Apparatus for the measurement of thermoluminescence

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Received 16 June 1976, in final form 21 July 1976

Abstract Apparatus for the measurement of thermoluminescence is described which generates glow curves with an overall reproducibility of $\pm 5\%$. Particular attention has been given to the design of a controller capable of accurately reproducing a chosen linear heating rate (0·1–99·9 °C s^{-1}) up to a predetermined final temperature (ambient to 990 °C). A manually operated 'hold' facility for intermediate temperatures is also provided. The construction of the light-measuring system and checks on its stability, sensitivity and linear response to very weak sources are also described.

1 Introduction

Thermoluminescence (TL) is the light emitted when many minerals and other crystalline solids are heated to temperatures below incandescence. The heat excites electrons held in 'traps' (lattice defects etc) to the conduction band, and when they fall to the valence band via a suitable 'luminescence centre' UV, visible or IR light may be emitted. The theory was first outlined by Randall and Wilkins (1945) who pointed out that the 'glow curve' – a plot of the intensity of emitted light against temperature – could be used to investigate the distribution of trap energies. The detailed nature of the traps and luminescent centres is still under discussion (Medlin 1968) but it is clear that electrons may be excited to traps by any ionizing radiation; TL is therefore a function of both the radiation environment and the thermal history of a specimen.

These two factors make TL particularly suited to the study of lunar samples and meteorites, and the apparatus described here was designed with the latter in mind. However, published applications of the technique range far and wide (McDougall 1968), notably to the dating of ancient pottery (Aitken *et al* 1964, 1968b). Previous descriptions of apparatus for the measurement of TL have been published by Vaz and Zeller (1966), Bonfiglioli (1968) and Labeyrie *et al* (1968). The instrumentation described here incorporates a number of new features in construction and operation to give improved accuracy, efficiency and adaptability.

The equipment is required to heat a powdered sample in a controlled manner in a vacuum or inert gas atmosphere. The latter is preferred because chemiluminescence occurs in the presence of oxygen (Aitken *et al* 1968a) while the low thermal conductivity of powders in vacuum hinders their uniform heating. The emitted low-intensity light falls upon a cooled photomultiplier tube (PMT) of suitable wavelength response. The PMT signal is amplified and plotted against the temperature of the sample to produce the 'glow curve'. A schematic diagram of the apparatus is presented in figure 1.

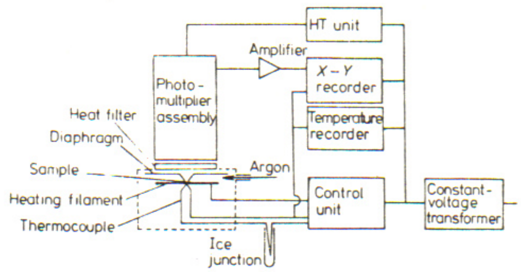


Figure 1 Schematic diagram of the thermoluminescence apparatus

There has been considerable debate on the need for a linear heating rate, some authors claiming that all that is required is that the heating regime be reproducible. However, Houtermans and Liener (1966) showed that the slightest deviations from linearity could result in perfectly reproducible but nevertheless spurious 'peaks' (figure 2). In the development of

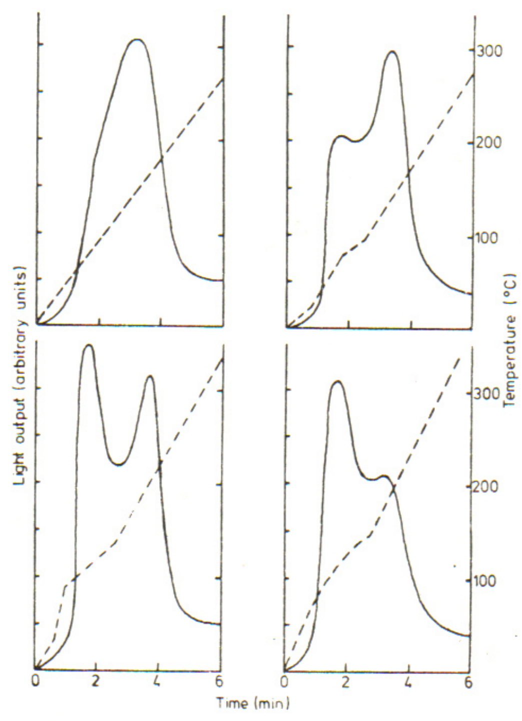


Figure 2 Effect of irregularities in the heating rate on the shape of the glow curve from identical samples. The diagonal plots show the temperature of the specimen (after Houtermans and Liener 1966)

the apparatus described here we have therefore emphasized the need for an accurate linear heating rate of preset slope, eventually holding constant at a predetermined final temperature. For this reason we preferred an electronic controller to mechanical systems. The excellent linearity achieved has enabled glow curves to be routinely generated with a reproducibility better than ±5%. It is thought that this controller would prove equally applicable to other techniques involving a steady linear increase in the temperature of a sample, e.g. differential thermal analysis.

2 Details of the equipment

2.1 *Specimen chamber and heating filament* (figure 9)

The chamber is a heavy-walled cylindrical vessel turned from aluminium alloy. Two copper electrodes support a 6 cm × 1 cm filament cut from 0·005 in molybdenum sheet, which is replaced every 150 runs or as soon as it is completely discoloured. A chromel–alumel thermocouple (using an ice junction) was used to measure and control the temperature of the filament, since it produces an EMF almost directly proportional to temperature from ambient to 500°C. Connections through the chamber wall were made with cast Araldite plugs made opaque with a black dye. A table supporting a conical aluminium diaphragm with a 6 mm aperture was placed over the sample to screen off unwanted IR radiation from bare portions of the molybdenum filament. A Chance HA3 heat filter was sealed in front of the photomultiplier tube to further reduce the effect of blackbody radiation, and also to act as a vacuum-tight window.

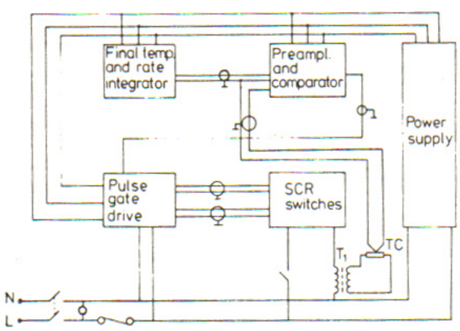


Figure 3 Block diagram of the linear heating control unit

2.2 *Heating control unit*

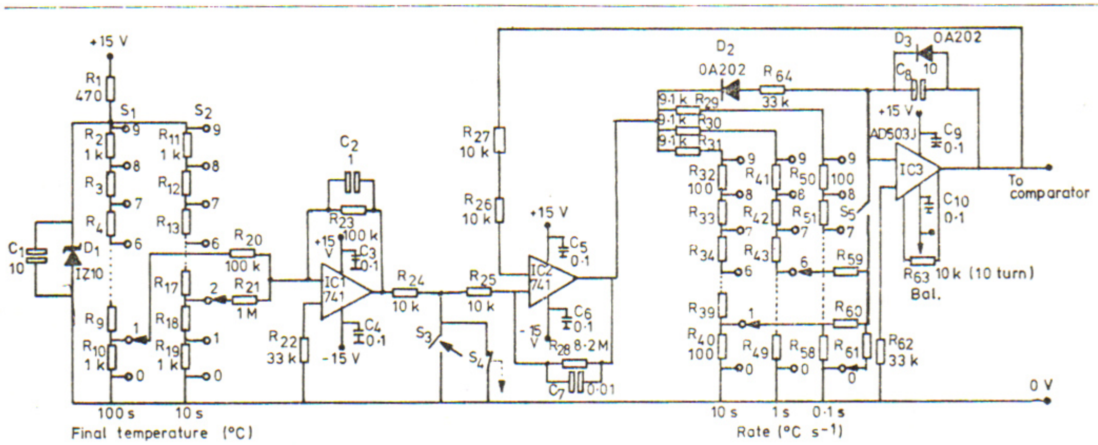
The linear heating controller comprises the five basic circuits shown schematically in figure 3. The required rate of rise of temperature and the final temperature are preset by the user. On operating the 'start' switch the voltage output of the 'set temperature and rate integrator' builds up at the appropriate rate to a proportional final value. This output is compared with the filament temperature (i.e. thermocouple EMF) in the 'preamplifier and comparator' circuit. A voltage level proportional to the temperature error is produced, and this controls the phase angle at which the 'pulse gate drive' generates a gate pulse to the SCR thyristors. As the required temperature increases so the SCR conduction angle is increased, thereby supplying more power to the heater.

2.2.1 *Set temperature and rate integrator* (figure 4) The stabilized +15 V supply is reduced to 10 V by the Zener diode D_1 to provide the 'set temperature' reference voltage. For setting purposes two decade switches S_1 and S_2 are provided, one for the 100–900°C range, the other for the 10–90°C divider. Any desired final temperature between ambient and 990°C may thus be set to within 10°C, although values exceeding 500°C were not required for TL applications.

The outputs of the two decade switches are summed in the ratio 1 : 1 and 1 : 10 at the inverting input of IC1, which also acts as a buffer to avoid loading the decade dividers. The amplifier feedback resistor R_{23} is shunted by C_2 to provide a 6 dB per octave roll-off at 10 Hz, reducing noise problems to a negligible level.

IC2 compares the output of integrator IC3 with the temperature demand voltage from IC1. So long as a difference exists the output of IC2 is a maximum, and provides a charging current via three decade switches to the integrator. The latter charges up at a rate set by these switches within the range 0·1–99·9°C s^{-1}, until its output is equal to that of IC1. The output of IC2 then drops to zero and integration ceases. The output of IC3 is therefore a function of the desired rate of rise up to the preset final temperature. To hold the temperature at any desired intermediate level the 'hold' switch S_5 is opened, removing the input to the integrator.

When either the 'reset' button S_3 or the 'output off' switch S_4 is operated the input to the comparator IC2 is taken to zero, and its output changes to maximum voltage of the opposite sign. The integrator then reduces its output towards zero at a fast rate set by R_{64}. Diode D_2 prevents interference with the



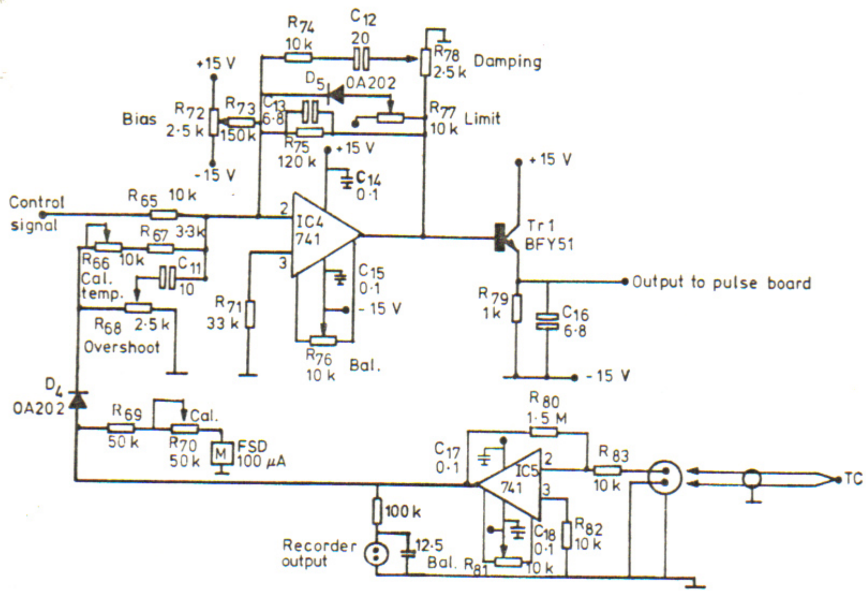


Figure 5 Comparator and preamplifier circuits

normal charge-up mode. The current offset in the integrator is trimmed out by R_{63}.

2.2.2 *Comparator and preamplifier* (figure 5) The output from the integrator acts as the control signal in a conventional servo system. The temperature-sensing element is the chromel–alumel thermocouple spot-welded to the underside of the molybdenum heating filament. Its voltage increases linearly from 1·0 mV at 25°C to 20·6 mV at 500°C. This signal is buffered by IC5 which is used as a DC inverting amplifier in the feedback path with a gain of about 150. The output of this preamplifier provides the feedback signal to the servo system, and also drives a panel meter and recorder output.

To ensure servo stability, a three-term control system is used. IC4 is provided with proportional feedback by R_{66}, R_{67} and differential feedback by R_{68}, C_{11}. The amplifier gain is preset by R_{75}, integral feedback is provided by R_{74}, R_{78} and C_{12}, while C_{13} gives high-frequency roll-off. DC offset bias is provided by R_{72}, R_{73}. To prevent a large output from IC4 under fault conditions (such as loss of temperature feedback signal resulting from a broken thermocouple) from developing excessive power in the heating filament, a diode D_5 is used to clamp IC4 to a maximum level set by R_{77}.

2.2.3 *Pulse gate drive and SCR switches* (figure 6) At the beginning of a mains half-cycle the negative voltage from the synchronizing transformer T_5 produces a current overriding that via R_{86} and causes TR2 to switch off. Capacitor C_{19} then commences to charge from two sources: the control voltage via R_{84} and the supply rail via R_{87}, R_{88}. The capacitor voltage rapidly reaches the control voltage, at which diode D_6 blocks and C_{19} continues to charge towards the supply rail. When the trigger level of the programmable unijunction transistor (PUT) is reached C_{19} discharges and produces a pulse across R_{89}. With zero control voltage a pulse is generated at the end of the mains period, and as the control voltage increases so a pulse occurs earlier in the period.

The pulse is amplified by the blocking oscillator Tr3 and T_2, and lengthened to 150 μs to avoid latching problems. Transformers T_2, T_3 provide isolated gate pulses for connection to the SCRs. Resistors R_{93}, R_{94} are selected to suit the gate characteristics of the thyristors.

When the SCRs (figure 7) receive a gating pulse they switch from an 'off' to an 'on' state, and the power source is connected to the load for the remainder of the mains half-cycle. At the next current zero the SCRs revert to the 'off' state and power is removed from the load. The load consists of the

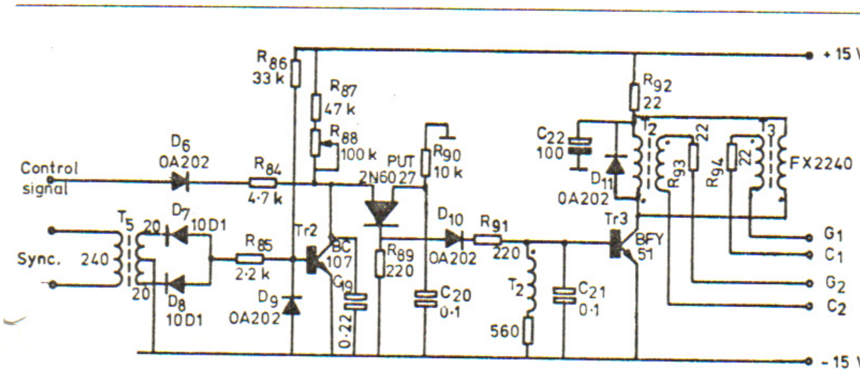


Figure 6 Pulse gate drive circuit

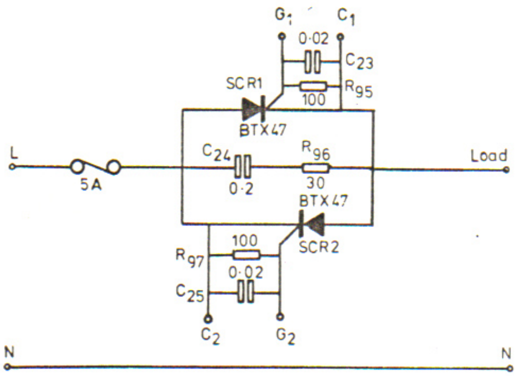


Figure 7 SCR switches

primary of a 90 : 1 resistance welding transformer (T_1 in figure 3), the high-current low-voltage output of its secondary being connected to the electrodes supporting the molybdenum heating filament by short copper cables of large diameter. Currents of up to 100 A passed through the filament.

2.2.4 *Power supply* (figure 8) The +15 V and −15 V power supplies are derived from L123 regulators. The negative

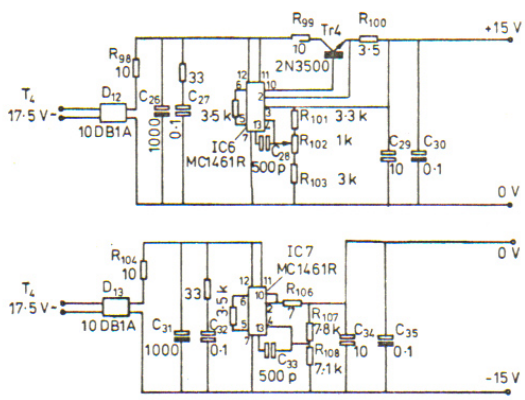


Figure 8 Power supplies

supply is rated at 100 mA but the positive is rated at 2 A and requires the external pass transistor Tr4. The output of the +15 V supply can be adjusted by R_{102} to be exactly equal to the −15 V potential.

2.2.5 *Construction notes* All circuits are built on printed circuit plug-in cards using an ISEP frame. The resistors are of the thin-film type for good stability. All parts around the integrator IC3 must be clean to minimize long-term drift. The gate leads to the SCRs must be screened and kept well away from power leads, while the SCRs themselves must be mounted on adequate heat sinks and protected with a high-speed fuse. It was found advantageous to operate all units from a constant voltage transformer of adequate capacity.

2.3 *Light-sensing assembly* (figure 9)

The choice of PMT was governed by the need for high sensi-

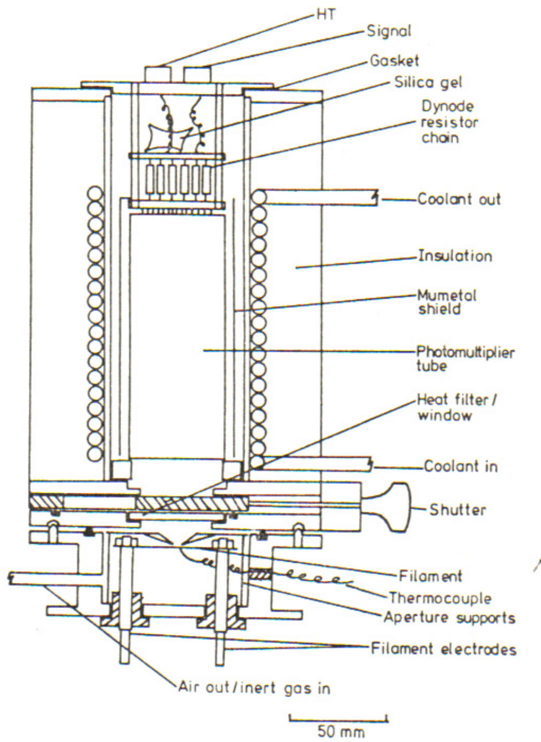


Figure 9 Scale drawing of the PMT housing and sample chamber

recommended by EMI Ltd for thermoluminescence applications was used, the quartz window version being considered unnecessary since meteorite TL does not include the UV wavelengths (Sippel 1971)†. Most meteorites (and all those for which quantitative data were sought) display a blue-green TL which is in the region of peak sensitivity for this photomultiplier. The associated resistor chain was built according to a circuit in the manufacturer's catalogue to produce a linear response to light. This called for a high negative voltage on the cathode, an earthed 13th dynode resistor, and no coupling capacitors. The PMT itself was prepared in accordance with the recommendations of James and Sternberg (1969). A Mumetal shield at cathode potential provided shielding from both magnetic and electric fields. The stabilized EHT supply to the PMT was provided by a Hewlett-Packard 6516A unit and was normally maintained at 1250 V. So far as possible it was kept switched on, for a number of workers have remarked that after an interruption a tube may take several days to settle down again. Instead, a shutter fitted to the housing was closed whenever the assembly was lifted from the filament chamber to load a sample.

† One referee has pointed out that this apparatus may be readily modified to detect UV emission without the necessity of purchasing a special PM tube and replacing the heat filter with a quartz window. All that is necessary is the application of a thin layer of sodium salicylate over the specimen side of the heat filter/window, this material giving a unit quantum conversion efficiency of UV to blue light over a wide range of wavelengths

The dark current was measured with various coolants flowing around the PMT assembly (e.g. alcohol cooled with solid carbon dioxide) but the improvement over mains water did not warrant the extra inconvenience. A typical dark current was 5 nA, whereas the current associated with meteorite TL was of the order of 10 μA.

The signal from the PMT was amplified with a MOSFET input operational amplifier with a current-to-voltage gain of 1000, occasionally raised to 20 000 when recording the glow curves of particularly weak emitters. This parameter was displayed on the Y axis of a Bryans X–Y recorder, with temperature (from the recorder output of the comparator circuit) on the X axis. A glow curve was thereby generated directly.

3 Checks on the apparatus and experimental technique

Well over a thousand glow curves have been recorded, many with simultaneous display of the heating rate. The latter was achieved by recording temperature against time on a separate chart recorder (TOA Polyrecorder). No deviations from linearity within our ability to detect them ($\pm 0{\cdot}05\,^{\circ}C\,s^{-1}$) were observed, an independent check of filament temperature being obtained by measuring the EMF of the thermocouple directly with a Pye precision potentiometer. A standard heating rate of $5{\cdot}0\,^{\circ}C\,s^{-1}$ gave the optimum balance between intensity and discrimination between peaks. Previous workers have employed rates varying between $0{\cdot}375\,^{\circ}C\,s^{-1}$ (Houtermans and Liener 1966) and $30\,^{\circ}C\,s^{-1}$ (Christodoulides *et al* 1970).

The linearity of response of the light-measuring assembly to very weak sources was checked with the system of integrating spheres shown in figure 10. This apparatus produced an enormous reduction (up to 10[illegible]) in the intensity of a white light source throughout the region of its spectrum which could affect the PMT. (Neutral density filters are notoriously unreliable for this purpose.) The spheres were constructed from four 10 in diameter Perspex hemispheres (manufactured by Duplus Domes Ltd, Leicester), the insides of which were treated with three coats of white photometric integrator paint (Rolls and Co., Edmonton, London). A 6 V lamp supplied by a constant voltage transformer illuminates one sphere, which contains a set of pinhole diaphragms through which light can enter a second sphere. An aperture in the second sphere acts as a dummy specimen chamber to support the PMT assembly. The response to light was checked every few months and no deviations from linearity were observed (figure 11).

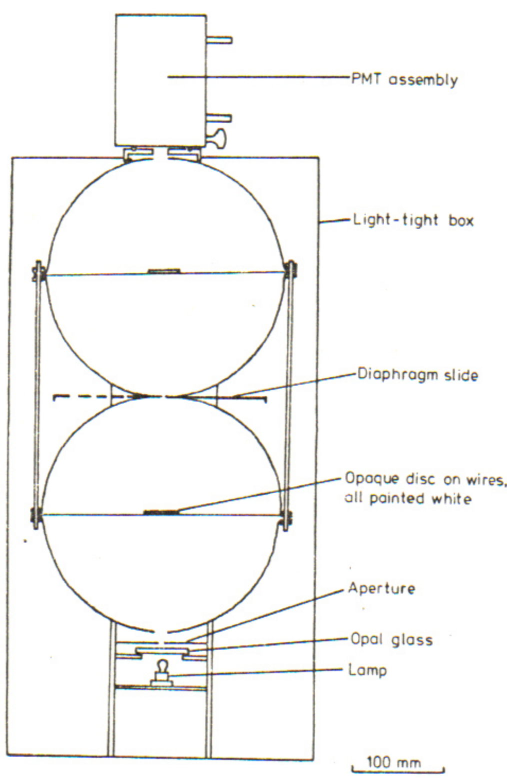


Figure 10 Schematic diagram of assembly used to check the linearity of response of the light-measuring system to very weak sources

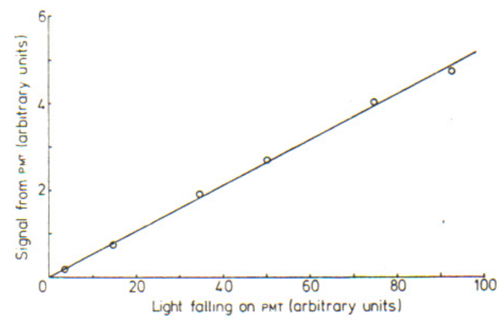


Figure 11 Linearity of response of light-measuring system. The abscissa is in arbitrary units of *ca* $10^{-11}\times$ intensity of lamp

A standard lamp is also desirable to check the day-to-day and long-term constancy of the sensitivity of the apparatus. A variety of designs has been tested, but none has been found to be wholly satisfactory. Best was a Saunders-Roe 'Betalight', a tiny tube in which an internal phosphor coating is activated by a tritium gas filling. This was covered by several neutral density gelatine filters (Kodak Ltd) to reduce the light level to that comparable with meteorite TL. The assembly was attached to a base which fitted over the filament in such a way that the light source was held in the same position each time. It was used at the beginning and end of each set of glow curve determinations, due allowance being made for the 12 year halflife of the tritium filling.

Meteorite samples are prepared by lightly crushing to disaggregate the constituent phases, and the magnetic portion is removed with a bar magnet. The mineral residue is ground in a glass mortar to pass a 50 μm nylon sieve. $10\pm0{\cdot}1$ mg of the powder are then weighed out and spread over an 8 mm diameter area of the filament with the aid of a stencil. The PMT assembly is placed over the chamber and the air evacuated. Dry argon is then bled in to a pressure of 100 mm Hg, and the glow curve recorded in this inert atmosphere. In common with other workers (Christodoulides *et al* 1970) we have been unable to detect any triboluminescence induced by the grinding procedure.

Aitken *et al* (1964) and Hoyt *et al* (1973) recommend working in red light when preparing samples for TL examination, to guard against the possibility of laboratory illumination draining some of the luminescence. We checked for this effect by placing two watch glasses of meteorite powder about three feet from fluorescent lamps, one sample being covered with an opaque lid to act as a control. Over a period of 11 h eight aliquots of each were taken and their glow curves recorded. No draining of the sample exposed to the strong illumination was observed, so we do not consider it normally necessary to work in red light.

4 Results

Representative glow curves produced by various classes of meteorite are shown in figure 12. These curves are very sensitive to fluctuations in the heating rate, and their smoothness independently testifies to the linearity we have achieved. The significance of the curves has been explored elsewhere (Sears and Mills 1974a, b, c, Sears 1974, 1975a).

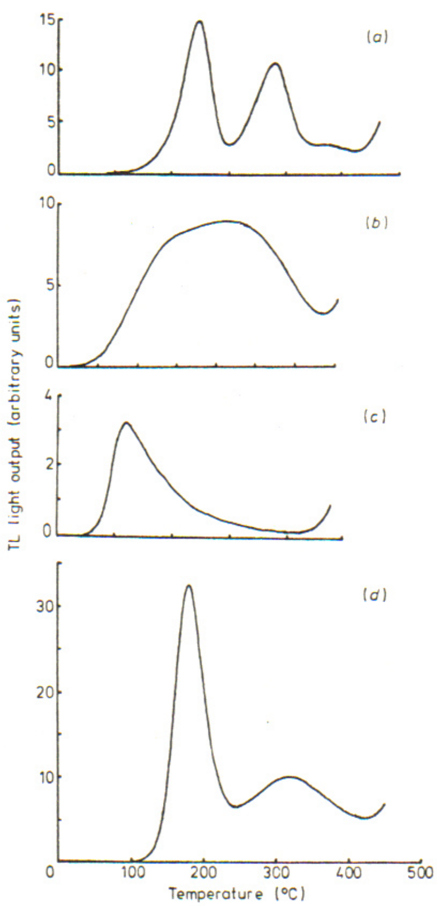


Figure 12 Glow curves for various classes of stony meteorites. (*a*) the Khor Temiki enstatite achondrite, (*b*) the Allende carbonaceous chondrite, (*c*) the Kapoeta pyroxene–plagioclase achondrite, (*d*) the Durala common chondrite

Although primarily designed for the quantitative examination of glow curves, the apparatus has also been applied to related investigations. Thus the 'hold' facility has enabled the effect on TL of a few seconds' exposure to various elevated temperatures to be tested. In this way it has been possible to derive the temperature gradients induced in meteorites during their atmospheric descent (Sears and Mills 1974c, Sears 1975b).

The variable heating rate, besides facilitating comparison with published results, has also enabled trap depths to be measured by the peak position against heating rate method (Braunlich 1968). Finally, the entire PMT assembly has on occasion been replaced by a glass window to allow visual and photographic examination of the thermoluminescence.

Acknowledgments

We are grateful to Mr G A Smith and Mr C Mason (Engineering Department, University of Leicester) for providing assistance with the design and construction of the heating control unit, and to the TL group at Birmingham University for their helpful suggestions. Financial support was provided by the Research Board of the University of Leicester.

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