Research Needs to Improve the Understanding and Application of Thermal/Optical Carbon Measurements

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AWMA, Xi’an, May 12, 2010
Background

• Thermal methods for OC/EC were first developed during late 1970’s.

• Thermal optical technique was first applied in IMPROVE, a visibility monitoring network in the U.S. in mid 1980’s.

Reference:
IMPROVE Protocol is used by USEPA networks.

Non-Urban U.S. EPA Interagency Monitoring of PROtected Visual Environments (IMPROVE) Network

Urban U.S. EPA Speciation Trends Network (STN)

Virgin Islands

Hawaii

Alaska
**IMPROVE Thermogram- 4 OC & 3 EC fractions**

**IMPROVE Protocol (Sample 02/14/03, medium loading)**

- **Wavelengths:**
  - He
  - 98% He/2% O₂

**Graphical Data**:
- **Y-axis (Carbon Evolved):** gC cm⁻² s⁻¹
- **X-axis (Analysis Time):** sec
- **Lines:**
  - Carbon (FID) (Green)
  - Reflectance (Pink)
  - Transmittance (Red)
  - Temperature (Black)

**Highlights**:
- **He and 98% He/2% O₂**
- **TOR split**
- **TOT split**
- **FID tailing**
- **Laser Reflectance, Transmittance, Temperature (ºC)**

**Additional Notes**:
- Improves understanding of chemical analysis techniques and their applications in environmental studies.
Research Needs:

Procedures are non-routine or under development

- Inorganic Carbonate Carbon (ICC)
- Organic Oxygen content
I. Carbonate Interference

- ICC is seldom measured
- Many carbonates in the environment decompose below 850°C.
- CO₂ from carbonate decomposition overlaps with OC fractions.
- Pretreatment with Conc. HCl vapor may not be complete and residual Cl⁻ can catalyze EC oxidation.
Differential Thermal Analysis of Carbonates

Calcite, CaCO₃
Siderite, FeCO₃
Smithsonite, ZnCO₃
Rhodochrosite, MnCO₃
Stronitanite, SrCO₃
Witherite, BaCO₃
Dolomite, CaMg(CO₃)₂
Magnesite, MgCO₃
Aragonite, CaCO₃
Cerussite, PbCO₃

Source: Cuthbert & Rowland (1947) Am. Mineralogist, V32 p.111
Injection of $H^+$ for Direct $CO_3^-= Measurement$
Carbonates by Sparging
II. Aerosol Organic Oxygen

Significance:

- Affects the scaling of carbon mass to organic mass – a large uncertainty
- May yield information on the nature and origin of the aerosol.
- Enhances source apportionment applications that, at present, rely only on the OC/EC fractions.
O Measurement Technique

• Incorporate a cracking reactor in analyzer:

\[
\begin{align*}
C_xH_y & \quad \triangleleft \quad xC + \frac{y}{2}H_2 \\
C_xH_yO_z & \quad \triangleleft \quad (x-z)C + \frac{y}{2}H_2 + zCO
\end{align*}
\]

• Reactor temperature: ~ 1200°C

• Catalyst: C, or Pt/Rh 90/10

• Measure CO directly by NDIR or conversion to CH\(_4\) for FID
III. Nature of OC fractions

Significance:

- In the course of analysis, some compounds are volatilized unchanged, and some pyrolyze.
- Provides information on the nature and origin of the aerosol.
- Work is tedious and may not be routine.
- Ongoing research by Prof. Ralf Zimmermann’s group at Universitat Rostock, Germany.
Analyzer Modifications

• Sample cross oven:

Add capillary tube to sample volatilized OC
Analyzer Modifications

- Add heated compartment for transfer line:

Before

After
Analyzer Modifications

Capillary for connection to fused silica capillary

To MS
MS to identify the compounds
SUMMARY

• ICC should be measured when samples are impacted by dust storm events.

• ICC is best measured by direct measurement of CO$_2$ released upon acidification.

• Organic Oxygen, when measured, reduces the aerosol organic mass uncertainty and enhances source apportionment applications.

• Organic oxygen can be measured with some modification to the analyzer.

• Nature of organic fractions is being investigated.