In Situ Growth of Pyrolytic Aerosol Particles.
Pinhole Camera Results.

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In December, 2002 we completed in situ SAXS and USAXS studies of nano-particle growth in silica and titania flames at ESRF using the High Brilliance Beamline (HBBL ID02). The results of this work are the first high spatial resolution in situ studies of nanoparticle growth in a flame as summarized below. While the Bonse-Hart (USAXS) studies allow for indispensable complete characterization of agglomerate, aggregate and primary particle structure on size-scales ranging from 1 μm to 1 nm, the measurement time of about 15 minutes on this camera limits the spatial mapping capabilities. Additionally, as noted in the adjoining report on the Bonse-Hart results, unexpected aggregate orientation in the laminar flow lines of the flame may have inhibited the ability of the ID02 Bonse-Hart camera from resolving the large-scale aggregate structure making the pinhole camera the more useful instrument. The pivotal issue of aggregate orientation has not been fully resolved since no orientation has been observed in the smaller size-scale pinhole 2D data.

The 20 millisecond exposure time using the pinhole CCD SAXS camera allowed rapid and more complete scanning of flames. However, the ESRF HBBL pinhole camera is somewhat limited in observable size-scales so that aggregate and agglomerate growth could not be fully characterized. Only the tail of the aggregate structure could be resolved in most cases, yielding the mass-fractal dimension but not the aggregate size. In the ESRF studies we were able to observed nucleation, coalescence, sintering, and aggregation phenomena on the millisecond time scale (through millimeter spatial resolution in the flame) as well as development of mass-fractal aggregate structure. We believe that significant orientation of aggregates may occur in the laminar flow lines of the flame especially at early stages of growth, low in the flame, which may have major implications for models and simulations of nanoparticle growth in flames (see attached comparison of ESRF and APS Bonse-Hart data). We have found that aggregates at early stages of growth (first 50 milliseconds) are of low mass-fractal dimension, close to linear structures. We are analyzing the 2D data obtained at ESRF to ascertain if there is any direct evidence for orientation of these aggregates along the laminar flow lines of the flame. Such a finding would have major implications for our understanding of nano-particle growth in flames. In general, this first study of in situ growth shows that first the experiment is possible and second that particle growth in flames can be controlled to produce narrow distribution nano-scale particles with either high or low degrees of aggregation. In general we observed that aggregates move to or grow at the outer fringes of the flame while, in well managed flames a uniform and slowly growing nano-particle population develops at the center of the flame. In diffusion flames a much richer mapping of nano-particle growth is observed compared to premixed flames.

Experimental:

The pyrolytic device is composed of 3 gas tanks, oxygen, methane and a dry nitrogen carrier gas. All gas streams are regulated with mass flow controllers and the fuel lines are fitted with flash back valves at several locations. The feed temperature of the nitrogen stream is often regulated to maintain the reactant vapor pressure. The nitrogen stream passes through a heated bubbler in order to saturate the nitrogen stream with the liquid silica precursor, hexamethyldisiloxane (HMDS). The reactant vapor and gas streams pass to the burner assembly which is composed of concentric quartz cylinders oriented vertically for a diffusion flame or a flame spray pyrolysis reactor, or the precursors are fed into a fritted burner for a premixed flame. The sustained premixed flame, SPF, used at ESRF is a hybrid of the diffusion and premixed burners. The flame temperature is on the order of 1200°C at the hottest point. Hot vapors, ceramic particles and reaction byproducts flow upward away from the burner and are typically collected in a vacuum tubing arrangement where the gasses cool, powders are separated in a bag filter and effluent gasses, are neutralized in a NaOH bath when HCl is produced (if $SiCl_4$ is used as the precursor) and released to a vent. The effluent gas stream which was fed to the exhaust vent was monitored to ensure a temperature below 30°C. The experiment required modification of the Bonse-Hart and pinhole hutches by addition of ventilation tubing, installation of a methane detector, additional fire extinguishers and installation of tubing and shutoff valves for the gas tubes. This process was conducted during synchrotron shutdown in about 1 day and was done twice during the run for the two cameras.

Typical reaction conditions are shown in the following table.

	Methane	**Oxygen**	**Nitrogen**	**N_2/HMDSO**	**Production rate**
	L/min	L/min	L/min	L/min	g/h SiO2
Flame A	0.4	1.4	5.0	1.0	14
Background A	0.4	1.4	3.0	1.0	0
Flame B	0.8	4.3	8.9	3.0	38
Background B	0.8	4.3	2.6	3.0	0

Table 1. Flow rates in liters per minute for various gas streams.

Summary of ESRF Results Using the ID02 Pinhole Camera:

Diffusion Flames:

Two flame types were involved in the December experiment. A diffusion flame was first observed. A diffusion flame is similar to a candle flame or the flame that results in environmental fires. In the diffusion flame a vapor stream rich in fuel, but containing little oxygen is fed to the burner. Oxygen must diffuse from either the environment or from an outer oxygen stream to a combustion front in the fuel stream. Simulations of diffusion flames indicate a symmetric growth front in the observed flame where fuel and oxygen meet. This was verified in the in situ experiments on the diffusion flame as shown below. Figure 1 shows the diffusion flame in the pinhole camera at ID02. The flame was moved using the HBBL sample stage by attaching the burner to the stage. Exposure times of 20 millisecond were sufficient to fully characterize the few particles present in the aerosol stream. Figure 1b shows particle size as a function of height above the burner at several lateral locations near the center of the flame. Linear growth is observed from which a linear growth rate can be determined. By comparison of measured temperature profiles and chemical composition in the flame (using in situ IR at ETH) a full understanding of nano-particle growth in the flame is being developed.

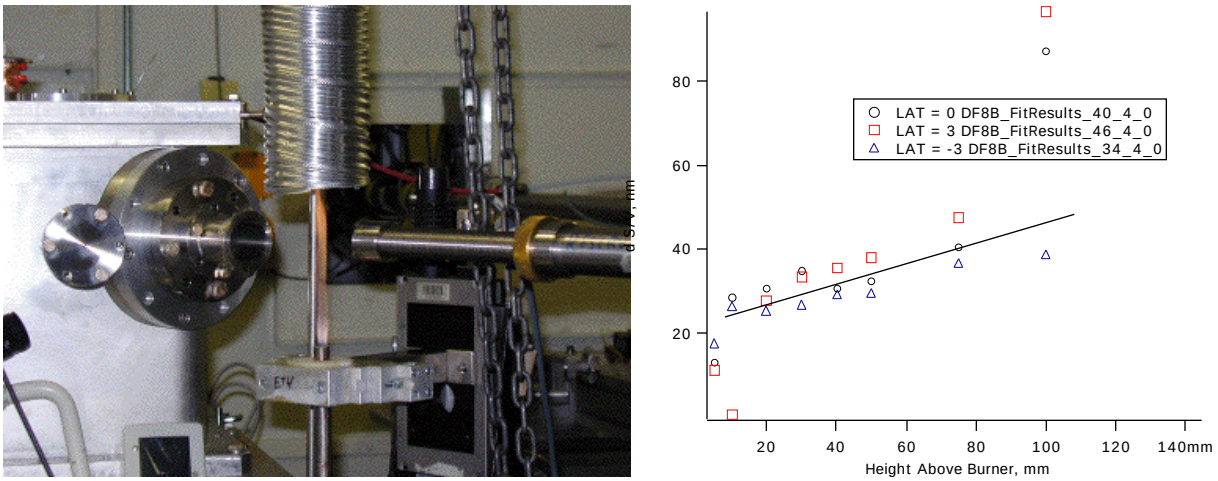

Figure 1. a) In situ pinhole measurements at ESRF, HBBL ID02 showing a diffusion flame. b) Primary particle size, R^3/R^2 for flame shown at three lateral positions in the flame and as a function of height above the burner. The initial points reflect nucleation where a high particle density exists. 10 mm corresponds to about 10 milliseconds growth time.

Figure 2 shows a summary of some of the results on the diffusion flame. The 2D mappings reflect a snap-shot of the flame as view from the various fit parameters using the Unified function. Primary particle density is determined using the invariant and the Guinier prefactor for the primary particles for instance. $D_{S/V}$ is determined from the Porod constant and the primary particle invariant and reflects the ratio of the third to the second moments of particle size. This size corresponds well to sizes obtained using gas absorption, for instance, and reflects a lower moment than measures such as the radius of gyration. Number density shows initial nucleation followed by coalescence and reduction in particle number density. This is followed by a second nucleation burst at about 50 mm in the center of the flame. At higher levels in the

flame a symmetric ring of nucleation is observed in the diffusion flame which is related to diffusion of fuel and oxygen in competition with combustion and formation of silica. Particle size also displays symmetric regions of relatively larger size at about 5mm from the center laterally.

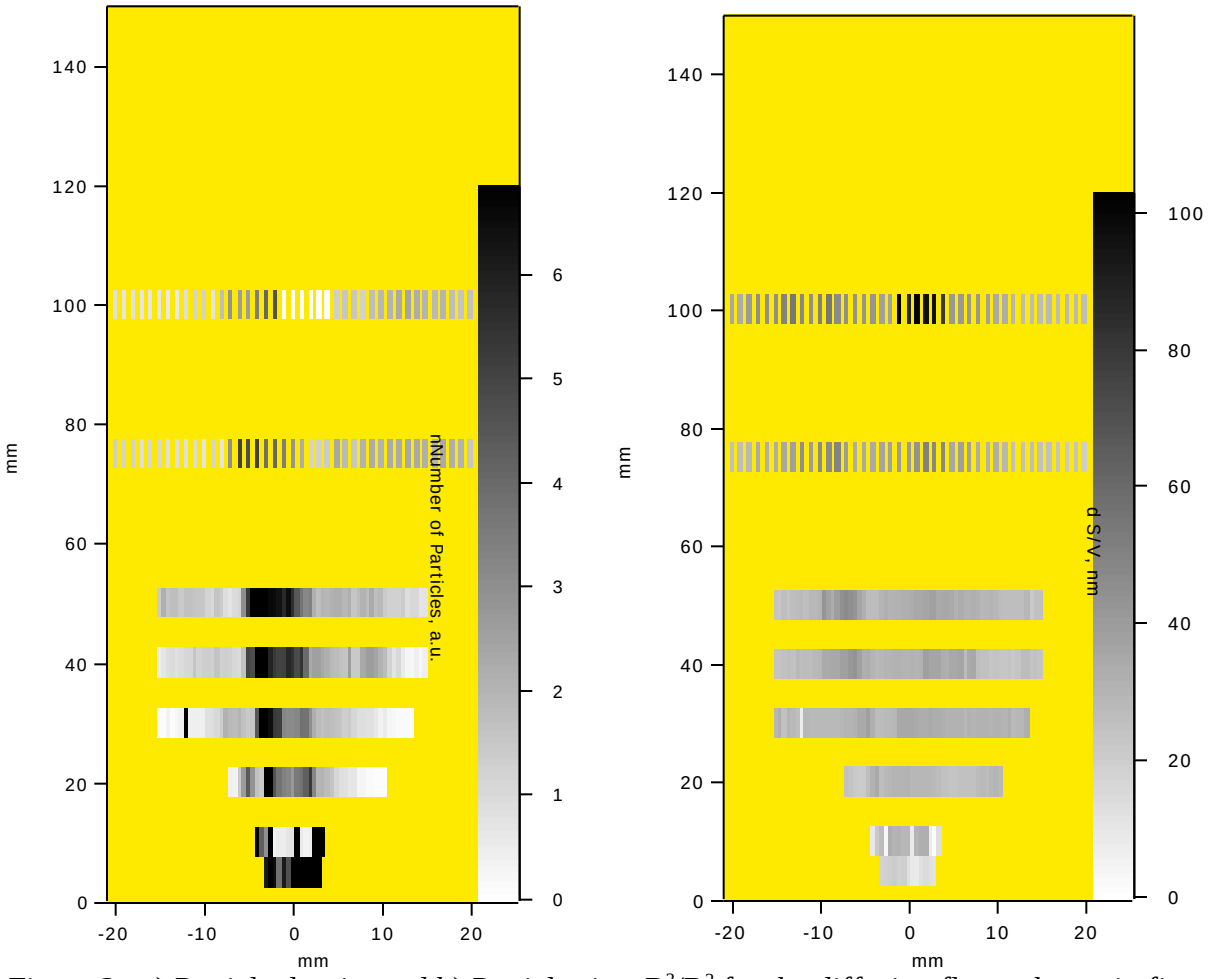

Figure 2. a) Particle density and b) Particle size, R^3/R^2 for the diffusion flame shown in figure 5. Initially, the nucleation stage shows high particle density and small size. Coalescence leads to a much smaller number and larger size. In the center of the flame particle size remains fairly static. The flame shows a diffusion front at + and - 5mm laterally where fuel and oxygen meet.

Although the aggregate size could not be observed, except for the earliest stages of the diffusion flame, the mass fractal dimension could be determined from the slope at low-q in the pinhole camera. Bonse-Hart measurements at APS and ID02 (described in the adjoining document) have allowed a fuller mapping of aggregate structure. The pinhole results show that the initial aggregates are linear in structure, figure 3. These linear aggregates appear to diffuse out of the central part of the flame where they initially form and to become branched in the cooler parts of the flame towards the outer fringes. The observed behavior indicates that aggregates form in a region where particle density is moderately high and where temperatures are moderately low. Higher temperatures or lower particle density both disfavor formation of mass-fractal aggregates and branching.

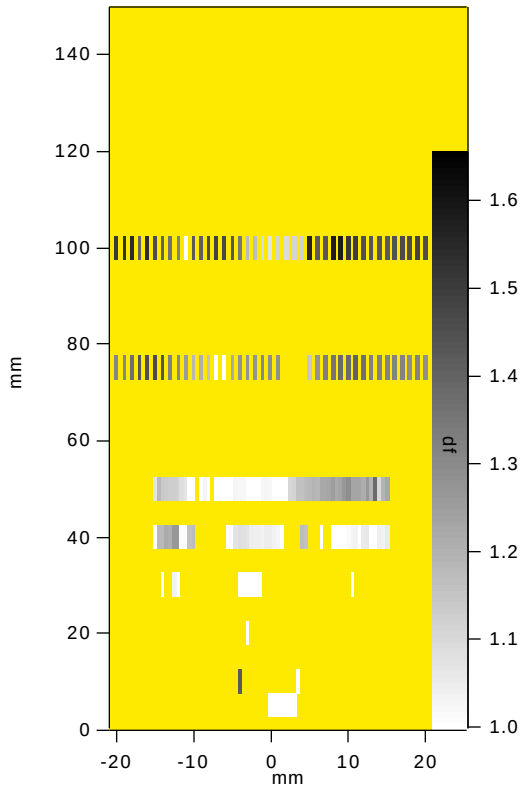

Figure 3. Aggregate dimension for flame shown in figure 1. Only the tail of the aggregate curve could be measured. Aggregates are too large to measure with HBBL camera. Initial aggregation of nuclei coalesce into larger particles at about 10mm above the burner. New aggregates form and diffuse outward at about 50mm above the burner. Larger aggregates form at outer fringe where particle density is low. In all cases the initial aggregates are fairly large (beyond range of instrument) and linear, $d_f = 1$.

Sustained Premixed Flames (SPF):

Whereas a diffusion flame is similar to the familiar candle flame, a premixed flame is more akin to a welding torch or a diesel engine where oxygen and fuel streams are mixed at a stoichiometric ratio prior to combustion. Since temperature is believed to largely govern particle size through control over particle sintering, it is sometimes advantageous to control the flame temperature with an external fuel stream that does not contain silica precursor. This is the so called sustained-premixed flame (SPF). Such a flame is also useful at high particle concentration where the inner fuel-oxygen mixture requires heating to fully combust under controlled conditions. Figure 4 shows an SPF flame installed in the pinhole camera at ID02.

Mappings of the SPF flames were conducted in only one direction from the center of the flame for the most part.

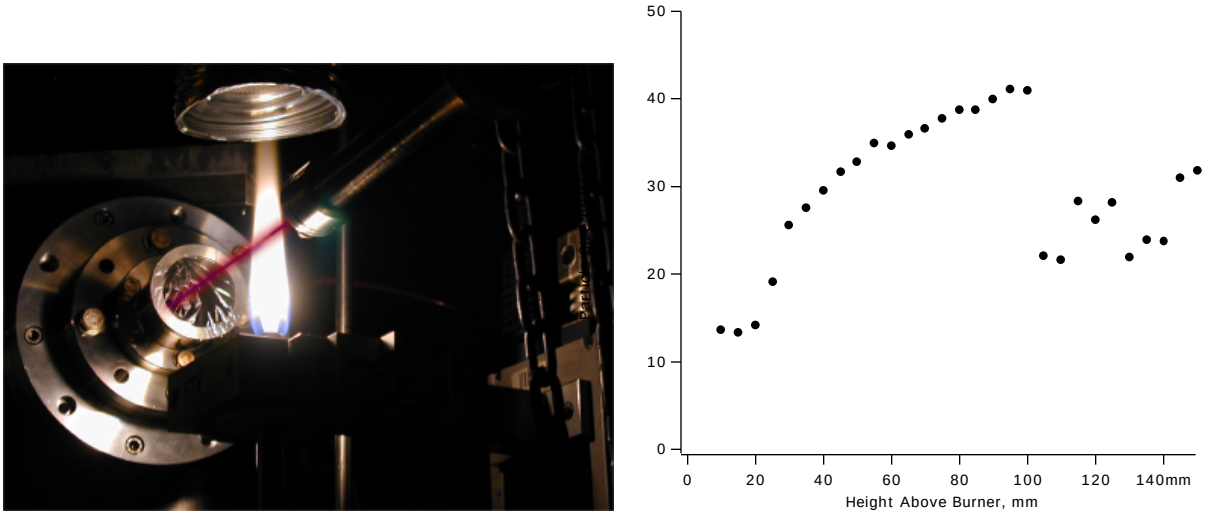

Figure 4. a) Sustained premixed flame (SPF). Red line is added to indicate the path of the synchrotron beam. Plastic wrap was used to protect sensitive optics. At the base of the flame the outer, sustaining flame can be seen to be distinct from the inner, particle generating flame. A nitrogen sheath stream separates the two combustion fronts. b) Particle size versus height above burner for the SPF flame. Lateral diffusion at about 100 mm above the burner leads to a drop in the average particle size. Initial nucleation is seen below 25 mm with a constant particle size. Coalescence and sintering lead to growth above 25 mm.

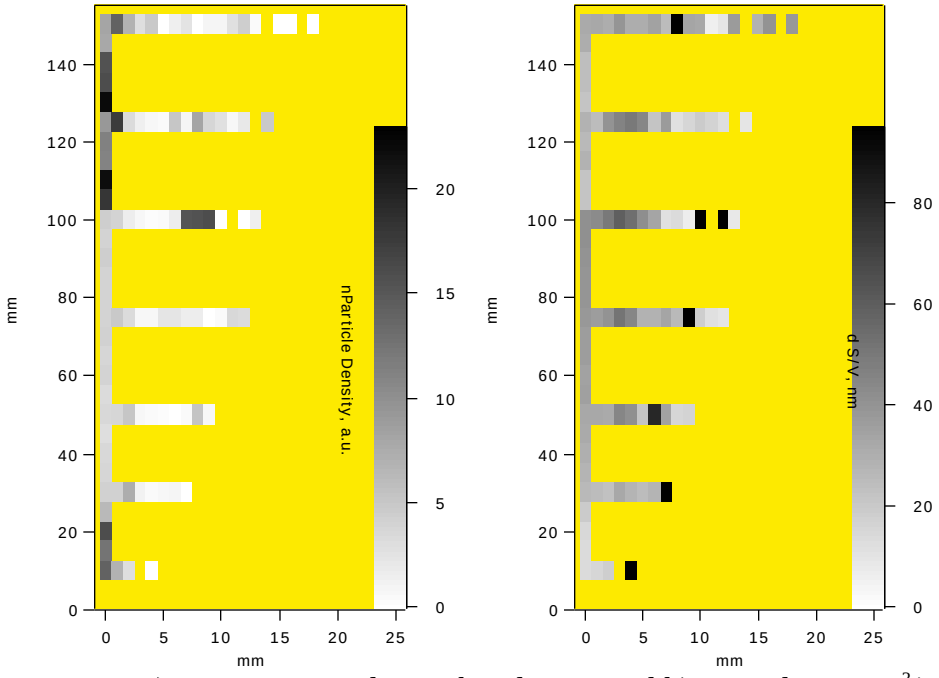

Figure 5. a) Primary particle number density and b) particle size, R^3/R^2, as a function of height above the burner and lateral position. Nucleation occurs up to 20 mm above burner with high particle density and small particle size. This is followed by a reduction in particle number and growth of particles. Large particles form at the hottest part of the flame near the sustaining flame at the outer fringe. Lateral diffusion occurs high in the flame, above 100 mm.

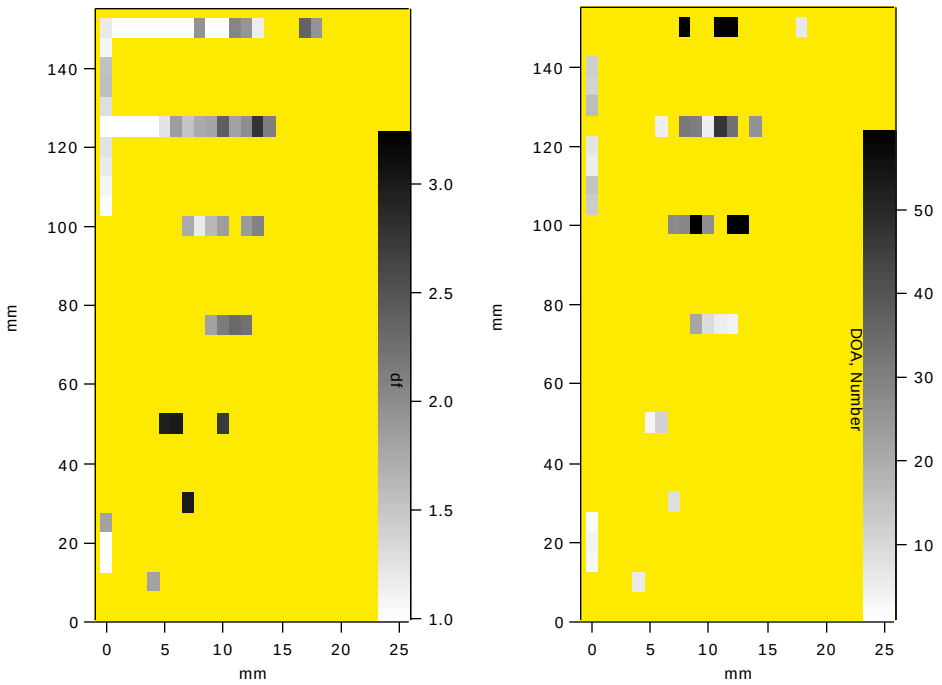

Figure 6. Aggregate structure for SPF4. a) Mass-fractal dimension and b) degree of aggregation, number of primary particles in an aggregate. Most aggregates form at the outer parts of the flame or high in the flame above 100 mm. Aggregate dimension is close to 1 for much of the flame except at the fringes.

Figure 7 shows a plot of primary particle number density and size for a larger SPF flame, SPF8. The size and number data seem to indicate that particles move laterally and upward in the flame. Particles nucleate and grow and then move laterally. There is a secondary nucleation at about 80mmHAB with little growth following this. Late nucleated particles are smaller and fail to significantly grow. A stagnation zone may exist at LAT 5 to 10 and HAB 0 to 35 where large particles form. Figure 7b) clearly shows nucleation, a large burst in particle density, followed by growth, a decay in the number density. This corresponds with growth in particle size. A second nucleation event occurs at about 55 HAB and 2mm LAT that then moves inwards perhaps following diffusion of reactants. The stagnant particles at the base of flame are small in number.

Figure 8a) shows the degree of aggregation, DOA (number of primary particles in an aggregate). A region of large aggregates at 8mm LAT and high in the flame is observed. Monotonic growth of aggregates occurs at the center of SPF8. Aggregates begin to form at 80mm in the center of the flame and at 40 mm at the edge. Figure 8b) shows that d_f increases generally with HAB and with LAT.

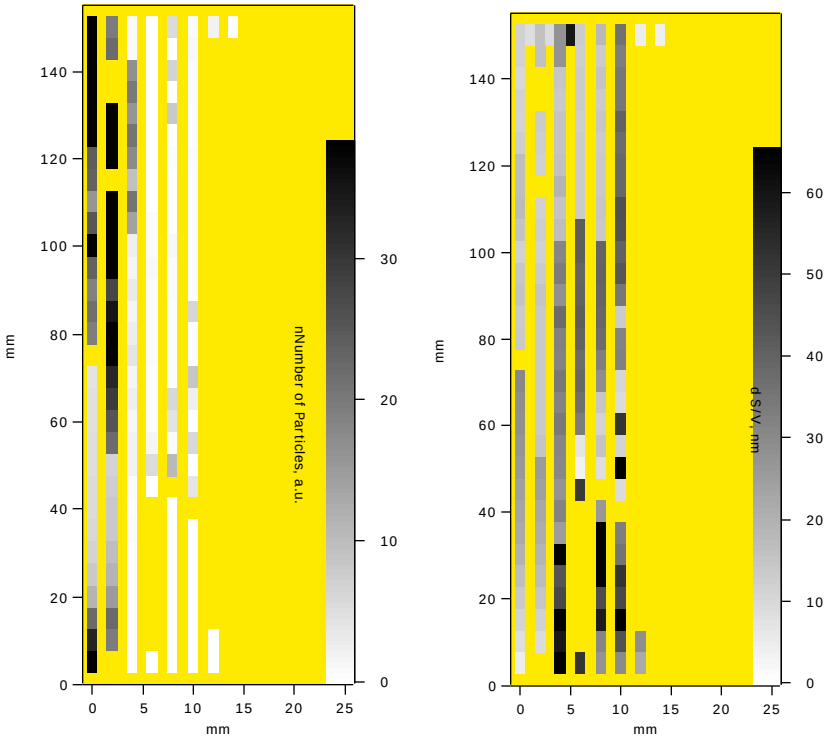

Figure 7. Similar results to Figure 5 for a larger flame, SPF8. a) Particle density and b) particle size.

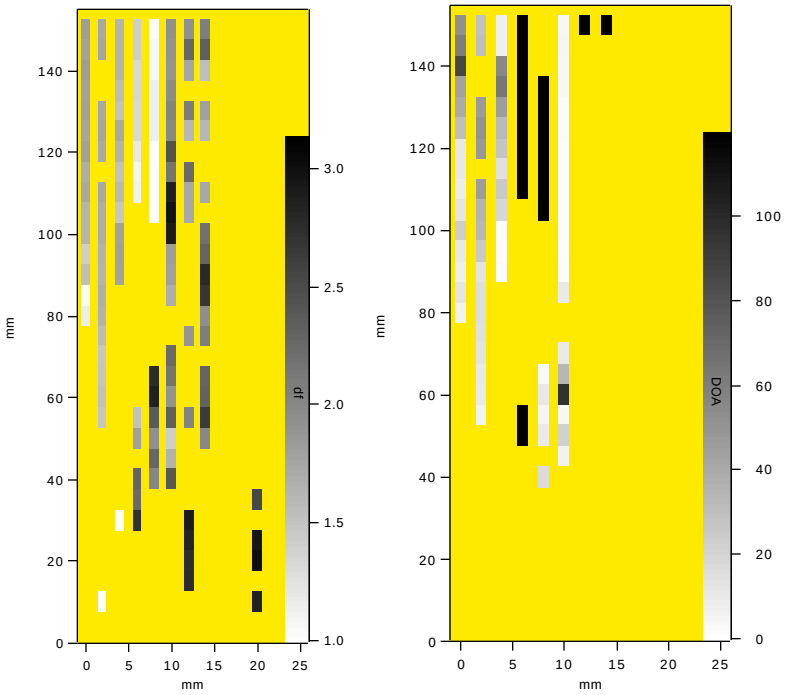

Figure 8. Similar results to figure 6 for a larger flame SPF8. a) df and b) DOA.

Summary:

The initial results using the pinhole camera are encouraging. We have demonstrated that in situ measurements using synchrotron radiation are possible even with the scant populations of particles in aerosol streams. The results have already verified many predictions of previous simulation studies and have brought into question some assumptions. Observation of nucleation times and position in the flame as well as direct observation of nano-particle growth rates are indispensable in shaping the future of pyrolytic synthesis of nano-particles. Pyrolytic synthesis is being used to produce a wide variety of nano-particles ranging from catalysts to fiber optics precursors. Additionally, the information pertaining to diffusion flames may be of importance to the design of low soot engines and may prove of use to those studying natural fire. In many ways those involved in this experiment feel that we are just at the tip of an iceburg in terms of the possible experiments that could be done using the ID02 facility and we hope that we can continue this work.

1 Spicer, PT, Artelt, C, Sanders, S, Pratsinis, SE, *J Aerosol Sci.* **29** 647 (1998).
2 Hyeon -Lee J, Beaucage G, Pratsinis SE, Vemury S., *Langmuir* **14** 5751 (1998).
5 Vemury S, Pratsinis SE, Kibbey L., *J. Mater. Res.* **12** (4) 1031 (1997).
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10 Streletzky KA, Zvinevich Y, Wyslouzil BE, Strey R *J. Chem. Phys* **116**4058 (2002).
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13. Several manuscripts describing the ESRF and APS results are in the process of preparation and submission.

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This is a report on some of the results obtained on the ID02 Bonse-Hart camera in December 2002. The experiments on the Bonse-Hart camera involved determination of the feasibility of in situ measurements on flames where nano-particles are being generated, comparison of the ID02 camera with a Bonse-Hart camera at the APS in Chicago and measurement of several different flame synthesis experiments if feasibility could be established. The experimental run was successful in many aspects but unexpected results, as described below, lead to the transfer of the pyrolytic instrument to the pinhole camera for about half of the allotted beam time. The pinhole results are outstanding and are reported in a separate document.

Comparison of ID02 and APS/UNICAT Bonse-Hart Cameras:

A comparison between the Bonse-Hart camera at APS, UNICAT and the ESRF ID02 instrument was attempted by running the exact silica powder samples that had been previously run at APS. Problems with sample alignment as well as possible contamination of the Bonse-Hart windows at ID02 by the in situ measurements may have corrupted this comparison. At least one case of exact one to one correspondence was found. The figure below shows a fumed silica sample that was run at both facilities with good agreement.

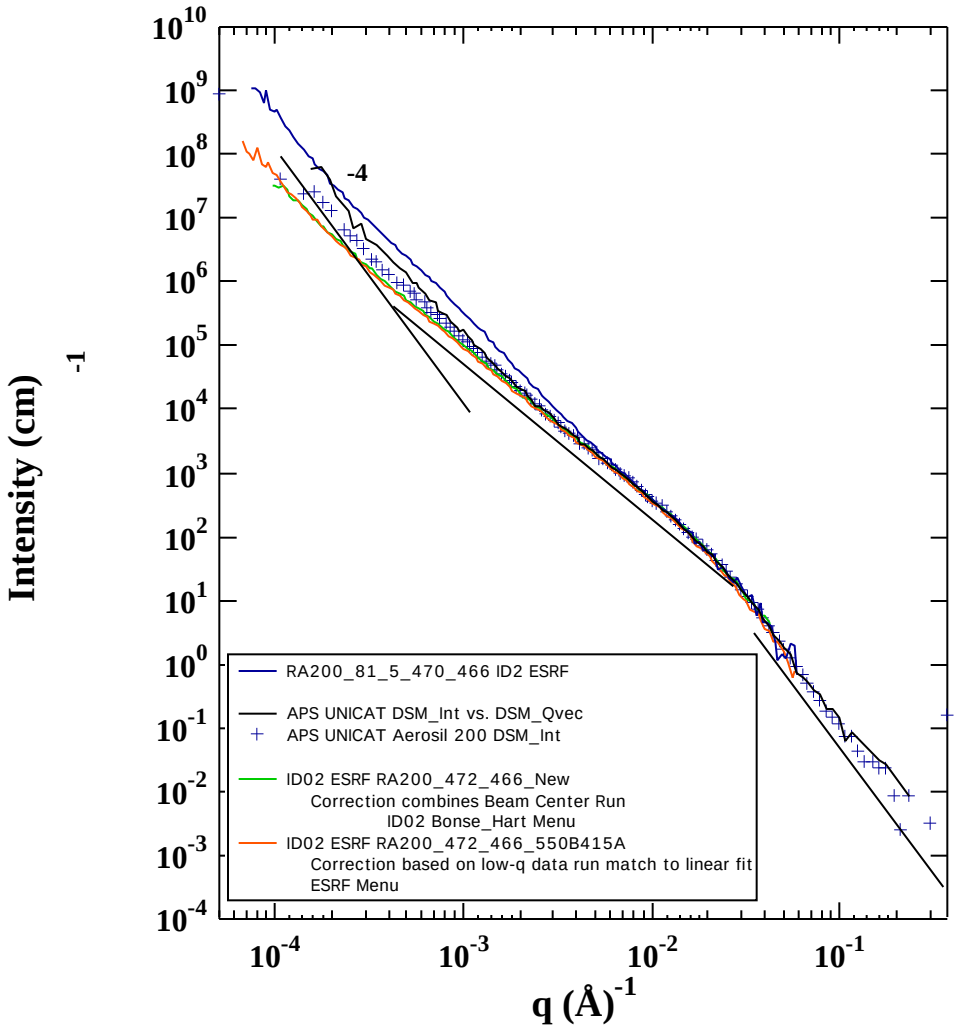


Figure 1. Comparison of USAXS data from APS, UNICAT and ID02. Top curve (blue) is a separate sample (81-5) where the cardboard may have been in the beam, sample alignment problem mentioned above. Black curve (second from top) is an APS run that may also have low-q interference. Blue plusses are the previous "good" run from APS, red and green are two reductions of ESRF data (using different software) that seem to be better than the "good" APS run. ESRF data seems to reach a somewhat lower scattering vector, in some cases below 10^{-4} $Å^{-1}$. APS data can reach a higher-q and this has advantages for some samples such as this fumed silica where the Porod regime for the primary particles is largely missing from the ID02 data.

In situ flame measurements on Bonse-Hart Camera:

In addition to the ESRF ID02 Bonse-Hart runs, we have recently conducted in situ measurements at APS using the UNICAT Bonse-Hart camera. A comparison between the results at APS and at ESRF leads to important information concerning the orientation of aggregates in pyrolytic synthesis. The APS and ESRF Bonse-Hart cameras both result in a line scan through reciprocal space. The scan at ESRF is in the horizontal direction, normal to the laminar flow lines of the flame for the in situ measurements. The APS, UNICAT instrument scans vertically, in the laminar flow direction of the in situ measurement, Figure 2. Figure 3 shows results from APS

and ESRF on premixed flames. Although a sustained premixed flame was used at ID02 and a self-sustaining premixed flame at APS, the patterns were chosen for comparable flow conditions and particle/aggregate structure.

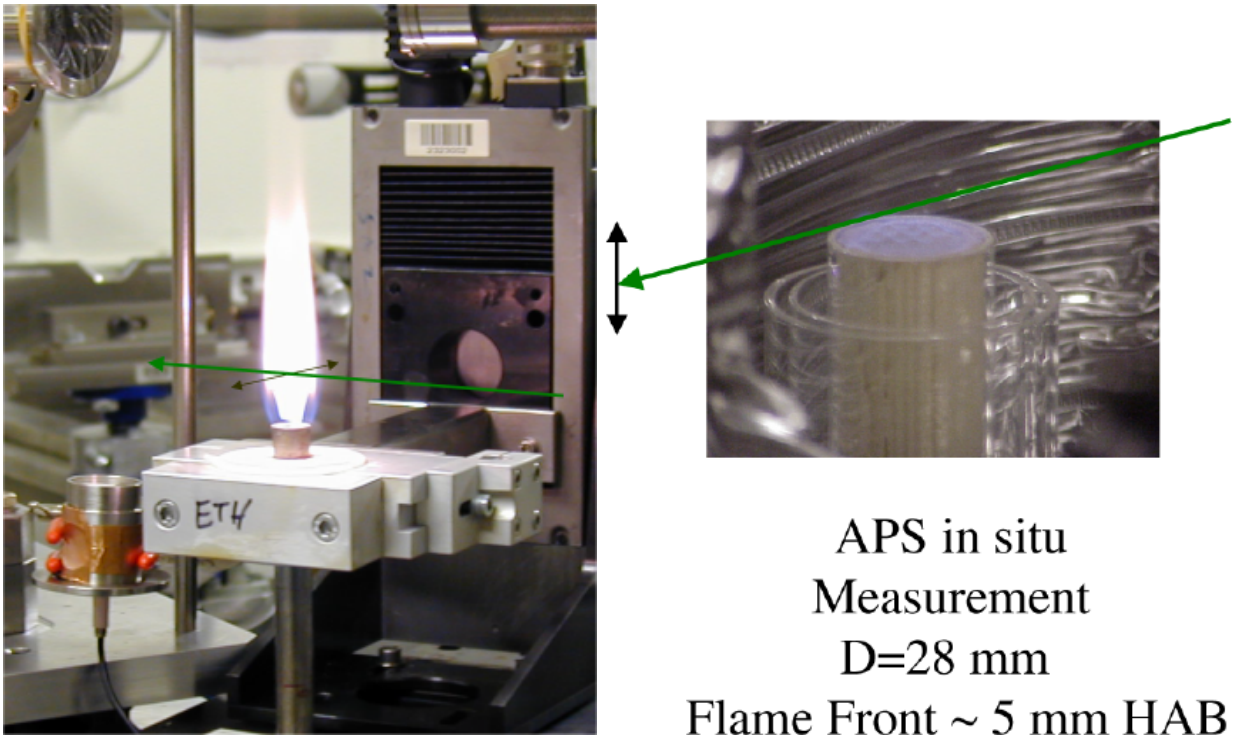
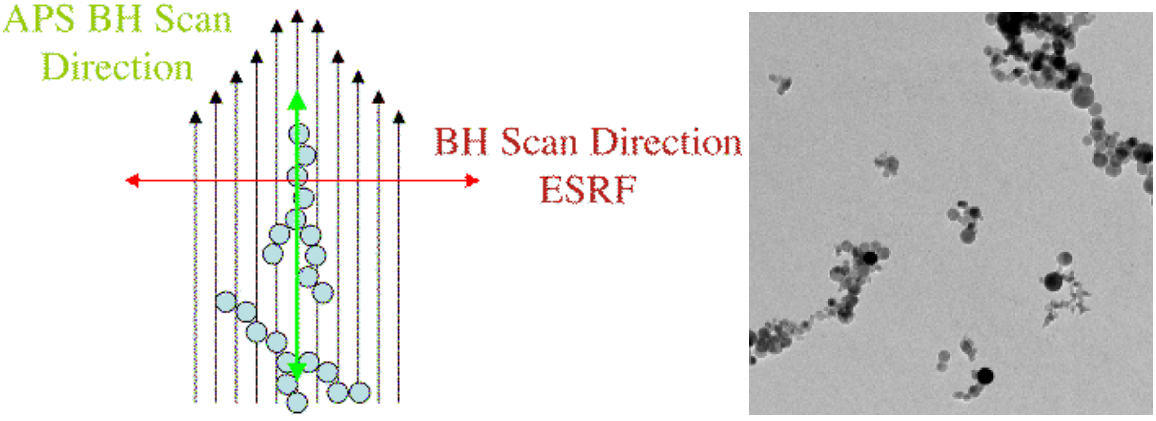
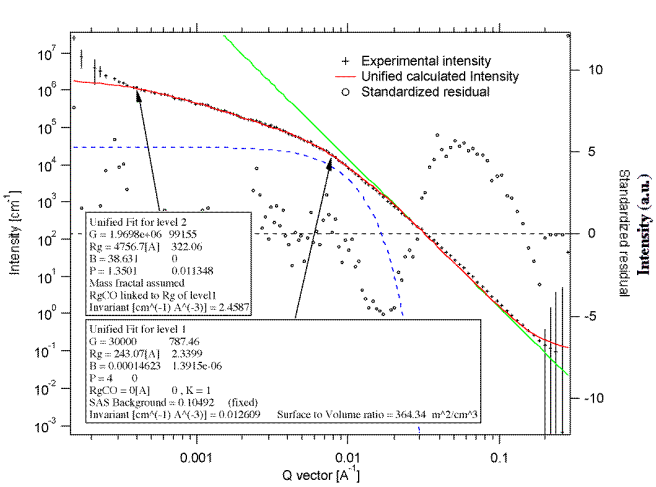
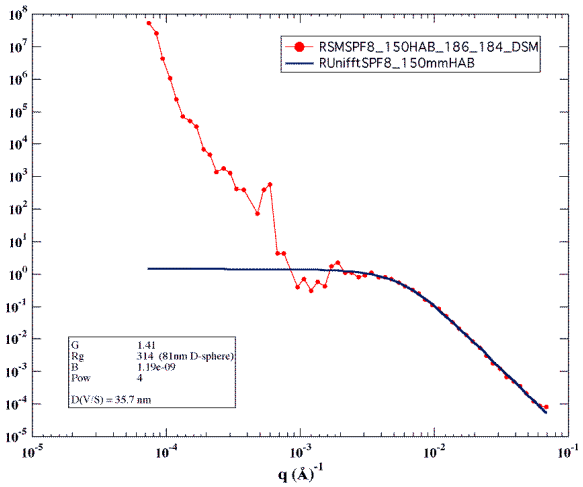


Figure 2. Left, ESRF ID02 Bonse-Hart Sample Stage, green arrow is the path of the beam from right to left, black arrow shows scan direction relative to the flame, scan is horizontal. Right, APS Bonse-Hart sample stage, green arrow is beam path from upper right to middle left, scan is vertical. Both flames are silica premixed flames using HMDS. Left is supported by an external fuel stream, SPF, right is a premixed self-sustaining flame.





APS, UNICAT In Situ Bonse-Hart Data.



ID02 ESRF In Situ Bonse-Hart Data.

Figure 3 a) Schematic of scan directions relative to aggregates in a laminar flow stream for ID02 and UNICAT Bonse-Hart cameras. b) Fumed silica similar to particles produced in the two flames shown in figure 2. c) and d) in situ data taken for the APS UNICAT and ID02 ESRF instruments showing dramatic differences in pattern which may be associated with aggregate orientation in the laminar flow stream of premixed flames.

Since the ID02 Bonse-Hart data showed dramatic differences with the UNICAT data and because issues concerning contamination of the Bonse-Hart windows at ID02 are largely unresolved for the existing data, we have focused attention on the pinhole results in mappings of pyrolytic synthesis. We hope to follow-up our initial studies using the ESRF ID02 Bonse-Hart camera with duplicate runs at APS and ESRF in the hope of determining the degree of aggregate orientation for aggregates of variable mass fractal dimension and aggregate size.

Summary:

The Bonse-Hart measurements demonstrated that USAXS experiments on aerosol combustion streams are feasible. Further, through comparison with APS Bonse-Hart and ID02 pinhole measurements it seems possible that the ID02 Bonse-Hart results support a high degree of orientation of nano-aggregates in the laminar streams of flame synthesis. This result remains to be verified by parallel measurements on the UNICAT Bonse-Hart camera and on the ID02 camera. We anticipate expanding our in situ studies to titania and mixed oxide flames where larger aggregates are produced and Bonse-Hart measurements will be pivotal.

1 Spicer, PT, Artelt, C, Sanders, S, Pratsinis, SE, *J Aerosol Sci.* **29** 647 (1998).
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