FT-IR: a promising method for checking consistency between Teflon and quartz channels and measuring OM on IMPROVE samples

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Consistency between IMPROVE sampling modules

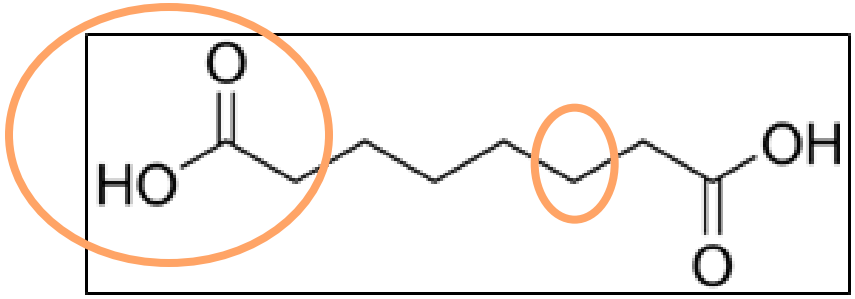
- Consistency checks identify issues:
  - Swaps of filter
  - Sampling/handling problems
- Teflon and nylon modules
  - comparison for sulfur and sulfate
- Teflon and quartz modules
  - PESA on Teflon measures total hydrogen
  - Subtract NH_4 assuming fully neutralized sulfate
  - Makes Teflon filters brittle, sometimes tear
  - Prefer non-destructive method does not require fully neutralized assumption

OM on IMPROVE samples

- Organic mass (OM) includes carbon, oxygen, hydrogen, nitrogen and sulfur
- OM used in estimating visibility from PM
- Current method for estimating OM
  - OM = (Measured OC) X (OM/OC)
    - OM/OC value applied to all samples in network
    - IMPROVE currently using 1.8 (used to use 1.4)
    - CSN proposing to use 1.4
- Prefer method that measures OM or OM/OC on each filter rather than assuming an OM/OC

Fourier Transform Infrared (FT-IR) Spectroscopy

- Non-destructive
- Quantifies organic functional groups



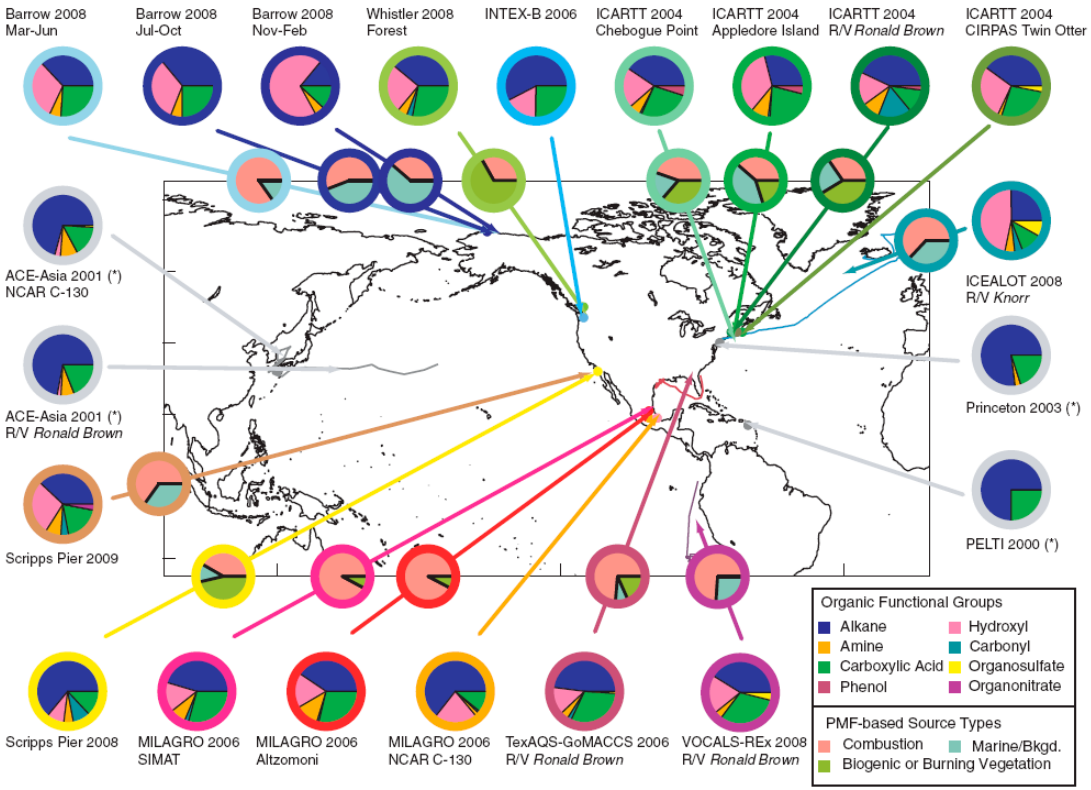
aliphatic C-H
aromatic C-H
carbonyl (C=O)
alcohol (O-H)
carboxylic acids
organosulfate
organonitrate
amines

- OC mass – use for Teflon/quartz consistency checks
- Sum of functional groups = OM
- Calculate OM/OC per sample

FT-IR - limitations

- Not organic compound specific (i.e., levoglucosan)
- No one has quantified graphitic carbon in particulate matter
- Interferants
  - Teflon filter material
  - Ammonium

FT-IR analysis of Teflon filters



Russell et al., PNAS (2011)

Simple Proof of Concept Analysis - IMPROVE samples

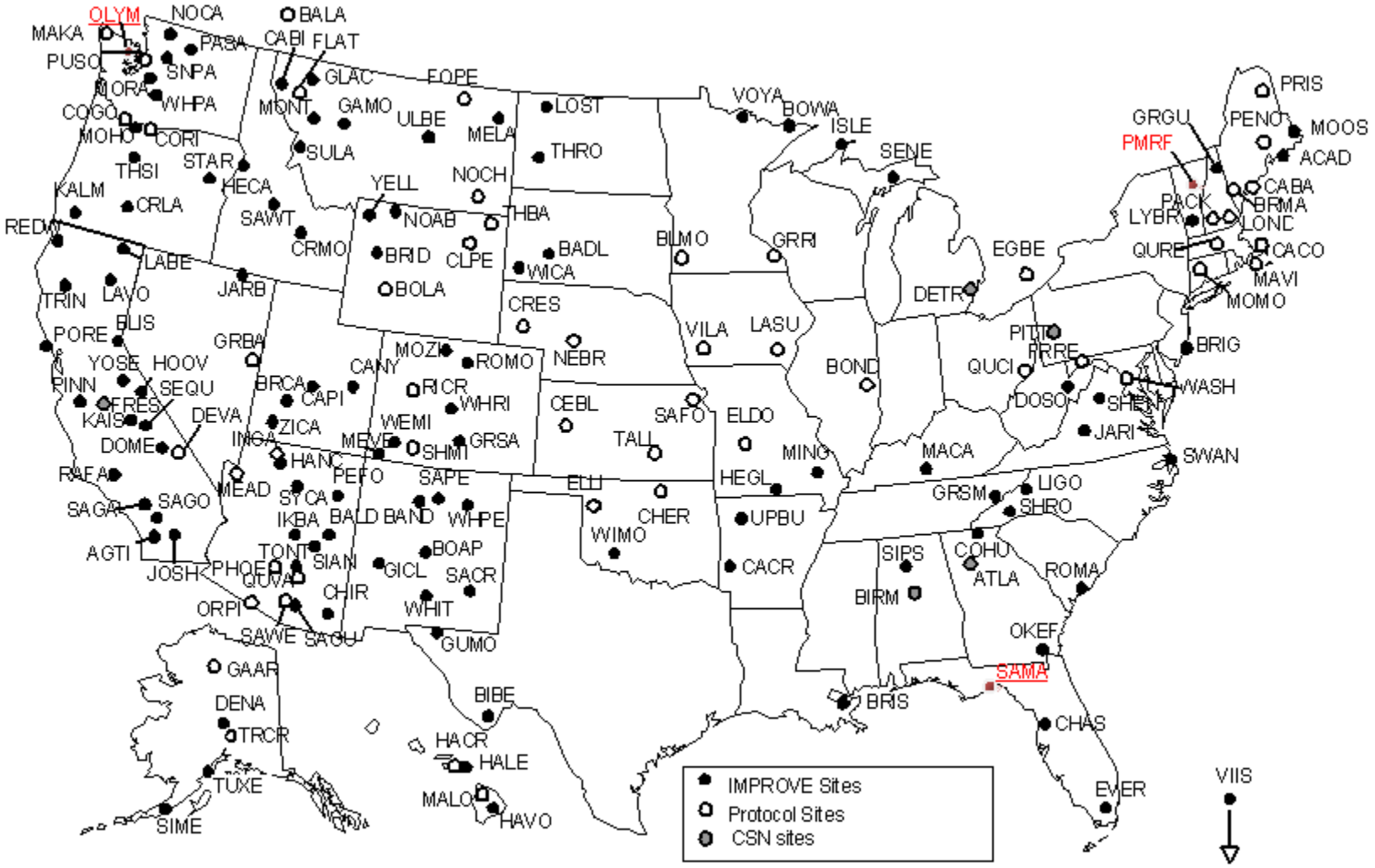
1. Does analysis provide reasonable results for OC across range of IMPROVE samples?
2. Can interferants be accounted for successfully?
3. Do samples exhibit differences that show variability in OM/OC?

Method

- Analyzed 136 IMPROVE Teflon filters from three sites + 10 field blanks
- Identified functional groups in spectra
- Subtracted ammonium from O-H and C-H region of the spectra
- Used peaks areas for C=O and C-H functional groups and %C in group to
  - estimate "absorbance" for OC and compare to TOR OC
  - (C=O + C-H)/C-H surrogate for OM/OC

IMPROVE samples

- Three sites - OLYM, PMRF, SAMA (map)
- Spring, summer, fall, 2010
- Sample data:
  - 5 – 186 μgOC (0.15 – 5.6 μg/m^3)
    - 10th %ile – 99th%ile in network
  - Sulfate: 2-300 μg (0.06 – 9.2 μg/m^3)
    - >90th%ile
  - EC/OC: 0.01 – 0.40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BALA
MAKA
PASA
CABI
FLAT
PUSO
SNPA
GLAC
EQPE
MORA
WHPA
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GAMO
LOST
VOYA
BOWA
ISLE
COGO
ULBE
MELA
MOHO
CORI
SULA
THRO
SENE
THSI
STAR
NOCH
KALM
HECA
YELL
CRLA
SAWT
NOAB
THBA
REDW
CRMO
BRID
CLPE
BADL
BLMO
GRRI
LABE
WICA
JARB
BOLA
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ACAD
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CACO
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MOMO
IMPROVE Sites
Protocol Sites
CSN sites
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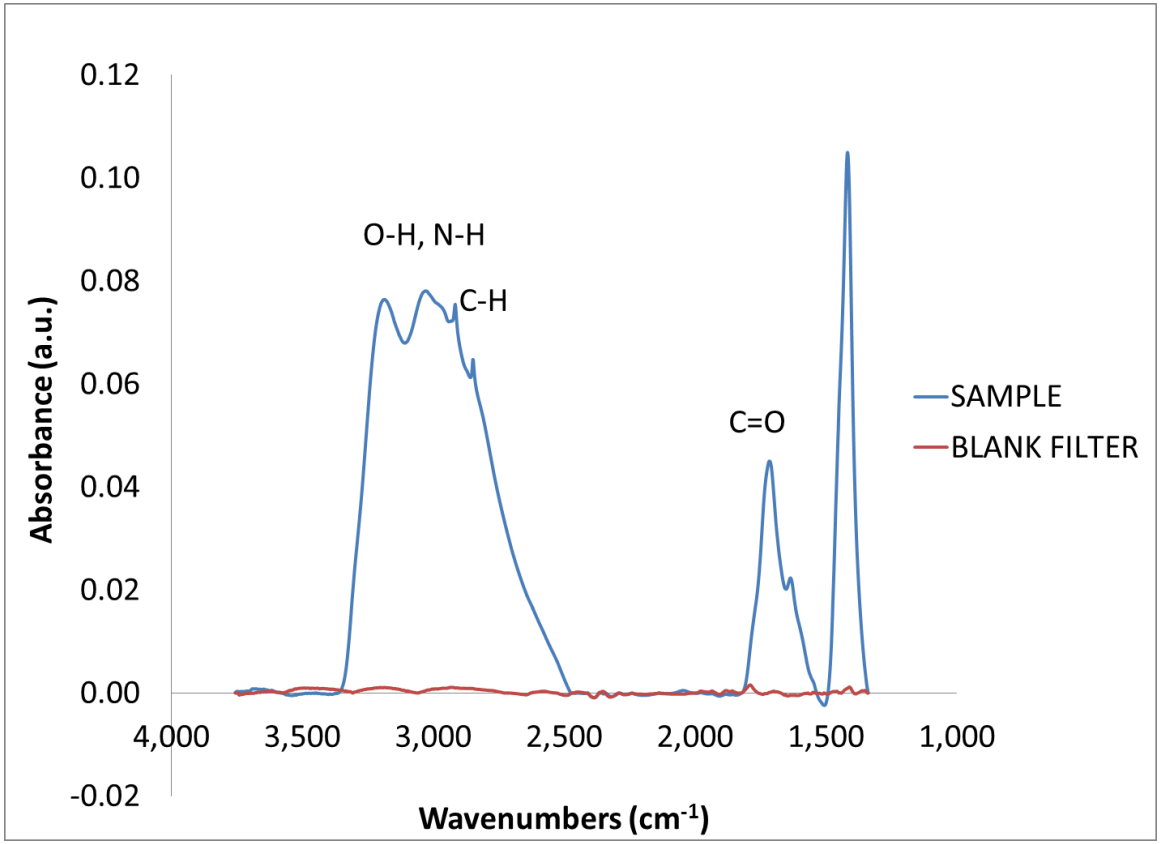
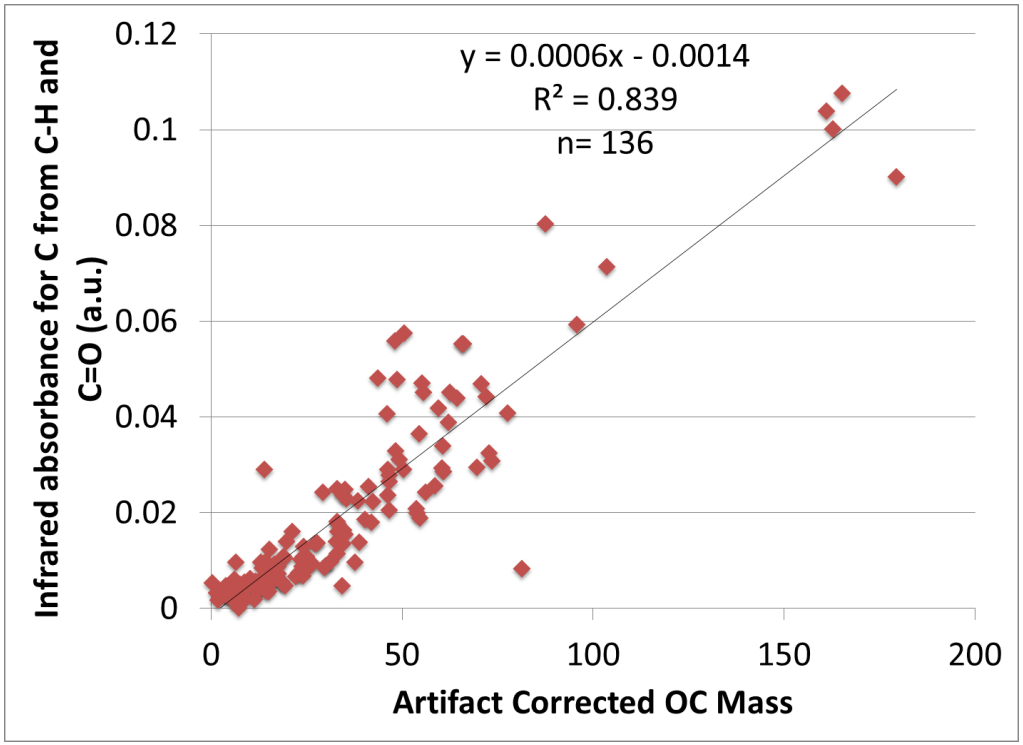
Example IR Spectra



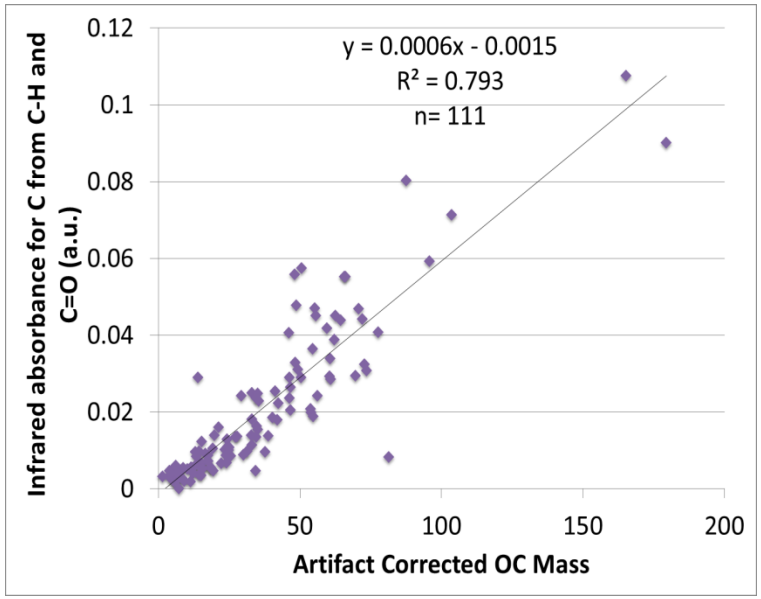
1. IMPROVE range



FT-IR calibration will enable comparison of carbon masses

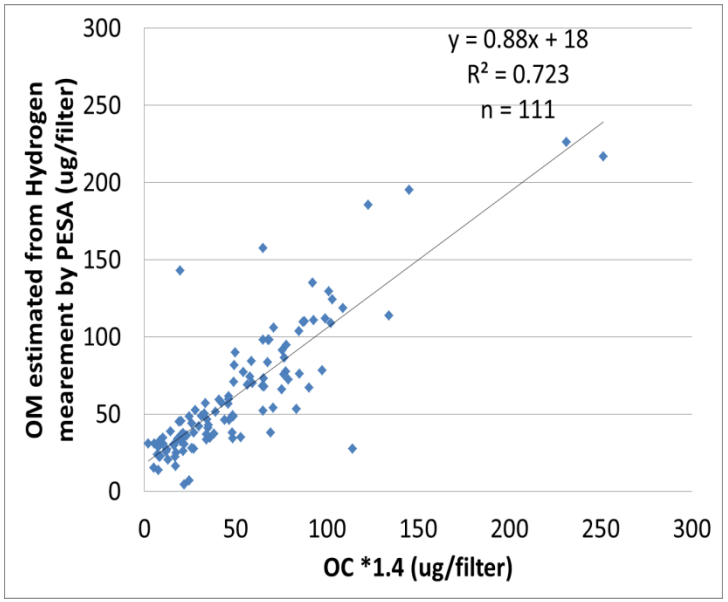
Consistency checking

OC absorbance from FT-IR vs TOR OC



FT-IR calibration will enable comparison of carbon masses

OM from PESA vs OM from TOR

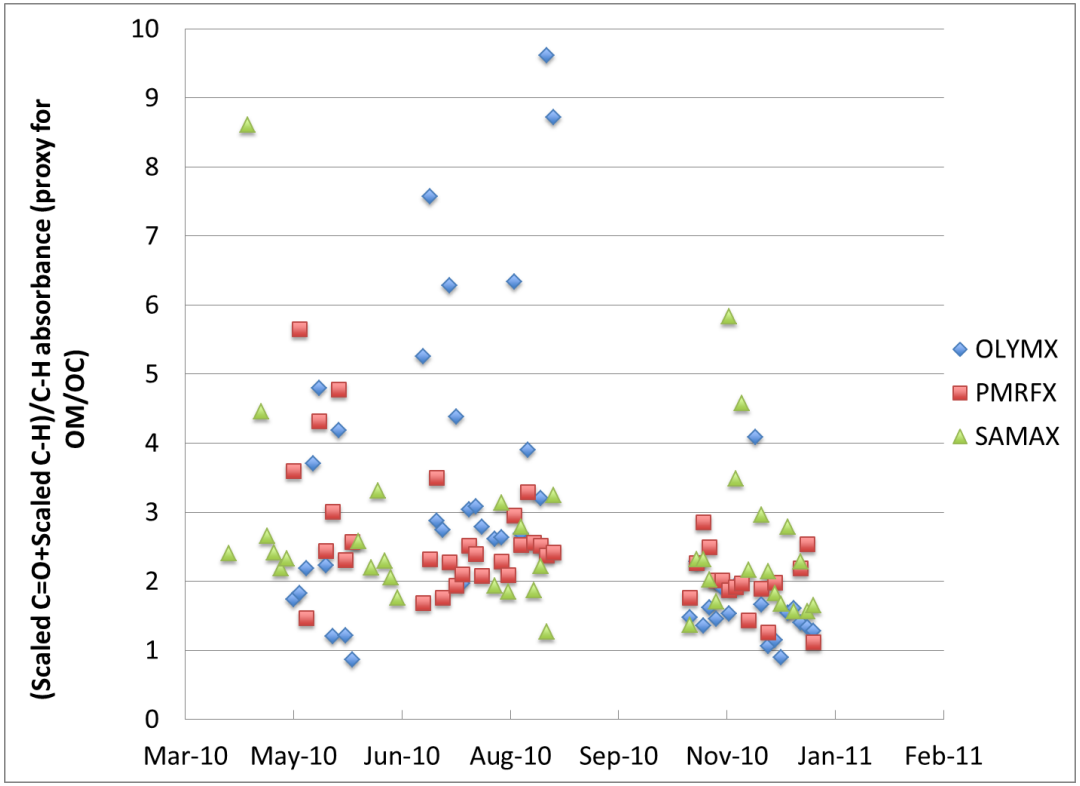


OM from PESA = 13.75*(H-S/4)

2. Interferants – ammonium, Teflon

- Ammonium
  - absorbs in OH and CH region of spectra
  - two methods to remove
    - Subtract scaled ammonium sulfate spectra (Russell et al.)
    - Include in calibration (Coury and Dillner)
- Teflon
  - exclude region from calibration (Russell and Dillner groups)
  - pre-scan Teflon and subtract from post-scan

3. Un-calibrated FT-IR proxy for OM/OC

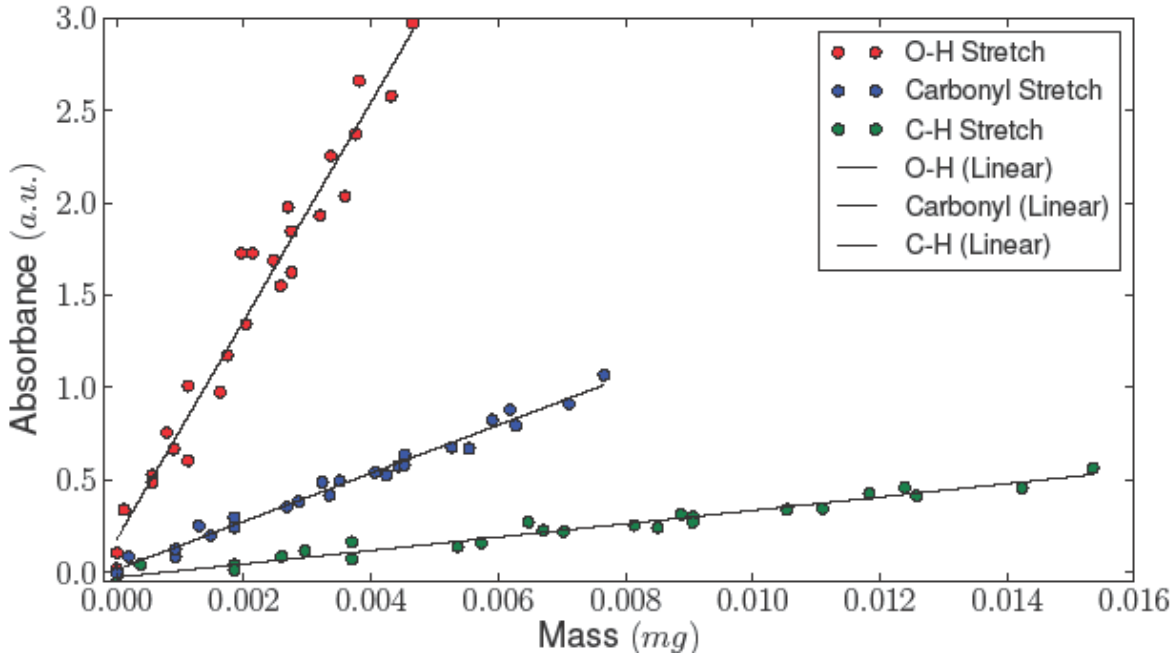


Calibration method development to date

- Created di-carboxylic acid standards
  - 5 acids of varying length
  - Mixtures of acids
  - Range of masses on filters
- Evaluated two calibration algorithms
  - Peak area absorbance vs. mass
  - Partial Least Squares Regression

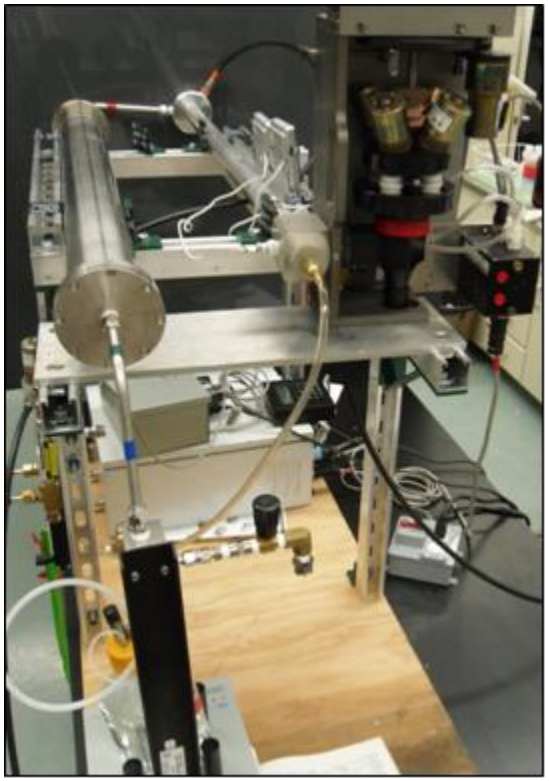
FT-IR absorbance vs. mass by functional group

Sebacic Acid – 10 carbon dicarboxylic acid



Plans for coming year to further develop method

- Create more standards
  - Functional groups
  - Range of masses (low)
  - Mixtures
- Evaluate/test algorithms
- Determine if pre-scan provides useful info.
- Analyze IMPROVE samples
  - Impact of XRF on OC



System for generating organic standards

Longer term plans

- Continue calibration method development
- Develop low cost auto-sampler for standards
- Test calibration method on:
  - Laboratory generated filters
  - well characterized lab-generated SOA samples
  - Ambient samples
- Continue to analyze IMPROVE samples
  - Compare to PESA and TOR

Feasibility of applying FT-IR analysis to network

- Automation of IMPROVE filter analysis
  - Considered in current automation of XRF and weighing
- One instrument can handle all IMPROVE filters
- Automation/QC of data analysis
  - To be developed after standards and algorithm established
- Possible new archiving method (cold?)
- Staff person to run samples/analyze data

Summary

- FT-IR analysis of Teflon filters useful for IMPROVE
  - Consistency check with quartz channel
  - OM/OC per filter
  - Functional group information – sources
- Non-destructive to Teflon filters
- Cost ≤ PESA
- Feasible to physically integrate into existing filter analyses at CNL