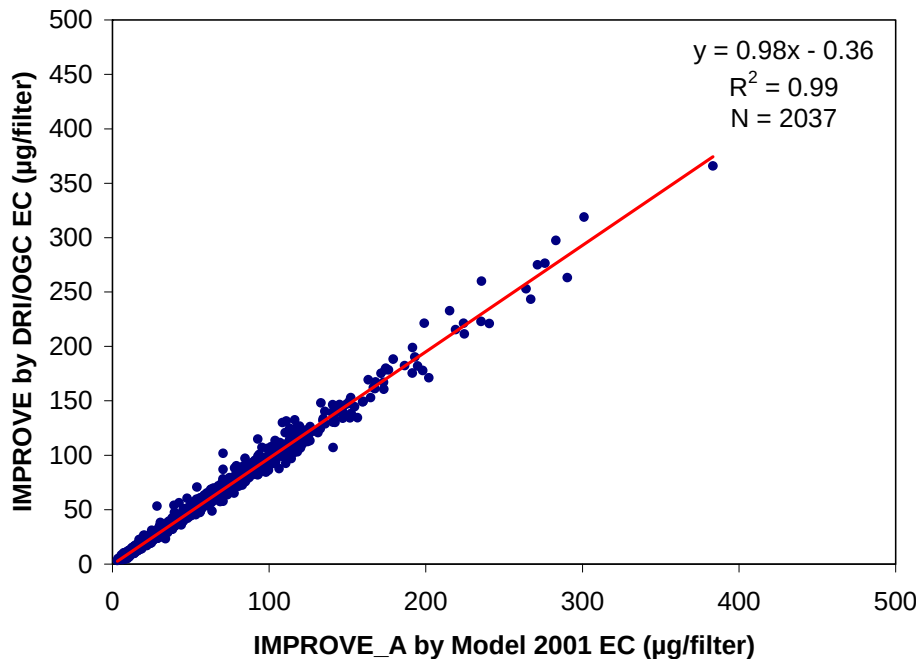
DRI Model 2001  
Thermal/Optical Analyzer

|          | IMPROVE_A*<br>(DRI Model 2001) | IMPROVE<br>(DRI/OGC) |
|----------|--------------------------------|----------------------|
| OC1      | 140 °C                         | 120 °C               |
| OC2      | 280 °C                         | 250 °C               |
| OC3      | 480 °C                         | 450 °C               |
| OC4      | 580 °C                         | 550 °C               |
| OP (POC) | TOR/TOT                        | TOR                  |
| EC1      | 580 °C                         | 550 °C               |
| EC2      | 740 °C                         | 700 °C               |
| EC3      | 840 °C                         | 800 °C               |

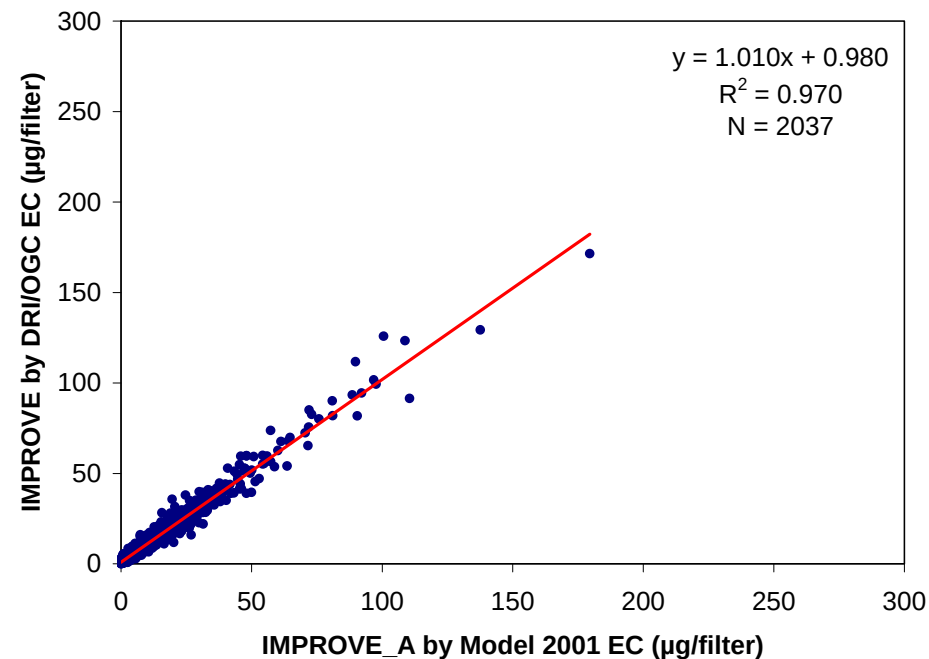
\*After temperature and O<sub>2</sub> calibration.  
Implemented for samples acquired after  
January 1, 2005

# No difference in OC/EC split between IMPROVE by DRI/OGC and IMPROVE\_A by Model 2001

OC\_TOR (Sample Date 3/1/2004 - 9/30/2006)



EC\_TOR (Sample Date 3/1/2004 - 9/30/2006)



# Effect on Carbon Fractions by Temperature and O<sub>2</sub> Level

- Low temperature OC1 (140 °C) and OC2 (280 °C) are sensitive to temperature independent of the oxidant level
- As O<sub>2</sub> > 100 ppmv in He atmosphere, changes in OC3 (480 °C), OP, and EC1 (580 °C) are found

# Laboratory Generated Carbon Sources



Diesel Generator

4 kW load  
Dilution ratios (DR)  
of 18, 40, 80 and  
150

sample time (T) of  
20 or 60 min

Source, Source +  
NaCl



Wood Stove

White Oak  
DR of 18, 40, 105

T of 20 or 25 min

Source, Source +  
NaCl



2-inch flame  
DR of 17

T of 20, 40, 70 min  
Source, Source +  
NaCl



Acetylene Flame

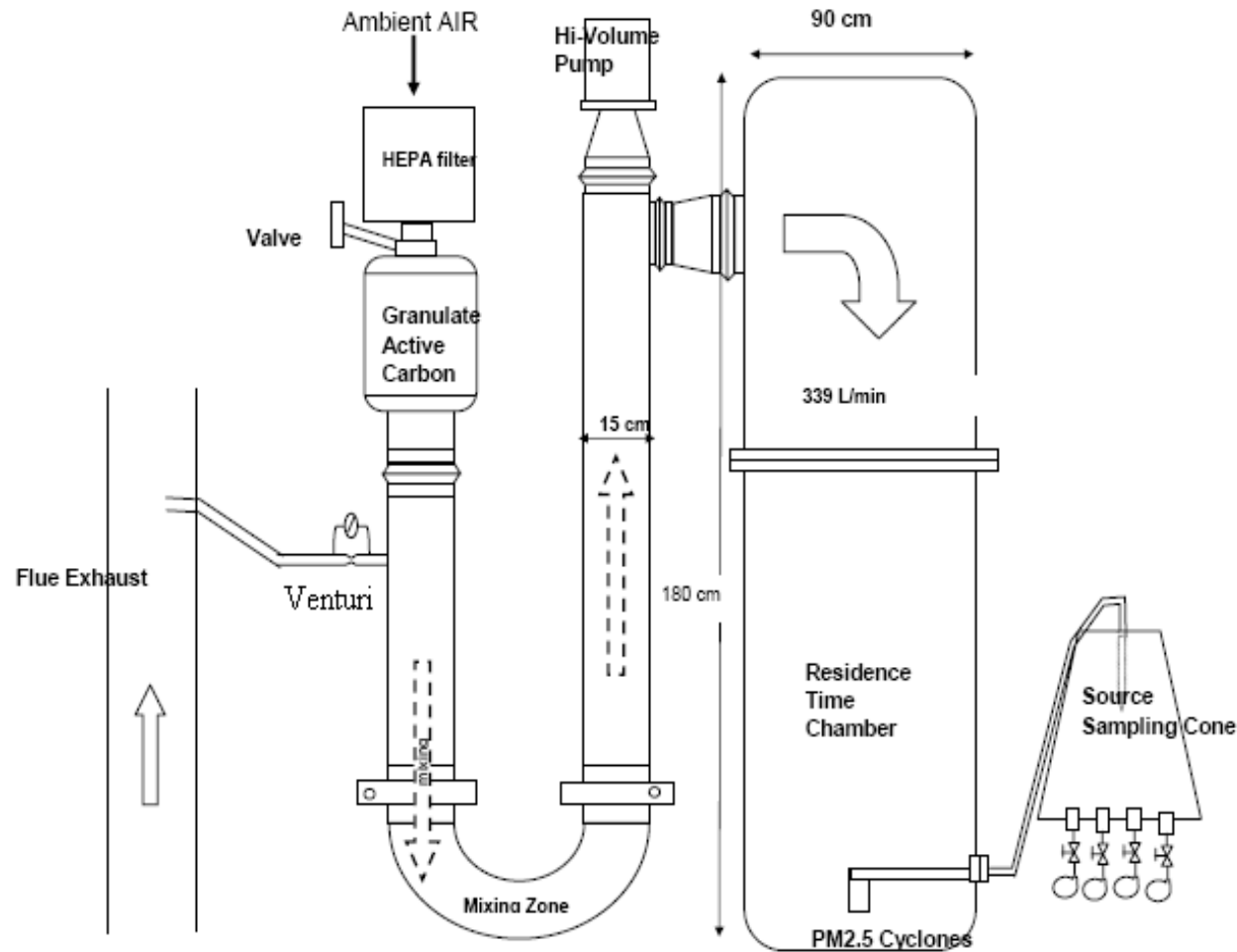


- Electric Arc Generator (PALAS) DR of 8; T = 20 or 40 min; Source, Source + NaCl



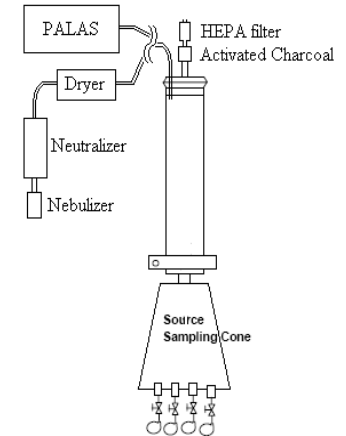
- Carbon Black and Graphite Powder

# Source Characterization Systems for Reference Samples



**Dilution Sampling System**

For Diesel Exhaust  
Acetylene Soot  
Wood Smoke

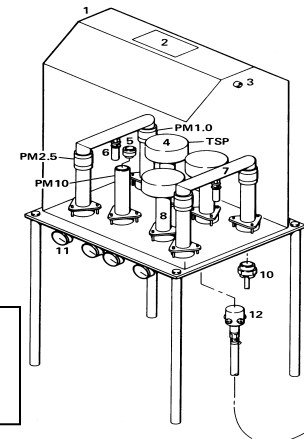


**Miniature Dilution System**

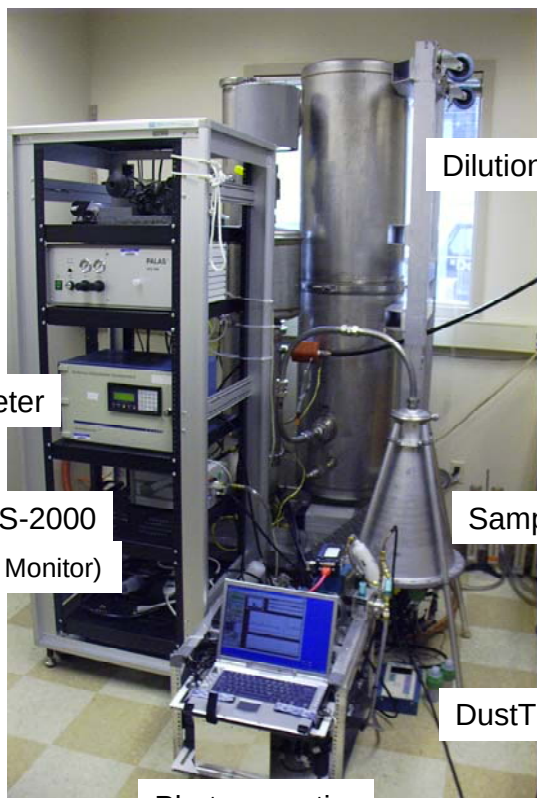
For Electric Arc Generator

**Re-suspension Chamber**

For Carbon Black and graphite powder



# Source Testing Instrumentation



Dilution System

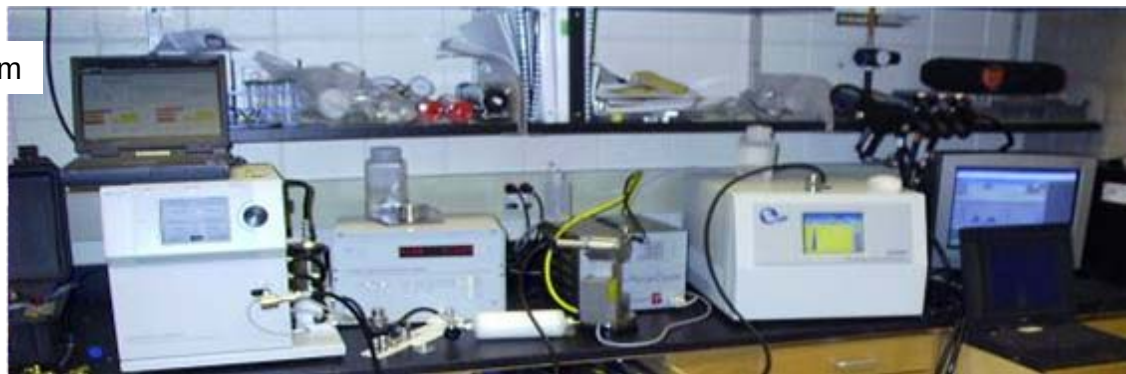
Aethalometer

PAS-2000  
(PAH Monitor)

Sampling Cone

DustTrak

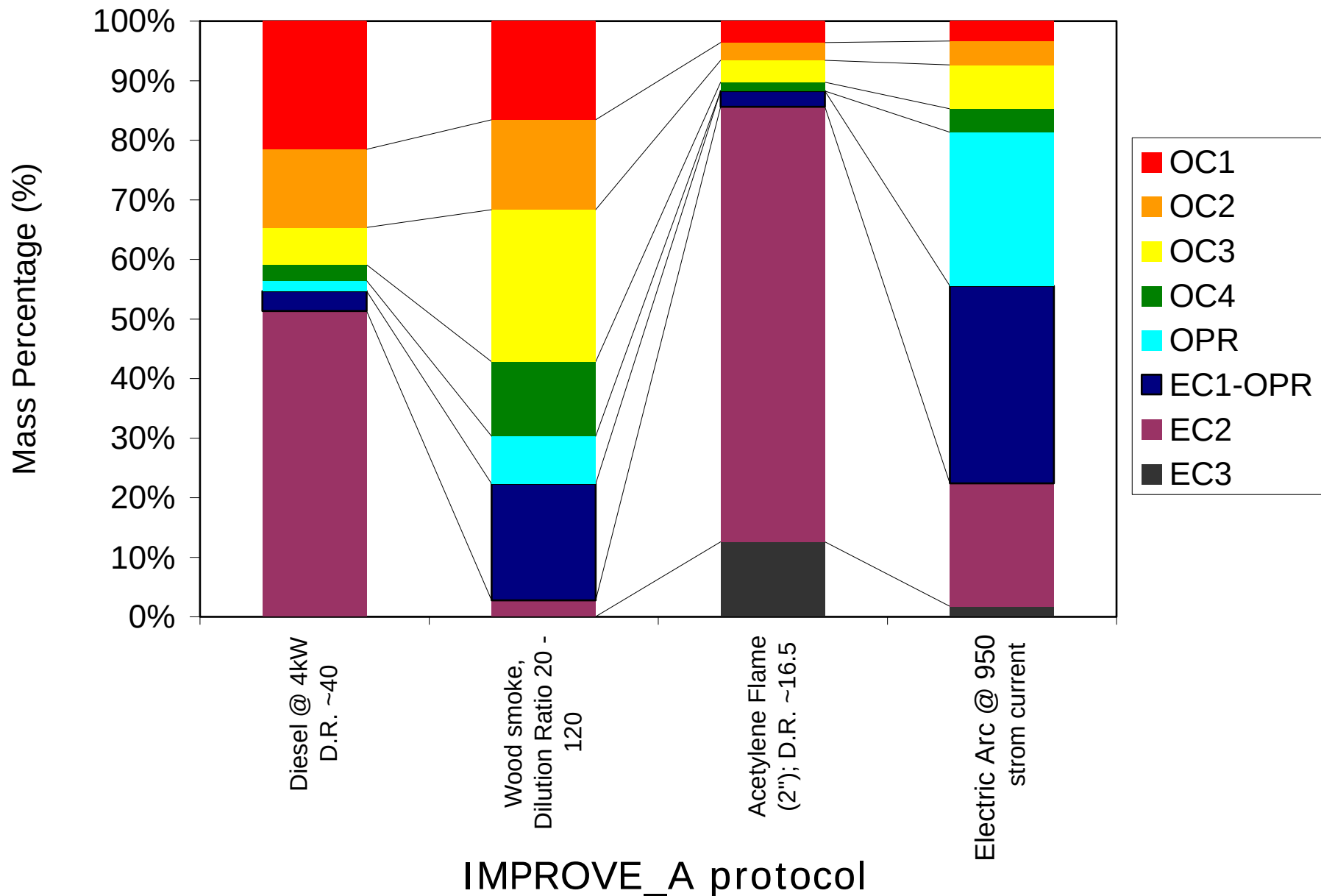
Photoacoustic



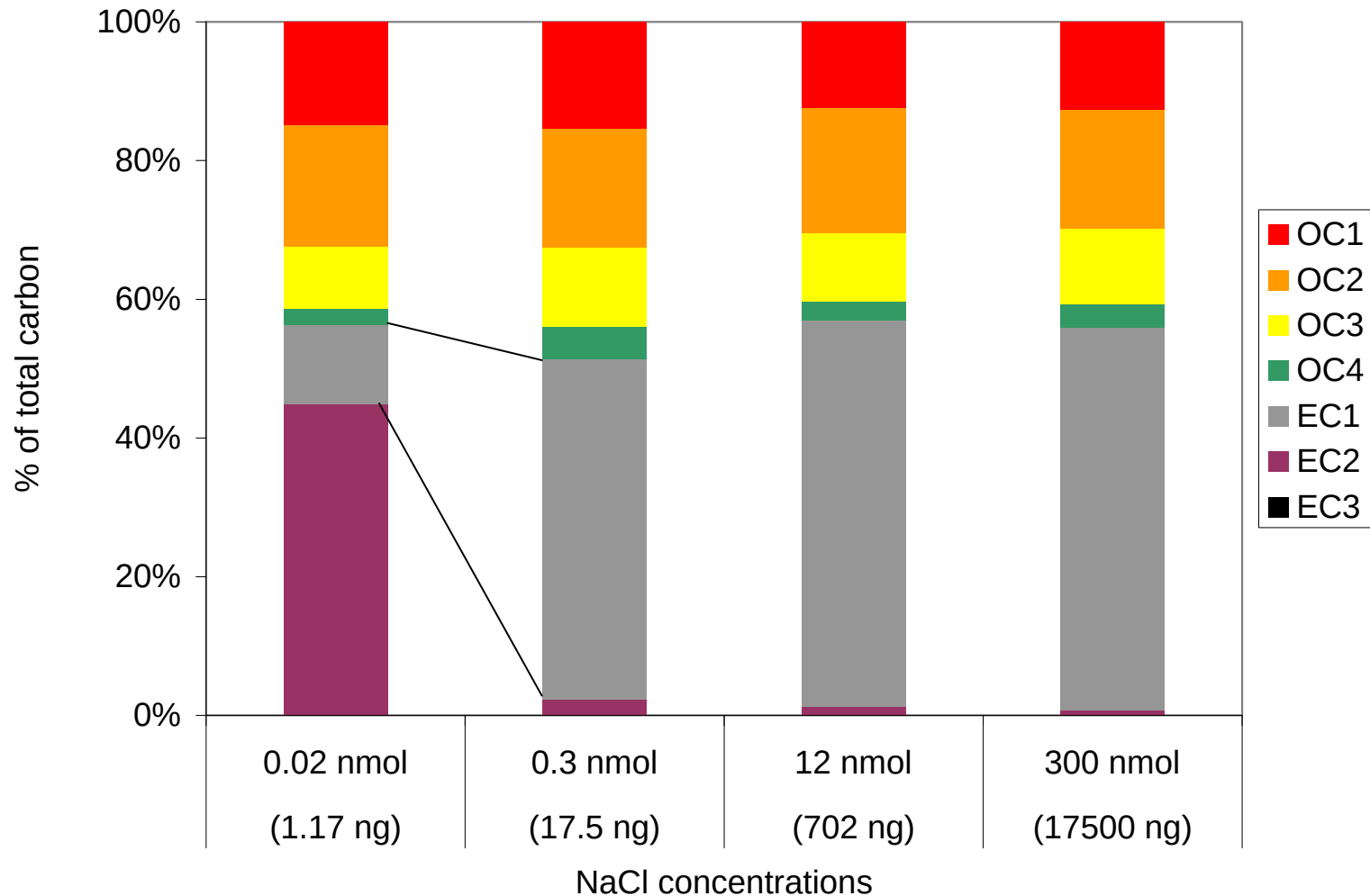
Particle Sizing Instruments (3 nm to 10  $\mu\text{m}$ )

- TSI Nano-SMPS (TSI, St. Paul, MN)
- Grimm SMPS+C (Grimm, Ainring, Germany)
- MSP Wide Range Spectrometer (MSP; St. Paul, MN)

# Carbon fractions vary by source



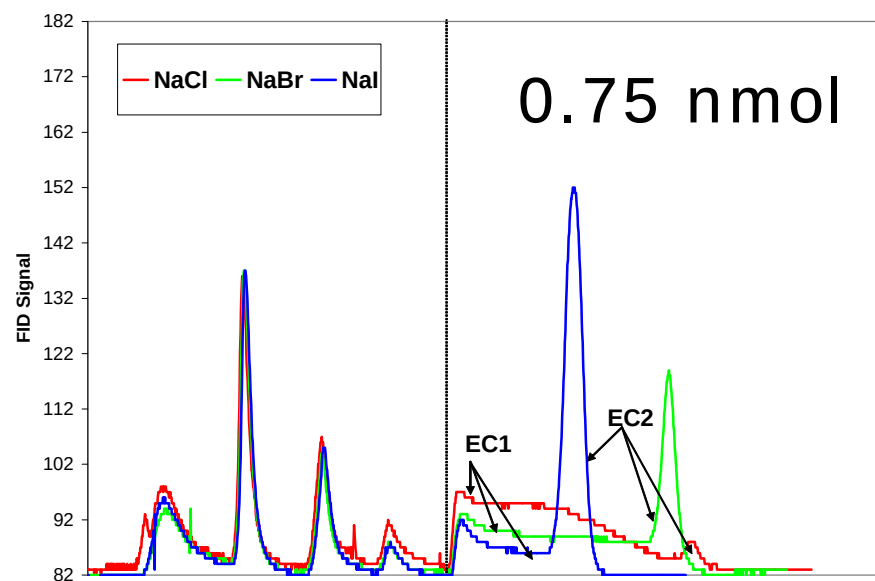
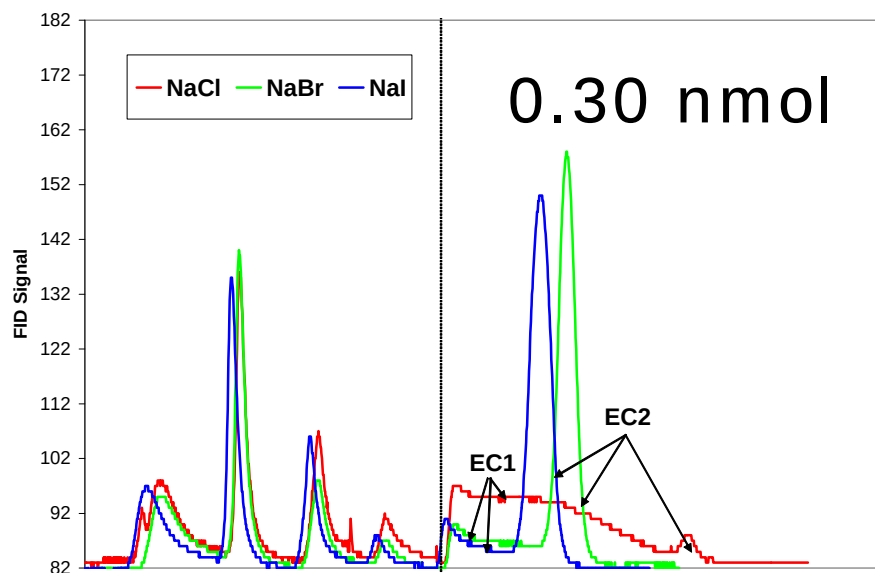
# Presence of NaCl shifts EC to lower temperature fractions\*



\* Higher NaCl -> greater shift from EC2 to EC1

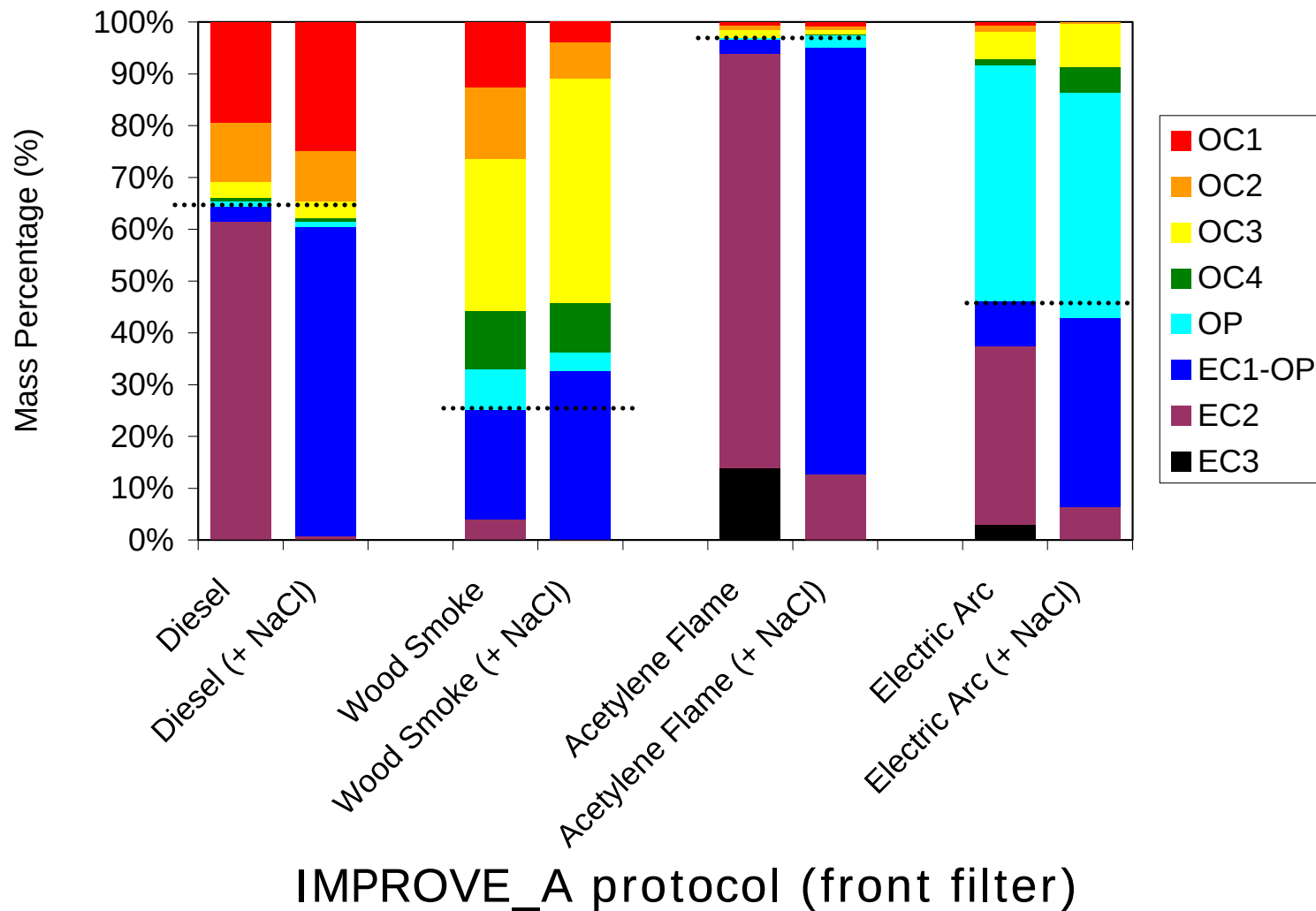
# NaCl has the largest effect among halogen salts on EC fractions

- For NaCl, shift of EC2 to EC1.
- For NaBr, no shift at 0.3 nmol but shift at 0.75 nmol
- For NaI, no shift for both 0.3 and 0.75 nmol

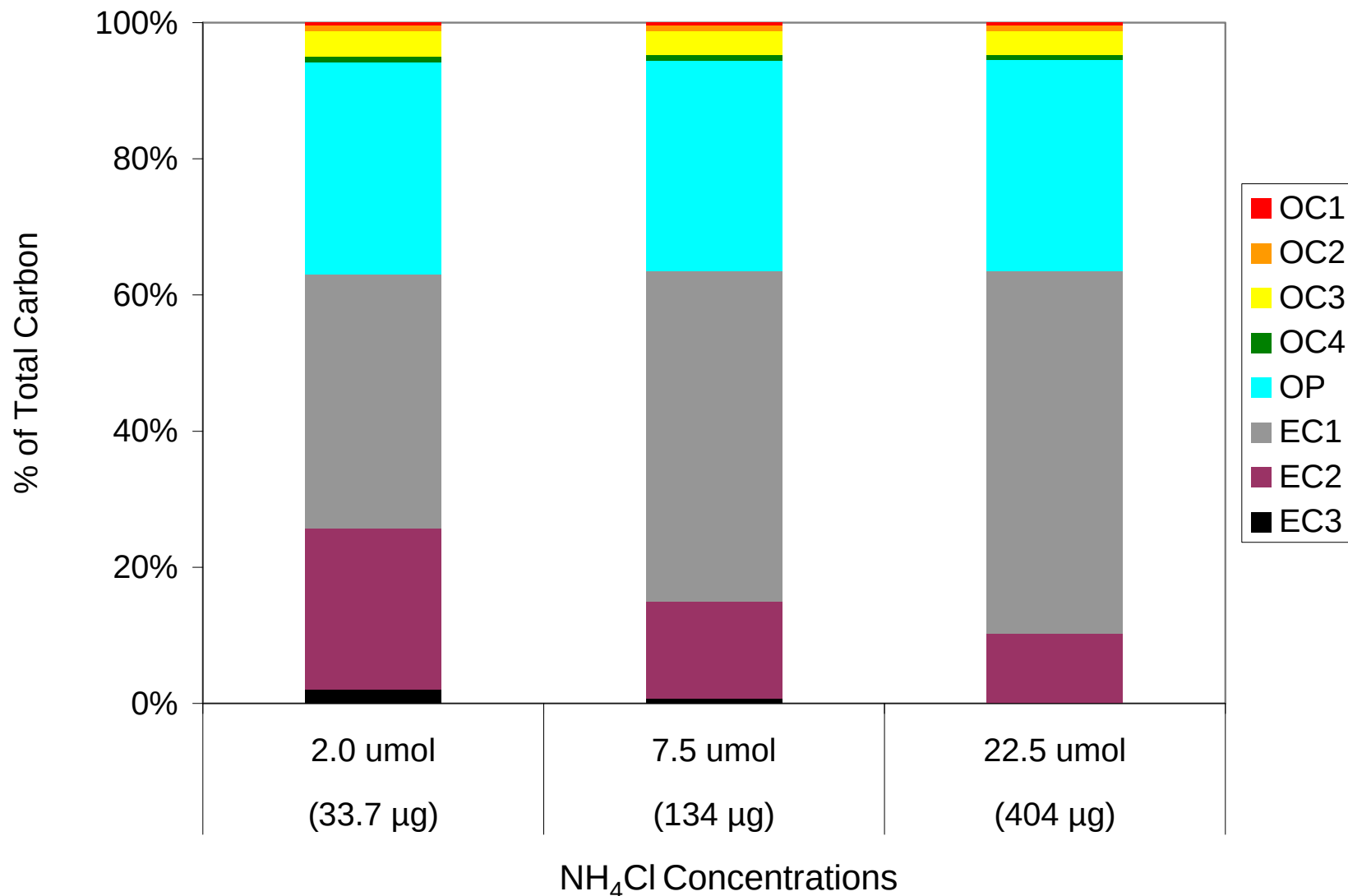


Catalytic reactivity: NaCl > NaBr > NaI

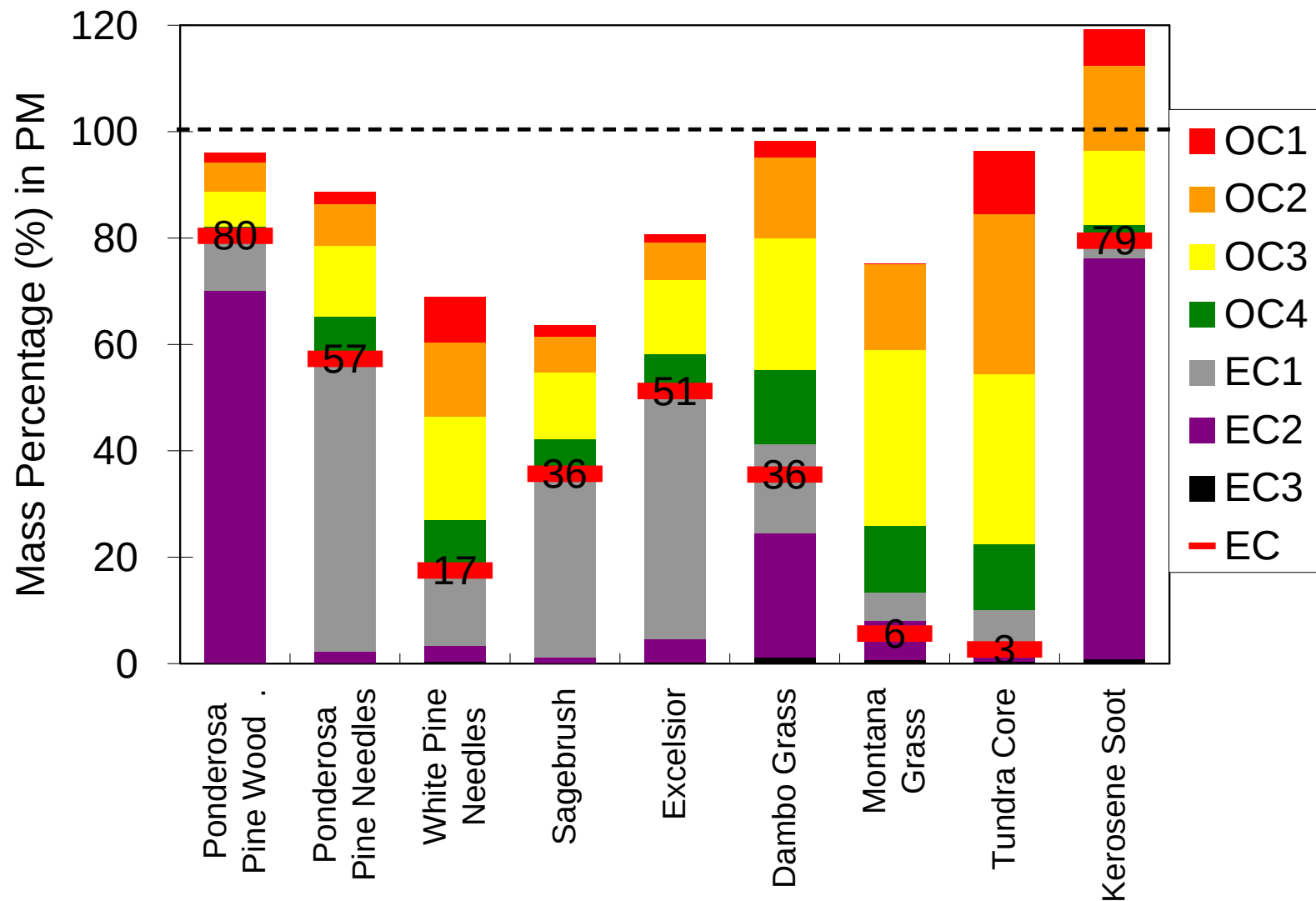
# Addition of NaCl shifts EC to lower temperature fractions



# Higher $\text{NH}_4\text{Cl}$ shifts EC2 to EC1 (No OC shift)



# Carbon fractions in biomass burning varied by fuel and combustion conditions

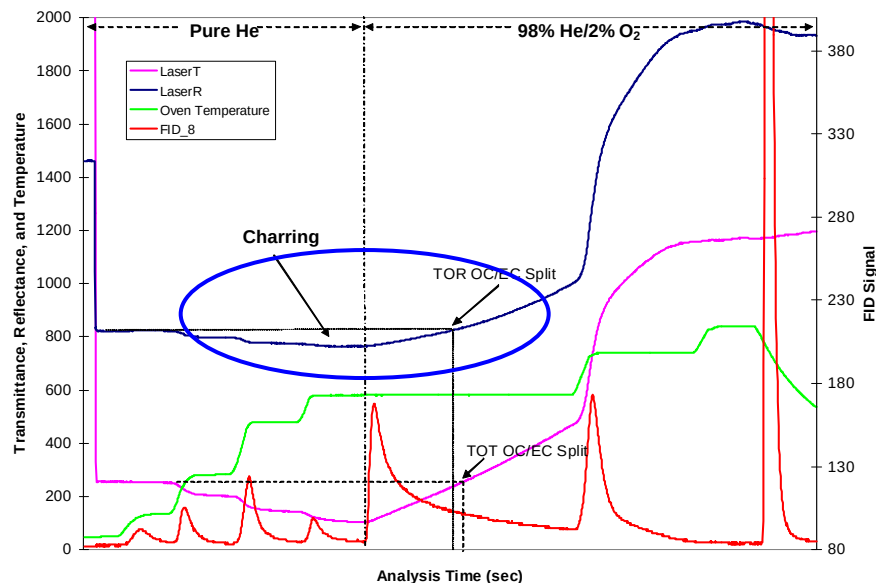


# Presence of $(\text{NH}_4)_2\text{SO}_4^*$ minimizes pyrolysis (No EC shift)

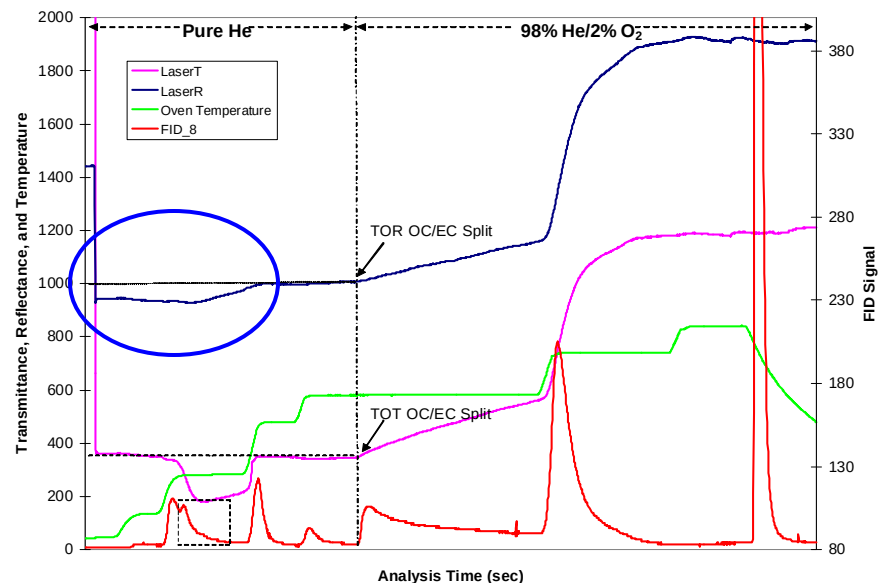
Original Filter

Spiked with 3.0  $\mu\text{mol}$  of ammonium sulfate

a)

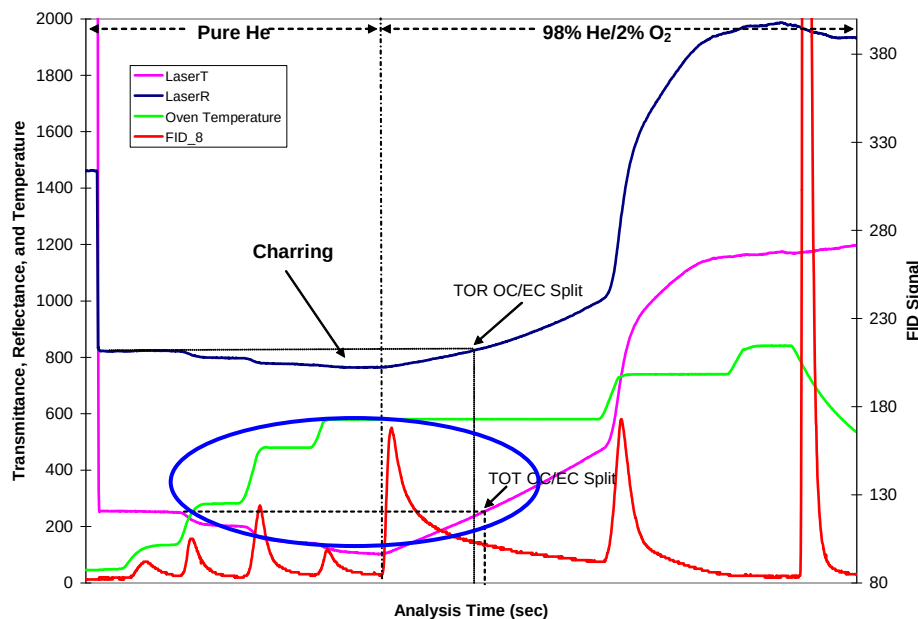


b)

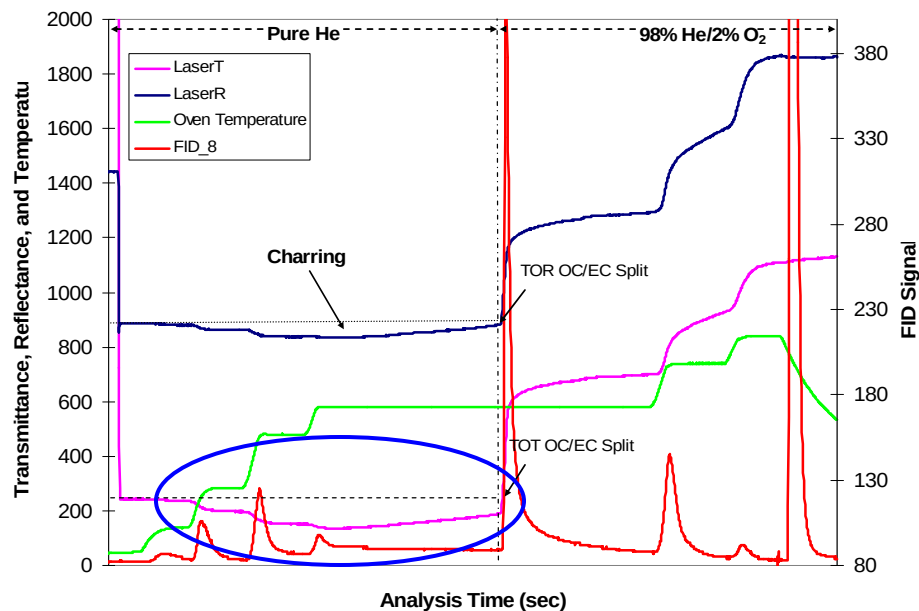


# $\text{Na}_2\text{SO}_4^*$ does not suppress pyrolysis (Shift EC1 to EC2)

Original Filter



Spiked with 3.0  $\mu\text{mol}$  of  $\text{Na}_2\text{SO}_4$



\* Melting point = 884 °C

# Conclusions

- The presence of salts in samples increases EC oxidation rate at lower temperatures, thereby shifting thermal carbon fractions to lower temperature plateaus.
- Charring is minimized in the presence of  $(\text{NH}_4)_2\text{SO}_4$ , but not  $\text{Na}_2\text{SO}_4$ .
- Due to the formation of char and EC decomposition at high temperatures w/o  $\text{O}_2$ , optical correction is necessary to separate OC from EC.