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Advancing the chemical characterization of carbonaceous aerosols for improving source-receptor modeling

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Characterizing carbonaceous aerosol

- both organic and elemental carbon components in aerosols are poorly understood
- develop health effects mechanisms (and apportion endpoints)
- atmospheric reactions and processing
- direct and indirect climatic effects of aerosols
- improved exposure estimates
- dispersion modeling

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General discussion focus

- analytical chemistry and source emissions aerosols
- chemical mass balance (CMB) modeling

- case examples
  - two-dimensional gas chromatography-mass spectrometry (2D GC-MS) for the identification and quantification of N-bearing molecules in biomass burning aerosols
  - GC with atomic emissions detection (AED) for organosulfur constituents in residential boiler effluents
  - high resolution-transmission electron microscopy (HR-TEM) for soot nanostructure determination
  - X-ray photoelectron spectroscopy (XPS) for determining aerosol surface chemistry and carbon chemical state

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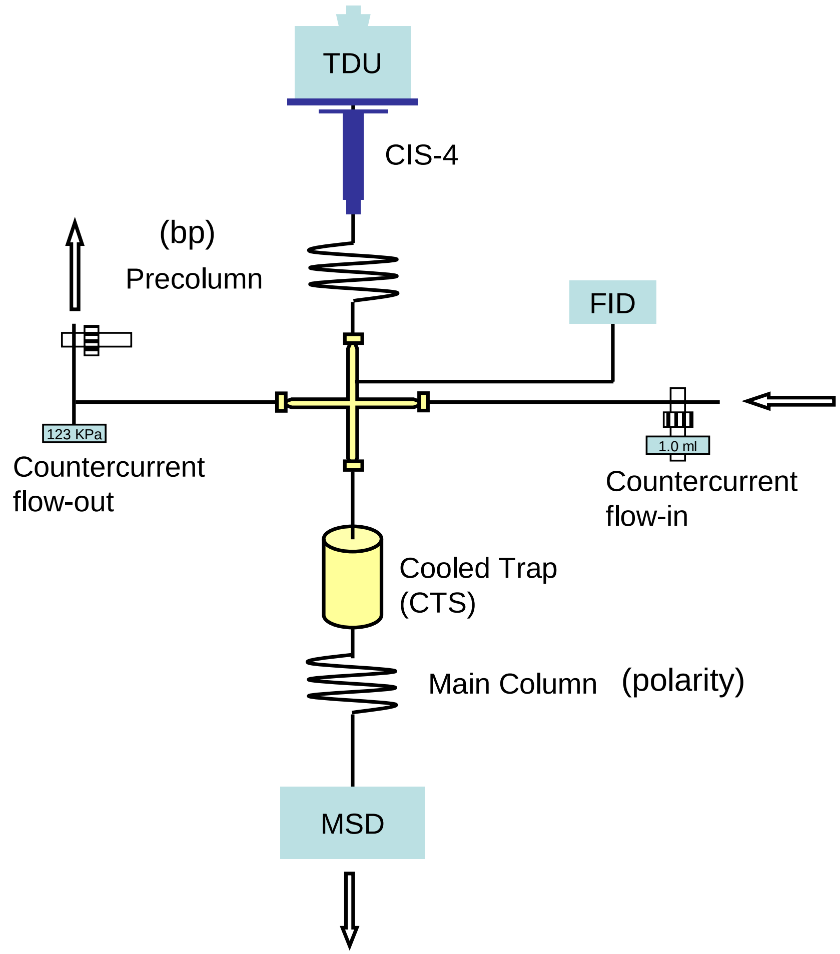
2D-GC-MS applied to aerosols

TE-2D-GC/MS system



Motivation

- deconvolve unresolved complex mixture (UCM) components
- develop thermal extraction (TE)-2D-GC/MS for characterizing PM2.5 source emissions

- apply heart-cutting method
- serial concentration
- column length adjustment
- traditional quantification possible

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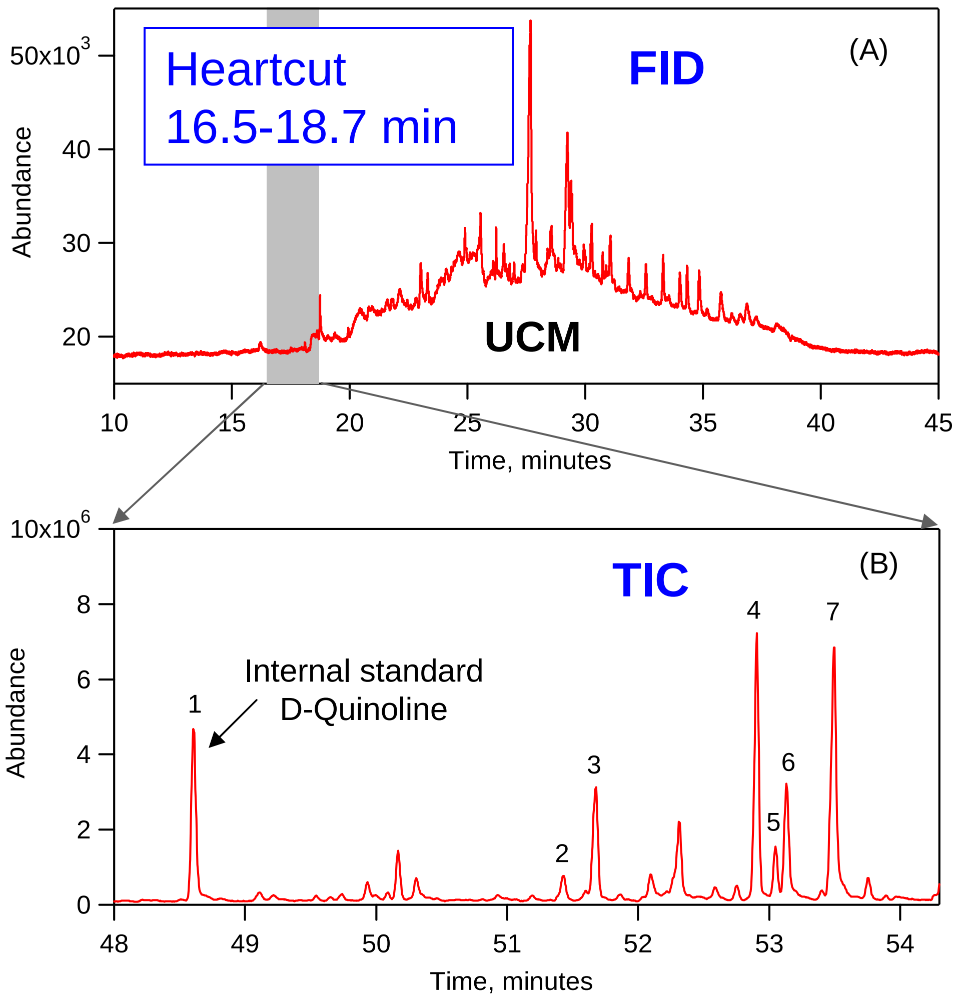
2D-GC-MS applied to biomass burning aerosols

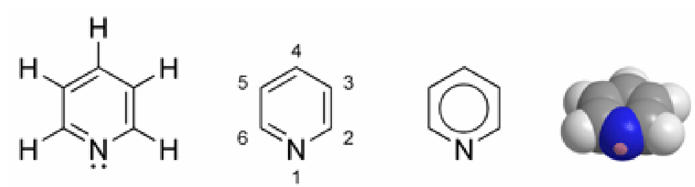
rice straw burning $PM_{2.5}$



direct identification of polar organic compounds in PM2.5 - typically detected as derivatives

Nitrogen-bearing organic compounds (NOCs)

Peak 6: 3-hydroxypyridine



anhydro sugar compounds

Peak 2: dianhydro-mannitol (polyol)

Peak 3: 2,3-anhydro-d-mannosan

Peak 4: 1,4:3,6-dianhydro-α-d-glucopyranose

furans

Peak 5: 2,3-dihydrobenzofuran

Peak 7: 5-hydroxymethyl-dihydro-furan-2-one

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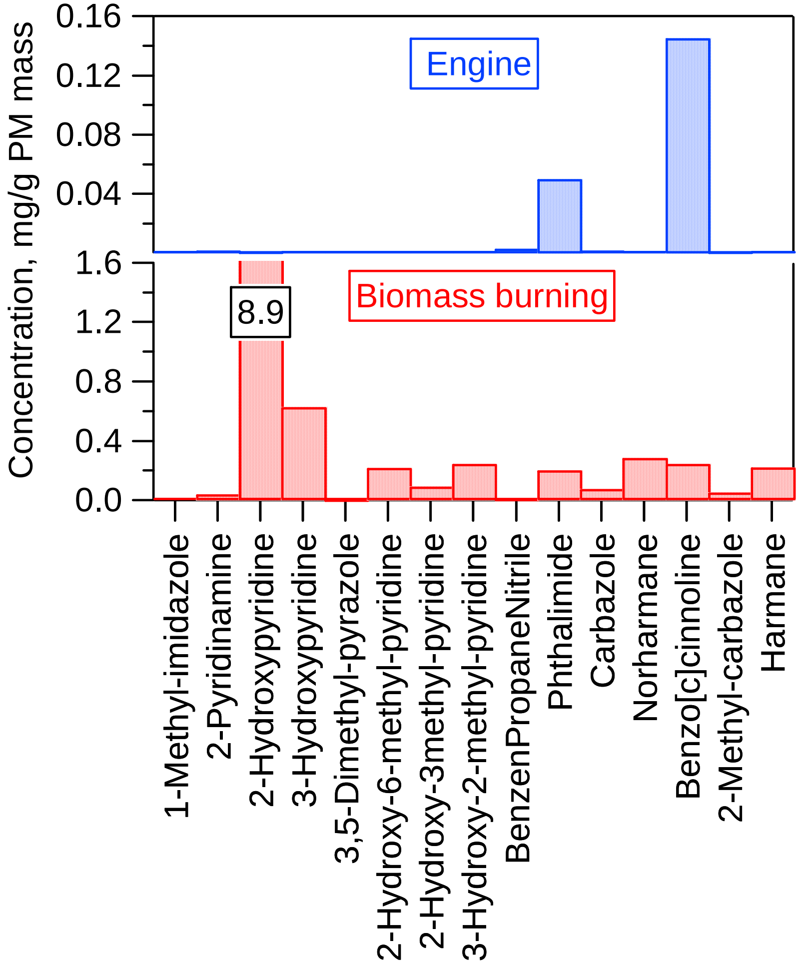
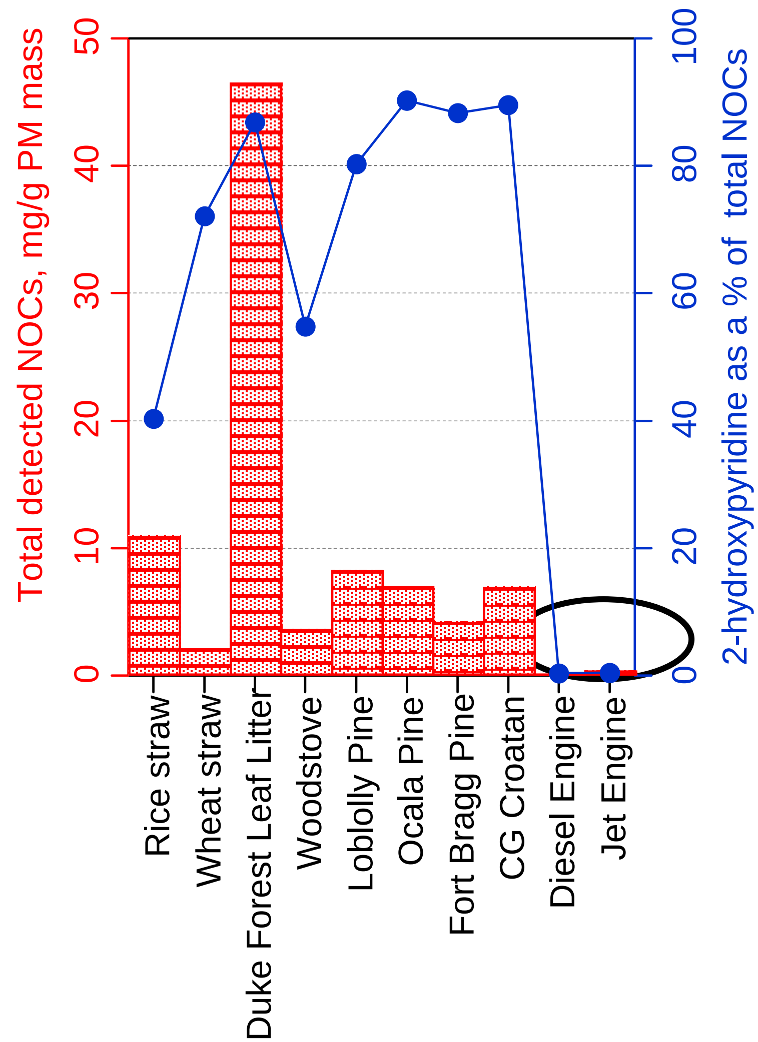
2D-GC-MS detected NOCs in source aerosols





- total NOCs range from 2.1 to 46.5 mg/g $PM_{2.5}$ mass for biomass burning
- 2-hydroxypyridine has the highest conc., 40-90% of total detected NOCs
- most NOCs specific to biomass burning PM2.5

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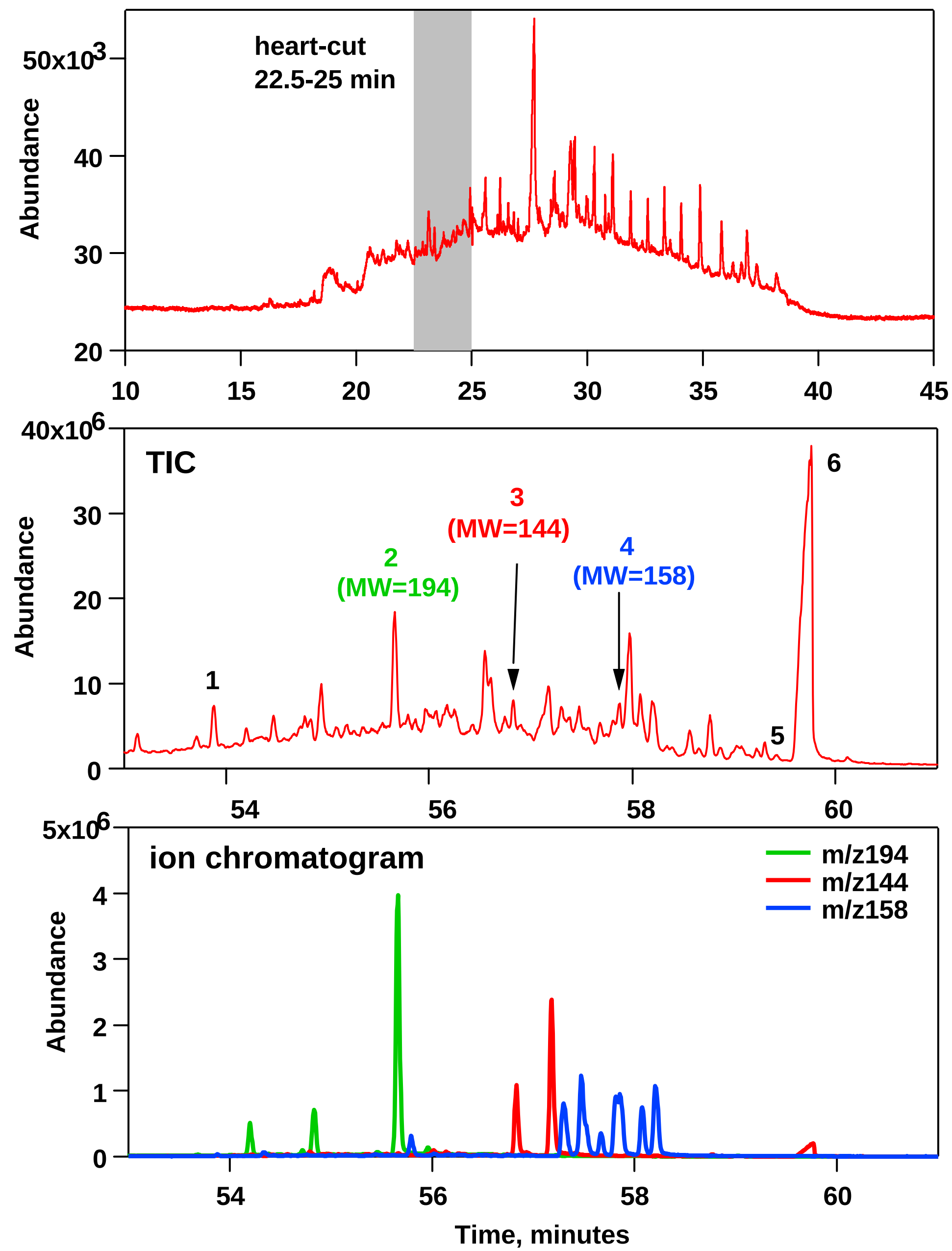
peak	compounds	match
1	dodecanoic acid	96
2	phenol, 2,6-dimethoxy-4-(2-propenyl),	93
3	1-naphthalenol	95
4	1-naphthalenol, 2-methyl	91
5	1,3-benzenediol, 4,5-dimethyl	94
6	**levoglucosan**	90



- heart-cut within the UCM
- levoglucosan and structural isomers resolved

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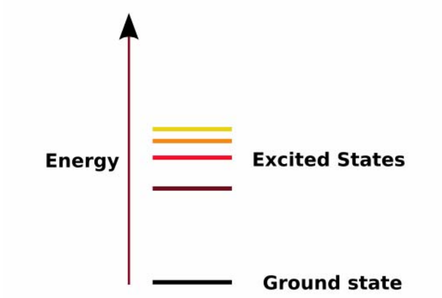
GC-AED applied to residential oil boiler aerosol

- AED (atomic emissions detector) - overlooked detection system
- column separation complemented by selective detection (pg/s)
- identify specific components in unresolved complex mixture (organometallics)
- element mass, empirical formulas, improved OM:OC ratio



- AED source – microwave-induced He plasma
- C, O, **S (181 nm)**, N, Hg, Ni, V, Fe, P, Sn, Cl, and Br
- sample – residential oil boiler (ROB) aerosol (solvent extract)
  - No. 2 distillate fuel
- GC method (Mazurek et al., Rogge et al.; Schauer et al.)

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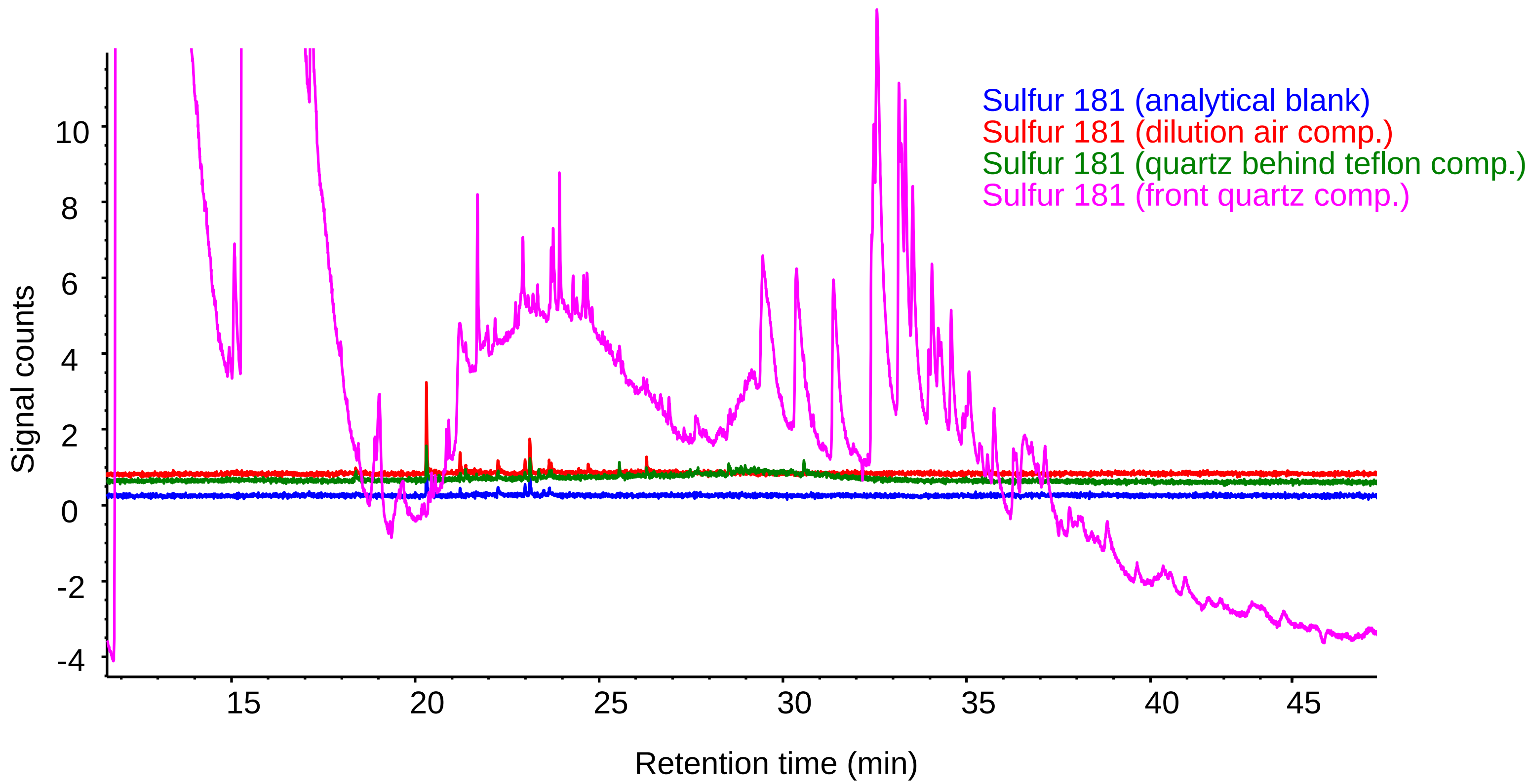
GC-AED applied to ROB aerosol



- ROB is a source of organosulfur compounds
  - unburned fuel
- UCM deconvolved (unidentified by GC-MS)
- empirical formula will require better separation
- 1% of S in fuel in PM (sulfate)
- fractionation and clean-up needed
- check more oil source emissions

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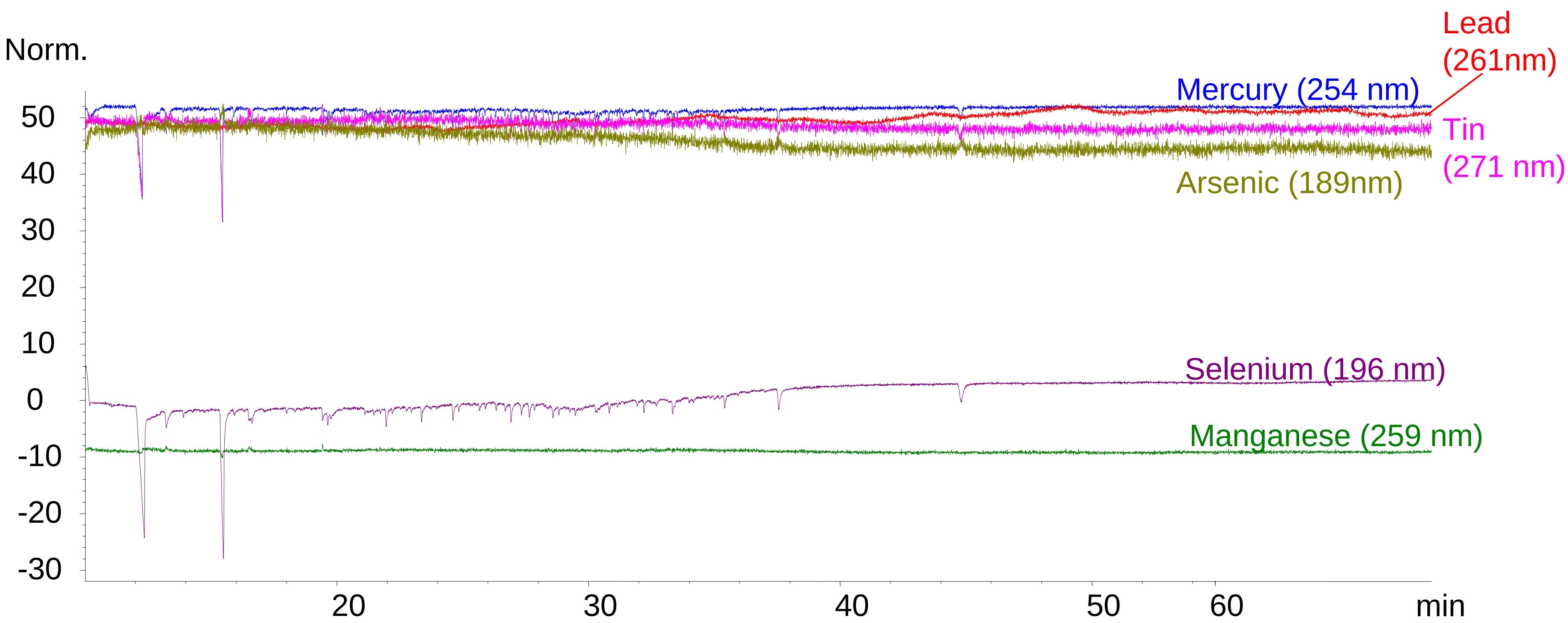
Check for Organometallics in ROB aerosol



- ICP-MS detected Pb, Mn, Sn, As, and Se
- metals below detection AED limits
- no evidence of organically bound metals

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HR-TEM (transmission electron microscopy for soot nanostructure determination

- resolves details of soot (EC) nanostructure (less than 1 nm)
- carbon atom arrangements (layer planes, segments, or lamella)
  - physical order (long and short range; graphitic or amorphous)
  - heteroatom inclusions, surface interiors, porosity
  - extent of mixing
  - quantify fringe or layer plane, separation distance, curvature, and tortuosity
- particle inception and growth
- mechanisms of particle uptake by biological samples
- apportion major sources of light absorbing EC
  - single particle sensitivity, EC is nonreactive, sources lacking organic matter

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Experimental details – HR-TEM

- seven filter samples (5 diluted source emissions and 2 atmospheric samples)
  - significant EC and aerosol mass sources
  - diesel, wildfire, oil boilers, jet engine, NFRAQS, Duke Forest
- wet or dry deposition process to TEM grid
- HR-TEM analysis (three or more sample locations depending on sample homogeneity)
- lattice fringe analysis – quantitative measure
- NASA Glenn Research Center

- the research questions:
  - is soot from different fuel and combustion sources homogeneous?
  - do atmospheric particles contain nanostructure that varies with fuel and combustion source characteristics?

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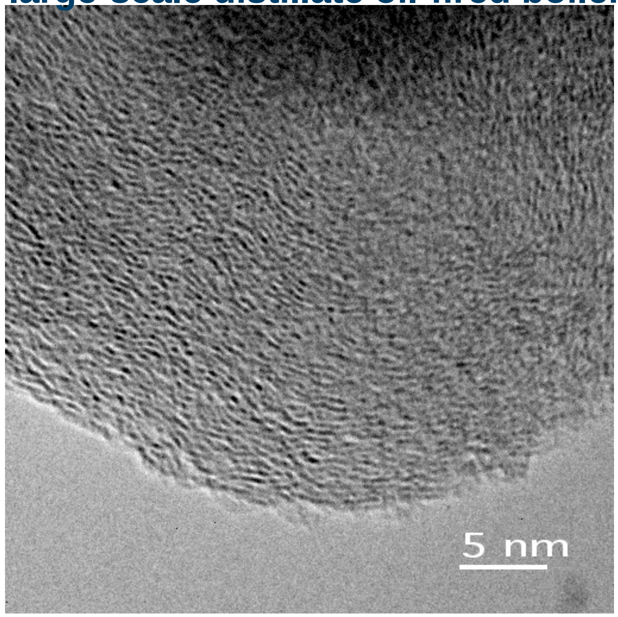
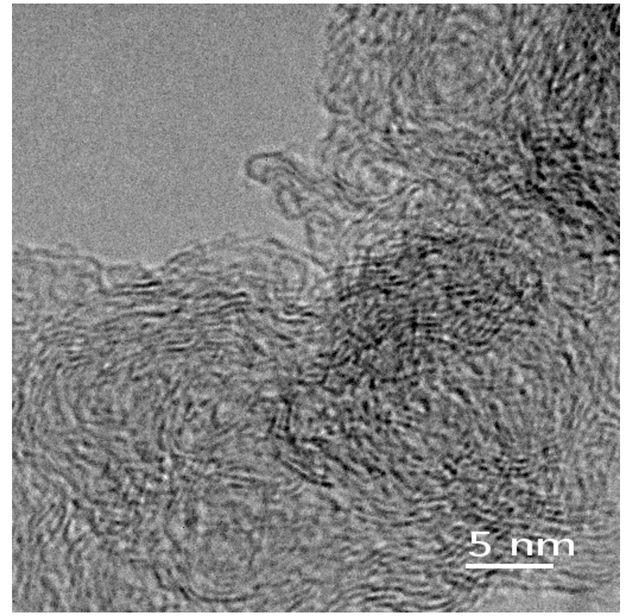
- EC is nanoheterogeneous
  - internal and external mixture
- interior-perimeter effects
- fullerenic structure – anthropogenic emissions
- fringe analysis confirmed subtle differences
- variety of soot types in atmospheric aerosols
- complement source-receptor modeling

- receptor model caveats
  - reactivity of amorphous soot
  - inter-source variation

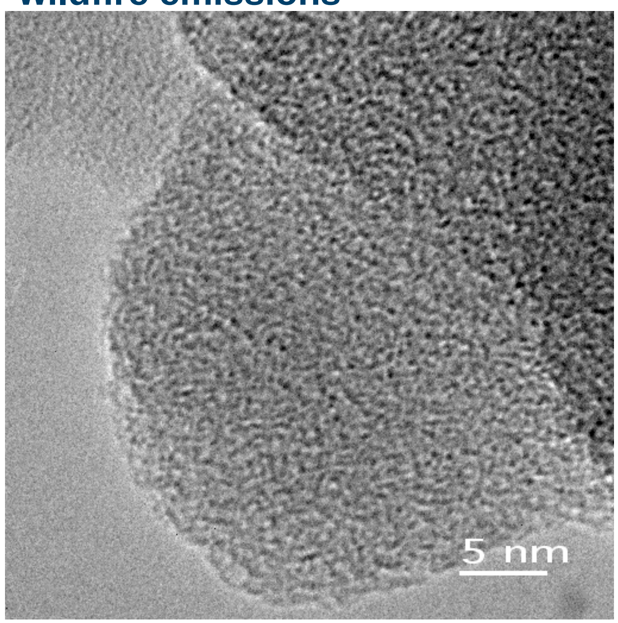
large-scale distillate oil-fired boiler



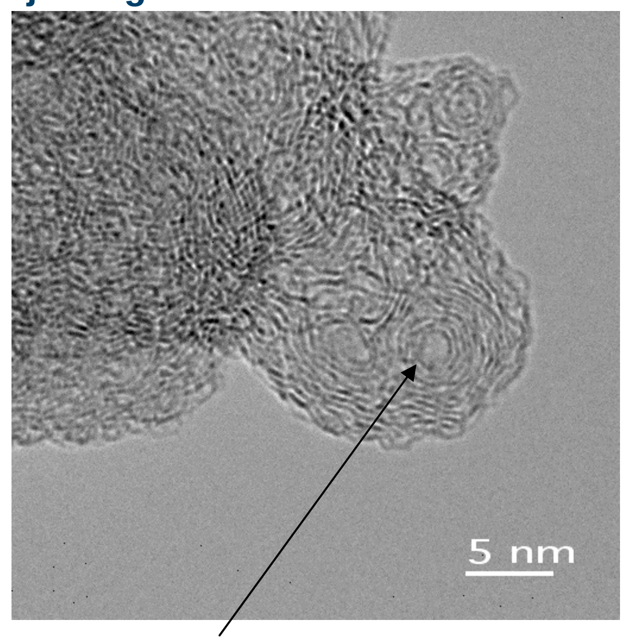
diesel truck exhaust



wildfire emissions



jet engine exhaust



fullerene structure

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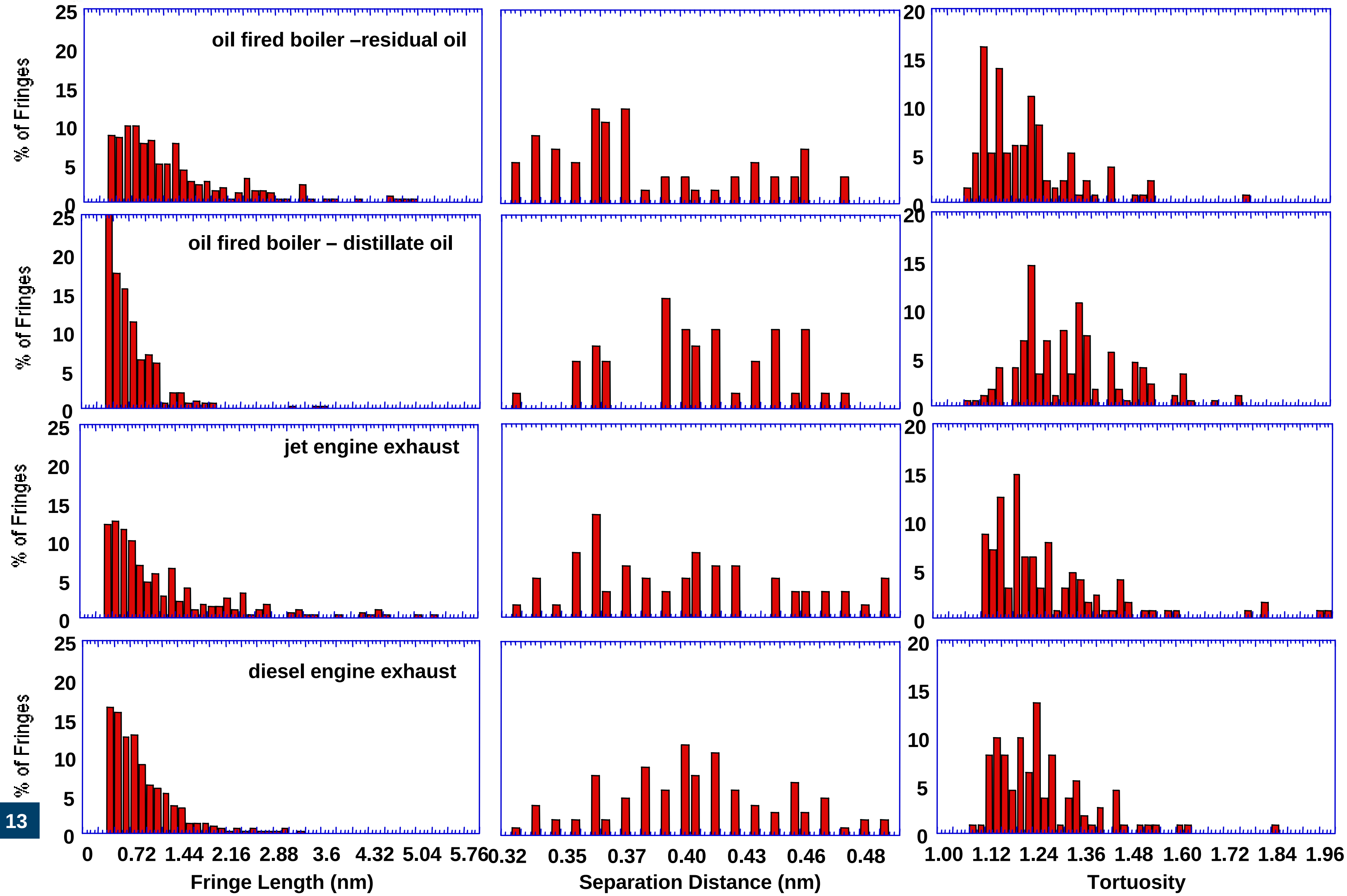
HR-TEM Fringe Analysis



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XPS (ESCA) for aerosol surface chemistry

- heteroelements, surface functional groups, carbon bonding states uncharacterized
- surface composition modulates SOA yield and particle oxidation rate
- organic matter concentrated at or near the particle surface
- health effects might be surface-related

- the research questions:
  - how do source particle surfaces differ compositionally (and with bulk chemistry)?
  - how does particle nanostructure convolve in tandem with its surface composition?

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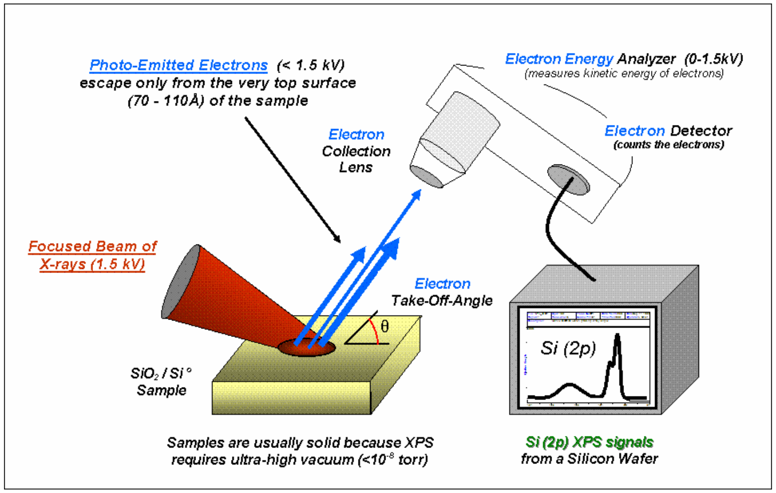
XPS technique and experimental details

- measured difference between ejected electron energy and incident beam = binding energy
- 1-10 nm sample depth
- survey scan and high resolution scan
  - elements determined to within ±0.1% (atomic)
  - HR scan for carbon bonding states and functional groups (10 sweeps 7 cycles)
  - curve fit C1s region
  - Lorentzian and Shirley fit



- examined emissions from plant-, institutional-, and residential-scale oil boilers, diesel and bio-diesel engine exhaust, wildfire, and aircraft engines

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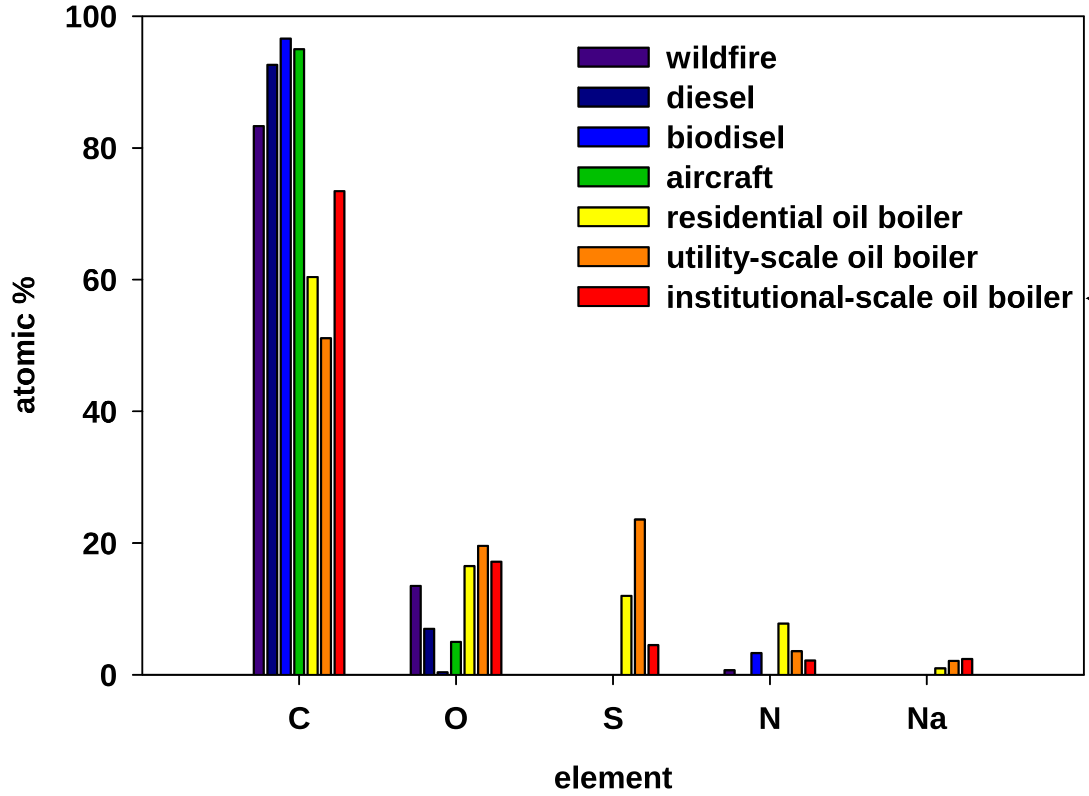
Surface composition of source aerosols



agreed with bulk S composition

- mostly surface carbon
- oil boilers show reduced C
    - contain S and O (sulfate)
- biodiesel lacked surface O
- wildfire - surface OM:OC ratio = 1.2

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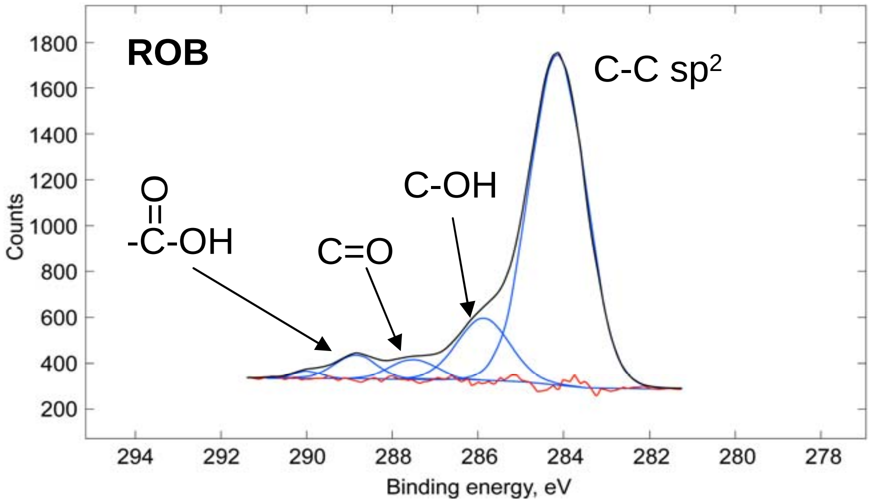
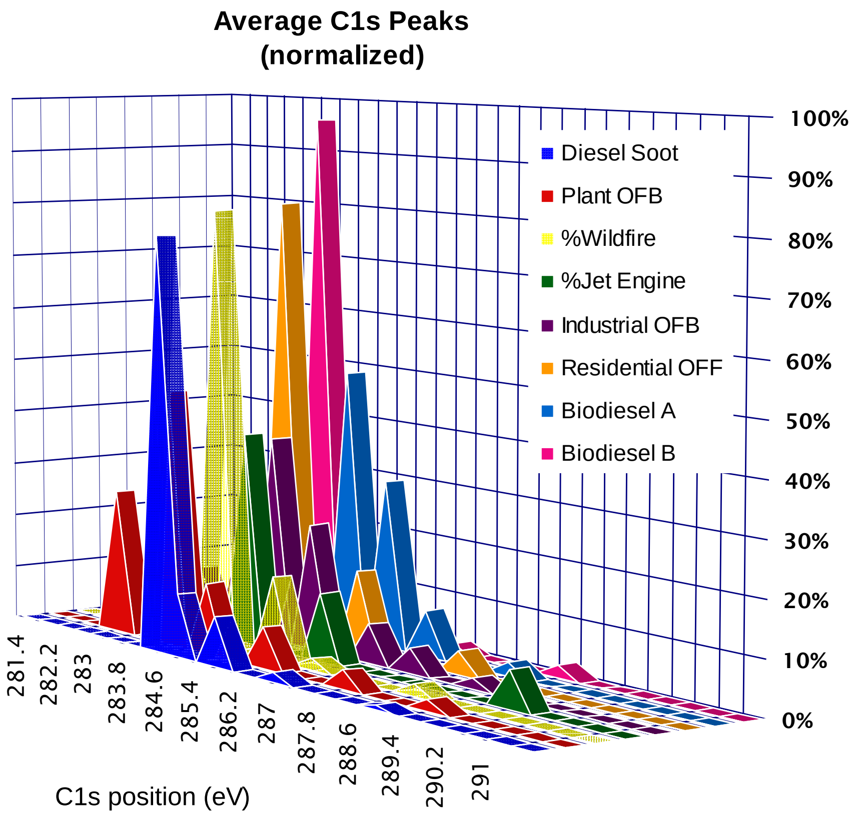
Surface functional group composition

high-resolution scan over C1S region





- slight shift in C1s binding energy indicate different oxygen functional groups
- percentages of carbon atoms apportioned to oxygen functional groups
- different carbon bonding states at the particle surface

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