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Application of small angle and wide angle X-ray scattering for the characterization of carbonaceous materials, aerosols, and particles

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Small angle X-ray scattering (SAXS) can provide quantitative information on internal surface areas, porosity, particle size, void size distributions, surface roughness and fractal dimension of surfaces, interfaces and particles and aggregate structures. Applied in-situ and ex-situ, SAXS even permits to derive kinetic parameters for chemical reactions and transformations. In particular homogeneous systems such as soot can be studied with SAXS, and carbonaceous materials have been widely used to develop this technique. Wide-angle X-ray scattering (WAXS) permits to measure crystallite sizes and to distinguish aromatic and aliphatic structures in carbon materials. WAXS was particularly applied for coal research. I present here studies that were made on diesel exhaust soot for combustion engineering and environmental science, as well as studies on model systems such as glassy carbon (pore size and connectivity evolution) and on aerogels (inclusion of third phases such as metal clusters).

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[1] A.W. Kandas et al, Carbon 2005, 43(2), 241-251.
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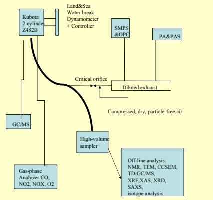
Objective

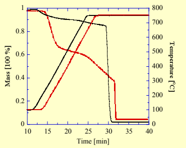
Scattering techniques, including light scattering (LS), provide statistically very robust data, complementary and often even superior to microscopy data. Small angle X-ray scattering (SAXS), when done at synchrotron radiation sources, can provide data very fast. At best, a scattering curve can be obtained in a fraction of 1 second. High resolution data may need about 15 minutes to cover a length scale from several microns to 1 nanometer. A shortcoming of scattering techniques is that they do require some minimum amount of material, such as milligrams, which always exceeds the amount necessary for TEM studies, which ultimately needs one tiny particle only. Also, SAXS cannot be applied very well for chemically very inhomogeneous systems. However, for soot studies, SAXS is perfect. Wide angle X-ray scattering (WAXS), pretty mch like SAXs, is a diffuse scattering technique which basically uses profile and background scattering analysis. It has been extensively applied for coal research with much success.



Left: Diesel exhaust from heavy duty truck. **Right:** Diesel soot sample generation at Univeritu of Utah.

Samples: Diesel PM from 50/50 Chevron/Phillips reference fuels T22/U15, oxygenated with DEC and ethanol, operated under idle/load. Oxygenated fuel is called "Mix A" and "Mix B". Addition of 1000 ppm ferrocene to some of the fuels was made to catalytically oxidize the soot and prevent graphitization.

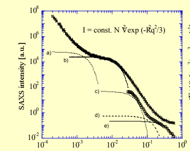
Thermogravimetric Analysis

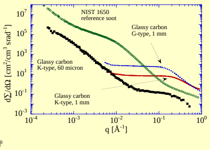


Sample	Moisture [%]	Volatile (Extract) [%]	Carbon [%]	Ash [%]
idle	1.757	23.78 (42.7)	70.521	4.699
load	1.145	14.36 (14.3)	80.150	3.490
idle, Mix B	1.917	56.19 (48.9)	36.077	4.733
load, Mix B	1.375	16.75 (10.5)	76.340	2.910
idle, Mix A	2.488	61.80 (31.6)	28.586	4.614
load, Mix A	1.025	14.09 (5.9)	77.772	2.138

Left: TGA profiles of load (black) and idle (red) soot from oxygenated Diesel, including the temperature profile TGA was operated with N_2, and at 750°C with O_2. **Right**: Summary of TGA results. Data in parentheses are based on Soxhlet extraction. Idle soot contains more volatiles.

Particle and pore size and porosity in diesel soot and GC





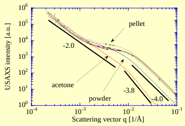
Left: Log-log plot of small angle scattering curves reveal at least 5 size ranges in Diesel PM, with size $L=2\pi/q$. Curve with open symbols was obtained after subtraction of Porod- and constant background scattering. Exponent of decay allows determination of fractal dimension, and was close to –4 for high q range and thus indicates smooth surfaces of primary particles and sub-units. For low q, exponents of decay are close to –3. **Right**: Comparison of scattering curves for soot and glassy carbon, a standard SAXS material with many micropores.

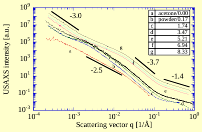
Quantitative data for diesel soot

Soot	Elementary units D[nm]	Sub units D [nm]	Primary Particles D [nm]	high q exponent	Fractal dimension	low q exponent	Fractal dimension
Diesel, idle	1.5	17.4	49.16	3.99	2.01	3.28	2.72
Diesel, load	1.6	14.5	41.50	3.86	2.14	3.12	2.88
Mix A, idle	1.9	21.1 (14.2	78.29	3.97	2.03	3.02	2.98
Mix A, load	1.4	13.8 (12)	36.78	3.96	2.04	3.09	2.91
Mix B, idle	2.0	14.3 (14.5	83.85	3.92	2.08	2.96	2.96
Mix B, load	1.4	22.0 (18.6	48.73	3.98	2.02	2.75	2.75

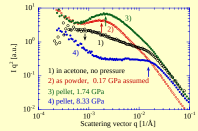
Elementary particles sizes 1-2 nm range. Form compact cluster to built subunits of 15-20 nm size. These build up larger structures (primary particles) of 40-80 nm, which form aggregates. Aggregates are found at q-values of 0.001 1/A, though harder to resolve in the SAXS curves. Idle soot has generally larger particles than load soot.

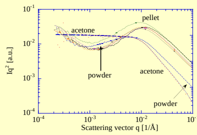
Pressure and compaction studies with USAXS



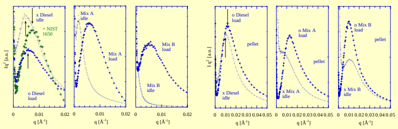


Left: SAXS scattering curves for diesel soot as poder, pressed pellet, and immersed in acetone. Sample environment modifies soot aggregation slightly and has impact on scattering curve. **Right:** Shift of characteristic structures in scattering curves upon pressurizing of samples indicates aggregate rearrangement.



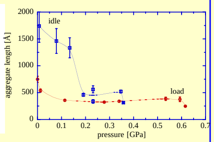


Maxima in Kratky plots of scattering curves provide information about compactness of soot particles and size of agglomerates: $L=\pi/q$.



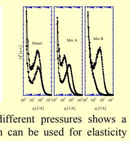
Pressure [GPa]	idle R_g [nm]	load R_g [nm]
0 (Acetone)	398 ± 224	376 ± 50
0.347 (Scotch Tape)	106 ± 22	105 ± 11
1.74	88 ± 15	22 ± 2
3.47	89 ± 23	16 ± 1
5.21	26 ± 5	17 ± 1
6.94	26 ± 4	18 ± 2
8.33	24 ± 4	21 ± 1

Table 1
Aggregate sizes for idle and load soot as obtained from unified fit.



Fuel	high q	high q, pellet	low q	low q, pellet
diesel, idle	3.99	3.89	3.28	2.89
diesel, load	3.86	3.86	3.12	3.16
Mix A, idle	3.97	3.77	3.02	3.36
Mix A, load	3.96	3.94	3.09	3.45
Mix B, idle	3.92	3.80	2.96	3.39
Mix B, load	3.98	3.95	2.75	2.80

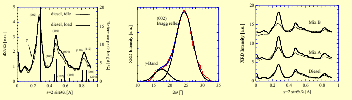
Fuel (pellets)	R_g [Å]	D [nm]	R_g [Å]	D [nm]	D [nm]	D [nm]
diesel, idle	5.95	1.5	55.40	14.3	13.7	30
diesel, load	6.46	1.7	39.51	10.2	11.8	25
Mix A, idle	7.42	1.9	81.75	21.1	19.4	86
Mix A, load	5.71	1.5	53.61	13.8	11.2	25
Mix B, idle	6.52	1.7	55.28	14.3	13.0	85
Mix B, load	6.42	1.7	85.13	22.0	14.1	27



Systematic scattering study on samples compacted at different pressures shows a systematic trend for aggregate size rearrangement, which can be used for elasticity estimation.

Wide Angle X-ray Scattering

Quantitative analysis of diffuse XRD diffractograms (WAXS) provides information on aromaticity (area under γ-band peak vs. the entire peak area, including (002) peak), ratio of crystalline/amorphous carbon (background scattering), and crystallite sizes (Scherrer Formula).



Left: X-ray diffractograms from load/idle soot, and reference Bragg peaks of graphite (2H Graphite PDF 26-1079). **Center**: Deconvolution of Peak into (002) and γ-sideband for determination of aromaticity. **Right**: Comparison of load/idle soot XRD from Diesel and oxygenated Diesel Mix A, Mix B.

Aromaticity *f* of diesel soot	diesel	diesel Mix A	diesel Mix B
idle	0.15	0.34	0.31
load	0.22	0.15	0.08

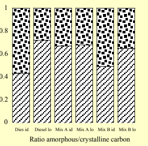
Aromaticiy of oxygenated and non-oxygenated diesel exhaust PM for idle and load engine conditions.

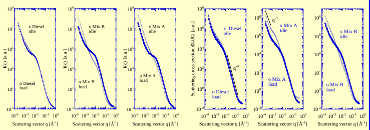
Sample	L_c (002) [Å]	L_a (110) [Å]	L_a (112) [Å]
Diesel, idle	11.10	8.67	17.24
Diesel, load	11.78	10.48	16.68
Mix B, idle	10.18	6.96	13.24
Mix B, load	12.86	8.64	14.92
Mix A, idle	8.64	8.93	6.24
Mix A, load	10.78	16.30	11.19

Idle soot particles have smaller crystallites than load soot. Aromaticity higher for idle soot from oxygenated Diesel (Mix A, Mix B). Idle soot contains more amorphous carbon than crystalline carbon. Adding oxygenates to fuel causes bigger differences in the structure between idle and load soot, in line with NEXAFS and TGA.

Soot structure depending on engine operation + fuel additives

Idle soot particles have smaller crystallites than load soot. Aromaticity is higher for idle soot from oxygenated Diesel (Mix A, B). Idle soot contains more amorphous carbon (upper part of column, grains) than crystalline carbon (lower part, planes). Adding oxygenates to the fuel causes bigger differences in the structure between idle and load soot, in line with observations form the NEXAFS and TGA.





Ferrocene is added to diesel fuel in order to prevent formation of graphitic soot structures. This facilitates subsequent soot oxidation in aftertreatment devices. WAXS data explicitly show that ferrocene soot lacks significantly in graphite-like structures. Instead, a large aliphatic gamma side-band is observed. Results in line with NEXAFS spectroscopy data, as shown in the Figure below.

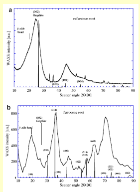
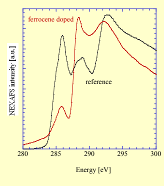


Fig. 1. WAXS pattern of reference soot (top, 6 ft-lb load, 2200 rpm) and ferrocene soot (6 ft-lb load, 2200 rpm). Reference soot contains indexed Bragg reflexes from graphite. Ferrocene soot contains indexed Bragg reflexes from maghemite.



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

Oxidation Studies

Porosity and Chord Length distribution

Porosity evolution of activated (right side) and non-activated GC (left) was studied by SAXS. Based on first geometric principles (*Rosiwals linear integration principle*, isotropic uniform random chord length distributions), porosities have been obtained, in contrast to more conventional techniques, by means of the second derivative of the small-angle scattering correlation function γ(r). Estimates of the porosity p are based on the range order L = 2.5 nm, which corresponds to a sequence pore/wall/pore by means of a so-called linear simulation model (bottom, blue, green). Specific assumptions about size, shape, pore topology, are not required.

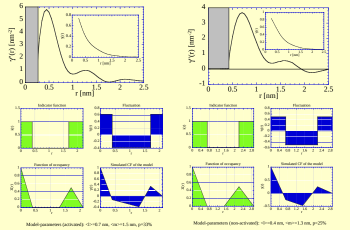
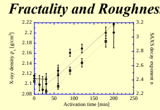


Figure 4

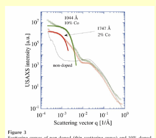
Figure 3

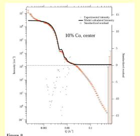
Fractality and Roughness

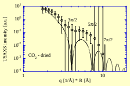


SAXS useful for soot oxidation studies. Here, GC is used as a model for soot oxidation to study the changes in surface fractal dimension and X-ray density with SAXS and WAXS as a function of oxidation time. While for extensive oxidation a compaction of the carbon structures are observed, an expansion of graphene sheets is observed in an initial phase.

Inhomogeneity and Metal Inclusions







Aerogel are ultrahigh surface area materials and allow for metal nanoparticle inclusions. Here we studied a Fischer-Tropsch fuel catalyst as a model for metal inclusion in high porous carbon (see for instance iron oxide inclusions in soot from ferrocene doped fuel). Cobalt-doped and non-doped silica aerogels show significantly different SAXS curves (upper, left).

Chemical reduction of samples alters SAXS curves, too. Anomalous SAXS permits to study solely the metal inclusions by contrast variation. Metal clusters can be modelled by spheres (bottom, left). Shape profile of particle size distribution suggests Ostwald ripening as coarsening process (upper, right).

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