


*Effects of Iron Oxides on the
Determination of Organic and
Elemental Carbon using Thermal
Optical Techniques*



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Speciation Principles

NIOSH or IMPROVE

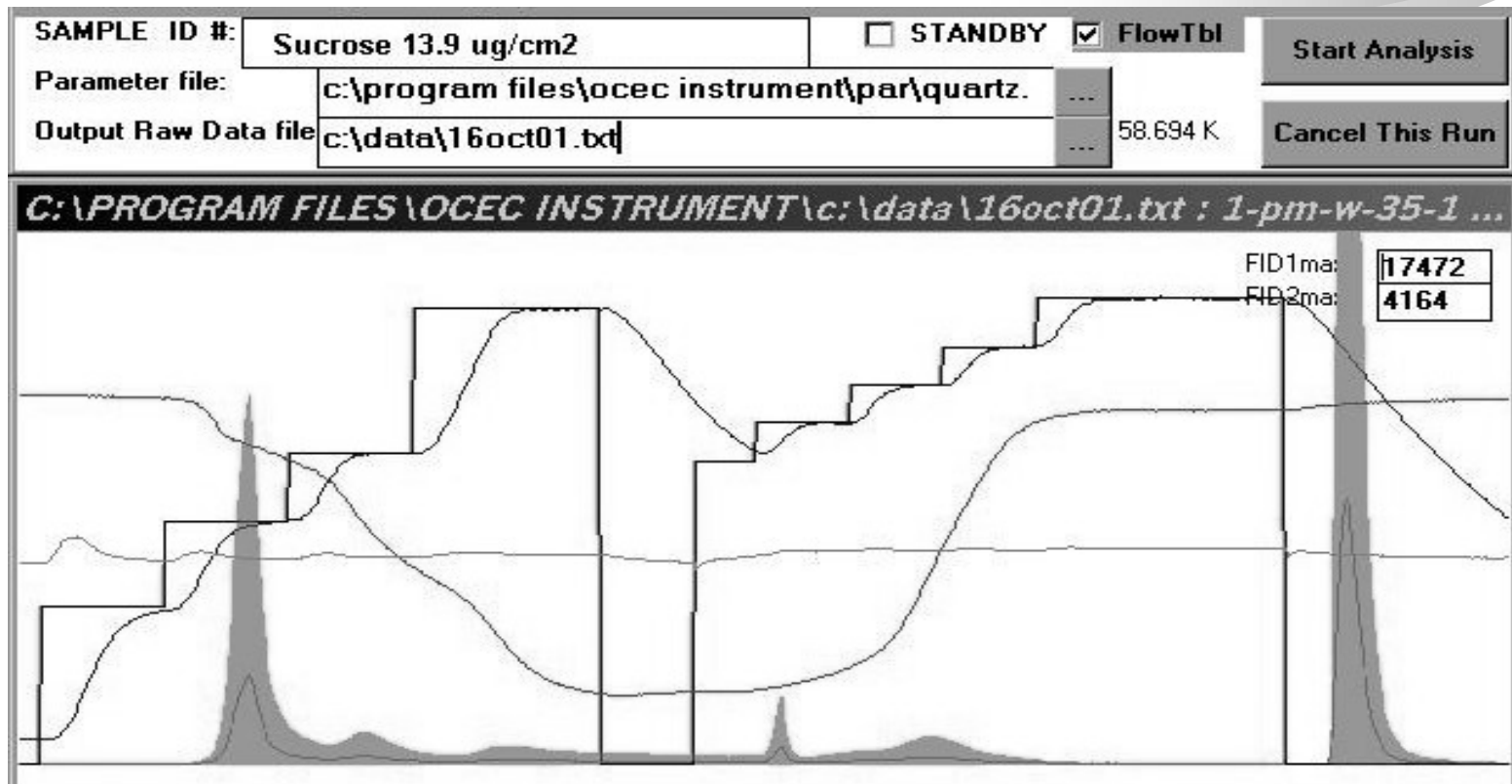
- OC is measured in He atmosphere.
- EC is the fraction of particulate carbon that is measured in O₂/He atmosphere when the laser signal is at the same level as the initial value.
- Laser R or T for pyrolysis correction

NIOSH Method



- Thermal volatilization, with pyrolytic correction by laser transmittance (T)
- 4 OC peaks: 250°, 400°, 550°, & 900°C in He (volatilization)
- 5 EC peaks: 600°, 675°, 750°, 825° & 920°C in 2% O₂/He (oxidation)

NIOSH thermogram

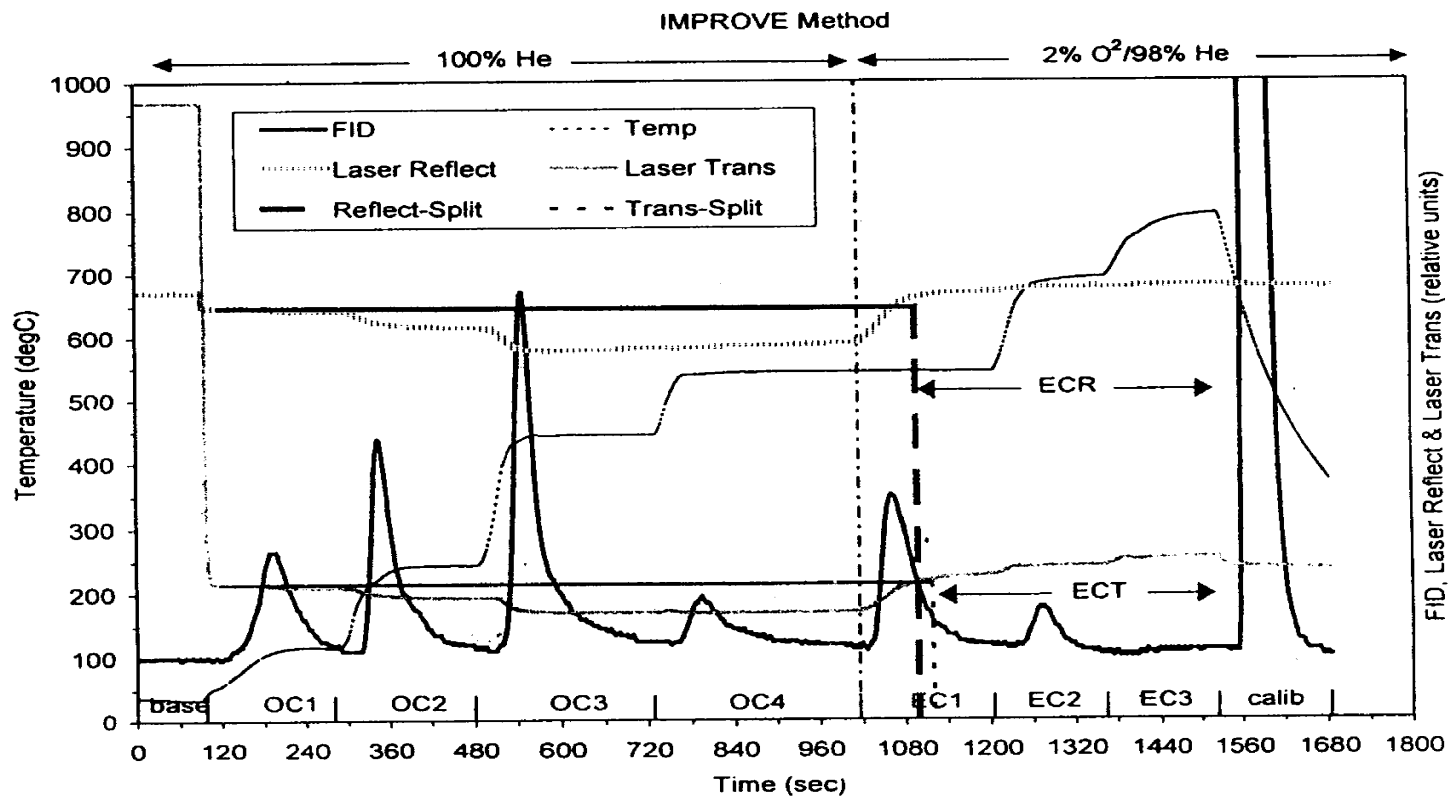


IMPROVE Method



- Thermal volatilization, with pyrolytic correction by laser reflectance (R)
- 4 OC peaks: 120°, 250°, 450°, & 550°C in He (volatilization)
- 3 EC peaks: 550°, 700°, & 800°C in 2% O₂/He (oxidation)

IMPROVE thermogram



Hypothesis for Difference in EC



- NIOSH $>700^{\circ}\text{C}$ for OC cause volatilization or oxidation of light absorbing carbon.
- Fe_2O_3 (& other metal oxides) as [O] donors or catalyst

Soot Generation

UC-Davis :

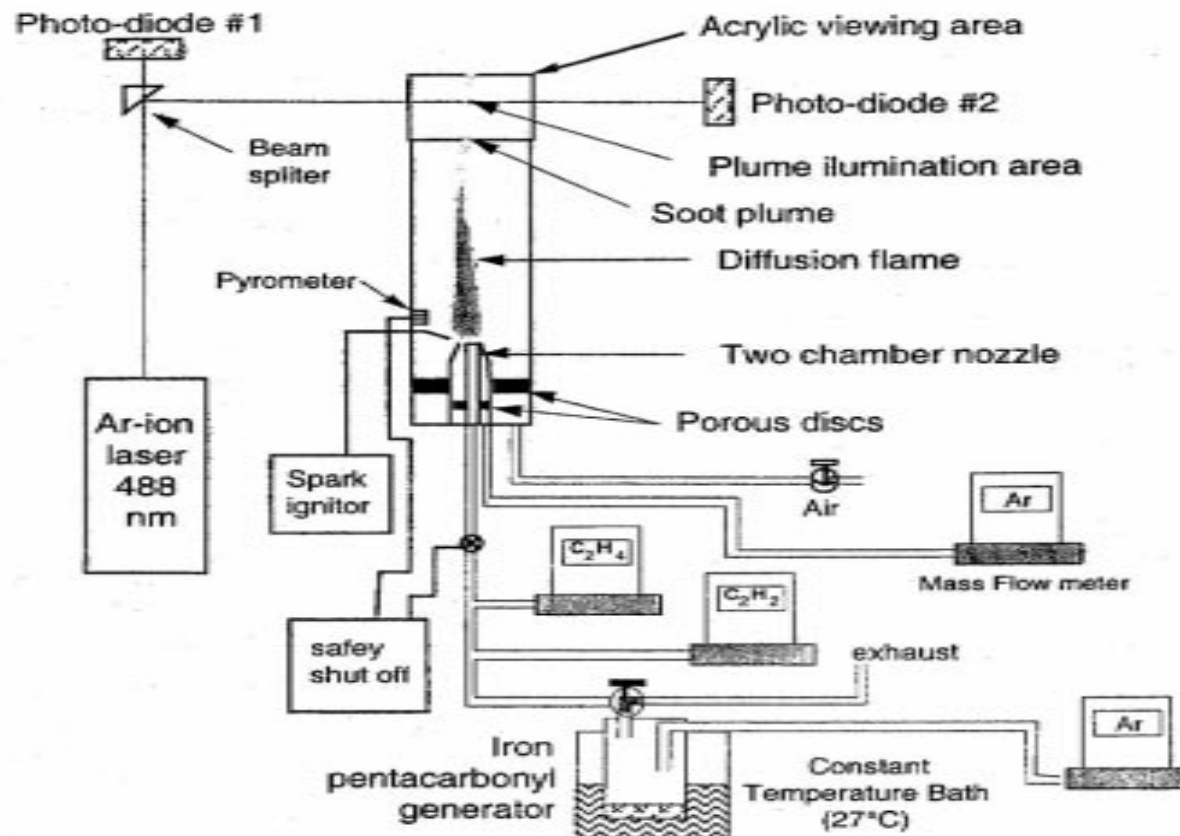


Figure 1. Diffusion flame apparatus.

Quartz filter, Fe oxides (~40nm)

- No acetylene in gas stream:



Quartz filter, Soot only

- No $\text{Fe}(\text{CO})_5$ in gas stream:



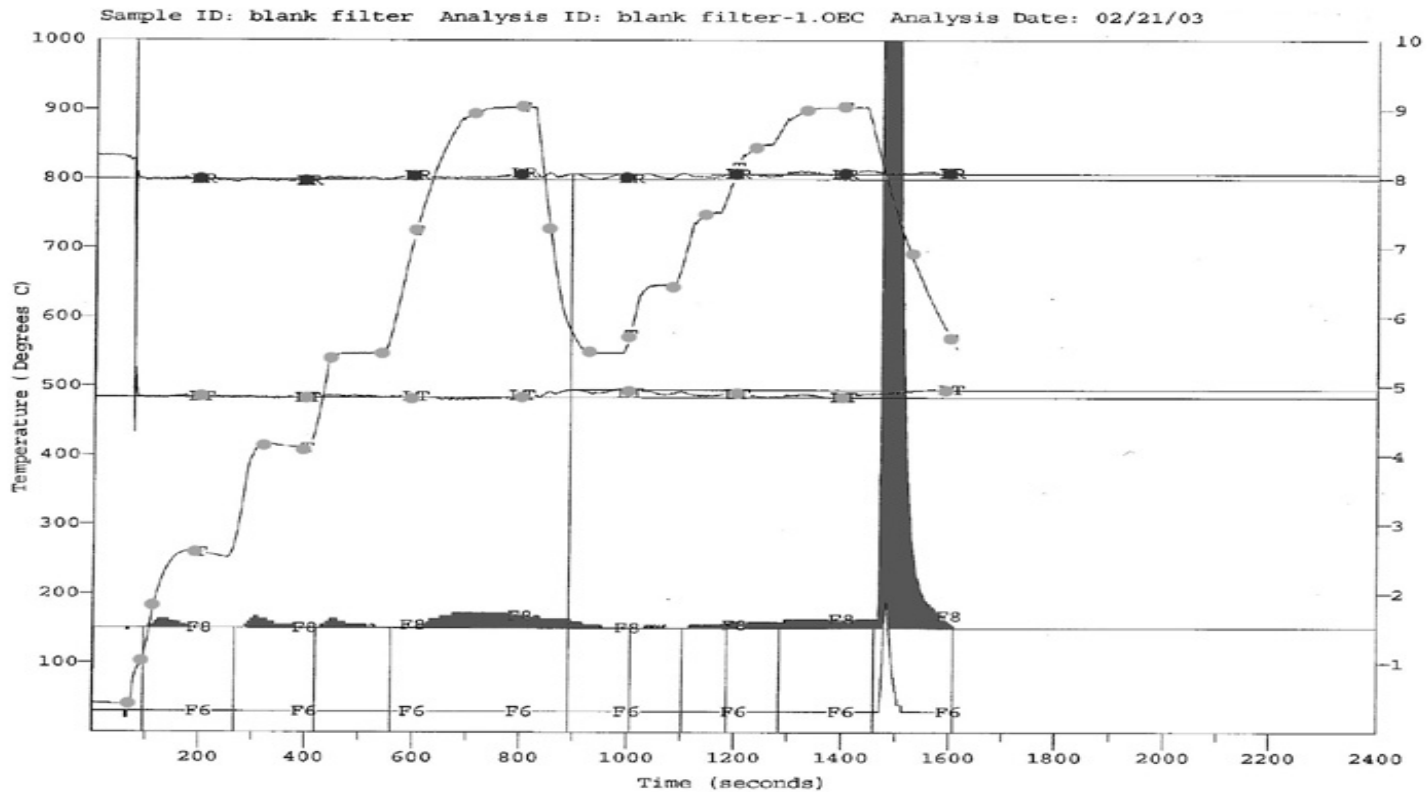
Quartz filter, Soot + Fe Oxides

- Ethylene + $\text{Fe}(\text{CO})_5$ + Acetylene:



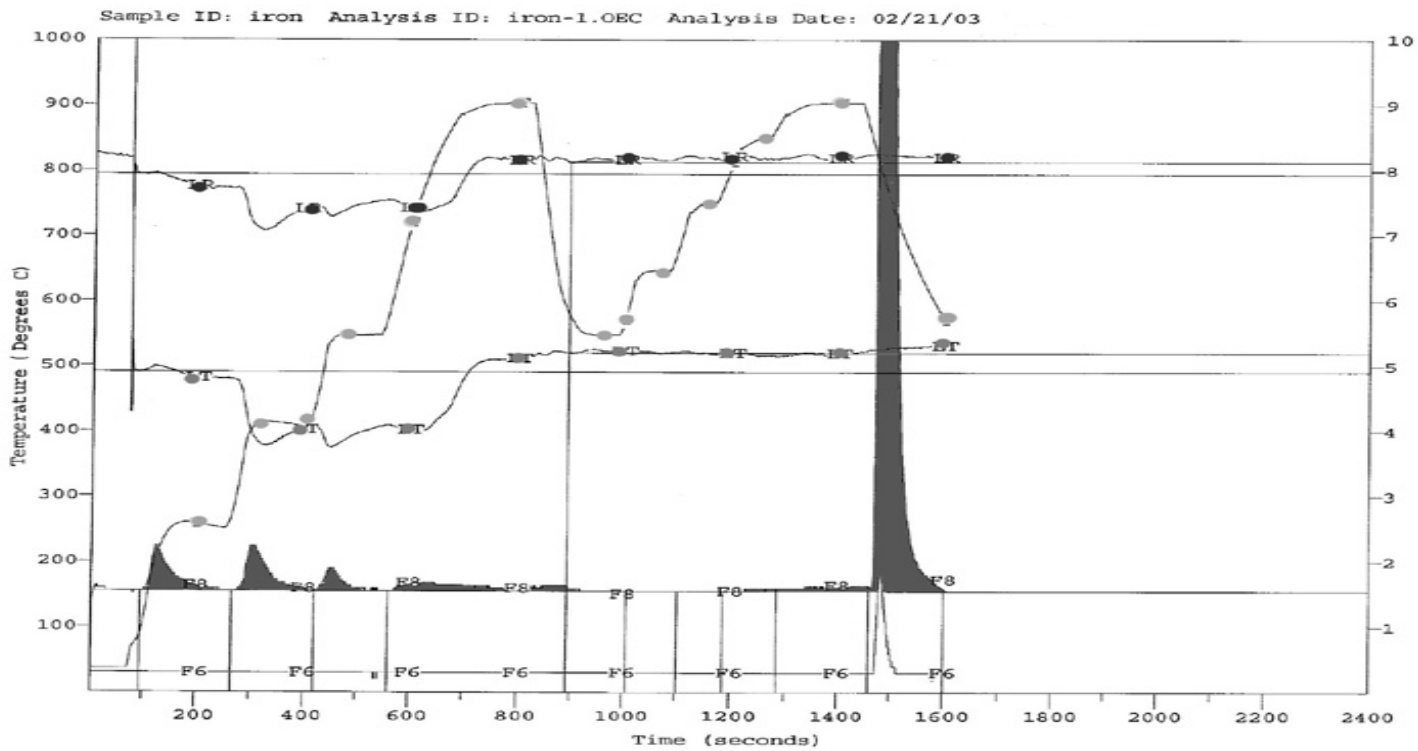
NIOSH - Filter Blank

- Flat laser R and T:



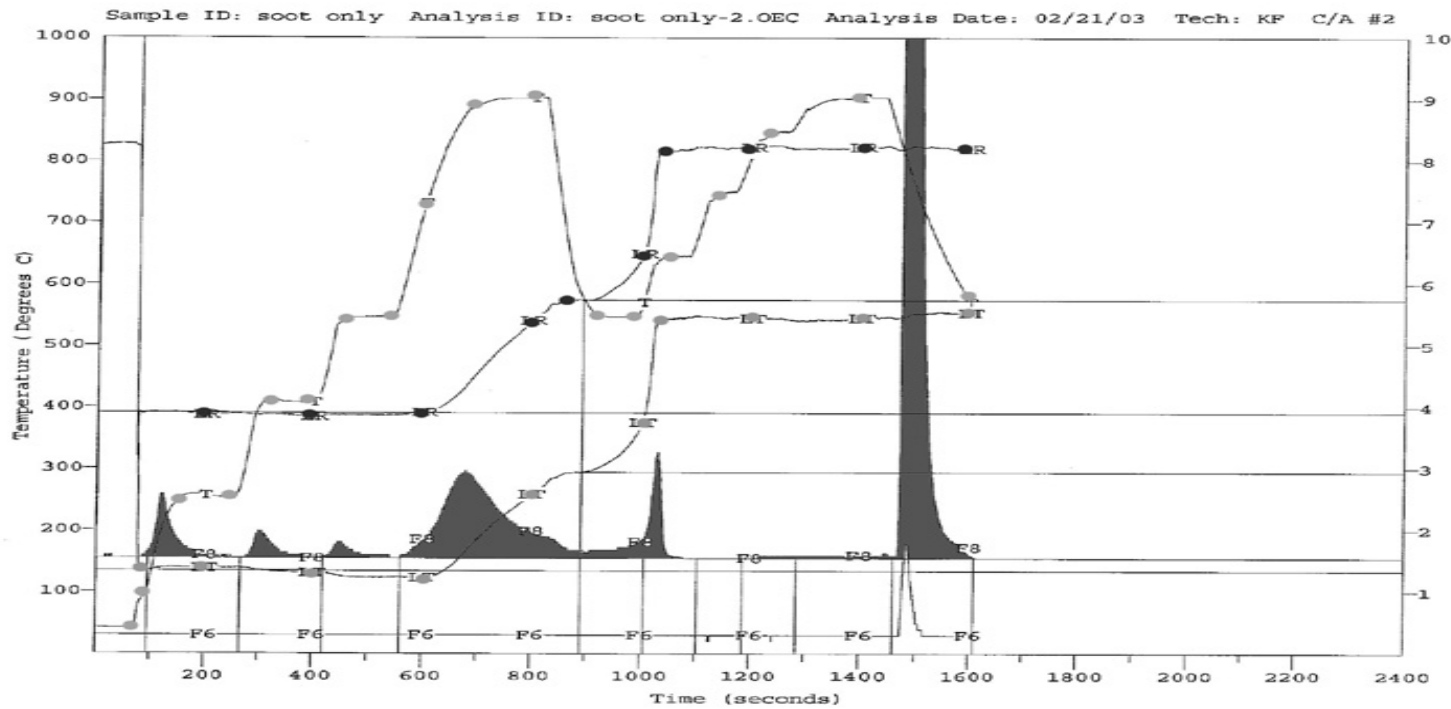
NIOSH - Fe Oxides

- Dipping of laser R and T up to $\sim 750^{\circ}\text{C}$
- No residue after analysis



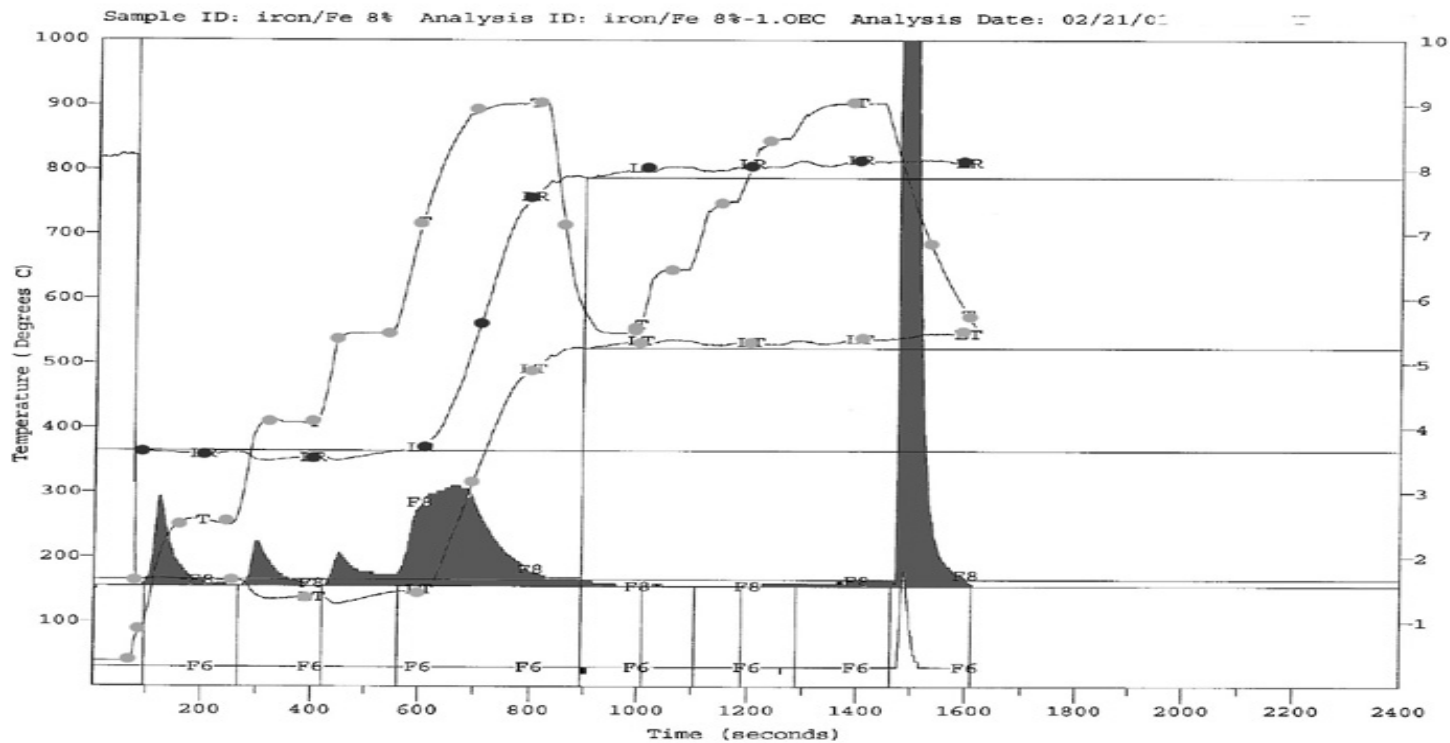
NIOSH - Soot only

- Flat laser R and T until $>700^{\circ}\text{C}$
- Light absorbing C in OC-4
- EC under O_2/He conditions



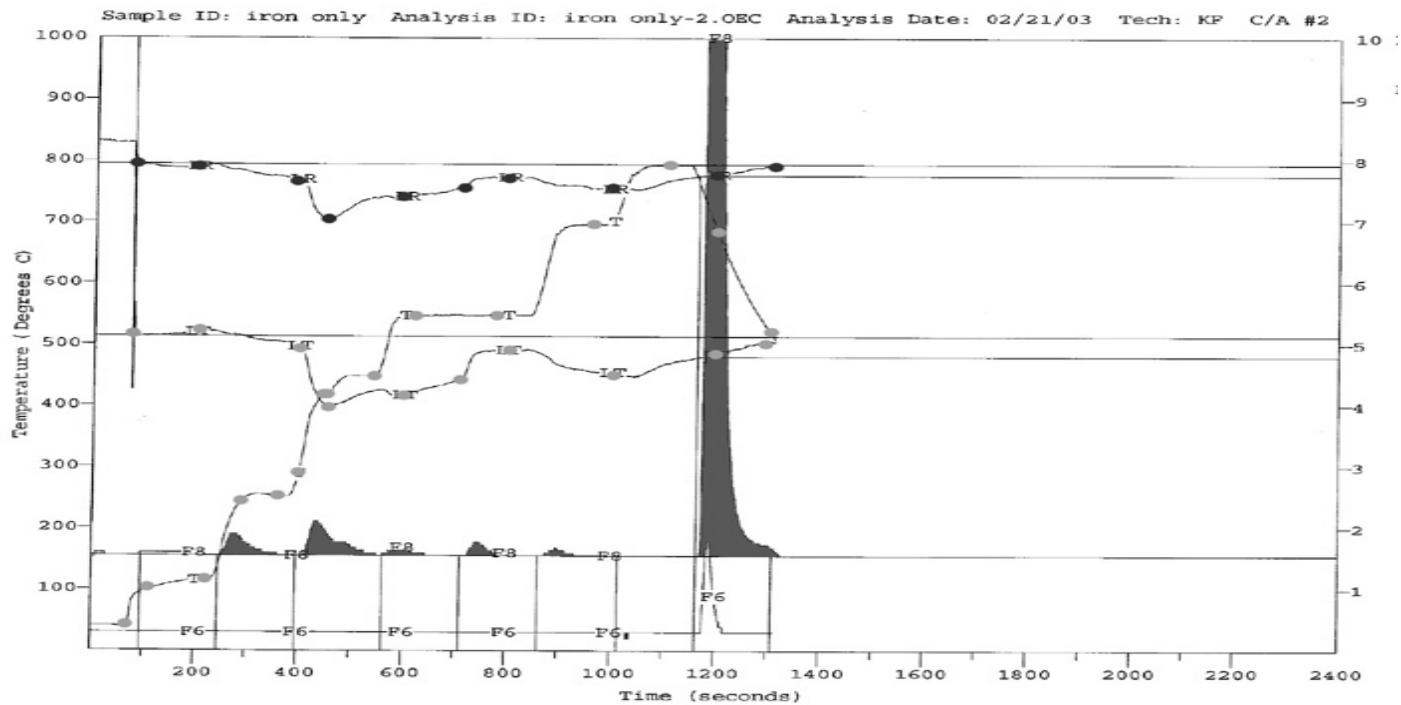
NIOSH - Soot with Fe Oxides

- Changes in laser R and T as in Fe-only filter
- No EC under O₂/He conditions - all as OC-4



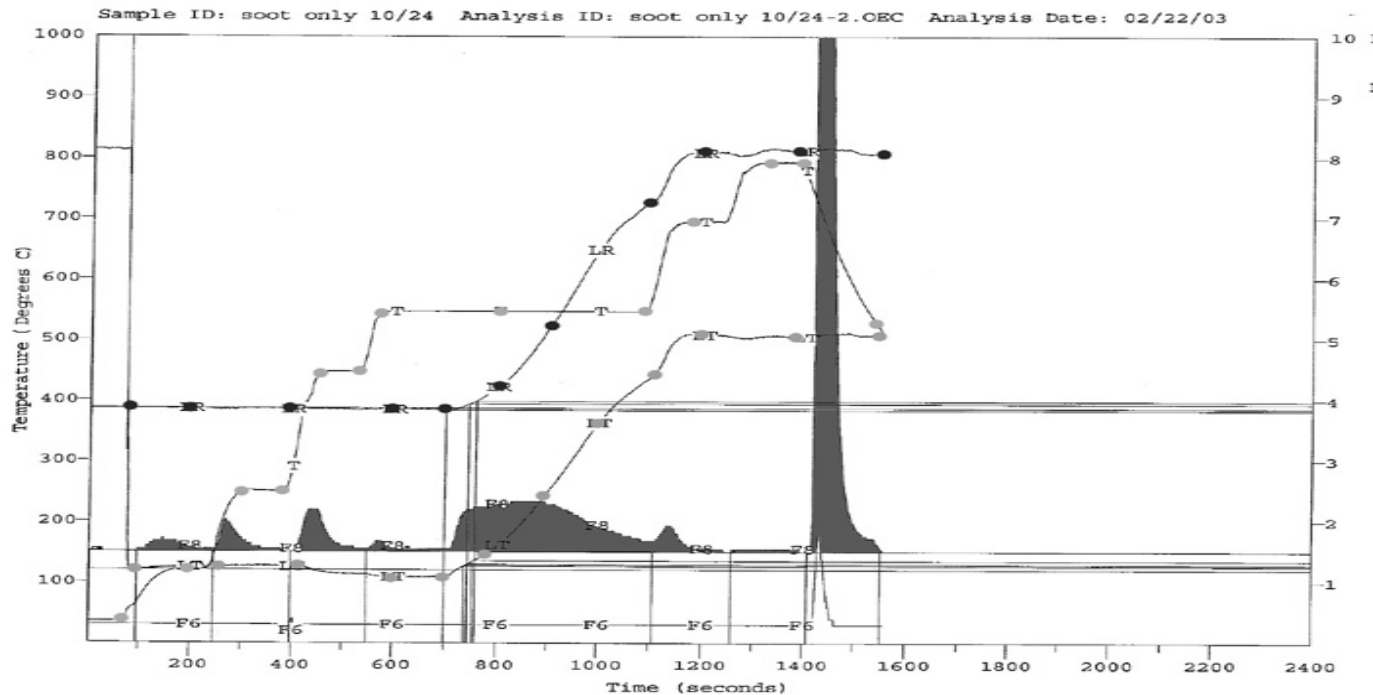
IMPROVE - Fe Oxides

- Laser R and T dip & rise in He & O₂/He
- Orange residue after analysis



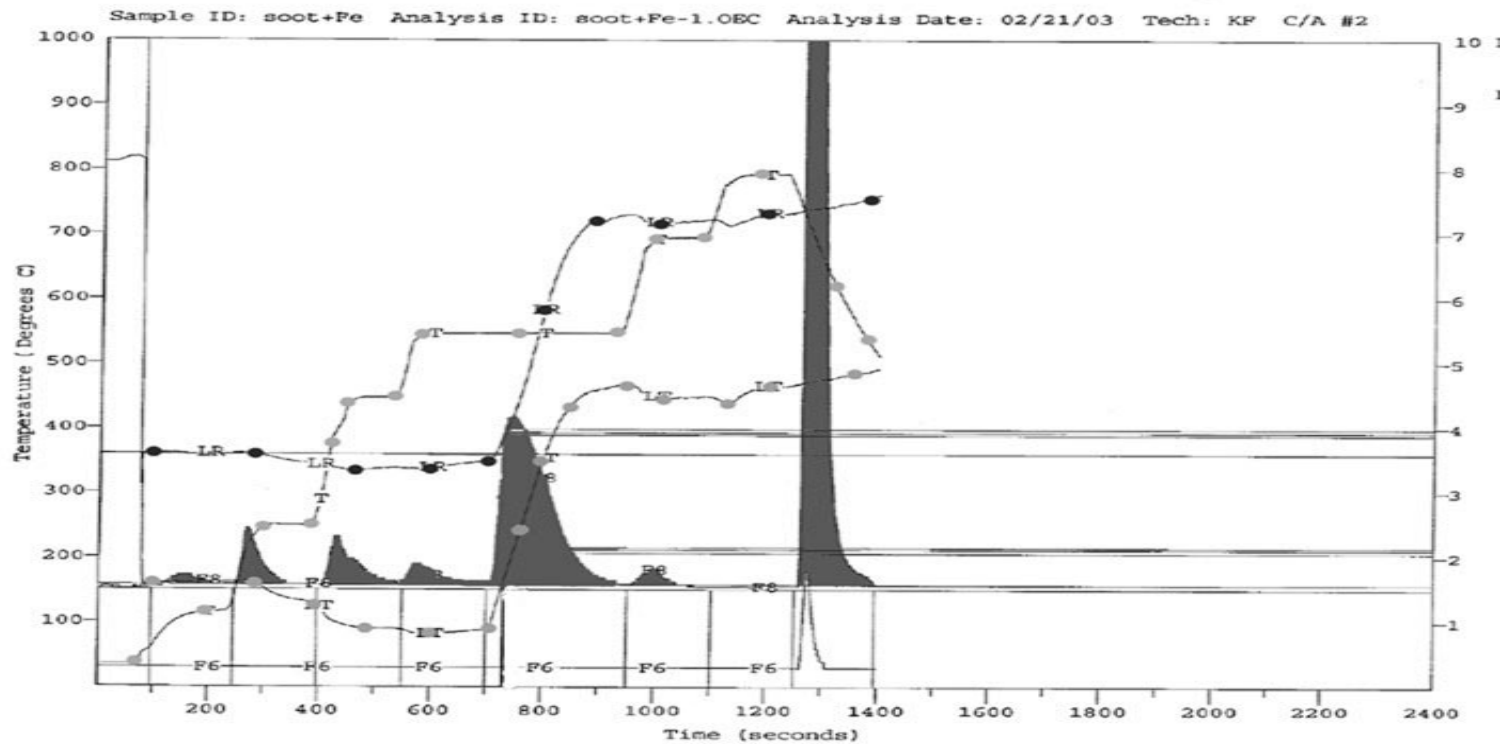
IMPROVE - Soot only

- Flat laser R and T until in O₂/He
- EC profile approximates NIOSH - 2 peaks
- Broad EC - slow [O] rate



IMPROVE - Soot + Fe Oxides

- Laser R and T show features of Fe-only filter
- EC profile - sharper EC-1 peak (catalysis)



Summary

Iron oxides in the sample

- attenuated laser signals in thermal optical techniques.
- May interfere with pyrolysis correction process.
- Oxidized EC at 700-900° as OC-4 in NIOSH.
- Catalyzed EC oxidation at 550° in O₂/He in IMPROVE.

Implications



- Other inorganic particles may have similar effects as iron oxides.
- Effects may be significant with dust storm samples.
- NIOSH results may be more appropriate to define EC by laser T signal only.