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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:** ***Testing of radiometric measurement system for rapid collection of viscosity data under high p, T conditions.***	**Experiment number**: MI-688
Beamline: BM29	**Date of experiment**: from: 18 Feb 2004 to: 24 Feb 2004	**Date of report**: 25/02/04
Shifts: 18	**Local contact(s)**: Simone de Panfilis	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Wilson A. Crichton, Simone de Panfilis, Mohamed Mezouar, Sebastien Pasternak and Thierry Martin.

ESRF

Report:

The subject of MI-688 was to test the utility of the Paris-Edinburgh large-volume press, mounted on a novel goniometer and combined with a fast fluorescence imaging system to detect and measure the velocity of spheres falling through liquid samples under high p, T conditions and to thus obtain the viscosity of the liquid through application of the Stokes Equation.

*From both a technical and scientific point of view, the system is operational and has the potential to be very successful and productive to the User community. As an illustration, we have obtained more than 100 data points at range of high p, T conditions in 4 days of testing (plus 2 days of setup and alignment). This represents a minimum of a **20-fold** increase in the amount of data that can be obtained by similar experiments at **any other 3GS**, and probably comes close to doubling the total number of viscosity data yet collected at high p, T by the radiographic method, from any x-ray source.*

We briefly outline some of our technical findings and improvements that could be added during User experiments, though we point out that the system as run below is entirely satisfactory and can be run as is.

Experimental Setup

With the setup mounted at BM29 (Figure 1.), the P-E press is mounted in the direct beam via a goniometer (normally used for ReflEXAFS measurements) that rotates about a horizontal axis perpendicular to the beam, so that the press can be turned top-to-bottom around the sample position. Behind the press, the SENSICAM (Detector Pool) camera is mounted with 4x microscope objective, focused on a fluorescent screen (Kodak mammography film). All control is external, for operation of press (p, T, position) and camera (exposure parameters, position) and the readout of the camera is buffered directly to memory, before writing to disc.

The experiment proceeds as follows; driving the press to the desired pressure, location of the camera in the direct beam path and setting of fast acquisition rate with suitable exposure time. This will be followed by step-heating until melting is encountered by observation of the sphere falling (normally the User will have little precise information of the melting curve in p, T-space and even less of the viscosity). When the sphere has dropped the sample is quenched and the press turned about for the second measurement. This will be the same, though the User now will have a good measurement of the melting point at pressure and can go directly to a sub-melting temperature and then heat rapidly to the desired temperature with a correctly adapted exposure, region of interest and

frame rate. After each measurement is finished the camera buffer can be written to disc for recovery and temperature, time curves recovered (e.g. for estimation of heating rate, etc.) as well as details of furnace characteristics (for continuous control of the state of the furnace, which is being heat and quenched 2-3 times per hour).

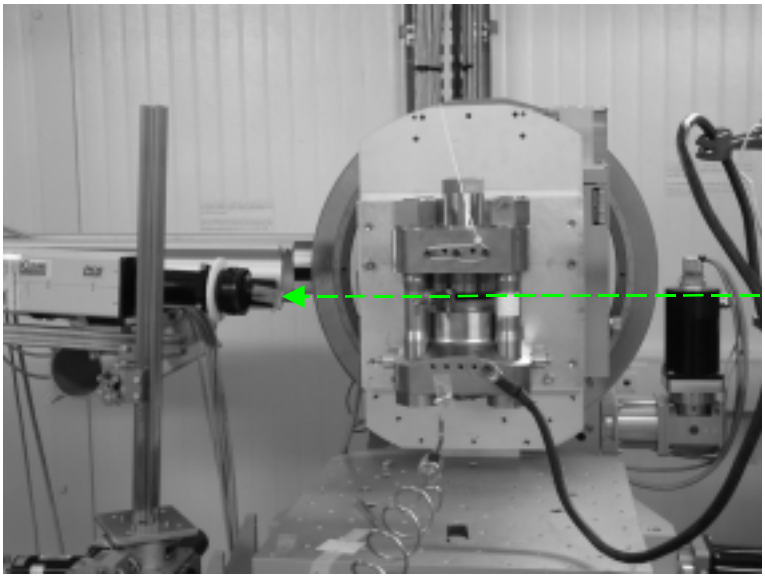


Figure 1.

Fast-imaging system coupled to Paris-Edinburgh press, as setup on BM29.

The incident beam passes from the right, through the anvil gap in the press, onto the fluorescent screen on the SENSICAM camera. The image is magnified and recorded in a memory buffer before writing to disc at the end of each run.

Using the goniometer, we can then turn the press and take further measurements.

Tested limits

We have tested the following, using liquid sulphur as sample:

1. Variation of energy on the visible contrast from, <15 to 35 keV
2. Measurement of velocities with a range of fall time from 0.1 seconds to 1000 seconds (> 15mins) over typically <500 μm, e.g. Figure 2.
3. Measured with exposure times from <5 ms to >1 second (i.e. frame rates of ~20Hz to < 1Hz, including deadtime)
4. Tested scintillators and fluorescent films; with the Kodak mammography film proving useful over full E and t range.
5. Variation of probe sphere size from 0.03mm to 0.4mm; any sphere smaller than 0.1mm was unusable at these E conditions.
6. Analysis of the 16-bit TIF images is most satisfactory using Fit2D.

There is no need to test the operation of the press, furnace nor the goniometer.

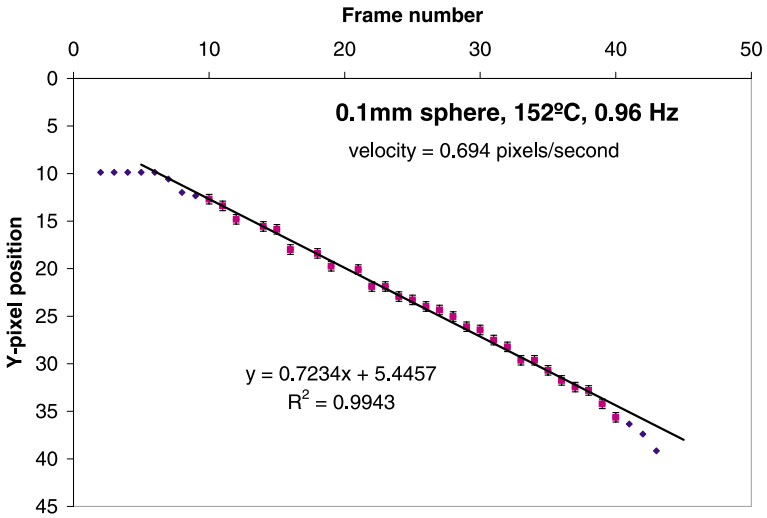


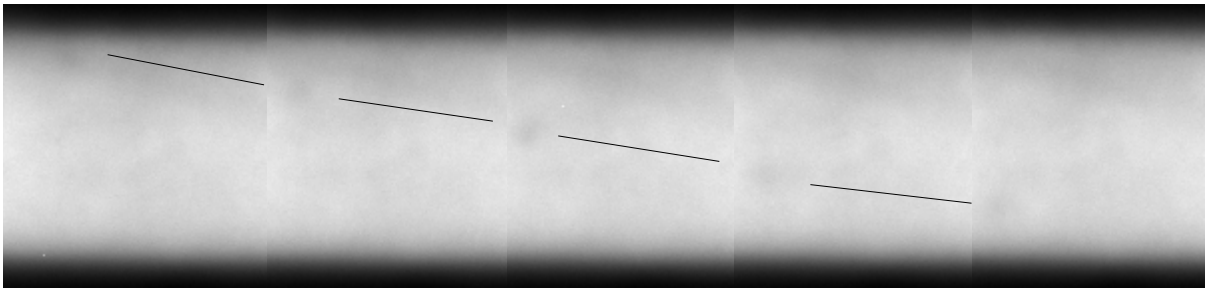
Figure 2.

Typical plot of image frame number versus 1-D pixel position, from which the real-space velocity can be calculated knowing the frame rate (in this case 0.96 Hz) and a calibrated pixel:mm scale. This data is taken from those frames shown in Figure 3.

To obtain the viscosity, we then require the density of the sphere and liquid and the size of the sphere only.

Figure 3.

Selected frames from a 0.1mm sphere falling through sulphur liquid.



Available measurements

It is self-evident that the melting curve can be measured with the largest contributing error (including; temperature overstep for visible sphere release, temperature measurement via thermocouples and the pressure effect on emf, pressure measurement via a marker, e.g. the BN or other capsule material) being that of the pressure measurement as it relies on its own equation of state in p, T space and depends on the same errors in temperature measurement in addition to those of estimation of unit-cell volume, or density, at high p, T conditions.

The viscosity can be measured, again with the largest error, we expect, being due to the estimation of density of sample liquid. The database is not sufficiently large to assess the accuracy of the measurement. However, with regard to the precision, we have obtained essentially identical fall rates at similar conditions during repeat experiments. Through the application of Stoke's Equation to a liquid at identical p, T conditions in the same container we would obtain the same viscosity with identical velocities.

The density of the liquid, or, a relative density could be estimated by the change in integrated intensity in a region though which the sphere passes, as per the method previously delineated by Katayama (1996).

For examples of falling spheres, see `U:\exp\crichton\viscosity\*.avi` files (onsite only).

Future additions and improvements

Several improvements can be envisaged for better control of p, T conditions and experimental resolution:

1. Addition of a detector for diffraction; this for example, at BM29 could be scintillation counter mounted on the same goniometer as the press; or an alternative, at the new high-pressure beamline, ID27, a fast CCD. With the short exposure time (a few seconds) this would give *in situ* measurement of:
    a. the falling sphere density, and
    b. the pressure with use of the thermocouple T, measurement, or,
    c. p and T through cross-calibration of marker densities - though this is less precise.
2. Use of monochromatic radiation tuned to the probe sphere K-edge for increased contrast (e.g. 78 keV in this instance), this would only be generally available at ID beamlines, though this could form part of the sphere selection criteria.
3. Camera with shorter deadtime; in many cases we were operating the camera with exposure time shorter than the read-out time. Thus the frame rate was limited by read-out time, which in the case of the long exposure SENSICAM was ~35ms.
4. Use of diamond and cBN anvils to increase the x-ray 'transparent' portion of the anvil gap.

It should be possible, at a high flux beamline (like ID27) to obtain structural measurements of the liquid by diffraction (either before or after the sphere passage). Though the limit in this case is that the viscosity must be such that the sample is heat and quenched over a timescale of several seconds; subsecond viscosity measurements would not permit such measurement. This kind of diffraction measurement would indeed be disadvantaged compared to data collected during a dedicated diffraction measurement, but should reflect gross structural features; such as those presented by sulphur at various stages of polymerization.

For the future…

At a high-flux beamline, with defocused monochromatic beam tuned to probe sphere K-edge, it may be possible, and is perhaps something to aim for, to collect simultaneously:

i./ image of sphere passage – viscosity;
ii./ fast diffraction to obtain;
    1. sphere density during passage – reduces error in deriving density from calculation
    2. pressure marker density – pressure (and temperature) condition, and
    3. liquid signal – gross structural measurement

iii./ liquid density, though Katayama's method, by integrating detector counts over a region of interest through which sphere falls.