MEASUREMENT OF THERMAL
PROPERTIES OF IRRADIATED
FUEL AT AEA TECHNOLOGY

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SUMMARY

Three fuel thermal properties measurement techniques developed at AEA Technology are
described; melting point, thermal diffusivity and specific heat. The first two techniques are
already in use for both unirradiated and irradiated fuels (including MOX). Specific heat
apparatus, capable of measurements on irradiated fuel, is currently under development and
will be commissioned for active use later in 1994. It is believed that this facility will be the
first of its kind world-wide.

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1.0   Introduction

In order to underwrite all stages of the fuel cycle and assess all safety implications it is important to obtain comprehensive data on fuel thermal properties under both normal and off-normal conditions for all fuel variants. This is especially necessary for MOX $(U,Pu)O_2$ or $(U,Gd)O_2$ fuels to be used in advanced reactor designs and conventional thermal reactors because the thermal properties of uranium dioxide (UO_2) based fuel may vary significantly as a function of dopant/Pu concentration, irradiation, or stoichiometry. Two of the key thermal properties are melting point and thermal conductivity.

Safety studies of fault conditions/accident scenarios must assess the likelihood of fuel melting and the consequent effects of molten fuel relocation. It is therefore important to have data on the melting point (T_m) of different fuel variants. Melting point measurement on irradiated fuel is a relatively specialised technique which is carried out at AEA Harwell.

Thermal conductivity has a wider importance since, for a given power rating, it controls operating fuel temperatures which in turn affect all aspects of fuel performance. Fuel thermal conductivity (k) values may be derived from measurements of thermal diffusivity (α), specific heat (C_p) and bulk density (ρ) via the relationship: $k = \alpha \cdot C_p \cdot \rho$.

Fuel density is a parameter which is measured routinely during Post-Irradiation Examinations (PIE) at most laboratories. Thermal diffusivity measurements on irradiated fuel are carried out at only a small number of PIE laboratories world-wide, of which AEA Windscale is one. At present, it is common practise to use unirradiated values of C_p in the above expression to determine fuel thermal conductivity since no laboratory is currently capable of making measurements of specific heat on irradiated fuel. However, AEA Windscale has been developing such equipment which will be installed in a hot cell in mid-1994 and commissioned by the end of the year.

This paper describes techniques/apparatus developed and used by AEA Technology for measurement of T_m, α and C_p for irradiated fuel.

2.0   Melting Point Measurement

2.1   GENERAL

Equipment for measuring the melting point of irradiated fuels under carefully controlled conditions has been designed and constructed at AEA Technology's Harwell Laboratory. Experience of measurements in this facility have been gained over the last four years.

The thermal arrest technique is used. For a two-phase solid such as UO_2, melting occurs as a two-stage process at the solidus and liquidus temperature boundaries. The

measurement technique involves detection of the thermal arrests which occur at these boundaries.

2.2 SAMPLE PREPARATION

A fuel sample is typically around 10 g. No specific preparation of the sample is required, except that care must be taken to ensure that the fuel is not contaminated with any extraneous material which could affect measurements.

2.3 APPARATUS

A schematic diagram of the melting point furnace is shown in Figure 1.

Due to incongruent vaporisation at temperatures close to melting, the fuel sample is contained in a sealed tungsten capsule manufactured by vapour deposition techniques. This capsule forms the primary fuel containment. Careful regulation of the oxygen partial pressure within the capsules is required, since the phase diagram for UO_2 indicates a reduction in the melting temperature for hypo- and hyper-stoichiometric composition. The furnace is constructed such that the sealed capsules containing the fuel samples are heated by large electric currents induced by a radio-frequency (rf) powered work coil.

The capsules comprise an open ended tungsten tube to which an end-cap is welded before fuel loading. After insertion of the required fuel variant, a similar end cap is welded into the remaining open end forming a sealed unit. Both end caps include a re-entrant thermo-well so that capsules can be used in either vertical orientation within the furnace. The capsules are a sliding fit inside a cylindrical tungsten coil susceptor (approximately 15 mm inner bore and 38 mm long), wrapped with layers of 0.05 mm thick tungsten foil which operate as an effective radiant heat shield. The bottom of the furnace contains a lower heat shield formed from a 24 mm diameter, 0.05 mm thick, tungsten disc, with a 6 mm diameter central hole. This allows the sighting of a Land infra-red pyrometer sensor into the re-entrant thermo-well in the capsule base, for temperature measurement.

The capsule and susceptor are positioned within a single turn rf concentrator constructed from oxygen free, high conductivity, copper. Two vertical feed pipes supply cooling water to the concentrator from the furnace base. An upper heat shield pack comprising six 0.05 mm thick tungsten discs 24 mm diameter, housed in an alumina container, completes the assembly. These furnace components are enclosed within a vacuum envelope to reduce thermal losses and eliminate the formation of glow discharges, which may divert useful current to destructive arcing. A silica window, housed within a removable extended tube, passes through the furnace base plate on an 'O'-ring seal, and is changed after every melting point measurement to prevent signal losses due to fogging by condensed vapours.

The furnace is powered by a 12 turn, water cooled, insulated, copper work coil supplied by an rf generator with an operating frequency of 345 kHz and a maximum power output of 50 kW. Large alternating electric currents, induced by the work coil, are concentrated into the susceptor, heating the capsule contents by thermal radiation.

Power output, and hence furnace temperature, is varied by a 10 turn precision potentiometer. To detect solidus and liquidus temperatures (as thermal arrests) a motorised gearbox smoothly varies the rf power potentiometer, and hence furnace temperature.

2.4 METHOD

Fuel samples are sealed in tungsten capsules in an atmosphere of appropriate oxygen partial pressure. Before measurements are carried out on fuel samples the furnace must be calibrated. Calibration procedures are as follows:

Samples of pure metals with known melting points are encapsulated and heated to melting. By ramping calibration samples to controlled potentiometer settings and breaking them open for visual inspection, it is possible to relate potentiometer settings to known melting temperatures.

The furnace is then loaded with an encapsulated fuel sample and heated to melting. For detection of thermal arrests the heating rate is typically $20°C$ min^{-1}.

The temperature versus time data are then analysed to detect inflexions associated with thermal arrests corresponding to solidus and liquidus temperatures. An idealised typical melting point inflexion is illustrated in Figure 2.

3.0 Thermal Diffusivity Measurement

3.1 GENERAL

Apparatus capable of measurements on unirradiated and irradiated samples is located in a hot cell at AEA Technology's Windscale Laboratory. Experience with measurements on irradiated fuel have been gained over the last four years; during this period various improvements have been made to the apparatus, operating procedures and data processing methods.

The laser-flash technique is used. The basic method is to fire a laser at one face of a sample and to monitor the temperature history of the opposite face. The time taken for the heat pulse to pass through the sample characterises the thermal diffusivity of the material.

3.2 SAMPLE PREPARATION

Procedures for unirradiated and irradiated samples are similar, but for irradiated samples they are complicated by the cracked nature of the fuel.

Unirradiated fuel samples typically consist of a disc cut from a pellet with a diameter of around 10 mm. The sample is then ground to provide a parallel-sided disc around 1 mm thick.

For irradiated fuel, a sample is usually around 50 mg in weight. An uncracked fuel fragment must be obtained of size (planar dimensions) $\geq$ 3 mm. The fragment is

then ground to provide a parallel-sided sample typically 0.4 mm thick. The first stage of sample preparation usually involves selection of many fuel fragments of suitable size/appearance. However, during subsequent grinding and handling many samples become cracked or disintegrate and have to be discarded.

For both unirradiated and irradiated samples the thickness is measured at many points using a dial gauge and the results averaged.

3.3 APPARATUS

A schematic diagram of the equipment used is shown in Figure 3. The main features of the apparatus are described below.

A horizontal tube resistance furnace is enclosed in a water-cooled vacuum vessel which is evacuated to 10^{-5} - 10^{-6} torr. The sample is mounted in a graphite holder (Figure 4) held on three parallel molybdenum rods positioned to be on the centre line of the furnace. Temperature monitoring is effected by means of a tungsten-rhenium thermocouple.

An incident pulse of energy (of duration < 1 ms) is provided by a 12 mm Nd-glass laser which is situated outside the hot cell. The laser pulse passes through an aperture in the cell wall and into the vacuum chamber via a quartz window. The back surface of the sample is monitored by a In-Sb infra-red detector through a sapphire window and a CaF_2 lens. The detector's field of view is usually restricted to the central 2 mm of the sample. A germanium filter, placed immediately before the detector, is also used to prevent the possibility of any direct shine through of laser light damaging the detector.

The back surface signal response is amplified and stored on a magnetic disc by a computer. The data storage sequence is triggered by the laser beam. The signal from the detector is monitored by a storage oscilloscope whose main function is to establish that thermal stability has been obtained but also shows the heat pulse from the back surface of the sample.

3.4 METHOD

The method requires the solution of the dynamic heat flow equation, which for one-dimensional problems may be expressed as:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \qquad (1)$$

where: T is temperature (K)
         t is time (s)
         x is distance (m)
         α is thermal diffusivity ($m^2 s^{-1}$)

The solution of this equation is given in Carslaw and Jaeger[1] and based upon this, the usual measurement point is the time ($t_{0.5}$) when the temperature on the back surface of the sample has reached half its maximum value. At this point the thermal diffusivity (α) may be expressed as:

$$\alpha = \frac{0.13878 \ l^2}{t_{0.5}} \tag{2}$$

where: l is the sample thickness (m)
           $t_{0.5}$ is the time defined above (s)

The above expression applies for the case of an instantaneous heat pulse (at time t = 0) and zero heat loss from the sample. In addition, the gross temperature rise must be small so that any temperature dependent material properties affecting α can be neglected.

The raw data generated by the above equation are then subjected to a data processing procedure. There are two standard methods commonly used for this:

(a)   the Cowan[2] method which uses the trailing edge of the response curve; the correction at $5t_{0.5}$ is typically applied to minimise the effects of radial conduction heat losses.

(b)   the standard logarithmic method applied to the rise of the response curve, as specified by James[3] which utilises a Laplace Transform solution at short times and does not use heat loss corrections.

The Cowan method, which assumes that the heat loss is by radiation alone, will be better than the standard logarithmic technique at high temperatures. However, at low temperatures, where radial heat conduction contributes significantly to the total heat loss, the logarithmic method is more suitable (because at short times the effects of radial heat losses are less important).

As a result of recent work at Windscale[4] a unified analysis route, combining the beneficial features of the above two methods, has been developed so that it can be applied to both low and high temperature data. This technique comprises a modified version of the standard logarithmic method to include a heat loss correction term, which was derived empirically from fits to idealised data over the temperature range of interest.

A typical experiment consists of measurements between 400°C and 1600°C at 200°C intervals during heating and cooling cycles with 2 or 3 laser shots at each temperature. Figure 5 presents some typical measurements carried out on the Windscale apparatus for unirradiated UO_2. For comparison, the figure also shows previously reported measured data and theoretical data for unirradiated UO_2.

4.0 Specific Heat Measurement

4.1 GENERAL

AEA Technology has used the Differential Scanning Calorimetry (DSC) method for some time for unirradiated materials. Apparatus has now been adapted for measurements on irradiated samples and is about to be installed in a hot cell at the Windscale laboratory. Active commissioning will be complete before the end of 1994, after which the equipment will be used for measurements on commercial PIE contracts. It is believed that this facility will be unique world-wide.

The basic method employed with the DSC is to apply heat at a known rate to two similar crucibles (one contains the sample, the other being empty). The temperature rise in the crucible carrying the sample lags behind that of the empty crucible and the temperature difference is then related to the specific heat of the sample.

4.2 SAMPLE PREPARATION

For irradiated fuel, a typical sample would be around 100 mg in weight and would be selected from a position as close as possible to a complementary thermal diffusivity sample. Sampling procedures are similar to those for thermal diffusivity samples; fragments which are free from cracks must be obtained. However, a specific heat sample only needs to be polished flat on one face - the one which will be in contact with the bottom of the crucible. Sample diameter (planar dimension) should ideally be as near as possible to the internal diameter of the crucible (around 6 mm).

4.3 APPARATUS

A photograph of the equipment is shown in Figure 6. The central component of the system is a Netzsch DSC404 calorimeter, which has been adapted for remote use. The DSC contains a small platinum platform, supported by a slender alumina rod (see schematic diagram, Figure 7). Two platinum crucibles are placed accurately onto the platform. Two thermocouples (one under the centre of each crucible) are used to measure the temperature differential between the crucibles. This assembly is contained in a cylindrical furnace which is lowered over it. Due to the delicate nature of the DSC and the need to handle small irradiated samples remotely, an automated robot sample placement system has been developed.

The prepared sample is weighed by a precision microbalance, then placed in a platinum crucible. This crucible, together with an empty crucible of similar specification, is placed in a 'boat' which is moved along a sample transfer slide to a crucible placement robot. A 'centre find stylus system' is used to locate accurately the positions of the boat and the recesses in the platinum platform on top of the alumina stem. The robot then lifts the crucibles, one at a time using a vacuum tweezer device, and places them on top of the platinum platform; this must be done to an accuracy of ± 0.1 mm. Following crucible placement the furnace cover is remotely lowered into position. Measurements are carried out in an inert gas (normally argon). For measurements on irradiated fuel a flowing argon atmosphere will be used.

4.4   METHOD

The test procedure is normally conducted in three parts:

- The temperature range is scanned with the two crucibles in place, but empty (this establishes a base line).

- A standard (normally sapphire) is placed in one crucible and the temperature range is scanned again.

- The standard is replaced by the sample (eg UO_2) and the temperature range scanned again.

The same heating rate is pre-programmed for all three scans; any rate in the range 0.1 to 50 °C/min can be used. Measurements can be carried out over the temperature range ambient to 1400°C. The temperature differential (micro-volts) between the two thermocouples is measured during all three temperature scans and the data stored by the controlling computer. The specific heat, C_p (in $Jg^{-1}K^{-1}$) is given by the following expression:

$$C_p = \frac{dH}{dT} \cdot \frac{1}{m} \tag{3}$$

where: dH is enthalpy change (J)
            dT is temperature difference (K)
            m is mass (g)

Hence, the specific heat of the sample (C_p^{Sam}) is given by:

$$C_p^{Sam} = \frac{W_{Std}}{W_{Sam}} \cdot \frac{\Delta U_{Sam}}{\Delta U_{Std}} \cdot C_p^{Std} \tag{4}$$

where: C_p^{Std} is specific heat of standard ($Jg^{-1}K^{-1}$)
            W_{Std} is weight of standard (g)
            W_{Sam} is weight of sample (g)
            ΔU_{Std} is thermocouple voltage difference between the standard curve
                  and base line (μV)
            ΔU_{Sam} is thermocouple voltage difference between the sample curve and
                  base line (μV)

The computer uses equation (4) to calculate the variation of sample specific heat with temperature. Software is available to display the data directly in graphical form. A set of typical measured data for unirradiated UO_2 are shown in Figure 8 compared with a curve representing 'recommended' UK values.

5.0 Conclusions

Techniques developed by AEA Technology for measurement of melting point, thermal diffusivity and specific heat of irradiated fuel have been described. The first two techniques are already in routine use; the specific heat apparatus will be commissioned for active use later in 1994.

References

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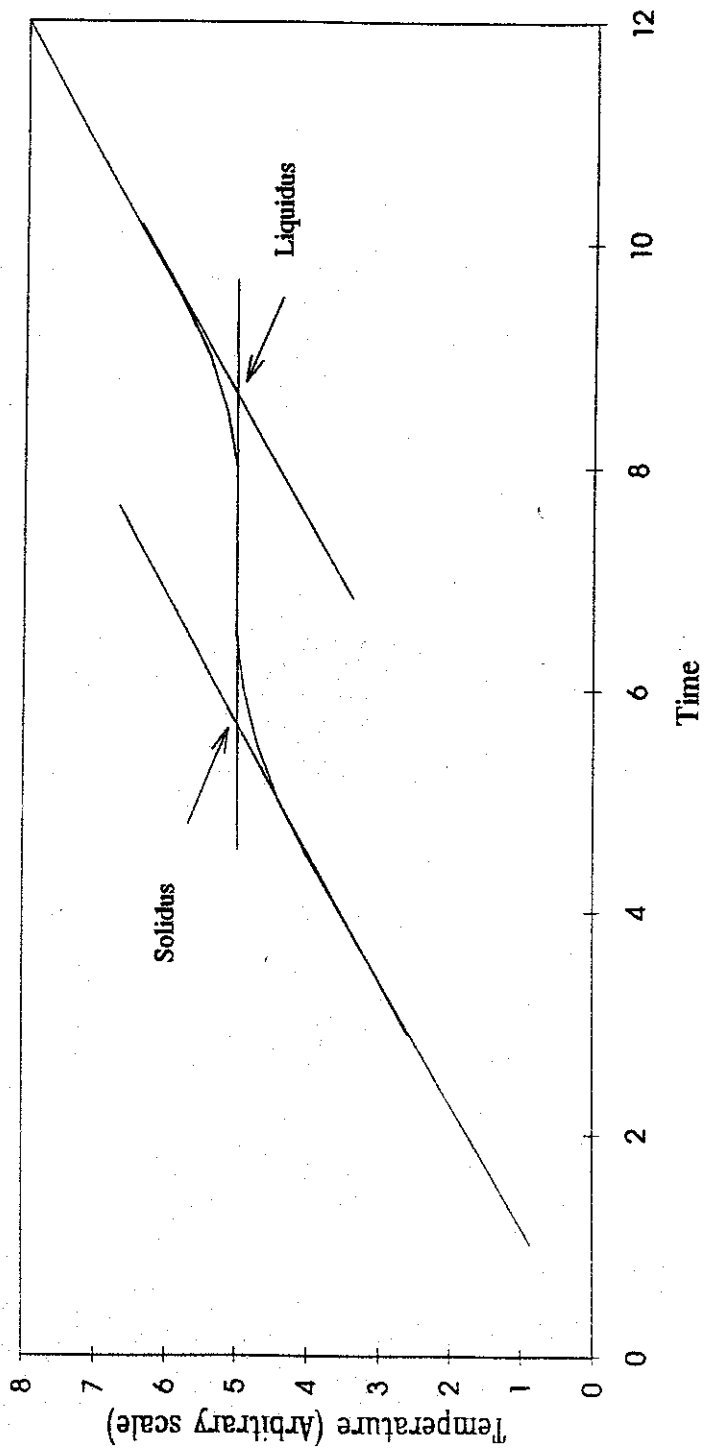
FIGURE 2

A TYPICAL MELTING POINT INFLEXION
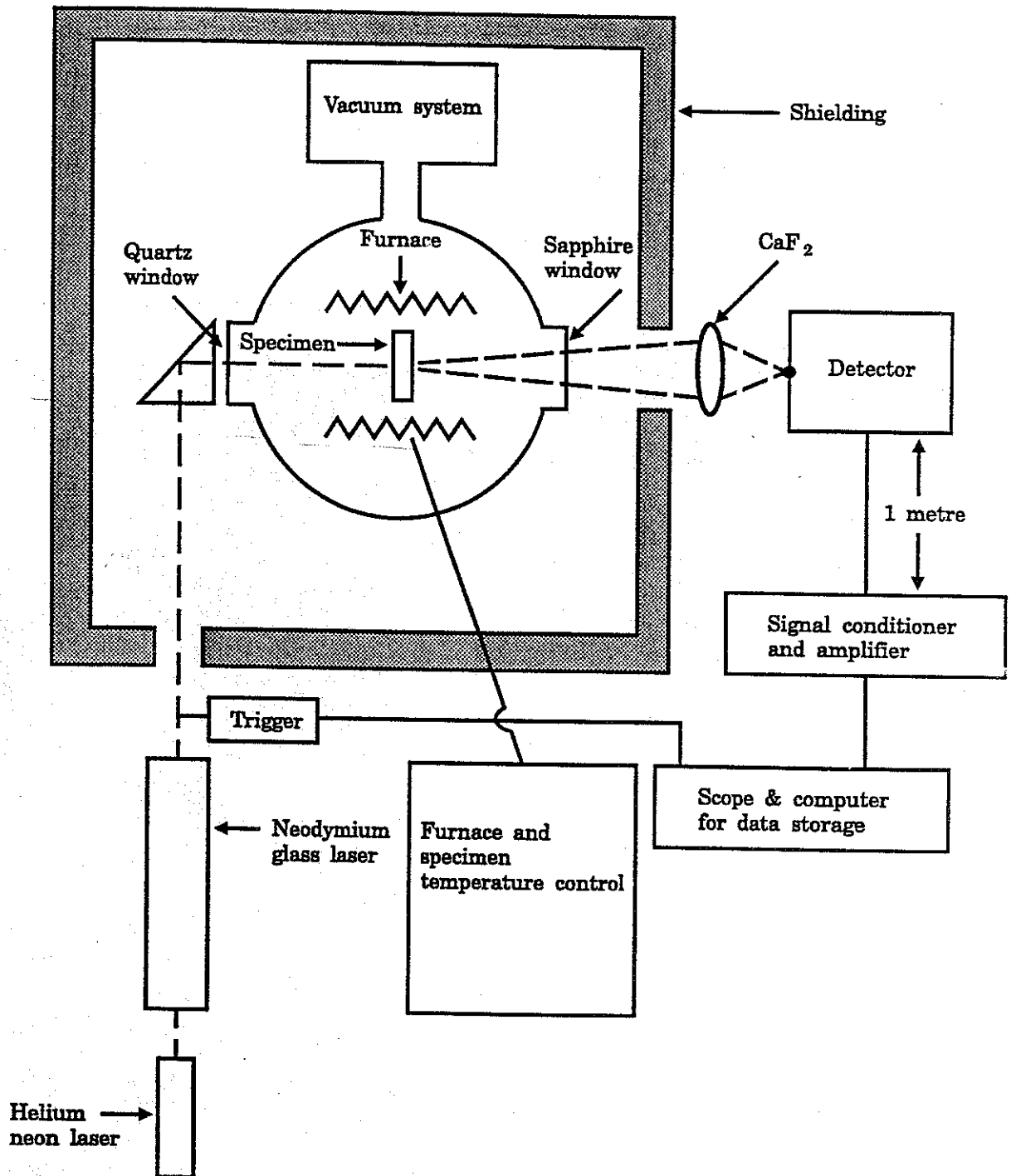
FIGURE 3

**SCHEMATIC DIAGRAM OF THERMAL DIFFUSIVITY
MEASUREMENT APPARATUS**

Detector

Incident
Energy
Pulse

Actual size
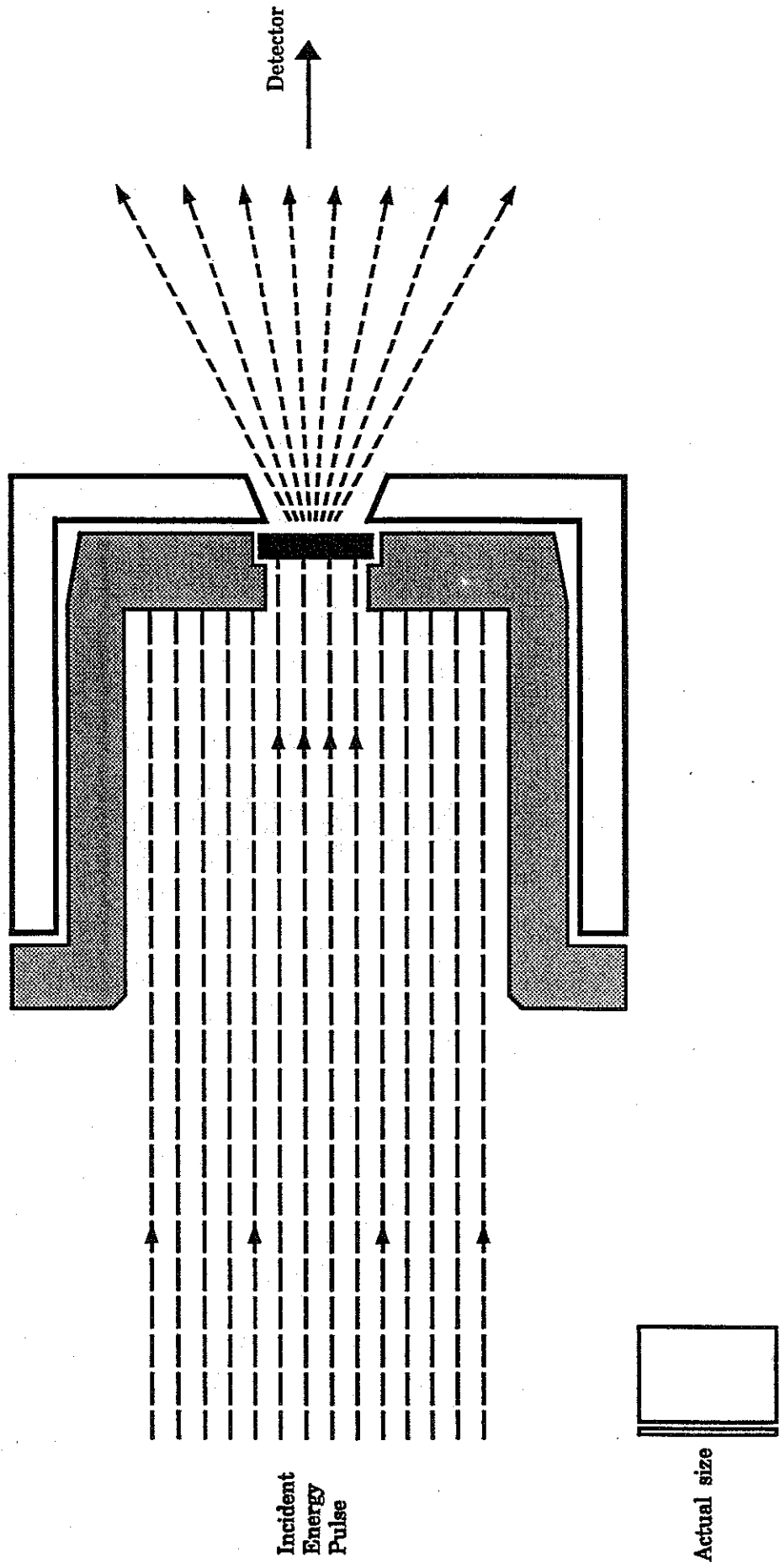
FIGURE 4

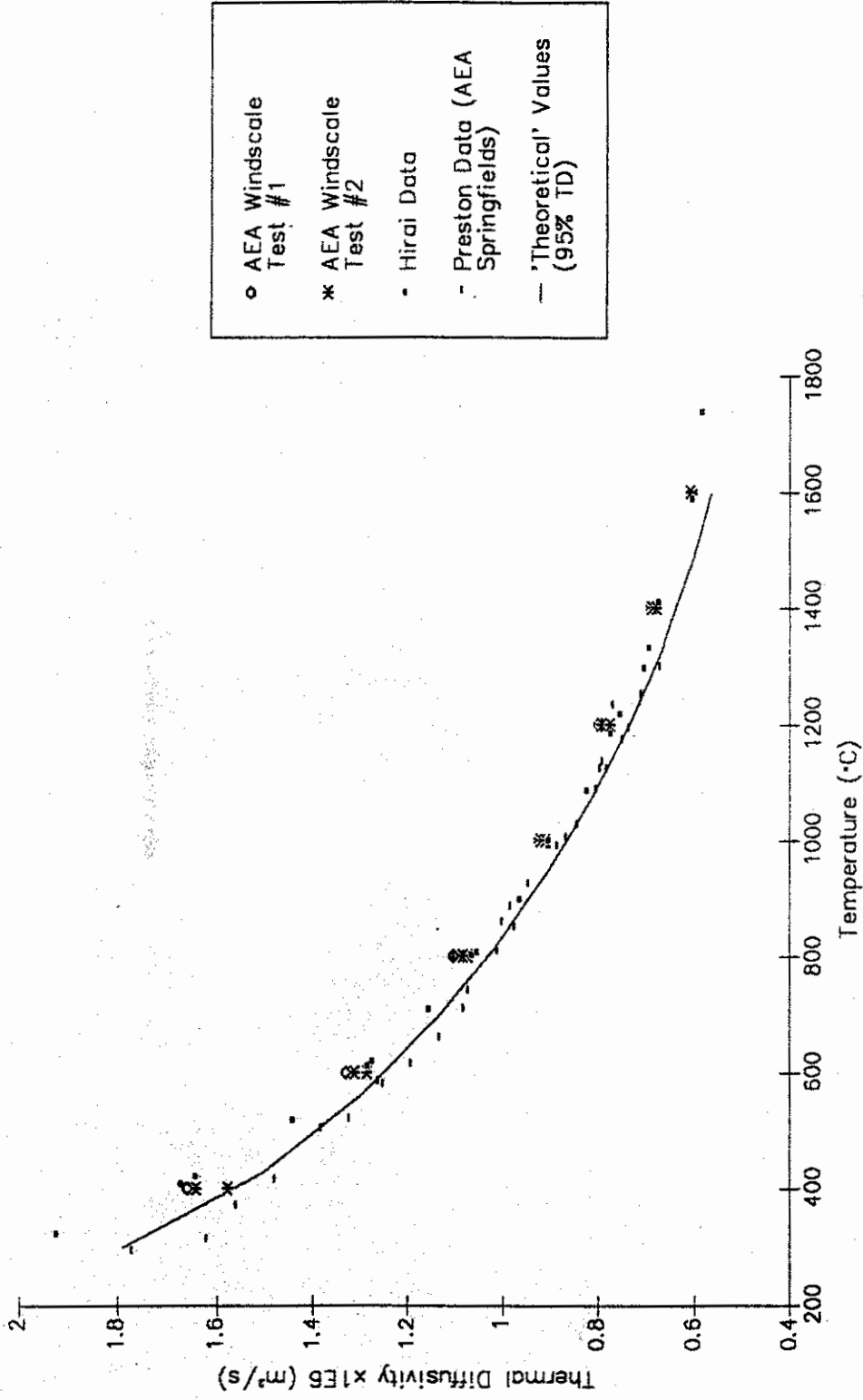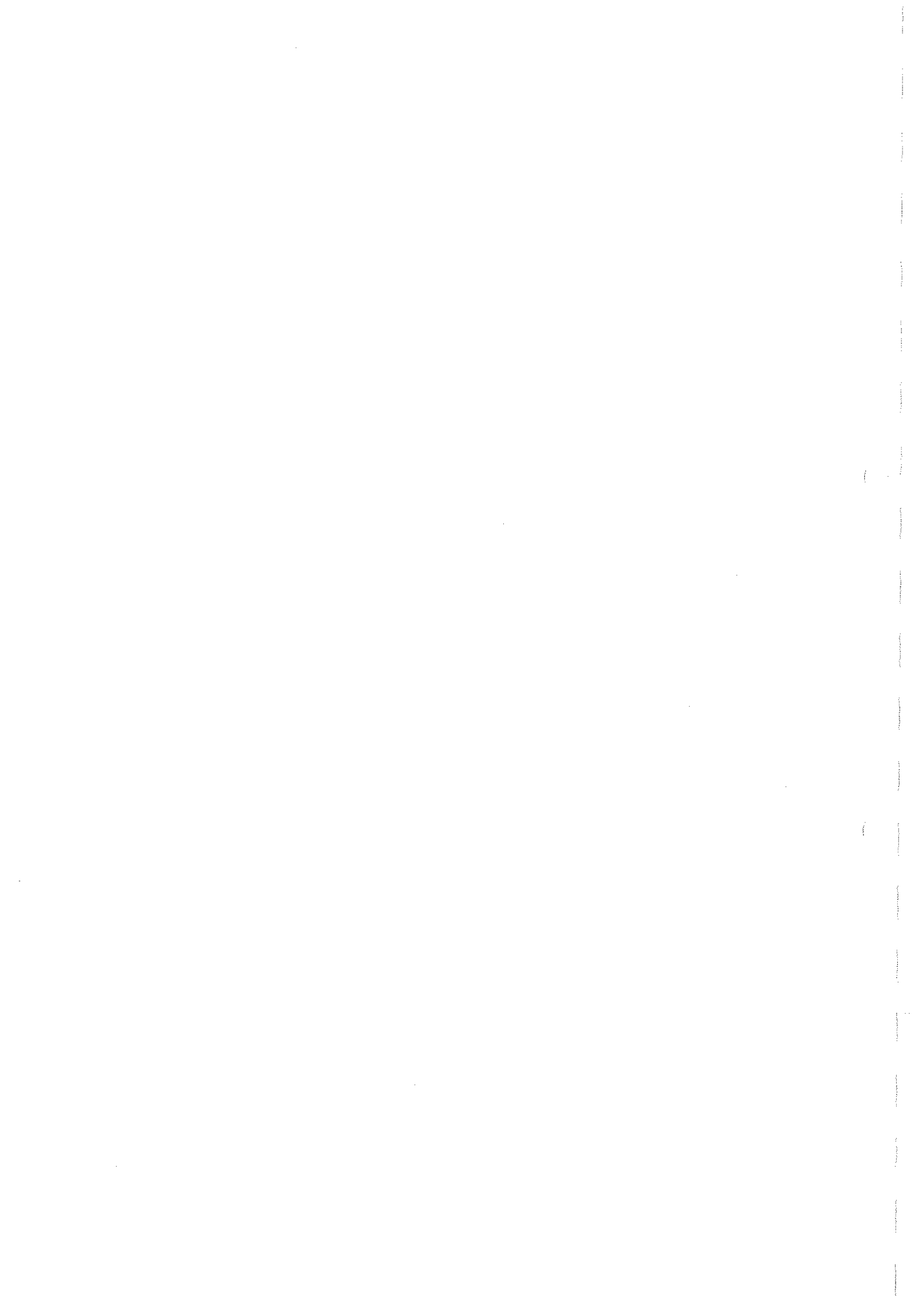SCHEMATIC DIAGRAM OF THERMAL DIFFUSIVITY SAMPLE HOLDER

FIGURE 5

TYPICAL THERMAL DIFFUSIVITY MEASUREMENTS FOR UNIRRADIATED STOICHIOMETRIC UO₂ COMPARED WITH PREVIOUSLY REPORTED DATA
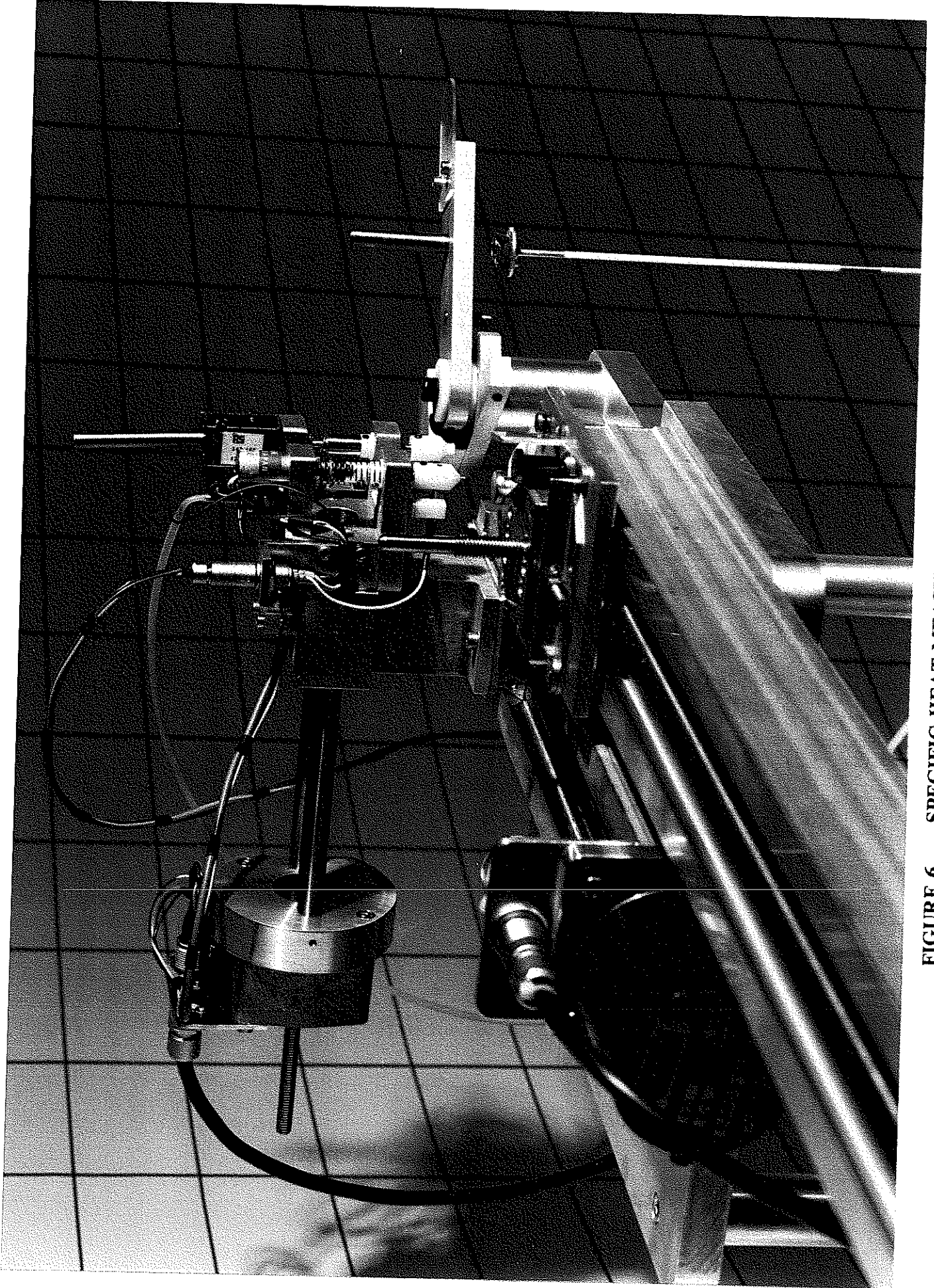
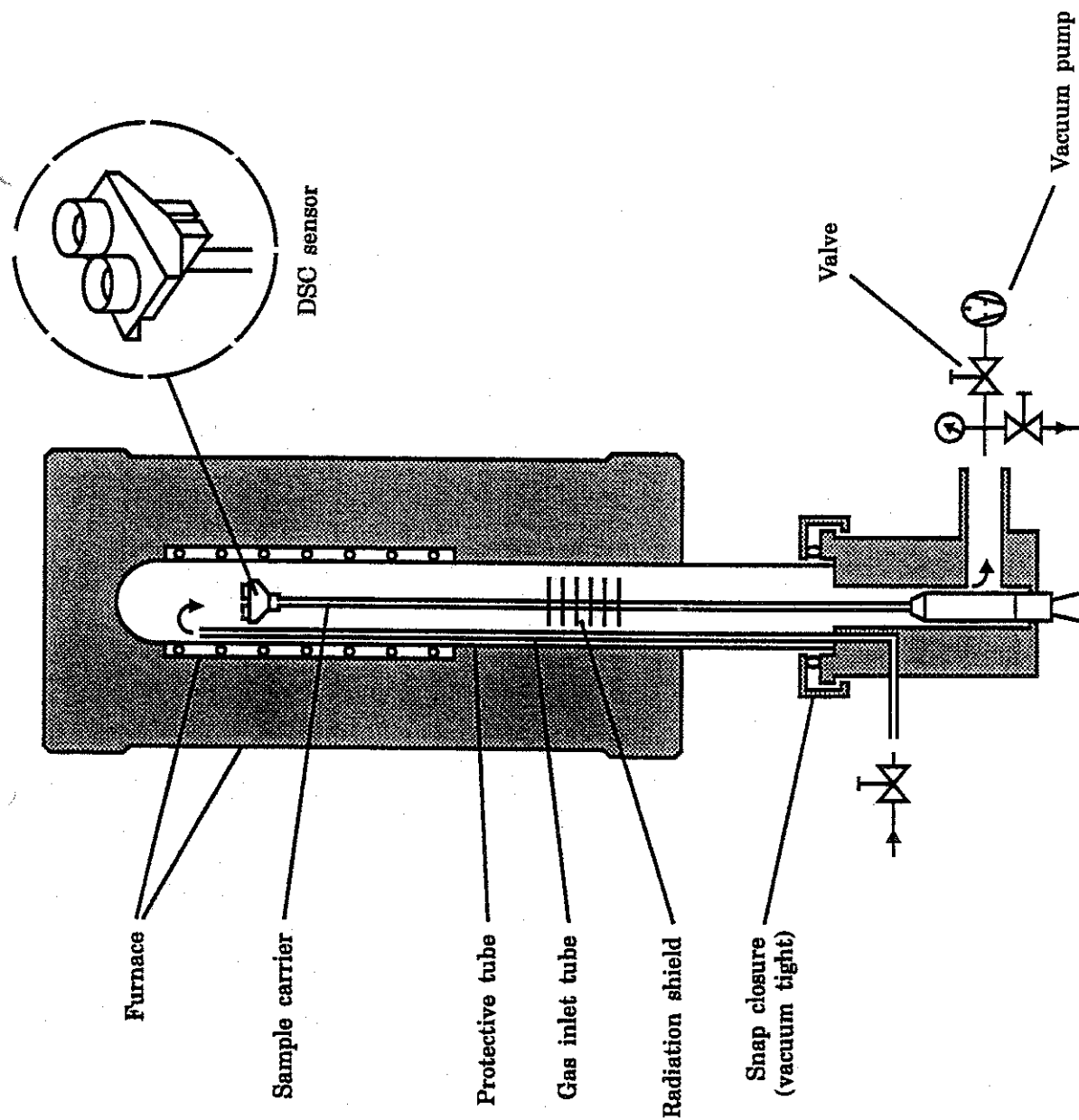FIGURE 6   SPECIFIC HEAT MEASUREMENT APPARATUS

Furnace

Sample carrier

Protective tube

Gas inlet tube

Radiation shield

Snap closure
(vacuum tight)

DSC sensor

Valve

Vacuum pump

FIGURE 7

SCHEMATIC DIAGRAM OF DIFFERENTIAL SCANNING CALORIMETER USED FOR SPECIFIC HEAT MEASUREMENT
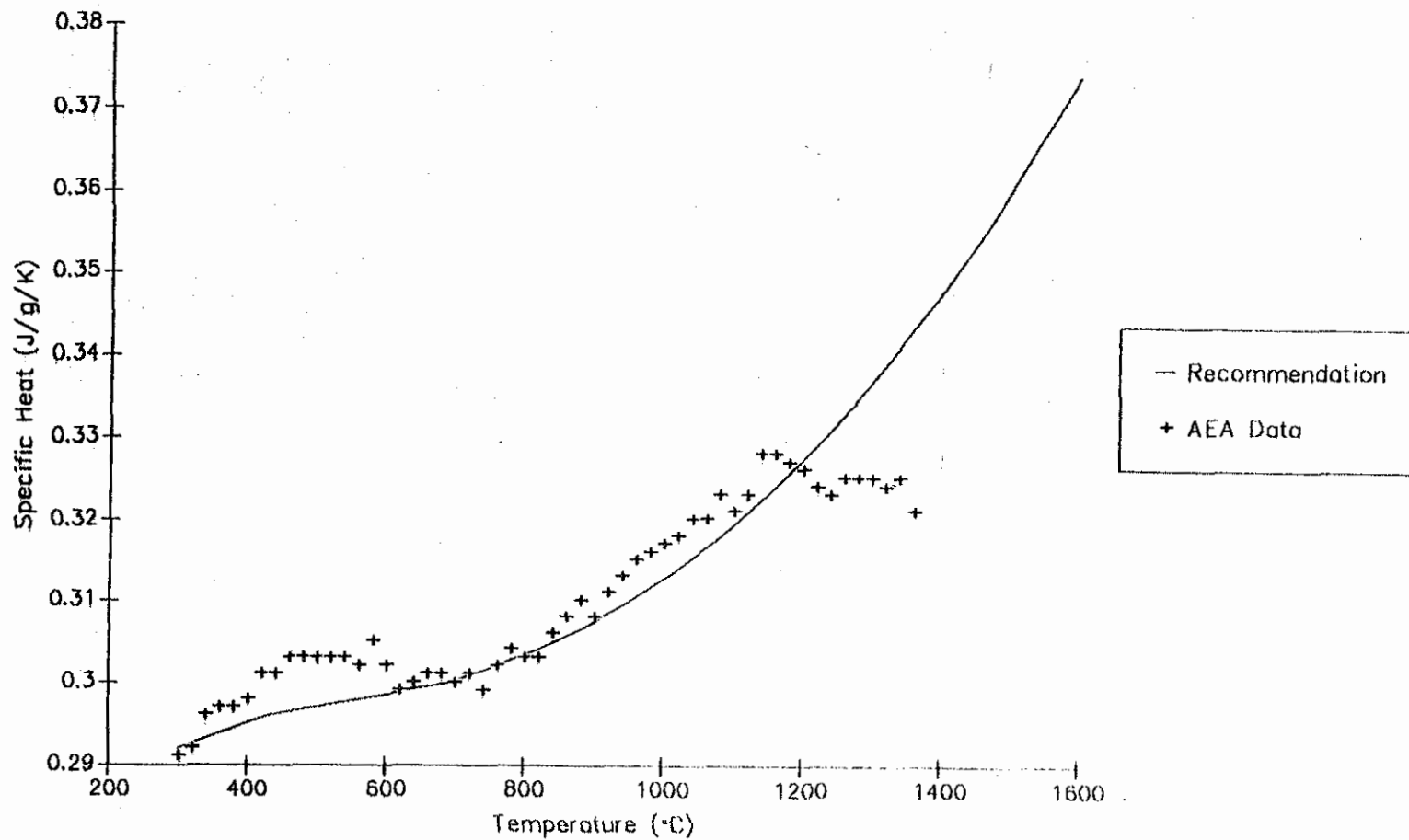
FIGURE 8

TYPICAL SPECIFIC HEAT MEASUREMENTS FOR UNIRRADIATED STOICHIOMETRIC UO$_2$ COMPARED WITH UK RECOMMENDED VALUES