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

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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. 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**


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

- **Teflon-membrane filter**
  - GRAV for mass
  - XRF for elements

- **Nylon-membrane filter**
  - IC, AC, and AAS for water-soluble ions

- **Quartz-fiber filter**
  - TOR/TOT for OC, EC, carbon fractions, and carbonate

Methods:
- AAS: Atomic absorption spectrophotometry
- AC: Automated colorimetry
- GRAV: Gravimetry (filter weighing)
- IC: Ion chromatography with conductivity detector
- TOR/TOT: Thermal-optical reflectance and transmittance
- XRF: X-ray fluorescence

- **Quartz-fiber backup filter**
  - Assess OC adsorption artifact
Most source profiles report similar measurements of elements, ions, and carbon, but these are insufficient for separating many sources from each other.
Organic components help with modern source apportionment, but source and receptor measurements are limited
Additional speciation can be applied to obtain marker compounds as part of the original analyses or on archived filters.

**Size-selective Inlet**
- HNO₃ denuder

**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)

**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

**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

**Impregnated cellulose-fiber filters (water extract)**
- NH₃ as NH₄⁺ by IC
- SO₂ as SO₄²⁻ by IC
- NO₂ as NO₃⁻ by IC

**Impregnated cellulose-fiber filter**
- HNO₃ as NO₃⁻ by IC

**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.

Dust

Biomass burning

Acetylene soot

PALAS arc generator soot

Diesel soot
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

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Absorbance peaks and/or region cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon peaks</td>
<td>1150-1300 (1156,1212), 640, 554, 517</td>
</tr>
<tr>
<td></td>
<td>Sharp peaks 1300-1950, 3480-3960</td>
</tr>
<tr>
<td>H₂O</td>
<td>1620-1640, 3350-3750</td>
</tr>
<tr>
<td>CO₂</td>
<td>1620-1640, 3350-3750</td>
</tr>
<tr>
<td>Aliphatic C-H</td>
<td>Sharp peaks 1370-1480, 2850-2950</td>
</tr>
<tr>
<td>Alkene C-H</td>
<td>2900-3100</td>
</tr>
<tr>
<td>Aromatic C-H</td>
<td>1000-1290, 3000-3100</td>
</tr>
<tr>
<td>Carbonyl C=O</td>
<td>Sharp peaks 1640 - 1850</td>
</tr>
<tr>
<td>Aldehyde -CHO</td>
<td>2700 - 2860</td>
</tr>
<tr>
<td>Alcohol/Phenol O-H</td>
<td>Broad peak 3200 – 3550, 1350, 650±50</td>
</tr>
<tr>
<td>Carboxylic acid C-OH</td>
<td>Broad peak 2500 - 3000</td>
</tr>
<tr>
<td>Organonitrate</td>
<td>Sharp peak 860, 1278, 1631</td>
</tr>
<tr>
<td>Organosulfur</td>
<td>Sharp peak 876</td>
</tr>
<tr>
<td>Sulfate SO₄²⁻</td>
<td>612-618, 1080-1140</td>
</tr>
<tr>
<td>Ammonium NH⁺</td>
<td>1400-1470, 2800-3400</td>
</tr>
<tr>
<td>Silicate SiO₃⁻</td>
<td>772-812, 1000-1200</td>
</tr>
<tr>
<td>Nitrate NO₃⁻</td>
<td>720, 840-810, 1340-1400</td>
</tr>
</tbody>
</table>

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

- Clark county paved road (REST1856)
- Vegas paved parking lot (REST0339)
- De-icing material (REST2102)
- Taconite dust

IR and UV-VIS spectra for biomass burning

- Litter composite (100% Wet, BIOTKF0102)
- Duff composite (100% Wet, BIOTKF088)
- Squaw carpet leaves (50% Wet, BIOTKF086)
- Bitterbrush stems (Dry, BIOTKF072)

Paved road  Parking lot  De-icing material  Taconite dust

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

Elemental detection sensitivity is optimized by excitation condition and analysis time. Longer analysis times reduce detection limits by $(t_{\text{usual}}/t_{\text{enhanced}})^{0.5}$. 
Rare-earth elements and isotopes can be quantified by Inductively-coupled Plasma-Mass Spectrometry (ICP-MS) but acid digestion destroys the filter.

**Isotopes**

<table>
<thead>
<tr>
<th>Lead</th>
<th>Strontium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{204}\text{Pb}$</td>
<td>$^{86}\text{Sr}$</td>
</tr>
<tr>
<td>$^{206}\text{Pb}$</td>
<td>$^{87}\text{Sr}$</td>
</tr>
<tr>
<td>$^{207}\text{Pb}$</td>
<td></td>
</tr>
<tr>
<td>$^{208}\text{Pb}$</td>
<td></td>
</tr>
</tbody>
</table>

**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)

<table>
<thead>
<tr>
<th>°C</th>
<th>Analysis Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC1</td>
<td>140 100% He (99.99% Purity)</td>
</tr>
<tr>
<td>OC2</td>
<td>280 100% He (99.99% Purity)</td>
</tr>
<tr>
<td>OC3</td>
<td>480 100% He (99.99% Purity)</td>
</tr>
<tr>
<td>OC4</td>
<td>580 100% He (99.99% Purity)</td>
</tr>
<tr>
<td>OP</td>
<td>Return to original reflectance/transmittance value</td>
</tr>
<tr>
<td>EC1</td>
<td>580 98% He/2% O₂</td>
</tr>
<tr>
<td>EC2</td>
<td>740 98% He/2% O₂</td>
</tr>
<tr>
<td>EC3</td>
<td>840 98% He/2% O₂</td>
</tr>
<tr>
<td>TC</td>
<td>OC (OC1+OC2+OC3+OC4+OP) + EC (EC1+EC2+EC3-OP)</td>
</tr>
</tbody>
</table>

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

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.

**Diagram Description:**
- Lasers: 405 –1000 nm
- 8-Leg Optical Fibers
- Filter Sample Heated up to 900 °C
- Quartz Light Pipes
- Tranmittance Photodiode
- Reflectance Photodiode

**Graphs:**
- Reflectance
- Transmittance
- Temperature
- Ion Signal (a.u.)
- Oven Temperature (°C)

**Images:**
- Smoldering
- Flaming
- Diesel
Light absorption patterns can be obtained as part of the normal carbon analysis.

The product of absorption optical depth ($A_b \cdot OD_\lambda$) and wavelength ($\lambda$) 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.

**Carbon (N=18)**

- Sulfanilamide: $y = 0.0463x$, $R^2 = 0.9983$
- L-Cystine
- CO2
- CH4

**Hydrogen (N=23)**

- Sulfanilamide
- L-Cystine
- (NH4)2SO4
- NH4NO3
- CH4
- $y = 0.1318x$, $R^2 = 0.9942$

**Nitrogen (N=19)**

- Sulfanilamide
- L-Cystine
- (NH4)2SO4
- NH4NO3
- $y = 0.0165x$, $R^2 = 0.9552$

**Sulfur (N=15)**

- Sulfanilamide
- L-Cystine
- (NH4)2SO4
- $y = 0.0120x$, $R^2 = 0.9933$

Sulfanilamide: $C_6H_6N_2O_2S$; 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.

- 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

- 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 cm² 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])

- Chloride (Cl⁻)
- Bromide (Br⁻)
- Nitrite (NO₂⁻)
- Nitrate (NO₃⁻)
- Phosphate (PO₄³⁻)
- Sulfate (SO₄²⁻)
- Ammonium (NH₄⁺)
- Soluble Sodium (Na⁺)
- Soluble Magnesium (Mg²⁺)
- Soluble Potassium (K⁺)
- Soluble Calcium (Ca²⁺)
Water-soluble organic carbon (WSOC) is related to cloud condensation nuclei, biomass burning, SOA, and health effects.

Total WSOC by TOC and WSOC classes

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

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

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

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

**Carbohydrates**
- Glycerol (\(\text{C}_3\text{H}_8\text{O}_3\))
- Inositol (\(\text{C}_6\text{H}_{12}\text{O}_6\))
- Erythritol (\(\text{C}_4\text{H}_{10}\text{O}_4\))
- Xylitol (\(\text{C}_5\text{H}_{12}\text{O}_5\))
- **Levoglucosan (\(\text{C}_6\text{H}_{10}\text{O}_5\)); Biomass burning marker**
- **Arabitol (\(\text{C}_5\text{H}_{12}\text{O}_5\)); Fungal biomarker**
- Sorbitol (\(\text{C}_6\text{H}_{14}\text{O}_6\))
- Mannosan (\(\text{C}_6\text{H}_{10}\text{O}_5\))
- **Mannitol (\(\text{C}_6\text{H}_{14}\text{O}_6\)); Fungal biomarker**
- Glucose (\(\text{C}_6\text{H}_{12}\text{O}_6\))
- Xylose (\(\text{C}_5\text{H}_{10}\text{O}_5\))
- Fructose (\(\text{C}_6\text{H}_{12}\text{O}_6\))
- Trehalose (\(\text{C}_{12}\text{H}_{22}\text{O}_{11}\))
- Arabinose (\(\text{C}_5\text{H}_{10}\text{O}_5\))
- Galactose (\(\text{C}_6\text{H}_{12}\text{O}_6\))
- Maltitol (\(\text{C}_{12}\text{H}_{24}\text{O}_{11}\))
Organic acids are related to biomass burning and cooking emissions

**Monocarboxylic acids:**
- Lactic acid (C$_3$H$_6$O$_3$)
- Acetic acid (C$_2$H$_4$O$_2$)
- Formic acid (CH$_2$O)
- Methanesulfonic acid (CH$_4$SO$_3$)

**Dicarboxylic acids:**
- Glutaric acid (C$_5$H$_8$O$_4$)
- Succinic acid (C$_4$H$_6$O$_4$)
- Malonic acid (C$_3$H$_4$O$_4$)
- Maleic acid (C$_4$H$_4$O$_4$)
- Oxalate (C$_2$H$_2$O$_4$)
Elemental analysis quantifies total C, H, N, S, and O for OM to OC ratios on liquids and quartz-fiber filters

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

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