Improved Optical and Chemical Characterization Methods for $PM_{2.5}$ Source Apportionment

Richard J. Tropp
Judith C. Chow
John G. Watson

Desert Research Institute, Reno, NV

Presented at:
EPA's National Ambient Air Monitoring Conference
Atlanta, GA
August 11-14, 2014

Objectives

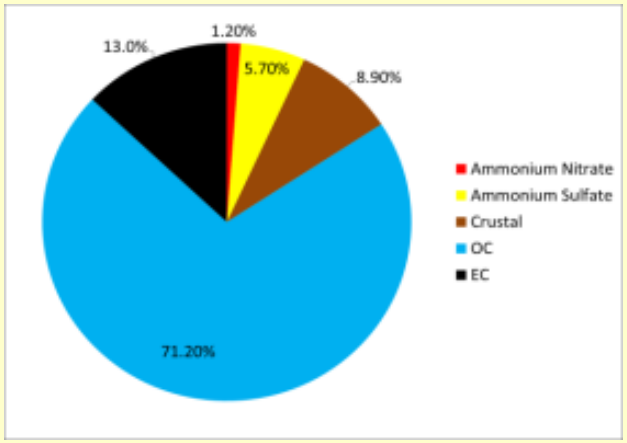
- **Review common chemical analyses for $PM_{2.5}$/PM_{10} networks**
- **Give overview of characterization methods for more specific source markers**
- **Give examples of source markers to better validate source apportionment results**
- **Goal is to provide additional information at minimal additional cost**

Major PM components are commonly characterized, but more specific markers are needed

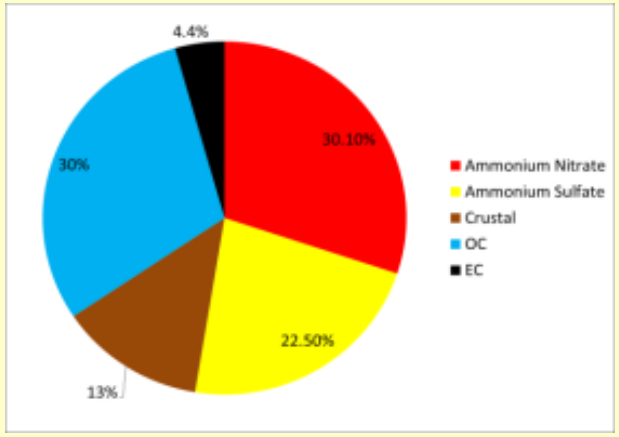
- Organic Carbon
- Elemental Carbon
- Nitrate
- Sulfate
- Ammonium
- Geological Material
- Sea Salt
- Liquid Water
- Other

Chemical composition differs by PM size fraction

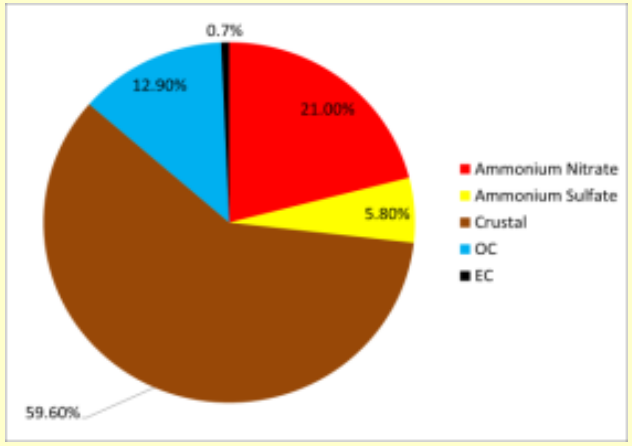
$PM_{0.1}$ (ultrafine PM)



$PM_{2.5}$ (fine PM)



$PM_{10-2.5}$ (coarse PM)

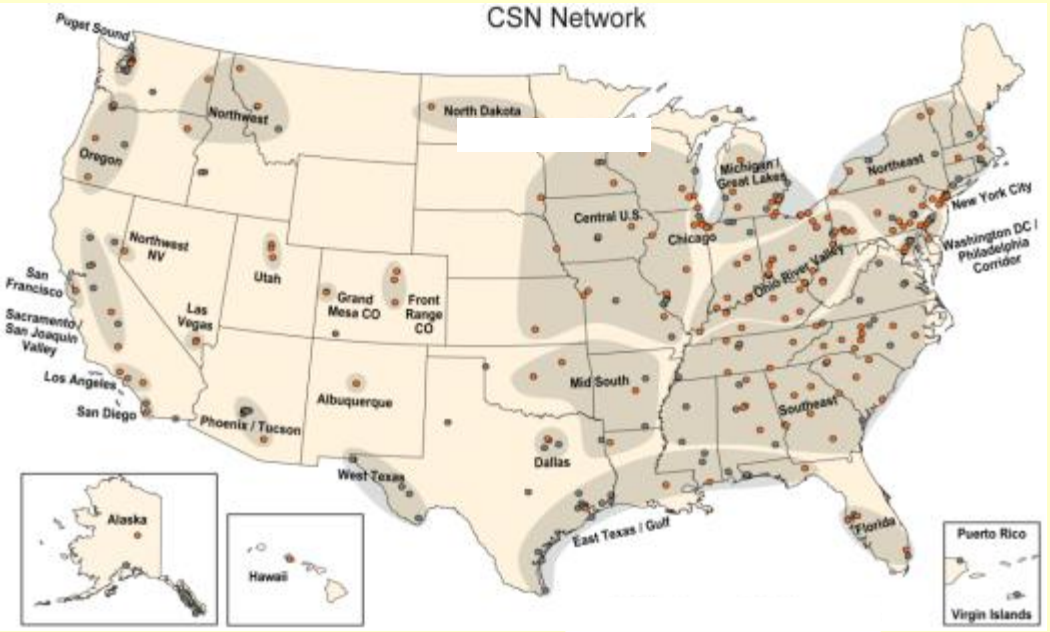


Los Angeles Supersite

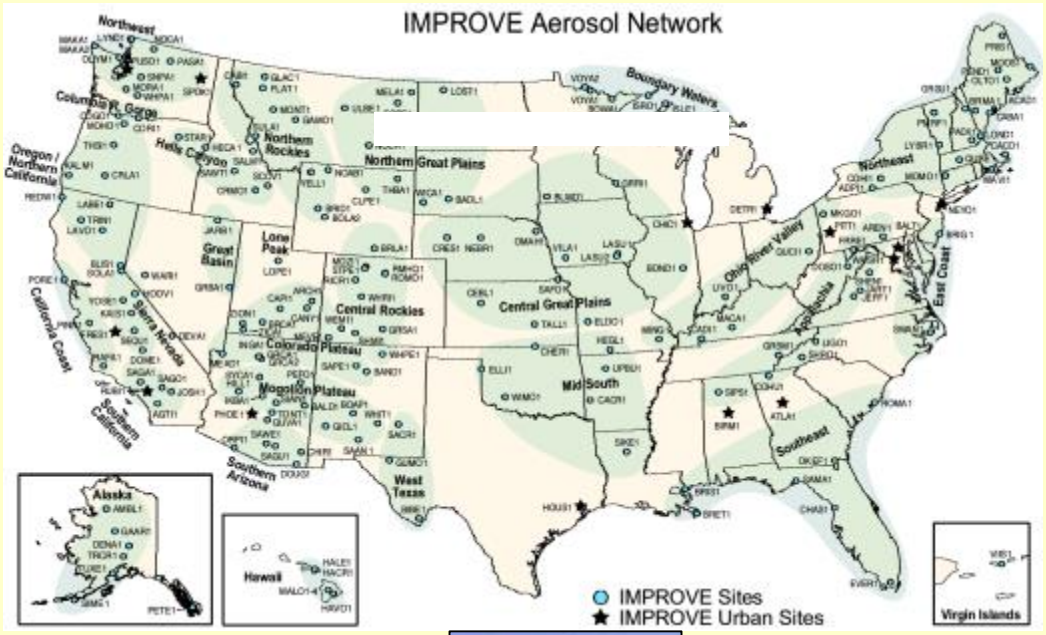
U.S. EPA Staff Paper (2005)

U.S. long-term chemical speciation networks obtain filter samples for $PM_{2.5}$ mass, elements, ions, and carbon

Chemical Speciation Network (CSN)



Interagency Monitoring of PROtected Visual Environments (IMPROVE) Network



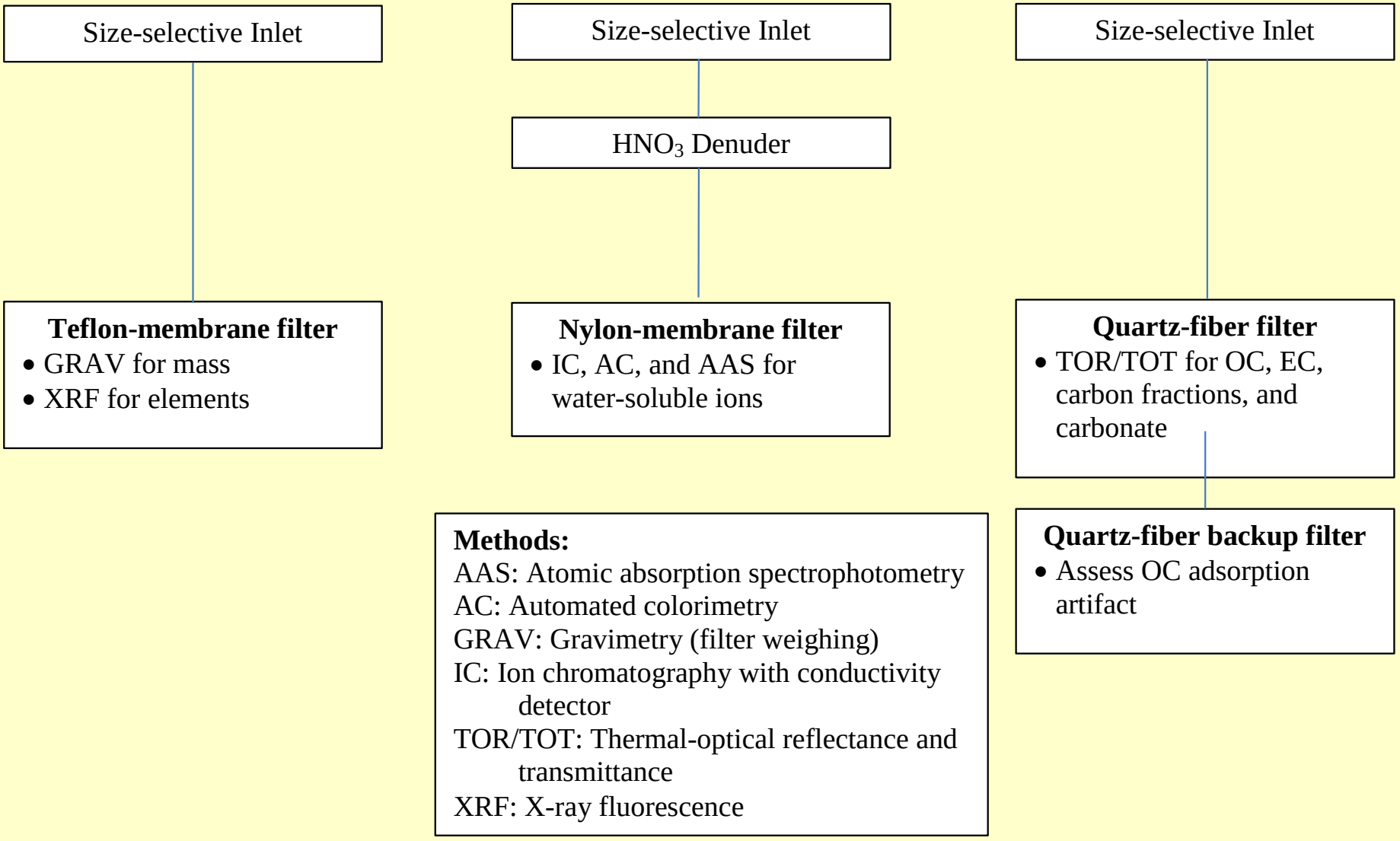
URG MASS | Andersen RAAS | MetOne SASS | URG 3000N | R&P Partisol

IMPROVE

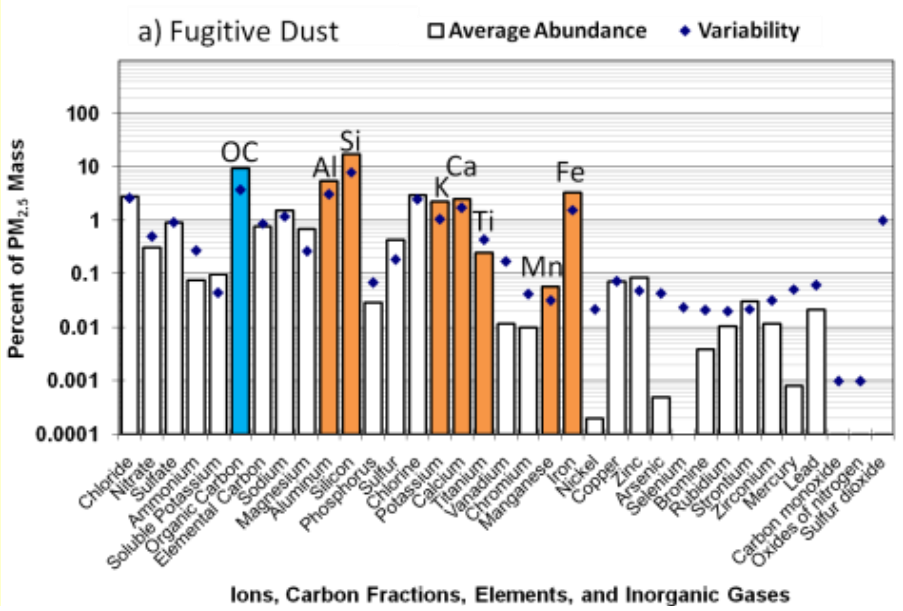
IMPROVE (2014). Interagency Monitoring of Protected Visual Environments. prepared by National Park Service, Ft. Collins, CO, http://vista.cira.colostate.edu/IMPROVE.

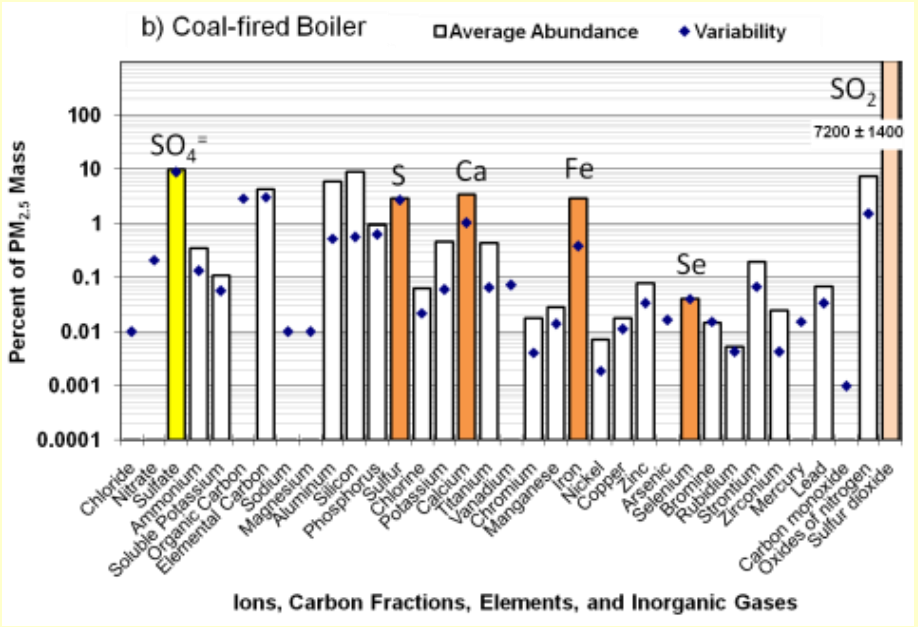
U.S.EPA (2014). Chemical speciation. prepared by U.S. Environmental Protection Agency, Research Triangle Park, NC, http://www.epa.gov/ttn/amtic/speciepg.html.

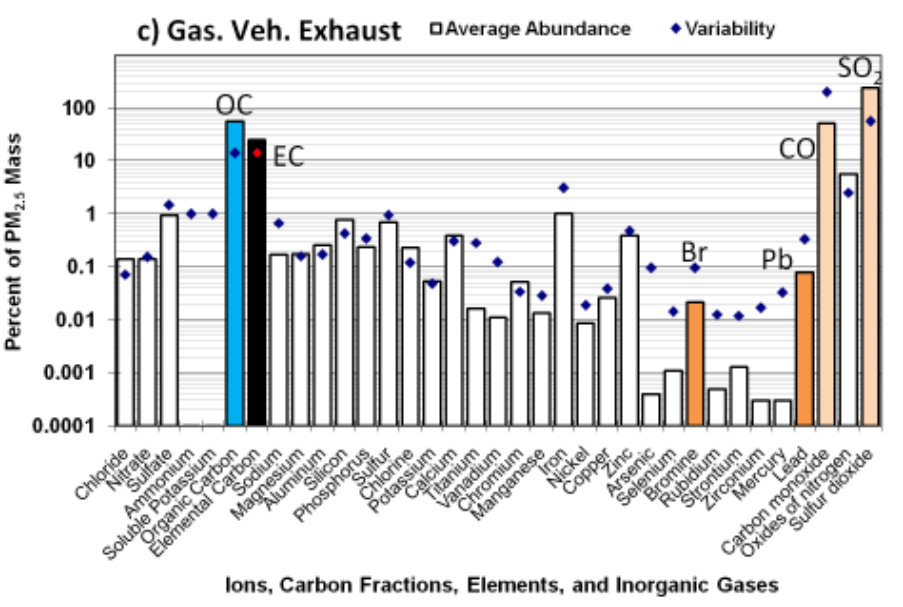
Current speciation networks use up to three filter channels for mass, elements, ions, and carbon fractions

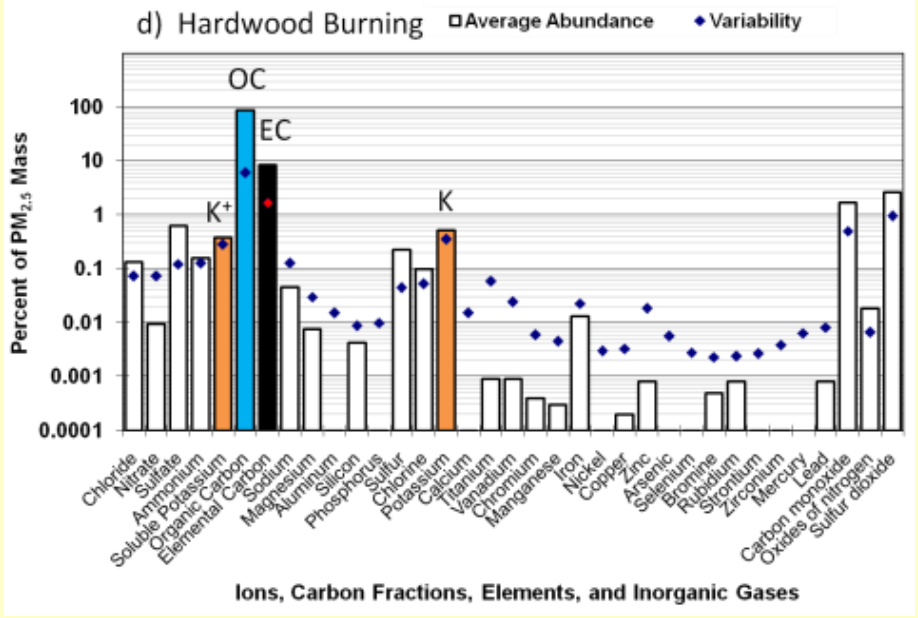


Most source profiles report similar measurements of elements, ions, and carbon, but these are insufficient for separating many sources from each other



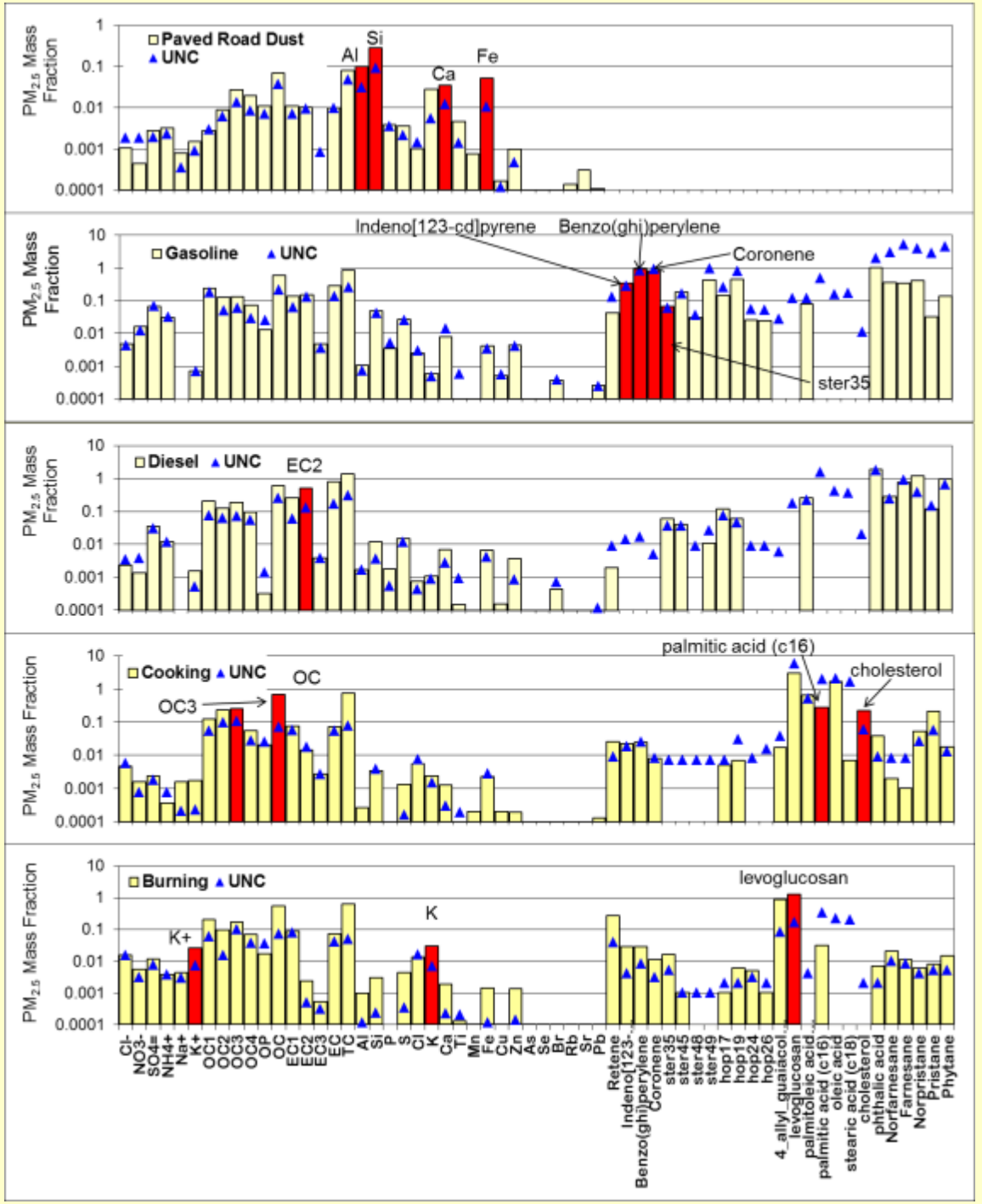






Watson and Chow (2007) 279–316

Organic components help with modern source apportionment, but source and receptor measurements are limited



Watson et al., 2008, *JAWMA*

Additional speciation can be applied to obtain marker compounds as part of the original analyses or on archived filters

Size-selective Inlet

Teflon-membrane filter

- GRAV for mass
- XRF for elements
- FTIR for organic functional groups
- UV-VIS for light transmittance/ reflectance
- ICP-MS for rare-earth elements and isotopes (acid extract)

Impregnated cellulose-fiber filters (water extract)

- NH_3 as NH_4^+ by IC
- SO_2 as $SO_4^=$ by IC
- NO_2 as NO_2^- by IC

Size-selective Inlet

HNO_3 denuder

Quartz-fiber filter (water extract)

- IC, AC, and AAS for anions and cations
- TOC for total Water Soluble Organic Carbon (WSOC)
- HPLC-TOC for neutral and basic WSOC classes
- HPLC-SEC-ELSD-UV-VIS for humic-like substances (HULIS)
- IC-PAD for sugars and sterols
- IC-ECD for organic acids

Impregnated cellulose-fiber filter (water extract)

- HNO_3 as NO_3^- by IC

Size-selective inlet

VOC denuder

Quartz-fiber filter

- TOR/TOT for OC, EC, carbon fractions, and carbonate
- TGA for volatile mass, moisture, fixed carbon, and ash
- TD-GC/MS or non-polar compounds
- D-TD-GC/MS for polar (oxygenated) compounds

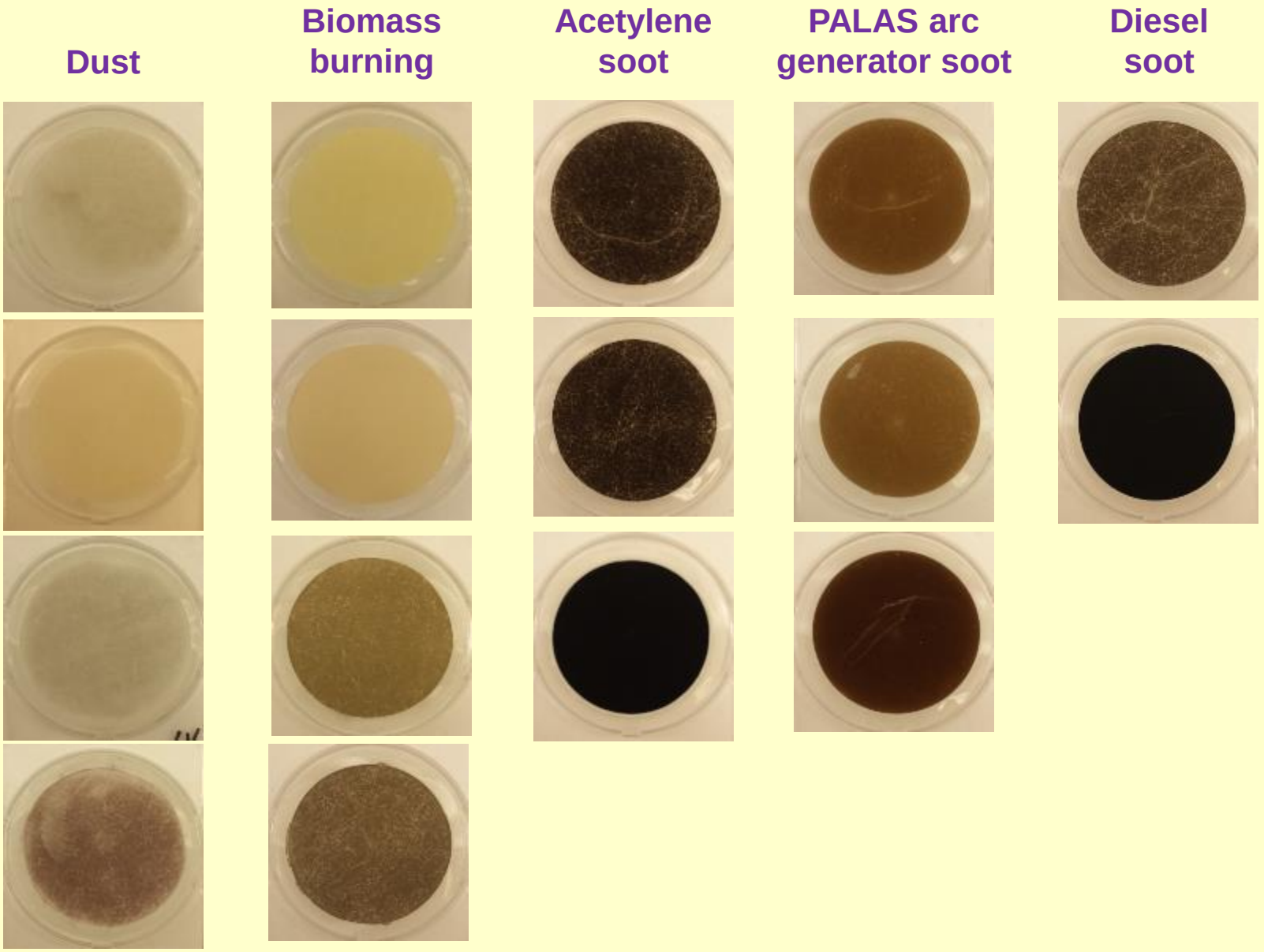
Quartz-fiber filter

- TOR/TOT for OC artifact assessment

Methods:

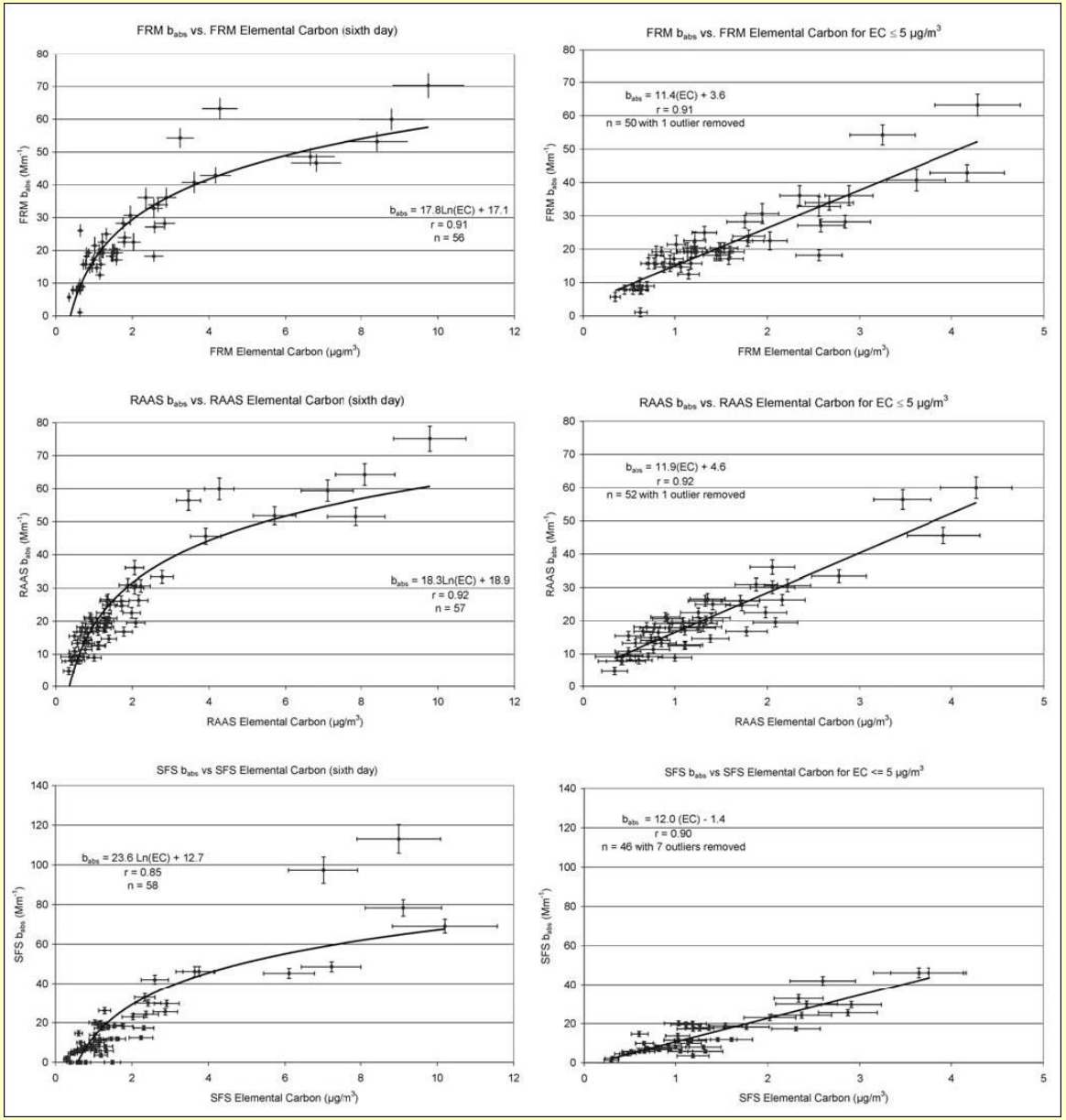
AAS: Atomic absorption spectrophotometry
AC: Automated colorimetry
D-TD-GC/MS: Derivitized-thermal desorption-gas chromatography/mass spectrometry
FTIR: Fourier Transform Infrared spectroscopy
GRAV: Gravimetry (filter weighing)
HPLC-SEC-ELSD-UV-Vis: HPLC-size-exclusion chromatography-evaporative light scattering detector-ultraviolet-visible light spectrometry
IC: Ion chromatography with conductivity detector
IC-ECD: IC-electrochemical detection
IC-PAD: IC with pulsed amperometric detection
ICP-MS: Inductively coupled plasma-MS
TD-GC/MS: Thermal desorption-gas chromatography/MS
TGA: Thermogravimetric analysis
TOC: Total organic carbon analysis
TOR/TOT: Thermal-optical reflectance and transmittance
UV-Vis: Ultraviolet-visible light spectrometry (λ=250–1100 nm)
XRF: X-ray fluorescence

More information can be obtained from Teflon-membrane filters than mass concentration



Filter transmittance (or reflectance as in British Smoke) has been added to mass as a soot indicator correlated with elemental carbon

Densitometer (TBX; Tobias Instruments, Ivyland, PA)

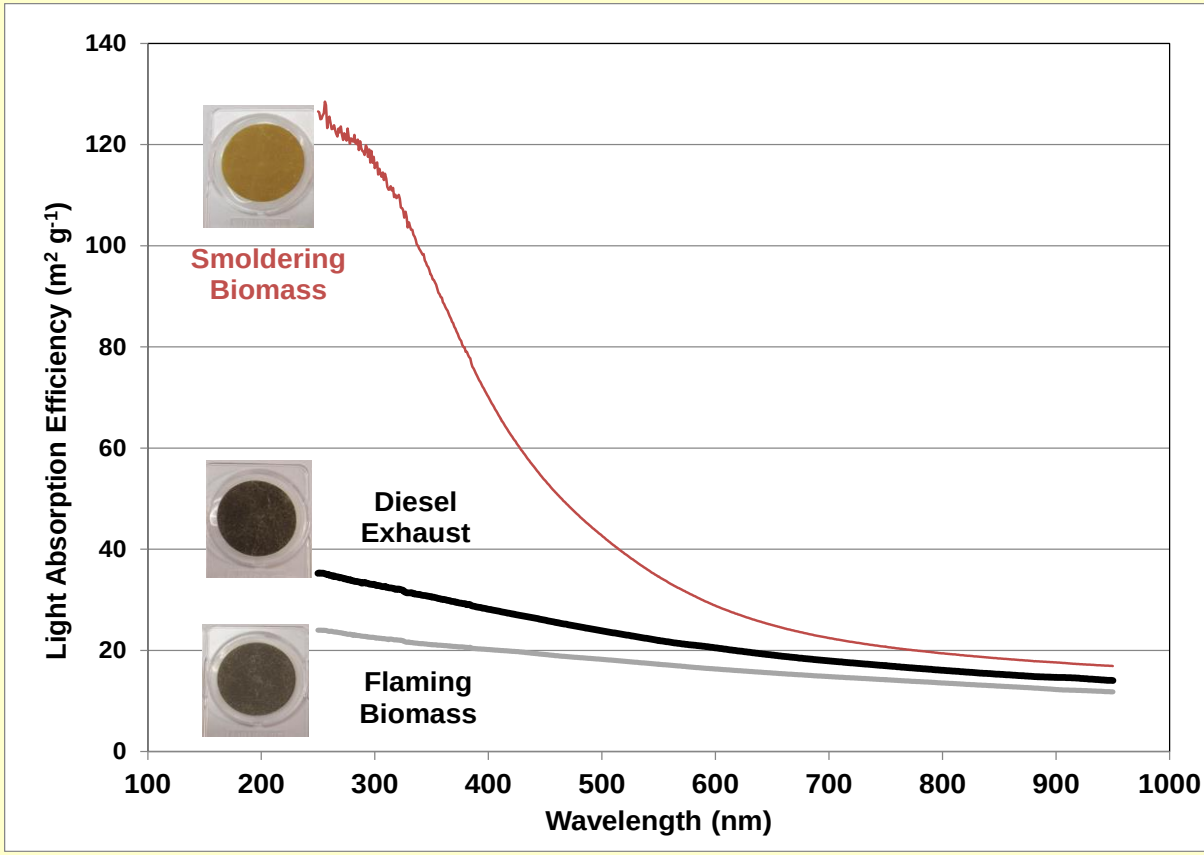


Dual wavelength light transmission through filters allows the separation of biomass smoldering (370 nm) from flaming/engine exhaust (880 nm)

Optical Transmissometer, (Magee Scientific, Berkeley, CA, USA)

Integrated sphere method quantifies light absorption/transmission at 250–1000 nm

UV/VIS spectrometer, (Lambda 35 , PerkinElmer, Waltham, MA, USA)

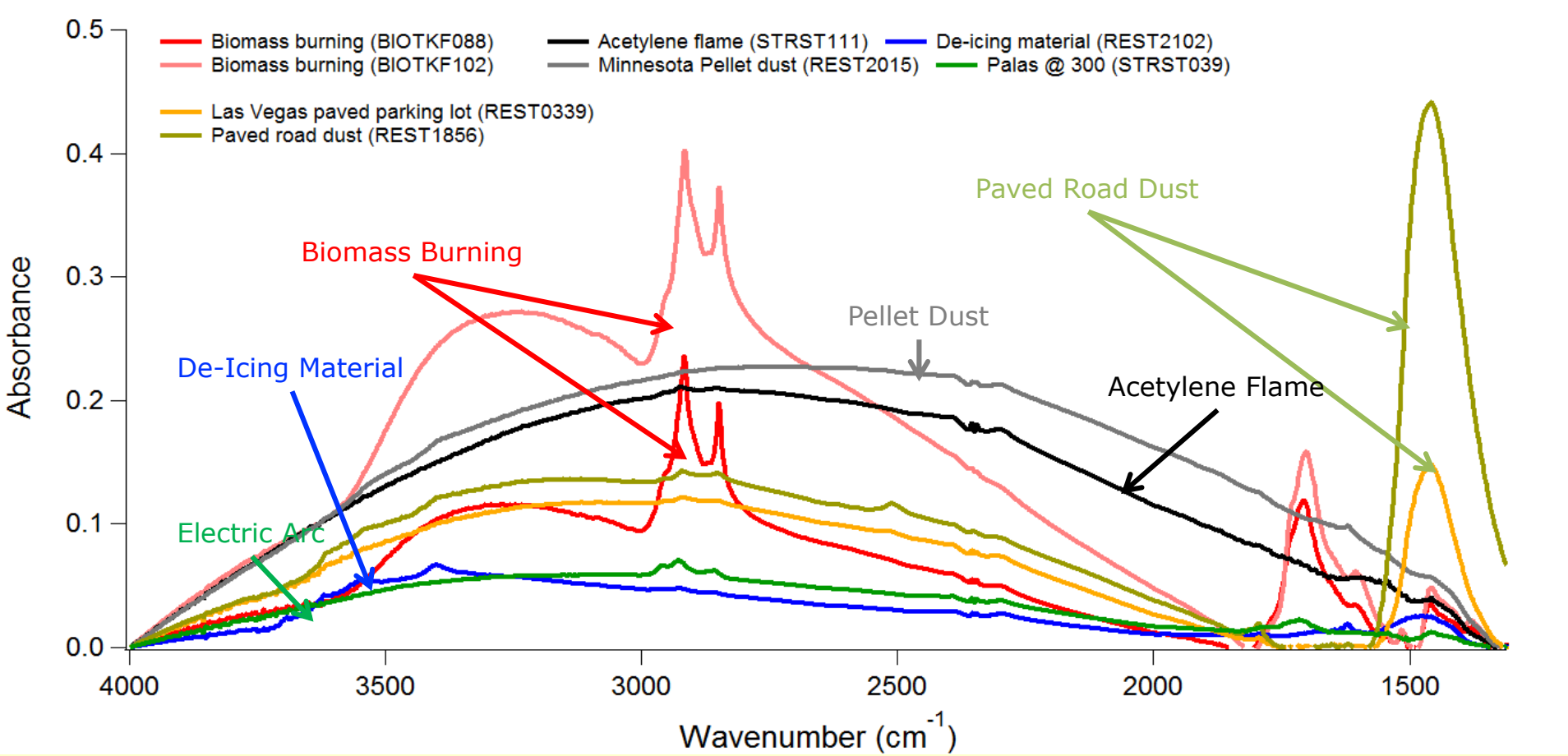


Organic functional groups can be quantified by Fourier-transform infrared (FTIR) spectrometry

Fourier-transform infrared spectroscope (Vertex 70 FTIR; Bruker Biosciences Corporation, Billerica, MA, USA)

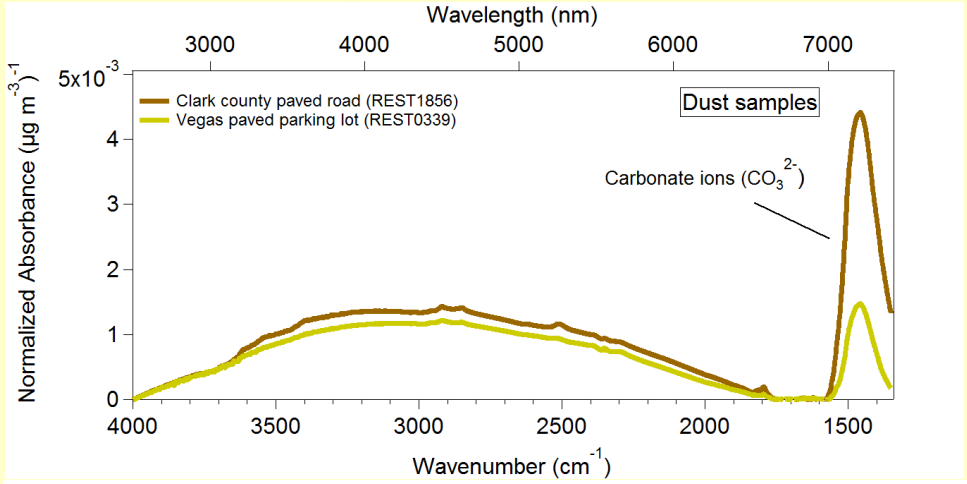
Functional group	Absorbance peaks and/or region cm^{-1}
Teflon peaks	1150-1300 (1156,1212), 640, 554, 517
H_2O	Sharp peaks 1300-1950, 3480-3960
CO_2	Sharp peaks 665-672, 2280-2390
Particle H_2O	1620-1640, 3350-3750
Aliphatic C-H	Sharp peaks 1370-1480, 2850-2950
Alkene C-H	2900-3100
Aromatic C-H	1000-1290, 3000-3100
Carbonyl C=O	Sharp peaks 1640 - 1850
Aldehyde -CHO	2700 - 2860
Alcohol/Phenol O-H	Broad peak 3200 – 3550, 1350, 650±50
Carboxylic acid C-OH	Broad peak 2500 - 3000
Organonitrate	Sharp peak 860, 1278, 1631
Organosulfur	Sharp peak 876
Sulfate SO_4^{2-}	612-618, 1080-1140
Ammonium NH^+	1400-1470, 2800-3400
Silicate SiO_3	772-812, 1000-1200
Nitrate NO_3^-	720, 840-810, 1340-1400

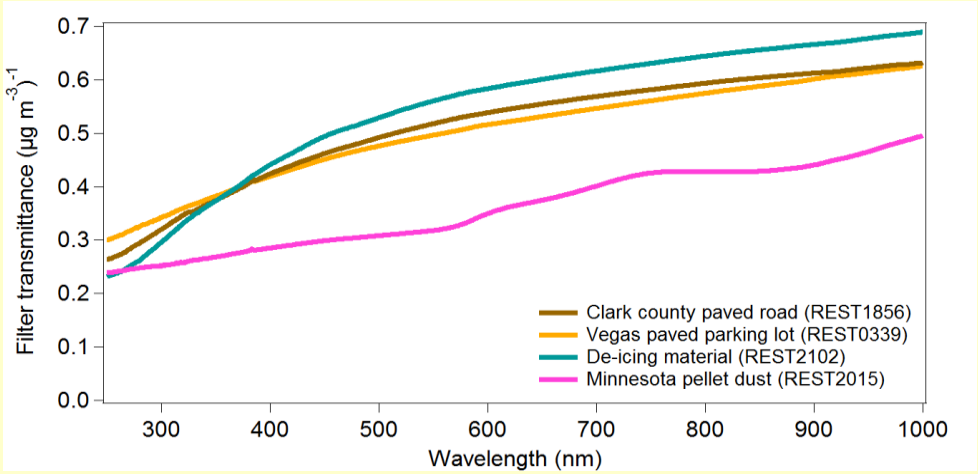
Functional group vary by pollution source and there is useful source apportionment information in unidentified parts of the spectrum



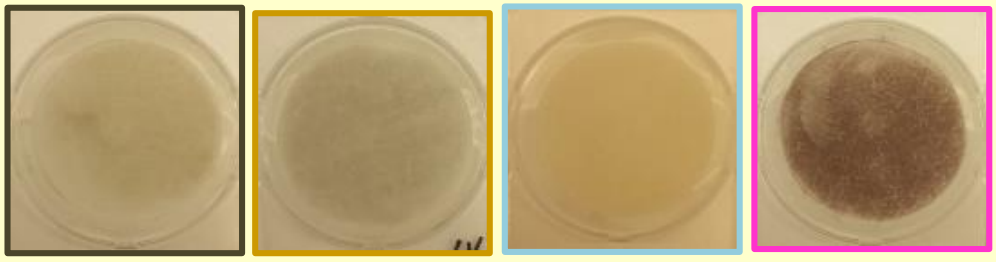
Absorbance for some blank filters can be as high as the actual signal from sample filters. Subtracting an average can create a problem.

IR and UV-VIS spectra for fugitive dust

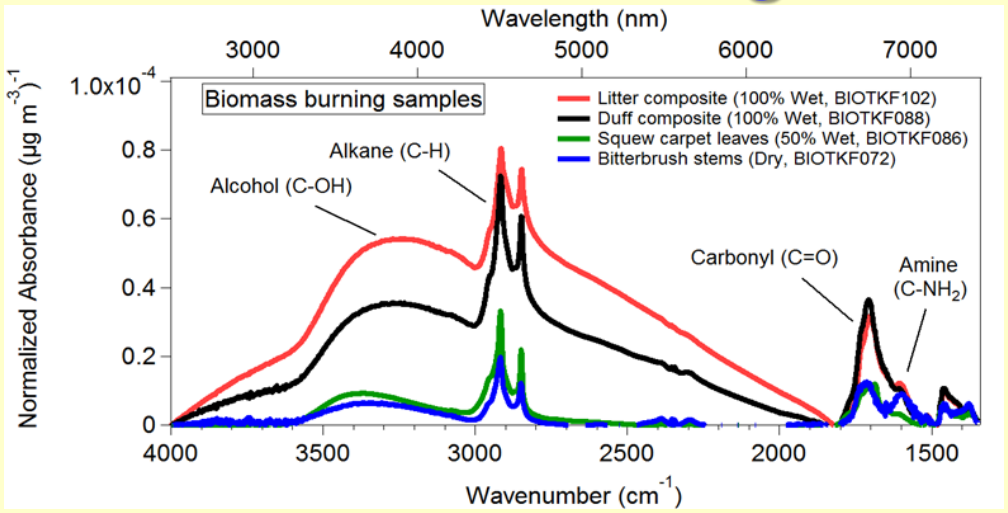


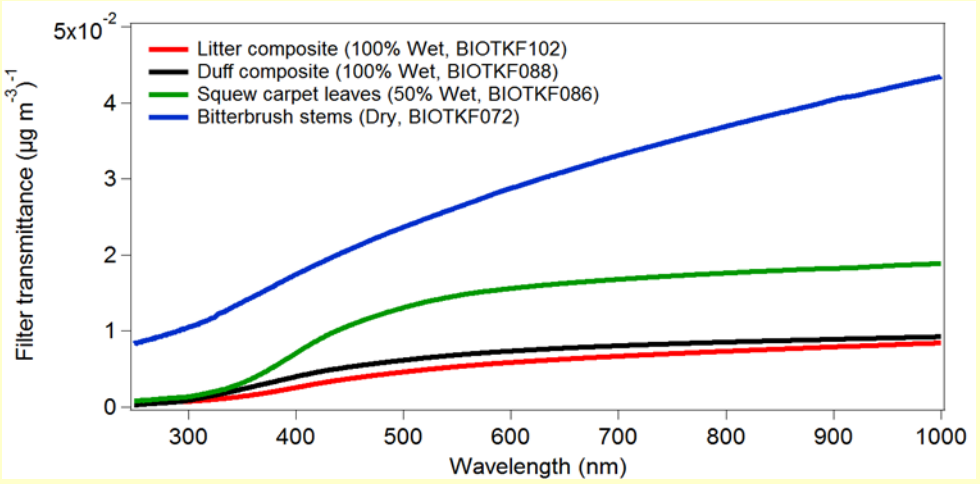


Paved road | Parking lot | De-icing material | Taconite dust



IR and UV-VIS spectra for biomass burning

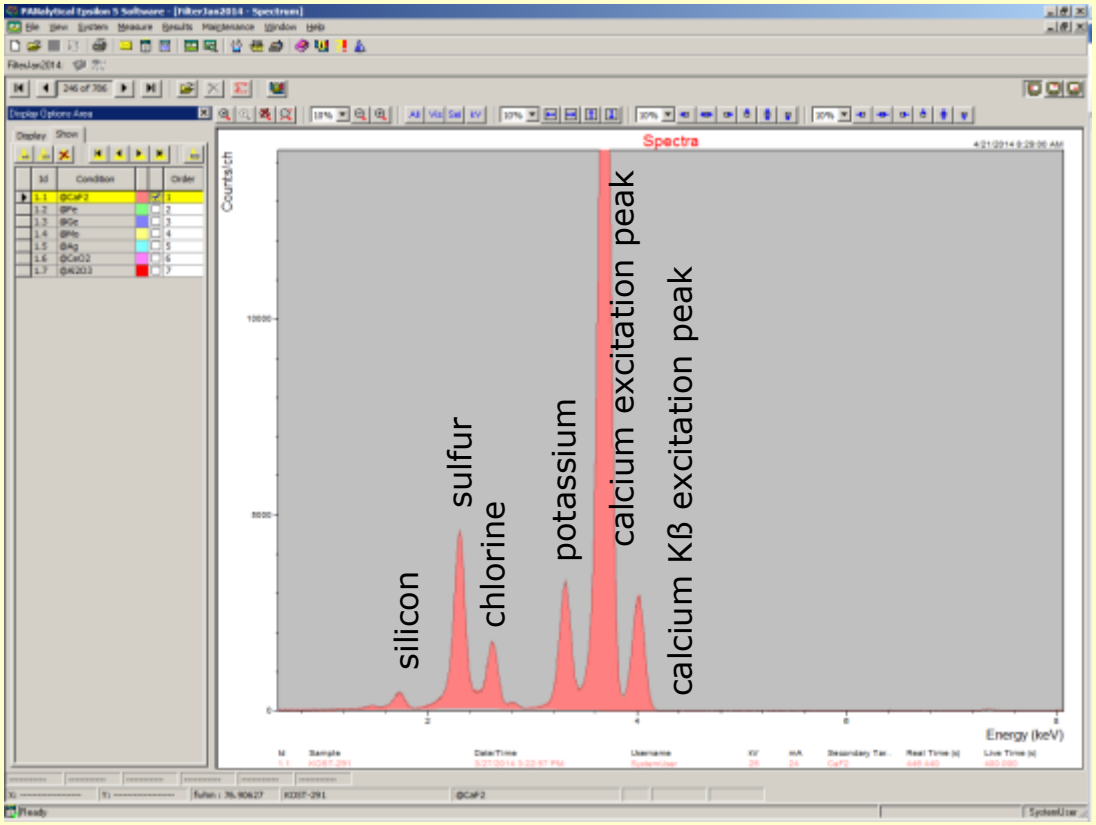




Litter | Duff | Squaw | Bitterbrush

X-ray Fluorescence (XRF) is non-destructive and acquires 51 elements (from Na to U)

X-ray Fluorescence analyzer (PANalytical Model Epsilon 5, Boulder, CO, USA)



Elemental detection sensitivity is optimized by excitation condition and analysis time. Longer analysis times reduce detection limits by $(t_{usual}/t_{enhanced})^{0.5}$

Rare-earth elements and isotopes can be quantified by Inductively-coupled Plasma-Mass Spectrometry (ICP-MS) but acid digestion destroys the filter

Inductively-coupled Plasma-Mass Spectrometry (Nexlon 300D ICP-MS; PerkinElmer, Waltham, MA, USA)

Isotopes

Lead:	*Strontium:*
^{204}Pb	^{86}Sr
^{206}Pb	^{87}Sr
^{207}Pb	
^{208}Pb	

Rare Earth Elements

Cesium (Cs)

Barium (Ba)

Lanthanum (La)

Cerium (Ce)

Praseodymium (Pr)

Neodymium (Nd)

Samarium (Sm)

Europium (Eu)

Gadolinium (Gd)

Terbium (Tb)

Dysprosium (Dy)

Holmium (Ho)

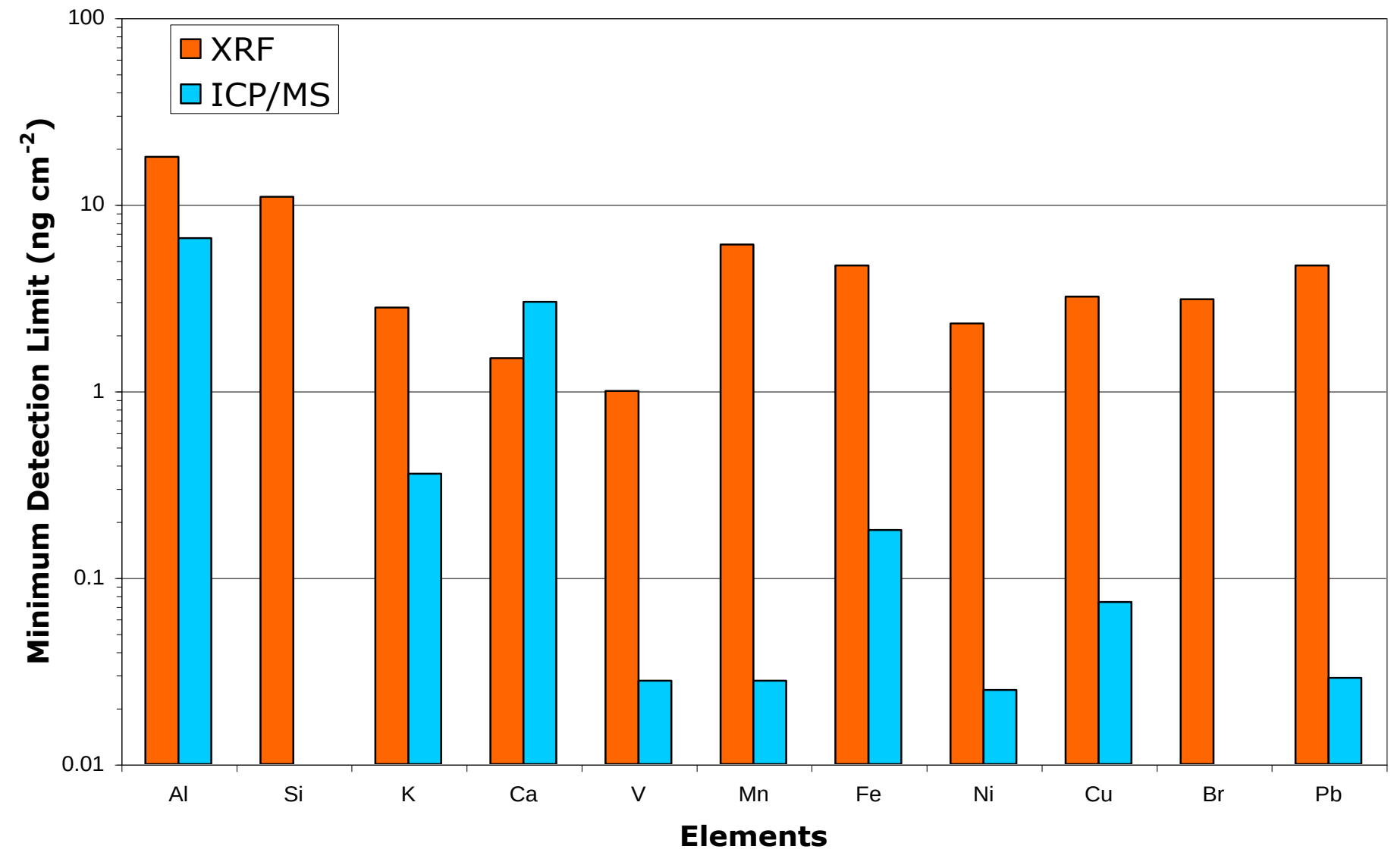
Erbium (Er)

Thulium (Tm)

Ytterbium (Yb)

Lutetium (Lu)

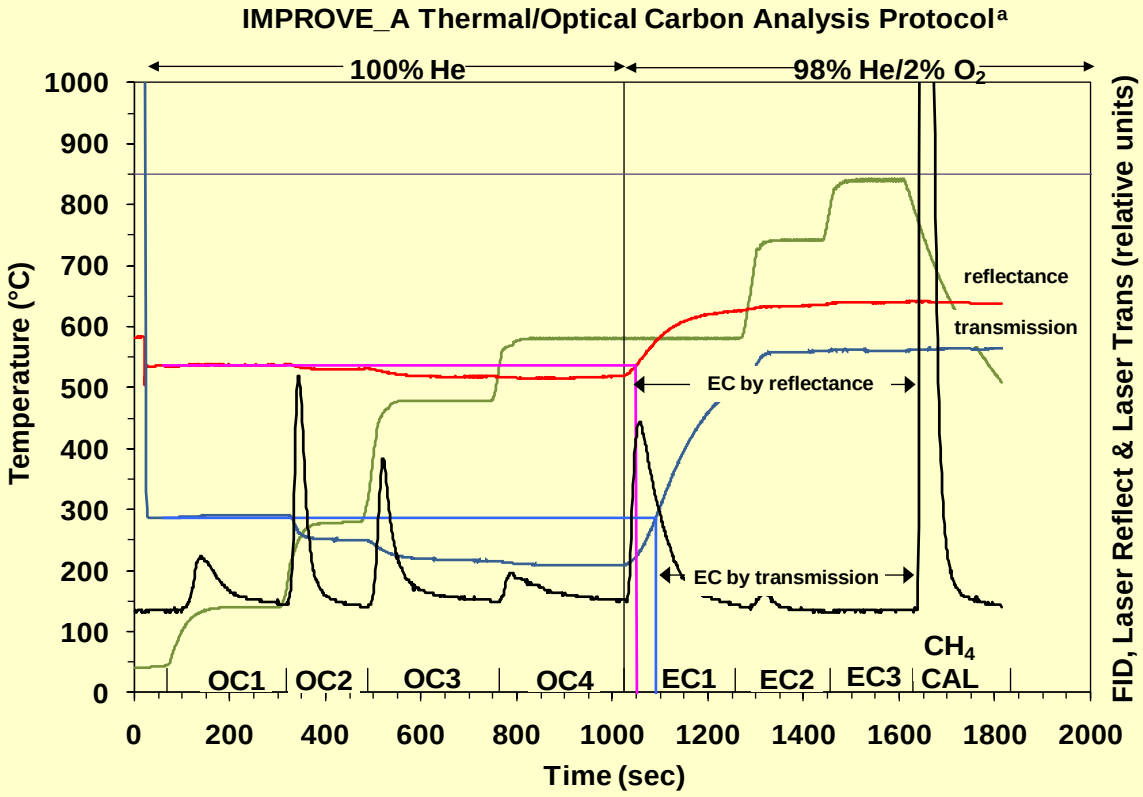
Detection limits for ICP-MS are lower than those of XRF for several elements



ICP-MS has difficulty detecting Si due to high background levels caused by the acid matrix

Thermal/optical reflectance/transmittance carbon analysis provides several carbon fractions

Thermal/Optical Analyzer (DRI Model 2001, Atmoslytics, Calabasas, CA)

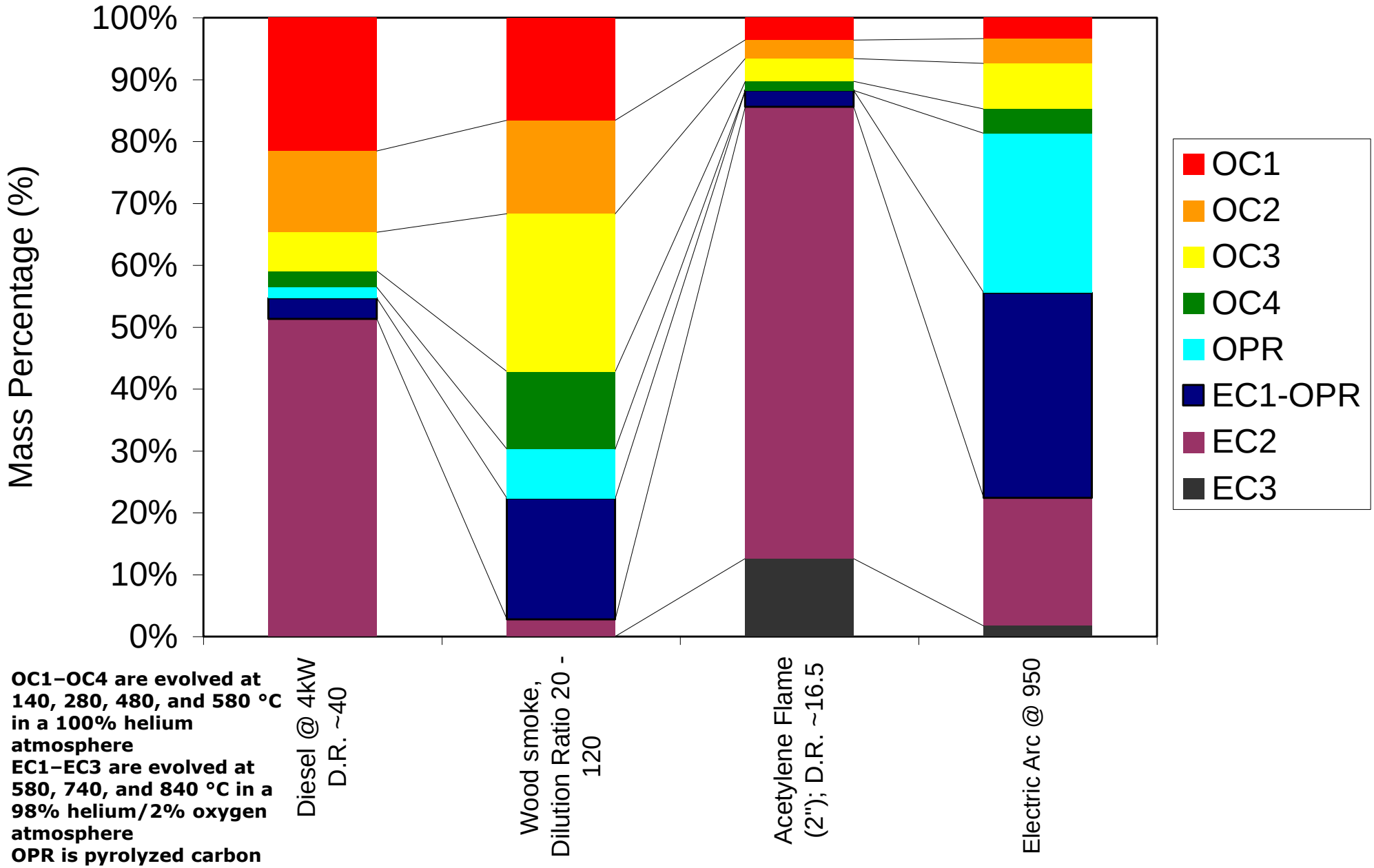


	°C	Analysis Atmosphere
OC1	140	100% He (99.99% Purity)
OC2	280	100% He (99.99% Purity)
OC3	480	100% He (99.99% Purity)
OC4	580	100% He (99.99% Purity)
OP	Return to original reflectance/transmittance value	
EC1	580	98% He/2% O_2
EC2	740	98% He/2% O_2
EC3	840	98% He/2% O_2
TC	OC (OC1+OC2+OC3+OC4+OP) + EC (EC1+EC2+EC3-OP)	

← **IMPROVE_A Thermal/Optical Protocol**

Chow et al. (2007) *JAWMA*

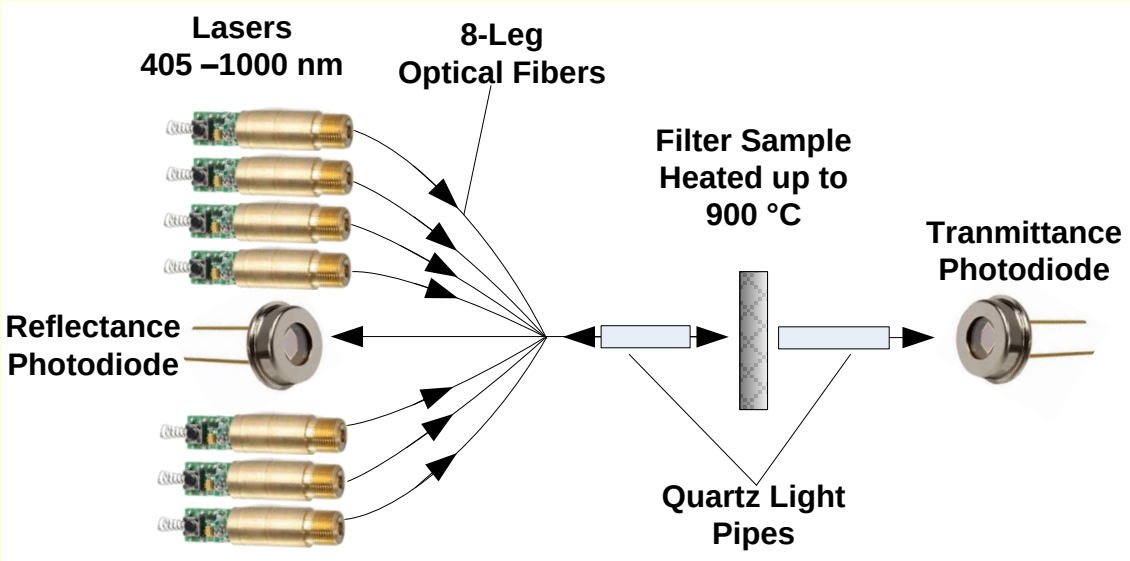
Abundances of thermal carbon fractions vary by source type

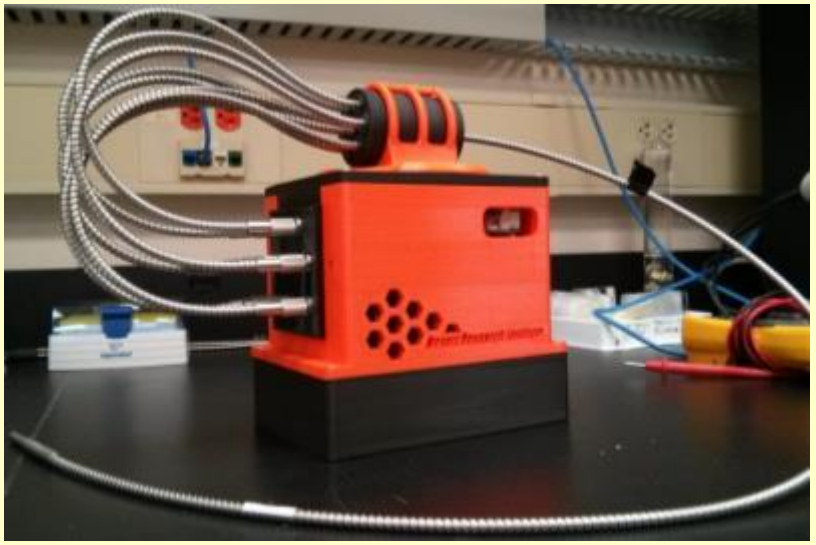


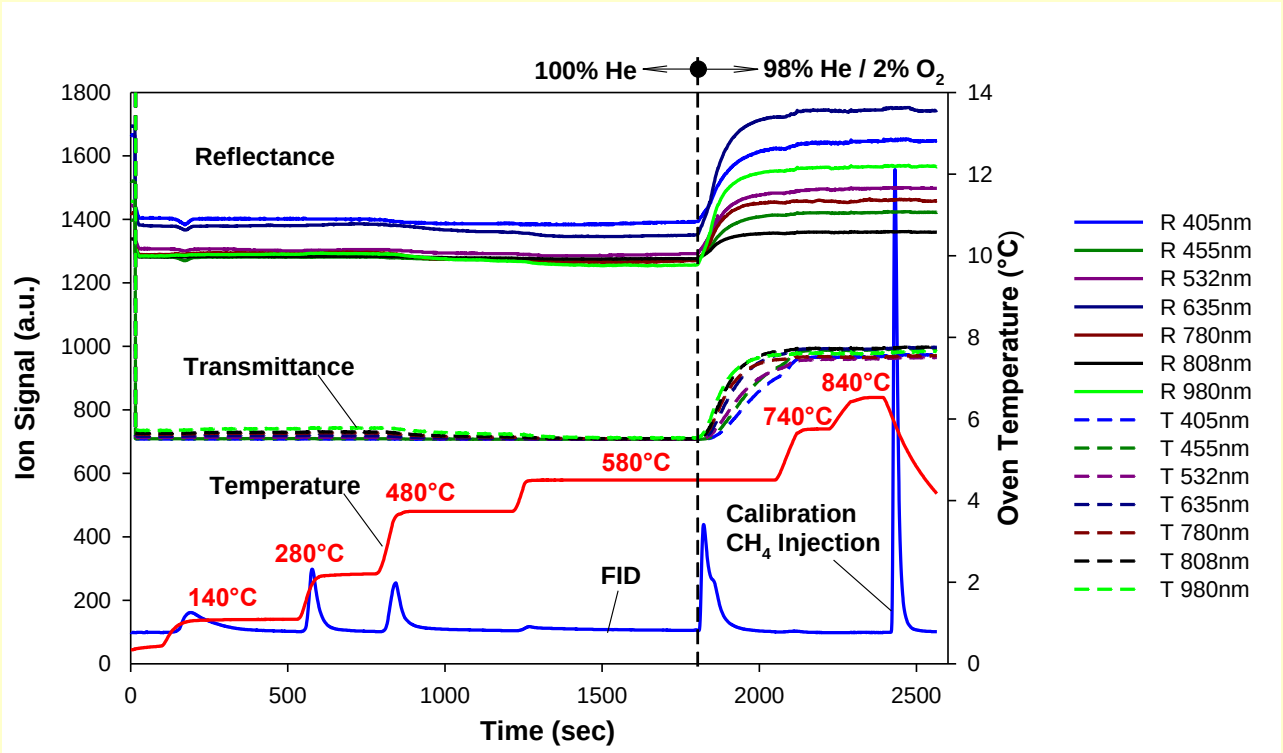
- **OC1–OC4 are evolved at 140, 280, 480, and 580 °C in a 100% helium atmosphere**
- **EC1–EC3 are evolved at 580, 740, and 840 °C in a 98% helium/2% oxygen atmosphere**
- **OPR is pyrolyzed carbon by reflectance**

Chow et al. (2007) *J. Environ. Sci. Health*

Thermal/optical analyzers can be adapted to obtain multiple wavelength information related to black and brown carbon



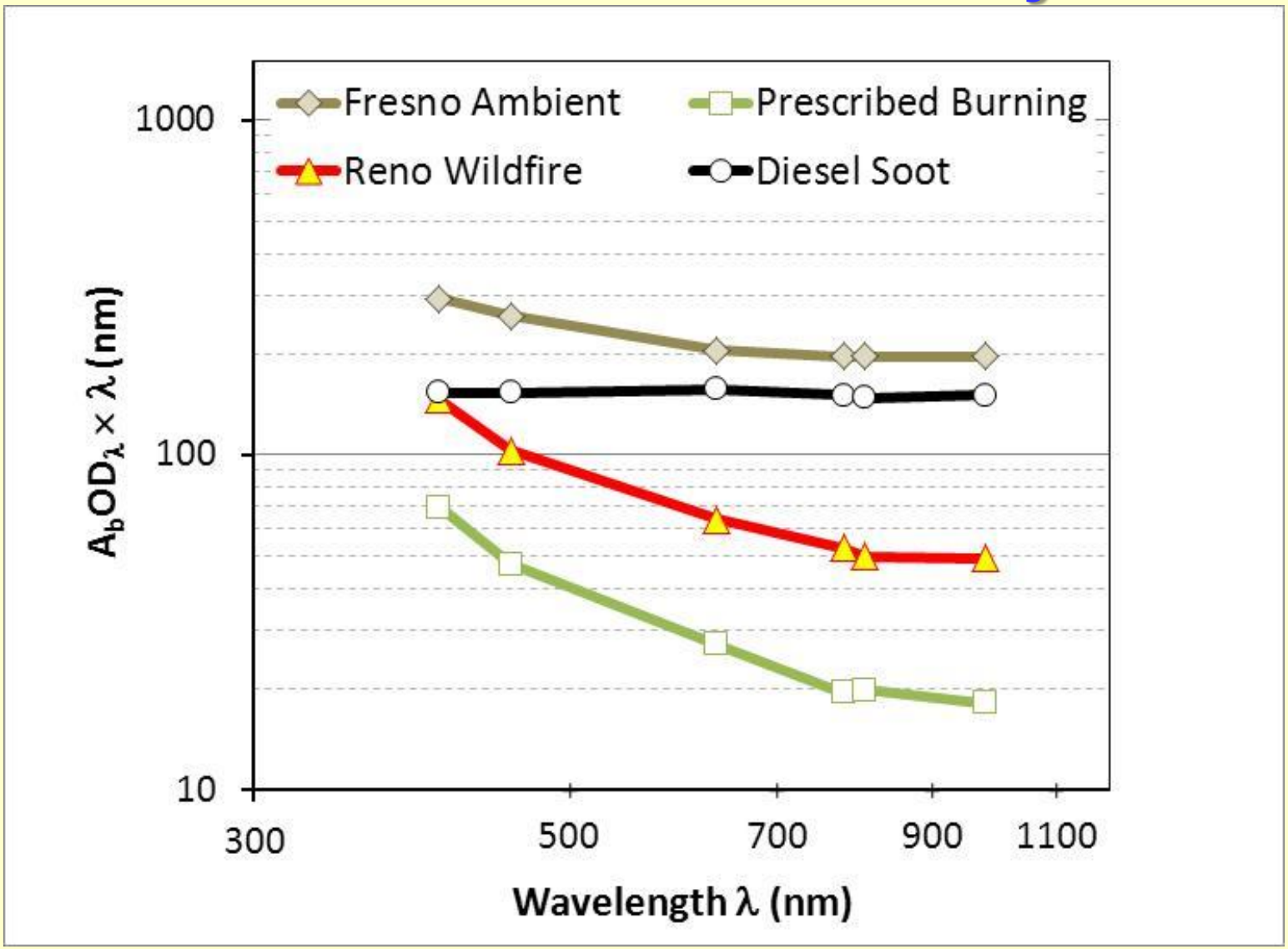




- Using laser diodes, λ are 405, 445, 532, **635**, 780, 808, and 980 nm
- Transmittance (T) and reflectance (R) analysis are normalized to the blank filter at end of analysis
- Black and brown carbon will be quantified for different temperature fractions

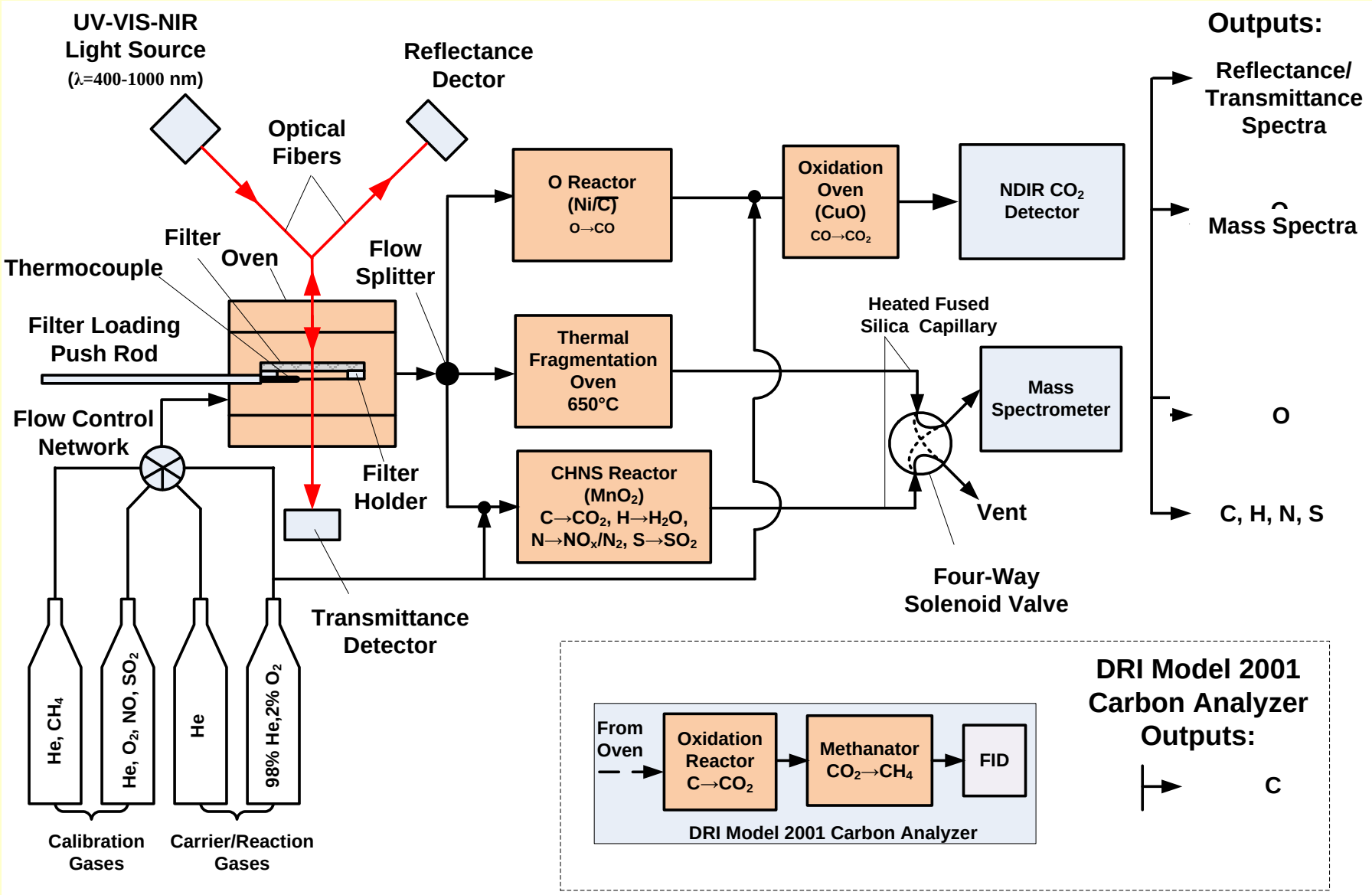
Smoldering Flaming Diesel

Light absorption patterns can be obtained as part of the normal carbon analysis



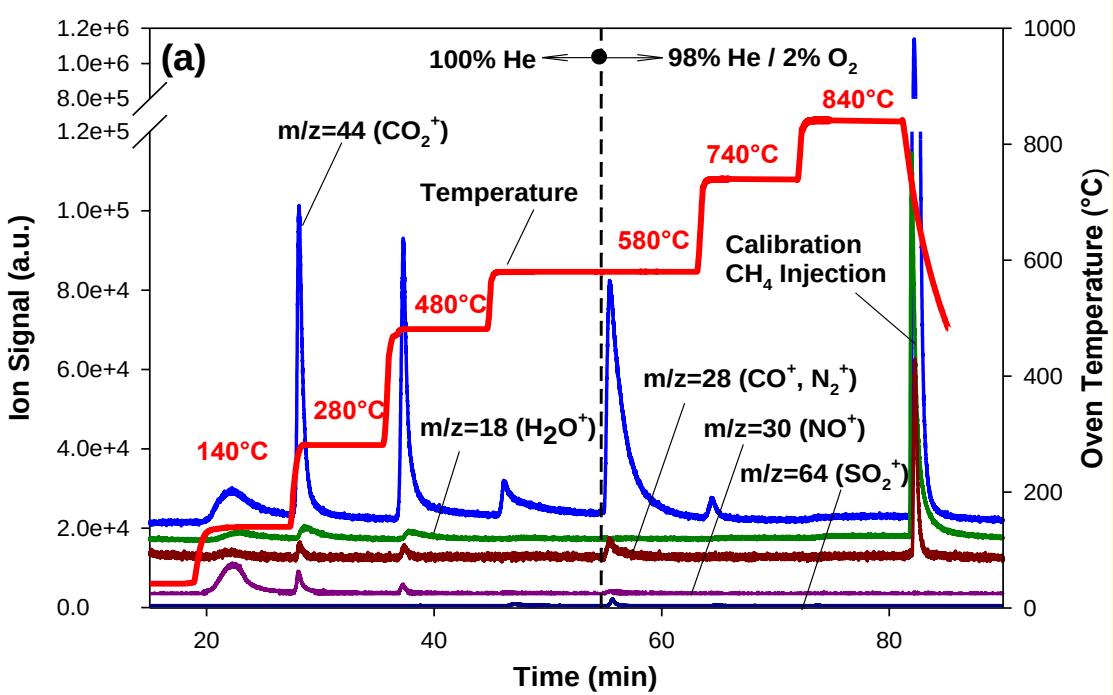
The product of absorption optical depth (A_bOD_λ) and wavelength (λ) accounts for scattering within the filter media

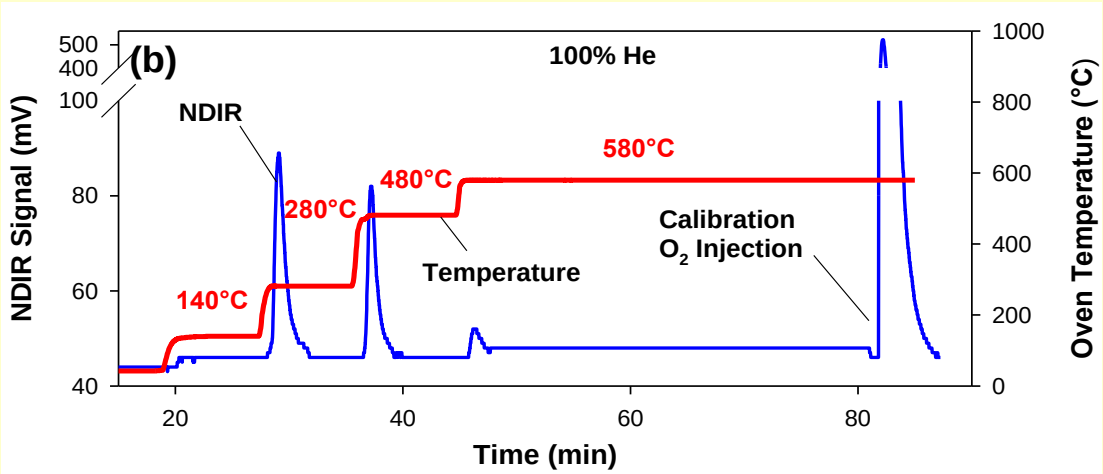
Can obtain H, N, S, and O along with OC, EC, and thermal fractions with the same analysis



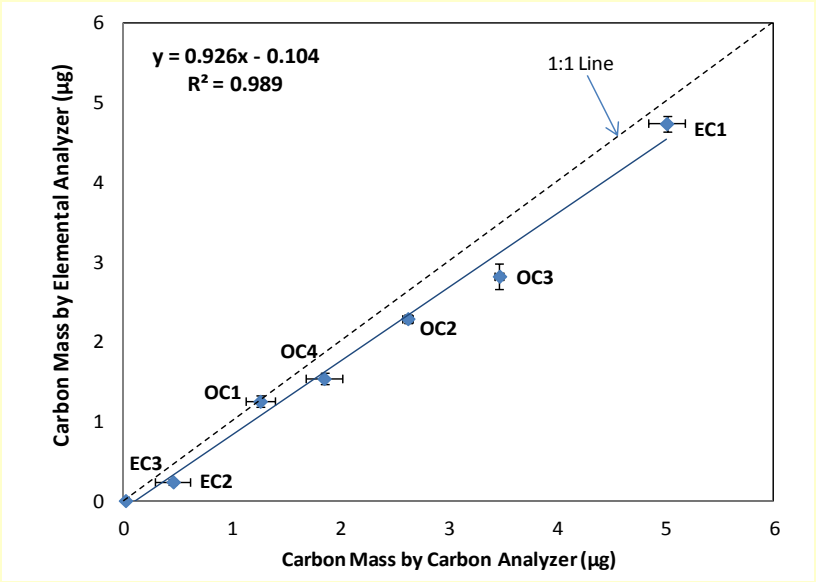
More information on PM can be gained from thermal/optical analyses with different detectors

C, H, N, S, and O can be quantified for each temperature fraction



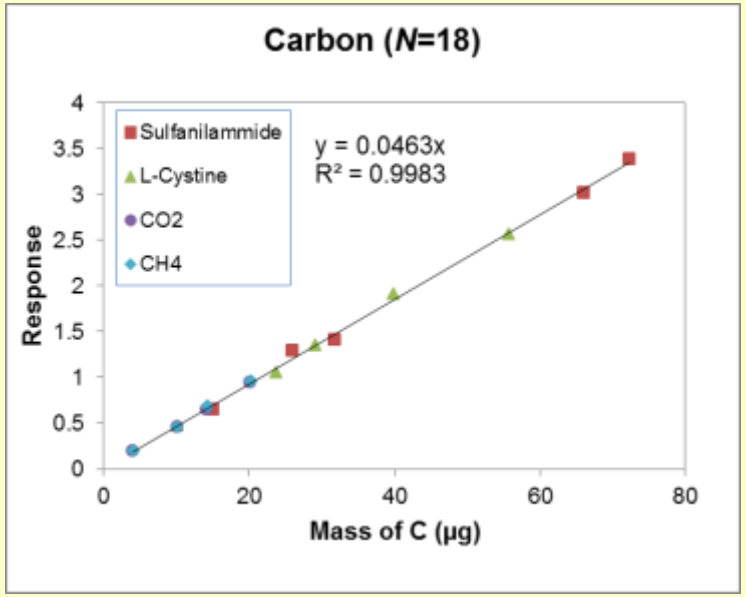


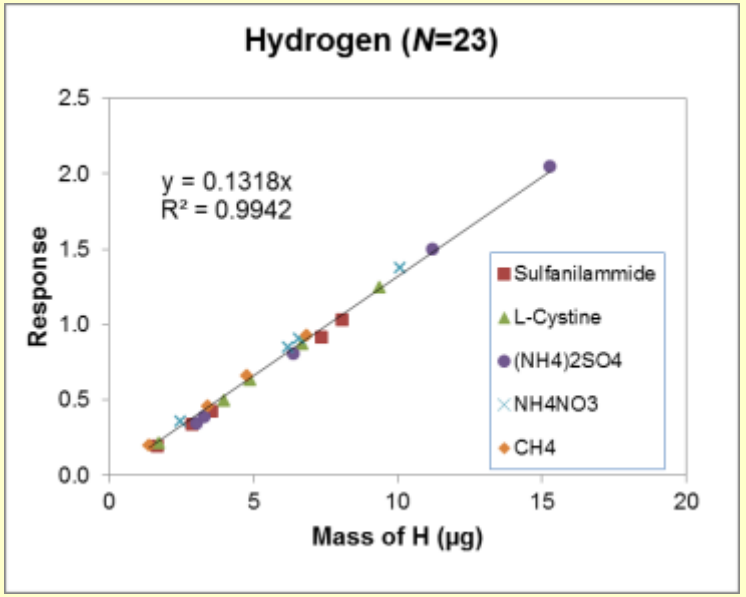
Thermogram of Fresno ambient aerosol sample for **(a) CHNS, and (b) O** following the IMPROVE_A protocol.

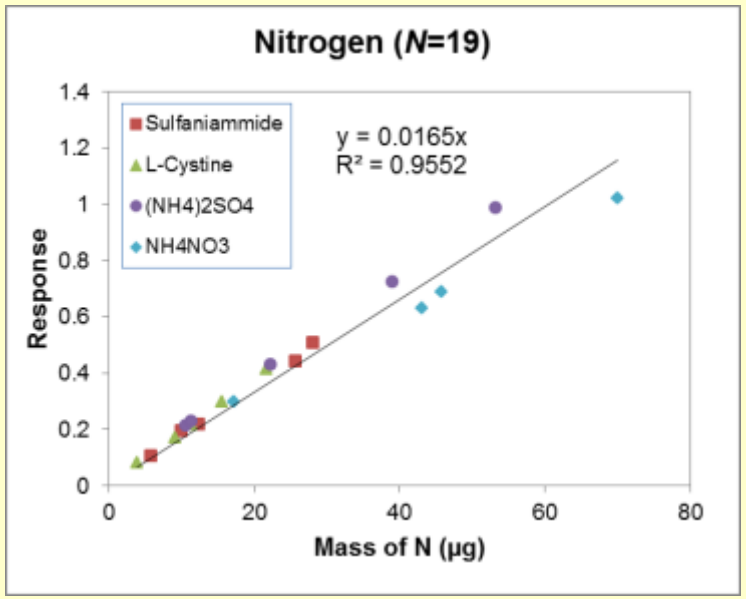


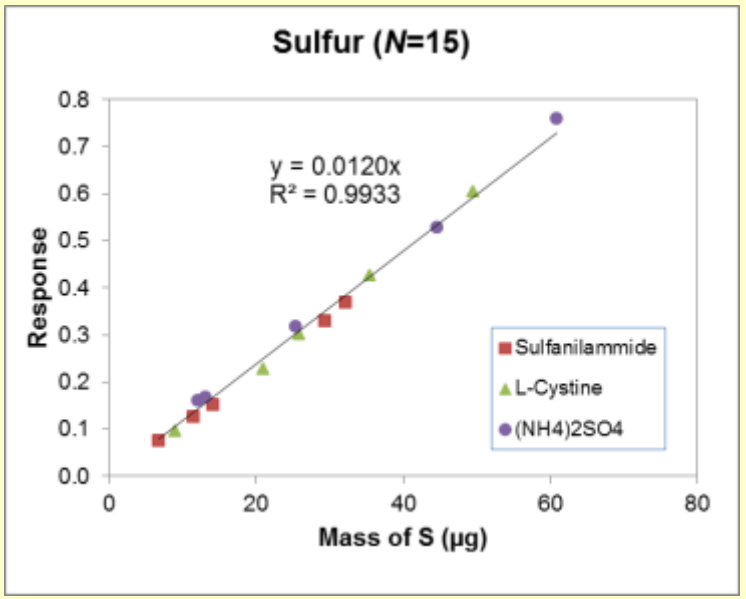
Comparison of carbon fractions measured by elemental analyzer and DRI Model 2001 carbon analyzer

Mass spectrometer signals are linear with C, H, N, and S quantities for calibration chemicals



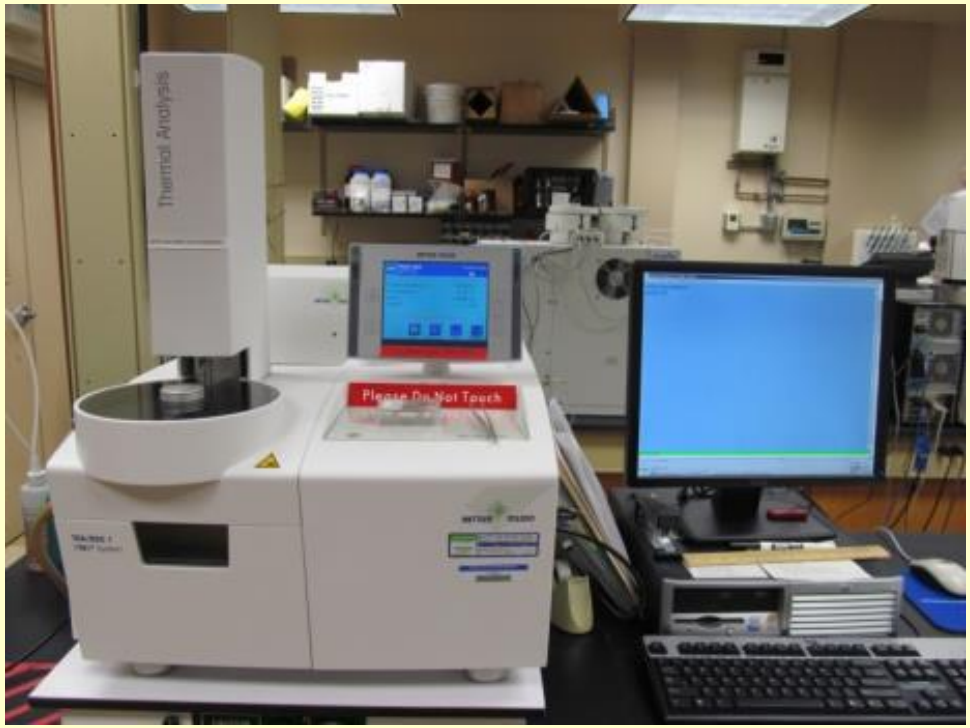






Sulfanilamide: $C_6H_8N_2O_2S$; L-Cystine: $C_6H_{12}N_2O_4S_2$

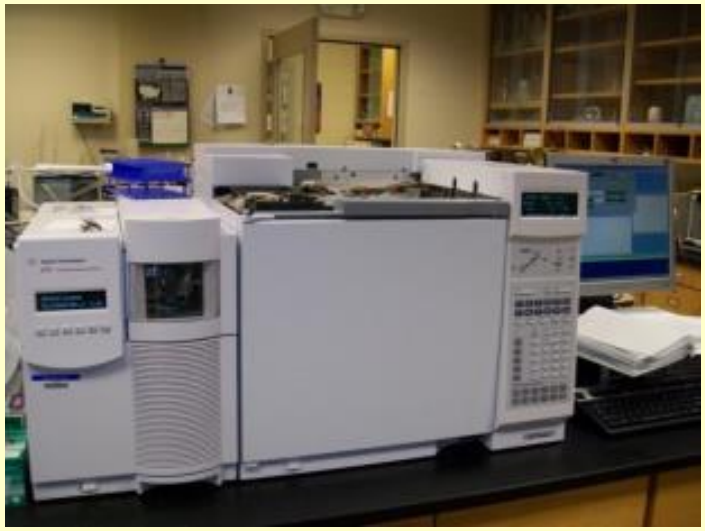
Evolved carbon as a function of temperature can be quantified by thermogravimetric analyzer (TGA) on quartz-fiber filter remnants



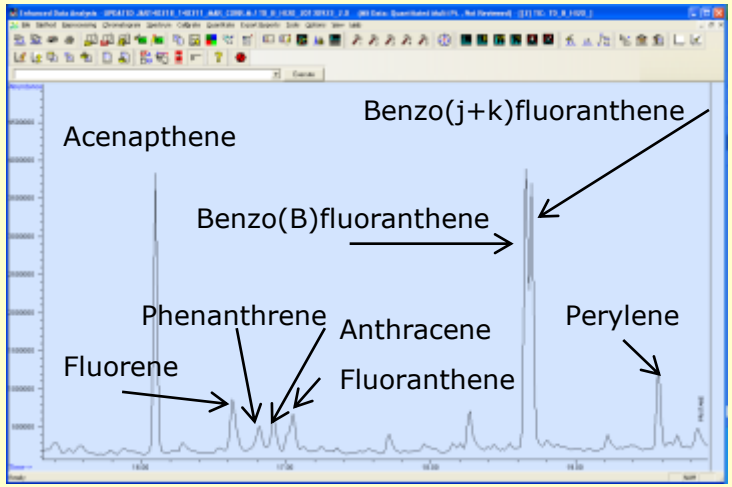
Thermal Gravimetric Analyzer (TGA/DSC-1 Mettler-Toledo International, Inc., Columbus, OH, USA)

- Percent Moisture
- Percent Volatile Matter
- Percent Fixed Carbon
- Percent Ash

Thermal desorption-Gas Chromatography/Mass Spectrometry (TD-GC/MS) can provide ~110 non-polar organic compounds[a]



Gas Chromatography with Mass Spectrometric Detector (Model 6890 /Model 5975C, Agilent Technologies, Santa Clara, CA, USA)



- 37 Polycyclic aromatic hydrocarbons (PAHs)
- 26 *n*-alkanes
- 10 iso/anteiso-alkanes
- 2 methyl-alkanes
- 3 branched-alkanes
- 5 cycloalkanes
- 1 alkene
- 18 hopanes
- 12 steranes

[a] Using ~1–2 cm^2 of filter aliquot without solvent extraction

Water- and acid-extracted solutions can be used for multiple analyses

Ultra-sonication

Sonicator (Branson Model 5200 Danbury, CT)

Mechanical Shaking

Sample shaker (Cole-Parmer Model 51401-00, Vernon Hills, IL)

Microwave Extraction

(MCEM Mars 5, Matthews, NC)

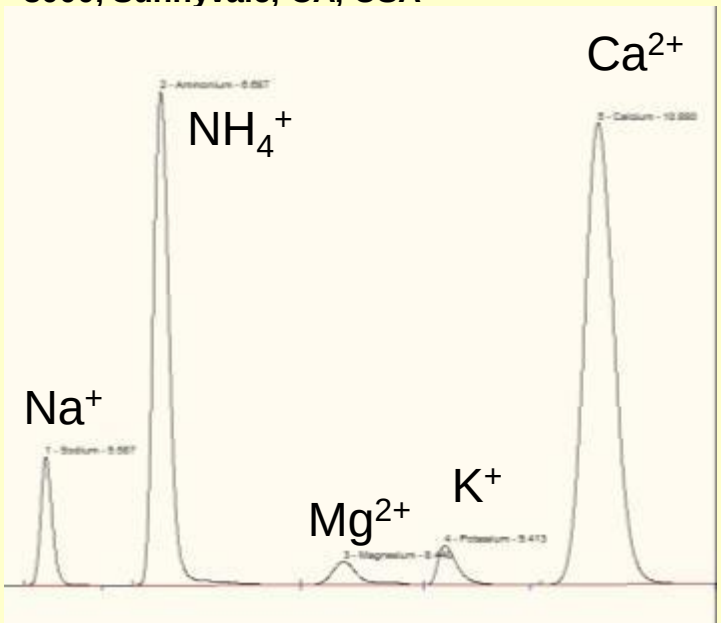
Acid Digestion

Hot block digestor (Environmental Express, Ventura, CA)

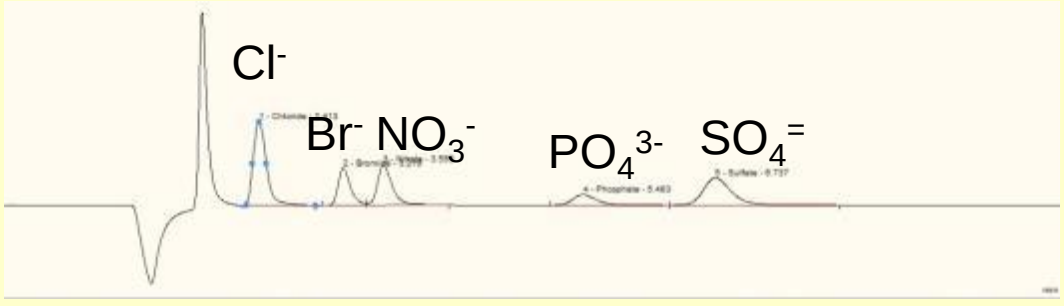
More ions can be quantified with the same analysis (Ion Chromatography with conductivity detector [IC-CD])

Ion Chromatograph (Dionex Model ICS 3000, Sunnyvale, CA, USA

- Chloride (Cl^-)
- Bromide (Br^-)
- Nitrite (NO_2^-)
- Nitrate (NO_3^-)
- Phosphate (PO_4^{3-})
- Sulfate ($SO_4^=$)



- Ammonium (NH_4^+)
- Soluble Sodium (Na^+)
- Soluble Magnesium (Mg^{2+})
- Soluble Potassium (K^+)
- Soluble Calcium (Ca^{2+})



Water-soluble organic carbon (WSOC) is related to cloud condensation nuclei, biomass burning, SOA[a], and health effects

Total Organic Carbon Analyzer (Model TOC-L, Shimadzu Corporation, Kyoto, Japan)

High Performance Liquid Chromatography System (A200 Series , Agilent Technologies, Santa Clara, CA, USA)

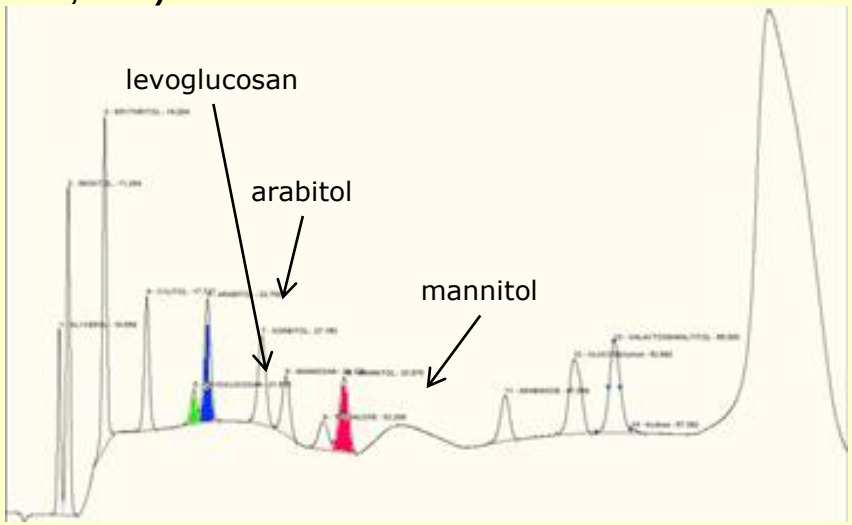
Total WSOC by TOC and WSOC classes

- **Neutral Compounds by HPLC-TOC[a]**
- **Mono- and Di-carboxylic acids by IC-PAD[a]**
- **Humic-like substances by HPLC-SEC-ELSD-UV/VIS[a]**

[a] SOA: Secondary Organic Aerosol; HPLC-TOC: High-performance Liquid Chromatography with Total Organic Carbon; IC-PAD: Ion Chromatography with Pulsed Amperometric Detector, HPLC-SEC-ELSP-UV-VIS: HPLC with Size Exclusion Chromotography and Evaporative Light Scattering Detector with Ultraviolet and Visible Light wavelengths

Carbohydrates are related to biomass burning and bioaerosols (Ion Chromatography-Pulsed Amperometric Detector [IC-PAD])

IC-PAD (Model ICS 3000 Dionex, Sunnyvale, CA, USA)

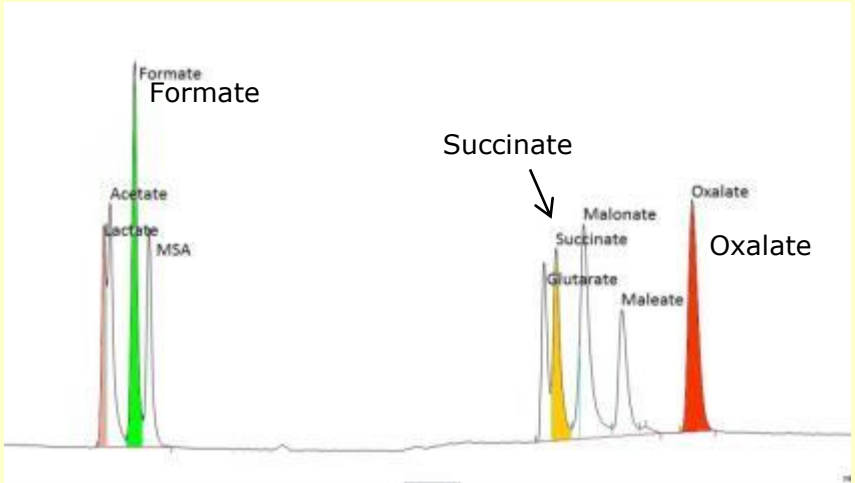


Carbohydrates

- Glycerol ($C_3H_8O_3$)
- Inositol ($C_6H_{12}O_6$)
- Erythritol ($C_4H_{10}O_4$)
- Xylitol ($C_5H_{12}O_5$)
- Levoglucosan ($C_6H_{10}O_5$); Biomass burning marker
- Arabitol ($C_5H_{12}O_5$); Fungal biomarker
- Sorbitol ($C_6H_{14}O_6$)
- Mannosan ($C_6H_{10}O_5$)
- Mannitol ($C_6H_{14}O_6$) ;Fungal biomarker
- Glucose ($C_6H_{12}O_6$)
- Xylose ($C_5H_{10}O_5$)
- Fructose ($C_6H_{12}O_6$)
- Trehalose ($C_{12}H_{22}O_{11}$)
- Arabinose ($C_5H_{10}O_5$)
- Galactose ($C_6H_{12}O_6$)
- Maltitol ($C_{12}H_{24}O_{11}$)

Organic acids are related to biomass burning and cooking emissions

Ion Chromatography with Electrochemical Detector (IC-ECD, Dionex Model ICS 2100 Ion Chromatograph, Sunnyvale, CA, USA)



Monocarboxylic acids:

- Lactic acid ($C_3H_6O_3$)
- Acetic acid ($C_2H_4O_2$)
- Formic acid (CH_2O)
- Methanesulfonic acid (CH_4SO_3)

Dicarboxylic acids:

- Glutaric acid ($C_5H_8O_4$)
- Succinic acid ($C_4H_6O_4$)
- Malonic acid ($C_3H_4O_4$)
- Maleic acid ($C_4H_4O_4$)
- Oxalic acid ($C_2H_2O_4$)

Elemental analysis quantifies total C, H, N, S, and O for OM to OC ratios on liquids and quartz-fiber filters

Elemental Analyzer (FlashEA 1112 , Thermo Fischer Scientific, Waltham, MA, USA)

- Carbon (C)
- Hydrogen (H)
- Nitrogen (N)
- Sulfur (S)
- Oxygen (O)

Conclusions

- **A large variety of analyses, especially for organic compounds, can be applied to recent or archived samples to verify source contribution estimates**
- **Teflon-membrane filters can yield much information from non-destructive IR and UV-VIS analysis. Rare-earth elements and some isotopes can be determined by ICP-MS after acid extraction**
- **Quartz-fiber filters can yield more optical and chemical information from routine thermal/optical analyses with multi-wavelength lasers and multi-elemental detectors. TD-GC/MS is an established and efficient method for non-extraction organic marker analysis**
- **Water extracts are amenable to several analyses for polar organics, including biomass burning and secondary organic aerosol markers**

Challenges for Enhanced Chemical Characterization of Filter Samples

- **Perfecting, evaluating, and making more efficient procedures for additional characterization**
- **Modifying instrumentation and procedures to incorporate more specific analyses methods into long-term chemical speciation networks to obtain more information from existing samples**
- **Maintaining continuity and consistency with the long-term trends data sets**
- **Developing more detailed source profiles with these methods for speciated inventories and source apportionment**

Questions?