DL/SRF/TM09

technical memorandum Daresbury Laboratory

DL/SRF/TM09

THE RADIATION DAMAGE RESEARCH PROJECT AT THE SRF

by

R.J. BOOTH* and M.C.R. SYMONS
Department of Chemistry, University of Leicester, Leicester LE1 7RH

and

D.J. BRADSHAW and K.R. LEA
Daresbury Laboratory

*Present Address: Department of Chemistry, University of Windsor, Windsor, Ontario, Canada.

MARCH, 1977

Science Research Council

Daresbury Laboratory

Daresbury, Warrington WA4 4AD

CONTENTS

1. INTRODUCTION

When non-conducting solids are exposed to vacuum ultra-violet or soft x-ray radiation, electrons may be ejected, and often both these electrons and the residual positive holes can become permanently trapped. The resulting centres are generally paramagnetic, and may be detected by electron spin resonance methods. A project to study radiation damage effects in a variety of materials, using synchrotron radiation, was approved in 1973.

The essence of the experiment is to irradiate a series of chemicals with light of different wavelengths so as to produce radiation damage; thereafter to detect the presence of radiation-induced centres using a highly sensitive electron spin resonance (e.s.r.) spectrometer. The trapping of the damage centres is temperature dependent, necessitating that the chemical samples be held at low temperature (liquid nitrogen temperature, 77°K) during and subsequent to the irradiation, so as to preserve the damage centres for extended periods. Warming of the samples to room temperature generally allows recombination processes to occur, with consequent disappearance of any damage signals originally present.

This memorandum describes the apparatus built for this research project, and records the operating procedures used in carrying out the experiment at the Daresbury Laboratory Synchrotron Radiation Facility (SRF).

2. EQUIPMENT

2.1 Cryostat

The cryostat comprises a vacuum vessel, in which a sample holder is mounted which can be cooled to liquid nitrogen temperature. The cryostat

was designed in conjunction with Mr. Ian Herbert of the Oxford Instrument Co. Ltd., and manufactured by Oxford Instruments. Figure 1 shows the salient features.

The main body of the 12.5 cm diameter outer vacuum case is made of stainless steel, and carries three FC50 and one FC38 vacuum flanges which are set at 90° to each other. These radial flanges are used for evacuation or irradiation purposes.

The cryostat has two concentric liquid nitrogen vessels, both of which are made mainly of stainless steel. The outer vessel takes the form of an annulus of outer diameter 11.43 cm, and inner diameter about 5.1 cm. It is supported and fed by three nitrogen ports which are vacuum insulated across the top plate, and has a capacity of about 1.2 litres. The inner wall of the annulus is made of 5.1 cm copper tubing, and extends to meet a copper support. This support is in turn partly located and supported by a stainless steel tube which is seated in a nylon bush, which fits into the bottom plate of the cryostat. The copper support has two radial holes for access of radiation to the samples and helps to provide a stable thermal environment for the samples.

The inner nitrogen vessel has a capacity of about 0.12 litres and is fed by a stainless steel tube which extends through a 5.1 cm diameter neck in the top plate to the very top of the cryostat. The top of the neck has a demountable flange which allows the complete insert to be removed. The main features of the insert are the following:-

(i) a vacuum insulated nitrogen fill point which includes a notch to act as a "keyway";

(ii) a hexagonal nut with internal thread which, in conjunction with a thrust bearing, is used to locate the insert vertically;

(iii) a sliding double O-ring seal with a pump-out access facility between the O-rings. This gives the necessary freedom for vertical and rotational motion of the insert, and the pump-out facility can be used as a safeguard against leakage past the O-rings;

(iv) the inner nitrogen vessel and support tube;

(v) the gold-plated copper sample holder. This allows up to 18 samples to be carried, in individual recesses around its circumference. The holder also has a single diametrically-drilled hole through it to allow radiation to traverse it for alignment purposes. The holder is demountable, but in use is held in contact with the lower edge of a hollow copper rod which forms a downward extension from the lower end of the inner nitrogen reservoir. Contact is maintained by a spring and retaining rod, while locating pins align it radially;

(vi) a spring-loaded cover cap or shroud. When the insert is lifted out of the outer vessel, the spring extends to its neutral position so that the shroud locates over the sample holder.

The topmost portion of the insert serves as a spindle for a gear wheel which is attached to it by two grub screws. The gear wheel, of 107 mm outside diameter, has 100 teeth, and carries a 360^{0} circular scale on its upper face. The insert can be made to rotate about its axis by means of a Rank-Pullen type 18/50 28 volt d.c. electric motor, an S.H. Muffett 3000 : 1 reduction gear, and a 50-tooth gear wheel which

couples to the 100-tooth wheel. The rotational position can be read off against a vernier scale fixed to the main body of the cryostat. By incrementing the scale reading in units of 18^{0}, successive samples may be moved into the path of the incident light beam. For two angular settings, 180^{0} apart, the diametrically-drilled channel in the sample holder lines up with the beam; monitoring the peak intensity of the transmitted light beam in this situation permits a reference "zero" on the angular scale to be determined.

Of the four ports 90^{0}-apart around the lower portion of the main body of the cryostat, one is used to admit the radiation, and the facing one is used for the transmitted light beam measurement. This is accomplished by a "fluorescent converter", a layer of sodium salicylate which has been sprayed (in a methanol suspension) on the inside surface of a glass viewport. Under irradiation by ultra-violet (uv) light, this fluoresces at longer wavelengths (blue light) for which the glass window is transparent. A photomultiplier (EMI 6256B) held in position against the outside surface of this window, and enclosed in a light-tight box, serves to measure the intensity of the fluorescent light, and hence gives a signal proportional to the uv light intensity.

2.2 Pumping Station

One of the four ports on the main body of the cryostat serves as a pumping port. Connection is made via bellows and an elbow piece to a high vacuum pumping station. The pumping system was specially built by Vacuum Generators Ltd. to a specification arrived at after extensive discussion between Daresbury Laboratory and the Company. The system is shown in outline in fig.2. It includes:

(i) a high vacuum section incorporating an Edwards 10.2 cm oil vapour diffusion pump and a CCT100 liquid nitrogen cold trap;

(ii) a rough pumping and backing section, incorporating an Edwards ED200 oil-sealed rotary pump, a foreline trap and diffusion pump backing ballast tank;

(iii) sundry valves, pressure gauges (Penning, thermocouple, and capsule dial), bellows sections and pipework;

(iv) an instrument console and control panel.

The whole system is mounted on a mobile mild steel frame which includes a platform on which to support the cryostat. The frame is fitted with four jacks, allowing it to be raised approximately 5 cm above the floor. Further small lateral and vertical adjustment of the cryostat position is built into the mounting system by which the base of the cryostat is attached to the support platform. Bellows sections in the vacuum system provide the necessary flexibility to permit these fine relative adjustments to be made.

The test specification of the pumping system alone was a base pressure of 1×10^{-7} torr or better, with the cryostat not attached. A description of the evacuation cycle and mode of operation of the pumping system is given later.

2.3 Liquid Nitrogen Filling System

Three reservoirs require liquid nitrogen, and to maintain these cold throughout an experimental run of two or three days, an automatic filling system was devised by members of the Daresbury Laboratory Cryogenics Section. This is outlined in fig.3.

The liquid nitrogen supply originates in a 160 litre storage dewar which has a back pressure of 2 to 3 psi over atmospheric pressure maintained by a nitrogen gas bottle and a 3 psi release valve for any excess pressure. Flexible, double-walled filling tubes (with evacuated interspace) run from the supply to the three reservoirs (cold trap on pumping station, and two reservoirs in the experimental cryostat). Each supply line has a liquid nitrogen valve. The opening and closing of each valve is controlled from liquid level sensors in the respective reservoirs. Two sensors are employed in each reservoir, for the upper and lower liquid levels respectively.

The filling system works reasonably well for the outer cryostat reservoir and for the diffusion pump trap, both of which have three inlets/vents. However, despite much effort, a reliable way of automatically filling the inner cryostat reservoir has not been found. The fact that the central trap is of small capacity and has only one narrow filling aperture means that there is a lot of turbulent bubbling of liquid nitrogen when it is being filled. During the filling cycle, such turbulence can cause the upper detector to be surrounded with liquid momentarily, and cause the liquid supply to be switched off prematurely. Also, the switching levels of the liquid sensing diodes seemed to drift appreciably with time for no accountable reason. In practice, the inner cryostat trap is filled by hand from a small thermos flask every 3-4 hours. At these times, opportunity is taken to manually trigger off the filling cycle of the outer cryostat trap. This can be initiated by momentarily shorting out the diode in the lower liquid level detection circuit.

It is found that after one filling, under good vacuum conditions, neither of the cryostat traps runs dry over a 5½ hour period, and the

sample temperature is held low throughout. The temperature of the sample holder was found to be less than 80°K prior to irradiation. Exposure to the synchrotron light is not expected to increase the sample temperature significantly. The trap on the pumping station has a holding time of upwards of 12 hours.

2.4 E.s.r. Spectrometer

Radiation damage is detected using a Varian E3 X-band e.s.r. spectrometer at the University of Leicester Chemistry Department. This instrument will not be described here.

3. EXPERIMENTAL PROCEDURE

3.1 Sample Preparation

The chemical samples used are in the form of cylindrical pellets, 3 mm in diameter and 5 to 10 mm long. They are prepared by compacting finely ground powder in a specially designed press. The bottom half of the press consists of a cylindrical piece of metal with a 3 mm diameter hole drilled through its centre. The bottom of the hole is threaded and fitted with a bolt. The top part of the press is a long 3 mm diameter rod or "plunger", which will move up and down within the hole of the lower press.

Finely powdered chemicals of the highest available purity are placed in the bottom die and compacted down by the plunger. The bolt of the bottom die is then removed and the plunger used to drive the pellet all the way out. When making pellets of different chemicals the dies are carefully cleaned when changing chemicals. The first two pellets made from a new chemical are normally discarded. This precaution is necessary because much of the damage induced by the radiation lies in the surface layers.

Up to eighteen of these pellets can be placed in the sample holder for each experimental run. The same chemical can be exposed to light of eighteen different wavelengths, or eighteen different chemicals to light of the same wavelength, etc. The sample holder is then attached by the spring and retaining rod to the base of the insert portion of the cryostat. It is useful to note the approximate position of each sample with respect to the gear wheel's 360° scale, as this scale will later be used in setting up the sample positions inside the cryostat.

3.2 Setting-up

Before introducing the insert, with attached sample holder, into the cryostat, the cryostat and pumping station are located in the right position in the Synchrotron Radiation Facility to receive light from the exit slit of a monochromator. Two monochromators are used in this research:

(i) a "normal incidence" horizontally-dispersing Wadsworth mounting, offering a wavelength range from 250 to 5000 Å, and a beam height of 1.52 m above the floor;

(ii) a grazing-incidence, vertically dispersing Miyake-West design[1], covering the wavelengths 40 to 400 Å in four overlapping ranges. The two shorter wavelength ranges have a beam height of 1.44 m, and the two longer wavelength ranges have a beam height of 1.33 m.

To accommodate these different beam heights, the vacuum pipework of the pumping system includes a removable section in the vertical portion connecting to the cryostat, and the platform on which the cryostat rests has a removable spacer, and fine adjustment screws. Flexibility for small lateral and vertical movements is provided by bellows sections in the high-vacuum line. In addition, the coupling between the monochromator

exit port and the cryostat front port is made with a short bellows section. It is important to minimise the distance between cryostat and monochromator because the divergence of the light emerging from the exit slit of the monochromator reduces the light intensity on the sample the further it is away.

In order to set the height of the cryostat to match beam height, it is convenient first to provide ready access to the interior of the cryostat by removing the photomultiplier and window from the rear flange, and the coupling bellows from the front flange. The frame on which the whole experimental apparatus is built is then raised off the floor by means of the four screw jacks around its base. Setting to the correct height is conveniently determined by use of the helium-neon gas laser, shining down the beamline and through the monochromator, the latter being set to transmit the "zero-order" of diffracted light. The bright spot of laser light is made to fall centrally over the hole in the shroud inside the cryostat, and the apparatus levelled so that the beam passes out through the rear hole in the shroud. The insert is then lowered into the cryostat body, and, when seated, checked to ensure that the sample holder presents its apertures at the same height as the hole in the shroud. If necessary, this condition can be achieved by resetting the height-adjusting nut on the neck of the insert. When the optical alignment is satisfactory, the frame of the pumping trolley is clamped rigidly to the floor. The photomultiplier, window, and coupling bellows section are re-connected to their respective cryostat flanges, and the complete system made vacuum-tight.

Pump-down procedure is as follows. The cryostat is roughed out by the mechanical pump I, via valves 1, 2, and 5 (see fig.2). In addition, the interspace between the double O-ring seal on the cryostat insert is

evacuated via valve 4. This reduces the pressure to 10^{-2} to 10^{-3} torr. At these pressures, the capsule dial gauge P1 and the Pirani gauge P2 indicate their lowest pressure scale readings, whilst the needle of the cryostat Penning gauge P5 may just register an on-scale pressure reading ($\sim 10^{-3}$ torr).

The diffusion pump (H), and trap (G), are roughed out by opening valve 3, but keeping valve 6 closed. The Pirani gauge P3 should then give the same pressure reading as P2. The diffusion pump cooling water and power are then turned on, and the trap (G) filled with liquid nitrogen. After about 10 minutes, the diffusion pump Penning gauge P4 starts to indicate a low pressure. Valve 5 is then closed, and valve 6 opened, thereby evacuating the cryostat with the diffusion pump. Penning gauge P5 then registers a low pressure which approaches the 10^{-6} to 10^{-7} torr level over a time of order 1 hour. It is sometimes helpful to rotate the insert in its double O-ring seal, to release any residual air traps there. When the cryostat vacuum is compatible with that in the monochromator and beam line, valve 8 on the exit side of the monochromator may be opened, connecting the two vacuum systems.

The filling system for the two liquid nitrogen reservoirs in the cryostat is then activated. It is best to cool the outer reservoir first. This is filled through one inlet, and short lengths of plastic tubing are placed over the other two inlets to deflect the blast of escaping cold gas. Without this precaution, the gas impinges on the flange directly above the inlets, cooling it, and eventually freezing the O-rings in the rotary seal. This can cause a vacuum leak to develop. The automatic filling system for the inner reservoir did not prove 100% reliable, and this reservoir is generally filled from a hand flask of liquid nitrogen every 3-4 hours.

The insert is rotated by an electric motor, for which the control unit is located some distance away. (For radiation safety reasons, all operations on the experiment when the synchrotron is beaming into the SRF area must be conducted remotely, from a shielded location, in this case from the mezzanine floor of the SRF.) A closed-circuit TV system is used to read the angular setting of the insert, and to observe the requisite 18° rotations between adjacent sample positions. The TV camera is focused on the vernier section of the 360° circular scale using a plane mirror to bend the light beam through approximately 90°.

Before irradiating samples, a check on the monochromator's performance is desirable. The photomultiplier current is measured (using an electrometer, or current integrator) and the insert is rotated to the "straight-through light" position. Two adjustments are then possible:

(i) the photomultiplier current is maximised as a function of rotation angle. This sets the sample holder in its zero position, and successive samples can be brought into the path of the light beam by incrementing the angular scale reading in units of 18°;

(ii) the photomultiplier current is maximised as a function of monochromator grating setting. This sets the grating to the zero-order diffraction position, which establishes a reference point for the wavelength scale of the monochromator.

In addition, it is useful to scan the full wavelength range of the monochromator, observing the photomultiplier response. This generally shows a broad maximum in the middle of the wavelength range, with an appreciable fall-off in intensity towards each end of the range. It is beneficial to run the experiment at monochromator settings in the middle

region, where the best flux is available. Such a scan on the grazing incidence monochromator (section 4) also shows a carbon K-edge absorption, which, together with the zero-order diffraction position, allows one to calculate the number of motor steps to change the monochromator wavelength by an Ångström.

3.3 Irradiation Procedure

The monochromator is set to the desired wavelength, and the exit slit width is chosen for the requisite band pass. The vacuum in the cryostat is checked, and the three liquid nitrogen reservoirs are checked. The regulation search of the SRF experimental area is conducted, the area locked up, and the beam shutter raised. From the photomultiplier response, it is verified that all intervening vacuum valves along the beam line are open, allowing synchrotron radiation to enter the monochromator, and monochromatic light to exit and pass through the clear channel in the sample holder. The first sample is brought into position by suitable motor-driven rotation of the cryostat insert, and the time at which irradiation commences is noted. The NINA operating parameters (electron energy, and mean circulating current) are recorded.

Once the experiment is underway, there is very little to do. Every few hours the liquid nitrogen reservoirs in the cryostat need servicing, unless the automatic filling system is in operation. It is desirable to check periodically that all beam line vacuum valves between the apparatus and the synchrotron remain open. In order to determine the accumulated radiation dose received by the samples, a record should be kept of all interruptions to the beam, as, for example, when other users have to go into the area to service their equipment. The NINA "history", a record of energy and current in the synchrotron at 2-minute intervals, is stored in the

main computer memory, and may be accessed via the TSO terminal, or a hard copy printed out if required. This history also includes the status of the SRF beam shutter, whether up or down, at the 2-minute intervals.

Successive samples are brought into the beam by rotating the insert; if necessary, the monochromator is driven to different wavelengths for different irradiations.

3.4 Sample Removal and Transfer

On completion of the series of irradiations, the following "shutdown" procedure is carried out. The vacuum valve 8 between the cryostat and the monochromator is closed, as are valves 2, 5 and 6 (see fig.2). The gear-wheel drive for the cryostat insert is disengaged, and the nuts which retain the insert against the top flange of the body of the cryostat are unscrewed. The liquid nitrogen feed line to the inner reservoir is removed, as is any other item that might impede the withdrawal of the insert. Dry nitrogen is admitted to the vacuum system via the air-release valve 7. With valve 4 open, the tubulation running to the double O-ring seal interspace is let up to atmospheric pressure, and disconnected from the cryostat insert. Subsequently, valve 4 is closed and valve 5 is opened to admit the nitrogen gas to the cryostat. As soon as the pressure reaches atmospheric (as observed on the capsule dial gauge P1) the insert is lifted clear of the cryostat body, and immediately lowered into a waiting dewar vessel containing liquid nitrogen. This transfer operation takes about 2 to 3 seconds. Prior to removal the inner reservoir is topped up with liquid nitrogen; it is found that a considerable amount of this is present after the transfer. With the sample holder safely submerged in the liquid nitrogen, the insert and dewar are taken out of the SRF area for further handling.

The pumping system is generally switched off, unless another series of sample irradiations is to follow immediately. Some condensation of atmospheric moisture may occur inside the cryostat on the liquid nitrogen-cooled surfaces. It is good practice to leave the nitrogen gas blowing through the cryostat for an hour or so. With the filling system switched off and the vessel at atmospheric pressure, the residue of liquid nitrogen in the outer reservoir quickly boils off, and the vessel returns to room temperature.

The samples have to be transported to the e.s.r. spectrometer at Leicester University. This is best done with the samples remaining encapsulated in the holder. Although the whole insert could be transported as one piece, it is more convenient to detach the relatively small sample holder, and ship only the latter. In practice, a U-shaped clip attachment (fig.4) is used, which, after pre-cooling, is fitted around the bottom of the sample holder, and also surrounds the shroud. Two springs are engaged across the top, so as rigidly to "sandwich" the holder between the shroud and the clip attachment. This combination is then released from the rest of the insert by pulling down on the retaining spring, and turning its locking bar through 90°. This latter operation is effected with a simple pair of small wire hooks, which are inserted through the hole in the clip attachment, and manipulated to engage the locking bar. With practice, this operation requires the sample holder (plus clip attachment) to be lifted out of liquid nitrogen for only a few seconds, before being re-submerged. The package is conveyed to Leicester in a large, slightly pressurised transport dewar of liquid nitrogen. When ready to transfer samples to the finger-dewar of the e.s.r. spectrometer, the clip attachment and shroud are removed from the sample holder, which is kept just submerged in a dish of liquid nitrogen. The sample pellets are extracted

from their recesses in the sample holder, using a fine wire as a lever. After an e.s.r. spectrum has been recorded, the pellet is warmed to room temperature, quenched back to 77°K, and the spectrum recorded again. A comparison of the two spectra then reveals the presence (or absence) of free radicals, unstable at room temperature.

4. OBSERVATIONS

The radiation damage project was allocated beam time in four NINA cycles, between August 1975 and June 1976.

During the first of these, light from a normal incidence monochromator (Horizontal Wadsworth I on SRF north beamline) was used. Although this provided a healthy photon flux, the photon energies (≤ 41 eV) proved insufficient to cause detectable damage in the samples.

When the equipment was transferred to the grazing-incidence monochromator[1], which provides photons with energies up to about 250 eV, radiation damage signals were obtained in a number of specimens. However, because these signals were weak, it was customary to irradiate some samples with zero-order light, in addition to those irradiated with monochromatic light. The zero-order light contained a wide spread of photon energies, extending up to the reflectivity limit of the diffraction grating, and generally produced relatively intense e.s.r. signals. These spectra were useful for "fingerprinting" the nature of the radicals produced, and served as reference spectra when searching for the weaker spectra arising from the same chemicals after exposure to monochromatic light. It nevertheless happened that some observations were uncertain. Various factors could account for variation in the results obtained. The pellet surface varied in compactness from sample to sample, even in the same chemical.

Unrecognised experimental accidents could occur, such as a scraping or chipping of the damaged pellet's surface, or a slight surface warm-up on transfer from the cryostat to the travel dewar, etc. Further, a poor vacuum in the beamline or experimental pumping system could cause the samples to become coated with impurities.

To guard against some of these uncertainties, it was customary to load two (or more) pellets of each chemical in the same holder for a given run. Then after using monochromatic radiation on one sample, its neighbour was exposed to zero-order light for a shorter period. If damage was seen in the latter, but not in the monochromatically-irradiated sample, then some of the above-mentioned uncertainties could be eliminated.

5. CONCLUSIONS

The equipment constructed for the radiation damage research project permitted some few preliminary results to be obtained[2]. The exposure times proved considerably longer than anticipated, necessitating periods of running extending over a couple of days, rather than a matter of hours. Only when access is available to substantially higher photon fluxes, as from an electron storage ring, will it be attractive to resume the project. Under such higher damage rates as would then be expected, the need to perfect the liquid nitrogen automatic filling system might be removed, in view of the shorter duration of the experimental runs. The considerably greater body of radiation damage data that might then be collected should permit a more systematic and quantitative investigation of cross sections and threshold energies for radiation damage processes to be made.

ACKNOWLEDGEMENTS

The contributions at the design stage of this equipment of J.A. Brivati (Leicester University) are gratefully acknowledged. The help of Mr. Ian Herbert (Oxford Instruments) and of Messrs. Ian Stagg and Reg Ellwood (Vacuum Generators) was also of great benefit. Members of the Daresbury Laboratory Cryogenics Section are thanked for their construction of the automatic filling system. Finally, the provision of synchrotron radiation facilities and experimental support at the Daresbury Laboratory is gratefully acknowledged.

REFERENCES

1. J.B. West, K. Codling and G.V. Marr, J. Phys. E7, (1974) 137.

2. R.J. Booth, M.C.R. Symons and K.R. Lea, submitted for publication.

FIGURE CAPTIONS

Fig.1 Sectional drawing of liquid nitrogen cryostat.

Fig.2 Schematic of vacuum pumping system.

Fig.3 Schematic of liquid nitrogen filling system.

Fig.4 Clip attachment.

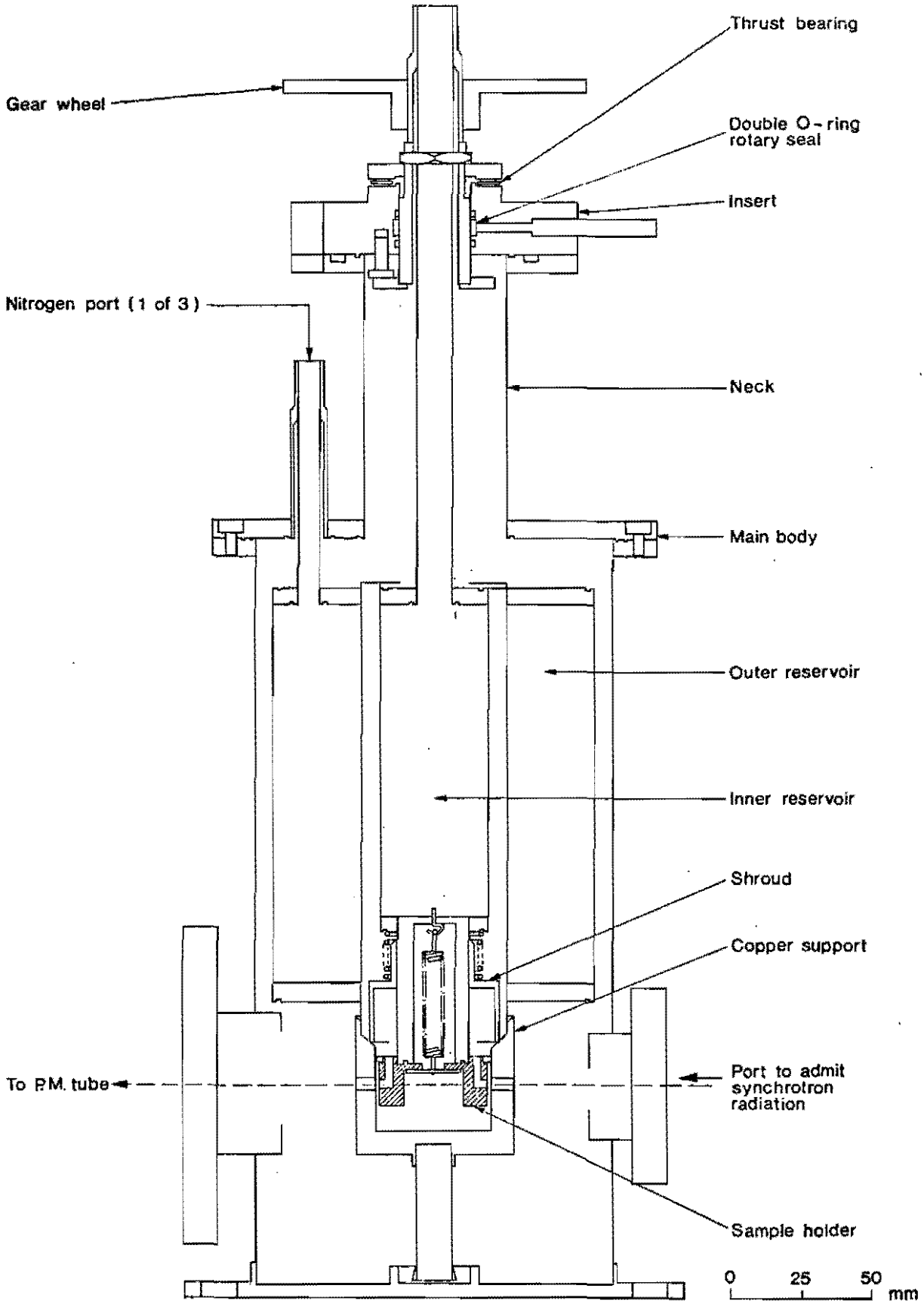
Thrust bearing
Gear wheel
Double O-ring rotary seal
Insert
Nitrogen port (1 of 3)
Neck
Main body
Outer reservoir
Inner reservoir
Shroud
Copper support
To P.M. tube
Port to admit synchrotron radiation
Sample holder
0
25
50
mm

Fig.1

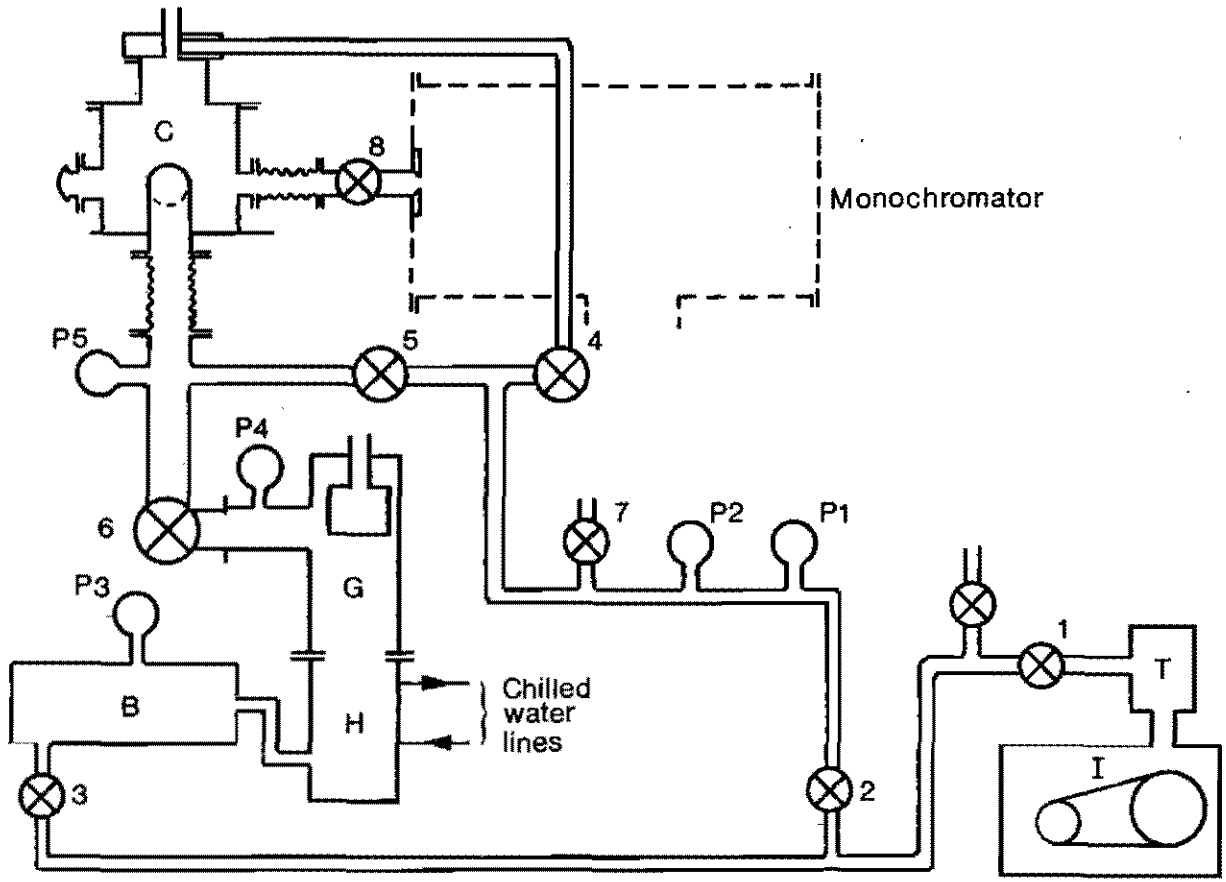
C
8
Monochromator
P5
5
4
P4
6
7
P2
P1
P3
G
B
H
Chilled
water
lines
1
T
I
3
2

Fig. 2

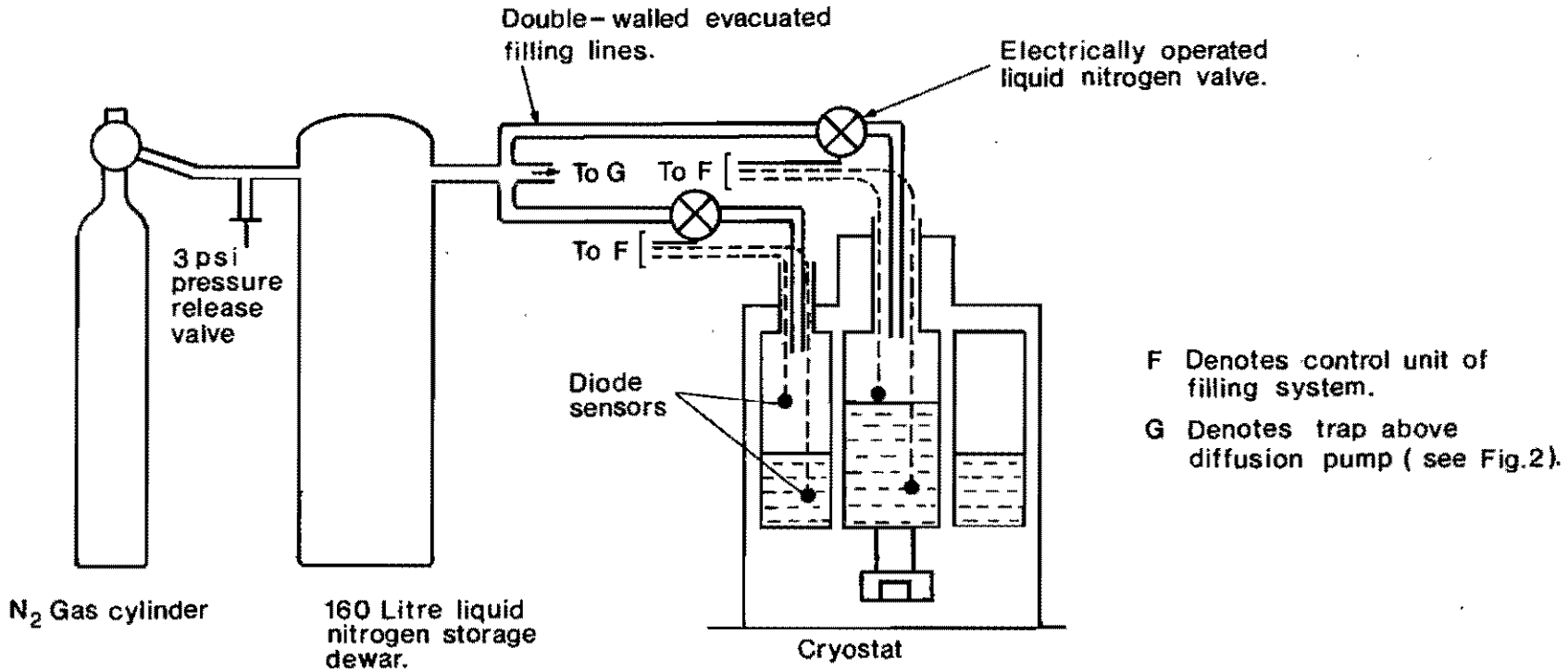
Double-walled evacuated filling lines.
Electrically operated liquid nitrogen valve.
To G
To F
To F
3 psi pressure release valve
Diode sensors
N_2 Gas cylinder
160 Litre liquid nitrogen storage dewar.
Cryostat
F Denotes control unit of filling system.
G Denotes trap above diffusion pump (see Fig.2).

Fig.3

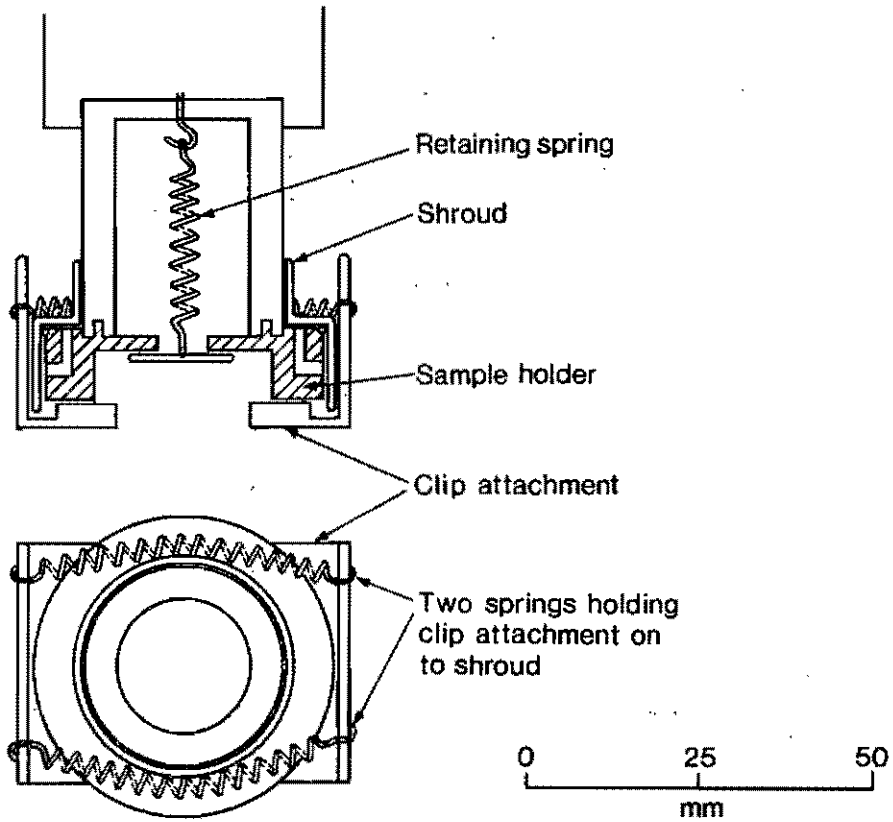
Retaining spring
Shroud
Sample holder
Clip attachment
Two springs holding clip attachment on to shroud
0
25
50
mm

Fig. 4