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 ($C_{24}H_{50}$ 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

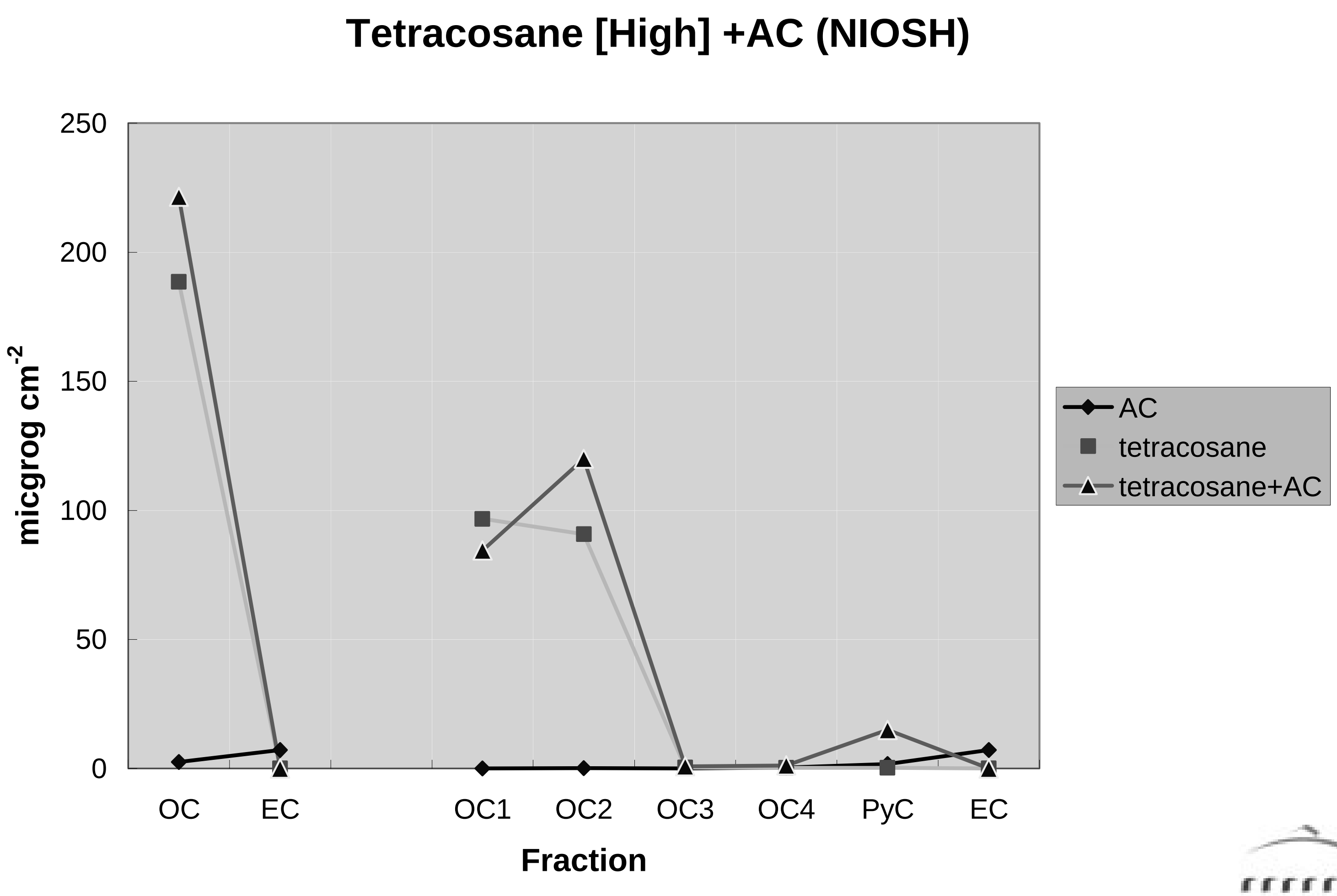
Standards + AC (‘back drawers) and new preps

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

Modified NIOSH 5040 TOT

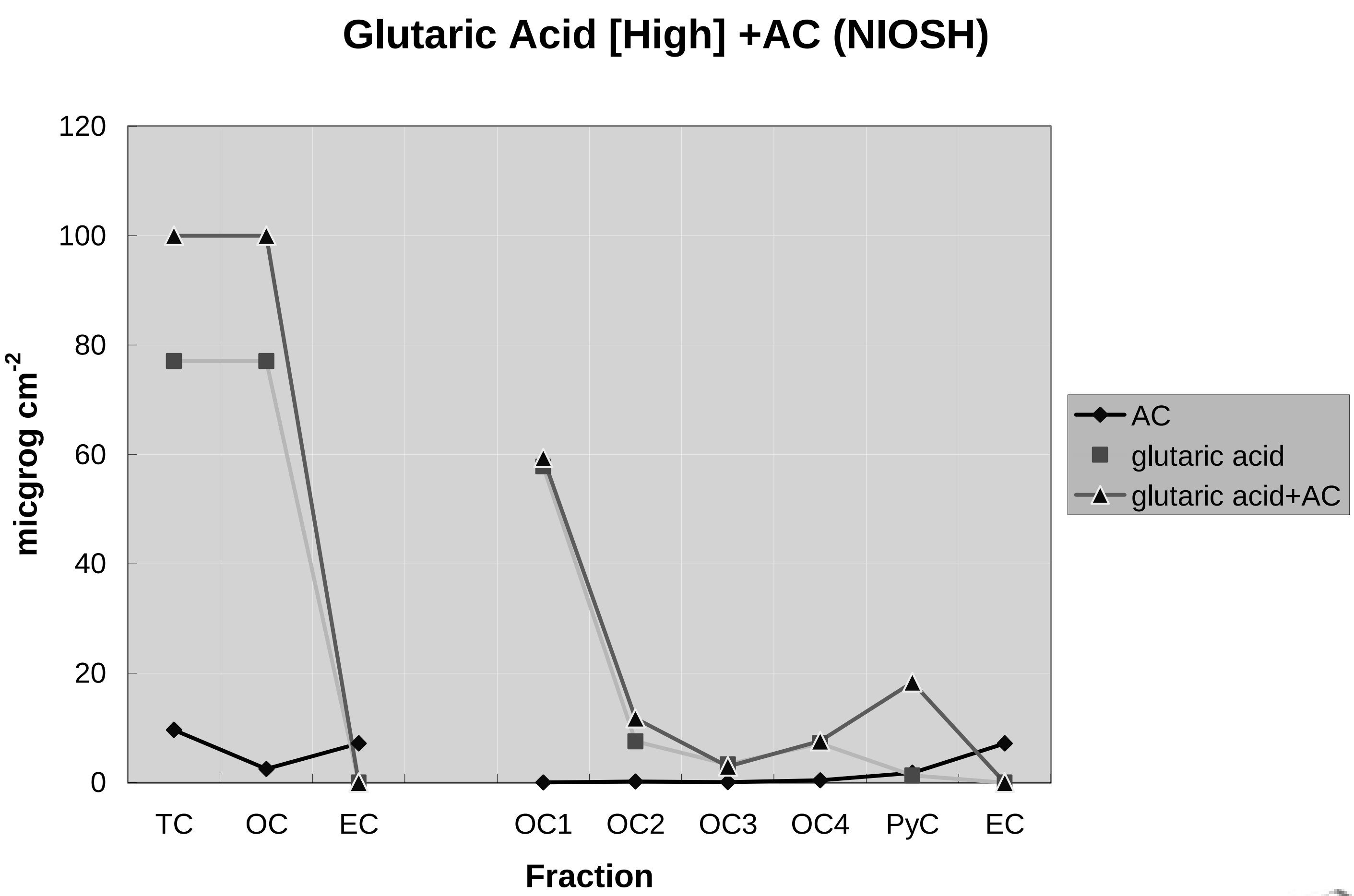
- OC1 (250 C, 60 s) Helium
- OC2 (500 C, 60 s)
- OC3 (630 C, 60 s)
- OC4 (870 C, 90 s)
- OP from light transmission decrease
- OC = Σ of the first 5 fractions
- Heat off 30 s, then 2% O_2 in He
- EC = difference between the carbon evolved in the presence of O_2 and the Pyr
- 500 C (10 s), 600 C (20 s), 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



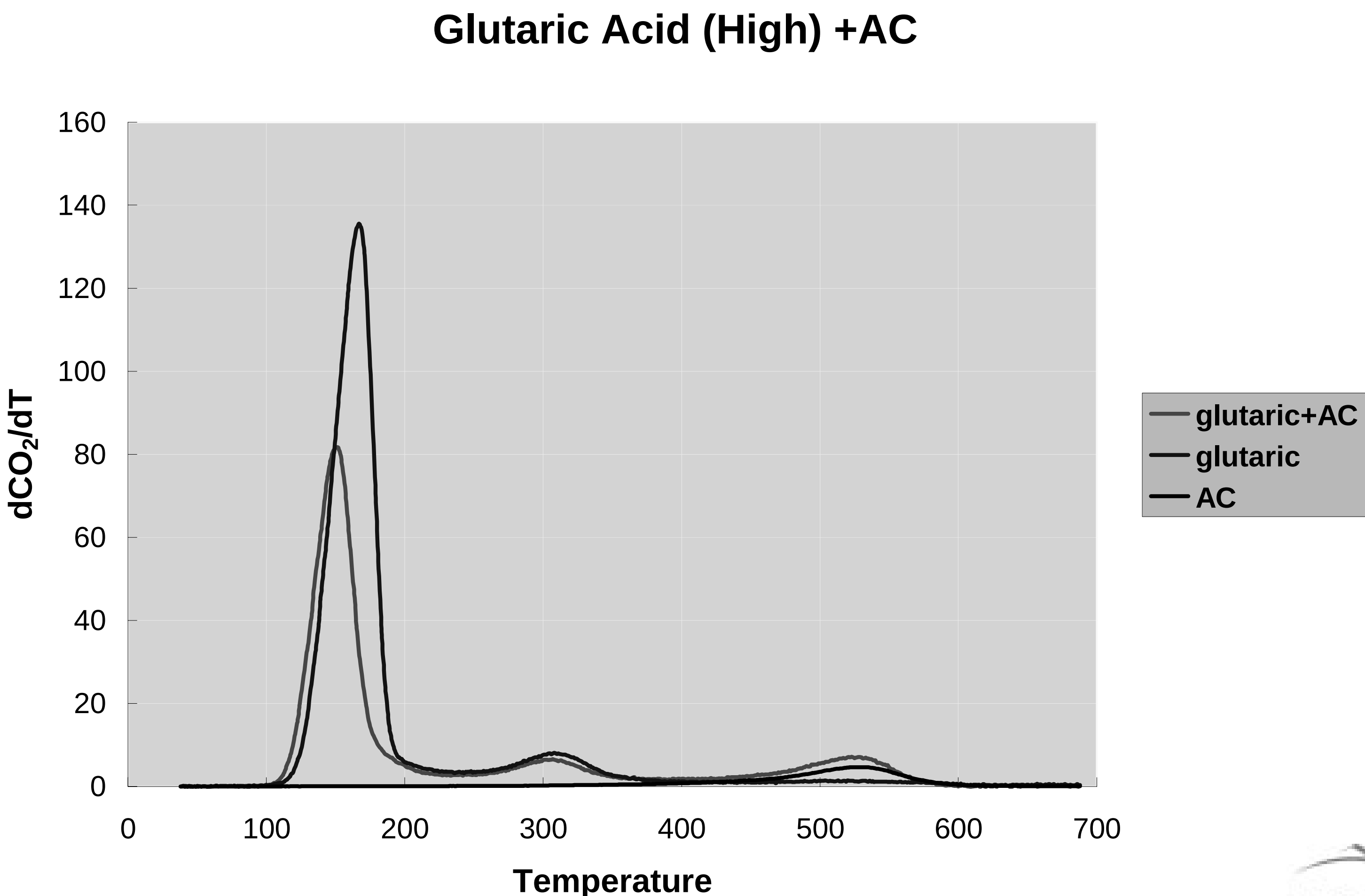
Tetracosane [High] +AC (NIOSH)
250
200
150
100
50
0
micgrog cm-2
OC
EC
OC1
OC2
OC3
OC4
PyC
EC
Fraction
AC
tetracosane
tetracosane+AC

Results



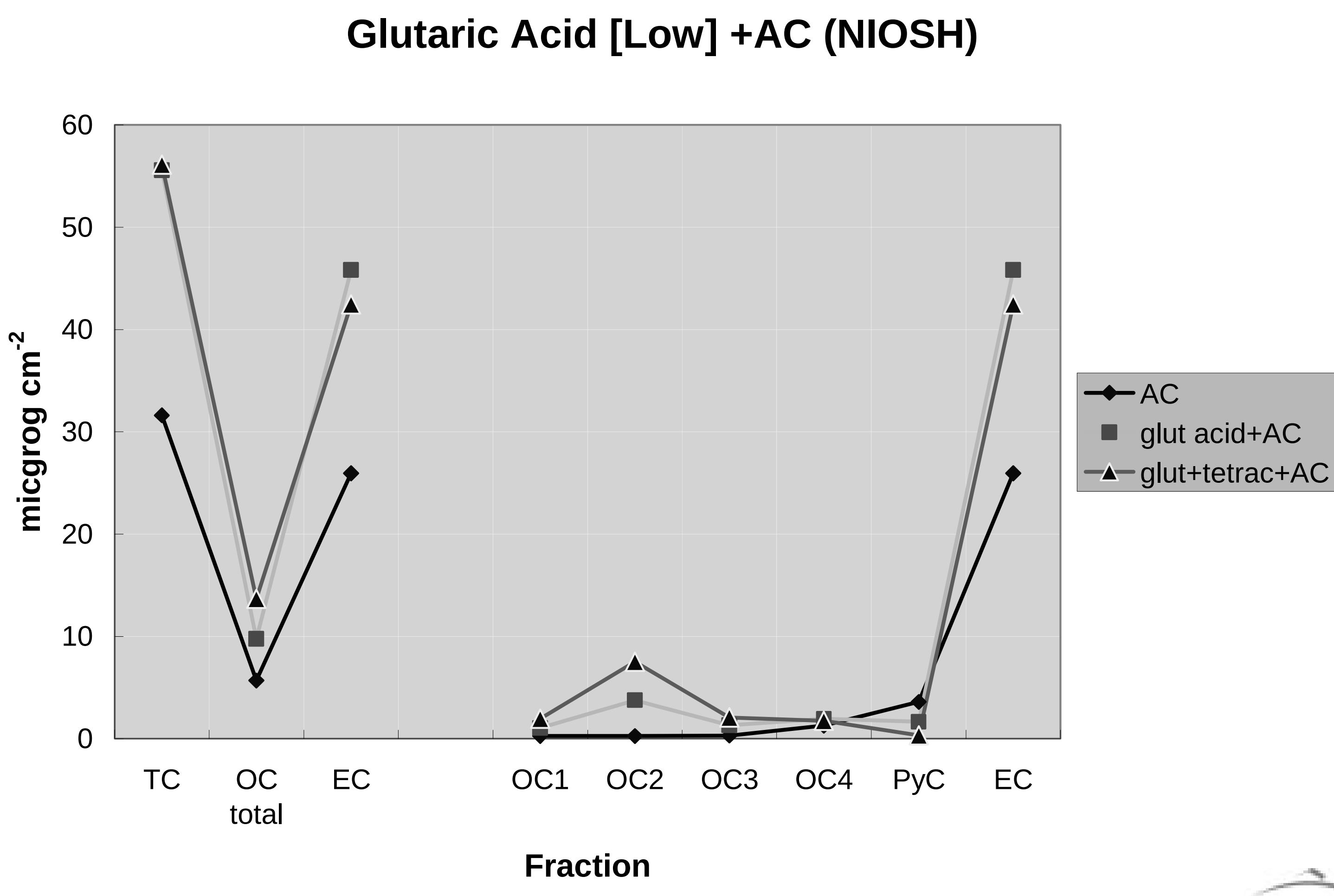
Glutaric Acid [High] +AC (NIOSH)
120
100
80
60
40
20
0
micgrog cm^{-2}
TC
OC
EC
OC1
OC2
OC3
OC4
PyC
EC
Fraction
AC
glutaric acid
glutaric acid+AC

Results

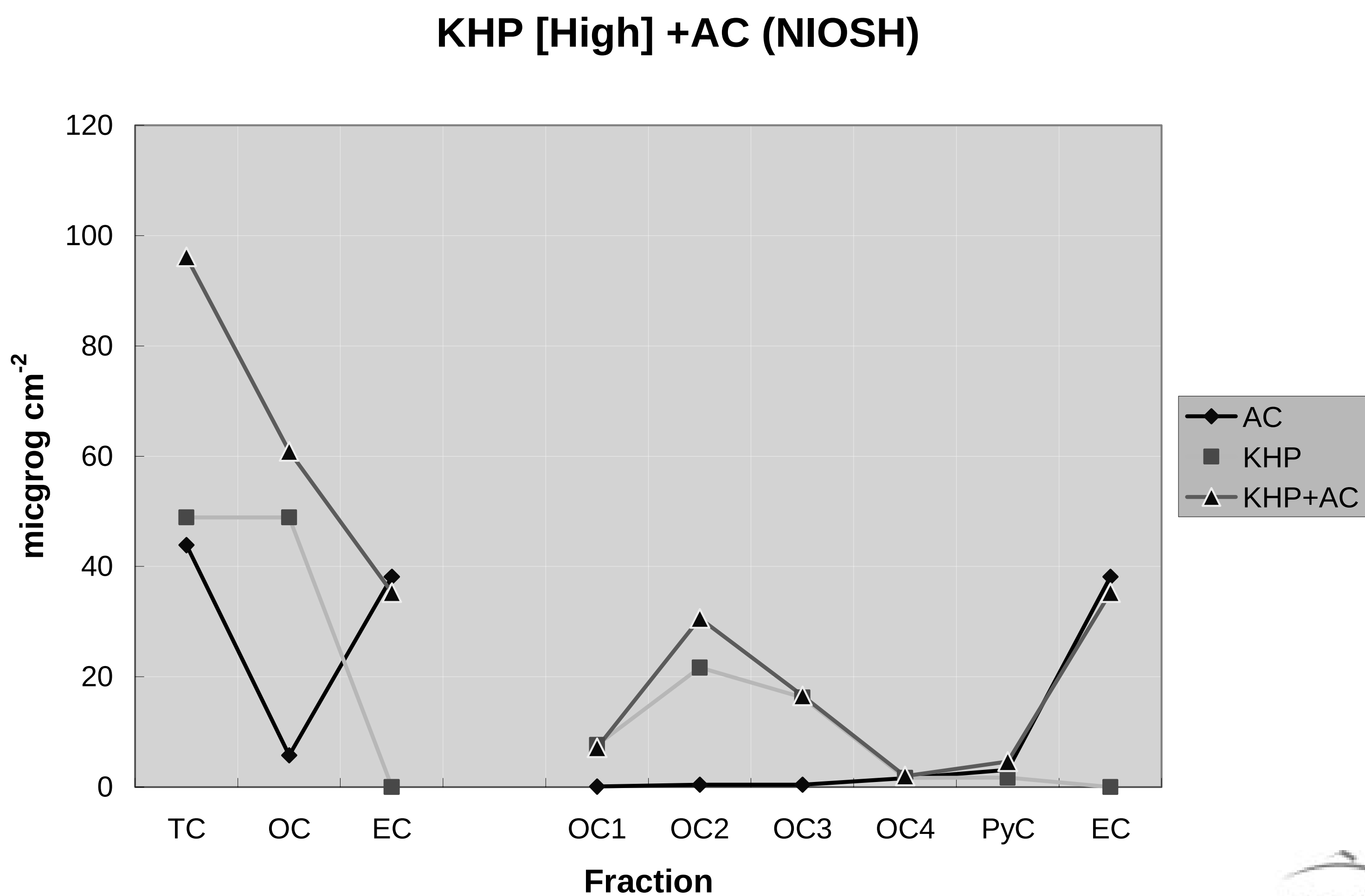


Glutaric Acid (High) +AC
160
140
120
100
80
60
40
20
0
0
100
200
300
400
500
600
700
Temperature
dCO2/dT
glutaric+AC
glutaric
AC

Results

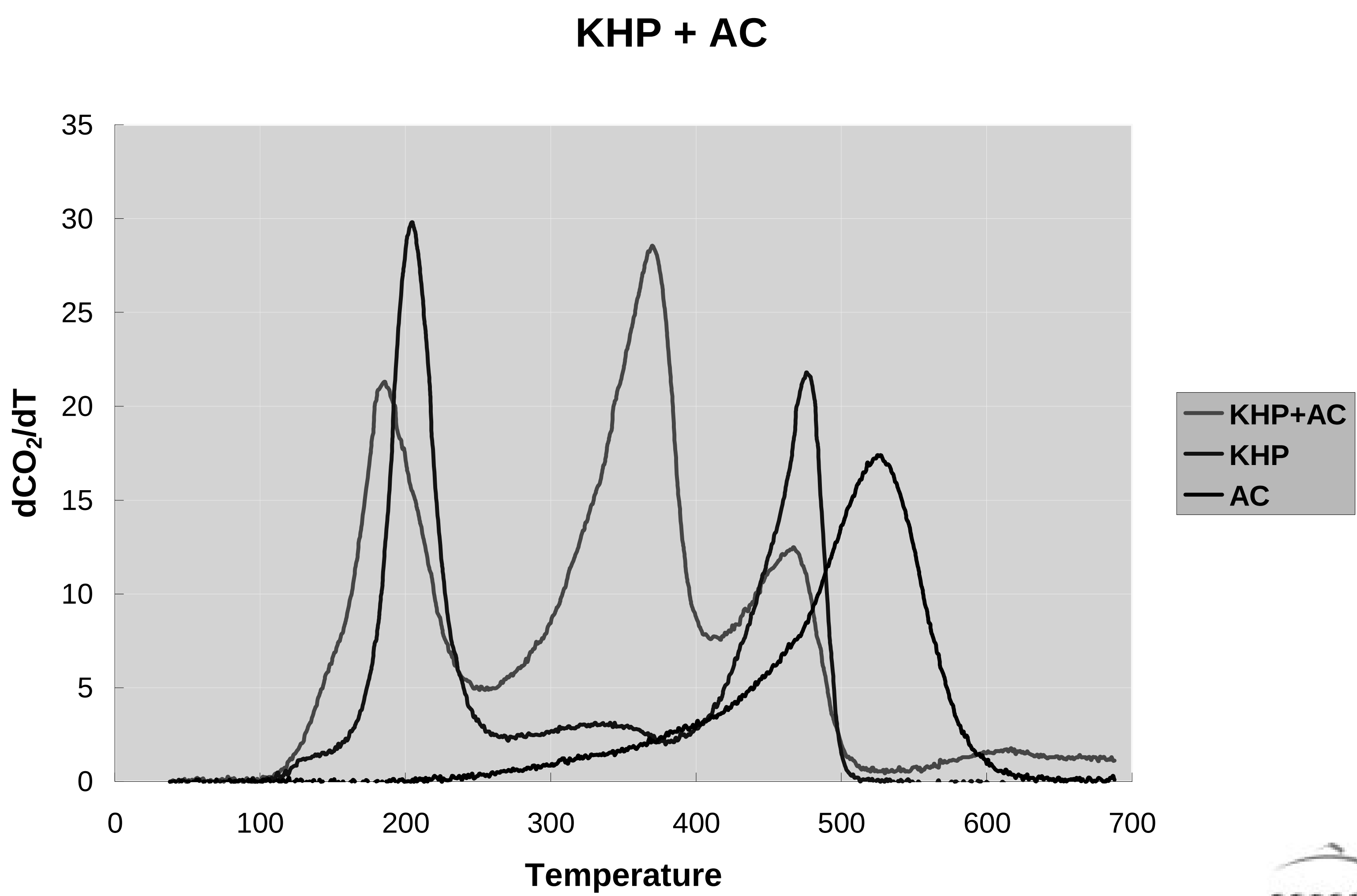

Glutaric Acid [Low] +AC (NIOSH)
60
50
40
30
20
10
0
micgrog cm-2
TC
OC total
EC
OC1
OC2
OC3
OC4
PyC
EC
Fraction
AC
glut acid+AC
glut+tetrac+AC

Results



KHP [High] +AC (NIOSH)
120
100
80
60
40
20
0
micgrog cm-2
TC
OC
EC
OC1
OC2
OC3
OC4
PyC
EC
Fraction
AC
KHP
KHP+AC

Results


KHP + AC
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
dCO2/dT
Temperature
KHP+AC
KHP
AC

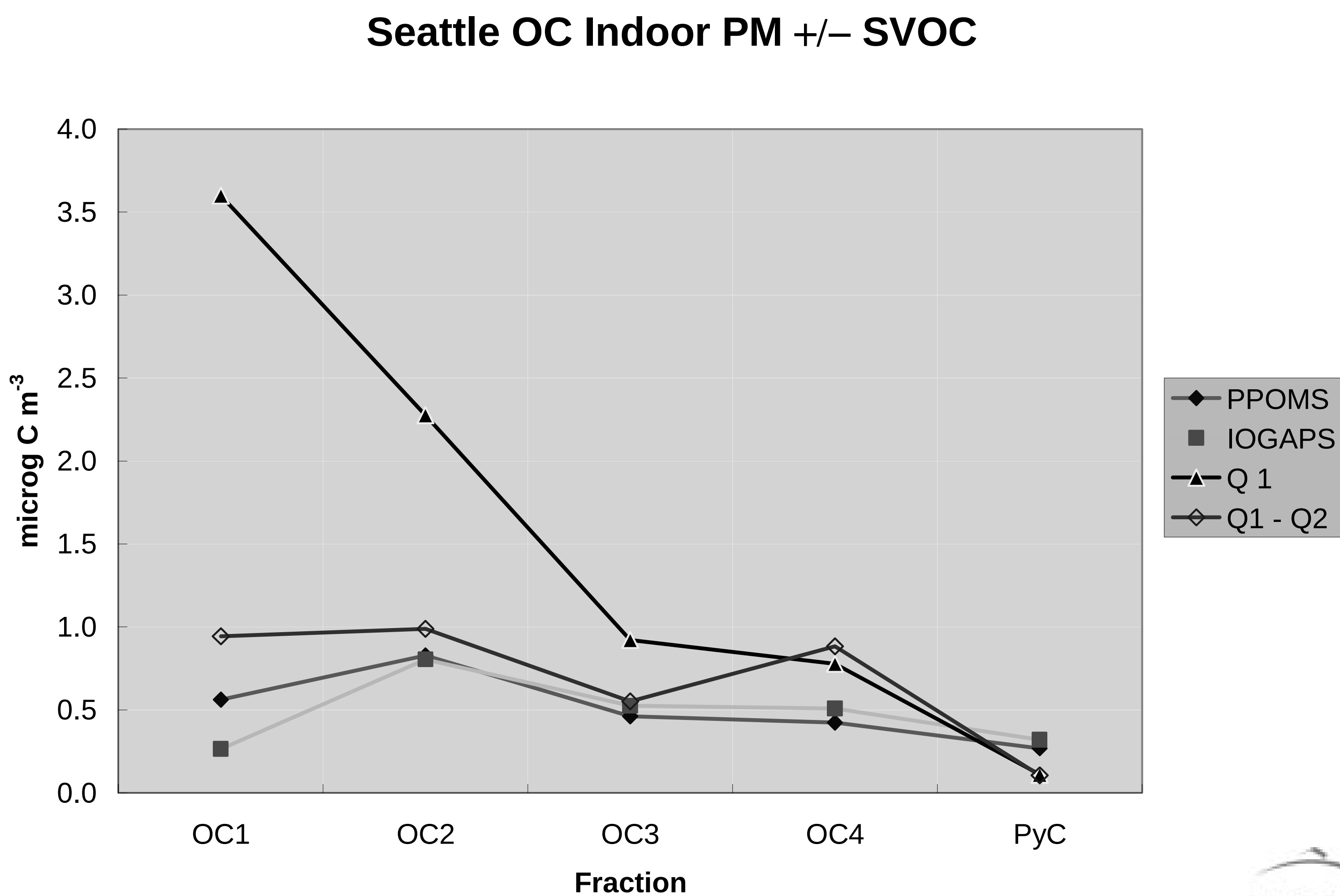
Results - Individual Compounds

- *OC1:* Volatility and MW, rather than class or functional group, controlled the evolution of OC <= 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



Acknowlegements

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