ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Investigation of Soot Particle Aggregation using Small Angle X-Ray Scattering	**Experiment number**: SC-1284
Beamline: ID09B	**Date of experiment**: from: 04/02/2004 to: 08/02/2004	**Date of report**:
Shifts:12	**Local contact(s)**: Michael Wulff	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

A SAXS experiment has been performed using the ID09B beamline and the special image plate CCD MAR345 detector available at that beamline. The set-up was adjusted to deliver an X-ray beam of 16 keV (λ=0.7749 Å) and 12 keV (λ=1.0332 Å) with a beam spot size of 0.120×0.020 mm. An ethylene diffusion flame is used as the target (See Figure 1) and is scanned vertically along the center axis by varying the vertical coordinate, z and horizontally along the radial coordinate, r. A flux of about 70 ml/min of ethylene is fueled in a burner with an inner diameter of 11 mm The origin of the vertical coordinate is fixed at the burner mouth. The flame was stabilized by a co-annular flux of air (44 l/min). The length of the visible ethylene-air diffusion flame thus generated was about 30.4 mm as measured with an optical short-distance telescope available at the beamline.

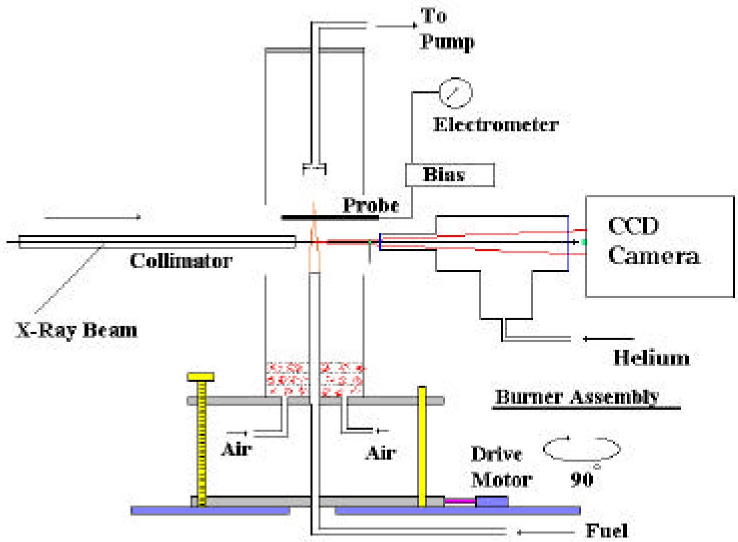

Fig. 1.

Several exposures per point were used in order achieve a sufficiently high signal-to-noise ratio. The raw data were subtracted for background and normalized to a reference signal. The background was measured at each *z* by adjusting the radial coordinate *r* so that the probing volume was about 3 mm out of the visible flame. The primary X-ray beam passed through the flame, and intersected a 0.5 mm diameter beam-stop. Scattered x-rays passed through a helium filled chamber, which was used to minimize extraneous scattering by air molecules. The acceptance angle of the scattered X-beam was about 14 deg. The distance between the flame and the MAR detector was fixed at 755 mm. The scattered intensity $I(q)$ is plotted in figure 1 vs. the modulus of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, also termed the scattering length. The scattering angles admitted in the experimental set-up correspond at E=16 keV to an available q-range from 0.02 to 0.15 nm^{-1}. The $I(q)$ and $q^4 I(q)$ are then plotted vs q^2 and q, respectively. In the first case the reduced data are fitted with an exponential decay in the small-angle or low-q limiting regime by the Guinier equation $I(q) = A\,exp\left(-q^2 R_g^2/3\right)$. This procedure returns an estimation of the largest particles present in the scattering volume. It should be stressed that Rg is not the direct size of the particle but is related to it. For instance in the case of a sphere, the diameter is $D=R_g\times(5/3)^{1/2}$. The structural information is also found from the presence of dips in the intermediate range between the Guinier and Porod regimes as already observed by Hessler et al. [1]. In this case, the scattered intensity predicted for a homogeneous sphere of radius R is $I(q) = I_0\left[3(sin(qR) - qR\,cos(qR))/(qR)^3\right]^2$. Thus the positions of the dips correspond to the zeros of this equation, the first of which occur at $qR=0.07842$ rad. The pattern which is revealed is that the so-called soot primary particles actually consist of clusters of smaller particles (sub-primary particles) in agreement with previous TEM studies [2]. The primary particles come into existence at very low *z* (about 3 mm) under which only nuclei of about 1nm and sub-primaries of about 4 nm are observed. The size of the sub-particles constituting the primary particles is about 4.5 nm independent of the height-above-burner and is obtained by the scattering length q^* at which the transition between the power-law and the Porod regime is observed. The size of sub-primary units is evaluated as the inverse of q^*.

Primary particles increase their size by attaching subprimary particles and by surface growth from about 5 nm (at z=3 mm) to about 12 nm (at z=8 mm). At larger z's, an oxidative process begins that produces a slight reduction of the primary particle size from about 12 nm to about 9 nm, respectively, between 10 mm and 30 mm of height-above the burner.

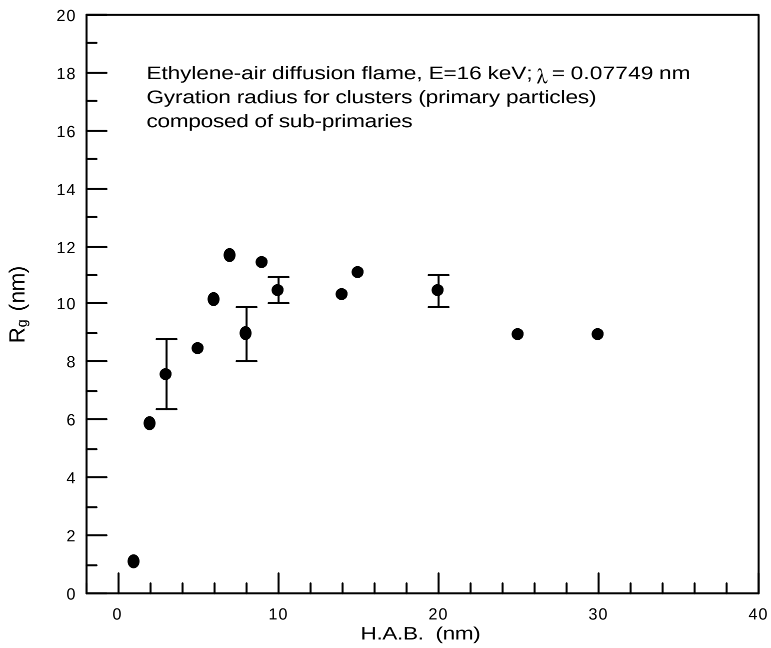

Fig. 2.

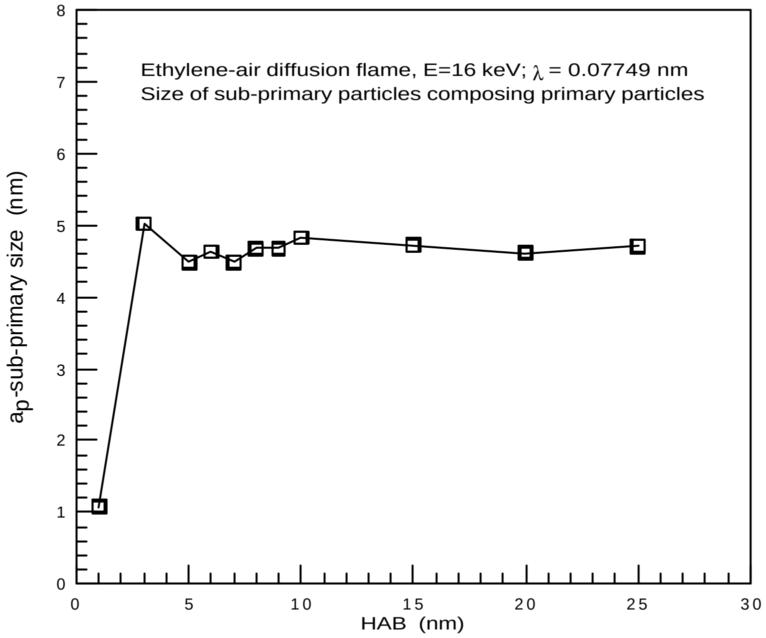

Fig. 3

A special feature of the ESRF with respect to other synchrotron radiation facilities, is the ability to deliver onto the target, a very narrow X-ray beam (0.079×0.024 mm) with very high energy. This will allow us to investigate the formation and growth of primary particles, sub-primary and soot nuclei with high spatial/temporal resolution. In order to have an idea of the huge potential of the ESRF source to shed light on these phenomena, we point out that from preliminary measurements at ID-09B we have observed that the primary particle growth takes place within something like 2 mm of height above the burner, i.e., on a time scale, of less than 100 ms. This *in-situ* method is definitely superior to *ex-situ* sampling (Electron microscopic-TEM analysis) owing to the fact that possible changes in primary particle structure may occur during the cooling and storing of the particles and, not less important, that it is mechanically difficult to take soot samples with such a fine spatial resolution.

Ionization current measurements were also performed using the same technique as in a previous ESRF measurement (SC809) [3, 4] except that a monochromatic (16 keV) beam was used instead of a white beam. The intensity of the x-ray beam was therefore smaller in the present experiment. The results are displayed in figure 4 and it

can be seen that the onset of the appearance of positive ions, resulting from the absorption of x-rays, coincides with the increase in the size of the primary particles. The increase in current above 25 mm is believed to be due to the increase in aggregate soot particle size, the result of agglomeration of the primary particles. Future experiments will seek to elucudate the mechanism of the ionization process in more detail as this is of great astrophysical interest, interstellar dust particles being similar in structure to fractal soot particles.

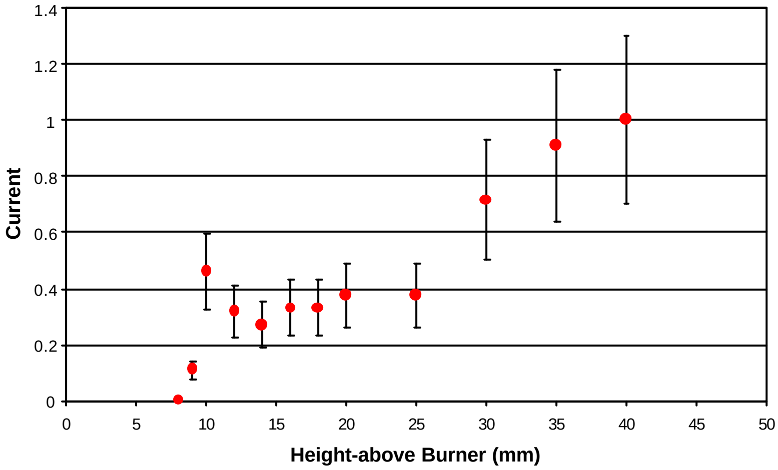

Fig. 4.

References

1. J. P. Hessler, S. Seifert, R.E. Winans and T.H. Fletcher, Faraday Discuss. 119 (2001) 395
2. S. di Stasio, Carbon 39 (2001) 109
3. J. B. A. Mitchell, C. Rebrion-Rowe, J-L. LeGarrec, G. Taupier, N. Huby and M. Wulf, Combustion and Flame, 131 (2001) 308.
4. J. B. A. Mitchell, C. Rebrion-Rowe, J-L. LeGarrec, G. Taupier, N. Huby and M. Wulf, Astronomy and Astrophysics 386 (2002) 743.