Investigating molecular structures contributing to organic and elemental carbon in monitoring network measurements

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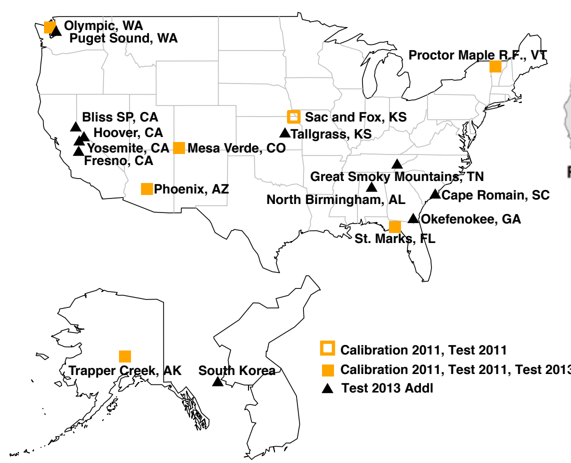
Predicting thermal optical reflectance (TOR) OC and EC with infrared spectra

- Collocated samples of PM2.5 on Teflon filters and quartz fiber filters
- TOR measurements on quartz by Desert Research Institute
- FT-IR spectra on Teflon by UC Davis

IMPROVE



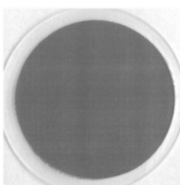
CSN

2011: 6 + 1 sites; 794 samples
2013: 6 + 11 sites; 2239 samples

2013: 10 sites; 927 samples

Analysis of samples collected on Teflon (PTFE) filters

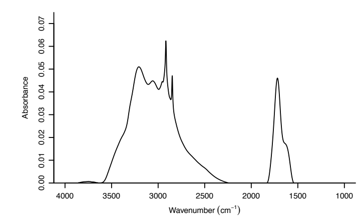
Standard substrate for gravimetric mass measurements in regulatory monitoring in the US



gravimetric mass

elemental composition
(e.g., X-ray Fluorescence)

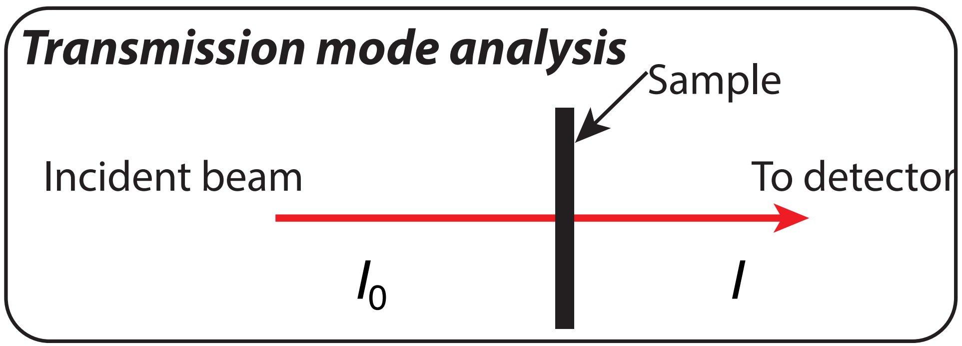
FT-IR spectrum

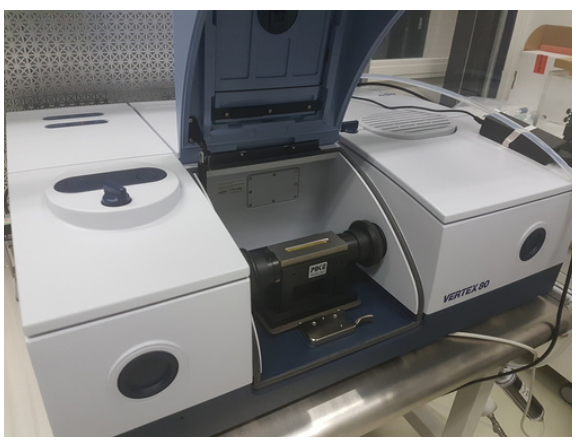


other (ions)

- No sample prep
- Non-destructive
- Rapid (few minutes per sample)
- Inexpensive
- *Integrate into PM analysis chain*

Fourier Transform Infrared Spectroscopy (FT-IR)
How does it work?





- Measures abundance of absorbing vibrational modes in molecules
- Basis for quantitative analysis – Beer Lambert law

$$A = -\log_{10}\frac{I}{I_0} = \sum \varepsilon \frac{n}{a}$$

Early infrared spectroscopy

Composition of Organic Portion of Atmospheric Aerosols in the Los Angeles Area

(1952)

PAUL P. MADER, ROBERT D. MACPHEE,
ROBERT T. LOFBERG, AND GORDON P. LARSON
Los Angeles County Air Pollution Control District, Los Angeles, Calif.

INDUSTRIAL AND ENGINEERING CHEMISTRY Vol. 44, No. 6

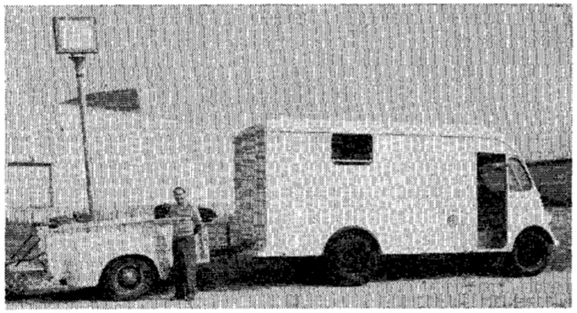


Figure 1. Large Mechanical Filter

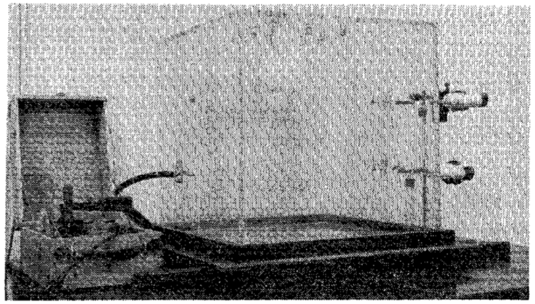
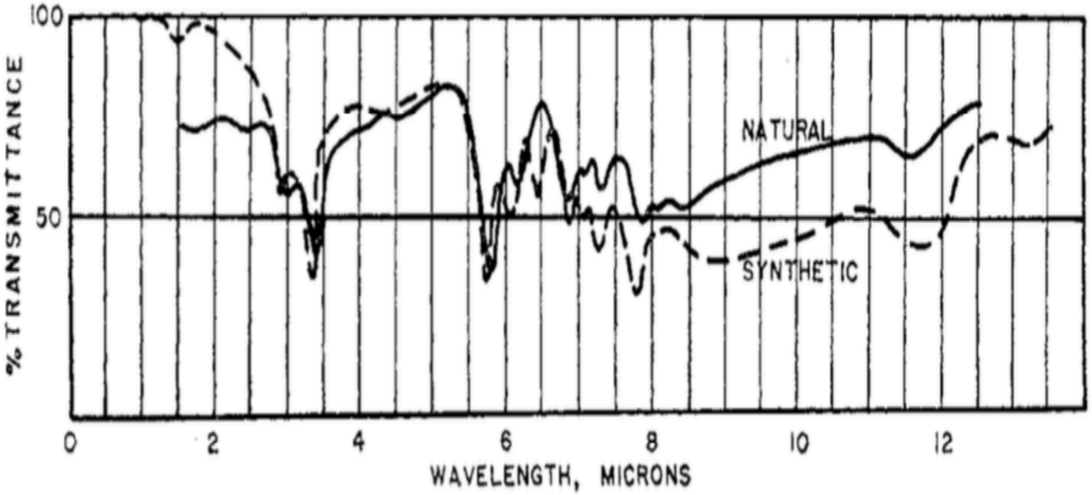
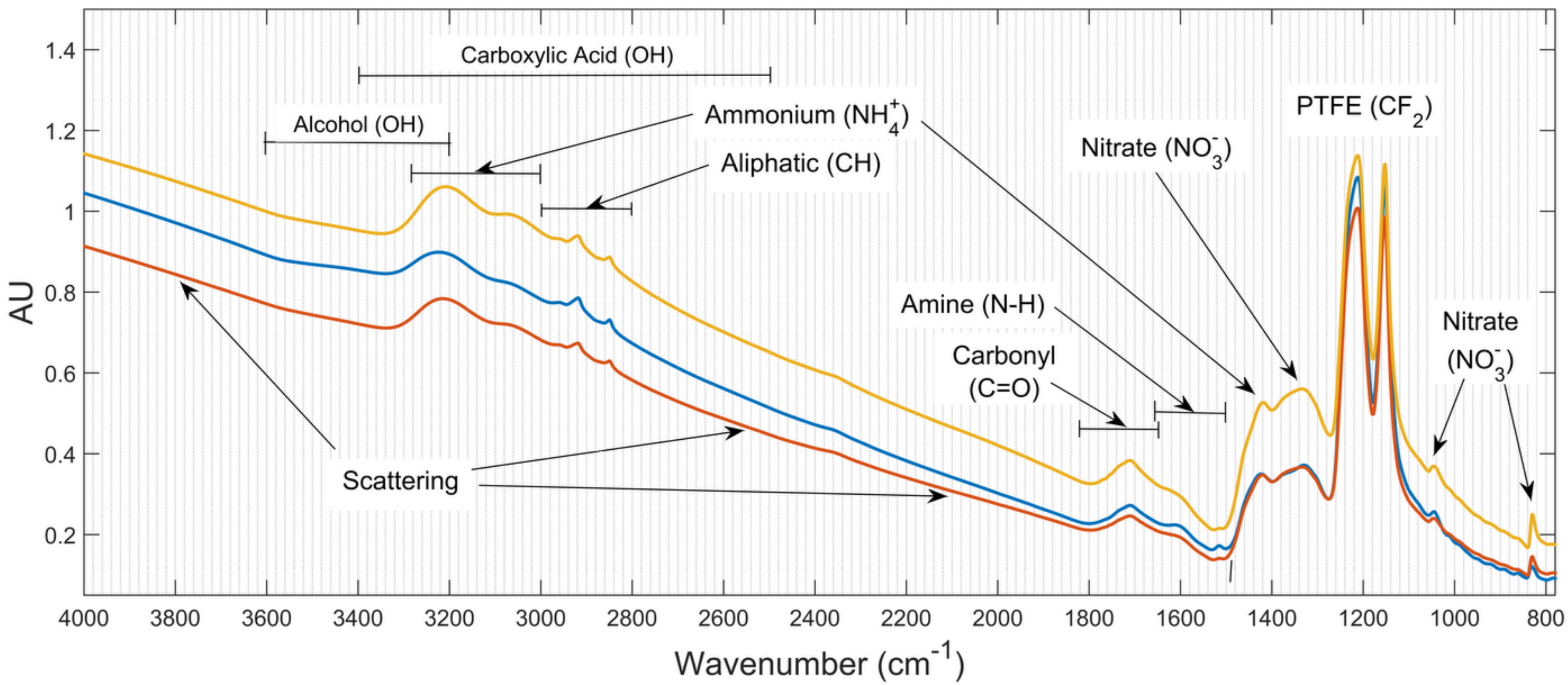


Figure 2. Plastic Chamber

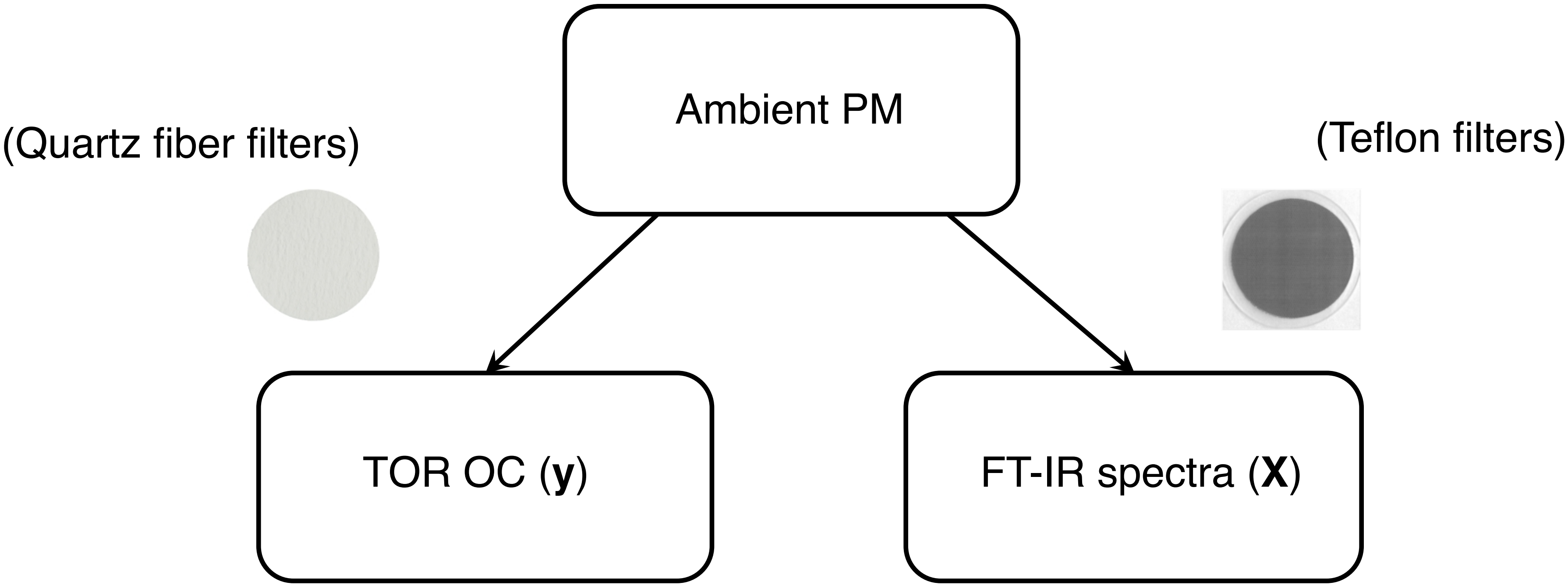


Complexity of PM spectra makes quantitative interpretation challenging



Example IMPROVE spectra

Method of calibration



collocated OC or EC

regression coefficients

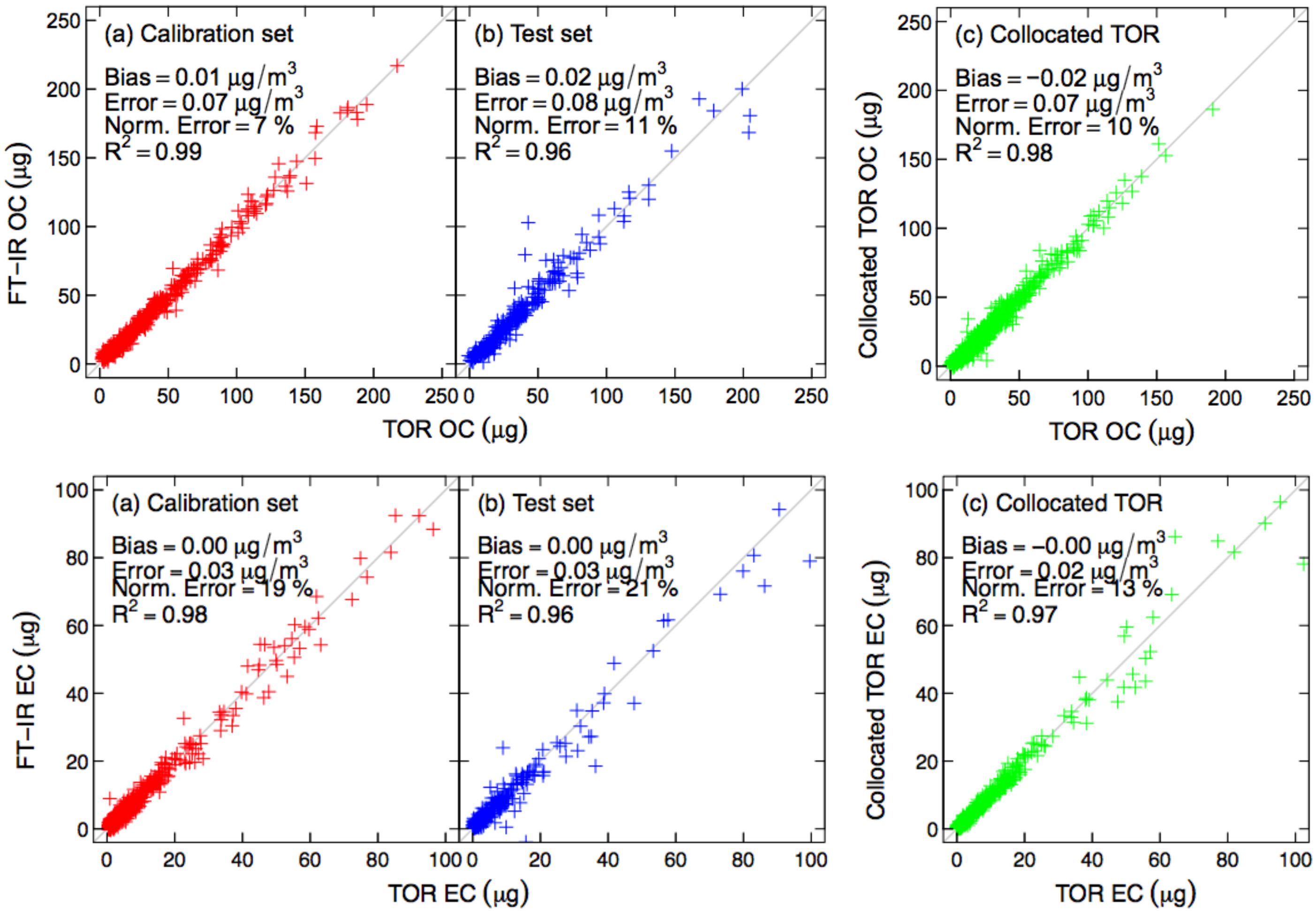
Linear calibration model

$$\mathbf{y} = \mathbf{X}\mathbf{b} + \mathbf{e}$$

spectra matrix

residual

Model predictions
IMPROVE 2011 (7 sites)

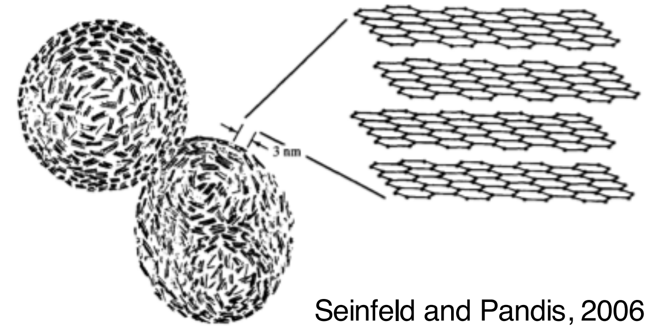


Dillner and Takahama, *Atmos. Meas. Tech.*, 2015a (TOR OC)
Dillner and Takahama, *Atmos. Meas. Tech.*, 2015b (TOR EC)

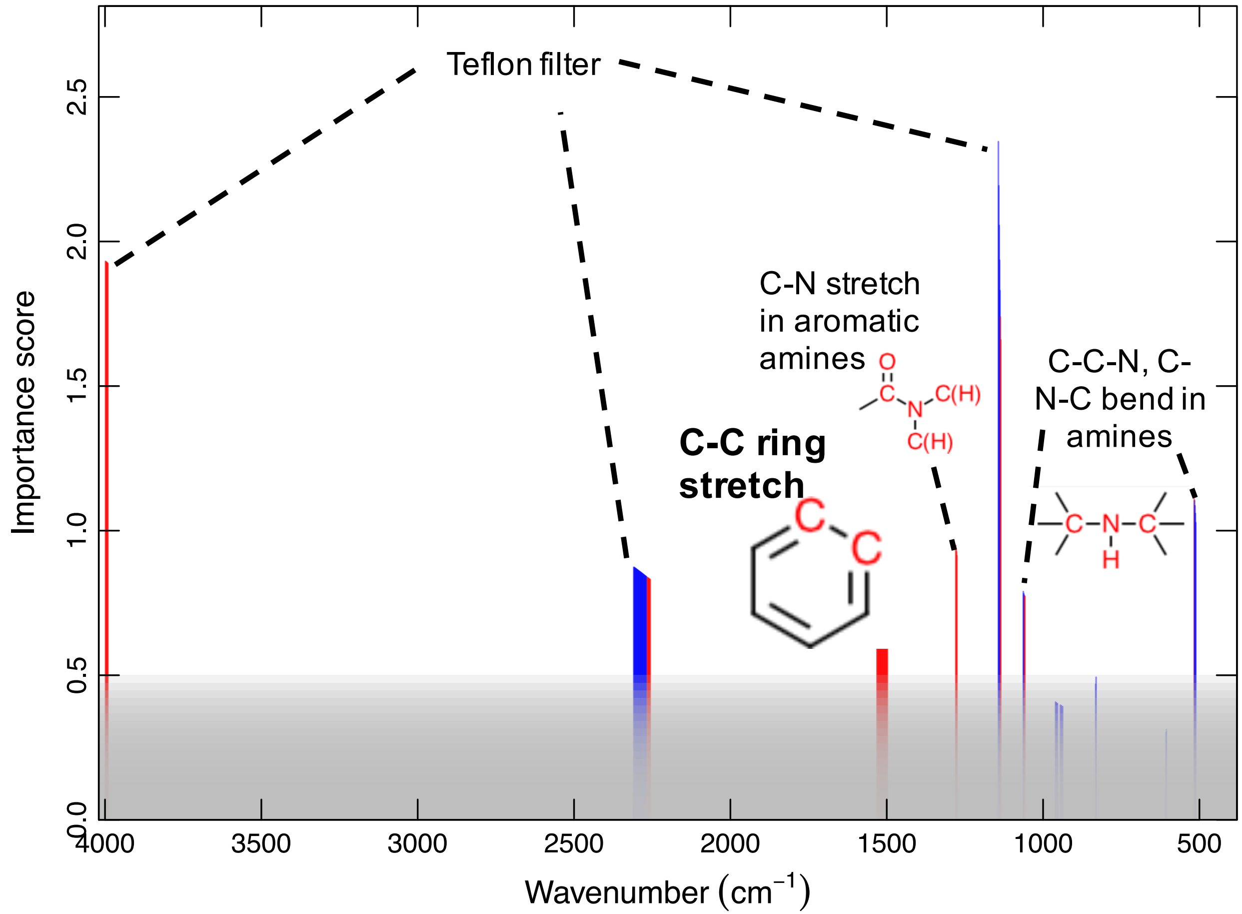
Strategies for molecular understanding

- Examine regression coefficients
  - eliminate unnecessary regression coefficients
  - interpret remaining regression coefficients:
    - vibrational modes for target analyte
    - vibrational modes for interfering substances
- Examine spectral components that explain variation in TOR OC or EC

What are the critical structures for predicting TOR EC? *IMPROVE 2011*



Seinfeld and Pandis, 2006



Elemental carbon:

- *chemical definition*: sp^2 carbon not bonded to other elements
- *probable interpretation*: subset of light-absorbing, low-volatility substances emitted primarily from combustion

Peak near ~1600 cm^{-1} observed for ground graphite, graphene:

- *C-C ring stretch*

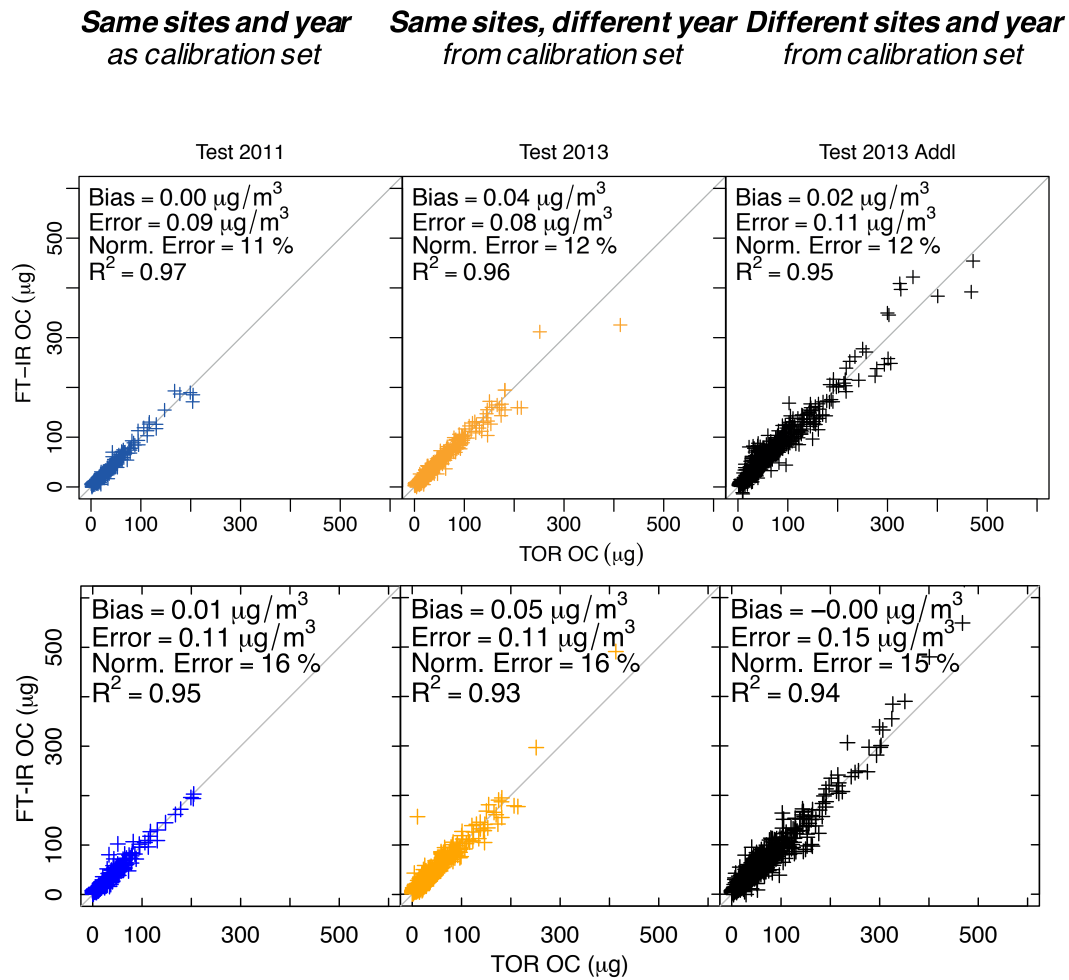
Takahama, Ruggeri, Dillner, *Atmos. Meas. Tech.*, 2016

What are the critical structures for predicting TOR OC? *IMPROVE 2011*

Calibration set:
530 samples for model training
Test set:
2503 samples for independent evaluation (*shown below*)

Baseline corrected spectra (1800+ wavelengths)

Baseline corrected spectra + wavelength reduced spectra (10 wavelengths)



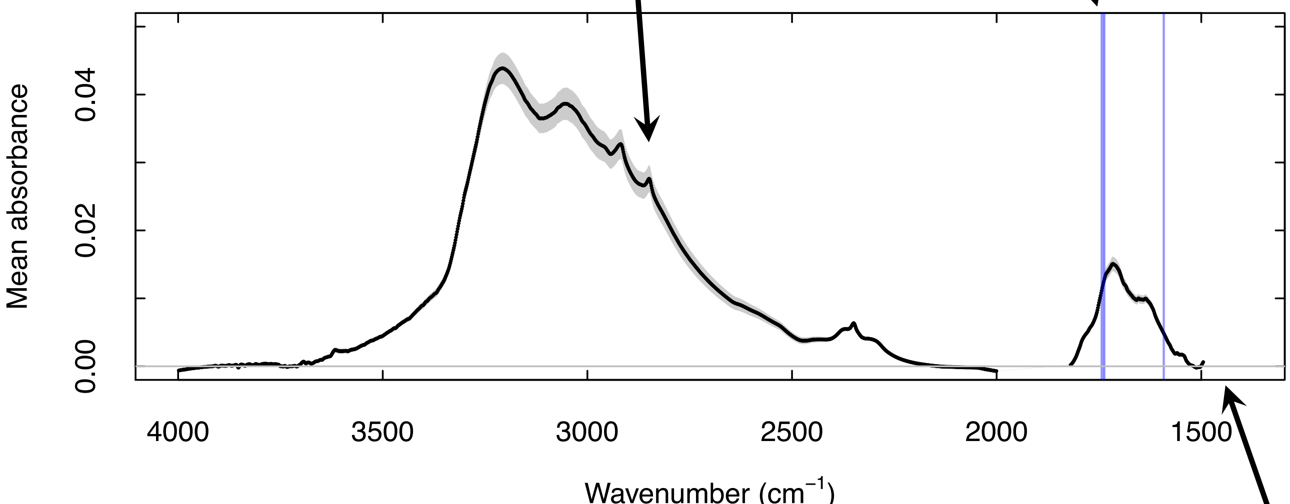
Reggente, et al., *in prep.*, 2016

10 wavenumbers confined to a narrow wavelength region

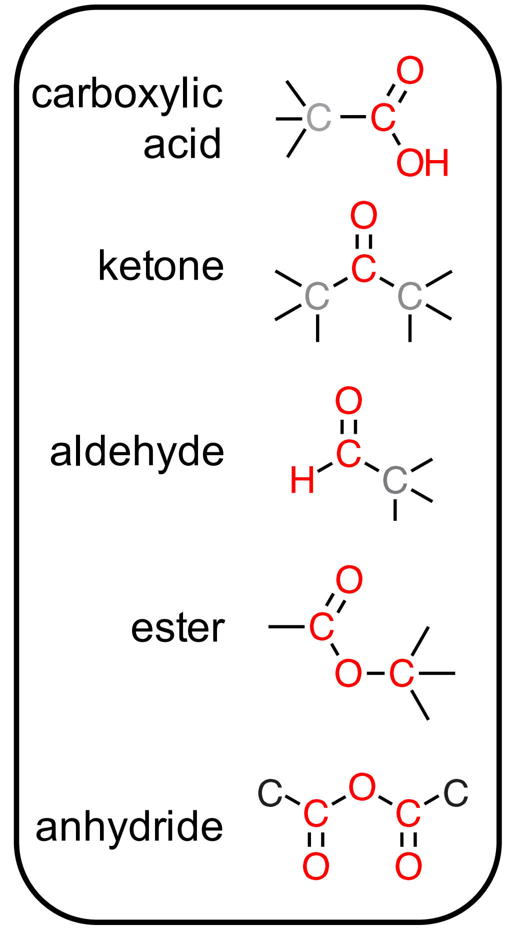
Selected from calibration with
530 IMPROVE 2011 collocated samples

alkane CH stretch
(not used)

carbonyl C=O
stretch

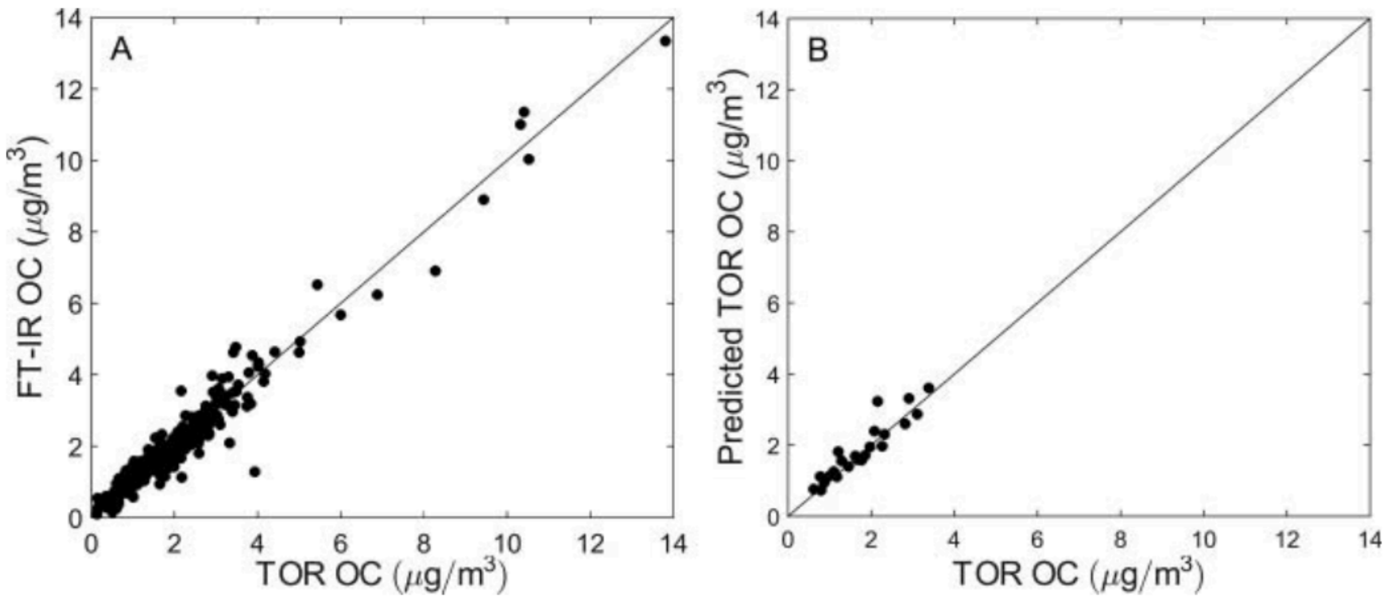


alkane CH bending
(not used)



Reggente, et al., *in prep.*, 2016

Model predictions
Chemical Speciation Network (10 sites)



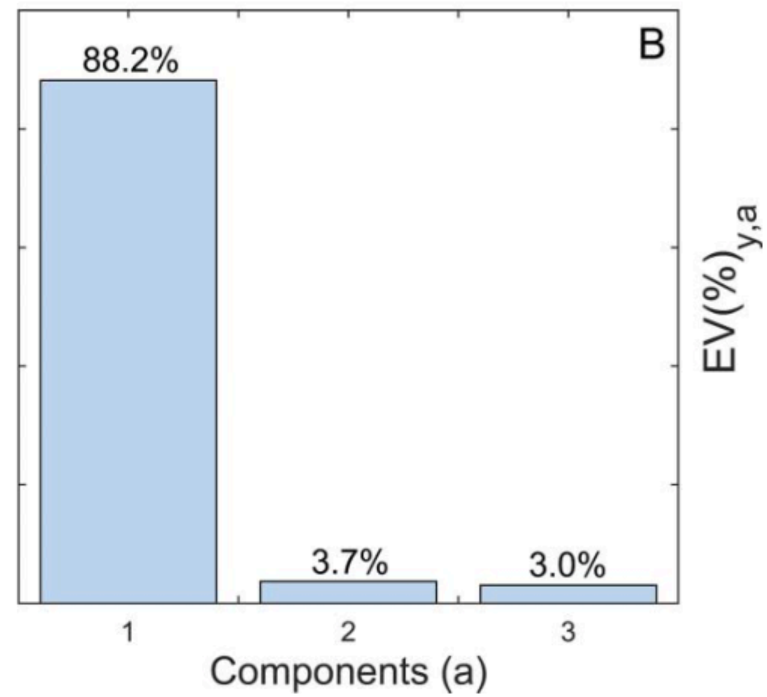
Weakley, Takahama, Dillner, *Aerosol Sci. Tech.*, 2016

Interpretation of underlying components in spectra *CSN 2013*

Three spectral components explain 95% of variation in TOR OC

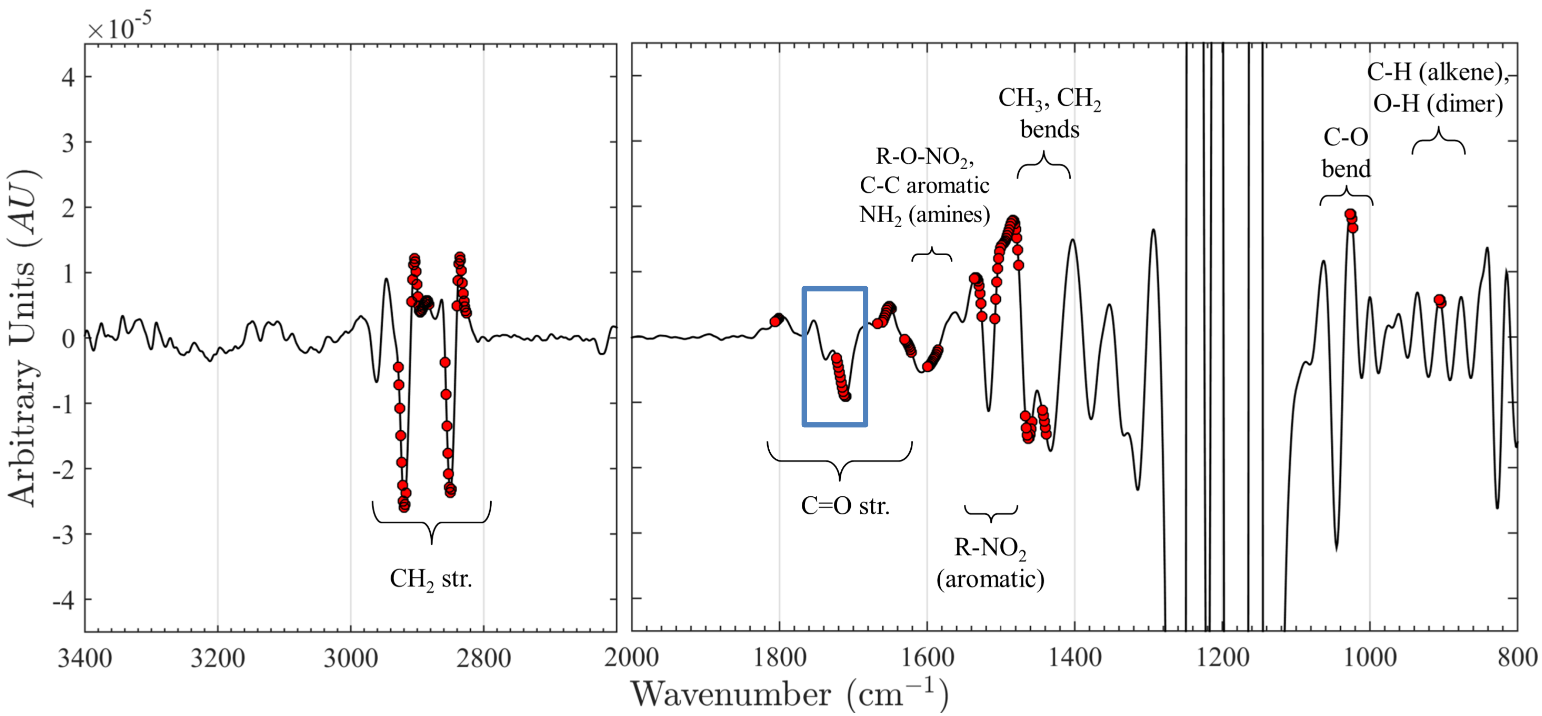
$y_{\text{TOR-OC}}$ = Organics
+ Teflon interferences
+ ammonium interferences
+ residual

Explained variation of TOR OC by individual components



What are the critical structures for predicting TOR OC? *CSN 2013*

Aliphatic C-H and carbonyl C=O are prioritized



Thank you for your attention

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