Impact of ferrocene on the structure of diesel exhaust soot

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We report on the structure of a set of diesel exhaust samples that were obtained from reference diesel fuel and diesel fuel mixed with ferrocene. The reference diesel soot shows a pronounced graphite-like microstructure and molecular structure, with a strong (002) graphite Bragg reflex and a strong aromatic C=C resonance at 285 eV. The mineral matter in the reference soot could be identified as Fe_2O_3 hematite. The soot from the diesel with ferrocene has an entirely different structure and lacks significantly in graphite-like characteristics. NEXAFS spectra of such soot barely show aromatics but pronounced contributions from aliphatic structures. WAXS patterns show almost no intensity at the Bragg (002) reflection of graphite, but a strong aliphatic γ-side band. Owing to the nanometer size of particles and the fact, that the relatively high surface energy enters the thermodynamic equations for crystal grwoth, the iron from the ferrocene transforms to Fe_2O_3 maghemite, rather than the bulk form hematite.

Our research team has recently published a number of studies on the morphology and molecular structure of diesel exhaust particulate matter (diesel soot) with results obtained from X-ray and synchrotron radiation based characterization techniques. Diesel soot is frequently believed to be a major constituent of carbonaceous airborne particulate significant matter in the environment, known to cause adverse health effects and suspected to have a impact on global climate change. It is the unwanted solid carbonaceous byproduct of combustion of diesel fuel, in particular from diesel engines that power heavy equipment, cars, trucks, busses, railway locomotives and maritime vessels. The size of soot particles is an important quantity both for access to lung and for abatement devices in vehicles.

Experiments with ferrocene as a fuel additive have been reported before on methane and ethylene flames, and more recently on diesel fuel. Surprisingly, when we mix diesel fuel with ferrocene, the emerging soot lacks significantly in graphitic characteristics. Our WAXS and NEXAFS data indicate clearly that ferrocene prevents the carbon during diesel combustion from forming aromatic structures with double bonds, with a drastic impact on the formation of soot particulates. This seems a surprising finding since ferrocene is known to promote graphitization and used for such in industrial applications. The aim of the current study is to show how ferrocene, when added to diesel fuel, modifies the crystallite size and structure of the soot particles.

In summary, adding ferrocene to diesel fuel has a dramatic impact on soot formation processes and on the molecular structure and nano-structure of soot. The graphitic structure of soot is dramatically altered in favor of aliphatic structures. According to the WAXS data, aromatic graphene sheets still seem to be present, but at a very small stack height. The majority of the ordered carbon comes in aliphatic structures. The iron persists as maghemite, but in significantly greater quantity. The carbon NEXAFS data support findings about the carbonaceous material, in particular the formation of aliphatic structures during combustion in the presence of ferrocene. Higher engine speeds make a significant difference on the graphite- like carbon formation, this is, at higher engine speeds ferrocene suppresses formation of the nanocrystalline graphite-structures, and enhances the aliphatic structures. This holds at least for the speed range studied here: 1500–2200 rpm. The soot from non-doped fuel seems to be largely unaffected by the change in speed. A similar effect has been observed with oxygenated fuels. Graphite is a thermodynamically and kinetically stable form of carbon that can persist for long times in the environment, the atmosphere and even in the universe. It resists more to oxidation than other forms of solid carbon. In contrast, aliphatic carbon can be much more easily oxidized. Since mixing diesel fuel with ferrocene generates soot with less graphitic but more aliphatic structure, this may be a route to accelerating oxidation of soot. However, with respect to the respiratory toxicity of ferrous oxides, which can be present in the soot and in the ash, subsequent exhaust filtration to prevent release of toxic agents into the atmosphere, is mandatory.

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References

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[3] Garry S, Nesslany F, Aliouat EM, Haguenoer JM, Marzin D. Mutat Res–Gen Toxicol Environ Mutag 2004;563(2):117–29.
[4] A. Braun, N. Shah, F.E. Huggins, G.P. Huffman, K.E. Kelly, A. Sarofim, S.B. Mun, S.N. Ehrlich, *Impact of ferrocene on the structure of diesel exhaust soot as probed with wide-angle X-ray scattering and C(1s) NEXAFS spectroscopy*, Carbon, in press, doi:10.1016/j.carbon.2006.05.051.
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See also Poster # 57 „Traffic Exhaust or Wood Smoke ?“
by M. Heuberger-Vernooij et al.

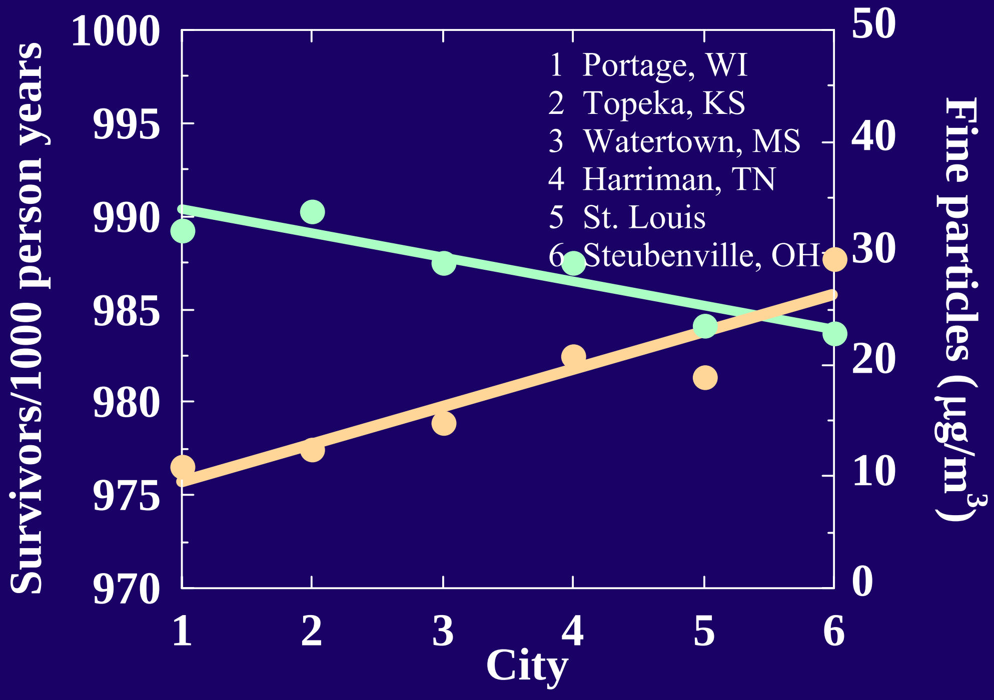
This talk will be presented again this week at
EMPA Dübendorf, LA 373
14:00, Friday, August 25, 2006

Airborne fine particulate matter - *Feinstaub*

Direct correlation: Particle concentration ~ Mortality ratio

Suspected role in global climate forcing

"The 6 Cities Study"
D.W. Dockery et.al., New Engl. J. of Medicine (1993):329/24 1753-1759.



Soot takes center stage
W.L. Chameides, M. Bergin;Science (2002) 297 2214

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- J. Macdonald, Lovelace Respiratory Research Institute
- S. di Stasio, Istituto Motori, Napoli, Italy
- A. Kubatova, EERC Univ. of North Dakota

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Motivation

Interest in iron-catalyzed combustion of diesel fuel, such as by ferrocene$(C_5H_5)_2Fe$

Purpose: improve exhaust aftertreatment

promote oxidation of diesel soot trapped in a particulate filter

Significant effect on size + amount of particle emissions:

- PM mass substantially reduced, but larger number of ultrafine particles
- Size range of PM greatly shifted towards smaller particles

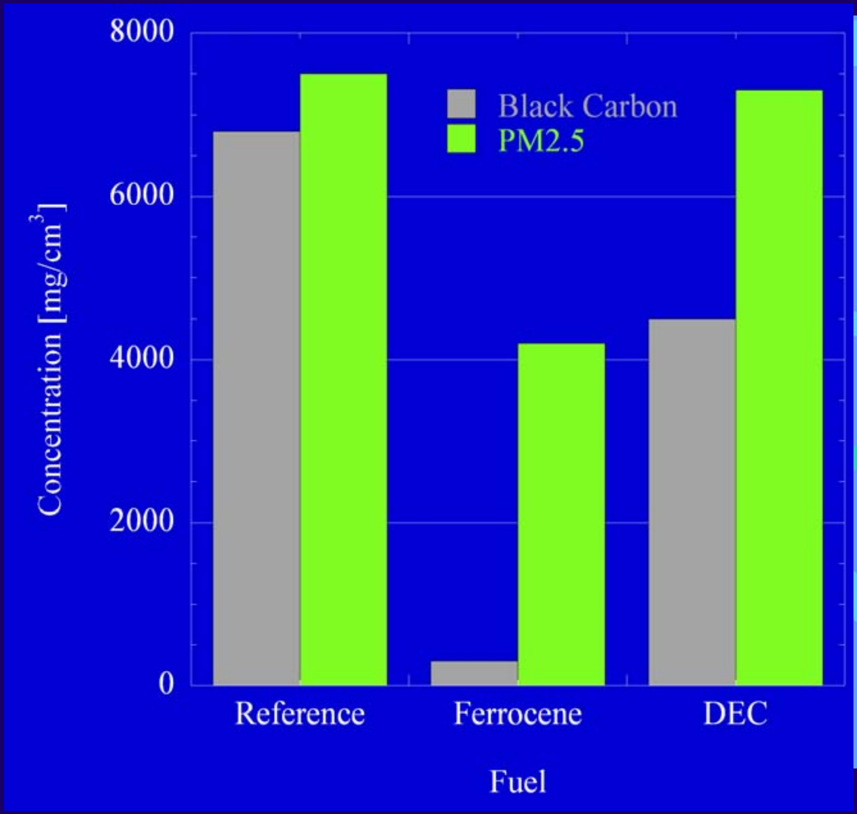
Here:

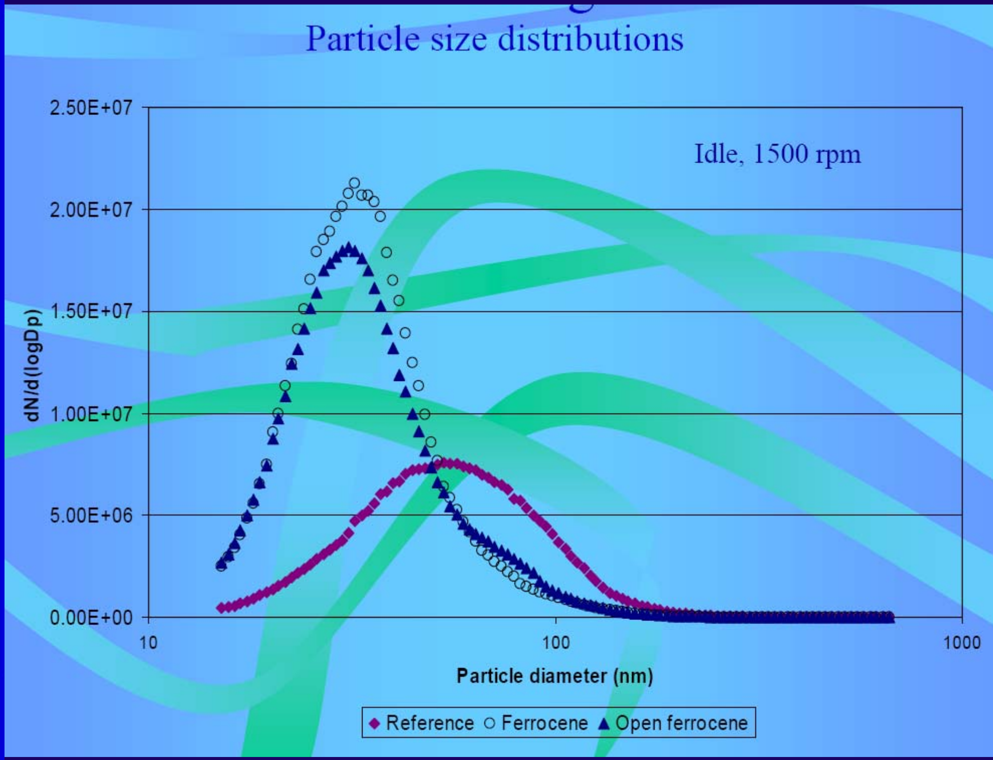
Investigation of soot molecular structure and nano-/microstructure with X-ray spectroscopy and X-ray scattering

References:

- Burtscher et al., Characterization of particles in combustion engine exhaust. J Aerosol Sci 1998;29(4):389–96
- SAE papers by P. Richards et al., Octel Company

Particle Size & Concentrations



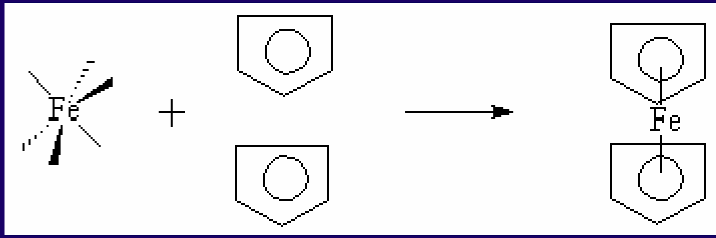


Courtesy: Kerry E. Kelly Univ.of Utah

Soot Sample Generation

- Diesel test engine facility at the University of Utah
- 2-cylinder, 492 ccm, direct injection Kubota model Z482B, rated at 10.8 kW brake horse power at 3600 rpm
- 50:50 mixture of Chevron/Phillips reference fuels T-22, U-15
- operated idle at 1500 rpm
- load conditions 1800 rpm and 3 ft-lb, and 2200 rpm, 6 ft-lb
- a reference fuel, and the reference fuel plus 1000 ppm ferrocene
- oxygenates added, such as DEC etc.

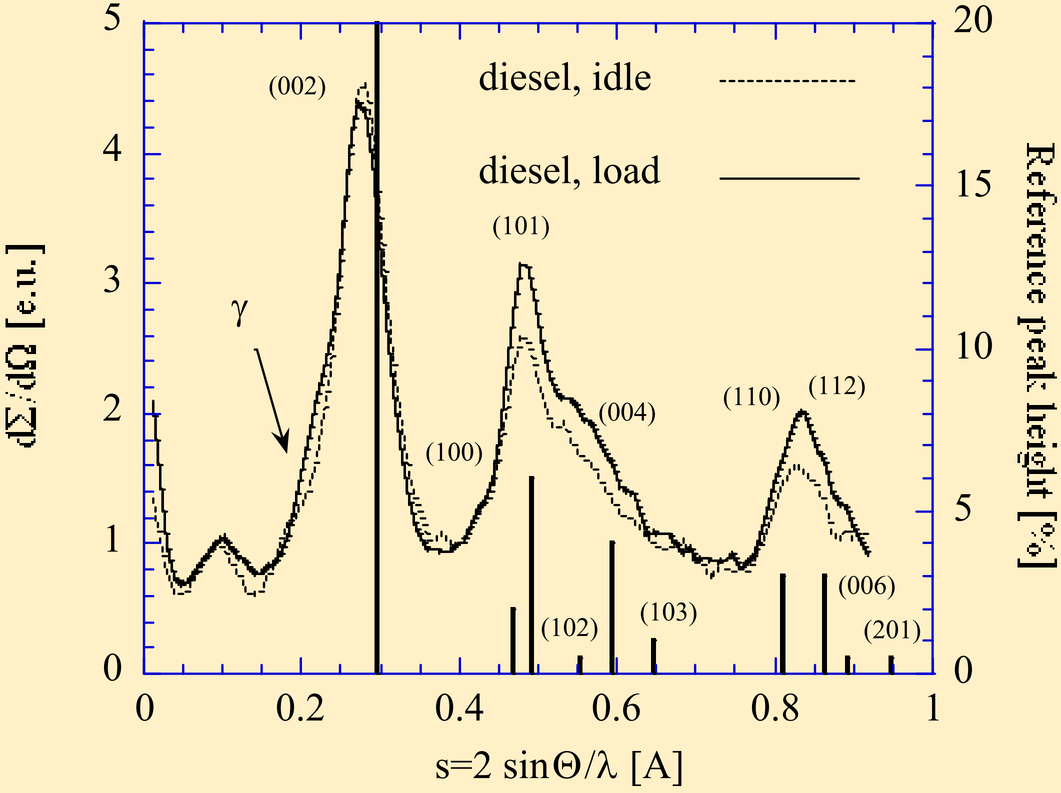
Ferrocene
Metastable molecule = **iron** atom sandwiched between two cyclopentadienyl rings.



Dramatic decrease of C=C bond contribution in soot; increase in aliphatics *aka XRD*

WAXS - Wide-angle X-ray Scattering

My global statement: Diesel soot looks „graphite-like“ in WAXS.



WAXS = Similar to X-ray diffraction, but diffuse scattering. Not crystallography, but profile analysis and information on microsctructure.

WAXS curves of *idle* and *load* diesel soot display some differences.

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Soot from oxygenated fuels

Deconvolution into graphitic and aliphatic contributions yields crystallite sizes and aromaticity

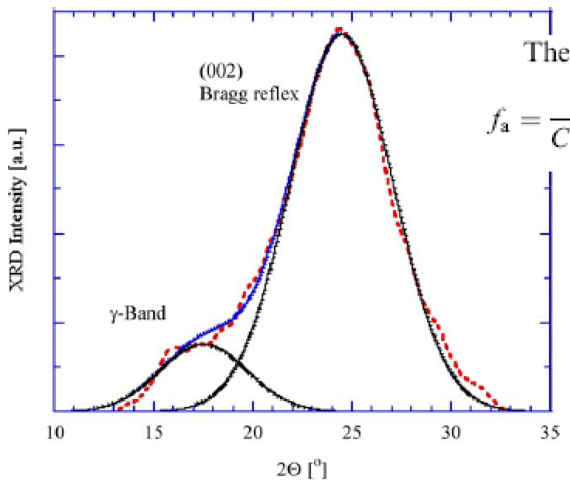
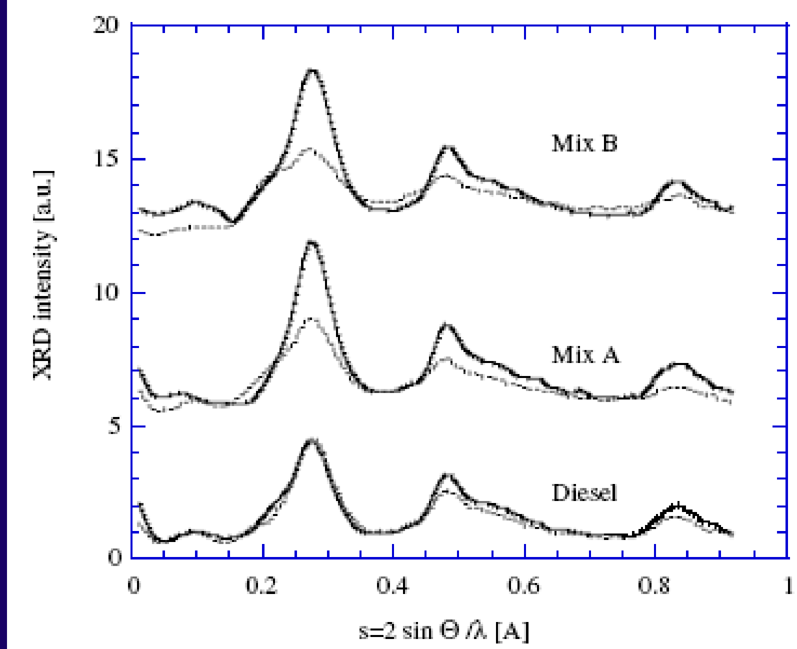


Fig. 6. Deconvolution of graphite (002) Bragg reflex and γ-band.

The *aromaticity* can be defined as

$$f_a = \frac{C_{ar}}{C_{ar} + C_{al}} = \frac{A_{(002)}}{A_{(002)} + A_\gamma}$$

$$w = \frac{a \cdot \lambda}{b \cdot \cos(\Theta)}$$



Systematic changes can be quantified.

Structural changes in idle / load soot more drastic when oxygenates added.

Oxygenates + load = larger crystallites

Table 4
Comparison of crystallite sizes determined from WAXS

Sample	$L_c(002)$ [Å]	$L_a(110)$ [Å]	$L_a(112)$ [Å]	Ordered [%]
Diesel, idle	11.10	8.67	17.24	62.0
Diesel, load	11.78	10.48	16.68	70.0
Mix B, idle	10.18	6.96	13.24	53.6
Mix B, load	12.86	8.64	14.92	64.6
Mix A, idle	8.64	8.93	6.24	54.2
Mix A, load	10.78	16.30	11.19	58.8

X-ray scattering and spectroscopy studies on diesel soot from oxygenated fuel under various engine load conditions

Carbon 43 (2005) 2588–2599

Ferrocene can *dramatically* alter soot characteristics

Diesel soot looks „graphite-like“
(*this* was *my global statement*) –
unless you add ferrocene

Changing engine settings or adding oxygenates can alter the structure and thus the WAXS patterns.

Most dramatic changes observed when ferrocene added to the fuel. Soot lacks entirely graphitic characterstics !

No graphitic structure.
Strong aliphatic side band.
Strong mineral peaks.

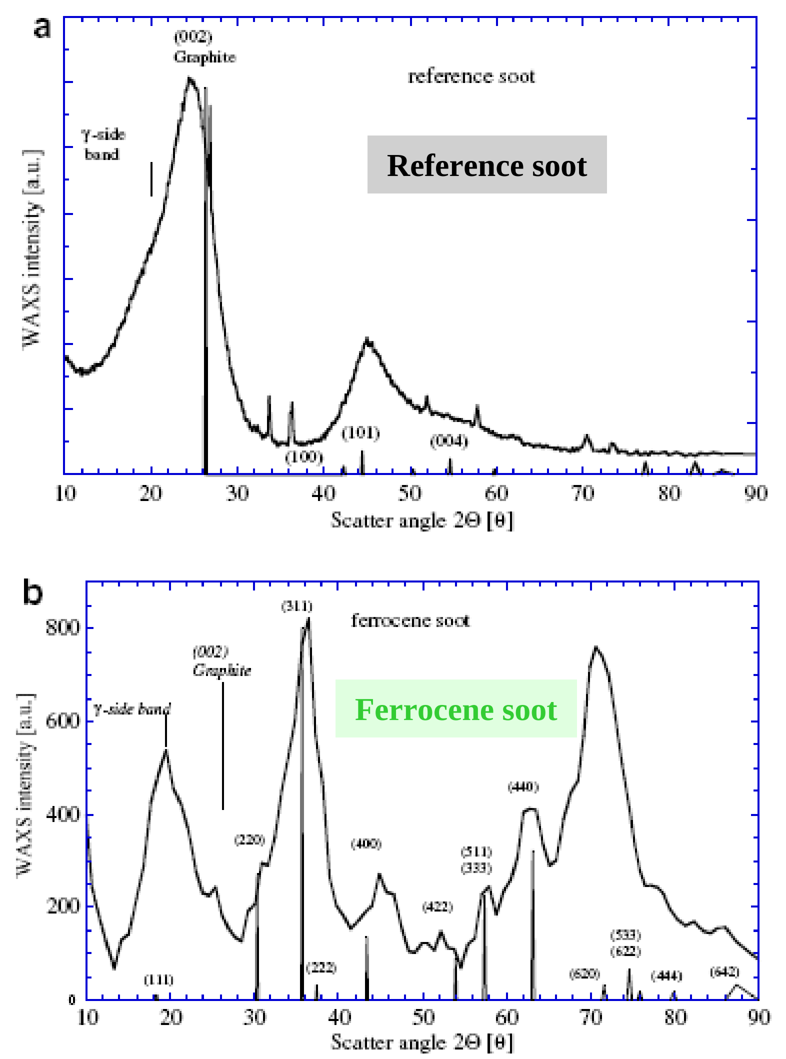


Fig. 1. WAXS pattern of reference soot (top, 6 ft-lb load, 2200 rpm) and ferrocene soot (6 ft-lb load, 2200 rpm). Reference soot contains indexed Bragg reflexes from graphite. Ferrocene soot contains indexed Bragg reflexes from maghemite.

Carbon, in press; doi:10.1016/j.carbon.2006.05.051

Quantitative analysis of Fe

Reference soot: Inorganic crystalline phase hematite $\alpha\text{-}Fe_2O_3$
Crystallites very coarse, size around 250 nm.
Source: likely engine wear-off

Ferrocene soot: Hematite $\alpha\text{-}Fe_2O_3$, very broad peaks, → phase assignment difficult.
Magnetite Fe_3O_4 could not be ruled out on basis of WAXS alone.

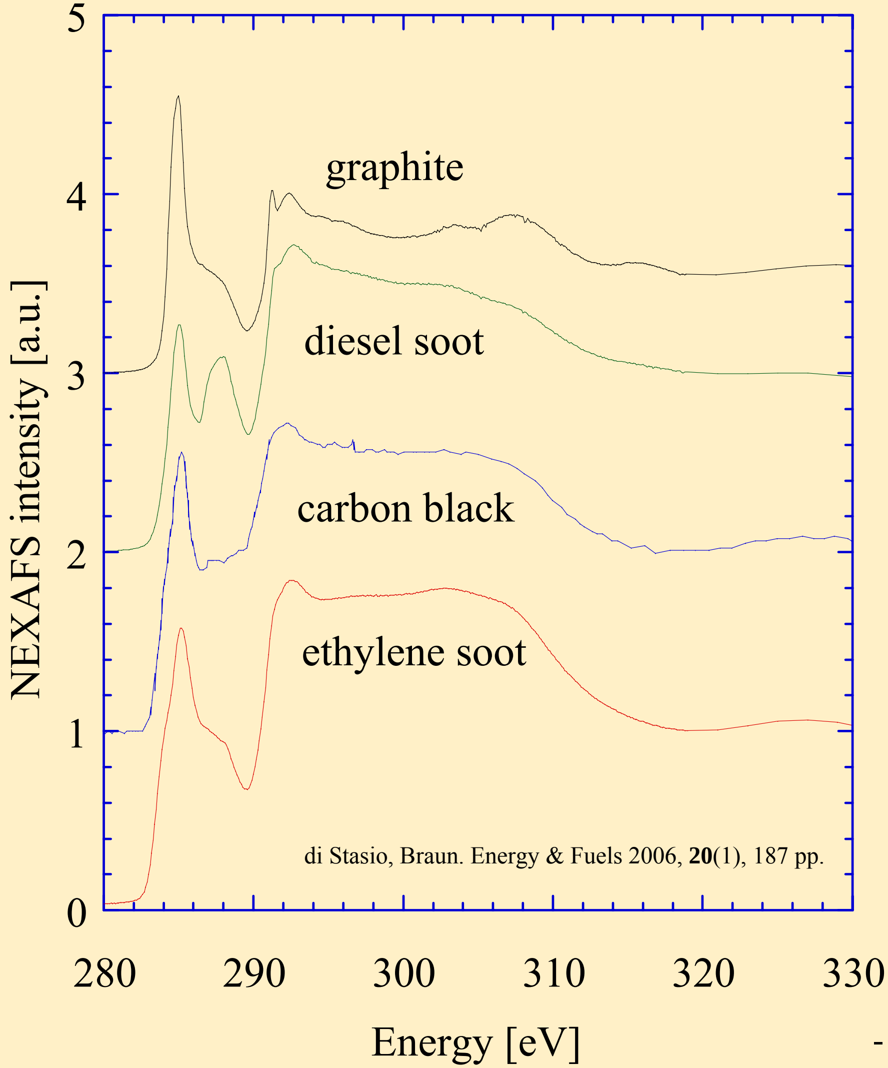
But Fe (L2,L3)-NEXAFS show Fe^{3+} prevalent species → no magnetite !

Controversial picture. Clarification when looking at nanosize-induced polymorphs.
[1] Nanoparticles have high surface energies. *Nanoscale* Fe-oxide with Fe^{3+} ***likes*** to be „Maghemite".

- Maghemite $\gamma\text{-}Fe_2O_3$ nanoparticles, 1.5 nm in large quantity from ferrocene
- Hematite $\alpha\text{-}Fe_2O_3$ submicron particles from iron wear of engine

[1] reviews on thermochemistry by A. Navrotsky, UC Davis, American Mineralogist 2003, 88, 846-854.
Detailed Moessbauer study on these samples supports WAXS+NEXAFS results, to be published soon.

C(1s) NEXAFS spectroscopy



- Element specific

• Sensitive to molecular structure

• Soot shows strong peak at 285 eV from C=C double bonds such as graphite or PAH

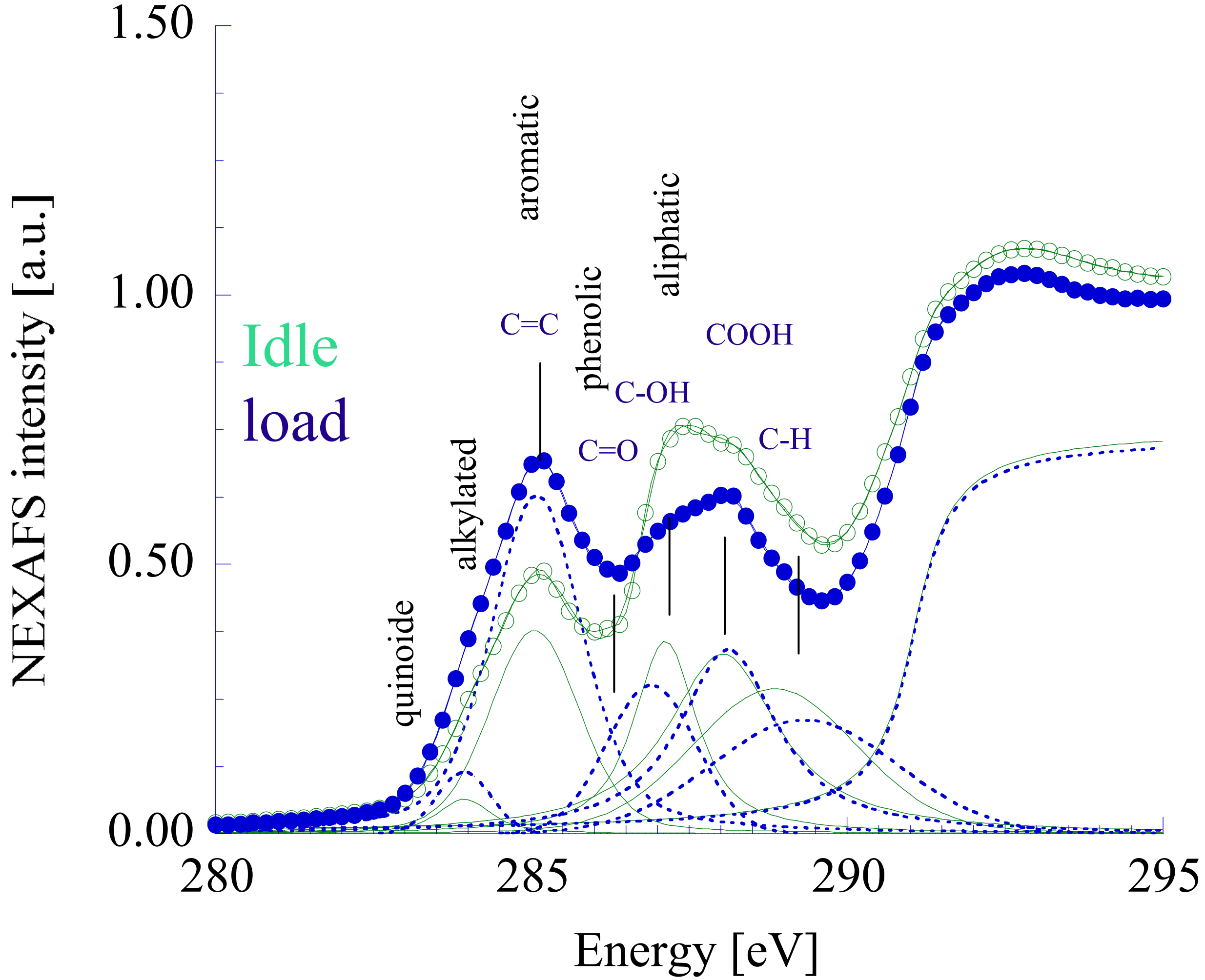
• Surface functional groups, SOM

• Goal: molecular fingerprint for source attribution

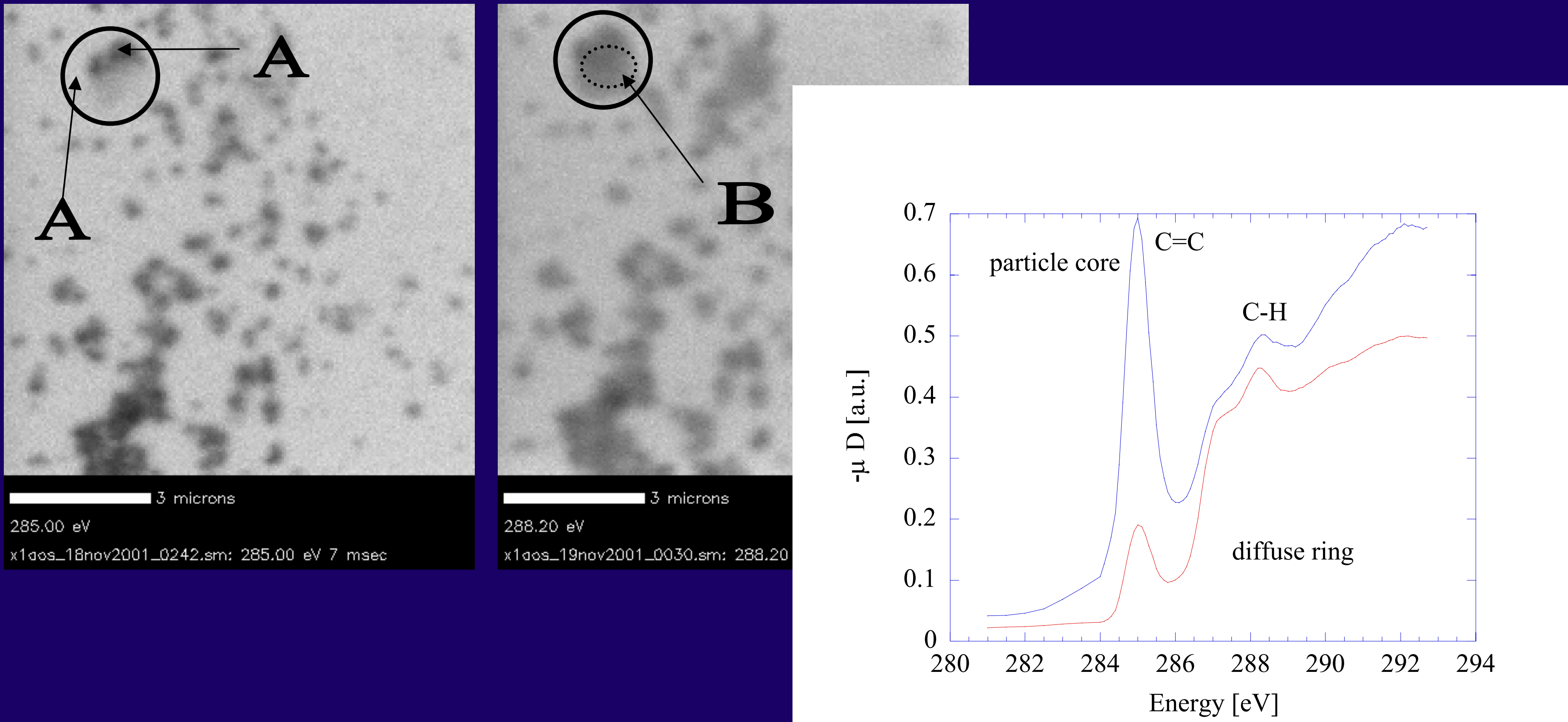
- J. Stöhr, NEXAFS Spectroscopy, Springer Verlag, 1992, New York.
- S.C.B. Myneni, Rev. Miner. Geochem. 49 (2002) 485.
- A. Braun, J. Env. Monitoring., 2005, **7**(11), 1059-1065.

NEXAFS of idle and load diesel soot

Load soot contains more graphitic material. Idle soot contains significantly more aliphatic material, incl. volatiles, residual oil, fuel, soluble organic matter, … .



Scanning Transmission X-ray Micro-spectroscopy

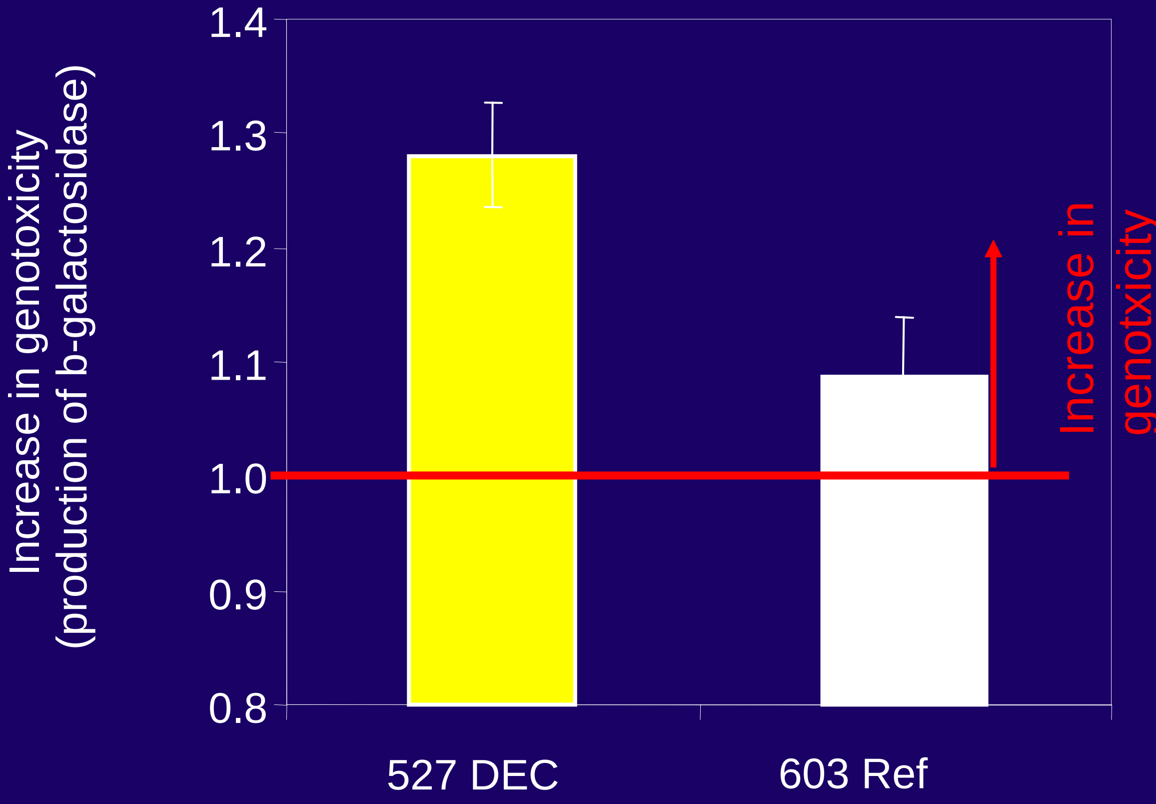


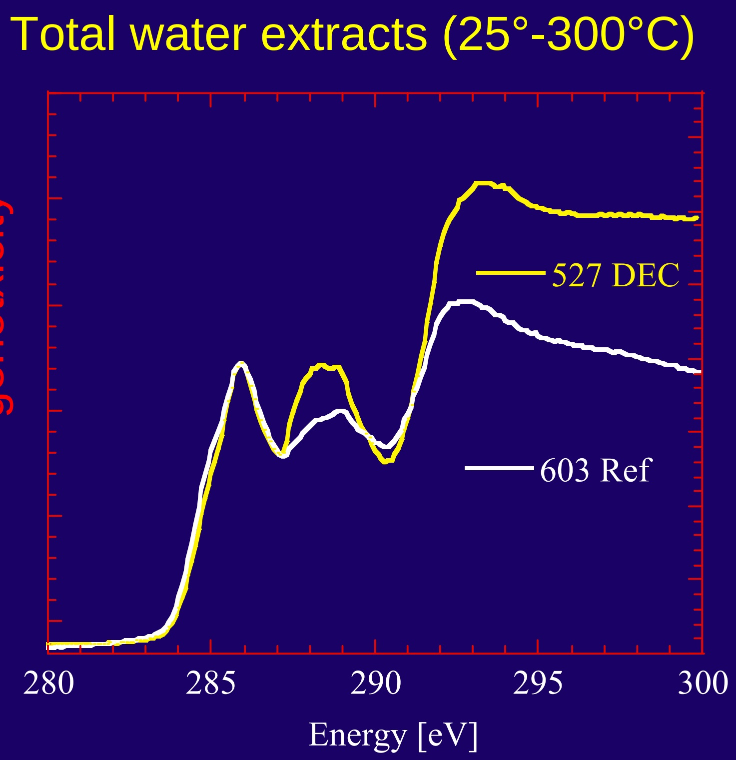
STXM is X-ray microscopy with chemical contrast

Resolution: ~ 100 nm, and chemical contrast of ~ 0.1 eV

Study of fine diesel particulate matter with scanning transmission X-ray spectroscopy.
Fuel (2004) **10** 7/8 997-1000.

Diesel exhaust PM generated with oxidizer has higher genotoxicity

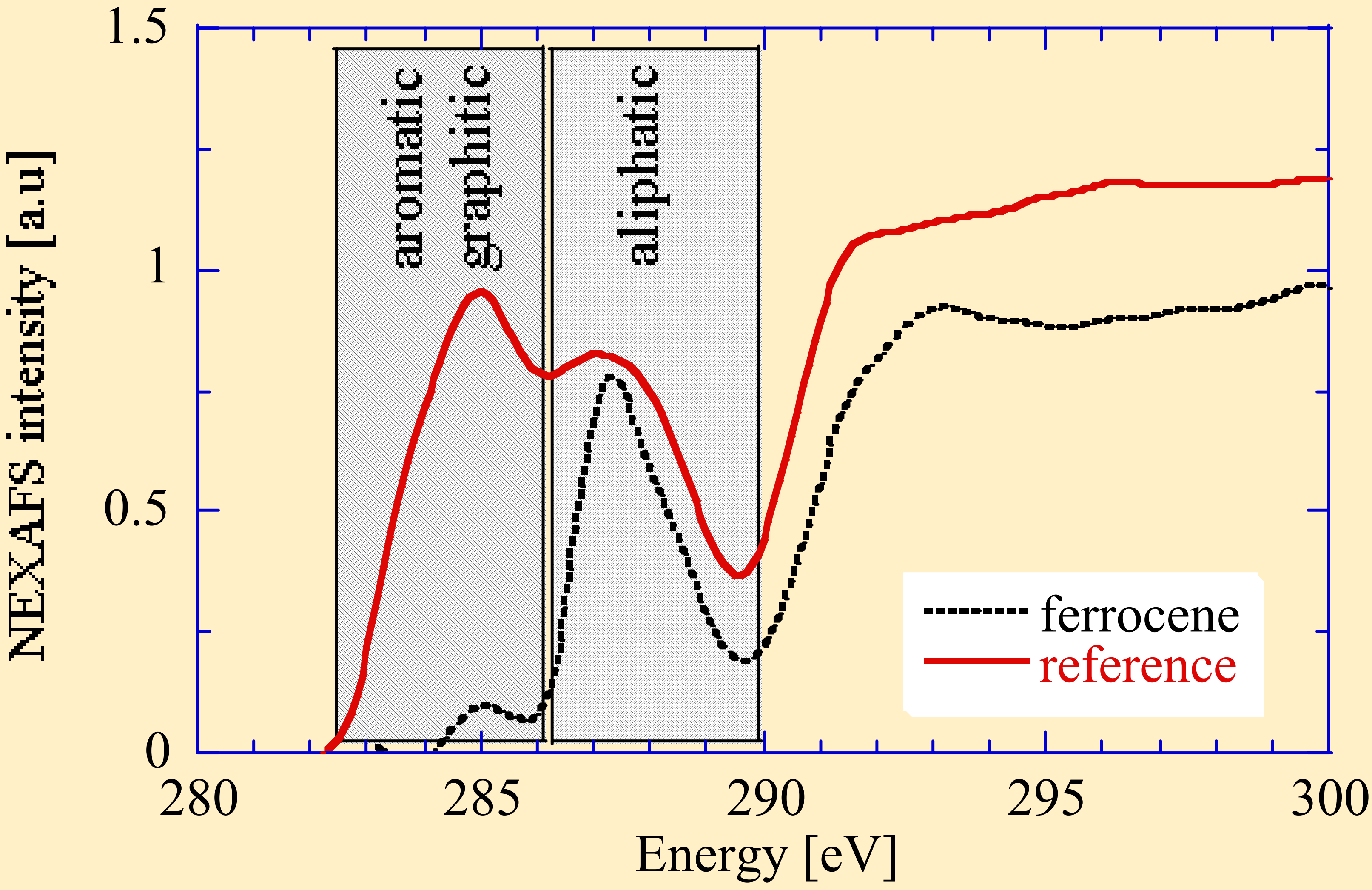




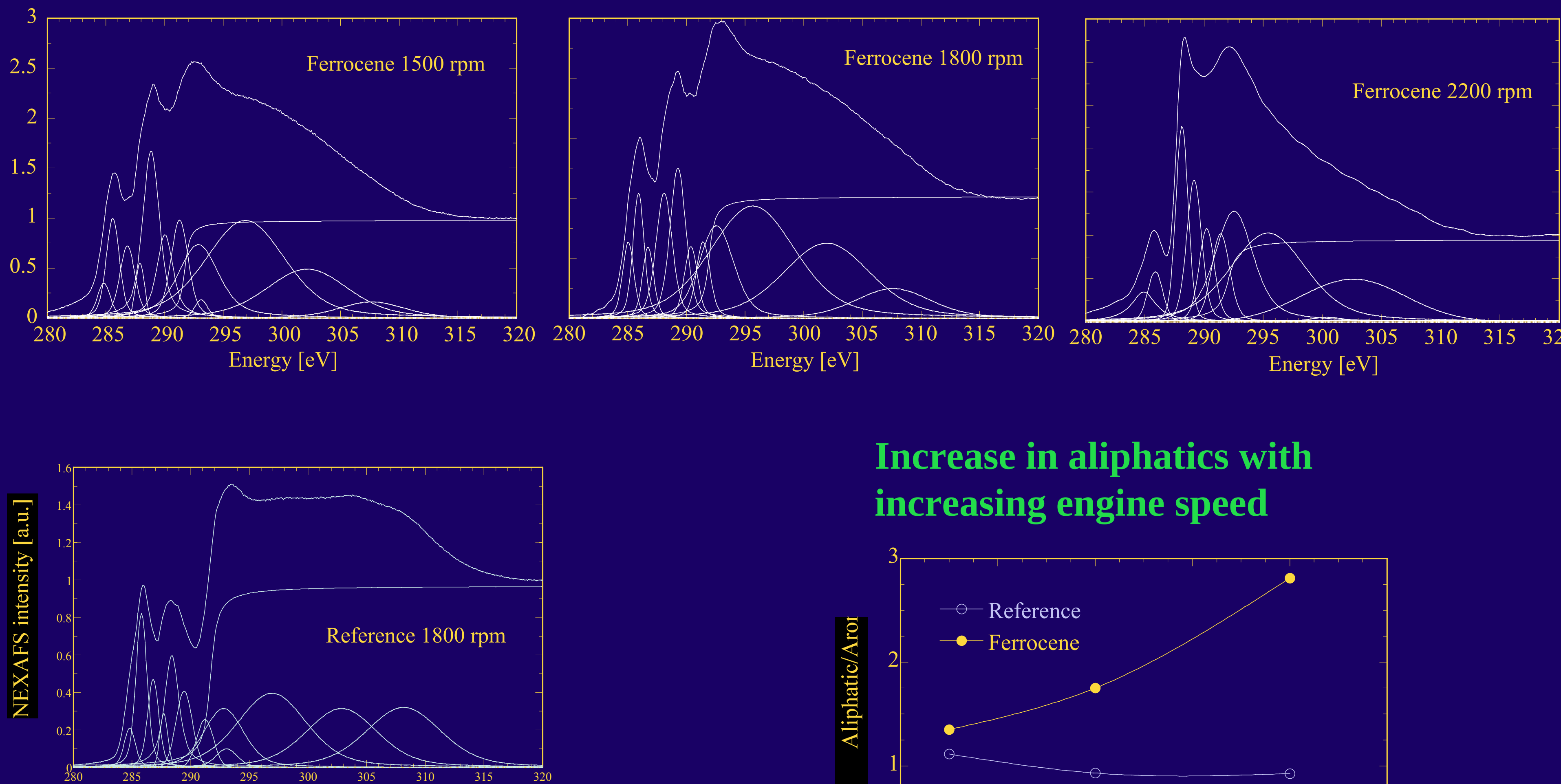
A. Kubatova, A Braun, in preparation

De Marini et al., Bio-assay directed fractionation and mutagenicity of exhaust particles, Env. Health Persp. 2004, 112(8), 814-819

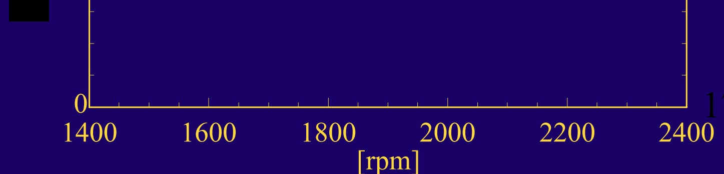
C(1s) NEXAFS confirms WAXS results: catalytic suppression of soot formation by ferrocene



Diesel + ferrocene
Spectral changes upon speed changes



Increase in aliphatics with increasing engine speed



Conclusions

- Adding ferrocene to diesel fuel makes exhaust less graphitic,
  → easier to oxidize for after-treatment
- Enhanced effect at higher engine speeds
- Less mass, but larger number of ultrafine particulates
  → [1] higher concentration of cytotoxic surface functionalities
- Ferrous nanoparticles generated in ferrocene diesel
  → [2] respiratory and genotoxicity of ferrous oxides

- Suggestion: soot from diesel plus ferrocene additive could be more harmful to human health than soot from diesel without ferrocene.

1 Boland et al. Cellular effects induced by diesel exhaust particles, Toxicology in vitro 2001, 15, 379-385.
2 Garry et al. Hematite (Fe_2O_3) acts by oxydative stress and potentiates benzo[a]-pyrene genotoxicity. Mutat Res–Gen Toxicol Environ Mutag 2004;563(2):117–29.
Braun et al, CARBON, in press.

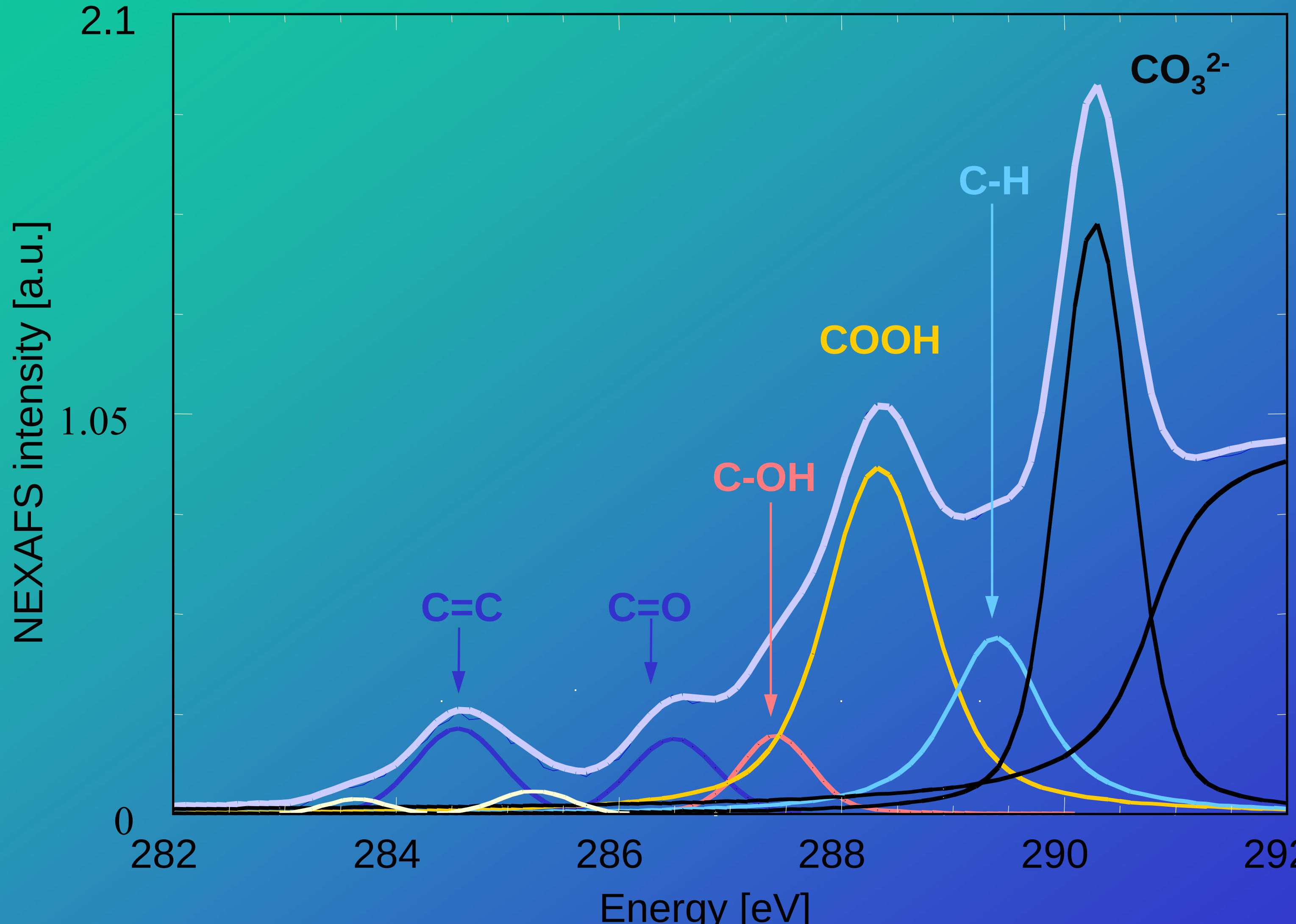
Suggestion: soot from diesel + ferrocene could be more harmful to human health than soot from diesel without ferrocene.

This talk will be presented again at

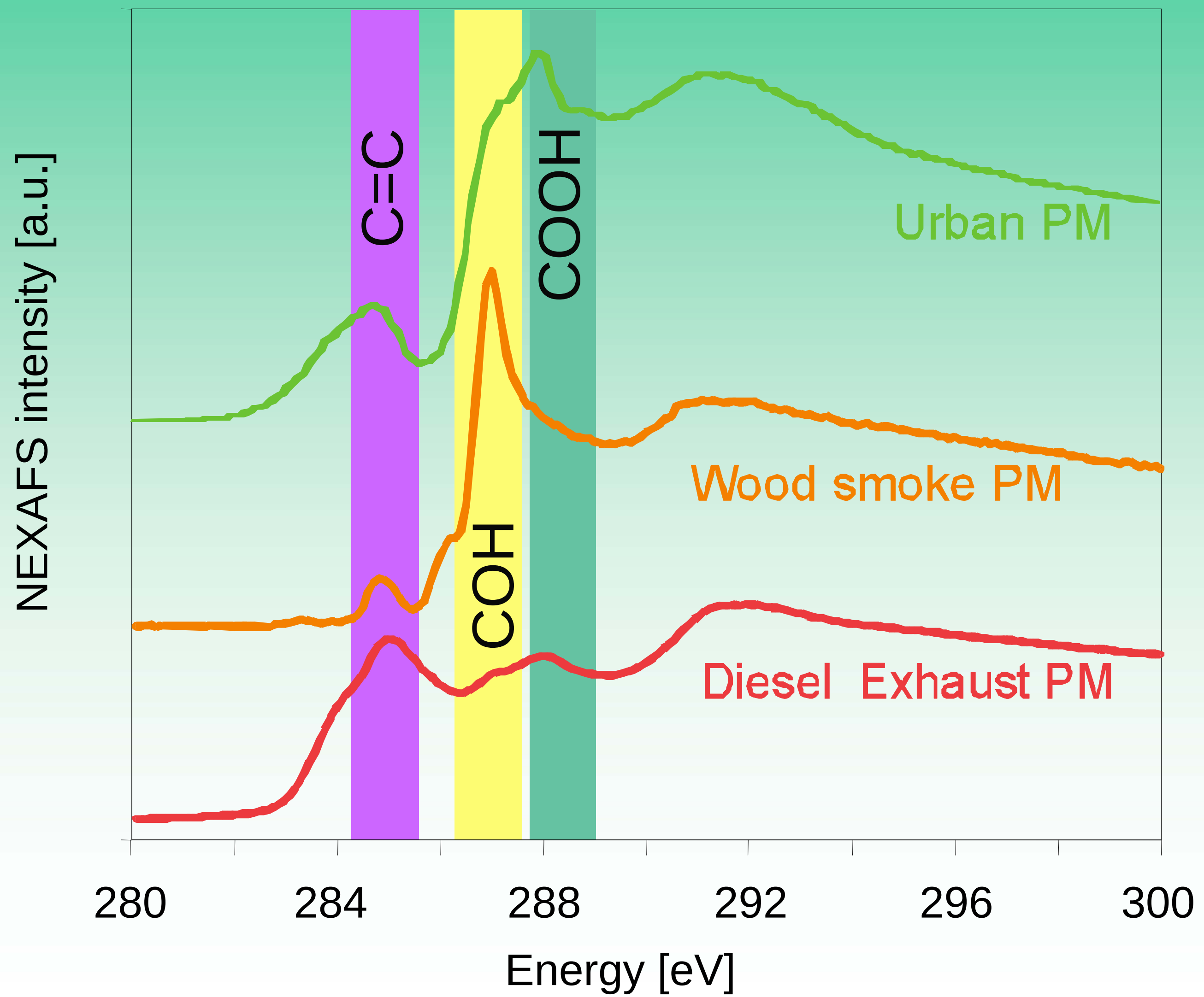
EMPA Dübendorf, LA 373

14:00, Friday, August 25, 2006

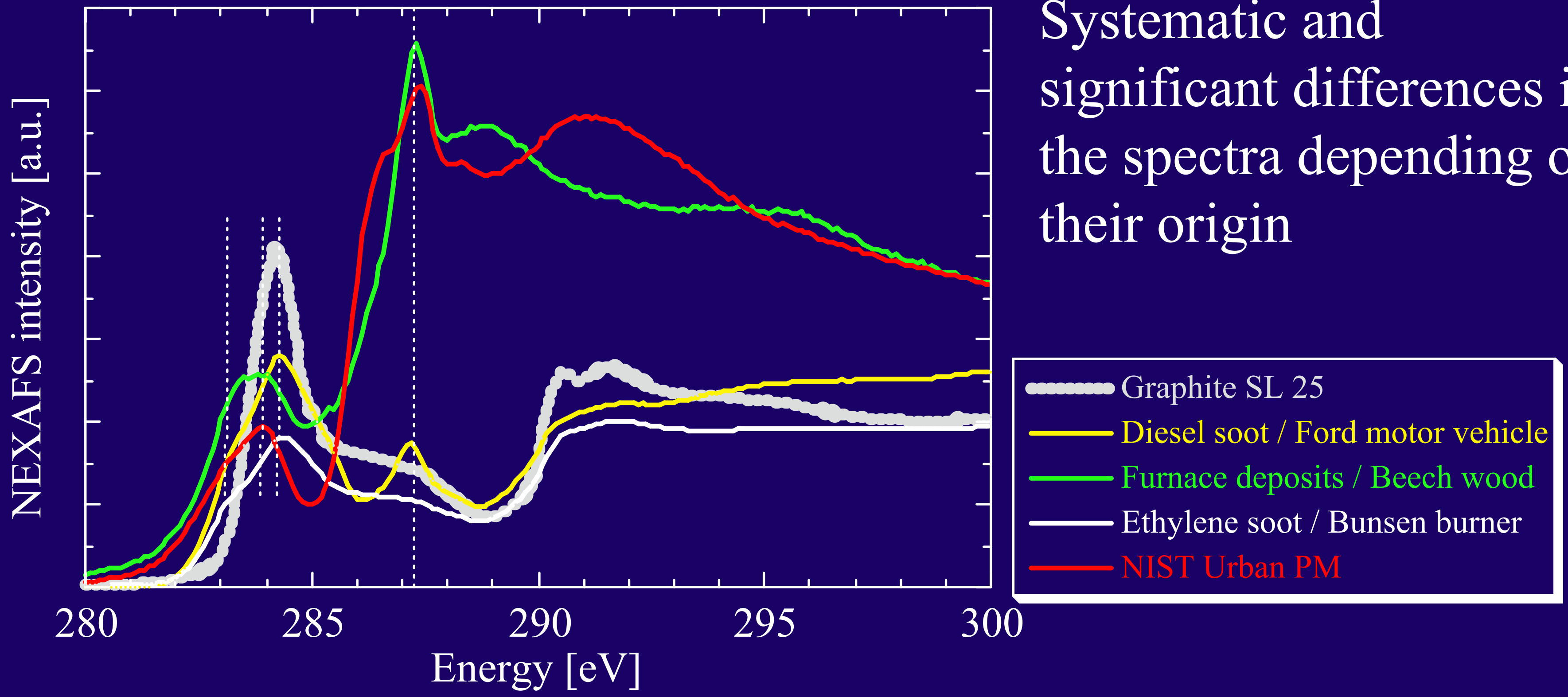
Suggested NEXAFS Peak Assignments for DPM Extract



Different PM samples show complex patterns in NEXAFS which cannot be easily attributed to the PM polarity



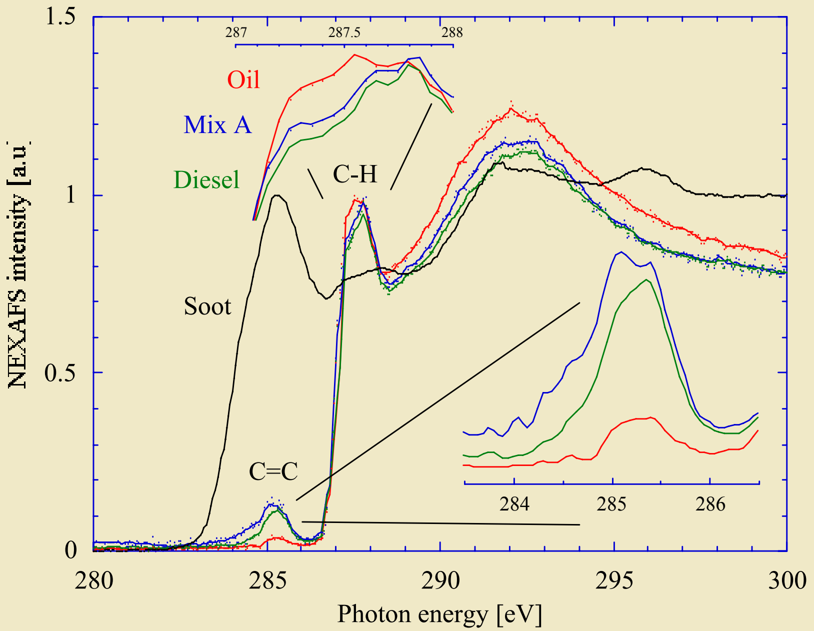
Spectra of some solid carbon samples



Systematic and significant differences in the spectra depending on their origin

Soot spectra contain significant intensity from C=C bonds ~ 285 eV.
Urban PM and wood creosote spectra contain significant intensity from aliphatics ~ 287 eV.

NEXAFS of soot, oil, and fuel



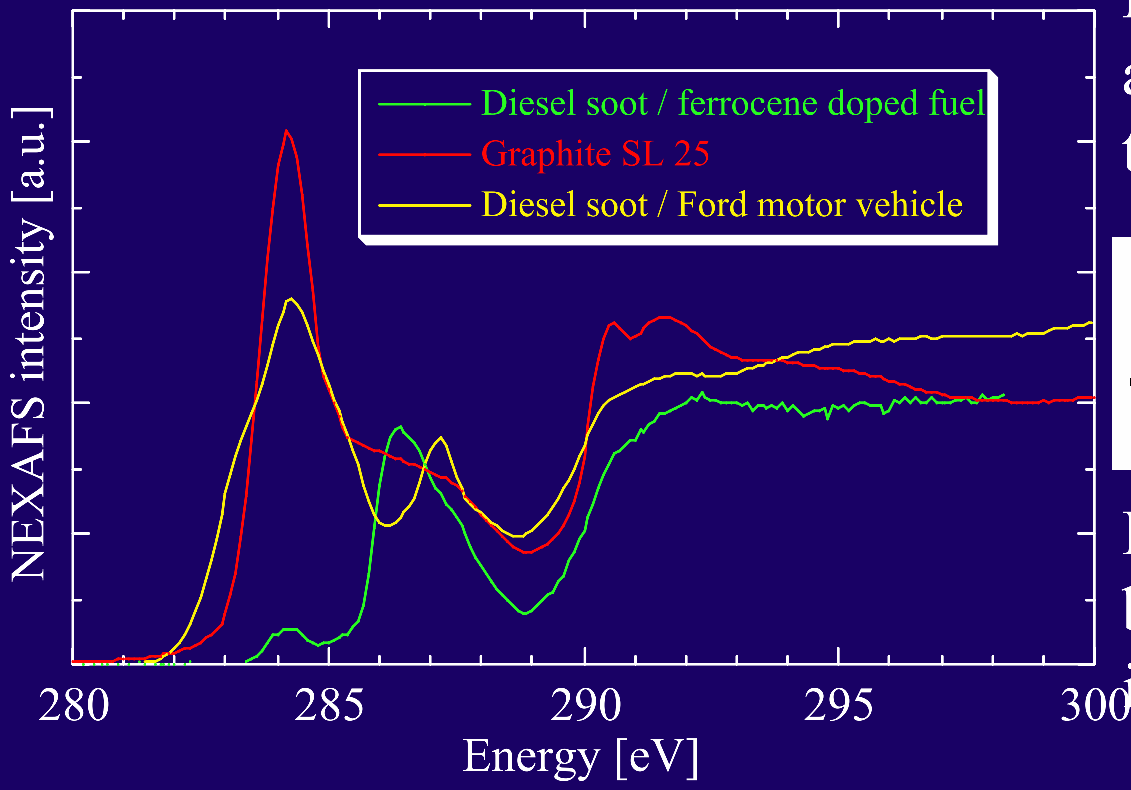
Spectra of soot, lubricant, fuel.

Allows for chemical speciation of samples, and determination of oxidation states.

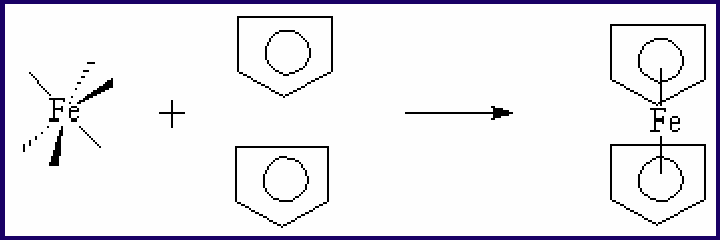
Braun et al. Study of fine diesel particulate matter with scanning transmission X-ray spectroscopy. Fuel (2004) **10** 7/8 997-1000.

Catalytic suppression of soot formation in diesel engines

Mixing diesel fuel with ferrocene

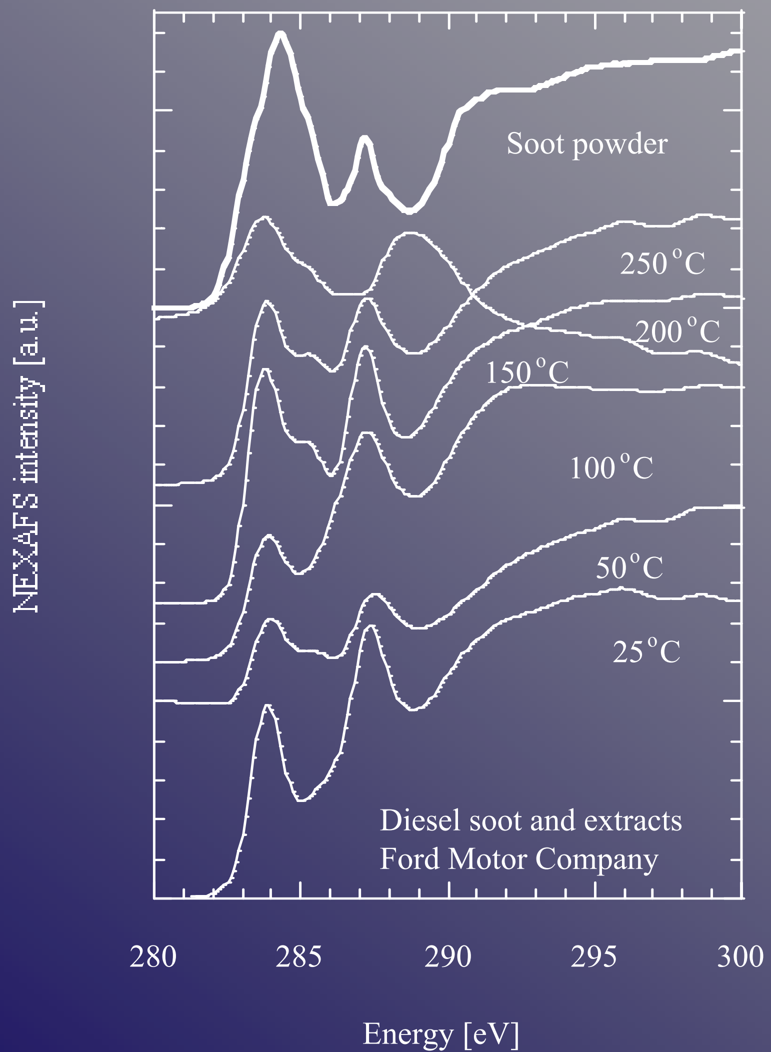


Ferrocene
Metastable molecule = **iron** atom sandwiched between two cyclopentadienyl rings.

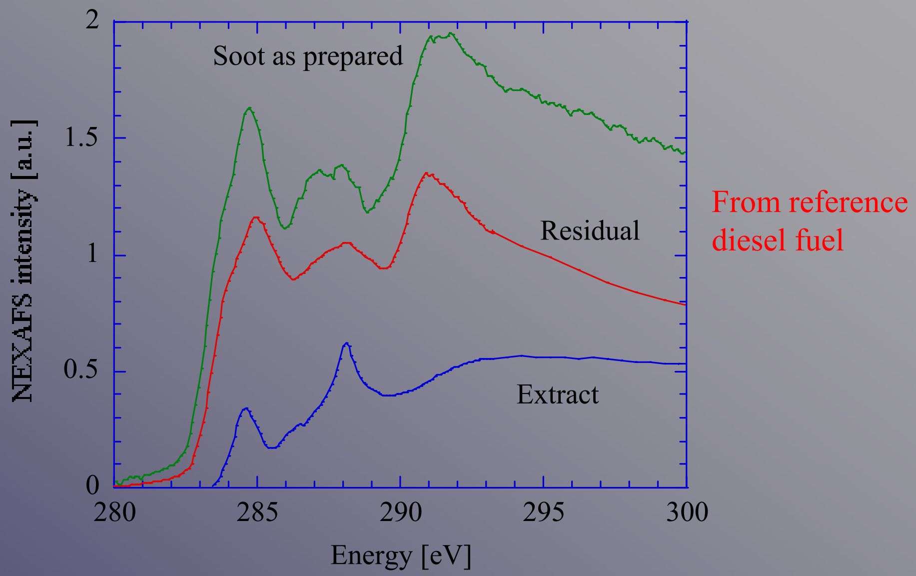


Dramatic decrease of C=C bond contribution in soot; increase in aliphatics

Soot Extracts



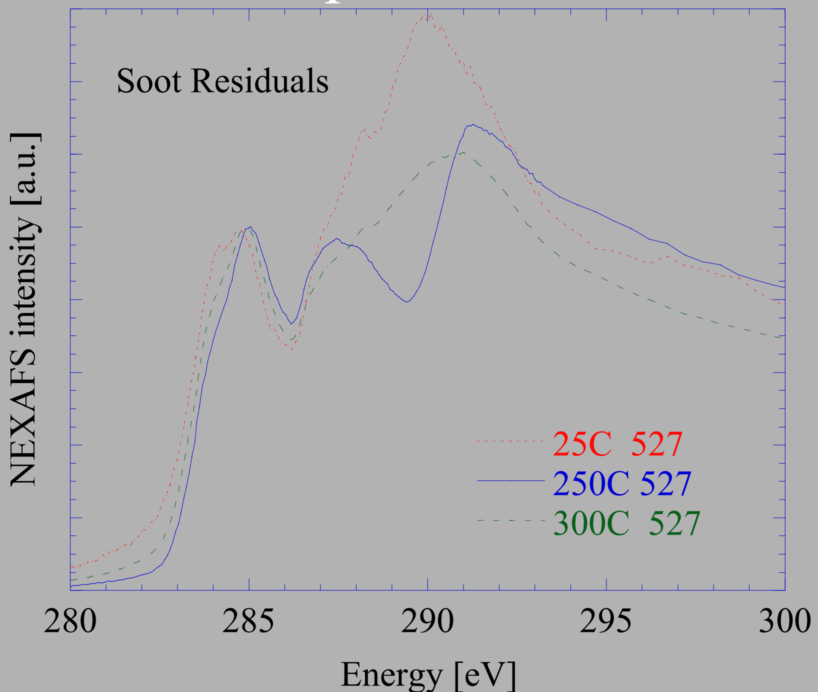
Separation of diesel soot into solid core and volatile fractions with sub-critical water facilitates subsequent decomposition of NEXAFS spectra.



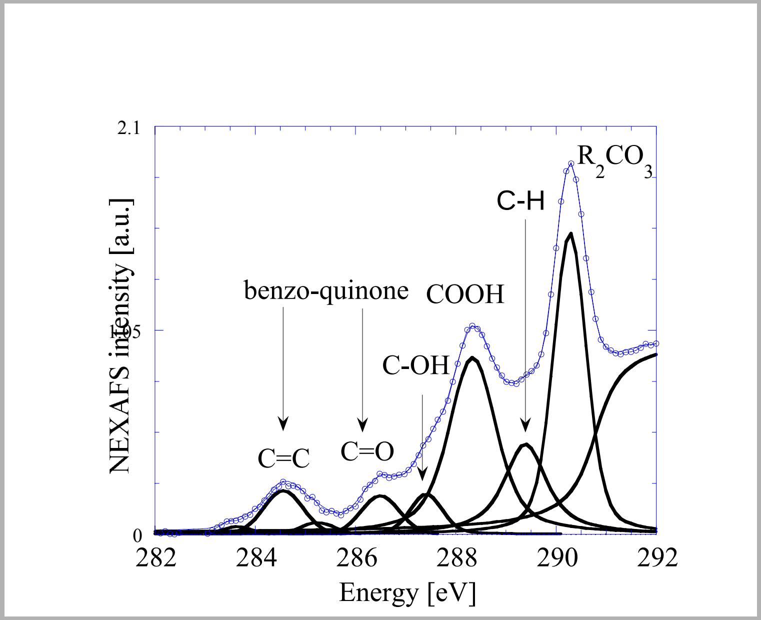
Extracts do contain material with C=C bonds

Soot Residuals

Separation of diesel soot into solid core and volatile fractions with sub-critical water facilitates subsequent decomposition of NEXAFS spectra.

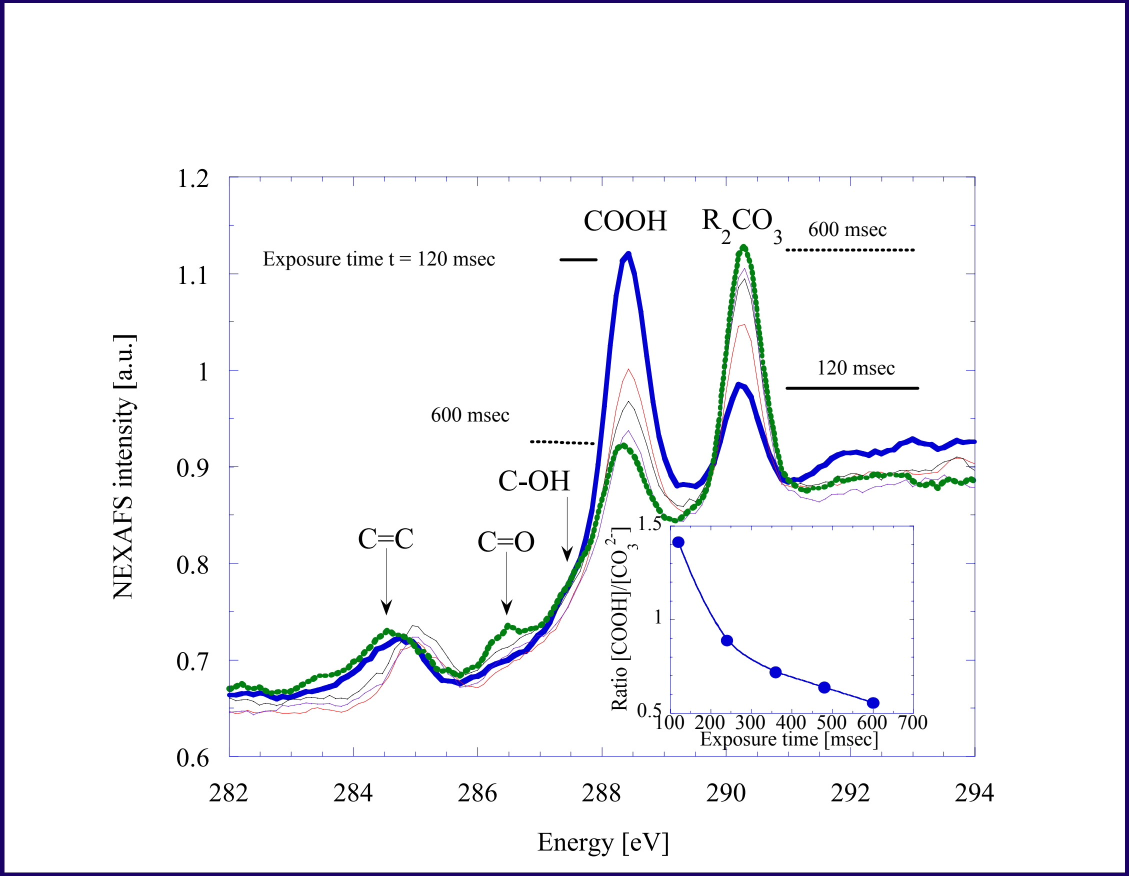


At low temperatures polar species like carboxylates and quinones are extracted.



Proposed peak assignment for extracts.

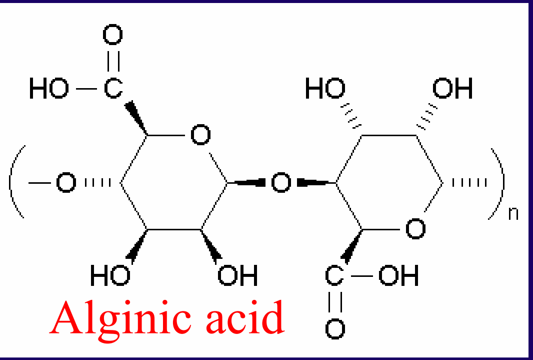
Photochemistry and De-carboxylation



Intense X-ray beam of the STXM microscope generates nascent oxygen from air.

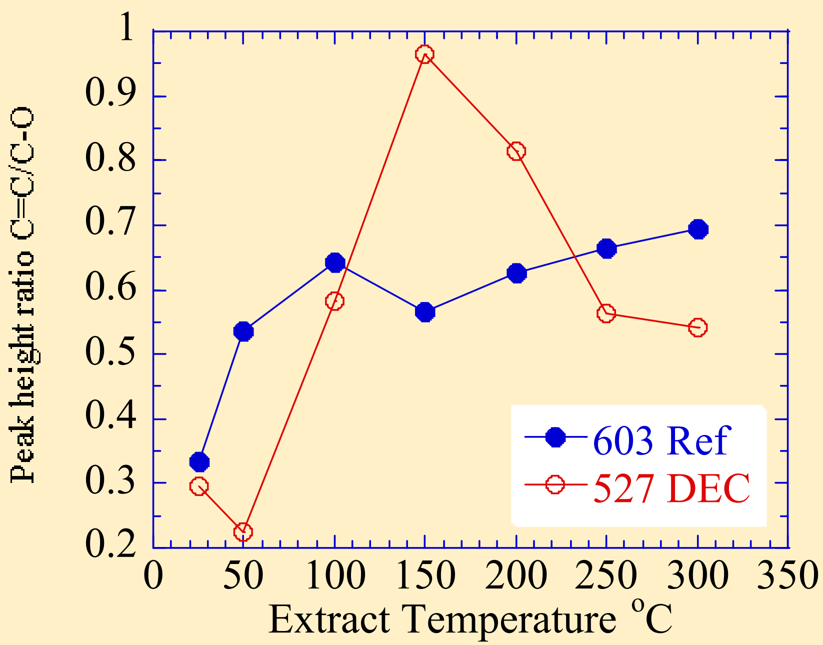
Upon irradiation, COOH carboxyl peak intensity decreases, and new peak evolves - probably from an organo-carbonate.

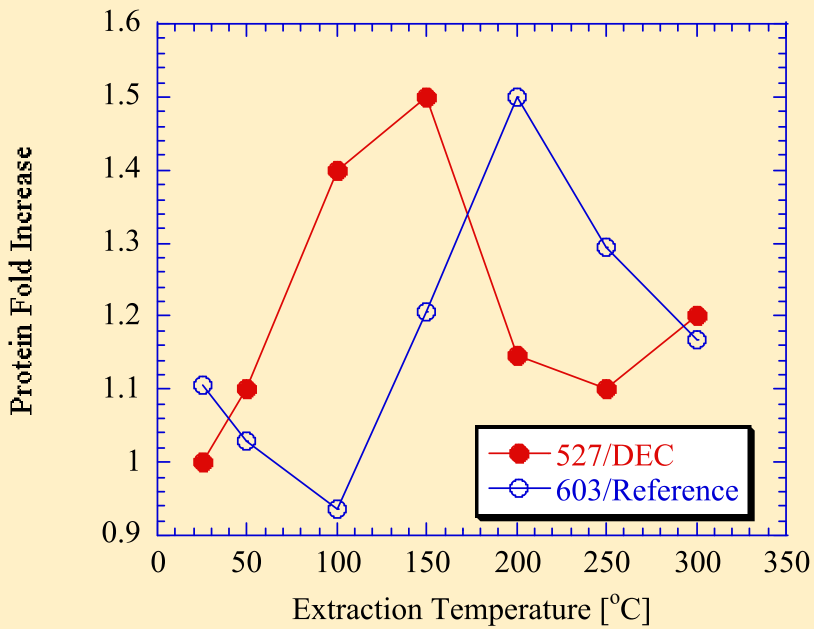
Potential tool for in-situ reaction studies !
(ozone + soot, etc…)



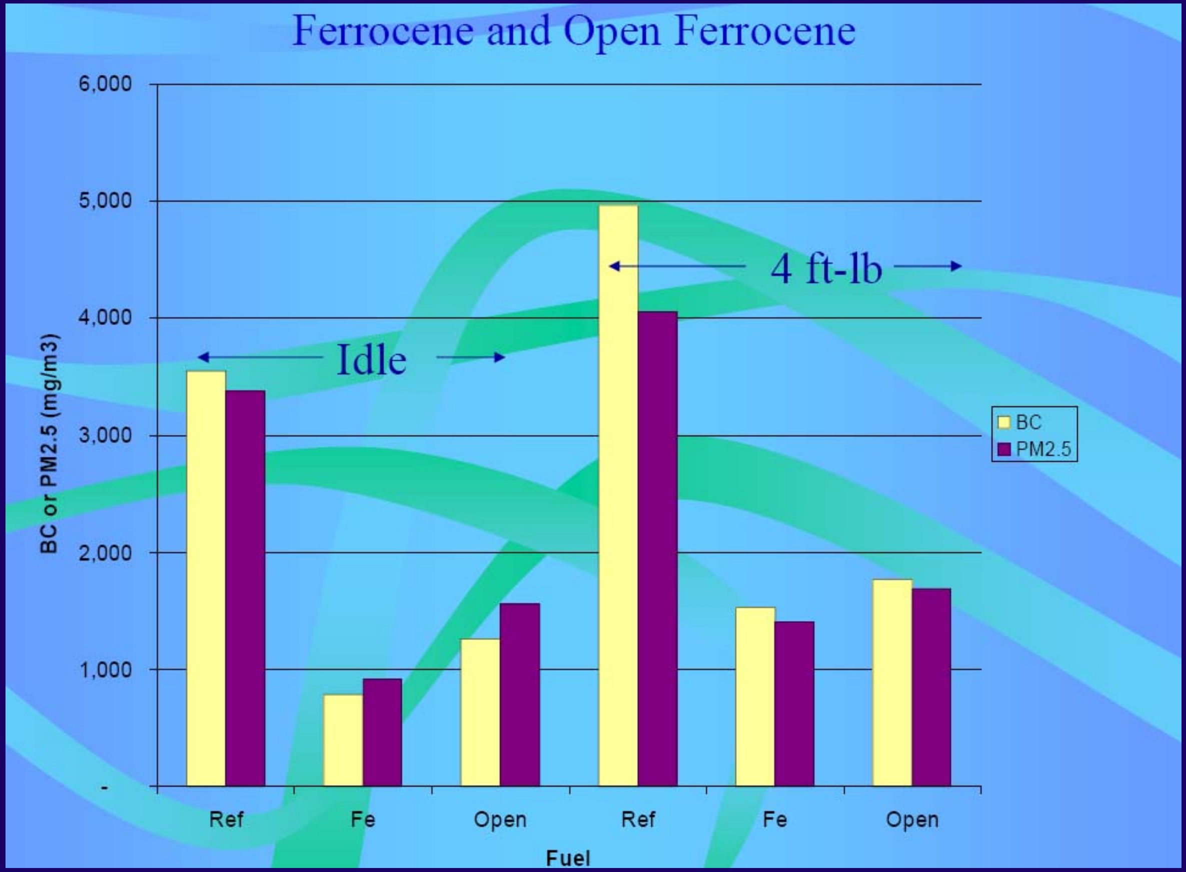
Correlation of Toxicological Results and Spectra ?

Cell cultures exposed to a series of subcritical water extracts.
Protein fold increase is a measure for toxic response.

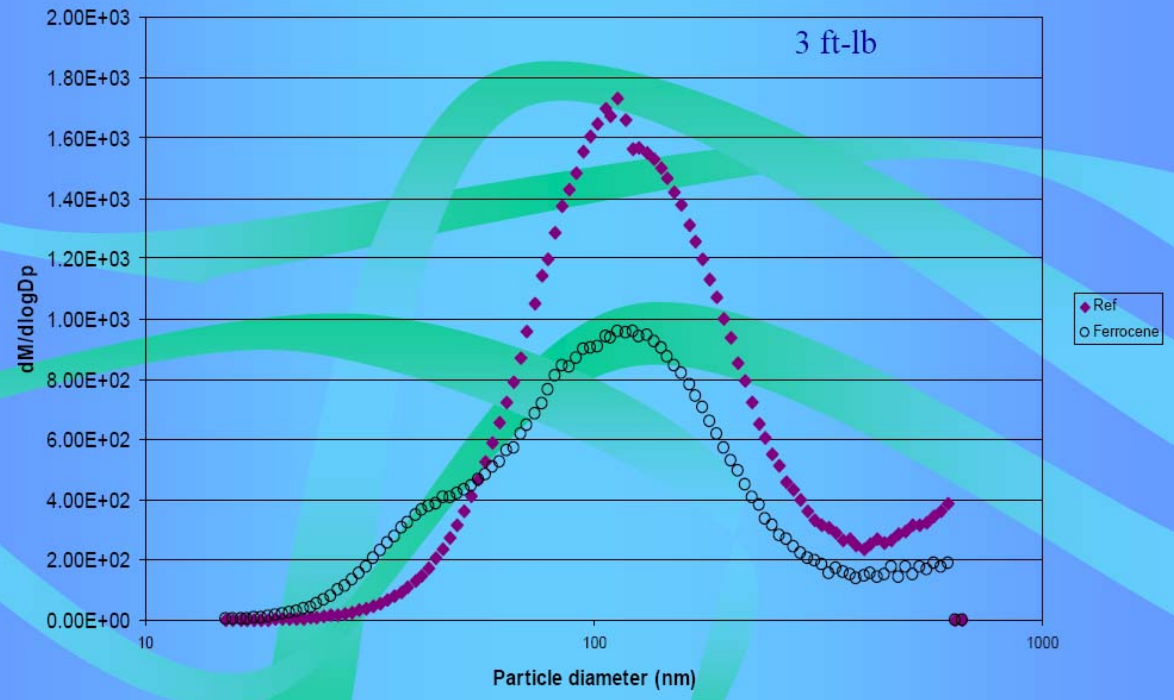


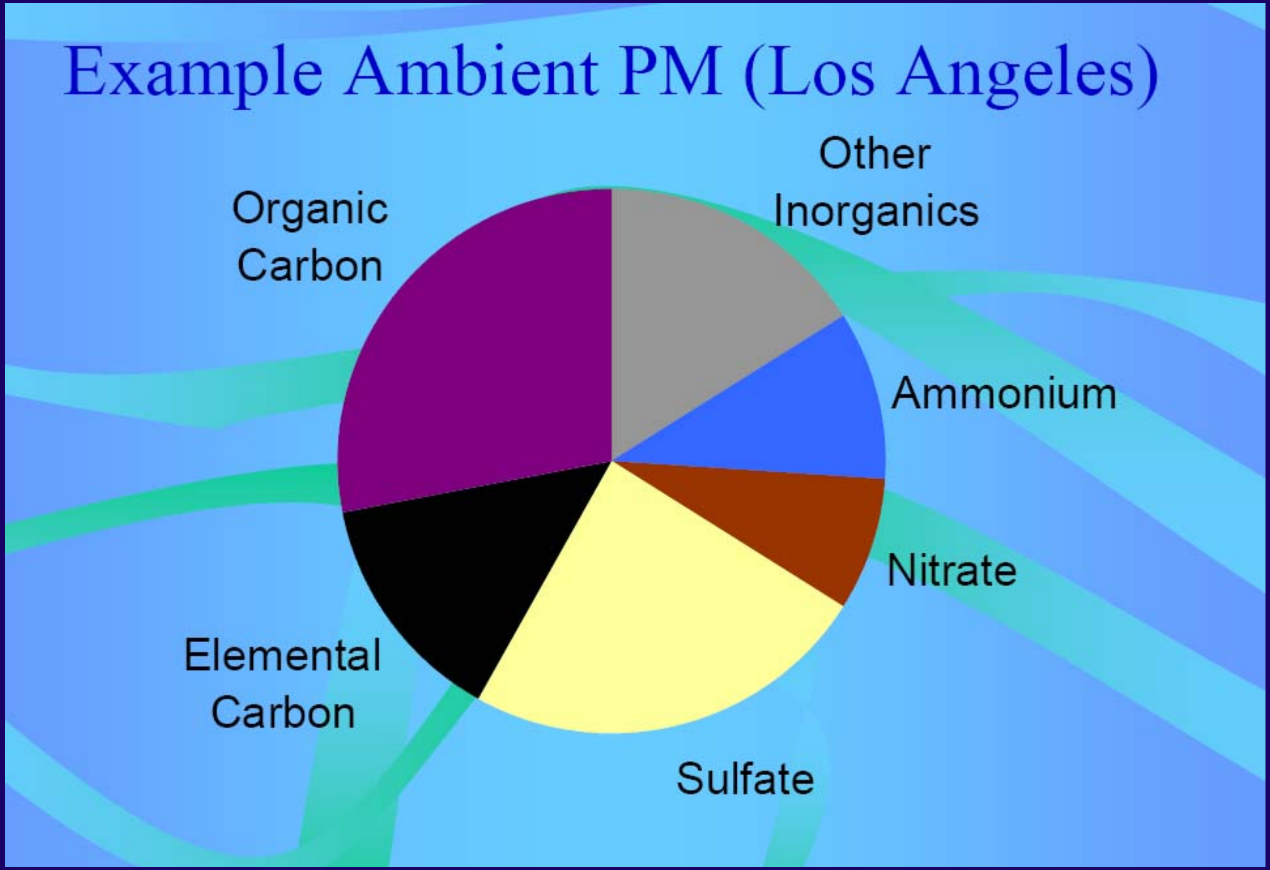


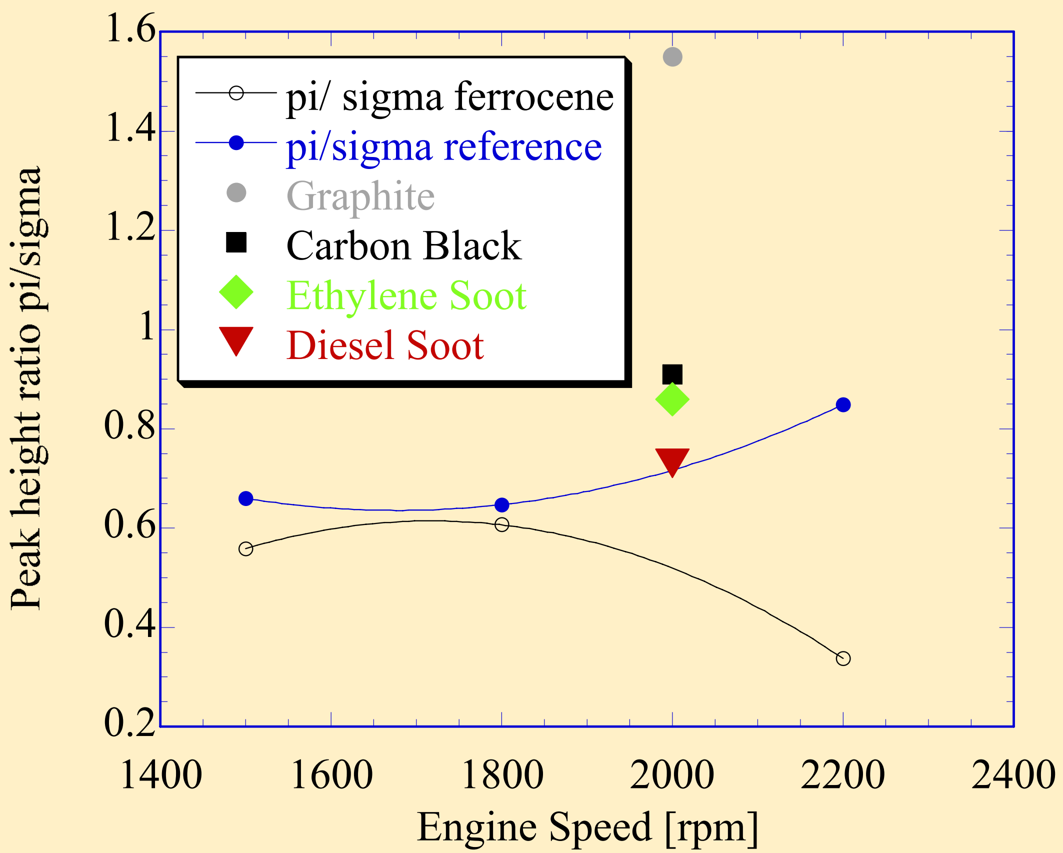
A. Kubatova, A Braun, in preparation


Ferrocene and Open Ferrocene
6,000
5,000
4,000
3,000
2,000
1,000
-
BC or PM2.5 (mg/m3)
Idle
4 ft-lb
BC
PM2.5
Ref
Fe
Open
Ref
Fe
Open
Fuel

Particle size distributions




Example Ambient PM (Los Angeles)
Other
Inorganics
Organic
Carbon
Ammonium
Nitrate
Elemental
Carbon
Sulfate



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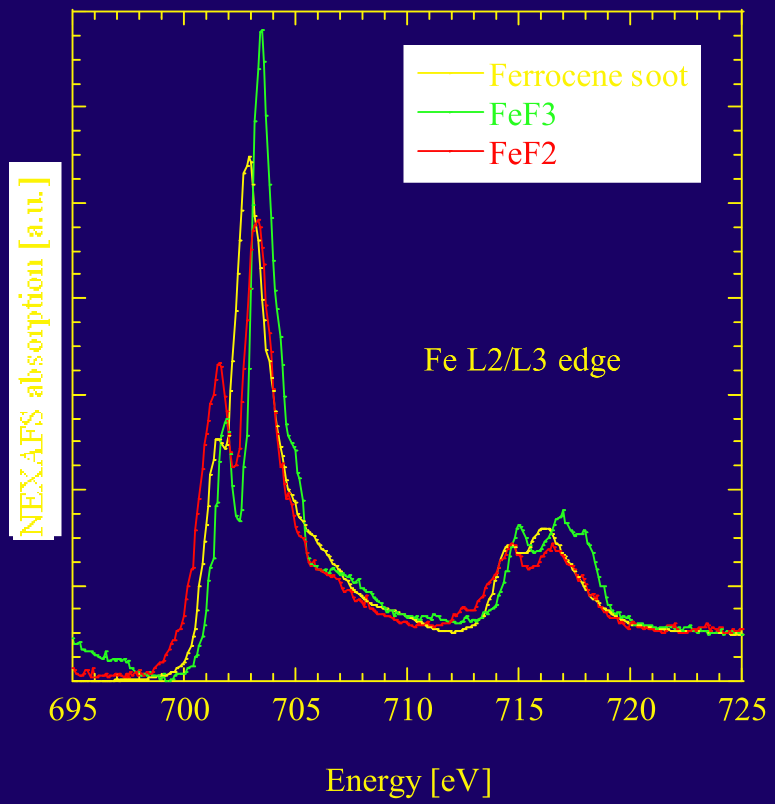
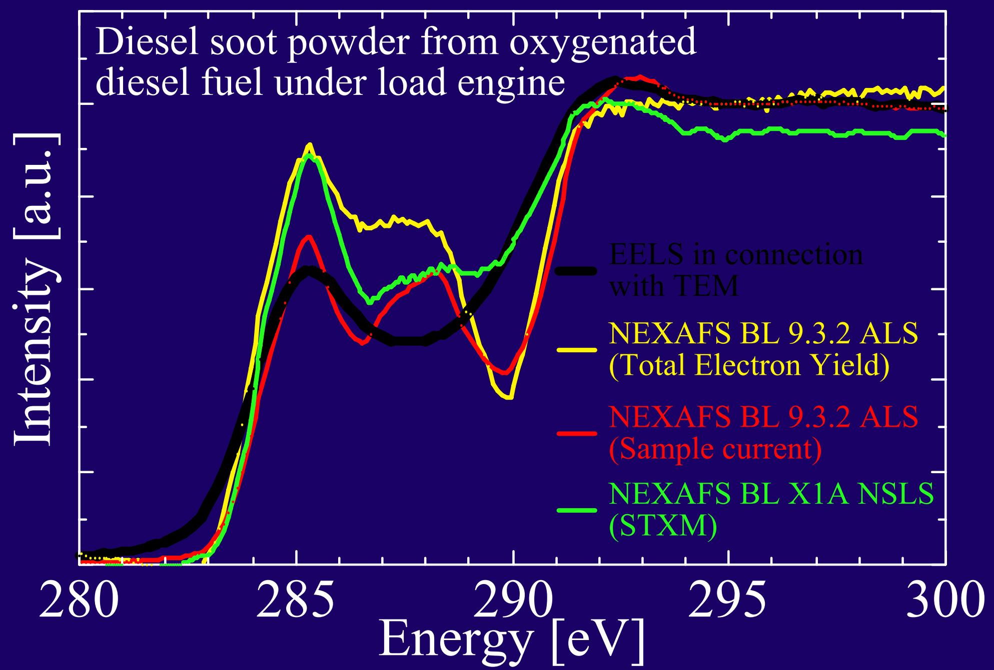

Ferrocene soot
FeF3
FeF2
Fe L2/L3 edge
NEXAFS absorption [a.u.]
695
700
705
710
715
720
725
Energy [eV]

NEXAFS vs. EELS



EELS and NEXAFS have similar spectra. TEM microscopes often come with an EELS spectrometer. But EELS spectra from TEM look blurred, almost entirely useless for quantitative studies.

Advantages of soft X-ray absorption over TEM-EELS - A Comparative study on diesel soot with EELS and NEXAFS; Carbon, **43**(1), (2005) 117-124.

Note: this concerns not ISEELS such as the ones by Hitchcock & coworkers

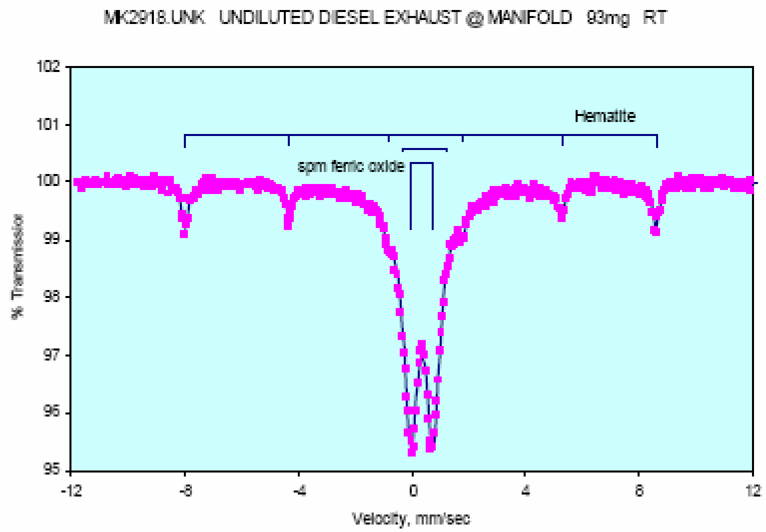


Figure 6: Room temperature Mössbauer spectrum of diesel PM collected undiluted at the exhaust of the University of Utah diesel test engine facility. The six-line spectral component represents hematite, whereas the two central doublets represent a superparamagnetic ferric oxide. The spectrum of the sample collected under conditions of N_2 dilution at the engine manifold was virtually identical.

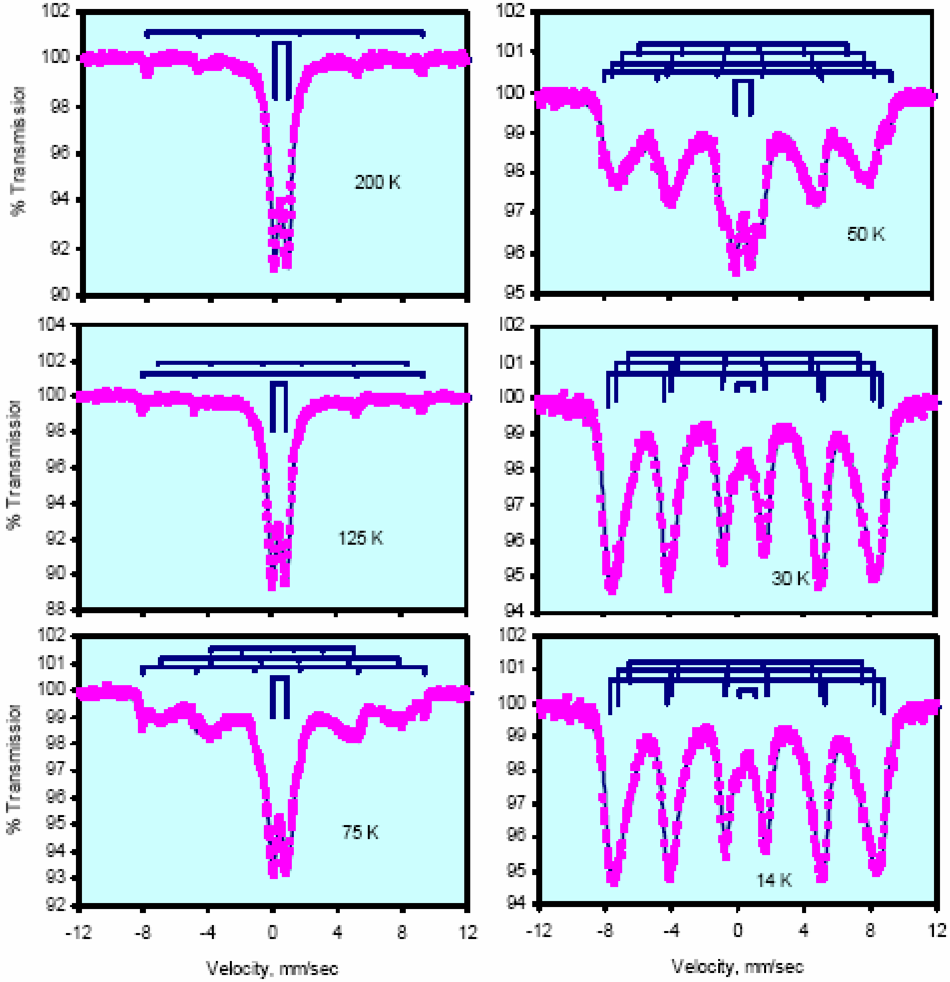


Figure 7: Suite of Mössbauer spectra taken at different temperatures for the undiluted PM sample collected at the exhaust of an engine consuming diesel fuel to which 1000 ppm of ferrocene had been added.

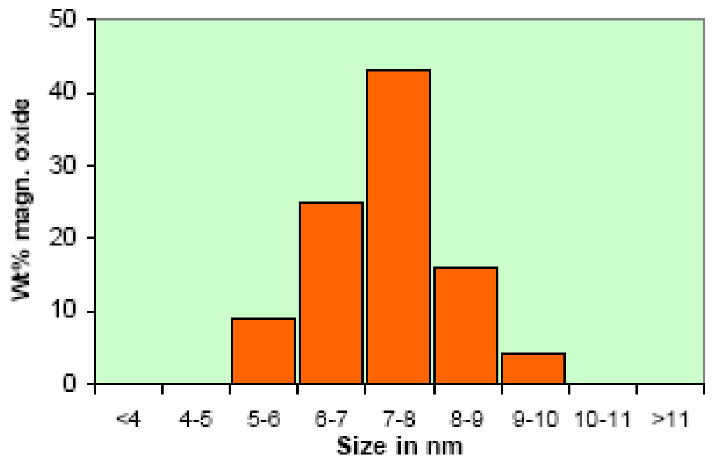


Figure 10: Size-distribution profile estimated for γ-Fe_2O_3 derived from the temperature dependence of the spm component in iron Mössbauer spectra of PM from combustion of a diesel fuel doped with 1000 ppm of ferrocene in a diesel test engine. Sample was collected at the exhaust without dilution under N_2.