IMPROVE Carbon Analysis

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Presented at

the IMPROVE Steering Committee Meeting

Frostburg, MD

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Objectives

- Report status and improvements of IMPROVE carbon analyses

- Show results from recent carbon analysis research

Summary of Carbon Lab Operations

- Maintained 24 hours per day/6-7 days per week operation with five staff
- Average 17 days from sample receipt to carbon analysis (Jul 2010 to Jun 2011)
- Averaged ~800 samples per month in the queue (fluctuated between 0 and 1800); work schedule is adjusted accordingly
- Analyzed ~22,000 IMPROVE samples (Jul 2010 to Jun 2011)
- Started new contract April 2011

IMPROVE Carbon Analysis following the IMPROVE_A[a] Protocol

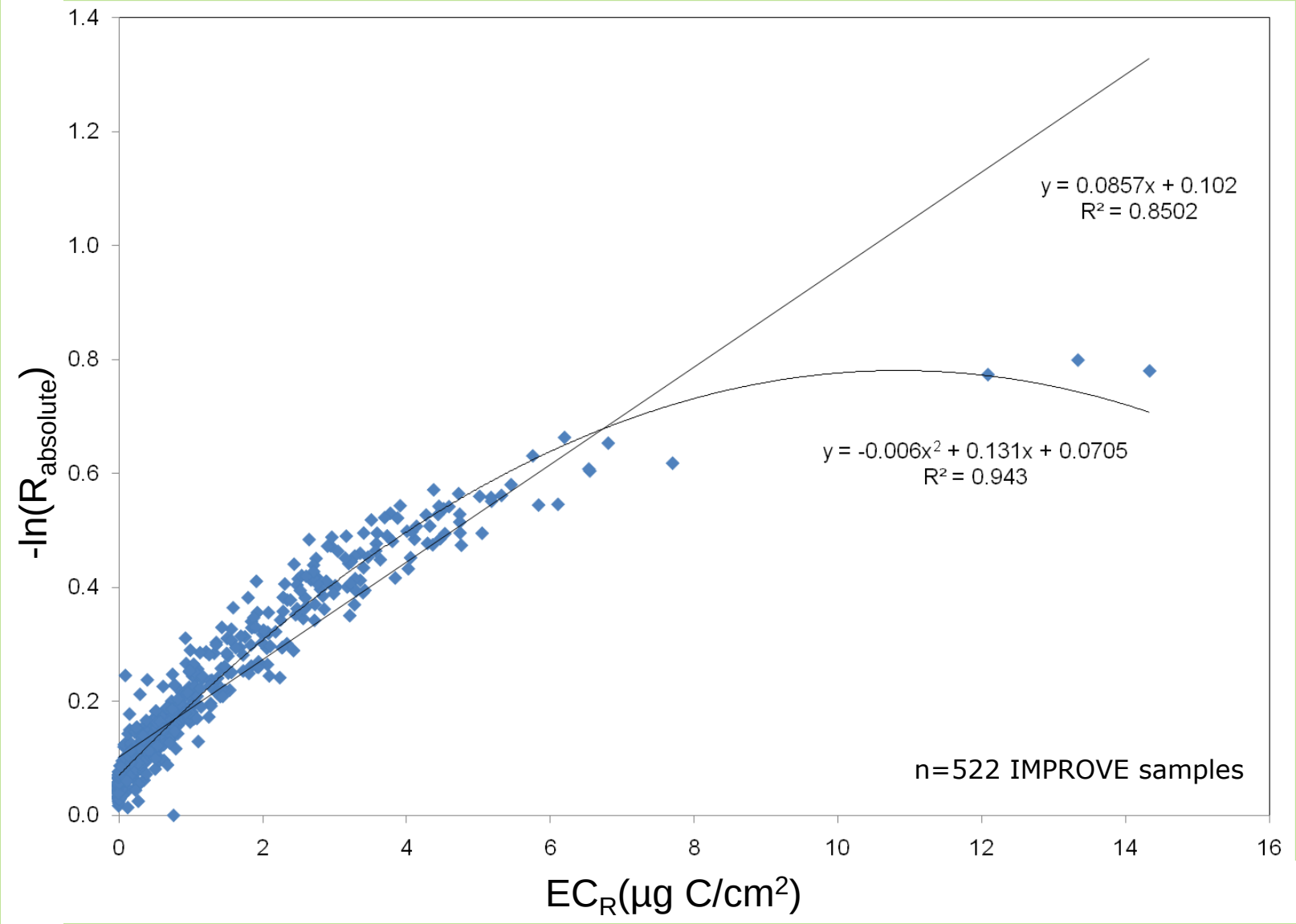
(7/10 – 6/11)

Sampling Period	Samples Received	Analysis Completion Date[b]
7/1/10-12/31/10	11,013	2/3/11
1/1/11-6/30/11	11,046	8/29/11

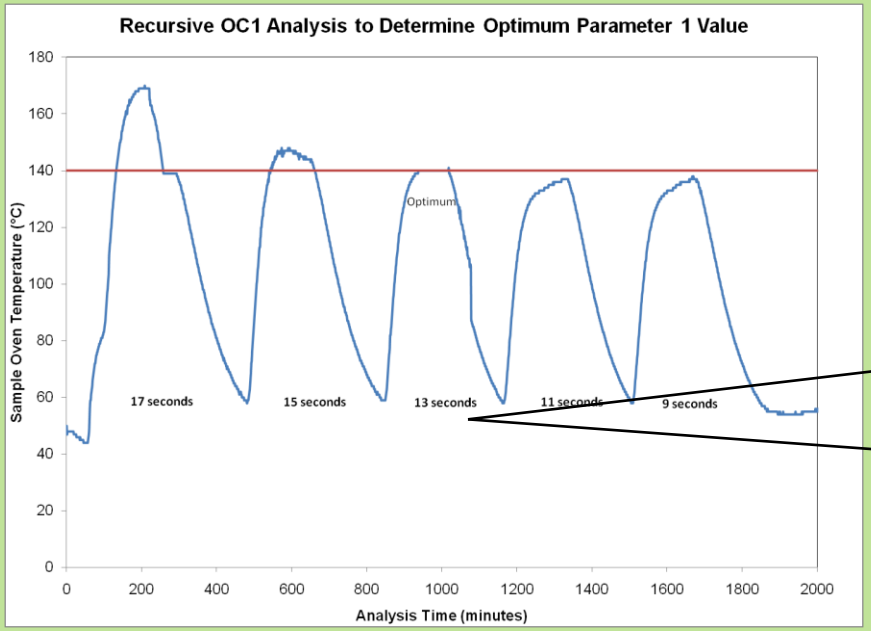
[a] Chow et al. (2007)

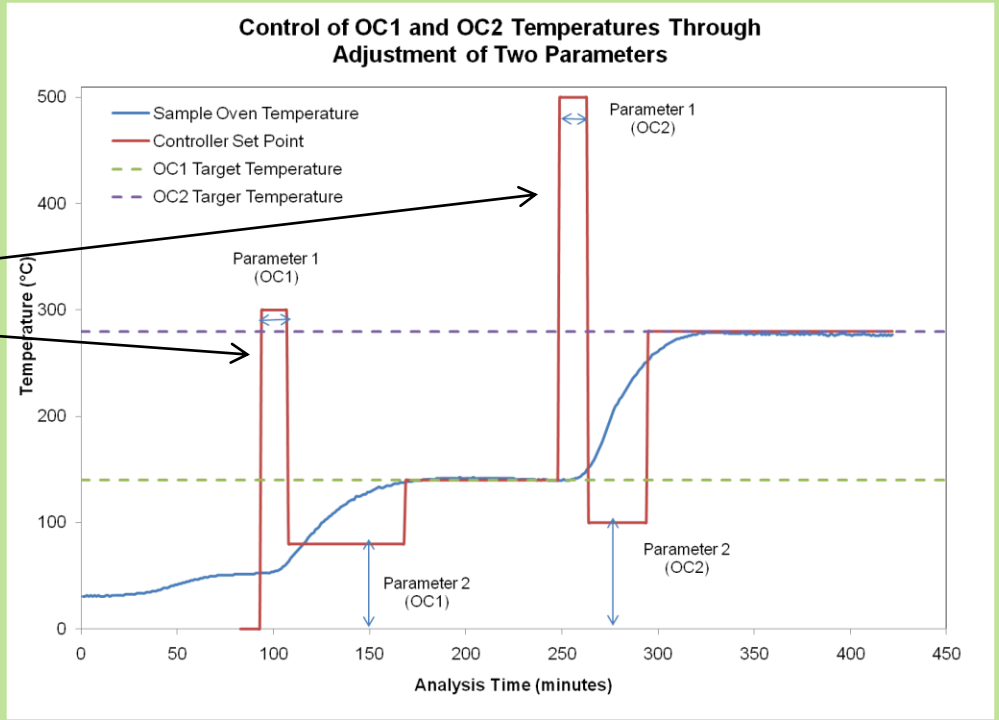
[b] Currently analyzing July 2011 samples (latest batch received)

Absolute laser reflectance highly correlates with EC_R measurements



Recursive testing allows the optimization of OC1 and OC2 Temperatures





SOP revisions to be completed by December 2011

- Verify carbon standards (sucrose and KHP) with the TOC analyzer (within ±5% of 1800 ppm C).
- Shorten carbon standard usage from 40 days to 30 days (documented in the electronic maintenance logbook).
- Purchase sieved MnO_2 for packing (size range 0.066 to 0.251 mm)
- Use Brillo Pad to smooth push rod to prevent sticking
- Enhance documentation of laboratory blank analysis

Additional QA/QC activities are added to SOP

Requirement	Calibration Standard	Calibration Range	Calibration Frequency	Performed By	Acceptance Criteria	Corrective Action
System Blank Check	N/A	N/A	Beginning of analysis day.	Carbon Analyst	≤0.2 μg C/cm^2.	Check instrument and filter lots.
Leak Check	N/A	N/A	Beginning of analysis day.	Carbon Analyst	Oven pressure drops less than 0.52 mmHg/s.	Locate leaks and fix.
Laser Performance Check	N/A	N/A	Beginning of analysis day.	Carbon Analyst	Transmittance >700 mV; Reflectance >1500 mV	Check laser and filter holder position.
Calibration Peak Area Check	NIST 5% CH_4/He gas standard.	20 μg C (Carle valve injection loop, 1000 μl).	Every analysis.	Carbon Analyst	Counts >20,000 and 95-105% of average calibration peak area of the day.	Void analysis result and repeat analysis with second filter punch.
Auto-Calibration Check	NIST 5% CH_4/He gas standard.	20 μg C (Carle valve injection loop, 1000 μl).	Beginning of analysis day.	Carbon Analyst	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.
Manual Injection Calibration	NIST 5% CH_4/He or NIST 5% CO_2/He gas standards.	20 μg C (Certified gas-tight syringe, 1000 μl).	End of analysis day.	Carbon Analyst	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples
Sucrose Calibration Check	10μL of 1800 ppm C sucrose standard.	18 μg C.	Thrice per week (began March, 2009).	Carbon Analyst	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples
Multiple Point Calibrations	1800 ppm C Potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH_4/He, and NIST 5% CO_2/He gas standards.	9-36 μg C for KHP and sucrose; 2-30 μg C for CH_4 and CO_2.	Every 6-months or after major instrument repair.	Carbon Analyst	All slopes ±5% of average.	Troubleshoot instrument and repeat calibration until results within stated tolerances.
Sample Replicates	N/A	N/A	Every 10 analyses.	Carbon Analyst on same or different analyzer	±10% when OC, EC, TC ≥10 μg C/cm^2 or <±1 μg/cm^2 when OC, EC, TC <10 μg C/cm^2	Investigate instrument and sample anomalies and rerun replicate when difference > ±10%.
Temperature Calibrations	Tempilaq (Tempil, Inc., South Plainfield, NJ, USA).	Three replicates each of 121, 184, 253, 510, 704, and 816 °C.	Every 6-months, or whenever the thermocouple is replaced.	Carbon Analyst	Linear relationship between thermocouple and Tempilaq values with R^2>0.99.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Oxygen Level in Helium Atmosphere	Certified gas-tight syringe.	0-100 ppmv.	Every 6-months, or whenever leak is detected.	Carbon Analyst using a GC/MS system.	Less than the certified amount of He cylinder.	Replace the He cylinder and/or O_2 scrubber.



Anal Bioanal Chem
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ORIGINAL PAPER

Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon

Judith C. Chow · John G. Watson · Jerome Robles · Xiaoliang Wang · L.-W. Antony Chen · Dana L. Trimble · Steven D. Kohl · Richard J. Tropp · Kochy K. Fung

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Abstract Accurate, precise, and valid organic and elemental carbon (OC and EC, respectively) measurements require more effort than the routine analysis of ambient aerosol and source samples. This paper documents the quality assurance (QA) and quality control (QC) procedures that should be implemented to ensure consistency of OC and EC measurements. Prior to field sampling, the appropriate filter substrate must be selected and tested for sampling effectiveness. Unexposed filters are pre-fired to remove contaminants and acceptance tested. After sampling, filters must be stored in the laboratory in clean, labeled containers under refrigeration (<4 °C) to minimize loss of semi-volatile OC. QA activities include participation in laboratory accreditation programs, external system audits, and interlaboratory comparisons. For thermal/optical carbon analyses, periodic QC tests include calibration of the flame ionization detector with different types of carbon standards, thermogram inspection, replicate analyses, quantification of trace oxygen concentrations (<100 ppmv) in the helium atmosphere, and calibration of the sample temperature sensor. These established QA/QC procedures are applicable to aerosol sampling and analysis for carbon and other chemical components.

Keywords Thermal/optical carbon analysis · IMPROVE_A protocol · Aerosol · Organic carbon · Elemental carbon · Pyrolysis · Quality assurance · Quality control

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Atmoslytic, Inc., 24801 Alexandra Court, Calabasas, CA 91302, USA

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Introduction

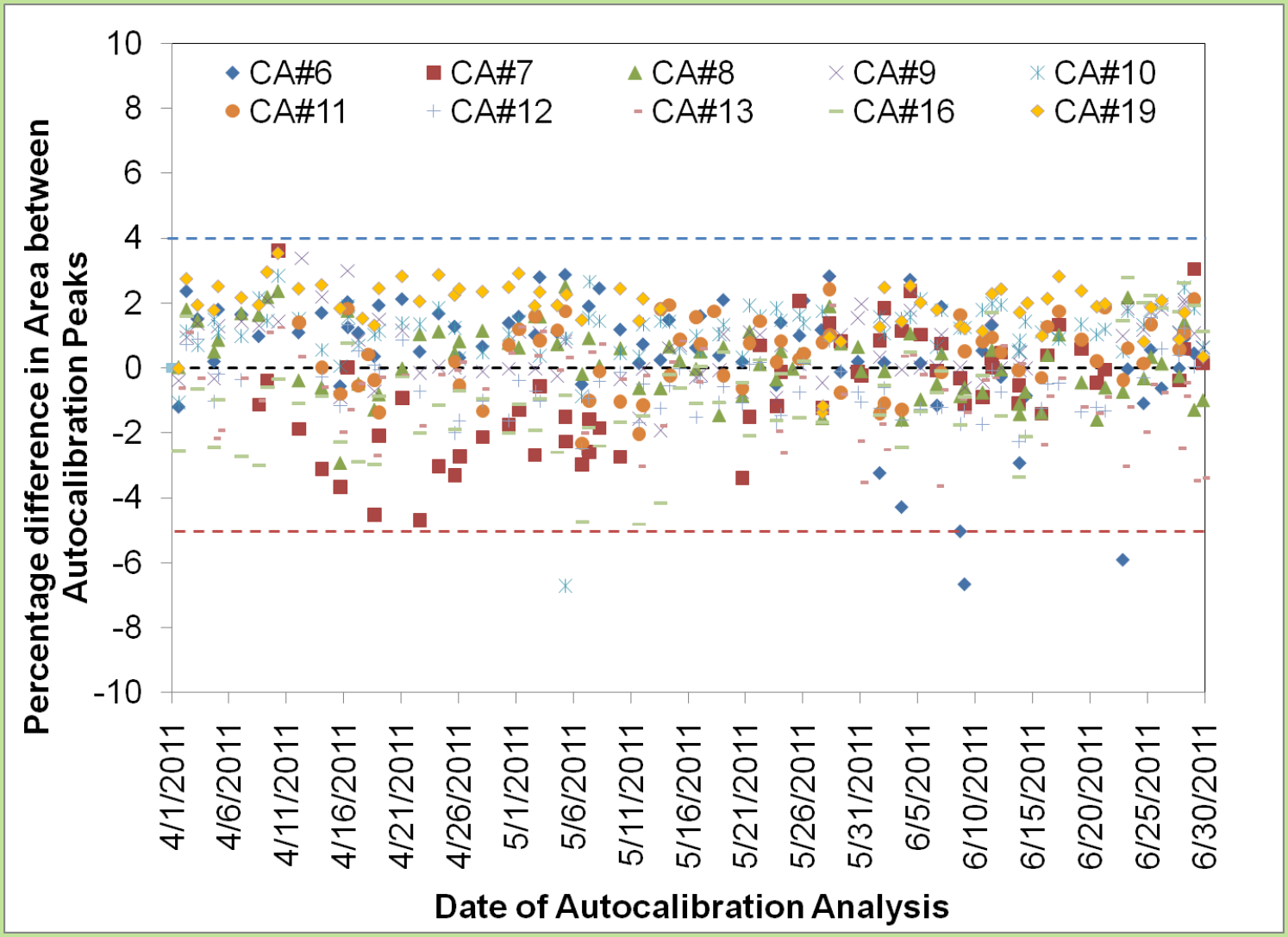
Organic and elemental carbon (OC and EC, respectively) are important components of suspended particulate matter (PM), especially the respirable fraction with aerodynamic diameters (d_p) of less than 2.5 μm ($PM_{2.5}$). Excessive OC and EC concentrations can adversely affect human health [1–3], visibility [4, 5], climate [6–8], materials [9–11], and biotic systems [12–16]. Bioaerosols such as plant wax, insect parts, spores, pollens, fungi, and endotoxins can be important contributors to the OC fraction(s) [12–16]. The ultrafine-size (d_p<100 nm) fraction also contains OC and EC [17, 18], and the fraction of PM carbon increases as particle size decreases [3]. OC and EC are measured in air quality monitoring networks and special studies using more than 20 variations on the evolved gas analysis (EGA) method [19]. These methods have been found to produce equivalent values for total carbon (TC=OC+EC), but dissimilar values for OC and EC.

Ambient air and source emission samples are collected onto a heat-resistant filter substrate and a portion of each filter is submitted to EGA for carbon determination. During heating under various temperatures and atmospheres, PM carbon in the sample volatilizes and combusts to carbon-containing gases that are oxidized to carbon dioxide (CO_2).

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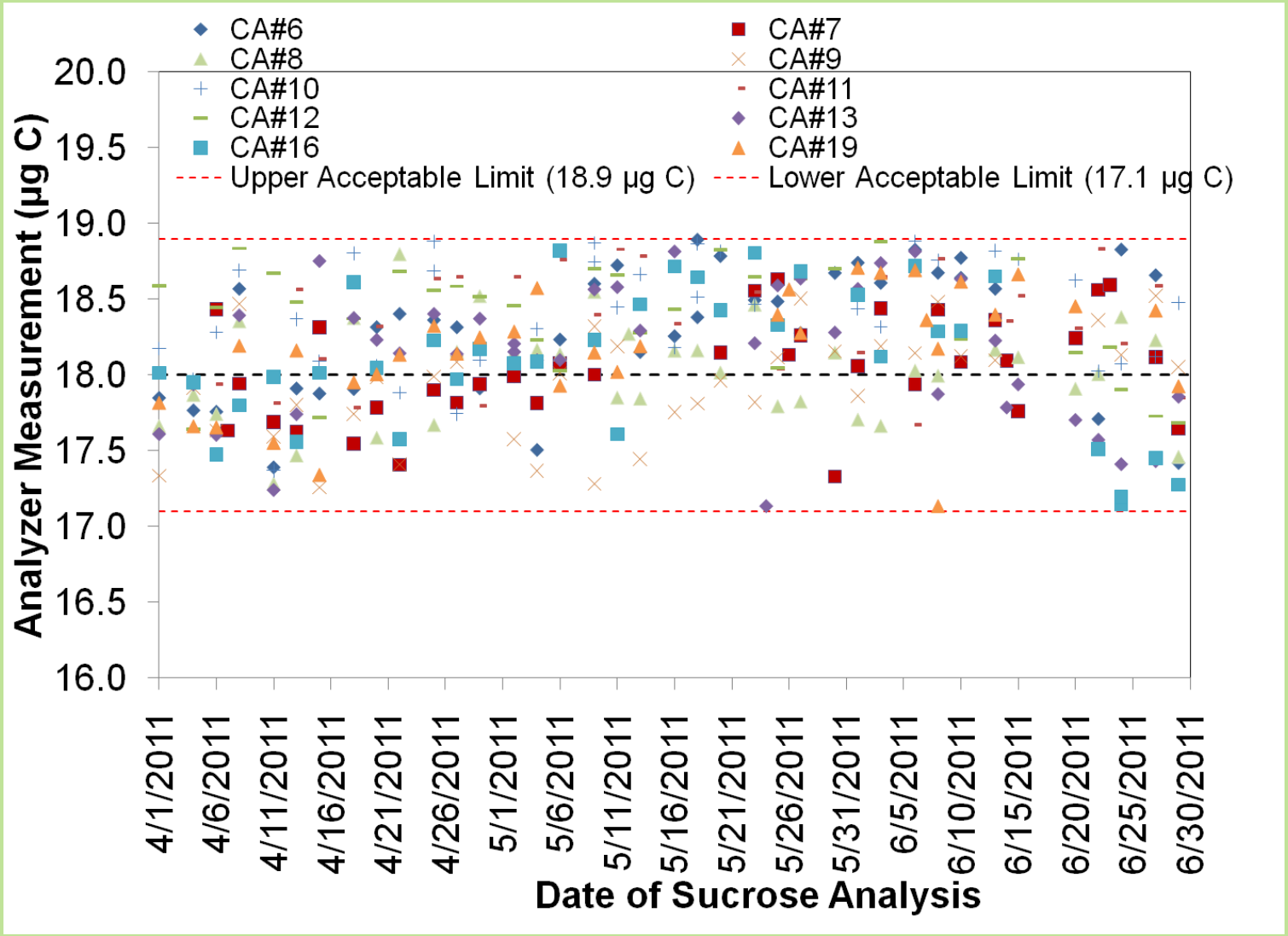
Chow et al., *ABC,* 2011

Daily instrument auto-calibration is within ±5%



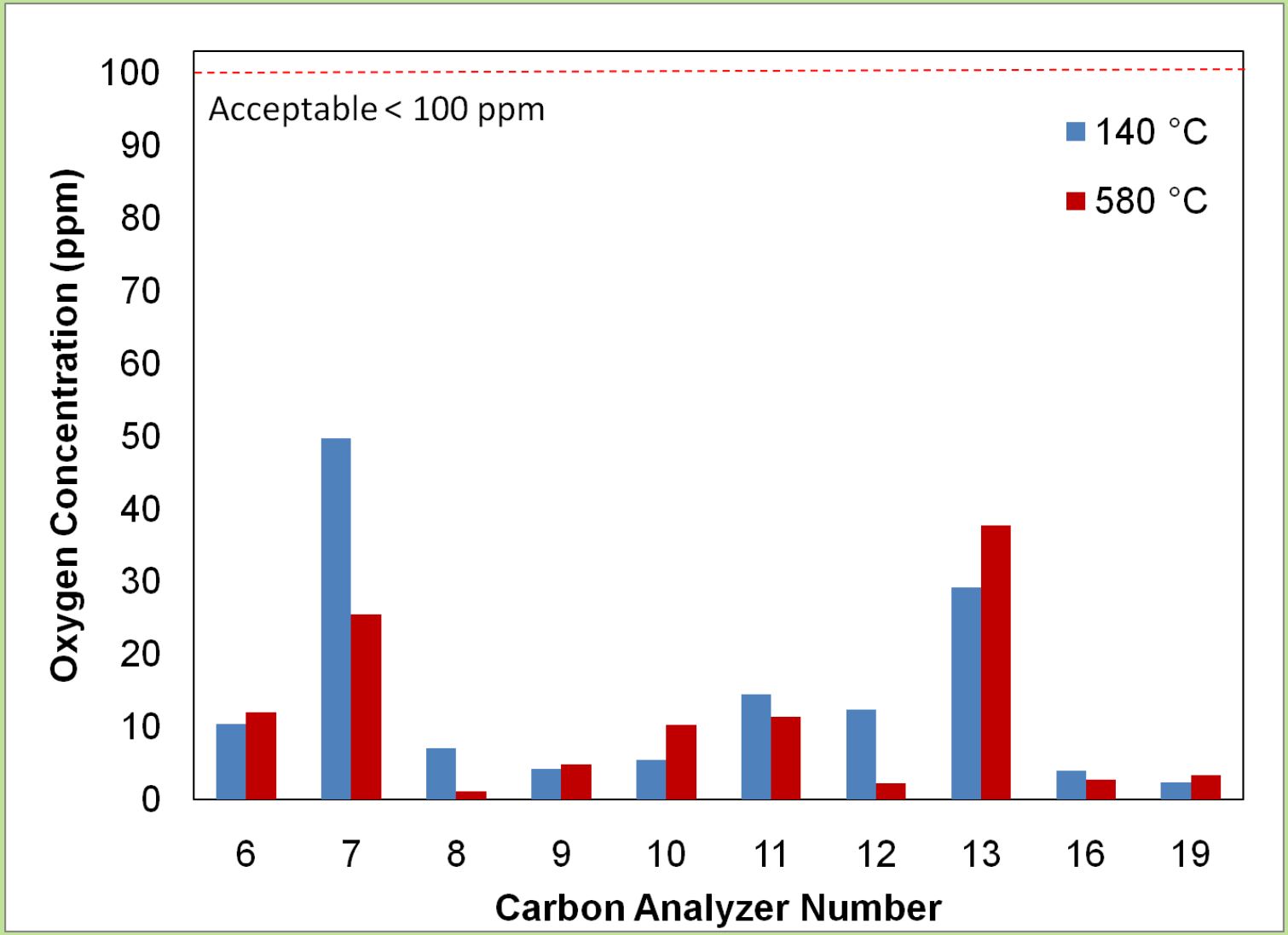
Quarterly calibration is within ±5%

(Sucrose; thrice per week)



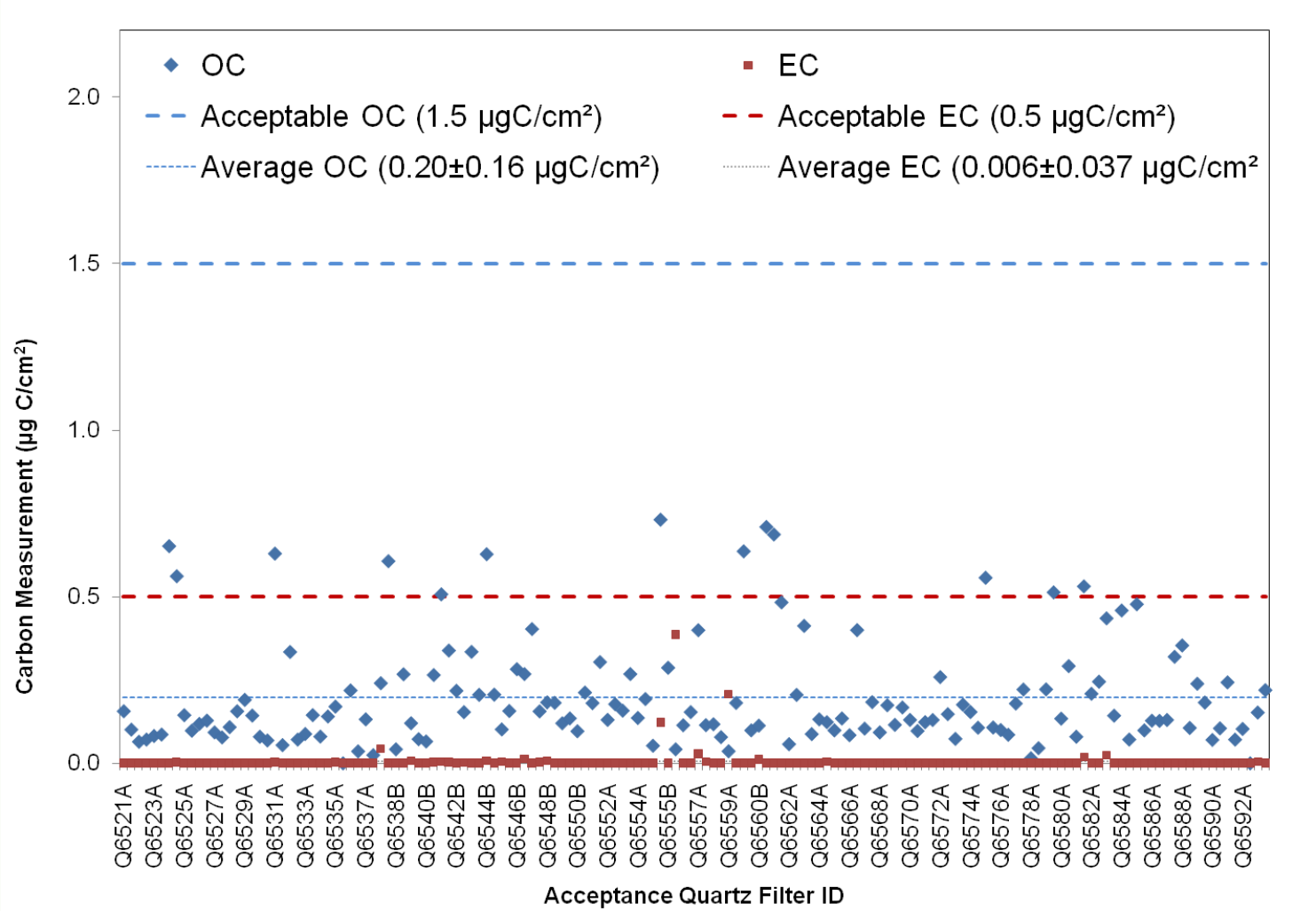
Oxygen content in OC analyses is well below 100 ppb

(Tested every six months, April-June 2011)



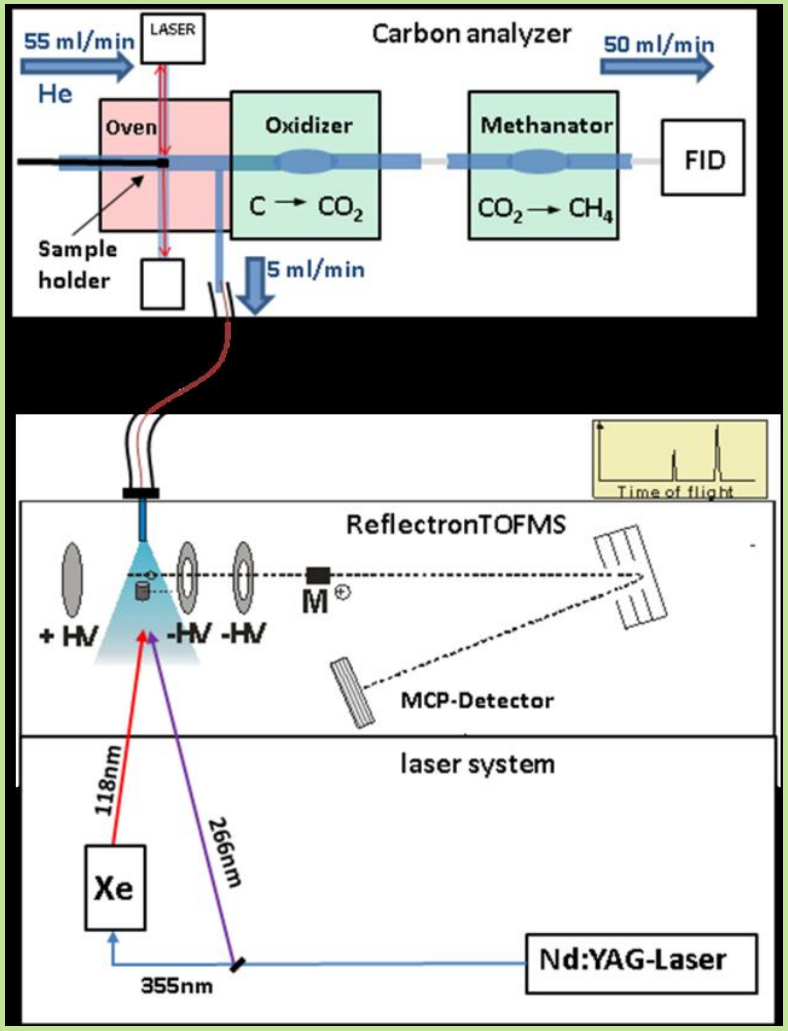
Low OC and EC levels found on pre-fired quartz-fiber filters

(Acceptance testing, April-June 2011)



Model 2001 DRI carbon analyzer integrated with photoionization-time-of-flight mass spectrometer

(PI-TOFMS; U. of Rostock, Germany)

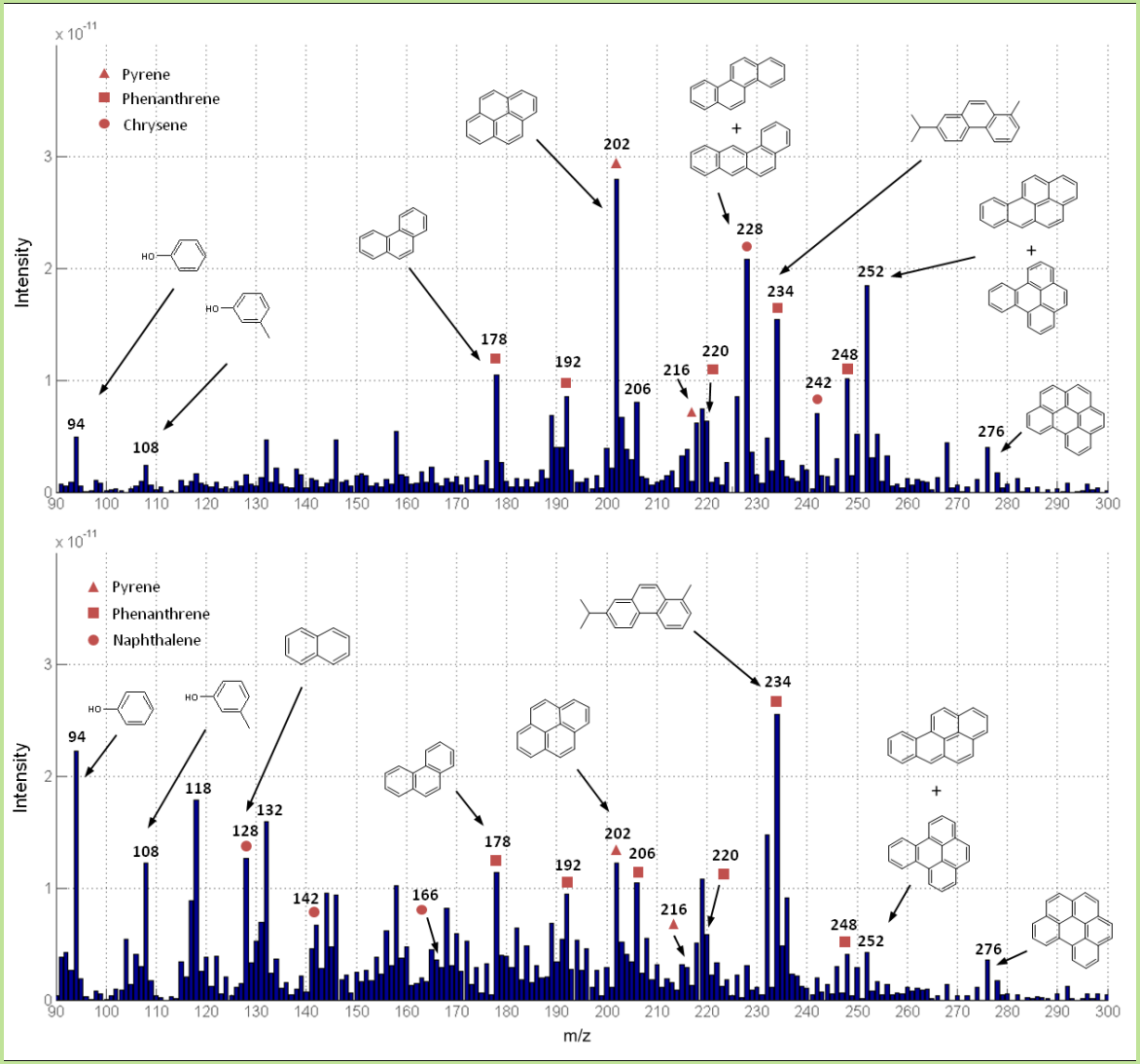




Pure Helium		Helium / 2 % O_2	
OC1	120°C	EC1	550°C
OC2	250°C	EC2	700°C
OC3	450°C	EC3	800°C
OC4	550°C		

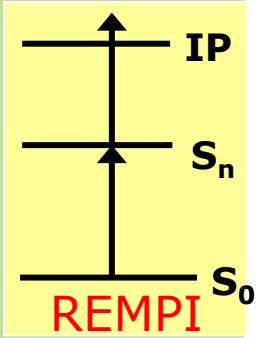
Grabowski, ABC, *submitted*

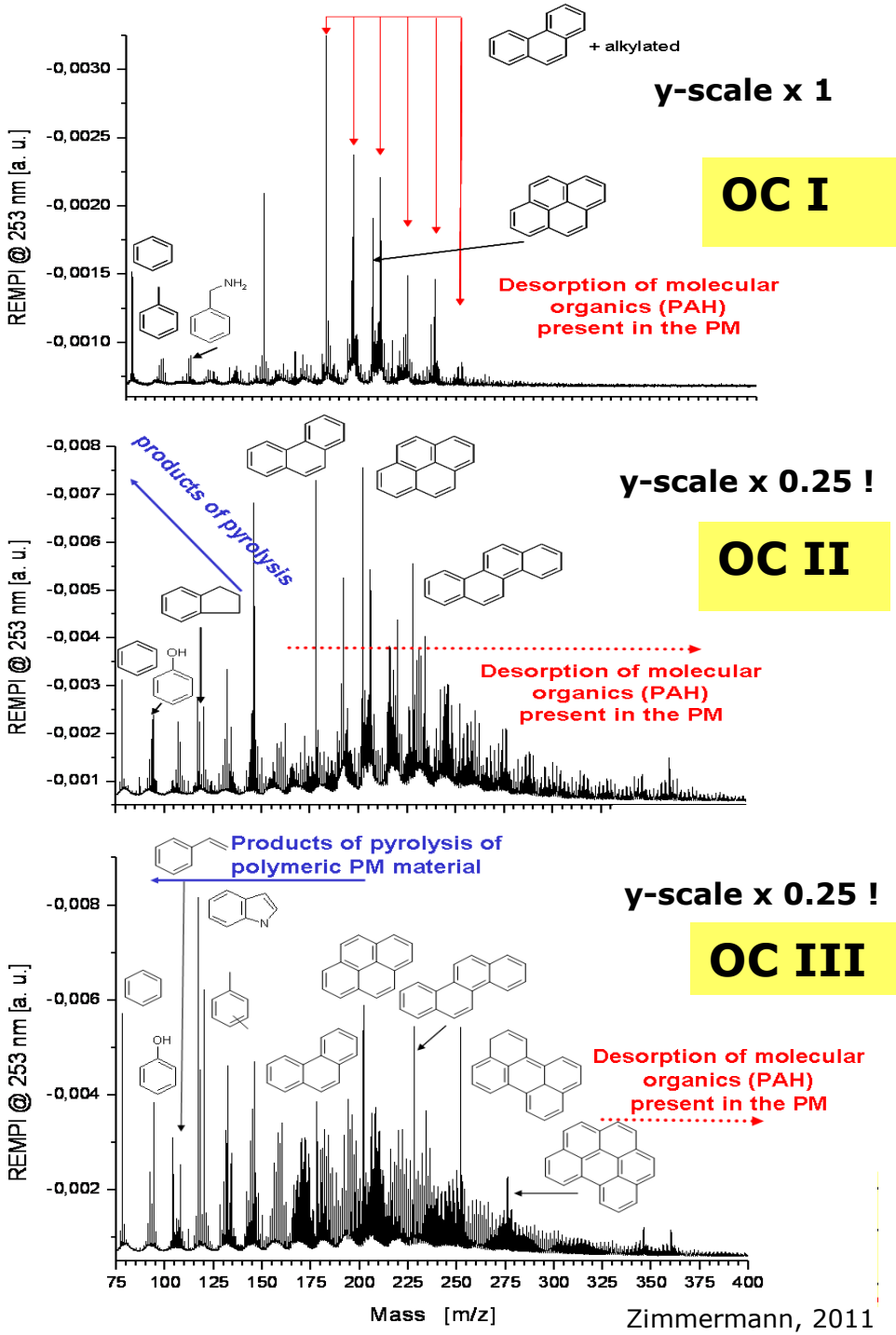
Resonance Enhanced Multi-Photon Ionization-Time-of-flight-Mass Spectrometry (REMPI-TOFMS) allows identification of compounds in each thermal fraction



Grabowski et al., 2011, ABC, *accepted*

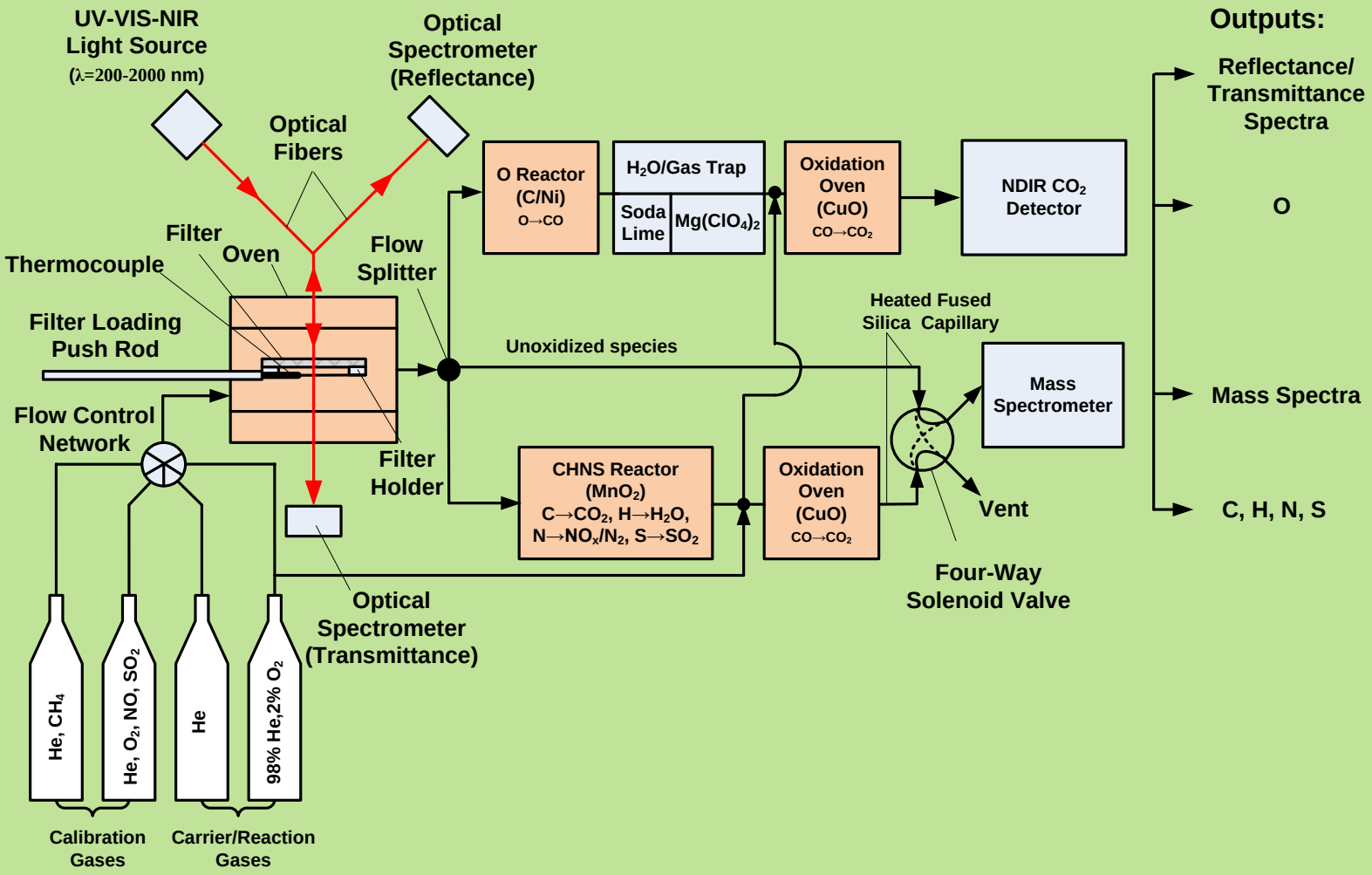
Mass spectra for thermal fractions from Model 2001 with REMPI-TOFMS detector



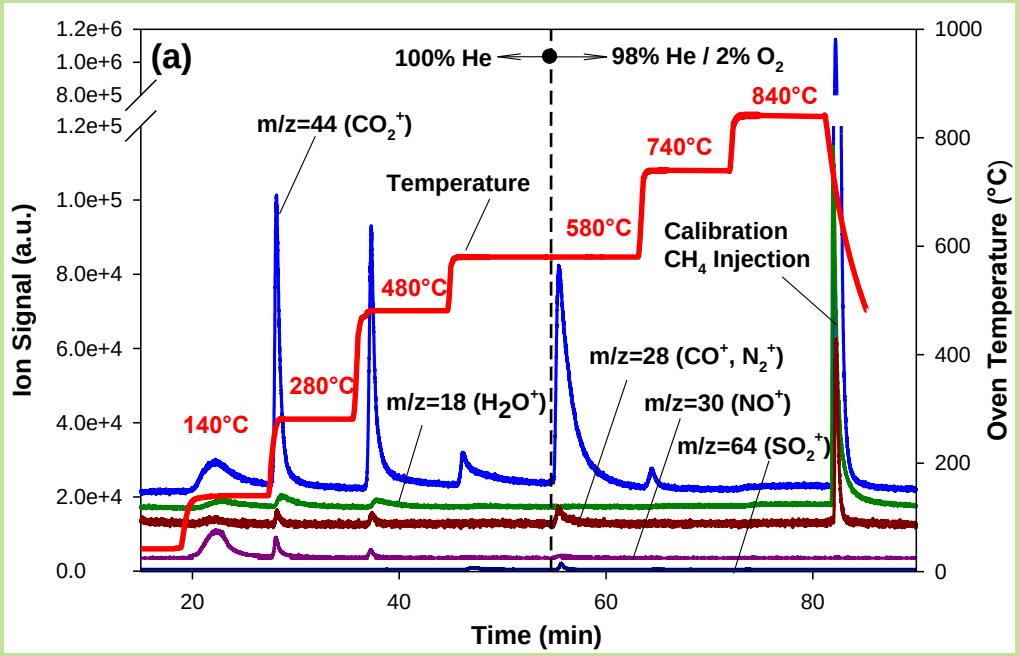


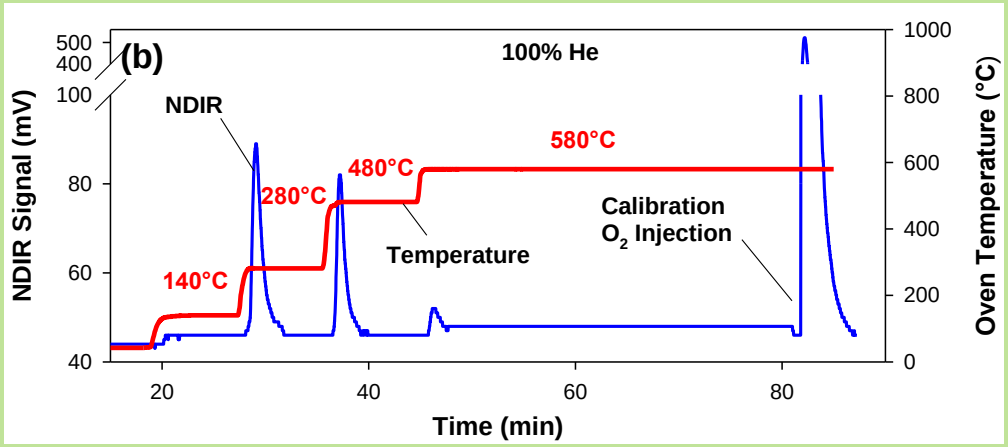
Zimmermann, 2011

Potential configuration for next generation of thermal/optical analysis for elemental and optical properties



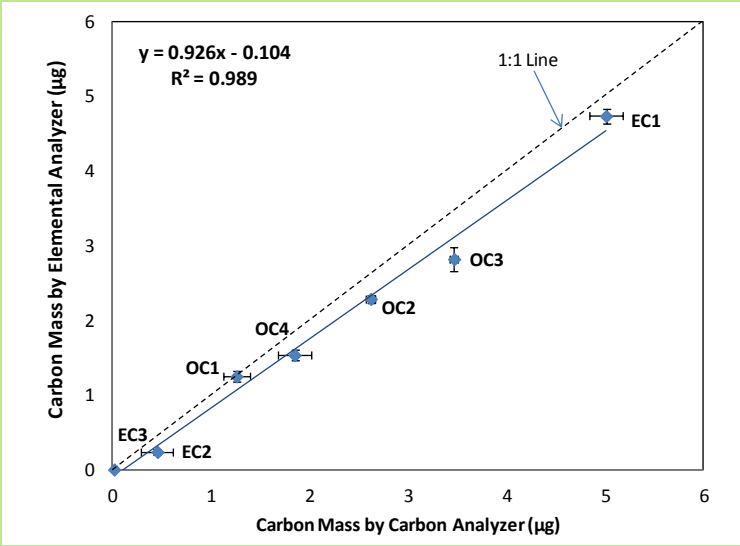
C,H,N,S, and O can be determined using current processes



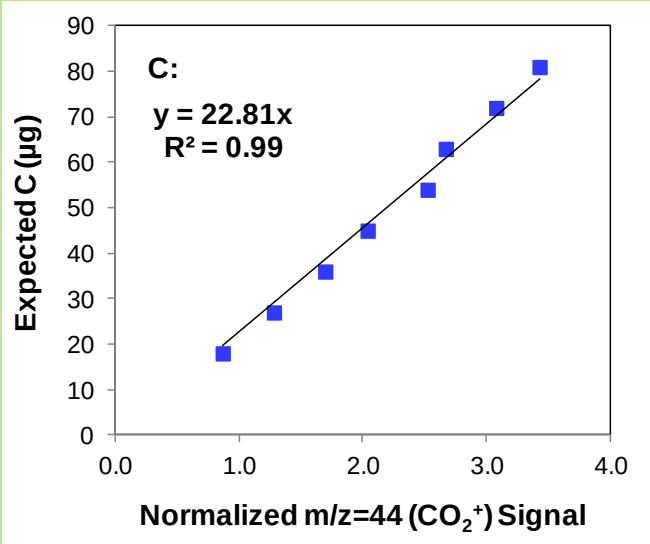


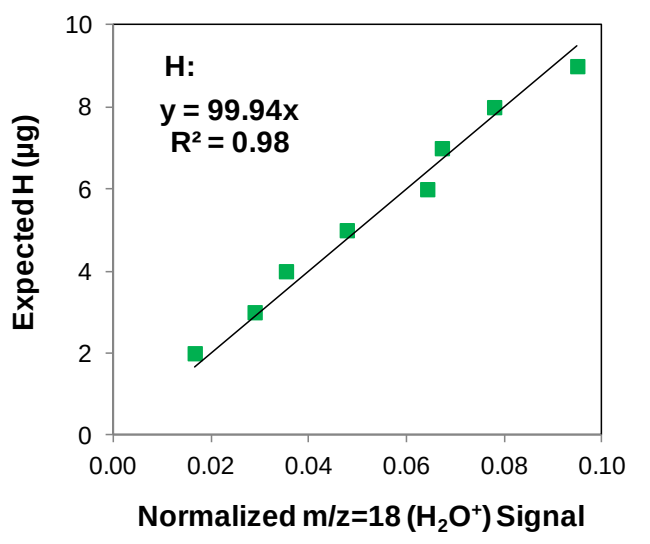
Thermogram of Fresno ambient aerosol sample for (a) CHNS, and (b) O following the IMPROVE_A protocol.

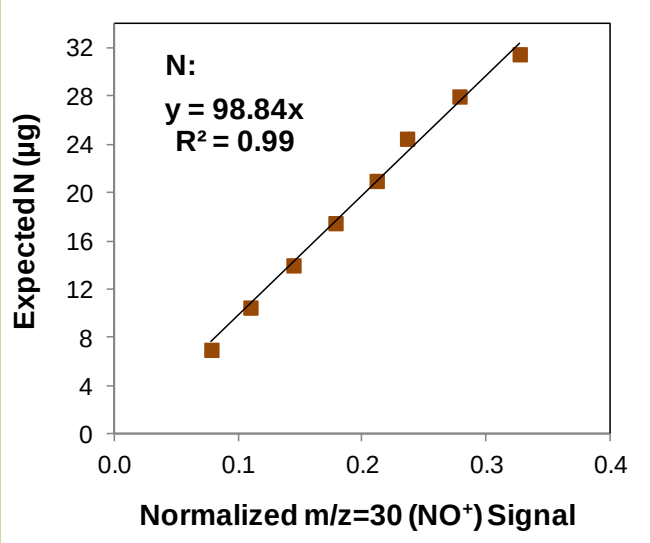
Comparison of carbon fractions measured by elemental analyzer and DRI thermal/optical carbon analyzer

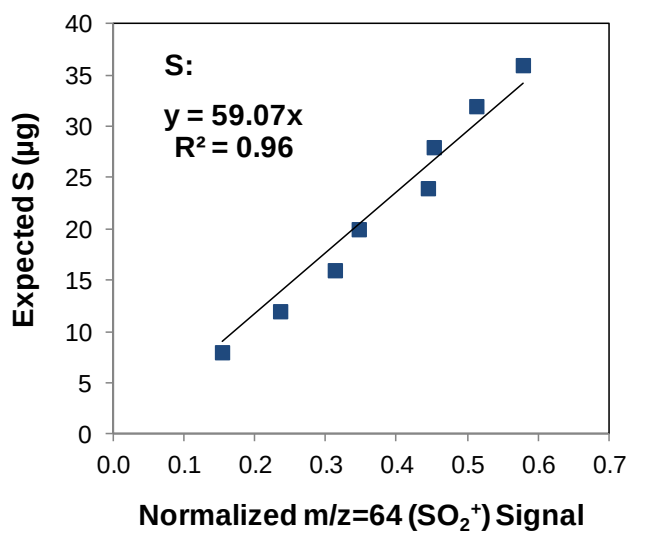


C,H,N,S Calibration of MS-TOA instead of FID using Sulfanilamide ($C_6H_8N_2O_2S$)

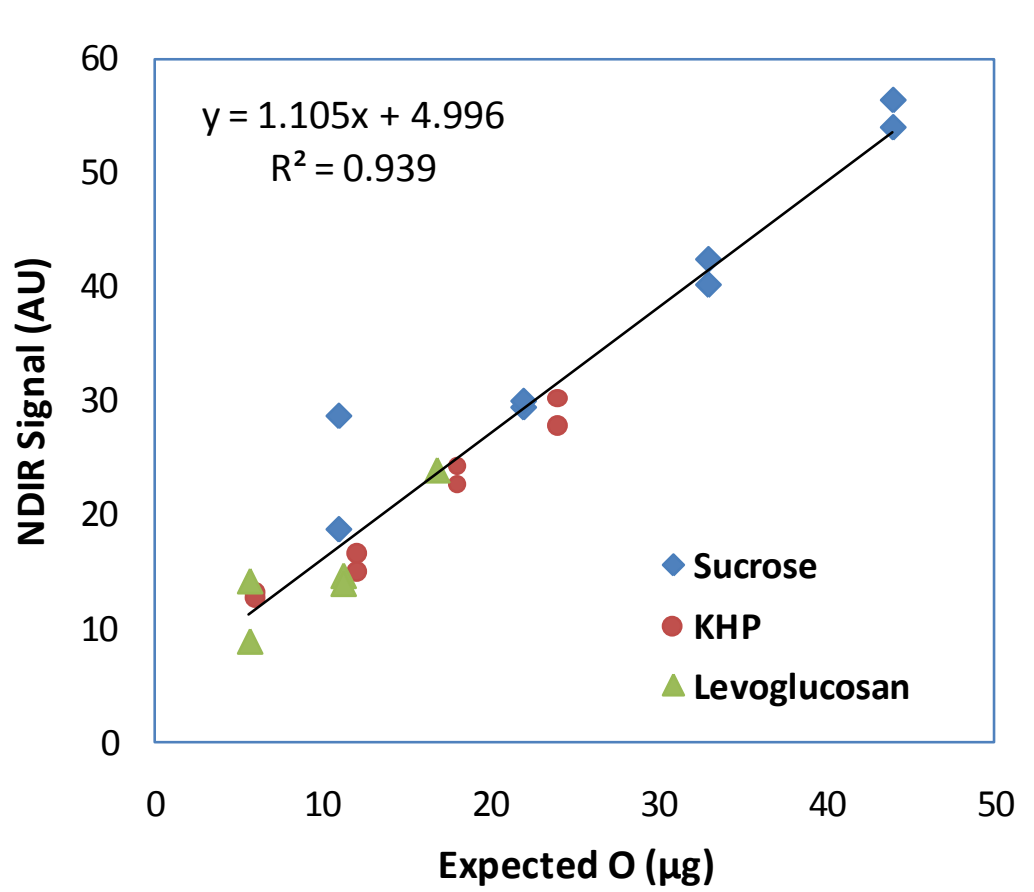




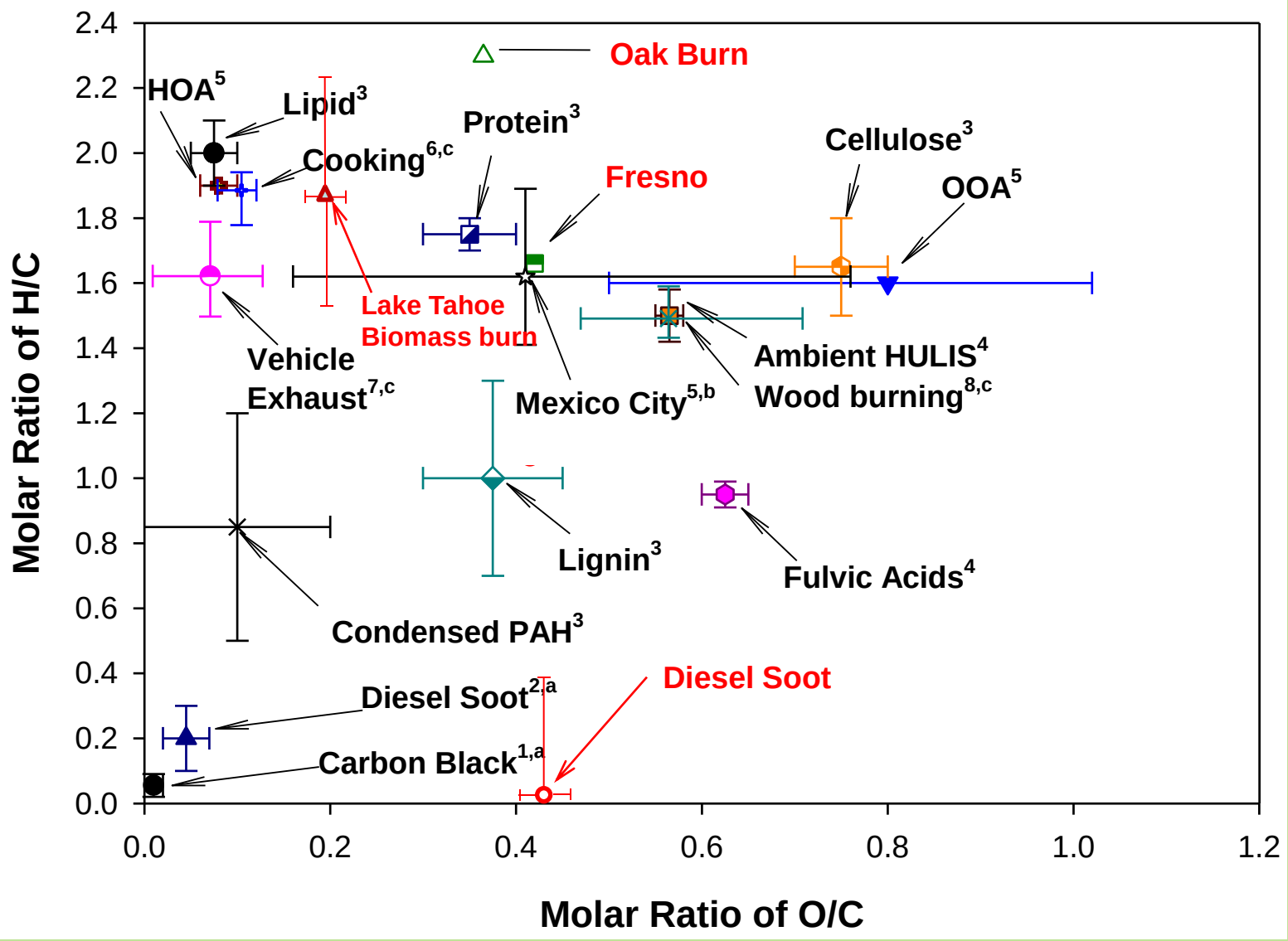




O Calibration of MS-TOA

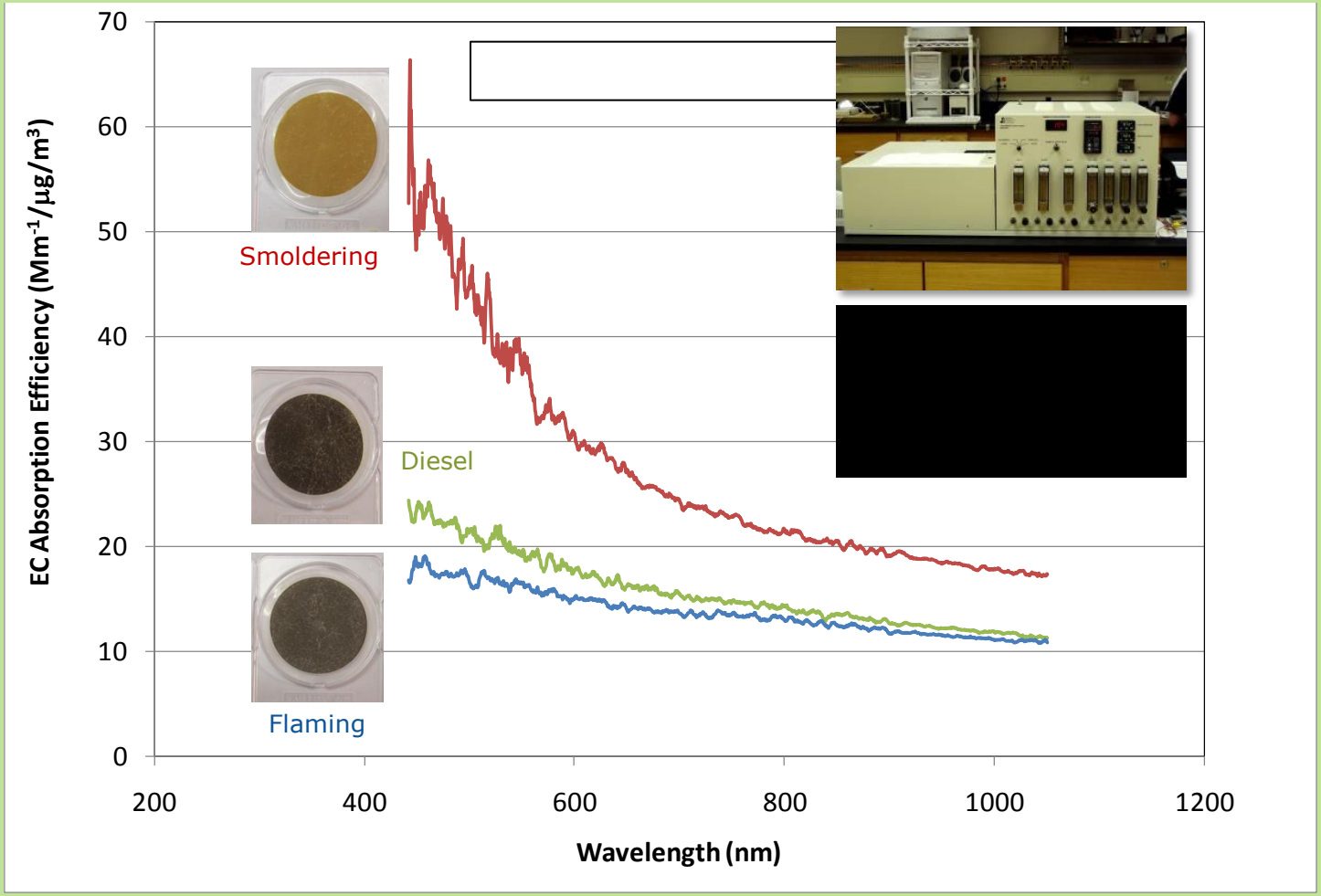


H/C vs. O/C molar ratios varied by source



Extending from single to multiple wavelengths can obtain more information on IMPROVE samples

(EC absorption efficiency varies by source and wavelength)



Experimental Configuration Using Laser Diodes with Different Wavelengths

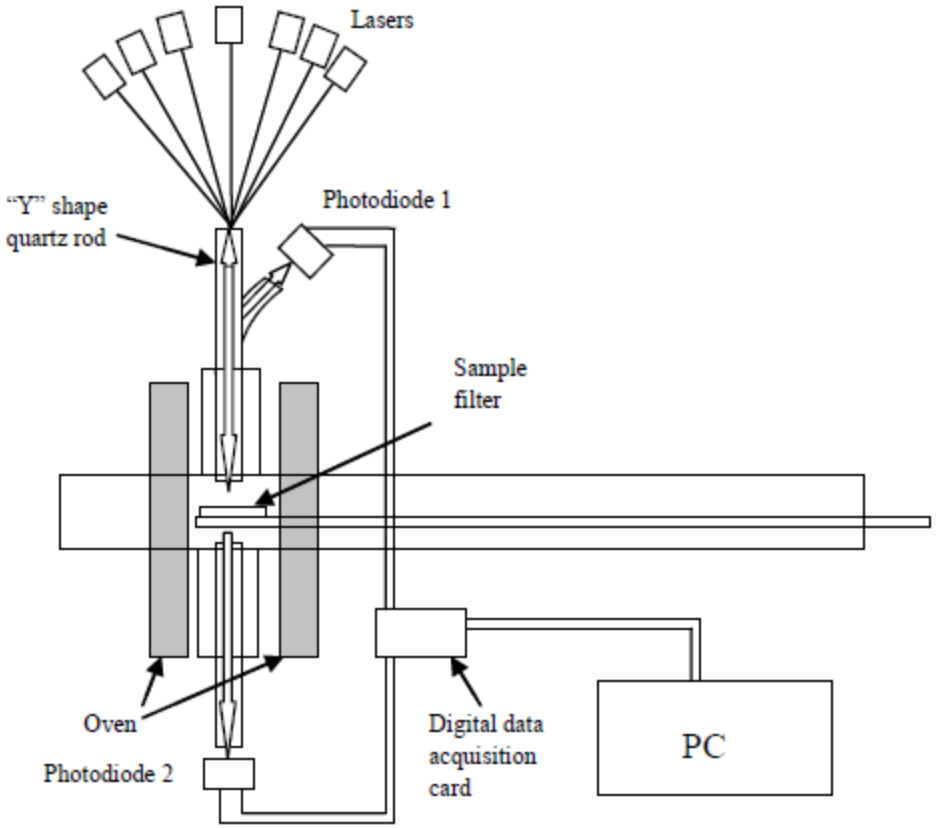


Figure 3. Schematic diagram of multi-wavelength carbon analyzer. Instead of the two branch optical fiber, A "Y" shape quartz will be used to guide the incident light to the sample filter and the reflected light to photodiode 1. Photodiode 2 is used to measure the transmitted light. Signals are collected by a Digital data acquisition card. A computer is used to read the data and process signals from different lasers using Fourier transform.

Proof of concept: Multi-wavelength transmittance and reflectance during charring of sucrose

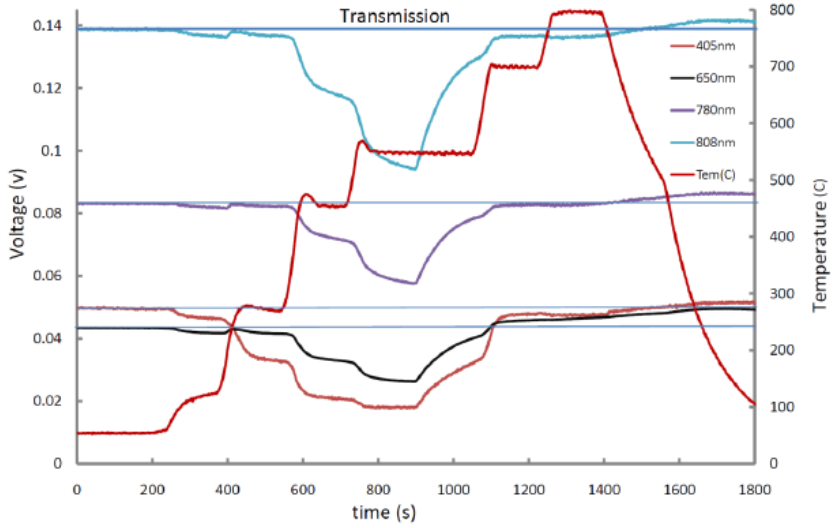


Figure 4. Preliminary transmission signal through a sucrose sample filter in the carbon analyzer at four different wavelengths (405 nm, 650 nm, 780 nm, and 808 nm) when the sample was heated following the modified IMPROVE_A protocol.

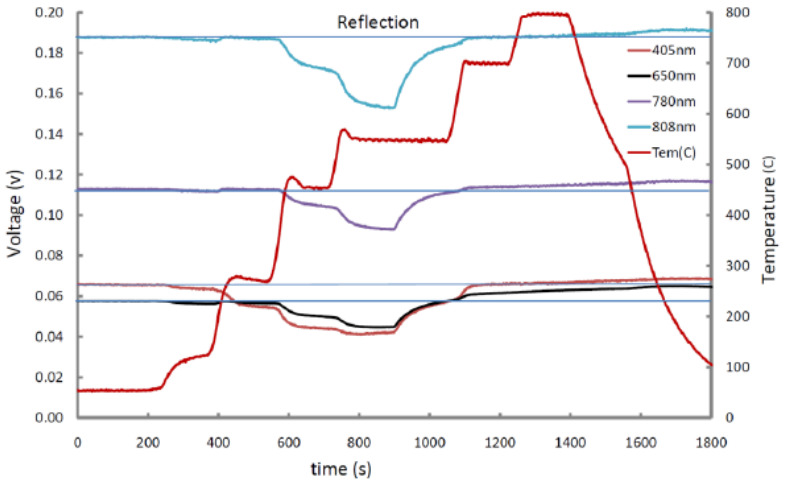


Figure 5. Preliminary reflection signal through a sucrose sample filter in the carbon analyzer at four different wavelengths (405 nm, 650 nm, 780 nm, and 808 nm) when the sample was heated following the IMPROVE_A protocol.

Publications using IMPROVE data and carbon analysis methods since last meeting

Aerosol and Air Quality Research, 11: 70–79, 2011
Copyright © Taiwan Association for Aerosol Research
ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2010.10.0088

Chemical Composition of Indoor and Outdoor Atmospheric Particles at Emperor Qin's Terra-cotta Museum, Xi'an, China

Jun-ji Cao[1,5*], Hua Li[1,4], Judith C. Chow[2], John G. Watson[2], Shuncheng Lee[3], Bo Rong[4], Jun-gang Dong[6], Kin-fai Ho[1]

Contents lists available at ScienceDirect
Atmospheric Environment
journal homepage: www.elsevier.com/locate/atmosenv

Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels

Jun-ji Cao[a,b,*], Judith C. Chow[a,c], Jun Tao[d], Shun-cheng Lee[e], John G. Watson[a,c],

TECHNICAL PAPER
ISSN: 1047-3289 *J. Air & Waste Manage. Assoc.* 61:1–14
DOI: 10.1080/10473289.2011.619082
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$PM_{2.5}$ Source Apportionment: Reconciling Receptor Models for U.S. Nonurban and Urban Long-Term Networks

L.-W. Antony Chen, John G. Watson, Judith C. Chow, and Dave DuBois
Division of Atmospheric Sciences, Desert Research Institute, Reno, Nevada, USA

Lisa Herschberger
Minnesota Pollution Control Agency, St. Paul, Minnesota, USA

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Journal of Hazardous Materials
journal homepage: www.elsevier.com/locate/jhazmat

Characteristics and source apportionment of PM_1 emissions at a roadside station

Y. Cheng[a,b,c,*], S.C. Zou[d], S.C. Lee[c], J.C. Chow[a,b,e], K.F. Ho[c], J.G. Watson[a,b,e], Y.M. Han[b], R.J. Zhang[f], F. Zhang[a], P.S. Yau[c], Y. Huang[c], Y. Bai[a], W.J. Wu[a]

Contents lists available at ScienceDirect
Atmospheric Environment
journal homepage: www.elsevier.com/locate/atmosenv

$PM_{2.5}$ source profiles for black and organic carbon emission inventories

Judith C. Chow[a,b,*], John G. Watson[a,b], Douglas H. Lowenthal[a], L.-W. Antony Chen[a], Nehzat Motallebi[c]

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ISSN:1047-3289 *J. Air & Waste Manage. Assoc.* 60:1365–137
DOI:10.3155/1047-3289.60.11.1365
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Filter Light Attenuation as a Surrogate for Elemental Carbon

Judith C. Chow and John G. Watson
Division of Atmospheric Sciences, Desert Research Institute, Reno, NV; and Aerosol and Environmental Division, Institute of Earth Environment, Chinese Academy of Science, Xian, People's Republic of China

Mark C. Green
Division of Atmospheric Sciences, Desert Research Institute, Reno, NV

Neil H. Frank
Air Quality Assessment Division, U.S. Environmental Protection Agency, Research Triangle Park, NC

Anal Bioanal Chem
DOI 10.1007/s00216-011-5103-3

ORIGINAL PAPER

Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon

Judith C. Chow · John G. Watson · Jerome Robles · Xiaoliang Wang · L.-W. Antony Chen · Dana L. Trimble · Steven D. Kohl · Richard J. Tropp · Kochy K. Fung

Atmos. Chem. Phys., 11, 4679–4686, 2011
www.atmos-chem-phys.net/11/4679/2011/
doi:10.5194/acp-11-4679-2011
© Author(s) 2011. CC Attribution 3.0 License.

Decreases in elemental carbon and fine particle mass in the United States

D. M. Murphy[1], J. C. Chow[2], E. M. Leibensperger[3], W. C. Malm[4], M. Pitchford[5], B. A. Schichtel[6], J. G. Watson[2], and W. H. White[7]

Contents lists available at ScienceDirect
Science of the Total Environment
journal homepage: www.elsevier.com/locate/scitotenv

Chemical compositions and source identification of $PM_{2.5}$ aerosols for estimation of a diesel source surrogate

Manoranjan Sahu[a], Shaohua Hu[a], Patrick H. Ryan[b], Grace Le Masters[b], Sergey A. Grinshpun[b]

Atmos. Chem. Phys., 11, 4425–4444, 2011
www.atmos-chem-phys.net/11/4425/2011/
doi:10.5194/acp-11-4425-2011
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Evaluation of the carbon content of aerosols from the burning of biomass in the Brazilian Amazon using thermal, optical and thermal-optical analysis methods

L. L. Soto-García[1,2], M. O. Andreae[3], T. W. Andreae[3], P. Artaxo[4], W. Maenhaut[5], T. Kirchstetter[6], T. Novakov[6], J. C. Chow[7], and O. L. Mayol-Bracero[1]

Atmos. Chem. Phys., 10, 5223–5239, 2010
www.atmos-chem-phys.net/10/5223/2010/
doi:10.5194/acp-10-5223-2010
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Quantification of $PM_{2.5}$ organic carbon sampling artifacts in US networks

J. C. Chow[1,2], J. G. Watson[1,2], L.-W. A. Chen[1], J. Rice[3], and N. H. Frank[3]

Future Activities

- Test specific source samples for C, H, N, S, and O
- Improve understanding of compounds evolving in each temperature fraction
- Examine EC absorption efficiencies as a function of wavelength on laboratory-simulated vegetative burning samples
- Determine practicality of enhancing information from IMPROVE sample analyses while maintaining consistency with the long-term database