Insights from Thermal Analysis of Individual Organic Compounds, Mixtures, Black Carbon Surrogates, Airborne PM and Extracts

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Objectives

1. Compare thermograms of organic compounds, ambient, source and ‘surrogate’ particulate matter.

2. Shed light on the chemical characteristics of the temperature-defined carbon fractions in relation to what is known from detailed speciation efforts for organic compounds in source and ambient PM.
Approach

- Dip quartz filters into solutions of representative compounds and slurries of compounds and fine activated carbon
- Compare NIOSH 5040 and combustion EGA for stds, AC and stds+AC
- Compare to combustion EGA for more stds, as well as source and ambient PM
- Compare to combustion EGA for extracted PM and extracts
Organic Compounds: NIOSH & Combustion EGA

- Tetracosane ($\text{C}_{24}\text{H}_{50}$ alkane)
- Glutaric acid
- Methylcellulose
- Cholesterol
- Potassium hydrogen phthalate (KHP), often used for calibration of OCEC
Surrogate PM

- ‘Surrogate PM’: mixture of fine activated carbon (AC) particles and one or more known compounds
- Coated onto filters from slurries
- Dried at < 50 C
Combustion Constant Heating - Novakov

Temperature programmed combustion in pure $O_2$

- Concurrent light transmission (1980’s)
- Tom Kirchstetter now enabling multi-wavelength TOT

Standards + AC (‘back drawers) and new preps

- No light transmission in very recent preps
- Standards and fine AC coated on filters from solutions & slurries
Modified NIOSH 5040 TOT

- OC1 (250 °C, 60 s) Helium
- OC2 (500 °C, 60 s)
- OC3 (630 °C, 60 s)
- OC4 (870 °C, 90 s)
- OP from light transmission decrease
- OC = Σ of the first 5 fractions
- Heat off 30 s, then 2% O₂ in He
- EC = difference between the carbon evolved in the presence of O₂ and the Pyr
- 500 °C (10 s), 600 °C (20 s), 670 °C (20 s), 740 °C (20 s), 810 °C (20 s), 860 °C (20 s), and 920 °C (120 s)
- TC = OC + EC
Results

Tetracosane [High] + AC (NIOSH)

Fraction

microg cm\(^{-2}\)

0 50 100 150 200 250

OC EC OC1 OC2 OC3 OC4 PyC EC

- AC
- tetracosane
- tetracosane + AC
Results

Glutaric Acid [High] + AC (NIOSH)
Results

Glutaric Acid (High) +AC

![Graph showing dCO₂/dT versus Temperature for Glutaric Acid (High) +AC]

- Glutaric + AC
- Glutaric
- AC

Environmental Energy Technologies
Results

KHP [High] +AC (NIOSH)

![Graph showing microg m⁻² for different fractions: TC, OC, EC, OC1, OC2, OC3, OC4, PyC, EC. The graph compares AC, KHP, and KHP+AC with overlaying lines.]

Environmental Energy Technologies
Results

KHP + AC

![Graph showing the rate of change of CO₂ concentration with respect to temperature for KHP and AC. The graph includes multiple peaks at different temperatures, indicating different reaction rates and behaviors. The x-axis represents temperature in Kelvin, and the y-axis represents the rate of change of CO₂ concentration (dCO₂/dT).]
Results - Individual Compounds

- *OC1*: Volatility and MW, rather than class or functional group, controlled the evolution of OC \(\leq 250\) C.
- *OC1*: The higher the MW and greater the O content, the more likely the compound was seen in more than one fraction.
- *OP*: formation of OP was more likely for polyfunctional compounds with at least one aromatic ring.
- *OP*: Some complex oxygenated molecules with saturated rings also pyrolyzed readily.
Results: Surrogate PM

- Reconstruct any profile with AC + a few compounds
- Different ratios of OC and EC influence fractions
- Aromaticity and oxygen) influence fractions
- Surrogate PM may still have uses.
Results: Indoor PM

Seattle OC Indoor PM +/- SVOC

![Graph showing the comparison of OC concentrations across different fractions (OC1, OC2, OC3, OC4, and PyC) with and without SVOC. The graph plots microg C m\(^{-3}\) against Fraction.]
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