AN EXPERIMENTAL STUDY OF TECHNIQUES IN THERMOLUMINESCENCE DATING

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By

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The phenomenon of thermoluminescence (TL) cannot yet be said to be completely understood, and cases of anomalous results from TL dating programmes are not infrequent, although explanations are rarely given. It is therefore useful to put TL dating into a firmer physical framework in which all relevant phenomena can be adequately described, whence the best action can be taken to avoid spurious results. However, TL dating embraces many varied aspects of physics, and a solution to all the problems is not a simple task. This thesis is intended to be an experimental study of some of the main physical techniques in thermoluminescence dating. Following a brief review of the whole field, selected areas presented here have been investigated in more detail.

A new TL reader has been implemented with novel design features, including microprocessor controlled heating cycles, a switch-mode power supply direct current heating, all based on a modular concept to facilitate future improvements in the hardware. The use of a microprocessor as the heating controller should enable further development (eg. data collection and processing) to be a straightforward task. Non-linear heating profiles can be generated for glow curve analysis and for providing pre-heat zones.

The radioisotope content of ceramics and soils is important in TL dating, and a comparison of commonly used radio assay techniques has been made with the aim of assigning a minimum detectable activity to
each technique for a given required accuracy. The analytical methods have been applied to various ceramic samples, and the derived dose rates within the shards are calculated and presented for comparison.

Some theoretical aspects of TL described in this thesis include a computer model to simulate common TL phenomena, which is used to investigate the effects of varying the model parameters. A complete solution of the equations determining glow curve shapes produced by hyperbolic heating profiles is presented, with techniques for extracting the mathematical constants describing the model, from them.

A brief intercomparison of five quartz samples of differing origins is presented with a trace element analysis of the samples to determine whether there exists a correlation between trace element concentration and the magnitude of the TL properties.
To my mother and father
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In the field of radiation dosimetry, thermoluminescence (TL) techniques have been greatly developed over the last decade for the measurement of low radiation doses. When a thermoluminescent material is subjected to ionising radiations, the induced free electrons and holes may be trapped at lattice imperfections (trapping levels). Depending on the energy band structure of the material, and the position the traps have in this structure, thermal energy will eventually release the trapped charges, and their recombination may give rise to energy released as visible light.

For natural geological TL phosphors (e.g. quartz, calcite, zircon, feldspars etc.) trapped charges will be accumulated due to the constant radiation field it experiences from surrounding materials, cosmic rays and its own radioisotope concentration. The natural dose received by the TL material may be calculated by a calibration experiment to determine the TL sensitivity (light output per unit radiation dose), and measuring the TL signal due to the accumulated dose since the phosphor was formed, or heated to a high temperature in nature. In the case of ceramics, a time zero is set when the pottery is fired to a high temperature.

This rather simple description of TL dating has been found to hide many problems. The technique essentially divides into two parts: 1) Dosimetry, and 2) TL signal measurement and interpretation of results.

The dosimetry problem could be described as follows for a typical buried ceramic shard. An irregularly shaped shard is buried in a wet soil producing a non-homogeneous radiation field having seasonal variations due to ground wetness, and associated radioactive gas escape. The shard itself contains thermoluminescent crystals of sizes varying from 1µm to 2mm. These minerals are distributed in a random
manner in a clay matrix. This matrix contains natural radioisotopes in various concentrations and equilibrium conditions distributed in an unknown (often assumed homogeneous) way.

An exact solution to these problems is an impossible task, therefore useful approximations must be devised if this technique is to yield accurate dates. The following section gives a brief description of the dating techniques used at present, with some mention of the problems which have been encountered in their use.

It may be noted that the units of physical quantities used throughout this thesis have been chosen to be in line with current usage in thermoluminescence work. In particular, the unit used for radiation dose is the 'rad', and not the 'gray'.

1.1 DATING TECHNIQUES

The complexity of the dosimetry problem is such that a simplification is necessary if a practical solution is to be found. Some techniques are presented below which enable certain simplifying assumptions to be made, and hence obtain an estimate of the dose received by the phosphor grains in the ceramic.

1.1.1 The Fine Grain Method

The fine grain dating technique is most frequently used for ceramics in which large quartz inclusions (50\(\mu\)m to 200\(\mu\)m) are absent in the matrix. Because of the limited ranges of the various ionising radiations causing the natural dose (PROFIO, 1979), particularly alpha particles and to a lesser extent beta particles (MEJDAHL, 1979), fine grains only are used to ensure that negligible attenuation within each
grain has occurred, and a homogeneous dose distribution exists throughout the phosphor. ZIMMERMAN (1967, 1972), has developed this technique with some success and reports an accuracy of 10% (AITKEN, 1968a).

By careful crushing (to ensure large inclusions are not reduced to fine grains), and acetone liquid separation (AITKEN, 1972), grains in the size range 1μm to 8μm may be collected and deposited on an aluminium disc, ready for TL read-out and the administering of an artificial calibration dose. Allowance must be made for the lower TL signal produced by alpha particles (i.e. lower TL efficiency), than would occur with beta or gamma radiations (MUREY, 1961, ZIMMERMAN, 1972).

1.1.2 Inclusion Dating

To remove the alpha contribution to the TL signal, the inclusion technique is frequently used (FLEMING, 1970). Phosphor grains of the order of 100μm are selected to ensure that the alpha dose is restricted to the outer regions of the grain (due to the short range of the alpha particle), whereas the beta and gamma dose is much more evenly distributed.

By acid etching of the grains (hydrofluoric acid in the case of quartz), the outer 5μm to 10μm are removed with a consequent reduction in the region of the grain that has experienced an alpha dose. This reduces the alpha dose down to between 10% and 20% of its original level. As the TL efficiency of alpha particles relative to beta or gamma radiations is of the order of 10%, the total alpha will contribute approximately 1 - 2% to the TL signal in the etched phosphor grain, which is dominated by the beta and gamma dose assumed to be homogeneously distributed throughout each grain. The etching
process also improves the grain transparency and removes some apparent surface traps which give rise to many small satellite peaks.

1.1.3 Pre-dose Dating

Some TL phosphors (particularly quartz) exhibit a phenomena known as pre-dose sensitisation (FLEMING, 1971), in which certain peaks of the glow curve have an enhanced TL sensitivity after heating which is dependent on its previous radiation history. This effect, which is related to the dose acquired since antiquity, is then activated by heating to high temperatures (in the region of 500°C for quartz). The pre-dose effect is clearly seen in the low temperature peak of quartz (110°C peak of FLEMING, 1969). The trap giving rise to this peak is not found to be populated in the natural sample, due to its fast fading rate at room temperatures. However, the sensitivity variation of this peak due to heating may be measured, and the information used as a basis for a dating method.

In experimental terms, the signal under a glow peak exhibiting the pre-dose effect is measured in the virgin material ($S_0$) after administering a small test dose (small relative to the total dose). The sample is then heated to a high temperature to activate the sensitivity increase. Again, an identical test dose is given to yield a second, enhanced signal ($S_N$). The sensitivity is then measured for a third time after giving a sensitising dose ($S_{N+\beta}$), where $\beta$ is of the same magnitude as the dose received in antiquity. The subtraction of $S_{N+\beta} - S_N$ is a measure of the sensitivity increase due to the sensitising dose $\beta$, and $S_N - S_0$ is a measure of the enhancement caused by the archaeological dose. Assuming a linear relationship, the archaeological dose can then be determined.
1.1.4 Photo-transferred TL

A technique which is far from completely understood, but has many possibilities is known as photo-transferred thermoluminescence (PTTL). This phenomenon has been shown to exist in a few minerals useful to TL dating (SCHAYES, 1967; BOWMAN, 1979; SCHLESINGER, 1965).

For dating purposes, a PTTL phosphor, when irradiated and subsequently heated to remove a TL temperature region, will exhibit a re-excited TL signal if illuminated by ultra-violet light. It is generally understood that this excitation is produced by the energetic U.V. quanta releasing some of the trapped charges (those not effected by the normal heating procedure) from 'deep' traps, and re-distributing a fraction of them among the traps present in the phosphor, which will include shallower traps. This PTTL signal has been found to be proportional to the initial received dose for a constant U.V. exposure and wavelength.

Two possible advantages of this technique are: 1) The ability for repeated reading of the TL signal by using multiple transfers from deeper traps. 2) Heating to temperatures in the region of 200°C are required for the low temperature quartz peak, thus reducing the problems of blackbody interference encountered with the high temperature peaks.

An intriguing possibility would be to use such a method for practical measurement of the primordial trapped electron population in very deep traps (if they exist), which may have been only partially emptied during the firing process. In principle, the firing temperature could be deduced from such measurements.
1.1.5 Subtraction Dating

Subtraction dating (FLEMING, 1971b, 1973) is a combination of the inclusion and fine grain methods. This technique removes the need to know the radiation dose due to the burial condition of the shard.

The accumulated fine grain dose (F) and inclusion dose (I) are both separately measured, and by subtraction of F - I, the alpha dose component (A) can be found, and knowing the alpha dose rate, the age of the ceramic may be calculated. Allowance can also be made for the attenuation of beta particles in the grain size being examined in the inclusion tests (MEJDAHL, 1979). Hence a simple equation results:

\[
A = \frac{F - I}{1 + (1 - f) \cdot \frac{b}{a}} \quad \cdots (1-1)
\]

where, \( f = \) beta attenuation factor. (see section 1.3.1)
\( a, b = \) annual alpha and beta dose rate respectively

It should be noted that equation (1-1) is gamma dose independent, which would be almost entirely due to the surrounding burial soil. Attractive though this technique may seem, it suffers from all of the problems of inclusion and fine grain dating, and is consequently seldom used.

1.1.6 Age Equations

It can be shown that for the three dating techniques described in sections 1.1.1, 1.1.2 and 1.1.5, the resulting 'age' equations are:

\[
T = \frac{(E.D)_{\text{f}}}{k \cdot D_{\alpha} + D_{\beta} + D_{\gamma} + D_{c}} \quad \cdots \text{fine grain}
\]
T = \frac{(E.D)_i}{D_B + D_Y + D_c} \quad \text{.. Inclusion}

T = \frac{(E.D)_f - (E.D)_i}{k.D_a} \quad \text{.. Subtraction}

where T = \text{Age [years]}

(E.D) = \text{Equivalent dose [rads]}

f, i = \text{Subscripts indicating fine grain (f) or inclusion (i) }

D = \text{Dose rate for alpha (\alpha), beta (\beta) gamma (\gamma) and cosmic (c) radiation}

k = \text{'k-value'. The ratio of TL efficiency for alpha and beta particles}

1.1.7 Non-Ceramic Materials

Although most of the TL studies in this thesis are concerned with ceramics, the knowledge gained can be used to study non-ceramic materials such as lavas (SABELS, 1962), sediments (WINTLE, 1979) and burnt stones (HUXTABLE, 1976). Some interesting, though rarely studied, non-geological materials are bone and shell (DRIVER, 1979). Both of these biological materials contain TL phosphors (apatite in the case of bone, and calcite/aragonite in the case of shell), which after formation, store a TL signal. Loess deposits (wind blown sediments) have recently been studied (WINTLE, 1981), where the mechanism for erasing the geological TL is by exposure to sunlight during wind transport.
It has been assumed during section 1.1 that for dating purposes, the TL response (TL signal versus dose) of the phosphors found naturally in ceramics is linear and not saturable. This simple view is found not to be true, although with careful experimental techniques, this problem may be overcome in most cases.

### 1.2.1 Supralinearity and saturation

A typical TL growth curve for quartz is shown in figure (1.1). The graph shows three regions of interest in TL dating: 1) A non-linear region in which the TL signal produced per rad increases with dose received. 2) A extended linear region over which the TL signal per rad is constant, and 3) Saturation, where the TL produced per rad decreases with dose and finally becomes zero. Although the archaeological dose is generally found in region 2, these three regions of the TL growth curve must be taken into account when the TL response is to be calibrated.

There seems to be some confusion in the literature concerning the use of the word 'supralinear' as applied to regions 1 and 2. Workers in medical TL dosimetry, describe region 2 as being supralinear (McKINLAY, 1981), whilst workers in scientific archaeology describe region 1 as being supralinear (ZIMMERMAN, 1971a). In the former case, it is often found that region 1 is linear from the dose origin, and therefore a second linear region could be termed as supralinear. In the latter case, the initial region is not found to be linear, but is termed supralinear because of its increasing radiation response with dose. In this thesis, the latter use of the word (ie. region 1 is supralinear) has been adopted in order to be in line with other
workers in the field of TL dating.

**Figure (1.1)**

A Typical Quartz Glow Curve

To avoid changes in response due to the TL read-out process altering the calibration, an additive procedure can be used as shown in figure (1.2a), (AITKEN, 1972). For this technique, two or three samples are given an artificial dose increment (b) in addition to that acquired naturally (N), and a graph of TL signal versus dose received is plotted. Hence by extrapolation to the zero signal axis, the equivalent dose (E.D) can be determined. This assumes that no supralinearity occurs, and that the natural plus artificial dose lies in the linear region of the growth curve. This latter criterion should be self-evident if sufficient samples are measured.

For materials exhibiting an initial supralinear region, the natural dose will have been underestimated by an amount I (see figure (1.2b)), when using the additive procedure described above. Replotting the
Figure (1.2a) The additive procedure (AITKEN, 1972)

Figure (1.2b) Changes in sensitivity (AITKEN, 1972)
growth curve after TL read-out by giving increasing artificial doses to each sample, the intercept giving I can be determined, assuming there is no change in the TL sensitivity for the particular glow peak region analysed. The corrected archaeological dose is therefore the sum of E.D. plus I.

1.2.2 Pre-dose sensitisation

As described in section 1.1.3, some TL phosphors exhibit a pre-dosing phenomena where the efficiency of the phosphor is changed by the dose received in antiquity. The degree of sensitivity change varies between different phosphors and glow curve peaks. The degree of enhancement is also dependent on the temperature to which the phosphor is raised, to activate the pre-dose effect (FLEMING, 1971a).

1.2.3 Dose rate and temperature of irradiation

The dose rate received by TL phosphors in antiquity is many orders of magnitude less than that received during dose calibration (approximately $10^7$), and whether this influences the TL signal must be determined.

Experiments using very high dose rates ($10^{10}$ rads per second) have shown lithium fluoride (a man made phosphor) to be dose rate independent (TOCHILIN, 1966), and many other natural phosphors have been found to exhibit little or no dose rate dependence. After the work of KHAZAL (1977), the dose rate independence of quartz was put into doubt, and further work (GROOM, 1978) showed that the quartz TL peaks had varying dose rate dependences. However, in general, for
total doses of less than 5 krad, the TL response is found to be dose rate independent. Further studies are required for other natural TL minerals.

The temperature during irradiation in the laboratory and in antiquity may not be closely similar, and with the TL minerals used for dating, tests must be made to determine whether there are measureable effects due to variations in irradiation temperature. A temperature dependent sensitivity has been reported by BURKE, (1974) and McKEEVER, 1978, in the latter case for quartz, although the effects are shown to be negligible for the temperature range found due to conditions in the natural climate. Temperature dependence studies of TL response may however be useful in analysing the kinetic processes which occur in these minerals.

1.2.4 Stability of TL signal

An implicit assumption in TL dating is the stability, over long time periods, of the accumulated charges which give rise to the TL signal. Use of the simple equations of RANDALL, (1945), which have been found to apply to more complex models, yields a stability (fading rate) which is dependent on three constants, two of which are unique to each mineral and glow peak in a particular mineral. Peak lifetimes for varying values of these constants are shown in figure (1.3). By analysing the glow curve to determine these constants (see sections 3 & 4) the validity of the assumption can be tested.

For complex glow curves (as encountered in fine grain dating), accurate determination of the lifetimes of the many overlapping glow peaks is not possible. An alternative approach is to plot the ratio of natural to artificial TL which should yield a plateau for the region of the glow curve in which little or no decay of the natural TL
Figure (1.3) Stability of the TL signal

Note:

Calculated from the equation:

\[ \tau = S^{-1} \cdot \exp \left( \frac{E}{kT} \right) \]

where:
- \( \tau \) = Mean lifetime of trap (s)
- \( E \) = Trap depth (eV)
- \( k \) = Boltzmann's constant (k=8.618×10^{-5} eV.K^{-1})
- \( T \) = Temperature (K)

signal has occurred (AITKEN, 1968b). This is known as the ordinate ratio or plateau test.

Some minerals occasionally exhibit an accelerated fading of the TL signal which is not predicted by glow peak analysis, but nevertheless 'passes' the plateau test. This phenomenon, which causes the calculated TL age to be too young, is known as anomalous fading, and
must be recognised in a sample if gross errors in TL dates are to be avoided. At present, the extent of anomalous fading in a TL sample is estimated by comparing the TL signal from a freshly irradiated sample with that from a sample that has been stored at room temperature for several weeks.

A typical sample exhibiting this anomalous behaviour shows an initial period of accelerated fading (found to be non-radiative), with a loss of 20% of the TL signal (calculated by glow curve measurements to have a lifetime of 1 million years) within 10 hours at liquid helium temperatures (WINTLE, 1977). A proposed mechanism to explain anomalous fading at low temperatures may involve temperature independent, direct transfer between the trapping sites and luminescence centres.

Minerals identified as possibly displaying anomalous fading are: feldspars (MEJDAHL, 1972), zircon (SUTTON, 1976), and fluorapatite (BAILIFF, 1977). Minerals not showing this phenomenon are: Quartz and calcite (WINTLE, 1973). A technique used to overcome the problem of anomalous fading is phototransfer (BAILIFF, 1976), where it is found that the deep traps associated with the PTTL, decay less than those responsible for 'conventional' TL.

1.3 DOSIMETRY

As described in the introduction, the problems of determining the dose received by a TL phosphor by exact calculation cannot reasonably be done. The techniques of 'fine grain' and 'inclusion' dating, allow some simplifying assumptions to be introduced and hence remove certain grey areas in the calculation. However great care must still be exercised in order to derive accurate dose rates. Some of the problems of which those active in TL dating programs must be aware, are outlined...
1.3.1 Attenuation of dose in quartz

Figure (1.4) shows the attenuation of alpha particles in a typical pottery matrix for spherical quartz grains (AITKEN, 1972). A grain of diameter 4μm will have an alpha dose of about 5% less than in the surrounding matrix. Allowing for the low efficiency of alpha particles in producing TL (ZIMMERMAN, 1971), which is in the region of 10% relative to fast electrons, and the fact that quartz grains are receiving substantial additional beta and gamma doses, typical values for which are shown in appendix (A), the effect of alpha attenuation is quite small. Therefore, by using a grain size range of 1μm - 8μm, the alpha attenuation effect will only reduce the overall signal by approximately 2%.

By contrast, when using large quartz grains in the inclusion technique, the effect of alpha dose attenuation is very severe, and therefore the alpha dosed outer layer is etched away, thereby simplifying the dose calculation. However, due to the attenuation of beta radiation in these large inclusions, the dose received by the quartz will be less than the infinite matrix dose. Figure (1.5) shows the results of the calculations performed by MEJDAHL, 1979, to determine the absorbed dose fraction, in a given grain size, of the theoretical infinite matrix dose for two natural radioisotope mixtures. From this figure, it can be seen that a 100μm quartz grain experiences an effective dose reduction of approximately 7%. This figure for dose reduction is not negligible, and therefore beta attenuation must be considered when using the inclusion technique. The very long mean free path for gamma absorption, ensures a uniform gamma dose for grains of typical size.
Figure (1.4)
Alpha dose attenuation in quartz

(Altkan, 1972)

Thorium

Uranium

Figure (1.5)
Absorbed dose fraction for Beta Particles in Quartz

(Mejdahl, 1979)

A: 12ppm Th, 3ppm U, 1% K₂O
B: 12ppm Th, 3ppm U, 2% K₂O
1.3.2 Water content of shard and soil

The environment of a shard during burial will be quite different from that in which laboratory measurements are carried out. In particular the water content during burial will effectively dilute the dose received by the phosphor inclusions in the shard, due to the dose fraction absorbed by the water. To correct for the effects of water uptake, the equation of ZIMMERMAN, 1971 may be used to find the wet shard dose rate.

\[
D_{(wet)} = \frac{D_{(dry)}}{1 + \frac{[\text{shard weight wet} - 1]}{\text{shard weight dry}}} S_a
\]

where \(a\) = Subscript indicating alpha, beta or gamma

\(D\) = Dose rate

\(S_a\) = Ratio of stopping powers for water and shard*. These values are approximately: 1.5, 1.25, 1.00* for alpha, beta and gamma respectively.

(* soil in the case for gamma radiation)

(+ BOWMAN, 1976)

In the case of soil, an average wet state must be assumed, whereas for the shard, the fine pore structure may be expected to retain water more effectively, and hence seasonal variations in water uptake are likely to be less than that occurring in the burial soil.

As an indication of the effect of ground water on absorbed dose between dry and saturation conditions (typically 10% and 20% water uptake in the shard and soil respectively), the absorbed dose reduction factor for wet conditions are respectively 0.86, 0.88 and 0.89.
0.80 for alpha, beta and gamma radiations.

1.3.3 Alpha particle efficiency

As was mentioned previously, the efficiency of alpha particles in producing TL is substantially less than that of beta and gamma (which are essentially equal). To apply the age equations of section 1.1.6, this efficiency (known as the 'k-value') must be determined for all samples to be dated using the fine grain technique. This is most easily done by administering two identical doses to fine grain samples using an alpha and beta source. The alpha source most frequently used is Po$^{210}$, however as the k-value is energy dependent, an allowance must be made for the difference between the energy spectrum from the Po$^{210}$ and natural radioisotopes found within the shard. ZIMMERMAN, 1971 determined a reduction factor of 0.85 to be applied to the apparent alpha particle efficiency as measured using Po$^{210}$. 
For the accurate measurement of TL signals, two fundamental pieces of apparatus are necessary; a light detection system capable of measuring at low levels of illumination (a detection limit of 100 photons per second is a reasonable target specification), and a heating device having a reproducible heating profile (not necessarily linear).

For ultra-sensitive light measurement, the only currently suitable device is a photomultiplier with its associated electronics for recording the train of output pulses. A carefully chosen and correctly used photomultiplier is capable of measuring light intensities well below that generally experienced in TL dating. For example, OLIVER (1968) has measured a signal of 0.043 counts per second which, assuming a quantum efficiency for the photocathode of 20%, implies a photon flux of approximately 0.22 photons per second.

The most common technique for obtaining a reproducible temperature rise in a TL phosphor is by contact heating with a resistively heated metal strip. With this method, a good control can be exercised over the temperature using analogue feedback circuits, TITE (1962). The heating of non-ohmic conductors such as graphite is also possible. Other techniques for heating which are more difficult to control are hot nitrogen gas flow, and radiative heating, in which a high power filament bulb is focussed onto the phosphor container.

Section 2.1 describes the development of the apparatus used throughout this thesis, and the following sections describe the tests on the final assembly and criteria for choice of the photomultiplier.
A new thermoluminescence apparatus has been constructed to allow low levels of TL to be measured. See figure (2.1a). The heating cycle is microprocessor controlled to enable reproducible, programmed heating profiles to be used. Light intensity and temperature are presented as digital signals to facilitate computer analysis of results. The whole system has been constructed so that future additions, and even fundamental changes, are made easy due to the modular design.

A cross-sectional diagram of the heating oven and the light collection and detection system is shown in figure (2.1b). A description of the components and their operation is given below.

2.1.1 The Vacuum Heating Oven

The construction details of the vacuum heating oven can be seen in figure (2.1b). The oven enclosure serves two purposes: firstly it excludes ambient light, so that the weak TL signal can be seen without interference, and secondly it provides the facility to evacuate the area around the heater and replace it with an atmosphere of oxygen-free nitrogen. Evacuation of the oven is carried out in order to reduce the non-radiation induced chemi-luminescence, by removing the oxygen from around the sample under test (ZIMMERMAN, 1970). This prevents oxidation reactions which are often associated with the emission of light. In a vacuum, there is a poor conduction of heat between the heating bit and the planchet holding the TL phosphor. Therefore the TL signals are recorded in an atmosphere of oxygen-free nitrogen (<5ppm) within the glow oven (AITKEN, 1963).

A continuous nitrogen gas flow is in fact used for two reasons:

1) To prevent the outside air leaking into the oven chamber (acts...
Figure (2.1b)

THERMOLUMINESCENCE READER

- Photomultiplier
- Shutter
- Filter holder
- Objective lens (quartz glass)
- Quartz glass plate
- Thin walled steel tube
- Gas inlet & vacuum outlet
- Perspex
- Heating bit
- Resistive carbon block
- Cooling gas (connected)
as an overpressure).

2) To cool the heating bit during operation. This gives the heater a quicker response to input power reductions. This also increases the cooling rate after the glow curve heating cycle is complete. Due to the minimisation of heat loss inherent in the heater design, cooling times of 10 minutes from 450°C to room temperature will result without a continuous gas flow.

2.1.2 The Heater

The heater contained within the glow oven is essentially a cylindrical graphite rod (6mm diameter) forming the resistive heating element, (based on the design of KELLY, 1978), in contact with a gold coated copper block which acts to conduct the heat from the graphite to the planchet placed upon it. The heating element and the block are supported on two concentric, thin walled stainless steel tubes to minimise heat losses. The supports are also used as the current electrodes and are therefore spaced by a sliding perspex bush. The whole assembly is mounted on a thick perspex disc by nylon screws, and this in turn is mounted on three brass legs with screw adjusters (spring-loaded) to enable careful positioning of the heater. The original design supported the inner steel tube on a spring, so that any thermal expansion and wear on the graphite cylinder would be taken up and prevent sudden variations in the total heater resistance during operation. However, the current was then carried by the spring in this configuration, and caused excessive heating within the spring which after a short period of use became weak and failed. The present design (as seen in figure (2.2)) has effectively a 'floating' outer tube, spring-loaded into contact with the graphite rod, which is
fixed. In this way, no current passes through the springs, and this
design has proved very reliable. Nitrogen gas cooling is simply fed
through the centre of the heater assembly, and passes through holes in
the inner tube to finally exit at the base of the outer tube.

This heater design attempts to minimise temperature gradients
across the planchet (KELLY, 1978), whilst the gold coated copper bit
helps to prevent tarnishing by oxidation, thus reducing possible
spurious luminescence signals, and changes in black-body emission due
to a slow variation in emissivity. This symmetrical design will
minimise field effects which may interfere with the operation of the
photomultiplier (FORSLO, 1974), although with the photomultiplier tube
so far removed from the heater in the design, this precaution is
probably unnecessary.
2.1.3 Light Collection and Detection

Light collection is accomplished by two fused silica UV-grade lenses (supplied by ORIEL corporation), having a 70% transmission at 185nm for a 10cm thickness. An f1 objective lens and f2 final lens (focal lengths of 38mm and 75mm respectively) give the maximum light collection obtainable with a conventional system. Fresnel lenses, with transmission in the UV would enable an f-number of less than unity to be used for light collection, but these lenses are manufactured from plastics and cannot be readily obtained in UV-grade glasses. For the wavelength region 400nm to 1100nm, these acrylic Fresnel lenses have a transmission of greater than 90%, and an effective f-number in the region of 0.6. For routine TL measurement these lenses would be suitable, and possibly preferable for phosphors with emissions well within the visible wavelength region.

The sample, being placed at the focal point of the objective lens produces a parallel beam between the two lenses, which passes through suitable optical filters before being focused onto the photomultiplier. Parallel light is necessary if interference filters are to be used for TL spectrum analysis. A camera shutter is placed between the focusing lens and the photomultiplier tube, in order that the light detection assembly may be removed to facilitate sample changing without having to reduce the voltage on the photomultiplier. This helps stabilise the gain and dark count. The photomultiplier used is an EMI 9893/350 with quartz end window and an effective 9mm photocathode. Its characteristics and performance are described in section 2.3.
2.1.4 Electronic Circuitry

A TRACOR NORTHERN (TN-1705) multi-channel analyser (MCA) operated in the multi-channel scaling (MCS) mode, is used to record the series of pulses representing the single photon pulse train. The circuitry used, is that shown in figure (2.12) for the 'fast' channel, recorded at the input of the MCA. The multi-channel analyser has 1024 channels, with a counting capacity of $10^6$-1 counts per channel. The dwell time between channels is adjustable from 0.1ms to 900ms. When using a linear heating profile, this will allow the TL output to be recorded between the temperatures 0-400°C with a range of heating rates from $0.43^\circ$C per sec, to values much faster than those required for TL measurements.

It was initially realised that the dead-time ($\tau$) in the MCS mode, would be far greater than that of any other component in the counting circuit, so a careful determination of $\tau$ was performed; Aliquots of varying masses were prepared from a natural quartz phosphor, and were washed and separated into the size range 75-150μm. These aliquots were all given an equal dose of Co$^{60}$ radiation, and read out on the TL apparatus. The peak heights of the high temperature peaks were subsequently plotted against the mass of the aliquot. See figure (2.3).

Assuming the curvature of this TL versus mass curve is due to dead-time effects only (ie. self absorption of the TL signal is negligible), then $\tau$ can be derived as follows.

$$N_0 = N/(1 - \tau N) \hspace{1cm} \ldots (2-1)$$

where $N = \text{Measured count rate.}$

$N_0 = \text{Actual input rate.}$
For aliquots of very small mass \( m \), it can be assumed that \( N_0 = N \), and that \( N_0 = K m \) where 'K' is a constant. Therefore from equation (2-1),

\[
\tau = \frac{1 - N / (K m)}{N}
\]

The value of 'K' may be found from the gradient of the curve in figure (2.3) at the intercept of the two axes (i.e. where the mass is small). Using this method, \( \tau \) was found to be equal to 3.3\( \mu \)sec.

For a count rate of \( 10^5 \) cps, a value of \( \tau = 3.3\mu \)sec will produce a dead time of approximately 11%. As such count rates are likely to occur, corrections will be necessary to all points on the glow curve before true peak areas and heights are determined. Because correcting 1024 points is a laborious task (even with the aid of a computer), it was decided to increase the effective dynamic range of the MCA. This could be done most simply in two ways: Optically reducing the TL
intensity (grey filters), or pre-scaling of the TL signal. The latter technique was chosen, as this would allow switchable values of pre-scaling to be instantly available (even during measurement of a glow curve). To optimise the characteristics of the pre-scaler, it is necessary to look at the timing characteristics of the associated electronics.

The timing filter amplifier (ORTEC 454), used for the initial amplification of the fast PMT output signal, has a minimum pulse output width of 4.5 nsec and a maximum gain of x200. The fast discriminator (ORTEC 463), processing the amplifier signal, has fast, negative logic output with pulse width of 5 nsec. As a suitable pre-scaler was not immediately available, a J&P NM131, 15 MHz scaler was converted to give 'switch selectable pre-scale ranges of divide by 1, 10, 40, 100, 400. This scaler required a positive pulse of duration not less than 60 nsec, therefore a trigger circuit was built into the module in order to convert the 5 nsec negative pulses produced by the discriminator, to 90 nsec positive pulses. This effectively produced an 11 MHz pre-scaler, and therefore causes a dead time of less than 1% for count rates of \(10^5\) cps.

The input requirement of the MCA is a positive pulse of duration not less than 1 nsec, although through experiment, the MCA was found to except a pulse width of 500 nsec in the multi-channel scaling mode. Therefore, the output of the pre-scaler was made to conform to a nominal 700 nsec positive pulse.

As the pre-scaling factor is increased, the pulses entering the MCA become less random, and consequently the \(\tau\) value approaches zero, and no dead-time is experienced. Running the pre-scaler at 10 MHz (close to its maximum), and at a pre-scale factor of 40, will cause the spacing of the 700 nsec output pulses to be greater than the 3.3 nsec required by the MCA, so that at this setting, the MCA dead-time will be negligible. There will be some small residual effect to the
dead-time, as the MCS mode requires a finite time to switch from one channel to the next. This switching time is however independent of the incoming count rate. A repeat of the experiment to find $\tau$ gave little deviation from a straight line with a divide by 40 pre-scale setting. See figure (2.3). For count rates where the dead-time of the pre-scaler becomes significant, optical filters can then be used.

2.2 TEMPERATURE CONTROL

The control of the desired heating profile for the equipment described in section 2.1 is accomplished using a MOTOROLA M6800 microprocessor; This is an 8 bit microprocessor having 8 kilobytes (8K) of accessible memory (expandable if more complex control programs or other functions are required), and contains four 8 bit parallel interfaces, and a programmable interrupt timer (1MHz to $3 \times 10^{-4}$ Hz interrupt frequency). Two of the parallel interfaces are connected to a 10 bit analogue to digital (ADC) converter, which converts the thermocouple analogue output to a digital value in the range 0-511. This requires 9 bits ($2 = 512$), the tenth bit being at present a safeguard against an accidental over-temperature, and therefore gives a resolution of $1 \degree C$ for the range $0 \degree C$ to $511 \degree C$. By relaxing the over-temperature safeguard, or changing the ADC for a 12 bit device, a temperature resolution of $0.5 \degree C$ and $0.125 \degree C$ respectively could be obtained. The resolution is effectively limited by the design of the thermocouple amplifier and the noise due to the power supply.

A third parallel interface controls the power supply to the heater. An output value in the range 0-255 will produce a proportional, constant DC current from 0-50 amps. Figure (2.4) shows the signal paths between the microprocessor and the supporting electronics.
Figure (2.4)

Microprocessor and Electronics
The microprocessor is used to determine two things about the dynamic state of the system:

1) The required temperature at any given time, and hence the difference between that temperature and the measured temperature.
2) The change in power requirement of the heater to correct for any temperature difference observed in 1).

A detailed discussion of the programming techniques used to produce a required temperature profile is given below.

2.2.1 Programming the MOTOROLA M6800

The MOTOROLA M6800 microprocessor unit, is an inexpensive 8-bit device with an addressing capability of up to $2^{16}(65536)$ bytes, designed to operate with any MOS or standard TTL components. It is used in conjunction with a monitor ROM (SWTFUG - Southwest Technical Products Corp.), and runs at a clock frequency of 1MHz. Some useful features of SWTFUG are breakpoint debugging and vectored software interrupts. SWTFUG also contains some useful input/output subroutines for single characters and strings.

It is quite conceivable that a useful program can be written using the SWTFUG ROM only, although an assembler or cross-assembler is preferable in most cases. The technique used for program development of the TLD reader was to use a microprocessor simulator (MICROSIM, developed by D.M. England and Partners). MICROSYM is run under the PRIME operating system, and uses existing M6800 assembly code to allow a developing program to be typed in and run without the need to assemble the code in the target microprocessor. This allowed for diagnostic error messages and syntax checking and consequently reduced the time taken to produce the necessary machine code. Program
segmentation was used, which enabled a modular approach to the programming with very little inefficiency caused in the final version.

It is envisaged in the future that the addition of floppy disk data storage and high-level language software will produce a free-standing system, not dependent upon a main-frame computer.

2.2.2 The Temperature Control Program

The program developed for the TLD reader described in section 2.1 is designed to allow the programming of any heating profile within the range of attainable heating rates. This requirement necessitates either a user defined algorithm describing the heating profile (difficult in the case of mixed linear/non-linear ranges within the same profile) or a pre-generated 'look-up' table, coded to produce the required profile. This latter technique was adopted, except for the case of simple linear heating, and the resulting program flow diagram is shown in figure (2.5). An assembled listing of the program is shown in appendix(B).

The look-up table is at present generated by the PRIME computer using FORTRAN programming language, with its output filed in the same format as required by a simple cross-assembler resident on the system. The assembled look-up table is then loaded into the microprocessor, along with the controlling program.

A series of tables have been pre-generated and are suitable for most general applications. If these profiles were stored on a small disk system, they could be quickly and simply loaded, making the complete TL reader free standing. Such a disk operating system would allow new look-up tables to be generated as required. The program steps describing the operation of the controlling microprocessor outlined in figure (2.5), is described in section 2.2.3.
Figure (2.5a)

Microprocessor Control Program

Determination of memory locations for program constants:

- Disable power supply.
- START J 0000
- Set table pointer to 1000H

Linear or non-linear?

- Linear
  - Set LNIN flag high.
  - Cut-off temperature equals 500°C.
- Non-linear
  - INPUT: Heating rate - Cut-off temperature -
  - G' to G' to ABD1

INPUT: Initial room temperature -

A1

A1. NON-LINEAR VECTOR AT ORG 0400H

- Disable interrupt.
- Fetch two adjacent words from look-up table.
- Increment look-up table pointer by 2.
- Decode to determine the heating rate and required temperature.

ZERO?

yes

no

A2

A2. LINEAR VECTOR AT ORG 0490H

- Increment time counter
- Calculate required temperature,
  \[ T = K \cdot C + T_{\text{ref}} \]

A3

STOP.
N.B. T_r and K are known at this stage, irrespective of route taken.

Begin hand-shake. 5p+ve logic pulse.

ADC control line low? yes

Input ADC signal.

Store temperature at 1 sec. intervals.

Determine T_r - T_a

Error > 25°C no

Set NEGFLAG

Change error to absolute value.

+ve or -ve error?

+ve

Fetch constants C, D determined by heating rate K.

Calculate power error factor.

Calculate constant power.

Add error power from constant power.

NEGFLAG high?

yes

Subtract error power from constant power.

Is flag high? yes

Is temperature cut-off reached?

no

Discrete power supply.

STOP.

yes

Is end of linear range reached?

no

Output power level.

IF X0, then P=0

IF P>255, then P=255

Clear flag.

Set interrupt vector to 0400H (N A000 - A001)

Enable interrupt.

Return from interrupt.

Figure (2.5b)

Continuation of the Microprocessor Control Program
Figure (2.5c)

*Loading of the Control Program with the Screen Display of a Typical Linear Heating Cycle*

(The user is attached to PRIME)

RUN LOADMICRO

GIVE THE FILENAME

CONT (Name of control program)

YOU HAVE 10 SECONDS TO SWITCH TO POSITION 2

(Position 2 allows interfacing between the PRIME, M6800 & VDU)

(Program is loaded)

SWITCH TO POSITION 3 & USE J COMMAND)

J0040 (Jumps to memory location 0040, the start location)

UNIVERSITY OF SURREY

MICROPROCESSOR CONTROLLED HEATER

G. G. COLVIN. 1981

N.B. GAIN AT MEM.LOC. 0617H

N.B. AFTER RESET.. J0040H

N.B. TEMP. AT OAOOH IN 1 SEC INTERVALS. 2 BYTES

HIT ANY KEY TO START

DO YOU REQUIRE NON-LINEAR HEATING.. N (or Y)

INPUT HEATING RATE.. 02 (2 degrees per second)

INPUT CUT-OFF TEMP IN HEX.. 0190 (400 C)

INPUT ROOM TEMP IN HEX.. 14 (20 C)

HIT G TO GO, A TO ABORT.. G (or A)

00A3 (Time elapsed during heating, in hexadecimal)

* Underlined words are typed by user

* Comments are in parenthesis
2.2.3 The Programming Method

The major programming steps described by figure (2.5) are fully described below. Figure (2.5c) shows a typical VDU display during operation of the TL reader.

STEP 1. Assign addresses for constants used throughout the program, and set table pointer to 1000H. Extensive use is made of the SWTBUG input/output routines to enable the constants to be entered as answers to a series of questions and commands. These are:

1) Is non-linear heating required? - Set NLIN flag high if answer 'Y' (YES).
2) Input heating rate (K) for linear heating.
3) Input room temperature (Tr).
4) Input cut-off temperature (Tc).
5) Is the operator ready to 'GO'? - Press 'G' character to begin heating profile. Any other character causes the program to halt.

STEP 2. This step enables the power supply. For reasons of safety, the power supply has a control line which if disconnected, floats at +5V and is thus disabled. To enable the power supply, the control line CA2 from the parallel interface is made to go low, and stays in this state until the program is halted for any reason.

NB. On 'RESET' of the microprocessor, the value set on the lines controlling the output power is undetermined, but control line CA2 will always be high, thus disabling the supply until the program is started.
STEP 3. A MOTOROLA MP-T interrupt timer has been assembled in the microprocessor. This device can be software programmed to select timed interrupt pulses in the range 1μs to approximately 1 hour. This program sets the interrupt rate at 10Hz, where each interrupt starts the temperature measurement and error determination. In this way, temperatures are read every 100ms, and the power supplied to the heater adjusted accordingly.

Depending on the state of the NLIN flag (set high if non-linear heating is required), the memory locations A000H-A001H (the address from which SWTBUG determines the interrupt vector address) are loaded with the following constants:

1) 0400H for non-linear heating (NLIN=high) –Proceed to STEP 4
2) 0490H for linear heating (NLIN=low) –Proceed to STEP 5

The program now waits for an interrupt.

STEP 4. This is the beginning of the interrupt routine for non-linear heating. The interrupt timer is first masked to prevent an interrupt signal being processed during the routine. Next, two adjacent bytes in the look-up table are fetched and decoded after the table pointer is incremented to the next pair of values.

The bytes fetched from the look-up table are coded as follows:

<table>
<thead>
<tr>
<th>MSW</th>
<th>LSW</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Bits 3(MSW) to 0(LSW) are used to store the required temperature multiplied by 10 (see note 2). With a maximum temperature of 500°C, the value 5000 will be the largest number contained in these locations. This value requires 12 binary digits for representation.
The remaining 4 bits of the most significant word are used to hold the heating rate required at that current time. Thus the program now has the values for required temperature (T) and heating rate (K), and will proceed with STEP 6.

If the values fetched from the table are both zero, then a second set of values are fetched and acted on according to table (2.1).

Table (2.1)

<table>
<thead>
<tr>
<th>1st Values</th>
<th>2nd Values</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSW 0 LSW 0</td>
<td>MSW 0 LSW 0</td>
<td>Disable power supply. STOP.</td>
</tr>
<tr>
<td>MSW 0 LSW 0</td>
<td>MSW K LSW Tc</td>
<td>K = Linear heating rate. Tc = Linear to non-linear changeover temperature. FLAG = High.</td>
</tr>
</tbody>
</table>

As seen from table (2.1), the second pair of table values being zero will halt the program after disabling the power supply. However, if they are not zero, then they are decoded as K and Tc, where K is the linear heating rate required, and Tc is 10 times the temperature at which non-linear heating will be resumed. A flag (FLAG) is set high in this case, and the interrupt vector is changed to that of the linear routine (ie. 0490H). The program now proceeds with STEP 5.
STEP 5. A record of the number of interrupts occurring in the linear mode is updated to keep track of the number of seconds in this linear mode. The counter is thus incremented every 100ms, and therefore the program works in units of 1/10th of a second and 1/10th of a degree centigrade, so that,

\[ T = K \cdot C + Tr \]

where \( T \) = Temperature required (0.1°C),
\( K \) = Heating rate (°C/s),
\( C \) = Time (0.1s),
\( Tr \) = Room temperature (0.1°C)

The maximum size of \( T \) will be approximately 500°C, which requires more than one byte to represent it, thus \( T \) is stored as two adjacent bytes.

STEP 6. The ADC for converting the analogue thermocouple signal to digital form, requires a positive 5μs pulse to initiate the conversion. The conversion takes approximately 25μs, therefore the microprocessor must wait for a 'ready' signal from the ADC before it can read the digitised thermocouple voltage. This is accomplished by establishing a CA2 control line of the parallel interface as an output, and producing a low/high/low transition lasting 5μs. A CA1 line is configured as an input to sense the high/low transition from the ADC signalling completion of the conversion. This transition on the CA1 line causes a bit to be set in the control register of the parallel interface, and it is this bit which is continually tested to determine when the reading of the ADC can commence.

STEP 7. Temperature conversion of the thermocouple amplifier voltage is accomplished using a 10 bit ADC, calibrated to give each binary digit as 1°C (bit 10 is currently used as an over
temperature safety device). Once converted, the thermocouple voltage is input using both A & B ports of a parallel interface. The temperature units of $1^\circ$C are internally represented as $1/10^\circ$C units to be compatible with the determined 'required temperature' units. A subroutine is included to store the measured temperature every second, thus enabling a check to be made on the accuracy of the desired heating profile.

STEP 8. The difference between the required and actual temperature is evaluated in order to determine the power required to maintain the desired profile. If this error is greater than $25^\circ$C, the program will halt, as an error will be assumed to have occurred. For negative errors, a flag (NEGFLAG) is set and the absolute error value used.

The required current is determined as the sum of two variables, one having a dependence on the actual temperature and heating rate ($P_c$), and the other having a dependence on $P_c$ and the temperature error ($P_e$).

\[
P_c = \frac{(T_a + A)}{B}
\]

\[
P_e = \frac{E.(T_a + A)}{(B \times X)} = \frac{E.P_c}{X}
\]

where $E$ = Absolute temperature error ($^\circ$C).

$A, B$ = Constants depending on the heating rate $K$. $A, B$ are fetched from a small look-up table. See section 2.2.4.

$T_a$ = Actual temperature sensed by the thermocouple ($^\circ$C).

$X$ = Gain factor.

Thus the required power 'P' is equal to the sum of $P_c + P_e$. $P_e$ is subtracted from $P_c$ if the error is negative (ie. NEGFLAG=high). The gain factor $X$ must be chosen to prevent oscillating power values developing, although if overdamped, the actual temperature will be constantly trying to 'catch up' with the required temperature.
STEP 9. The temperature now reached is compared to the cut-off temperature (FLAG=low) or the linear to non-linear change over temperature (FLAG=high) and implemented if reached. In the latter case, the interrupt vector is set back to 0400H, and FLAG is cleared. The power value derived from STEP 8 is checked to determine whether it is in the range 0-255 and if so is output to the power supply. If out of this range, P<0 is set to zero, and P>255 is set to 255.

Finally, the interrupt mask is removed, and an RTI instruction (return from interrupt) is implemented.

NOTE 1 It is conceivable that higher sampling rates be used (50Hz for example), as a single cycle of the interrupt routine requires less than 5ms to complete. This may be necessary if stability problems are encountered. As the thermal mass of this heater design is large, little will be gained by an increased sampling rate, whereas with other designs, this may not be the case.

NOTE 2 The interrupt frequency is 10Hz, therefore using units of 1/10th degree centigrade makes computations simpler and helps to avoid significant rounding errors, as all calculations use integer mathematics only.

2.2.4 Determination of Heater Constants

In the program description of section 2.2.3, an equation was presented for determining the power necessary to produce a required heating profile. This equation involved two constants (A,B) which are dependent on the heating rate. These constants are unique to any given heater, and an experiment must be done to determine their
By setting a constant value (0-255) on the power supply control (accomplished by using some of the routines from the temperature control program) a series of temperature versus time plots were constructed. Some of these curves for this heater are shown in figure (2.6), where 0=zero amps and 255=50amps. The actual power delivered depends on the heater resistance, and assuming it to have the average value over the range 0°C to 500°C of 0.05ohms, it is of the order of 125Watts maximum. 

The switch-mode power supply is in fact capable of delivering a maximum power of 250Watts. This could be achieved by increasing the heater resistance to approximately 0.1ohms by either wasting the diameter of the block, or drilling a hole through its centre. A good thermal and electrical contact between the carbon and the copper bit must be maintained at all times, therefore the latter method of increasing the resistance may be preferred.

From figure (2.6), an intermediate plot of heating rate versus current setting at various temperatures was constructed, from which a graph of temperature against current at set heating rates was derived, and is shown in figure (2.7). By approximating this latter curve to a linear representation (a polynomial was not found to be necessary), a simple \( y=mx+c \) equation will yield two constants:

\[
T = B \cdot P - A
\]

where \( T \) = Temperature

\( A, B = \) Constants

\( P = \) Current setting

Therefore to achieve a given heating rate \( K \), the value of the current setting can be determined by:

\[
P(K) = \frac{(T + A(K))}{B(K)}
\]
Figure (2.6) Constant Current Settings

![Graph showing constant current settings with temperature on the y-axis and time on the x-axis. The graph includes lines for different current settings marked as max, .3 max, .375 max, .188 max, and .125 max.]

Figure (2.7) Constant Heating Rates

![Graph showing constant heating rates with temperature on the y-axis and time on the x-axis. The graph includes lines for different heating rates marked as 1°C/s, 2°C/s, 3°C/s, 4°C/s, 5°C/s, 6°C/s, and 8°C/s.]

Current Setting (0 - 255)
The values derived thus for A and B are given in table (2.2).

Table (2.2)

Heating Rate Constants

<table>
<thead>
<tr>
<th>K(°C/s)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>826</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>448</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>316</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>335</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>330</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>367</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>384</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>423</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>505</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>524</td>
</tr>
</tbody>
</table>

N.B. Above values are rounded to the nearest integer.

2.3 CHOICE OF PHOTOMULTIPLIER TUBE

When detecting low intensity light signals using photomultiplier tubes (PMT), two methods are used for recording the output level at the anode, these being, current measurement, and photon counting. As the TL system is to measure low signal levels, the optimum choice must be made between these techniques.

The output from a PMT consists of a signal from two sources; That derived from the electrons liberated from the photocathode by direct
illumination, and a spurious noise signal (dark current or dark count) caused by thermionic emissions within the PMT, ionising radiations, ion pulses etc.

SPANNE (1974) calculated the theoretical improvement of photon counting over charge integration to be a factor 2, although in practice, the difficulty in optimisation of the charge integration circuits gives a more realistic experimental improvement of a factor of 10 (LASKE, 1973). Photon counting also lends itself more naturally to digital techniques, as the anode pulses can be directly counted (after suitable amplification), using digital circuits and consequently making analysis of results simpler. Also, discrimination against PMT noise and ionising radiation events is better.

Hence, a photon counting technique was preferred over charge integration. Constraints on the choice of PMT's, and suitability tests for photon counting are described below.

2.3.1 Spectral Response of the PMT

To maximise the number of anode pulses per TL photon incident on the photocathode, the quantum efficiency (Q.E) of the PMT (see figure 2.8), must be as high as possible, and carefully matched to the range of wavelengths in the incident light. TL emission spectra have been measured for some common minerals used in TL dating (BAILIFF, 1977a, and DAVID, 1977), and the wavelength range 350nm to 500nm is found to encompass them. The majority of commercial photo-tubes are suitable for such wavelengths.

At longer wavelengths (visible red and beyond), a low quantum efficiency is an advantage in order that the signal derived from the black-body glow of the sample and heater at elevated temperatures, is reduced to an absolute minimum. This is particularly important in
archaeological and geological TL dating, where the long-lived, high temperature peaks are to be measured, which suffer more from black-body interference than the lower temperature peaks employed when using man-made TL phosphors. From the various PMT constraints, only the bialkali photocathode materials are suitable in commercially available photomultiplier tubes. These tubes combine high quantum efficiency over the required range, with extremely low noise.

The use of optical filters to further reduce the range over which
the photocathode is effectively sensitive, will improve rejection of the near-infrared black-body signal. An infrared rejection filter may be used in most applications, although such a filter will reduce the near-UV wavelengths quite considerably as may be seen in figure (2.8).

2.3.2 Dark Count and Noise

When a photomultiplier tube is operated in 'complete' darkness, there will be present at the anode, a significant signal known as the 'dark count'. This dark count ultimately sets a lowest limit to the intensity of the TL signal that may be measured.

A major contributor to the dark count is thermionic emission from the photocathode. This component is dependent on temperature, cathode area, and the thermionic work function of the cathode material. Fortunately, the wavelengths of emitted light from most TL materials are in the high energy region of the visible spectrum, and it is therefore unnecessary to have low work function photocathode materials, as these have high thermionic emission rates compared to high work function materials. A reduction in the temperature of the photocathode will reduce the dark count, although below -10°C for bialkali materials, any residual dark counts are due to causes other than thermionic noise.

Multiplication variation is evident when the RMS variation of the anode charge, is found to be greater than that predicted by simple Poissonian statistics. This is due to the statistical spread in the coefficient of secondary emission of the dynodes. The fluctuations at the first dynode are the most significant in this process, and minimising this fluctuation is most important for obtaining a good single electron response. This may be achieved by increasing the first dynode gain, see figure (2.9), and hence an improved
discrimination against low amplitude pulses not derived from the photocathode is possible. In this way, low amplitude, multi-electron events due to weak scintillation signals around the photo-cathode (caused by environmental radiation), can be discriminated against.

2.3.3 Tests on the EMI 9893/350 Photomultiplier

The photomultiplier chosen for the apparatus described in section 2.1 was the EMI 9893/350. This device has a bialkali photocathode with a quartz window, and a fourteen BeCu dynode structure. The effective cathode diameter is 9mm (chosen to minimise the thermionic emission), and has a peak quantum efficiency of 26.5% at 380nm.

Single electron response (SER) differential pulse height and
integral pulse height spectra are shown in figure (2.10). The value $N(0)$ at which the integral curve intercepts the channel zero axis, is the number of electrons entering the multiplier structure (MORTON, 1968). If a rectangle of height $N(0)$ is drawn with an area equal to that under the integral pulse height spectrum, then its intercept on the abscissa is $eG$ (where 'e' is the electronic charge, and 'G' is the gain on the PMT), because the area under this curve is equal to the total charge produced by $N(0)$ electrons. From a knowledge of amplifier gain, G can then be determined. The measured values of G for this PMT are shown in figure (2.11) as a function of anode to cathode voltage. Figures (2.9) and (2.11) show a good SER and gain may be achieved with this photomultiplier.

A graph of SER for two photocathode to first dynode voltages has been shown in figure (2.9). From this it is seen that a higher voltage gives an improved resolution in the differential pulse height spectrum. However, the maximum permissible cathode to first dynode voltage determined by the manufacturer, must not be exceeded, because of possible increases in noise and the possibility of insulation breakdown. This maximum voltage for 50mm envelope PMT's is 450 Volts (EMI, 1979), and the EMI 9893 is run at 300 Volts in this application.

Two output circuits are used in this apparatus; A 'slow' channel to facilitate the determination of a suitable discriminator setting, and a 'fast' channel for signal collection during TL experiments.

The 'slow' channel is so-called, because of the long time constant due to the RC combination used in the output circuit from the last dynode. The positive pulse produced from this circuit, decays to 1/10th its maximum in approximately 0.1msecs. Such a pulse would also be suitable for photon counting, although pulse pile-up will occur at relatively low count rates ($>10^4$ cps).

The 'fast' channel is derived from the anode, and has an RC network producing a short time constant with pulses of 5nsec duration.
Figure (2.10)
SER (Integral and differential)

Figure (2.11)
Gain of PMT (EMI 9893/350)
Figure (2.12)

The Fast and Slow Channels of the PMT

Figure (2.12) shows the use of both output channels for setting the values of the lower level discriminator. The 'fast' channel is used to gate the 'slow' channel signals into the multichannel analyser, therefore the effect on the pulse height spectrum caused by the discriminator setting can be viewed and adjusted to the desired level.

2.4 TEST AND SPECIFICATIONS OF THE TL EQUIPMENT

A series of tests were carried out on the newly-assembled TL apparatus, to determine whether any serious design faults had occurred, and to ascertain whether stability and reproducibility were suitable for TL work. A careful consideration of the conditions under which the apparatus will be used is necessary to prevent any systematic errors occurring under certain conditions. An example of this type of problem
was highlighted by FORSLO (1974), where apparent thermal quenching was later found to be due to PMT magnetisation with increased AC currents in the heater.

The tests described below give an indication as to how well this apparatus will perform when used for routine dating purposes.

2.4.1 The Constancy of TL Collection

The constancy of light collecting from the heater tray is most important, as small movements in the field of view of the photomultiplier optics must not produce any significant variation in the TL intensity measured. To determine whether this was true for this apparatus, a single photon light source was necessary. This could then be placed on the heater tray at varying positions to determine the variations in the collected flux.

The light source used for this purpose was a single crystal of natural fluorite, with an approximate volume of $8\text{mm}^3$. This was given a dose of 200 rads and placed on the heater tray. By using suitable grey filters, the room temperature TL light flux reaching the PMT was adjusted to be well within the dynamic counting range of the associated electronics. Although this light source is a single photon emitter, it was found to decay fairly rapidly. By measuring the flux at various times at a constant position within the TL apparatus, a decay curve was constructed from which the half life (2.25 hours) was determined. With this information, changes in flux due to this ambient fading behaviour, can be calculated.

The flux was measured at nine different positions within the heater tray using this light source, and the results (normalised to the flux rate at position A) are shown in figure (2.13a). For completeness, this was repeated outside the heating tray field, using a thin plastic
Figure (2.13a)
Sample Movement

B

F G

D A E

H I

C

Position in Planchet

<table>
<thead>
<tr>
<th>Position</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
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</thead>
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<tr>
<td>Normalised Signal</td>
<td>1</td>
<td>.97</td>
<td>.99</td>
<td>1.00</td>
<td>.97</td>
<td>.95</td>
<td>.96</td>
<td>.99</td>
<td>.98</td>
</tr>
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</table>

Figure (2.13b)
Sample Movement

A B C D E

1cm

Position in Grid

<table>
<thead>
<tr>
<th>Position</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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</thead>
<tbody>
<tr>
<td>Normalised Signal</td>
<td>.98</td>
<td>.97</td>
<td>.99</td>
<td>1.00</td>
<td>.94</td>
</tr>
<tr>
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</tr>
<tr>
<td>2</td>
<td>.98</td>
<td>.99</td>
<td>1.00</td>
<td>.99</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>1.01</td>
<td>1.02</td>
<td>1.00</td>
<td>.98</td>
</tr>
<tr>
<td>4</td>
<td>.98</td>
<td>.99</td>
<td>1.00</td>
<td>.95</td>
<td>.96</td>
</tr>
</tbody>
</table>
film to hold the crystal, on which had been scratched a positioning grid. These results are shown in figure (2.13b).

The slight reduction in flux, measured at the edges of the heater tray (B to I) are probably due to shadowing of the light by the raised edges of the tray, as this is not seen when using the flat, plastic film. Therefore it can be concluded positional variations averaged over the sample can be kept to less than 2%.

2.4.2 Reproducibility of TL Signal

The high temperature peak areas of natural fluorite phosphors with a dose of 10 rads, were measured using the new TL apparatus. Various conditions of the experiment were changed, including ambient temperature of equipment, HT power supply for the PMT, heating rate and nitrogen gas flow rate. Results are shown in figure (2.14), and are normalised to the mode value. The fluorite samples were weighed to an accuracy of 1%, and were in the range 5-7mgm. Pre-scaling was used to ensure linearity of the MCA.

From these results, none of the conditions produced a systematic error of any observable significance.

2.4.3 Reproducibility of Heating Profile

The temperature recorded by the program described in section 2.2.3, was graphically compared to the desired temperature for linear heating in the range 1-10°C per second from room temperature to 400°C. An absolute error of greater than 1°C only occurred above 300°C on heating rates greater than 5°C per second.
Tests for Reproducibility

For non-linear heating profiles, change over from the initial linear ramp to the hyperbolic temperature rise, was always settled within 1 second of the predicted time, with temperature errors being the same as the linear case.
Finally, the specifications of the TL reader described within section 2 are summarised below.

**APPARATUS DESCRIPTION** - Digital TL reader.

**COUNTING ELECTRONICS** - Amplifier and multichannel scaling system.

M.C.A. - TRACOR NORTHERN (TN 1705)

AMPLIFIER - ORTEC 454, timing filter amplifier.

DISCRIMINATOR - ORTEC 463, fast discriminator.

PRE-SCALER - J&B (NM 131). Altered for divide by 2, 10, 40, 100, 400.

**HEATER** - Resistive graphite block heater.

POWER SUPPLY - Switch-mode DC power supply.

MAX POWER RATING - 200 Watts.

**TEMPERATURE CONTROLLER** - Microprocessor and thermocouple.

MICROPROCESSOR - MOTOROLA 6800 plus programmable interrupt timer.

THERMOCOUPLE - Chromel/alumel.

ADC - ANALOGUE DEVICE AD 571 JD. 12 bit ADC. 25μs conversion time.

TC AMPLIFIER - <1/2% error.

MAX HEATING RATE - 8°C/s (up to 500°C) for power supply rated at 125 Watts.

PROGRAMMING - Linear and hyperbolic heating rates.

**LIGHT MEASUREMENT** - PMT and lens system.

PMT - EMI 9893/350 - QB.

OPERATING VOLTAGE - 1800V.

TYPICAL SER RESOLUTION - 90%.

DARK COUNT - 60 cps at room temperature.

LENS SYSTEM - Quartz glass. Focal lengths 38mm (f1) and 75mm (f2).

LIGHT COLLECTION - <2% intensity variation over heater tray.
The importance of theoretical considerations in thermoluminescence dating is mostly concerned with the long term stability of the TL signal, and predictions of the non-linearity in the growth curves of useful phosphors. Without adequate stability and linearity, conventional TL dating would be prone to many errors. This section collects together some useful methods for determining the trapping parameters for glow peaks of TL phosphors. It should be noted that even an accurate knowledge of these parameters will not predict the fading mechanisms of certain phosphors (see section 1.2.4) under all conditions (WINTLE, 1977).

3.1 SIMPLE THEORY

It is possible to describe the phenomenon of thermoluminescence using the simple band structure model of an insulator. This model assumes two regions of energy continua (the valence and conduction bands), separated by a region of quantum mechanically forbidden energy values. The conduction band represents the free electron states, whereas the valence band is representative of all the bound states of the outer electrons. Assuming the forbidden energy region is sufficiently large, the probability of an electron possessing enough thermal energy to be promoted to the conduction band, will be small unless certain conditions (e.g., the presence of a radiation flux) prevail.

However, in a real insulating crystal having many defects in its lattice, energy levels (we will consider only discrete energy values, (KIVITS, 1978)) do exist within the 'forbidden gap'. It is at these energy levels that electron/hole pairs may be trapped and later
released to recombine with the emission of a photon of light.
Figure (3.1)

The simplest model for thermoluminescence is that described by
RANDALL & WILKINS (1945), and is diagramatically represented in
figure (3.1).

The production of TL in a material exposed to ionising radiation can
be considered as a two stage process:

1) An ionisation process followed by trapping of the free
electron/hole pair.

2) A recombination process giving rise to emission of light
photons.

Therefore, we can consider an electron from the valence band being
promoted to the conduction band upon irradiation, before being trapped
at a trapping level T of energy depth E. Similarly, the complimentary
hole can move through the valence band until it is captured by a hole
trapping centre, labelled L in figure (3.1). A TL glow is produced
when the trapped electron at T is given sufficient energy to re-enter
the conduction band before recombining at a luminescence centre where
the transition may be accompanied with the emission of light. The
luminescence centre L has been previously activated during irradiation
by capturing a hole. Retrapping of the electron at T, once removed
from the trap is assumed to be negligible (first order kinetics).
Using the classical Boltzmann equation, the probability of an electron escaping from a trapping level to the conduction band is given by:

$$p = S \cdot \exp \left( \frac{-E}{kT} \right) \quad \ldots \quad (3-1)$$

where

- $p$ = Probability of escape of trapped electrons [s$^{-1}$]
- $S$ = Constant [s$^{-1}$]. Often referred to as the frequency factor, or attempt to escape frequency.
- $k$ = Boltzmann constant [eV.K$^{-1}$] = 8.6178x10$^{-5}$ eV.K$^{-1}$
- $E$ = Energy level of metastable trap below the conduction band [eV]
- $T$ = Temperature [K]

The rate of emptying of electrons from this trap will be:

$$\frac{dn}{dt} = -n \cdot p \quad \ldots \quad (3-2)$$

where

- $n$ = Concentration of electrons in traps [cm$^{-3}$]

Therefore, 

$$\frac{dn}{dt} = nS \cdot \exp(-E/kT) \quad \ldots \quad (3-3)$$

Using equation (3-3), and solving for $n$ with a linearly increasing temperature gives:

$$n = n_0 \cdot \exp \left\{ -\int_{T_i}^{T} \frac{S \cdot \exp(-E/kT)}{b} \cdot dT \right\} \quad \ldots \quad (3-4)$$

where

- $b$ = Heating rate [K.s$^{-1}$] = $dT/dt$
- $n_0$ = Concentration of trapped electrons at time zero [cm$^{-3}$]
- $T_i$ = Initial temperature [K]

The rate of recombination $-dn/dt$ is proportional to the intensity of light produced, so that combining equation (3-4) into (3-3) gives:

$$I(T) = n_0S \cdot \exp(-E/kT) \cdot \exp \left\{ -\int_{T_i}^{T} \frac{(s/b) \cdot \exp(-E/kT)}{b} \cdot dT \right\} \quad \ldots \quad (3-5)$$

In the case where retrapping of liberated electrons is not assumed to be negligible (second order kinetics), equation (3-5) must be modified. The probability of retrapping will depend on the number of traps not occupied by electrons. Assuming that the probability of retrapping and recombination is equal, then at any time, there will be $(N-n)$ empty traps (where $N$ is the total number of traps), and $n/((N-n)+n) = n/N$ will be the probability of an escaped electron being
retrapped (GARLICK, 1948), so that:

$$ I = -\frac{dn}{dt} = \left(\frac{n^2}{N}\right)S \exp(-E/kT) \quad \cdots (3-6) $$

solving equation (3-6) for $n$ with a heating rate $b$, gives:

$$ I(T) = n_0^2 S \exp\left(-\frac{E}{kT}\right) / N \left[ 1 + \left(\frac{n_0}{Nb}\right) \int_{T_i}^{T} S \exp\left(-\frac{E}{kT}\right) \, dt \right]^2 \quad \cdots (3-7) $$

The difference between the glow curve shapes for first order and second order kinetics is shown in table (3.1).

Table (3.1)

First and second order glow curves

<table>
<thead>
<tr>
<th>CASE</th>
<th>FIRST ORDER</th>
<th>SECOND ORDER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant $S, n_0, b$</td>
<td>Temperature at peak max, proportional to $E$.</td>
<td>As first order case.</td>
</tr>
<tr>
<td>Given $E, n_0$</td>
<td>Max emission temperature varies with $b$, and $S$. (eg. As $S$ increases, $T_m$ decreases.)</td>
<td>Variation as first order case.</td>
</tr>
<tr>
<td>Varying $n_0$</td>
<td>Area under glow curve proportional to $n_0$.</td>
<td>As 1st order case with shape change.</td>
</tr>
<tr>
<td>Initial rise with linear rate $b$.</td>
<td>$I = n_0 S \exp(-E/kT)$</td>
<td>$I = (n_0^2/N)S \exp(-E/kT)$</td>
</tr>
</tbody>
</table>

Many techniques have been devised and compared for the determination of the parameters $S$ and $E$ from glow curves (NICHOLAS, 1964., CHEN, 1969a., DUSSEL, 1967., SANDOMIRSKII, 1967), and the order of reaction (GARLICK, 1948., HALPERIN, 1960). A result from many
determinations of the reaction order resulted in some workers (MAY, 1964) finding neither first or second order kinetics, but a non-integer order between the values of 1 and 2. An empirical formula (equation (3-8)) was successfully applied by HILL,(1955) on inspection of the equations (3-3, 3-6).

\[ I = n^r S \exp(-E/kT) \] ...

where \( r \) = Order of reaction.

\[ S' = \text{Constant (equivalent to frequency factor)} \]

The solution to equation (3-8) is:

\[ I = S'n^r \exp(-E/kT).[1+((r-1)S'/b)\int_0^T \exp(-E/kT) - \frac{T}{T_i} \exp(-E/kT)]/(r-1) \] (3-9)

This solution is not valid for the value \( r=1 \).

Although this simplified model helps to explain the glow curve shapes and peak positions, detailed consideration of trapping processes during irradiation and glow curve read-out is necessary for a more complete picture. The phenomena of supralinearity and dose sensitisation are described by models which consider the changes of electron distribution among traps (SUNHERALINGHAM, 1969) and spatial correlation between traps (FAIN, 1977). The deep trap model of Suntheralingham assumes a more efficient, saturating trapping level of large trap depth \( E \), coexisting with the level producing the glow curve which empties during the glow experiment. Fain proposes a single trap/centre system which only interact with adjacent systems as their concentration increases with dose.

Further modifications to these models are sometimes necessary to be able to compare experimental with theoretical results. Some examples are: variation of frequency factor with temperature, and a process whereby trapped electrons radiatively and non-radiatively de-trap independently of the phosphor temperature (anomalous fading).
3.2 DETERMINATION OF TL PARAMETERS (isothermal)

Using the equation for first order kinetics of RANDALL,(1945) shown in equation (3-3), and integrating with respect to time for a constant temperature T, yields the following after rearrangement:

\[-\ln(\frac{n}{N_0})/t = S \cdot \exp(-E/kT) \quad \ldots \ldots (3-10)\]

Equation (3-10) can be regarded as a decay constant \(L(T)\) on the left-hand side, so a plot of \(\ln(\frac{n}{N_0})\) against time will yield \(L(T)\) at the temperature T. Hence it can be seen from equation (3-10) that a plot of \(\ln(L(T))\) versus \(1/T\) will yield a slope of \(-E/k\) with an intercept of \(\ln(S)\).

In the second order case, equation (3-6) must be solved for \(n\) with constant temperature. The result is:

\[
(\frac{1}{n} - \frac{1}{N_0}) = (S/N)t \cdot \exp(-E/kT) \quad \ldots \ldots (3-11)
\]

Using the same method as that applied to equation (3-10), second order kinetics yields \(L(T)\) for a plot of \(1/n\) versus time. Therefore plotting \(\ln(L(T))\) versus \(1/T\) gives a gradient of \(-E/k\) and an intercept of \(\ln(S/N)\).

Finally, for kinetics of general order, the following steps will yield the constants \(r, E\), and \(S^*\).

1) Plot \(\ln(\frac{1}{n} - \frac{1}{N_0})\) vs \(\ln(t)\) to give a gradient of \(1/(1-r)\).
2) Plot \((\frac{1}{n} - \frac{1}{N_0})^a\) vs time to give \(L(T)\), where \(a=1/(1-r)\).
3) Plot \(\ln(L(T))\) vs \(1/T\) to give \(-E/kT\) and an intercept of \(S^*\).

3.3 DETERMINATION OF TL PARAMETERS (linear heating)

Many techniques have been used to extract the TL parameters from glow curve shapes produced by phosphors experiencing a linear heating profile. An examination of some of these are given by NICHOLAS,(1964) and KIVITS,(1978). Most of these methods are based on the position and...
shape of the glow peaks with varying heating rates. Approximations to
glow peak shapes make solutions to the model equations possible

A simple technique for the determination of the parameters E and S
is that first advocated by GARLICK, (1948), and is known as the 'initial
rise' method. It approximates the glow curve intensity to the
equation (3-12).

\[ I = (\text{constant}) \cdot \exp(-E/kT) \]  \hspace{1cm} \ldots(3-12)

This equation applies only when the electron traps are beginning to
empty and is independent of the order of kinetics. A plot of ln(I)
against 1/T on the rising slope will yield a gradient of -E/k.
HAKE, (1957) comments on the range of temperatures for which
equation (3-12) is valid. In some cases, thermal quenching (changes in
luminescence efficiency with temperature) has made this method
difficult to apply (WINTLE, 1977).

Another technique reported to be independent of reaction kinetics is
that of HAERING (1960). Differentiating the glow peak expression to
find the condition for the temperature \(T_m\) at the glow peak maximum
\((dn/dt=0)\), then substituting this condition into the expression for the
glow peak, equation (3-13) results after using an asymptotic expansion.

\[ I_m = A \cdot \exp(-E/kT_m - 1) \]  \hspace{1cm} \ldots(3-13)

Equation (3-13) shows that from a number of glow peak measurements
using varying heating rates, a plot of ln\(I_m\) against the reciprocal
of \(T_m\) produces a gradient of -E/k.

Assuming first order kinetics, HOOGENSTRAATEN, (1958) determined an
equation relating the maximum peak temperature and heating rate:

\[ \ln(b/T_m^2) = \ln(kS/E) - E/(kT_m^2) \]

Thus a plot of ln\(b/T_m^2\) versus 1\(T_m^2\) yields a straight line of
gradient -E/k and intercept of ln(kS/E).

GROSSWEINER, (1953) developed a technique for first order kinetics
whereby the trap depth and frequency factor could be determined from a
single glow curve as shown in equations (3-14,3-15):

\[ E = 1.51kT_m T_1/(T_m - T_1) \] .... (3-14)

\[ S = \frac{3 T_0}{2 N_0 T_m} \left[ \frac{\exp(E/kT_m)}{(T_m - T_1)} \right] \] .... (3-15)

where \( T_1 \) = Temperature at half maximum height on the rising slope.

Approximating the glow curve shape to a triangle, HALPERIN,(1960) produced two equations to determine \( E \) for both integer orders of kinetics:

First order \[ E = (1.72/(T_m - T_1)) k T_m^2 (1 - 2.58 d) \] .... (3-16)

Second order \[ E = (2.0/(T_m - T_1)) k T_m^2 (1 - 3d) \] .... (3-17)

where \( d = 2kT_m /E \)

Equations (3-16,3-17) can be solved by measuring the values of \( T_m \) and \( T_1 \). Halperin determined two inequalities to distinguish between the two kinetic cases:

First order \[ m < e^{-1}(1 + d) \]

Second order \[ m > e^{-1}(1 + d) \]

where \( m = (T_2 - T_m)/(T_2 - T_1) \) .... (3-18)

\( T_2 \) being the temperature at half the maximum peak height on the falling slope of the glow curve.

CHEN,(1969a) developed a method utilising the parameters of 'halfwidth', \( w = (T_2 - T_1) \) and the peak temperature \( T_m \). Some consideration for a possible variation of frequency factor with temperature was made. See table (3.2).

For general order kinetics, CHEN,(1969b) produced a set of equations incorporating the methods of HALPERIN,(1960), CHEN,(1969a), and LUSHCHIK,(1955).

\[ E_g = C_g (kT_m^2 /a) - D (2kT_m) \] .... (3-19)

where \( g \) is the subscript representing one of the three methods.
Table (3.2)
Halfwidth determination of trap depth

<table>
<thead>
<tr>
<th>CASE</th>
<th>FIRST ORDER</th>
<th>SECOND ORDER</th>
</tr>
</thead>
<tbody>
<tr>
<td>S constant</td>
<td>$E = 2kT_m (1.25T_m /w - 1)$</td>
<td>$E = 2kT_m (1.756T_m /w - 1)$</td>
</tr>
<tr>
<td>$S = S T^{-2}$</td>
<td>$E = 2kT_m (1.26T_m /w)$</td>
<td>$E = 2kT_m (1.758T_m /w)$</td>
</tr>
<tr>
<td>$S = S T^{+2}$</td>
<td>$E = 2kT_m (1.26T_m /w - 2)$</td>
<td>$E = 2kT_m (1.758T_m /w - 2)$</td>
</tr>
</tbody>
</table>

Halperin
- $C_g = 1.51 + 3(m - 0.42)$
- $D_g = 1.58 + 4.2(m - 0.42)$
- $a = T_m - T_1$

Chen
- $C_g = 0.975 + 7.3(m - 0.42)$
- $D_g = 0$
- $a = T_2 - T_m$

Lushchik
- $C_g = 2.52 + 10.2(m - 0.42)$
- $D_g = 1$
- $a = T_2 - T_1$

$m$ is defined in equation (3-18)

The probable order of kinetics $r$, may be found by comparing the value of $m$ to the calculated values given by CHEN, (1969b, page 1256).
Hence $S$ can be estimated from equation (3-20):

$$bE / kT_m^2 = S \exp(-E/kT_m) \cdot (1 + (r-1)y) \quad ....(3-20)$$

where $\frac{y}{2kT_m} = \frac{E}{2E}$

N.B. The value of $y$ is small and affects the calculated value of $S$ by less than 5%.
The trapping parameters for a sample of green quartz (Cornwall; supplied by R.F.J. Parkinson & Co., Somerset) were determined using two methods described in section 3.3. These were the initial rise method, and that of CHEN (1969b). See equation (3-19).

This sample was chosen for analysis because of its complex glow curve as shown in figure (3.2). The glow curve shows that only one of the glow peaks (at 92°C) is resolved sufficiently to determine \( t_m \), \( t_1 \) and \( t_2 \) and the initial rising slope of the peak. The technique first used to overcome this problem was to employ simple peak cleaning, whereby the initial rise portion of the glow peak to be analysed, has the lower temperature peaks annealed by heating to a temperature just below the TL maximum. This was found to be successful for the initial rise analysis for the glow peaks with temperature ordinates at 92°C and 160°C.

However, for the higher temperature peaks, a simple peak cleaning did not produce a linear plot for the initial rise method, so it was therefore assumed that higher temperature peaks had some contribution to the peak being analysed, perhaps to the extent that they could not be resolved. To overcome this problem, the rising slope of the next resolved peak (at a higher temperature) was determined by the simple peak cleaning technique, and then normalised at its peak temperature to the unresolved glow curve, before subtracting from the peak being analysed. This is shown schematically in figure (3.3).

Using this peak stripping technique for the remaining peaks yielded the theoretical trapping parameters \( E \) and \( S \), as shown in table (3.3).
Figure (3.2)  Glow Curve of Green Quartz

Figure (3.3)  Glow Peak Stripping

Cleaned peak = Glow1 - (I1/I2)Glow2
Table (3.3)

Derived trapping parameters

<table>
<thead>
<tr>
<th>Peak Temp(°C)</th>
<th>Initial rise method(eV)</th>
<th>CHEN(1969b) method(eV)</th>
<th>S (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>92°C</td>
<td>.89</td>
<td>.90</td>
<td>5x 10¹¹</td>
</tr>
<tr>
<td>160°C</td>
<td>1.07</td>
<td>1.00</td>
<td>7x 10¹⁰</td>
</tr>
<tr>
<td>204°C</td>
<td>1.18</td>
<td>1.10</td>
<td>1x 10¹⁰</td>
</tr>
<tr>
<td>291°C</td>
<td>1.31</td>
<td>1.21</td>
<td>3x 10¹¹</td>
</tr>
<tr>
<td>321°C</td>
<td>1.50</td>
<td>1.40</td>
<td>4x 10¹²</td>
</tr>
<tr>
<td>367°C</td>
<td>1.57</td>
<td>1.79</td>
<td>3x 10¹³</td>
</tr>
</tbody>
</table>

These results may be compared to those measured in section 4 (see table 4.1), where in general they are in agreement. Both the initial rise technique and that of Chen were simple to apply, although the latter relies on measurements from the falling slope of the glow curve peak which is more susceptible to interferences from higher temperature peaks, and the errors associated with the peak subtraction method described earlier.
An inspection of the first and second order kinetics equations of section 3 (equations (3-5), and (3-7)), show that for a linear heating rate \( \frac{dT}{dt} = b \), the solution involves an integral term \( \int \exp(-E/kT)dT \) which cannot be solved analytically. The methods for determining the trapping parameters as outlined in the previous section all therefore have to make approximations to arrive at a solution.

SHOEN (1958) showed that a hyperbolic heating profile of the form-

\[
\frac{1}{T} = \frac{1}{T_0} - gt
\]  

\( \cdots (4-1) \)

where \( T, T_0 \) = Temperature and initial temperature respectively \( ^\circ K \)

\( g = \text{Constant} \) \( K^{-1}s^{-1} \)

\( t = \text{Time} \) \( s \)

will allow the integral term of the TL equation to be readily solved. A solution for the first order case was presented by ARNOLD, (1959), who produced the heating profile of equation (4-1) using a manually driven VARIAC. However, his poor results were due as much to the materials being studied (chloroplasts) as to the irreproducibility of the heating profile. The equipment described in section 2 can produce this heating profile with good reproducibility, so it was therefore decided to study the possibilities of non-linear heating more closely.
4.1 THEORETICAL CONSIDERATIONS

The two equations describing the changes in concentration of trapped charge for a single trapping level in a TL material (using the nomenclature of section 3), are shown below for the first and second order processes.

FIRST ORDER  \[-dn/dt = nS.\exp(-E/kT)\] \(\ldots(4-2)\)
SECOND ORDER  \[-dn/dt = (n^2/N)S.\exp(-E/kT)\] \(\ldots(4-3)\)

Solutions to the above equations are presented below.

4.1.1 Solution for first order kinetics

Solving equation (4-2) as in section 3.1 gives:

\[n = n_0.\exp(-(\int S.\exp(-E/kT)dt))\] \(\ldots(4-4)\)

The solution to the integral in equation (4-4) is only analytically possible with certain functions of temperature. Using that of equation (4-1) gives:

\[n = n_0.\exp(Q(1 - \exp(at)))\] \(\ldots(4-5)\)

where \[a = (E_g)/k\] \(\ldots(4-6)\)

and \[Q = (S/a).\exp(-E/kT_0) = (S/a)\exp(-a/(gT_0))\] \(\ldots(4-7)\)

Assuming the TL intensity (I) is proportional to the rate of change of \(n\), then:

\[I = An_0aQ.\exp(Q(1 - \exp(at)) + at)\] \(\ldots(4-8)\)

where \(A\) = constant

The maximum value of \(I (I_m)\) will occur at \(t_m\), when:

\[dI/dt = aI(1 - Q.\exp(at_m)) = 0\] \(\ldots(4-9)\)

Equation (4-9) can be rearranged to give:

\[Q.\exp(at_m) = 1\] \(\ldots(4-10)\)

Substituting equation (4-10) into (4-8) produces:

\[I_m = Aan_0.\exp(Q - 1)\]
Therefore the ratio of intensities at varying times on a glow curve during a heating profile governed by equation (4-1) will be given by:

\[ \frac{I}{I_m} = \exp \left\{ 1 + a(t-t_m) - \exp(a(t-t_m)) \right\} \]  \hspace{1cm} (4-11)

4.1.2 Solution for second order kinetics

Solving equation (4-3) by using (4-1) results in the equation:

\[ n^2 = n_0^2 \left( 1 - \frac{n_0Q}{N} \right) \left( 1 - \exp(at) \right)^2 \]  \hspace{1cm} (4-12)

Hence, putting equation (4-12) into (4-3) yields:

\[ I = \frac{An_0^2aQ \exp(at)}{N(1 - \frac{n_0Q}{N}) \left( 1 - \exp(at) \right)^2} \]  \hspace{1cm} (4-13)

(assuming \( I = -A \cdot \frac{dn}{dt} \))

Equating \( \frac{dI}{dt} \) to zero gives:

\[ \exp(at_m) = \frac{N}{n_0Q} - 1 \]  \hspace{1cm} (4-14)

so that:

\[ I_m = \frac{An_0^2aQ \left( \frac{N}{n_0Q} - 1 \right)}{4N(1 - \frac{n_0Q}{N})^2} \]  \hspace{1cm} (4-15)

Hence:

\[ \frac{I}{I_m} = 4 \cdot \exp(-a(t-t_m)) \left[ 1 - \frac{\exp(at_m) + 1}{1 - \exp(at)} \right]^2 \]  \hspace{1cm} (4-16)

4.1.3 Time of maximum emission

Equations (4-10) and (4-14) give directly the time of maximum emission intensity for both first and second order kinetics, thus:

**FIRST ORDER**  \[ t_m = \frac{1}{a} \ln(1/Q) \]

**SECOND ORDER**  \[ t_m = \frac{1}{a} \ln\left( \frac{N}{n_0Q} - 1 \right) \]
4.2 DETERMINATION OF TRAPPING PARAMETERS (1st and 2nd order)

Using the equations derived above, some simple techniques present themselves for determining the trapping parameters $E$ and $S$.

For 1st order kinetics-

Equation (4-11) may be used to determine the value of 'a', and hence the trap depth $E$ from equation (4-6). The frequency factor can now be derived from the value of $Q$ which is to be found from equation (4-7). One simple method for finding 'a' is by plotting $\ln(I/I_m)$ versus $(t-t_m)$ on the rising slope of the glow curve and determining 'a' from the gradient. This assumes $\exp(a(t-t_m)) = 0$ for large $(t-t_m)$, (The rising slope below $I/I_m = .15$ ensures this component to be less than 5%). This graph will check that a 1st order peak is being analysed because the zero intercept will be unity on the ordinate scale in this case.

Equation (4-10) shows that:

$$Q \exp(at_m) = 1$$

therefore, substituting equations (4-6) and (4-7) into equation (4-10) yields:

$$\frac{(Sk/(Eg)) \exp(-E/kT_m) \exp(Egt_m/k)}{1}$$

which implies that:

$$\frac{(Sk/(Eg)) \exp(-E/(k(1/T_m - g t_m)))}{(Sk/(Eg)) \exp(-E/kT_m)} = 1$$

Equation (4-17) can be rearranged to give:

$$\ln(k/g) = E/(kT_m) - \ln(S/E)$$

Therefore, plotting $\ln(k/g)$ against $1/T_m$ for various values of $g$, will yield a gradient of $E/k$, and an intercept of $-\ln(S/E)$, hence $E$ and $S$ can be simply found.

For 2nd order kinetics-

As in the 1st order case, the value of 'a' may be determined from the equation describing $I/I_m$ (ie. equation (4-16)), and $Q$
found by rearranging equation (4-14) when the ratio \( n_0/N \) is known. It can be assumed that \( n_0/N \) is approximately unity when approaching saturation. Hence, \( E \) and \( S \) may be found.

A plot of \( \ln(I/I_m) \) versus \((t-t_m)\) on the rising slope will give the value of 'a' as in the 1st order case. Here, a check for 2nd order kinetics is to show that the zero intercept is 4 on the ordinate scale.

Using the approximation that \( \exp(a t_m) = N/(n_0 Q) \) (true before saturation), then:

\[
\ln(k/g) = E/kT_m + \ln(NE/(n_0 S))
\]

As in the first order case, the slope of \( \ln(E/g) \) versus the reciprocal of \( T_m \) will yield \( E \), and an intercept of \( NE/(n_0 S) \).

4.3 THE GLOW CURVE SECOND DERIVATIVE, 1st and 2nd order

By considering the second derivative of the glow curves produced using the hyperbolic heating profile of equation (4-1), more techniques for determining the trapping parameters become apparent.

For 1st order kinetics-

From equation (4-9), the second derivative is given as:

\[
d^2I/dt^2 = a^2I(1 - Q\exp(-at))^2 - Q\exp(at)
\]

and equating this to zero gives the two points of inflection '\( t_1 \)', where:

\[
(Q\exp(at_1))^2 - 3(Q\exp(at_1)) = 0 \quad \ldots(4-19)
\]

Solving equation (4-19) as a quadratic in terms of \( Q\exp(a t_1) \) results in:

\[
Q\exp(at_1) = 3/2 \pm \sqrt{5/4} = c_1
\]

So, \( t_1 = (1/a)\ln(c_1/Q) \) \ldots(4-20)
where \( q_i = 0.382 \) for \( i = 1 \) (ie. rising slope)
\( q_i = 1.618 \) for \( i = 2 \) (ie. falling slope)

The width of the glow peak \( D \) can be calculated from equation (4-20) to yield:
\[
a = 1.925/D \quad (D = t_2 - t_1)
\]

Therefore the value of 'a' (and hence E) may be found from the time to maximum slope on both sides of the glow maximum, and using these values in the equation above. By substituting the derived values of \( a, t_1 \) and \( t_2 \) into equation (4-20), the constant \( Q \) may be derived and hence the frequency factor 'S'.

For 2nd order kinetics -

Using the same technique as used above, the 2nd order kinetics gives:
\[
(1 - 2X)^2 + 2X^2 - 2X = 0
\]

where
\[
X = \frac{\exp(at_1)}{(\frac{N}{(n_0 Q)} - 1 + \exp(at_1))}
\]

thus giving
\[
t_1 = \frac{(1/a) \ln(\frac{N}{(n_0 Q)} - 1)}{(1/c_i - 1)} \quad \ldots (4-21)
\]

where \( c_i = 0.2113 \) for \( i = 1 \) (ie, rising slope)
\( c_i = 0.7887 \) for \( i = 2 \) (ie. falling slope)

As in the first order case, \( D \) will yield 'a'
\[
a = 2.634/D
\]

It may be noted that \( (t_m - t_1)/(t_2 - t_m) = 1 \) in both the first and second order cases, and may therefore be a useful check on the glow curve shape in order to determine whether glow curve interference is occurring (due to inadequate peak resolution for example).
4.4 HYPERBOLIC HEATING APPLIED TO A GENERALISED TL EQUATION

A generalised TL equation was proposed by May, (1964) and is shown below.

\[-\frac{dn}{dt} = S'n^r.exp(-E/kT) \quad \ldots \quad (4-23)\]

where \( S' \) = pre-exponential constant

\( r \) = order of kinetics (not necessarily an integer value)

The effect of changes in the constant 'r' on the glow curve shape is shown in figure (4.1).

Solving equation (4-23) with a hyperbolic heating profile yields:

\[n^r = \left[ \frac{n_0(r-1)}{1 - (r-1)Q(1 - \exp(at))n_0(r-1)} \right]^{r/(r-1)}\]

where \( r = 1 \)

Now as \( S'.exp(-E/kT) = aQ\exp(at) \), then from equation (4-23) can be obtained:

\[I = -A.dn/dt = AaQ\exp(at)n_0^r \quad \ldots \quad (4-24)\]

Finding \( t_m \) at maximum \( I \) where \( dI/dt = 0 \) gives:

\[\exp(at_m) = 1/( (r-1)n_0^{r-1}Q) - 1 \quad \ldots \quad (4-25)\]

So,

\[I_m = AaQn_0^r\left(1/(n_0^{r-1}Q) - (r-1)\right) \quad \ldots \quad (4-26)\]

\[\left( (r-1)^2n_0^{r-1}Q \right)\]

and the ratio \( I/I_m \) can be expressed as:

\[\frac{I}{I_m} = 2^{r/r-1}\exp(-a(t_m-t)) \left[ \frac{1 - 1/(\exp(at_m) + 1)}{1 - (1 - \exp(at))} \right]^{r/(r-1)} \]

From the second derivative, the points of inflection on the glow curve are \( t_i \).

\[t_i = \frac{1}{a} \ln \left[ \frac{1}{\left( (r-1)^2n_0^{r-1}Q \right) \exp(at_i)} \right] \]
where

\[ c_1 = \frac{3r(r-1) \pm \sqrt{(4r + r^2)(r-1)^2}}{2(2r^2 - r)} \]

(+ for rising slope, and - for falling slope)

Figure (4.2) shows the values taken by \( c_1 \) for various values of \( r \).

Now,

\[ D = t_2 - t_1 = \frac{1}{a} \ln \left( \frac{1/c_1 - 1}{1/c_2 - 1} \right) \]

therefore,

\[ a = \frac{\ln \left( \frac{1/c_1 - 1}{1/c_2 - 1} \right)}{D} \]

Equation (4-26) may be compared with that equivalent in the 1st and 2nd order cases in the previous section. A graph of the possible values of the constant \( \ln \left( \frac{1/c_1 - 1}{1/c_2 - 1} \right) \) are shown in figure (4.3). N.B. Although the solution to equation (4-23) is not applicable to the case where \( r=1 \), (monomolecular kinetics),
Figure (4.3) shows the log term of equation (4-26) to be identical to that derived directly from equation (4-20).

4.5 THE DETERMINATION OF THE GENERAL ORDER OF KINETICS

Figure (4.3) is very useful for the determination of the kinetic order from a single glow curve measurement. By finding the value of 'a' from a kinetics independent technique, equation (4-26) can be used to find the value of the log term and hence 'r' can be found from figure (4.3). Where the glow peaks are poorly resolved due to a complex spectrum, it can be assumed that the value of \( t_2 - t_1 = 2(t_m - t_1) \), as it can be shown that a glow peak produced by hyperbolic heating will have \( t_m - t_1 = t_2 - t_m \). See section 4.3 for the 1st and 2nd order case.

Two kinetics independent techniques for calculating 'a' are shown
1) From equation (4-24) it can be shown that:

\[ I = A n_0 a Q \exp(at) \quad \text{for } t << t_m \]

(i.e. on the low part of the rising slope)

therefore, plotting \( \ln I \) versus \( t \) will yield a gradient of 'a'.

2) The value of 'a' can be determined from a series of glow curves at various values of 'g' (heating constant). A change in 'g' will vary \( T_m \), hence from equation (4-25) and by substituting the expansions of 'a' and 'Q', it can be shown that a plot of \( \ln(k/g) \) versus \( 1/T_m \) will give a gradient of \( E/k \), and hence 'a'. This is achieved by the approximation \( 1/((r-1)n_0^{-1}Q) >> 1 \), therefore glow curves of unsaturated traps should be used.

With the knowledge of both \( E \) and \( r \), equation (4-25) may be used to yield \( Q \) and hence the frequency factor 'S' if the analysis is
applied to glow curves with saturated traps by measuring $t_m$. (ie. $S'=S/N^{r-1}$).

4.6 QUARTZ TRAPPING PARAMETERS USING HYPERBOLIC HEATING

Using the peak cleaning technique of section 3.4, a similar green quartz sample was analysed to determine the trap depth 'E', the order of reaction 'r' and the frequency factor 'S', using a hyperbolic heating regime. To make the direct subtraction of glow curves possible for peak cleaning purposes, the heating constant 'g' must have a value that will not lead to extreme heating rates in the temperature region of interest ($50^°C$ to $450^°C$ in the case of quartz). The constant 'g' was thus chosen to have the value $1.0x10^{-5}$, which yields a heating rate of $1.04^°C/s$ at $50^°C$ and $5.2^°C/s$ at $450^°C$. Both of these heating rates can be readily attained by the TL equipment used (see section 2). Figure (4.4) shows the glow curve over the whole temperature range.

The results for this quartz sample can be seen in table (4.1), giving the constants $E, r$, and $S$. These results may be compared to those in section 3.4.

<table>
<thead>
<tr>
<th>Peak Temp' (°C)</th>
<th>E(eV)</th>
<th>r</th>
<th>$S^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>92°C</td>
<td>0.67</td>
<td>1.24</td>
<td>$1 \times 10^{12}$</td>
</tr>
<tr>
<td>155°C</td>
<td>1.03</td>
<td>1.10</td>
<td>$2 \times 10^{12}$</td>
</tr>
<tr>
<td>212°C</td>
<td>1.20</td>
<td>1.41</td>
<td>$2 \times 10^{12}$</td>
</tr>
<tr>
<td>286°C</td>
<td>1.30</td>
<td>1.11</td>
<td>$7 \times 10^{11}$</td>
</tr>
<tr>
<td>326°C</td>
<td>1.56</td>
<td>1.22</td>
<td>$9 \times 10^{12}$</td>
</tr>
<tr>
<td>390°C</td>
<td>1.61</td>
<td>1.02</td>
<td>$1 \times 10^{13}$</td>
</tr>
</tbody>
</table>

(* 'S' is calculated from equation (4-25) at saturation)
Figure (4.4)  
Hyperbolic Glow Curve of Green Quartz
An example of the technique for glow curve analysis using hyperbolic heating is outlined below for the 92°C peak. Figure (4.5) shows the 92°C glow peak for green quartz. Comparing the glow curve shape with those expected from the TL model as seen in figure (4.1) suggests that the constant 'r' is in the 1st order region, as higher order glow curves tend to be more symmetric about the maximum emission time. The dotted line in figure (4.5) shows the absolute value of the glow curve derivative and gives the rising and falling derivative maxima at \( t_1 = 26s \) and \( t_2 = 47s \) respectively. The time of maximum TL signal is at \( t_m = 37s \).

Figure (4.5) 92°C Peak (hyperbolic heating)

\[ \frac{1}{T} = \frac{1}{313 - 10^{-5}t} \]

To check that this peak is caused by a single trap, the ratio \( \frac{(t_2-t_m)}{(t_m-t_1)} \) should equal unity, this being independent of the order of reaction. The value of the ratio is found to be 1.08 for this peak and hence it can be considered to be due to one trap only.
From the glow curve, a plot of lnI against time will yield a straight line of gradient 'a' when on the initial part of the rising slope. This yields a value of $a = 0.101 s^{-1}$ (NB. This is independent of the order of reaction). Hence 'E' can be determined from equation (4-6) to give $E = 0.87 eV$.

Equation (4-26) gives a method for determining the constant 'r' by using figure (4.3), as 'a' and $(t_2-t_1)$ are known. Using this equation shows that $\ln((1/a_1-1)/(1/a_2-1)) = 2.12$ and hence 'r' is found to be 1.24. With complex glow curves as in the higher temperature peaks of this quartz sample, it is often difficult to separate a glow peak on both the rising and falling slopes so that $t_1$ and $t_2$ can be measured. However, assuming simple peak cleaning has been applied, it may normally be assumed that the higher temperature glow peaks will not overlap significantly into the rising slope of the glow curve being analysed. Therefore using the knowledge that $t_m-t_1 = t_2-t_m$ for hyperbolic heating, the value of $t_2-t_1$ may be deduced by measurements on the rising slope only. (ie. $t_2-t_1 = 2(t_m-t_1)$).

From the results of table (4.1), it can be seen that the peaks at temperatures 155°C, 286°C and 390°C show 1st order kinetics within expected errors. The peaks at temperatures 92°C, 212°C and 326°C would be expected to show some of the 2nd order phenomena outlined in table (3.1). A simple test to show this would be to monitor the movement of peak temperature with varying dose. From the constants in table (4.1), the theoretical change in $t_m$ was calculated by using equation (4-25) with a varying $n_0/N$ ratio. The graph in figure (4.6) shows the results of these calculations. Experimentally, the quartz samples were given either a saturation dose or an approximate 1/10th saturation dose, and the times of maximum emission determined for the three peaks. Table (4.2) show these results.
Table (4.2)

Changes in peak Maximum with Varying Dose

<table>
<thead>
<tr>
<th>Peak Temp (fig(4.4))</th>
<th>t(s) obs</th>
<th>Theoretical t(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>92°C</td>
<td>-3</td>
<td>-5.7</td>
</tr>
<tr>
<td>212°C</td>
<td>-1</td>
<td>-6.8</td>
</tr>
<tr>
<td>326°C</td>
<td>0</td>
<td>-2.8</td>
</tr>
</tbody>
</table>

For the 326°C peak, no change in $t_m$ was observed, whereas the large change expected in the 212°C peak was not found to occur. The 92°C peak resulted in the most significant change, although only 53% of the expected value.

It is best to assume that the peak movement test is a more
sensitive method for determining whether departure from first order kinetics is occurring than the direct measurement of 'r', because of the ease in identifying the peak maximum. Quartz samples are seen to be difficult to analyse when determining 'r', although this technique is simple in application. For less complex glow curves, not requiring significant peak cleaning, non-linear heating provides a method by which the theoretical constants may be found without approximations in the glow curve shape.
It will have been seen from section 3, that the theoretical analysis of glow curves presented there does not provide a complete model for all observable TL phenomena. If the electron trap model is extended to include electron transport between traps, centres and bands during irradiation, such phenomena as supralinearity in the low dose region, and sensitisation of TL response due to previous dose history, can be predicted. A more complete model must include the filling of traps during irradiation, as well as de-trapping during read-out.

An ideal phosphor for TL dating would have a linear response with dose continuing well into the kilorad region, and a time stable signal (less than 1% fading in 10,000 years is adequate for the dating of ceramics, although not for geological dating). A prediction of any departures from this idealised phosphor would prevent erroneous results.

In the past, a typical approach to the solution of models for TL, has been to simplify the set of differential equations by making certain approximations (CHEN, 1978, ARAMU, 1975). It was therefore seen to be instructive to avoid any assumption based approximations, by using a numerical technique for the solution of a chosen model. The numerical technique used was a modified Adams-Bashforth predictor-corrector method, using a fourth order Runge-Kutte algorithm to start the solution. An allowance was made in the computer code for the variation of temperature during the experiment, both linearly and non-linearly. In this way, the program was effectively run twice to simulate trapping under irradiation conditions, and heating to produce glow curves.

The model chosen was a simplified set of the generalised equations of ARAMU (1975) describing a two trap system, with the addition of direct recombination between the conduction and valence bands.
Figure (5.1) shows the model schematically, and the equation set is shown below.

\[
\frac{dn}{dt} = n_c A (N - n) - G_n 
\] ....(5-1)

\[
\frac{dn_a}{dt} = n_c A_a (N_a - n_a) - G_a n_a 
\] ....(5-2)

\[
\frac{Dn_c}{dt} = X + (G_n + G_a n_a) - Dn_c n_v - n_c A_L n_L 
\] ....(5-3)

\[
\frac{dn_L}{dt} = n_v G_L (M - n_L) - n_c A_L n_L 
\] ....(5-4)

\[
\frac{dn_v}{dt} = X - n_c Dn_v - n_v G_L (M - n_L) 
\] ....(5-5)

where \( G = S \exp(-E/(kT)) \)
\[ G_a = S_a \exp(-E_a/(kT)) \]

The symbols used are as follows:

\( n, n_a \) = The concentration of electrons in the two trapping levels at any time (\( \text{cm}^{-3} \)).
\( n_L \) = The concentration of holes in the recombination centre at any time (\( \text{cm}^{-3} \)).
\( n_c, n_v \) = Concentration of electrons(\( n_c \)) and holes(\( n_v \)) in the conduction and valence bands respectively (\( \text{cm}^{-3} \)) at any time.
\( N, N_a, M \) = Initial concentration of electrons (\( N, N_a \)) and holes (\( \text{cm}^{-3} \)) in traps and recombination centres respectively.
\( A_A, A_L \) = Retrapping probability for electron traps (\( \text{cm}^{-3} \text{s}^{-1} \)).
\( A_L \) = Recombination probability of free electron with recombination centre (\( \text{cm}^{-3} \text{s}^{-1} \)).
\( G_L \) = Probability of hole trapping at recombination centre (\( \text{cm}^{-3} \text{s}^{-1} \)).
\( G, G_a \) = Probability of escape from electron traps by thermal energy (\( \text{s}^{-1} \)).
\( X \) = Rate of electron-hole production during irradiation (cm\(^3\) s\(^{-1}\)).
\( S, S_a, E, E_a \) = Frequency factors and activation energies for the electron traps. See section 3.
\( D \) = Probability of direct recombination (cm\(^{-3}\) s\(^{-1}\)).

5.1 A ONE TRAP MODEL

The simplest case was investigated initially, whereby only one electron trap exists \((A_a = 0)\), with no direct recombination \((D = 0)\), and detrapping during irradiation is negligible \((G = 0)\). Figure (5.2) shows some typical 'dose response' curves for the cases where \( A = A_L \) and \( A \ll A_L \). Both peak height and peak area growth curves are plotted.
For the first order case of $A \ll A_L$, (i.e., no retrapping), the peak heights follow the same form as the peak areas, and show linearity from zero dose, whereas for the second order case of $A = A_L$, (i.e., the retrapping and recombination probabilities are equal), the peak height response gives a supralinear rise at low doses. GARLICK (1948), showed that the glow curve shape depends on the initial concentration of the trapped electrons for the second order case (see table (3.1)), so that a departure from linearity is expected. Therefore in these cases, supralinearity is avoided by measuring peak area versus dose. Peak height may be used if first order kinetics is certain. By varying the $A/A_L$ ratio, and producing glow curves using non-linear heating, the 'effective' order of kinetics for each ratio was determined as described in section (4.5). The results are shown in figure (5.3).

To determine whether the irradiation rate effects the TL signal acquired per unit 'dose', the constant 'X' in equations (5-3) and (5-5)
Figure (5.3) Orders of Kinetics for Various $A/A_0$ Ratios

Figure (5.4) Effects of Dose Rate

- 2nd order
  - Dose $= 1 \times 10^{15} \text{ cm}^2$, $D=0$
  - Dose $= 5 \times 10^{12} \text{ cm}^3$, $D=0$
- 1st order
  - Dose $= 1 \times 10^{10} \text{ cm}^3$, $D=0$
  - Dose $= 5 \times 10^{9} \text{ cm}^3$, $D=0$
  - Dose $= 5 \times 10^{8} \text{ cm}^3$, $D=0$

$\log_{10} (\text{Irradiation Rate (cm}^3 \cdot \text{s}^{-1}))$
was varied for two values of the \( \frac{A}{A_L} \) ratio, namely first order, 
\( \frac{A}{A_L}=0 \), and second order, \( \frac{A}{A_L}=1 \). The results from this experiment for 
a constant total 'dose' are shown in figure (5.4).

The general trend of the curves in figure (5.4), that is an 
increased TL per unit 'dose' sensitivity with a decrease in irradiation 
rate, has been experimentally measured in quartz samples by 
KHAZAL (1977), where he found a rise in the TL sensitivity of \( \times 3 \) for a 
decrease in dose rate from \( 280 \text{ rads per hour} \) to \( 50 \text{ rads per hour} \). In the 
second order case, it is found that the decrease in sensitivity is less 
than in the first order case. The absolute values of accumulated TL, 
cannot be compared between the two cases in figure (5.4), as the 
trapping probabilities were varied between them.

Relating the results of figure (5.4) to real dose rates may be 
accomplished by assuming that 20eV (2x band gap) is required to produce 
an electron-hole pair in quartz (density = 2.6g.cm\(^{-3}\)). In this way, an 
electron-hole pair production rate of \( 10^{16}\text{cm}^{-3}\text{s}^{-1} \) results in a dose 
rate of 450 Krads per hour. The dose rate values reported by KHAZAL 
were from 100 to 800 Krads per hour. Within this range, the results of 
figure (5.4) show a TL sensitivity change of the same order of 
magnitude as that of KHAZAL. It was found that at values of \( \times \) lower 
than \( 10^{13}\text{cm}^{-3}\text{s}^{-1} \), rounding errors produced by the numerical technique 
became evident. It would be possible to extend the lower computational 
limit of this constant by using a double precision representation 
within the computer code.
Section 5.1 has shown that supralinearity in TL response, cannot be produced by the simple filling and glow-out of a single trap/centre system. A logical thought experiment, originally suggested by SUNTHARALINGHAM (1969), would be to assume the existence of a temperature stable trap, not detected when producing a glow curve, which is in competition with the visible trap for free electrons produced during irradiation. If the competing traps were either more efficient at trapping, or had a lower concentration than the visible trap, then it would be expected that during irradiation, the competing trap would begin to saturate, and hence the 'extra' electrons available to this trap would effectively cause an increase in sensitivity, thus giving rise to supralinearity.

To determine whether, and under what conditions, this will occur, a second much deeper trap was introduced into the model that would not be affected by the normal glow curve read-out. Typical response curves are shown in figures (5.5) and (5.6). The variety of possible responses produced, does indicate that the relative magnitudes of certain constants in equations (5-1) to (5-5) are critical in determining whether supralinearity will occur. CHEN (1978) reports three inequalities for a two trap model that are required to ensure the appearance of supralinear phenomena. These are:

\[ A_a > A_L \] \hspace{1cm} \text{...(5-6)}

\[ A_a > A \] \hspace{1cm} \text{...(5-7)}

\[ N_a * A_a^2 / (M.A) > A_L \] \hspace{1cm} \text{...(5-8)}

Figure (5.5) shows a supralinear response at low dose, and is consistent with the inequalities of CHEN. Reversing inequality (5-6) produces figure (5.6), which shows a sub-linear response. These inequalities, when obeyed, have produced supralinearity for all the cases tried, and can therefore be assumed correct.
Figure (5.5)
Supralinearity in the Two Trap Model

Figure (5.6)
Sublinearity in the Two Trap Model
It would be possible to extend this model to any multi-trap/centre system, so that the computer experiment may be used to test band models during initial trapping and glow-curve production, and hence determine whether a proposed mechanism will result in the phenomenon being studied. For example, ZIMMERMAN (1971b), has reported that enhancement of sensitivity in the low temperature peak of quartz, may be the result of a two trap/two centre system, in which the high temperature trap \( T_2 \) and high efficiency centre \( L_2 \), exists along with a low temperature trap/centre system \( T_1, L_1 \), and that heating to a temperature below that which would depopulate \( T_2 \), causes a transfer of holes from \( L_2 \) to \( L_1 \), hence increasing the sensitivity of the \( T_1, L_1 \) system. This model may be tested by the present computational method, by including an additional hole trapping centre \( L_2 \) to that shown in figure (5.1), such that at high temperatures, electrons from the valence band may be excited to neutralise some of the holes in the centre \( L_2 \), and hence the holes now transferred into the valence band, may be redistributed between \( L_1 \) and \( L_2 \), therefore effectively increasing the sensitivity of the \( T_1, L_1 \) system.

This computer experiment has been found constructive in testing hypotheses concerning the electron-hole transport in the TL model in order to determine the resulting TL responses. Its main use has been to investigate TL systems that cannot be solved analytically without approximations. By changing the differential equations describing the system, more complex TL models may be tried (not necessarily using "band theory") with ease in an attempt to improve the agreement between empirical models and experimental data. Best-fit models deduced in this way may be suggestive of the correct approach to a more fundamental understanding of the TL phenomena in given cases.
Next to the feldspars, quartz is the most abundant mineral in the earth's crust. It is common in most igneous, sedimentary and metamorphic rocks, and is therefore present in most unrefined ceramic samples. In some cases, sand-like materials were added to clay to produce a desired ceramic property, and hence the study of quartz allows us to apply any knowledge gained of this material, to most of the pottery dating problems likely to be encountered.

Even in a brief study of the crystallography of quartz, one soon realises the many various forms it can take in nature. By simple optical examination, the colour may range through yellow, rose, green, pink, smokey and colourless in the common cases. These colours are ascribed to the oxides of impurities present in the $\text{SiO}_2$ matrix, and as these trace elements affect the optical properties of the quartz, it could be suggested that the TL properties may also depend on the types of trace elements in the crystal.

### 6.1 Neutron Activation of Samples

In an attempt to link the TL properties of quartz to the trace elements found in the quartz, a simplified neutron activation analysis scheme was tried, to give some indication of their concentrations within the matrix. An absolute measurement technique was used rather than a spectrum comparison between sample and standard, due to suitable standards not being immediately available.

Sample preparation was accomplished by simple crushing, etching and sieving to a predetermined size fraction (75-150 $\mu$m) in the case of geological specimens (green and rose quartz). For the three ceramic samples W, X and Y, (See appendix (C)), a heavy liquid separation was
used (bromoform) after crushing and washing. The heavy fraction (mainly quartz) was then etched for two hours in 48% hydrofluoric acid, then washed and sieved to the same size fraction as the geological specimens. The five prepared specimens were finally weighed and sealed in clean polyethylene containers ready for irradiation. It should be noted that great care was exercised in reducing the level of sample contamination occurring due to the preparation procedures, although in the case of ceramic quartz samples, some contamination is unavoidable.

The samples were irradiated at the University of London Research Reactor at Silwood Park, where the conditions of irradiation were as follows:

Irradiation period- 10 mins
Flux- $2.0 \times 10^{12} \text{ cm}^{-2}$
Cooling period- 25 mins
Counting period- 15 mins

The cooling period of 25 minutes was chosen to allow for short lived isotopes to decay to negligible proportions. It was particularly important to allow the activities of $^19\text{O}$ and $^{29}\text{Al}$ (formed by the reactions $^{18}\text{O}(n,\gamma)^{19}\text{O}$ and $^{28}\text{Si}(n,p)^{29}\text{Al}$ respectively) to decay to a low level to avoid interference with the much weaker but longer-lived trace element activation products. The half-life of $^{19}\text{O}$ is 29 seconds, thus a cooling period of 25 minutes effectively allows this isotope to decay to zero. In the case of $^{29}\text{Al}$, the half-life is 6.56 minutes, hence the cooling period used reduced the activity of this isotope by approximately 1/600. Although $^{29}\text{Al}$ was the major active isotope present during the counting period, it was reduced to tolerable proportions by the 25 minute cooling time. The $^{29}\text{Al}$ peak was analysed to monitor the counts per milligram of sample due to the $^{28}\text{Si}(n,p)^{29}\text{Al}$ reaction. The normalised results are presented in figure (6.1a), and
Figure (6.1) Neutron Activation of the Five Quartz Samples

1a) $\text{Si}^{29}(n,p)\text{Al}^{29}$

1b) $\text{Na}^{23}(n,\gamma)\text{Na}^{24}$

1c) $\text{Ti}^{50}(n,\gamma)\text{Ti}^{51}$

1d) $\text{Ba}^{134}(n,\gamma)\text{Ba}^{135}$

1e) $\text{U}^{238}(n,\gamma)\text{U}^{239}$

1f) $\text{Se}^{80}(n,\gamma)\text{Se}^{81}$

1g) $\text{Zn}^{65}(n,\gamma)\text{Zn}^{66}$

1h) $\text{Ag}^{107}(n,\gamma)\text{Ag}^{108}$

1i) $\text{V}^{51}(n,\gamma)\text{V}^{52}$

1j) $\text{Sr}^{79}(n,\gamma)\text{Sr}^{80}$

1k) $\text{Sm}^{154}(n,\gamma)\text{Sm}^{155}$

1l) $\text{Eu}^{151}(n,\gamma)\text{Eu}^{152}$
show the expected equal silicon content per milligramme of quartz, for all five samples.

The normalised relative concentrations of the trace elements found to be present using this simple technique are compared in figures (6.1b) to (6.1p). Some simple observations from these comparisons are:

1) Of the three ceramic quartz samples, all of the analysed impurities are seen in sample X which usually shows the highest concentration. This is particularly true for titanium. On average, sample Y is shown to be the most trace element free ceramic quartz, for those elements which can be sensitively measured in this way.

2) Of the geological quartz specimens, the green quartz shows all identified impurities to be present (apart from bromine, although this may be an impurity introduced during sample preparation in the
ceramic samples) in significant quantities, whereas the rose quartz is relatively pure and is shown only to have significant concentrations of sodium and aluminium, with most of the other impurities not being detected.

6.2 TL PROPERTIES

An attempt has been made to compare the TL properties of the five quartz samples analysed in section 6.1, with their trace element compositions in order to determine any correlation factors. The glow curves of the five samples (figures (6.2a) to (6.2e)) all having received the same pre-readout treatment of 1 hour anneal at 500°C, plus 3 krad Co60 irradiation, are shown to be far from identical, although all five have similarities in peak temperatures. A discussion of some measured TL properties is given below. The theoretical TL parameters for the green quartz sample were determined using linear and non-linear heating techniques, the results of which are shown in sections 3 & 4.

6.2.1 Peak Sensitivities

Three particular features are present in all five glow curves. These are:

1) A high sensitivity peak at around 90-100°C. This is equivalent to the 110°C peak of FLEMING(1969).
2) A peak around 300-330°C.
3) A peak at around 120-150°C (rather higher in green quartz).
Figure (6.2) Glow Curves of the Five Quartz Samples

2a) Sample 'G'

2b) Sample 'R'

2c) Sample 'W'

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Although present in all samples, these peaks have differing sensitivities (TL signal per unit dose). Other peaks are evident in some glow curves (in particular green quartz and sample X), but not in others to any significant extent above the 'background' due to neighbouring more intense peaks.

Figures (6.3a) and (6.3b) show the normalised peak heights (by weight) for the 90-100°C and 300-330°C peaks. No obvious correlations between these figures and the sample trace element concentrations are strikingly apparent for any of the peaks. A correlation between the concentration of sodium and the 320°C peak sensitivity (figure (6.1b)) does appear to be possible, although
sample 'W' shows a high sensitivity if this were true. No anti-correlations (quenching) were found between the peak sensitivities and the trace element concentrations.

6.2.2 Phototransferred TL

In order to determine whether the TL signal generated on exposure to an ultra-violet light source is dependent on the trace element concentrations within the sample, the following experiments were carried out:

1) After measuring the gamma induced glow curve to 450°C, each sample was illuminated with a low power UV lamp for 30 minutes, and its TL signal measured.

2) The glow curve to 210°C was measured and thus removed the low temperature peaks. This was followed by exposure for 30 minutes to the UV lamp as used above. The glow curve was then remeasured to 210°C and the process repeated.
In the first experiment, very little re-excited TL was evident to any significant level, and hence it was concluded that either the UV light source emitted a spectrum with a low mean photon energy and could not therefore excite the 'deep' traps, or alternatively, the 'deep' traps themselves may not exist or may be present only in very small quantities. Further experiments with a high power, higher energy UV source are necessary to determine conclusively the existence of such 'deep' traps.

In the second experiment, a significant TL signal was regenerated by the UV exposure, even after two or three illuminations. The peak generated was found to be in the 90°C to 100°C range, and a simple 'initial rise' analysis on the glow curve gave the trap parameters that were determined in sections 4 and 3 when induced by gamma radiation.

The maximum intensities of the regenerated low temperature peaks for the five quartz samples are presented in figure (6.4a) (normalised by weight of sample). Normalising this result by the gamma induced low temperature TL peak sensitivity for each sample, produced figure (6.4b). Figure (6.4c) shows normalisation of figure (6.3c) by the high temperature peak sensitivity. Neither of these figures appears to be correlated to the trace element concentrations.

As well as giving rise to a PTTL mechanism, certain trace elements may 'quench' the phenomenon, thus an inspection was carried out for anti-correlations between trace element concentration and PTTL signals from the normalised results of figures (6.3) and (6.4). These are shown in figures (6.5a) to (6.5e). Similarities between the Al\(^{27}\) concentration and figure (6.1c) can be seen, which may show the quenching of PTTL by aluminium, although these results cannot be said to be conclusive.
Figure (6.4) Correlations between TL Properties and Trace Element Concentrations

4a) Normalised 100°C peak after UV irradiation
4b) As 4a), normalised by the 100°C peak sensitivity
4c) As 4a), normalised by the 320°C peak sensitivity

Figure (6.5) Anti-Correlations between TL Properties and Trace Element Concentrations

5a) Anti-correlation of 3a)
5b) " " " " 3b)
5c) " " " " 4a)
5d) " " " " 4b)
5e) " " " " 4c)
6.3 REMARKS ON THE QUARTZ COMPARISON

Although yielding much data, this comparison of the trace element concentration of five quartz samples with some of their TL properties, has produced no clear correlations. Unfortunately, time has not allowed a repeat of this experiment with more samples, although this would have improved the statistics of the measuring technique.

It may have been more constructive to measure the TL properties and impurities of a selection of geological quartzes, rather than quartz separated from ceramics, as these materials are simple to prepare, and are unlikely to contain any significant amount of foreign materials resistant to HF acid etching. In the case of ceramic quartz, any non-quartz material remaining after preparation, will upset the neutron activation analysis, especially if they are not similar in origin.

If these experiments were to be repeated and extended, there will be a need to subject the data to a more numerical correlation analysis. Such techniques are commonly used for determining correlations between style or provenance in archaeology.
There are many techniques for measuring radioisotope concentrations. The isotopes of interest in thermoluminescence dating are emitters of characteristic radiations, and it is the measurement of these radiations which allow concentrations of less than one microgram to be determined.

The chief radioisotopes found to contribute to the radiation background, and hence causing a TL signal in natural phosphors are shown in table (7.1).

Table (7.1) - (NCRP, 1976)

Natural radiation background

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Concentration (pCi/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>10</td>
</tr>
<tr>
<td>Rb</td>
<td>4</td>
</tr>
<tr>
<td>Th</td>
<td>.6</td>
</tr>
<tr>
<td>U</td>
<td>.7</td>
</tr>
</tbody>
</table>

The decay schemes of the isotopes in table (7.1) are shown in appendix (D), and shows that many radiations are emitted with which to characterise the active sample.

The techniques studied were chosen so that they may be applied to the low-level of radioisotope concentrations found in natural materials. These fall broadly into three categories:

1) Gamma spectrometry
2) Alpha counting
3) Neutron activation analysis
The merits of each of these techniques are outlined in the following sections, although the final choice of which to use in routine TL dating will be determined by availability of apparatus, required accuracy, ease of use and cost.

7.1 ALPHA SPECTROMETRY AND COUNTING

Uranium-238, uranium-235, and thorium-232 are the three naturally occurring parent isotopes emitting alpha particles in ceramics and soil. By measuring the alpha particles emission rate in a calibrated experiment, it is possible to quantify the concentration of emitters present in the sample.

The physical properties of alpha particles (highly ionising, short range) produces both advantages and disadvantages for analysis. A major advantage in all alpha detecting systems is that shielding from highly ionising particles not produced in the sample is easily accomplished. Alpha particles are monoenergetic when first emitted from the nucleus although self-absorption in the sample and energy loss through air soon produce a broad energy spread in the detected alpha flux. The short range of alpha particles therefore dictate that the amount of material (including air) between source and detector be minimised. To achieve this, methods involving vacuum chambers and close proximity of detector and source have been used. Also, attention has to be given to sample thickness and entrance window absorption in the detector.
7.1.1 Scintillation Counting

One of the simplest and earliest methods for alpha particle detection uses a zinc sulphide screen in close proximity to the sample. Although this technique has rather poor energy resolution of the alpha particles counted, a good intrinsic efficiency is achieved (approximately 100%) and is therefore useful for low activity alpha emitting samples.

TITE (1962) used this method for determining the dose received in TL dating by sprinkling silver-activated zinc sulphide onto transparent adhesive tape stuck to a circular perspex ring, and covering this with a 1mm layer of crushed pottery to achieve close sample/scintillator proximity. A little improvement in this technique is provided by using machine produced ZnS film (ZnS encapsulated using a mylar film) as described by HALLDEN (1960), which minimises the variations found in phosphor thicknesses in hand made screens (BOWMAN, 1976).

It can be shown (TURNER, 1958) that for a screen of area $A \text{ cm}^2$, the count rate for an infinitely thick sample is given as:

$$S = \frac{1}{4} A \sum_{i=1}^{n} N_i R_i D$$

where $S = \text{Count rate [s}^{-1}\text{]}$

$N_i = \text{Specific activity of i}^{th} \text{ alpha emitter in sample [counts.s}^{-1}.g^{-1}\text{]}$

$D = \text{Density of sample [g.cm}^{-1}\text{]}$

$R_i = \text{Range of i}^{th} \text{ alpha energy in sample [cm]}$

This equation assumes a 100% efficiency in counting all of the alpha particles striking the ZnS screen. In practice a discriminator threshold has to be applied to guard against spurious signals (beta particles and electronic noise) so that the magnitude of $S$ will be
By using the Bragg-Kleeman rule, which states that \( R.D \) \( [g\cdot cm^{-2}] \) varies as the square-root of the atomic weight \( A \), and knowing the range/energy relationship of a carefully measured element, the range/energy relationship for a pottery sample may be determined. By using the simple mixture rule, the effective atomic weight for a typical pottery matrix may be taken to be 21.4 (BOWMAN, 1976). A graph of alpha range against alpha energy is given in figure (7.1). This gives an effective alpha range of 6.94mg/cm\(^2\) for uranium, and 5.84mg/cm\(^2\) for thorium (AITKEN, 1975), averaged over all daughter alpha particles in the chain.

Figure (7.1) Alpha Range in a Ceramic Matrix
7.1.2 Determination of Electronic Threshold

To determine the optimum electronic threshold that should be applied to the counter, it is necessary to measure the signals due to noise and beta particles. By placing a blank scintillator onto the photomultiplier, and counting at various discriminator settings, it was found that electronic noise is negligible below a relative threshold of 0.97. However, for beta particles this was not found to be the case, since they give rise to larger output pulses than electronic noise.

A ZnS screen was prepared with the active surface covered with a plastic film of sufficient thickness to prevent the penetration of alpha particles. The screen was then filled with a mixture of precipitated silica and a standard uranium ore (BL-3, CANMET. See section 7.2.1), and counted for various discriminator settings. By this technique, a relative threshold of 0.85 was found necessary to prevent any beta induced pulses from being counted. As this figure is very close to that used by AITKEN (1975), it was decided to use his threshold value of 0.835, so that dose rates from the published results of BELL (1979) could be used.

7.1.3 Some Experimental Results (alpha counting)

Alpha counting results are shown in table (7.2). These include four pottery samples, and two samples made by diluting the standard uranium ore with silica.
### Table (7.2)

**Alpha counting results**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Count rate (1000s)</th>
<th>Predicted count rate (1000s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>14.9</td>
<td>-</td>
</tr>
<tr>
<td>X</td>
<td>22.8</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>14.7</td>
<td>-</td>
</tr>
<tr>
<td>Z</td>
<td>25.1</td>
<td>-</td>
</tr>
<tr>
<td>St'd-1</td>
<td>1910</td>
<td>1860.</td>
</tr>
<tr>
<td>St'd-2</td>
<td>1500</td>
<td>1490.</td>
</tr>
</tbody>
</table>

Scintillator area = 19.6 cm²  
Threshold = 0.835

7.1.4 Counting with Energy Resolution

By using an alpha detector able to resolve the energy of incident particles, the ratio of the uranium and thorium contents of the sample may be calculated, and also possible disequilibrium in the decay chain detected.

A silicon surface barrier detector (surface area 200mm²) for low activity alpha emitters has been routinely used by ROMAN (1963) to measure thin samples with concentrations of radioisotopes in the region of $10^{13}$Ci/mg for a 40-hour counting time with an energy resolution of 100keV at 5MeV. A pottery sample containing 3ppm $^{238}$U is equivalent to approximately $10^{15}$Ci/mg for each alpha particle, and hence the spectrometer described by ROMAN will be too insensitive, unless a technique for concentrating the U and Th decay series is used. Because of the problems of producing samples in solution and radioisotope concentration, this technique will prove difficult for ceramics and geological specimens on a routine basis.

An interesting alternative to the above method is the use of large area Frisch-gridded ion chambers, in which samples up to
200mm diameter (approximately 30,000mm²) can be counted with 20keV resolution, HOETZL (1973). However, a sample thickness of less than 0.1μm would be required for this resolution to be utilised, thus producing alpha activities of the order of 10¹⁵Ci, assuming such a thin sample can be prepared from a solid pottery sample.

Problems similar to those encountered using a surface barrier detector will occur in liquid scintillation counting. Effective surface area will be increased, and an absolute efficiency of 100% can be achieved, although sample and scintillator preparation are complex, and the high beta background must be removed using pulse-shape discrimination (THORNGATE, 1974). It thus appears that alpha spectrometry for routine work is not practical using these techniques.

7.2 GAMMA SPECTROMETRY

From appendix (D), it is seen that many gamma rays of various intensities and energies are emitted by the decay of uranium, thorium, and potassium. Appendix (D) shows only those gamma rays with a decay fraction greater or equal to 5%, although many less intense emissions exist.

Because of the complex nature and low intensity of the natural gamma ray spectrum from a ceramic matrix, a choice between high detector efficiency and good energy resolution must be made. A sodium iodide (NaI(Tl)) scintillation crystal has many applications for routine low level counting, but its relatively poor energy resolution limits its use for complex spectra (see section 7.3). Spectrum stripping is possible to some extent, but requires good statistics.

For a complete knowledge of the decay of U, Th, and K, a high resolution semiconductor detector is preferable. There are 38 gamma rays emitted by these radioisotopes with decay fractions greater than
5%, their energies ranging from 12.7 keV from Pa\(^{231}\) (a \(\text{U}^{235}\) daughter) to 2.6 MeV from Po\(^{212}\) (a Th\(^{232}\) daughter). As it is not currently possible to detect such a large range of energies using the same detector with any useful resolution for our purposes, two approaches should be taken:

1) For energies greater than 100 keV, a large volume germanium-
lithium Ge(Li) detector is suitable.
2) For energies less than 100 keV, an intrinsic (hyperpure) germanium detector will give the best resolution/efficiency combination.

The ratio of gamma rays having a decay fraction of greater than 5% above and below 100 keV is 22:16, therefore initial experiments were done using a 40 cm\(^3\) Ge(Li) detector situated in a large lead shield.

7.2.1 Use of the Germanium-Lithium Detector

The compilation of decay schemes for U, Th, and K by CARRIVEAUX (1978), list many intense gamma ray lines. If secular equilibrium in each chain is assumed, then a quantitative measurement of any one gamma-line will give the series activity, and using suitable conversion data (BELL, 1979), dose rates in the 'infinite matrix' may be determined. The choice of which gamma ray is the most suitable for analysis will be determined by that which minimises errors, maximises detector efficiency at that energy, and has a high decay fraction. This is discussed in more detail in section 7.6.

Standards, representative of pottery for the quantitative determination of U, Th and K, were made using active ore samples, and potassium salts. The ore samples were: BL-3 uranium ore (1.02% \(\text{U}^{238}\), 1% error), supplied by CANMET (Canadian Centre for Mineral and Energy Technology, Ottawa), and NBL-106 thorium bearing monazite sand (1% Th\(^{232}\), 1% error), supplied by the United States Dept. of Energy (New...
Brunswick Lab., Argonne, Illinois). Both of these materials are certified to be in secular equilibrium.

To keep the geometric efficiency of the detector constant between sample and standard, the matrix properties of the pottery and the artificial standard 'pottery' must be equivalent. Using the results of PERLMAN(1969), a 'typical' pottery matrix was determined, as shown below in table (7.3).

Table (7.3) - (PERLMAN, 1969)
'Typical' pottery matrix

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50.6</td>
</tr>
<tr>
<td>Si</td>
<td>30.0</td>
</tr>
<tr>
<td>Al</td>
<td>16.8</td>
</tr>
<tr>
<td>K</td>
<td>1.5</td>
</tr>
<tr>
<td>Fe</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Using the gamma ray attenuation coefficients reported by STORM(1970), the mass attenuation coefficients for the typical pottery of table (7.3) was determined between 50keV and 2MeV. On comparing these figures with the mass attenuation coefficients for SiO₂, little difference between them was observed over this energy range. It was therefore decided to use SiO₂ as an inert diluting medium for the concentrated (relative to real ceramics) standard area.

Accurately weighed amounts of BL-3, NBL-106, (in the region of 1.5g and 4.5g respectively), and potassium chloride (KCl) were made up to 10g with SiO₂, and sealed in 5cm diameter plastic petri-dishes, having a wall thickness of less than 1mm, which were subsequently heat-sealed in thin polyethylene. As the standard mixtures have approximately the same densities as crushed pottery samples, the geometric efficiency for all measurements will be closely similar.

From the results described in section 7.6.2, the optimum gamma ray
energies to be measured to determine the concentration of the parent isotopes \( \text{U}^{238} \), \( \text{Th}^{232} \) and \( \text{K}^{40} \) are as follows:

\[
\begin{align*}
\text{Th}^{232} & : 583\text{keV from the decay of TL}^{208} \\
\text{U}^{238} & : 352\text{keV from the decay of Pb}^{214} \\
\text{K}^{40} & : 1461\text{keV from the decay of K}^{40}
\end{align*}
\]

N.B. The 583keV line from TL\(^{208}\) was chosen in preference to the 239keV from Pb\(^{214}\) due to the weak interference of the latter from Pb\(^{214}\) and Ra\(^{226}\).

A typical standard uranium/thorium spectrum is shown in appendix H, recorded on an ND66 (Nuclear Data Inc.) multi-channel analyser. The FWHM resolution at 1.764MeV after a 64hour counting period is also shown.

Some typical results for various ceramics are shown in table (7.4), with derived infinite homogeneous matrix doses using the results of BELL(1979). Very little change was found in the recorded counts for each peak between measurements taken immediately after sample preparation or after a 30 day delay since sealing the sample, indicating a negligible change in the equilibrium level of these samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{U} )</th>
<th>( \text{Th} )</th>
<th>( \text{K} )</th>
<th>( \text{U} )</th>
<th>( \text{Th} )</th>
<th>( \text{K}(%) )</th>
<th>Dose* (rads/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>10.2</td>
<td>6.9</td>
<td>29.1</td>
<td>3.8</td>
<td>11.7</td>
<td>2.3</td>
<td>2.36</td>
</tr>
<tr>
<td>X</td>
<td>13.0</td>
<td>9.4</td>
<td>15.5</td>
<td>4.8</td>
<td>15.9</td>
<td>1.3</td>
<td>2.90</td>
</tr>
<tr>
<td>Y</td>
<td>7.6</td>
<td>6.7</td>
<td>10.8</td>
<td>2.8</td>
<td>11.3</td>
<td>0.9</td>
<td>1.87</td>
</tr>
<tr>
<td>Z</td>
<td>14.3</td>
<td>11.9</td>
<td>14.1</td>
<td>5.3</td>
<td>20.1</td>
<td>1.1</td>
<td>3.38</td>
</tr>
</tbody>
</table>

* Total dose from using BELL,1979 conversion factors.
+ 5% statistical uncertainty for an average 48hour counting period.
By using a Ge(Li) solid state detector, it is possible to determine the equilibrium state of the decay chains of U, and Th. The high resolution of this detector enables a more accurate estimate to be made of the dose received by a ceramic in antiquity. Secular equilibrium is attained when the parent isotope and its daughters decay at the same rate. If the condition is such that one of the daughter products is partially removed from the matrix, disequilibrium will result, and a quantitative determination of a daughter lower in the decay chain will lead to a false estimate of the matrix dose if this isotope decay rate is taken to represent the whole decay chain. Although a complete decay series may not be in secular equilibrium, some short lived isotopes will be in equilibrium with a longer lived parent. This allows the decay chain to be split into smaller groups all being in equilibrium among themselves. (ROSEHOLT, 1959).

Table (7.5) shows the uranium and thorium decay chains split into such groups. The isotopes Rn$^{220}$ and Rn$^{222}$ have been singled out as group parents because of their gaseous nature and hence increased probability of disequilibrium at this point. It is assumed that the $^3$H$^{235}$ chain is in equilibrium, although departure from this will have a negligible effect on the derived total dose rate. A detailed consideration of these groups is discussed below:

**Thorium-232 family**

$\text{Th}^{232}$ group (Th1) - A suitable gamma ray is emitted by Ac$^{228}$ in this group, with energy 969 keV and a decay fraction of 13.3%. This line is free from interference.
Table (7.5)

Sub-groups within the Uranium and Thorium Decay Chains

<table>
<thead>
<tr>
<th>Parent</th>
<th>Group Parent</th>
<th>Group Number</th>
<th>Daughter Isotope</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>U^{238}</td>
<td>U^{238}</td>
<td>U1</td>
<td>-</td>
<td>$4.5 \times 10^9$ y</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Th^{234}</td>
<td>24.1 d</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pa^{234}</td>
<td>1.14 m</td>
</tr>
<tr>
<td>U^{234}</td>
<td>Th^{230}</td>
<td>U2</td>
<td>-</td>
<td>$2.52 \times 10^5$ y</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>230</td>
<td>8.0 $\times 10^6$ y</td>
</tr>
<tr>
<td>Ra^{226}</td>
<td>Th^{230}</td>
<td>U3</td>
<td>-</td>
<td>1.662 y</td>
</tr>
<tr>
<td>Ra^{222}</td>
<td>Th^{230}</td>
<td>U4</td>
<td>-</td>
<td>3.825 d</td>
</tr>
<tr>
<td>Pb^{210}</td>
<td></td>
<td>U5</td>
<td>-</td>
<td>25 y</td>
</tr>
<tr>
<td>Pb^{210}</td>
<td></td>
<td>U6</td>
<td>-</td>
<td>138 d</td>
</tr>
<tr>
<td>Th^{232}</td>
<td>Th^{232}</td>
<td>Th1</td>
<td>-</td>
<td>$1.39 \times 10^9$ y</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ra^{228}</td>
<td>6.7 y</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ac^{228}</td>
<td>6.13 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Th^{228}</td>
<td>1.91 y</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ra^{224}</td>
<td>3.64 d</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Th^{220}</td>
<td>54.5 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Th^{220}</td>
<td>.518 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pb^{212}</td>
<td>10.6 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bi^{212}</td>
<td>60.5 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Po^{212}</td>
<td>$3 \times 10^{-7}$ s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tl^{208}</td>
<td>3.1 m</td>
</tr>
</tbody>
</table>
\textbf{Th}^{228} \text{ group} (\text{Th2}) - A gamma ray of energy 241keV (at 4.2\% decay fraction) is emitted by \text{Ra}^{224}. Two interferences exist at 239keV (\text{Pb}^{212} \text{ at 43.1\%}) and 242keV (\text{Pb}^{214} \text{ at 7.6\%}). After calculation of group \text{Th3} and group \text{U5}, their respective concentrations may be subtracted from the 241keV peak, although a large error is to be expected.

\textbf{Rn}^{220} \text{ group} (\text{Th3}) - An interference free gamma ray from \text{Tl}^{208} is emitted with an energy of 583keV (at 30.96\%). This strong decay line can be used to subtract the 239keV contribution to group \text{Th2}.

All groups in the \text{Th}^{232} \text{ family} can be measured using the 40cm\textsuperscript{3} Ge(Li), although the error likely to occur in the group \text{Th2} determination will be large.

\textbf{Uranium-238 family}

\textbf{U}^{238} \text{ group} (\text{U1}) - Two gamma rays from this group are emitted by \text{Th}^{234} at energies of 92.8keV and 92.3keV with decay fractions of 3.6\% and 3.2\% respectively. These can be taken together to determine the group \text{U1} concentration. Interference from \text{Th}^{228} and \text{Pb}^{214} occur, although these may be subtracted out.

\textbf{U}^{234} \text{ group} (\text{U2}) - This group has no gamma emissions with a significantly high decay fraction for measurement with either a Ge(Li) or intrinsic germanium detector.
**Th$^{230}$ group (U3)** - Group U3 has one gamma emission of sufficient intensity at 18.5keV (7.6% decay fraction). This energy is too low for measurement with Ge(Li) and is most suitably detected with a Si(Li) device.

**Ra$^{226}$ group (U4)** - A gamma ray of energy 186keV is emitted from Ra$^{226}$ (at 4% decay fraction). It should be noted that U$^{235}$ emits a gamma ray at this energy with a 54% decay fraction. Taking the natural U$^{235}$/U$^{238}$ ratio as 138:1, then the contribution from U$^{235}$ to the 186keV peak is 9.8%.

**Rn$^{222}$ group (U5)** - A 352keV gamma ray is emitted by Pb$^{214}$ with a decay fraction of 36% and is free from interference.

**Pb$^{210}$ group (U6)** - A low energy gamma ray at 46.5keV is emitted by Pb$^{210}$ at 4% decay fraction. This gamma ray is most suitably detected using an intrinsic germanium device.

If it is suspected that sample preparation may have changed the Rn$^{222}$ level in the ceramic, the group U6 concentration may be used to indicate the group U5 concentration during burial, as Pb$^{210}$ has a half-life of 25 years, and will not be effected during preparation for counting. Alternatively (and this is also true for group Th3) the sample can be remeasured after a suitable waiting period for the radon build-up to reach equilibrium. Appendix (E) shows the derived dose rates for each group (taken from BELL(1979) and CARRIVEAUX(1978)).

Table (7.6) show the results of this technique applied to three samples. The activities are all normalised to the decay rate of the isotopes chosen to yield the best accuracy, (see section 7.2.1). These are: Pb$^{214}$ from group U5, and Th$^{208}$ from group Th3. Activities were derived from the measured detector efficiency as...
described in section 7.6.1. The dose rates derived from table (7.6) shows good agreement with table (7.4), the greatest difference being in sample X which gave an 8% error on the equilibrium method. Table (7.6) shows a large spread of results for group U4 (due to strong interferences), but the group contribution to the total dose is on average less than 7% and will not therefore affect the accuracy of this technique significantly.

Table (7.6)

Equilibrium spectrometry results

<table>
<thead>
<tr>
<th>Group Number</th>
<th>Group Parent</th>
<th>Equilibrium level (L) E = measured activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>U1</td>
<td>U</td>
<td>1.03</td>
</tr>
<tr>
<td>U2</td>
<td>U</td>
<td>-</td>
</tr>
<tr>
<td>U3</td>
<td>Th</td>
<td>-</td>
</tr>
<tr>
<td>U4</td>
<td>Ra</td>
<td>1.34</td>
</tr>
<tr>
<td>U5</td>
<td>Rn</td>
<td>1.00</td>
</tr>
<tr>
<td>U6</td>
<td>Pb</td>
<td>-</td>
</tr>
<tr>
<td>Th1</td>
<td>Th</td>
<td>1.08</td>
</tr>
<tr>
<td>Th2</td>
<td>Th</td>
<td>1.38</td>
</tr>
<tr>
<td>Th3</td>
<td>Rn</td>
<td>1.00</td>
</tr>
</tbody>
</table>

N.B. Unmeasurable groups are taken to have the same decay rates as the preceding group in the decay chain.

7.2.2 Use of an Intrinsic Germanium Detector

Another type of gamma ray detector for equilibrium studies of U, and Th is a high purity (intrinsic) germanium, detector. An advantage this detector has over Ge(Li) is its ability to measure lower energies (down to 5keV), due to its thin entrance window and absence of dead layers. Hence, by using an intrinsic device, two of the 'missing' uranium groups can be measured (U3 and U6) to help complete the scheme of activities of the decay daughters.
Using the group nomenclature of table (7.5), the same gamma rays are measured using the intrinsic germanium detector as was described for the Ge(Li), with the following changes and additions:

Thorium 232 family

\( \text{Th}^{232} \) group (Th1) - An interference free gamma ray from \( \text{Ac}^{228} \) is emitted at 338keV with a 9.3% decay fraction.

\( \text{Rn}^{220} \) group (Th3) - \( \text{Pb}^{212} \) emits a gamma ray at 77.1keV (17.5% decay fraction), which is free from interference.

Uranium-238 family

\( \text{Th}^{230} \) group (U3) - A strong gamma ray emission at 18.5keV (7.6% decay fraction) can be used to determine the U3 group decay rate.

\( \text{Pb}^{210} \) group (U6) - An interference free gamma ray at 46.5keV from \( \text{Pb}^{210} \) (4% decay fraction) can be detected with this device.

Table (7.7) gives a brief description of the suggested measurable gamma rays for equilibrium studies using both Ge(Li) and intrinsic germanium detectors. Interfering emissions are included to allow for necessary subtractions from the required peak to be made. These subtractions may be made as follows:

If we have overlapping peaks with peak 1 being of interest, and interfering peaks \( n \), of known disintegration rate (found from the analysis of other gamma rays emitted from these isotopes), then the disintegration rate of
peak 1 is found from the equation-

\[ D_1 = \frac{A/E}{\sum_{n=1}^{n} \frac{D_n F_n}{F_1}} \]

where 
\( D_n \) = Disintegration rate of peak n
\( F_n \) = Decay fraction of gamma ray n
\( E \) = Absolute efficiency at peak energy
\( A \) = Detected complex peak count.

Table (7.7) 
Gamma Emissions for Equilibrium Measurement

<table>
<thead>
<tr>
<th>SUBGROUP No.</th>
<th>GAMMA PEAK FOR ANALYSIS (MeV)</th>
<th>DECAY FRACTION (%)</th>
<th>INTERFERING ISOTOPE EMITTER (MeV)</th>
<th>DETECTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1, Th(^{222})</td>
<td>1.239 Ge-228</td>
<td>3.9</td>
<td>Ge(Li)</td>
<td>Ge</td>
</tr>
<tr>
<td>T2, Th(^{238})</td>
<td>0.411 Re-224</td>
<td>4.2</td>
<td>Ge(Li)</td>
<td>Ge</td>
</tr>
<tr>
<td>T3, Ra(^{220})</td>
<td>0.583 Ti-208</td>
<td>31.0</td>
<td>T3</td>
<td>Ge(Li)</td>
</tr>
<tr>
<td>U1, U(^{238})</td>
<td>0.293 Th-234</td>
<td>6.8, 1.6</td>
<td>Ge(Li)</td>
<td>Ge</td>
</tr>
<tr>
<td>U2, Th(^{225})</td>
<td>0.185 Ti-230</td>
<td>7.6</td>
<td>Ge(Li)</td>
<td>Ge</td>
</tr>
<tr>
<td>U4, Ra(^{226})</td>
<td>0.406 Re-226</td>
<td>4.0</td>
<td>Ge(Li)</td>
<td>Ge</td>
</tr>
<tr>
<td>U5, Ra(^{226})</td>
<td>0.186 Re-226</td>
<td>4.0</td>
<td>Ge(Li)</td>
<td>Ge</td>
</tr>
<tr>
<td>K(^{40})</td>
<td>1.461 K-40</td>
<td>10.7</td>
<td>Ge(Li)</td>
<td>Ge</td>
</tr>
</tbody>
</table>

7.3 SCINTILLATION GAMMA RAY SPECTROMETRY

Although the energy resolution of NaI(Tl) is not sufficient to resolve the complex polyenergetic gamma rays emitted from U, Th, and K, with careful experimental design, certain energy regions,
representative of all three isotopes, can be resolved free of any major interference.

An advantage of NaI(Tl) detectors over Ge(Li), apart from cost, is its comparatively high efficiency. For a monoenergetic source where detector resolution is unimportant, a high efficiency is necessary for rapid and accurate quantitative measurement of low concentrations. However, with complex gamma spectra, there will be interfering contributions due to other gamma rays of similar energy, and also due to the Compton continuum from higher energy lines, thus decreasing the minimum detectable activity.

The three gamma rays most suitable for analysis using NaI(Tl) are for uranium, the 1.764MeV from Bi$^{214}$, for thorium the 2.614MeV from Tl$^{208}$, and for potassium the 1.461MeV from K$^{40}$. (MEAKINS, 1979). Corrections for background, Compton continuum, escape peaks and full energy peak interference can be made by determining three stripping constants. Equations (7-1 to 7-3) give the corrected count rates for the U, Th, and K peak regions.

\[
\begin{align*}
\text{Th}_C &= \text{Th} - \text{Th}_B \\
\text{U}_C &= \text{U} - \text{U}_B - a \cdot \text{Th}_C \\
\text{K}_C &= \text{K} - \text{K}_B - b \cdot \text{Th}_C - c \cdot \text{U}_C
\end{align*}
\] ....(7-1)

where: \(\text{Th}_C, \text{U}_C, \text{K}_C\) = Corrected count rates for thorium, uranium and potassium respectively.

\(\text{Th, U, K}\) = Uncorrected counts for thorium, uranium and potassium respectively.

\(\text{Th}_B, \text{U}_B, \text{K}_B\) = Background counts in the thorium, uranium and potassium windows respectively.

\(a, b, c\) = Stripping constants.
The stripping constants are defined as:

\[ a = \text{Counts in the U window per count in the Th window.} \]
\[ b = \text{Counts in the K window per count in the Th window.} \]
\[ c = \text{Counts in the K window per count in the U window.} \]

N.B. These constants were determined using the standard ores for thorium and uranium, and KCl for potassium.

It is assumed in equation (7-1) that the weak gamma ray emission from Bi\(^{214}\) at 2.438MeV (U\(^{238}\) daughter) having a decay fraction of 1.6%, will have a negligible effect in the Tl window for thorium if adequate detector resolution is obtained.

Some typical results for four ceramics are shown in table (7.8). A 3x3 inch NaI(Tl) detector was used, shielded over 3π by 5cm of lead. 10g samples were contained in a plastic petri-dish, and placed in contact with the detector. Infinite matrix dose rates are derived from the results tabulated by BELL (1977). No variation in the counting rate was found by sealing the samples and counting after periods of approximately 30 days to allow for radon gas build-up, this being the same result as found using the Ge(Li) gamma spectrometer described in section 7.2.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Counts/1000sec/10gm</th>
<th>PPM</th>
<th>Dose* (rads/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
<td>Th</td>
<td>K</td>
</tr>
<tr>
<td>W</td>
<td>18.8</td>
<td>15.3</td>
<td>320</td>
</tr>
<tr>
<td>X</td>
<td>28.1</td>
<td>21.3</td>
<td>193</td>
</tr>
<tr>
<td>Y</td>
<td>13.1</td>
<td>12.2</td>
<td>131</td>
</tr>
<tr>
<td>Z</td>
<td>29.3</td>
<td>20.1</td>
<td>150</td>
</tr>
</tbody>
</table>

* Total dose from using BELL, 1979 conversion factors.
The complex nature of the decay schemes of uranium and thorium provide many opportunities to detect radiations in time coincidence. Such correlations greatly increase the selectivity of the system and reduce the background signal, allowing low levels of activity to be measured in the presence of interfering emissions.

Beta-gamma and gamma-gamma coincidences are most frequently used for low level counting. Because of the solid form of ceramic samples, high efficiency techniques (e.g., gas-flow beta counter + NaI) cannot be used. However, the reduction in efficiency experienced with coincidence systems is offset to some degree by a large reduction in the background count rate.

An example of a simple beta-gamma coincidence system for the determination of uranium concentration in ores, is given by EICHOLZ (1952). This method is limited due to the continuous nature of beta particle energy spectra, but some improvement in selectivity may be gained from measuring gamma-gamma coincidences.

By reference to the NaI(Tl) spectra from uranium and thorium samples shown in figures (7.5b) and (7.6b), some intense gamma-lines are evident, along with a considerable continuum. From the decay schemes of the isotopes giving rise to these energies, it may be determined whether any pair of the visible gamma-peaks are emitted by the same isotope in coincidence.

It was found that both uranium-238 and thorium-232 have daughter products with decay schemes yielding coincidence gamma rays of sufficiently high intensity. These are:

- Uranium daughter, Bi$^{214}$ - see figure (7.2) - [1120keV-609keV]
- Thorium daughter, Tl$^{208}$ - see figure (7.3) - [583keV-2614keV]

The decay schemes in figure (7.2) and (7.3) (MARTIN, 1970) show...
the gamma-gamma coincidences which were studied to determine whether

such a technique could be used for routine analysis (the percentage figures are per disintegration of parent nuclide). Investigations into the minimum detectable activities that could be measured are discussed in section 7.6.2.

A schematic of the circuitry used for these coincidence experiments is shown in figure (7.4). Discriminator settings were determined after calibration of the 3x3 and 5x5 inch sodium iodide detectors using standard sources. The optimum delay setting of the delay amplifier was found experimentally by observing the amplifier output pulses using an oscilloscope triggered by the gate generator. A determination of the absolute efficiency of the detector pair was attempted using standard gamma sources of 1μCi activity. Such sources were found to be too active and caused pulse pile-up and distortion at detector distances that would be useful for low activity work.
Figures (7.5) and (7.6) show the spectra as recorded from the 3x3 inch NaI(Tl) detector in coincidence mode (1µs resolving time) for U and Th samples, and each is also shown with a normal singles spectrum for comparison. The two detectors were placed horizontally to prevent single cosmic ray events being recorded, and the petri-dish containing the sample was sandwiched between them. The coincidence spectra show a large reduction in background (including Compton interference) under the peaks of interest, although the time required to acquire a coincidence spectrum with a given number of counts in the main peak was approximately 20 times greater than when acquiring a normal non-coincidence spectrum.

A significant advantage of coincidence systems for low level radioisotope measurements is that it requires very little external shielding when compared to a conventional gamma spectrometer. It is envisaged that a single wall of lead bricks surrounding the two
detectors will be sufficient, whereas conventional spectrometers may require many tons of lead and steel to reduce background radiation levels to a minimum. A coincidence system would therefore be eminently suitable for a portable low level monitor.

7.5 NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis (NAA), is a powerful tool for trace element analysis. In the case of U, Th, K, and Rb, low concentrations have been measured with good accuracy using thermal neutron fluxes. Some examples of reported sensitivities are: 0.4 ppm U\textsuperscript{238} (MACKINTOSH, 1957), 0.02 ppm Th\textsuperscript{232} in meteorites (BATE, 1957), 0.1 ppm K\textsuperscript{40} (MORRISON, 1956) and 0.03 ppm Rb\textsuperscript{87} in geological specimens (CABELL, 1957).

Using a Ge(Li) detector, neutron induced gamma-emitting nuclides can be quantitatively determined without chemical separation, as the complex spectra emitted by neutron irradiated ceramics can be adequately resolved with this type of detector. The requirements to optimise NAA sensitivity are: high neutron flux, large reaction cross-section, suitable short-lived reaction products, and non-interfering gamma emissions. The thermal neutron capture reactions suitable for determining the concentrations of U, Th, K, and Rb are shown below:

\[ \text{S(n,} \gamma\text{), barns} \]

\[
\begin{align*}
90\text{Th}^{232}(n,\gamma) & \rightarrow 91\text{Pa}^{233} \rightarrow 92\text{U}^{233} \quad 7.4 \\
92\text{U}^{238}(n,\gamma) & \rightarrow 93\text{Np}^{239} \rightarrow 94\text{Pu}^{239} \quad 2.73 \\
92\text{U}^{235}(n,\gamma) & \rightarrow 90\text{Th}^{232} \quad 98. \\
19\text{K}^{41}(n,\gamma) & \rightarrow 20\text{Ca}^{42} \quad 1.5 \\
37\text{Rb}^{85}(n,\gamma) & \rightarrow 37\text{Rb}^{86} \rightarrow 38\text{Sr}^{86} \quad 0.8
\end{align*}
\]
The activity $A$ of a neutron capture reaction product can be calculated from equation (7-4).

$$A = \text{NSf}(1 - \exp(-0.693t/T_i))$$

where:

$N$ = Number of target atoms

$S$ = Cross-section of reaction $[\text{cm}^2]$ 

$f$ = Irradiation flux $[\text{neutrons.cm}^{-2}.\text{s}^{-1}]$

$t$ = Irradiation time $[\text{s}]$

$T_i$ = Product half-life $[\text{s}]$

Using this equation, the masses of $U$, $Th$, $K$ and $Rb$ required in a 50mg sample to produce an activity of 1000 dpm for a thermal flux of $2 \times 10^{12} \text{cm}^{-2}.\text{s}^{-1}$ is given in table (7.9).

<table>
<thead>
<tr>
<th>REACTION</th>
<th>CONCENTRATION (ppm) OF TARGET ISOTOPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{90}\text{Th}^{232}(n,\gamma)$</td>
<td>$^{233}\text{Th}$</td>
</tr>
<tr>
<td>$^{92}\text{U}^{238}(n,\gamma)$</td>
<td>$^{239}\text{U}$</td>
</tr>
<tr>
<td>$^{19}\text{K}^{41}(n,\gamma)$</td>
<td>$^{42}\text{K}$</td>
</tr>
<tr>
<td>$^{37}\text{Rb}^{85}(n,\gamma)$</td>
<td>$^{86}\text{Rb}$</td>
</tr>
</tbody>
</table>

The University of London Research Reactor is situated about 25 miles from the University of Surrey, and as the sample irradiation required would take no longer than 1 hour of the reactor facilities time, it was decided to devise a neutron activation analysis technique whereby the irradiated samples could be transported back to
the Surrey University Physics Department for counting. Although this precluded analysis using the short-lived isotopes produced by the neutron capture reactions, it was found to be possible to measure their daughter products. As 10 samples can be irradiated simultaneously, the resulting technique minimised reactor use.

The determination of U, Th, K and Rb concentrations were done by adopting the following techniques:

Thorium-232 - The neutron capture product Th$^{233}$ has a short half-life of 22 mins, and a weak gamma emission at 87keV. Therefore, the decay of the Th$^{233}$ daughter product Pa$^{233}$ was monitored. Pa$^{233}$ has a half-life of 27.5 days and yields an intense gamma ray at 311.8keV. The nearest likely interference to this energy is Np$^{239}$ (a weak 316keV gamma ray, T$_1$=2.3days)), which is the decay product of U$^{239}$. A good detector resolution and suitable choice of waiting time after irradiation will avoid problems due to this interference.

Uranium-238 - Conventionally, U$^{238}$ concentrations are measured by the decay of its neutron capture product U$^{239}$ ($T_1$ = 23.5 mins), being characterised by a 74keV gamma ray. However, as the half-life of this isotope is short, counting of the decay product of U$^{239}$ is more convenient. This isotope, Np$^{239}$, has a half-life of 2.35 days with strong gamma emissions at 106keV, 278keV and 228keV. The 106keV gamma may have an interference from Pa$^{233}$ (from Th$^{233}$), therefore it is more desirable to measure the 278keV and 228keV gamma rays.
Potassium-41 - The most abundant isotope of potassium, $^\text{39}\text{K}$, cannot be used for NAA as the activity of induced $^\text{40}\text{K}$ (already existing in 'large' quantities in the matrix) is very low. The neutron capture product of $^\text{39}\text{K}$ (6.88% natural abundance) is the gamma emitter $^\text{42}\text{K}$ with a characteristic emission energy at 1.53MeV. The half-life of $^\text{42}\text{K}$ is relatively short, being 12.42 hours, therefore potassium determinations must be performed fairly soon after irradiation.

Rubidium-85 - Rubidium concentrations may be determined from the decay of $^\text{86}\text{Rb}$ formed through the decay of $^\text{86m}\text{Rb}$ ($T_{1/2} = 1$ minute). $^\text{86}\text{Rb}$ has a half-life of 18.66 days and a gamma ray emission at 1.079MeV.

Figure (7.7) shows the relative build-up and decay of activity in the isotopes of interest, for a typical sample (3ppm U, 10ppm Th, 100ppm Rb and 1% K). Absolute concentrations were determined by comparison with standard mixtures. These were be irradiated simultaneously with the samples, thereby avoiding errors due to time variations in the neutron flux.

Standards were prepared from the chloride salts of potassium and rubidium, and standard ores (see section 7.2.1) of uranium and thorium with known isotopic concentrations. These standards were mixed with precipitated silica to simulate the pottery matrix. Concentration errors in the standards were less than 1% for U and Th, but were greater for the potassium and rubidium salts because of difficulties in producing homogeneous mixtures.

When counting times are not an insignificant fraction of the half-life, the assumption that the mean time $t_1$ at which the count is taken is $t_1 = t_0 + dt/2$ (where $dt$ is the counting interval, and $t_0$ is...
Figure (7.7)

Build-up and Decay of Activity for Radiolabels in Ceramics

Log$_{10}$ (Disintegration rate) vs Time after Irradiation (hours)

- Rb$^{86}$
- $\text{Pa}^{233}$
- $\text{Np}^{239}$
- $K^{42}$
the start time) is not valid and must be corrected for. Table (7.10) shows some NAA results on four ceramic samples. These should be compared to the results for gamma spectrometry and alpha counting on the same ceramic samples. The derived dose rate results are intercompared in table 7.13).

Table (7.10)

Neutron activation analysis results*

<table>
<thead>
<tr>
<th>Sample</th>
<th>U(ppm)</th>
<th>Th(ppm)</th>
<th>K(% nat k)</th>
<th>Rb(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>3.2</td>
<td>11.7</td>
<td>2.1</td>
<td>81</td>
</tr>
<tr>
<td>X</td>
<td>4.8</td>
<td>15.0</td>
<td>1.3</td>
<td>98</td>
</tr>
<tr>
<td>Y</td>
<td>2.7</td>
<td>11.0</td>
<td>0.9</td>
<td>49</td>
</tr>
<tr>
<td>Z</td>
<td>5.0</td>
<td>18.1</td>
<td>1.2</td>
<td>75</td>
</tr>
</tbody>
</table>

* Statistical errors in the peak counts were of the order of 3%.

7.6 MINIMUM DETECTABLE ACTIVITY

For a given measuring instrument, it is desirable to be able to calculate the minimum detectable activity (MDA) the detector can measure within a set confidence limit. In this way, a direct comparison between detectors would be possible when measuring the same source.

The generalised detector system envisaged is one in which the total signal counts $S$ includes both a background count $B$ and a derived signal count $D$. The background is either found from a second experiment (as in alpha counting), or subtracted directly from the total signal distribution (as in gamma spectrometry), where its presence can be recognised by the shape of the energy spectrum.

A definition of this minimum detectable activity (WALFORD,1972) is
'that activity which will allow a desired precision to be attained in a
set counting period'. The desired precision C, will therefore be
declared as follows:

\[ C = \text{That fractional standard deviation giving a probability 'p', that the interval contains the true value of the activity.} \]

\[ C = K(p)\frac{Z_t}{D} \quad \ldots(7-5) \]

where \( K(p) \) is the constant, depending on the probability p. This constant is obtained from the Gaussian probability distribution and is tabulated in appendix (F).

\[ Z_t = \text{Overall absolute standard deviation of the signal counts} D. \]

Now, \( S = D + B \), and the total absolute standard deviation is given as

\[ \sqrt{Z_s^2 + Z_B^2} = \sqrt{S + B} = \sqrt{D + 2B} \]

From equation (7-5), \( C = K(p)\frac{(D + 2B)^{1/2}}{D} \), therefore:

\[ D = \frac{(K(p)C)}{K^2(p)} \cdot (D + 2B)^{1/2} \quad \ldots(7-6) \]

Squaring equation (7-6) gives a quadratic equation in D. The positive root yields:

\[ D = \frac{k^2(p) \cdot (1 + \left(1 + 8C^2B\right)^{1/2})}{2C^2} \]

The derived minimum detectable activity, A, will depend on the absolute detector efficiency for the radiation being measured \( E \), the duration of the experiment \( T \), and the fraction of disintegrations yielding the radiation to be measured \( f \).

\[ A = \frac{k^2(p)}{2C^2ETf} \cdot \left[ 1 + \left(1 + 8C^2B\right)^{1/2} \right] \quad \ldots(7-7) \]

Before equation (7-7) may be applied to a real system, the detector efficiency must first be determined.
7.6.1 Efficiency of Detectors

To be able to apply equation (7-7) to the detectors used in sections 7.1 to 7.3, their absolute efficiencies have to be determined. We therefore have four cases:

a) Alpha counting

In the case of alpha counting, we assume the intrinsic efficiency of the ZnS phosphor is 100%. A ZnS screen with semi-infinite matrix has effectively a π geometry (TURNER, 1958), and using a value of 0.83 for the threshold setting of the apparatus, results in an absolute efficiency of 21%.

b) Germanium-Lithium solid-state detector

For Ge(Li) detectors, there is no standardisation in crystal sizes as is true for NaI(Tl). Added to this, the many existing drift geometries make theoretical calculations of efficiency unique to a given detector, and only approximate in any one case. As the Ge(Li) detector has a far better resolution than NaI(Tl), it was decided to use a simulated pottery standard of high activity (30mg U²³⁸ and 100mg Th²³²) to measure the efficiency in the geometry used for sample measurements. The results over the energy range 200keV to 2.5MeV are shown in figure (7.8).

c) Sodium Iodide detector

Due to the non-availability of gamma-ray standard sources of appropriate activity for the geometry to be used for routine pottery analysis, it was decided instead to calculate the expected absolute efficiency of the NaI(Tl) detectors. The complex pottery standard made to measure the efficiency of the 40cm³ Ge(Li) was not suitable for this purpose, because of the relatively poor resolution of NaI scintillation crystals. With the assumption of a 2π geometry and using the results of HEATH (1964) for a 3x3 and 5x5 inch NaI(Tl) crystal, an approximate absolute efficiency can be calculated, and is
Figure (7.8)
Absolute Full Energy Peak Efficiency for Ge(Li) Detector

- Experimental points

\[ \text{Efficiency} = \exp(1.87 - 4.38E + 4.88E^2 - 3.27E^3 + .731E^4) \]
d) Coincidence system using NaI(Tl) detectors

Figure (7.9) shows the calculated efficiencies for the two detectors used in the coincidence system. An accurate experimental calibration of the geometric efficiency for a close geometry (1cm apart) could not be done with standard sources due to source strength problems causing saturation of the detector electronics, so an estimate of 40% of all coincident emissions are assumed to be incident on the detectors.
7.6.2 Minimum Detectable Concentration (MDC) Calculations

Using the calculated, or measured efficiencies of section 7.6.1, and equation (7-7), it is possible to estimate the minimum detectable activities for alpha counting and gamma spectrometry.

a) Alpha counting

Absolute efficiency - 21%
Background - 0.4 counts per 1000 seconds
K(68%) - 1.0
Decay fraction - 1
T - 80,000 seconds (22.2 hours)
Precision - 10%

Using the values above with equation (7-7) will give:

\[ A = 8.6 \text{ disintegrations per 1000s} \]

This activity corresponds to 1.86 ppm U^{238} and 5.87 ppm Th^{232} assuming the Th/U activity ratio to be unity. These figures for the minimum concentrations of uranium and thorium detectable using an alpha counter are smaller than those expected from an average pottery sample.

b) The germanium-lithium spectrometer

The high resolution obtainable using Ge(Li) solid state detectors produces the dilemma as to which of the many observed gamma rays give the most sensitive activity measurements. The effects of changing the parameters C, K(p), and B on the derived values for MDA according to equation (7-7) (assuming EfT to be unity) are shown in figures (7.10, 7.11). To convert these to minimum detectable concentrations of the parent isotope (in ppm) for various gamma ray energies emitted by U, Th and K, a conversion constant G (for a 10g sample) is shown in table (7.11), which will convert those minimum activities of figure (7.10, 7.11) to the concentration of radio-isotope which gives rise to that activity. This constant should
Figure (7.10)

Theoretical MDA Values

- $H$
Figure (7.11)

Theoretical NDA Values

Minimum Resonant Rate (d.p.s.)

Log_10 B

3000

2000

1000

0

1

2

3

4

a... 10% 68%
b... 20% 68%
c... 5% 68%
d... 10% 90%
e... 20% 90%
f... 5% 90%
be divided by the duration of the experiment (in seconds).

Table 7.11

<table>
<thead>
<tr>
<th>Source</th>
<th>Energy (MeV)</th>
<th>1/(E.f)</th>
<th>G (10 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(^{234})</td>
<td>0.928</td>
<td>694</td>
<td>5642</td>
</tr>
<tr>
<td>Th(^{234})</td>
<td>0.923</td>
<td>781</td>
<td>6350</td>
</tr>
<tr>
<td>Ra(^{226})</td>
<td>1.846</td>
<td>772</td>
<td>6276</td>
</tr>
<tr>
<td>Po(^{214})</td>
<td>0.352</td>
<td>122</td>
<td>992</td>
</tr>
<tr>
<td>Po(^{214})</td>
<td>0.295</td>
<td>205</td>
<td>1691</td>
</tr>
<tr>
<td>Po(^{214})</td>
<td>0.242</td>
<td>506</td>
<td>4150</td>
</tr>
<tr>
<td>Bi(^{214})</td>
<td>2.204</td>
<td>12820</td>
<td>104228</td>
</tr>
<tr>
<td>Bi(^{214})</td>
<td>1.764</td>
<td>2877</td>
<td>23390</td>
</tr>
<tr>
<td>Bi(^{214})</td>
<td>1.120</td>
<td>1081</td>
<td>8747</td>
</tr>
<tr>
<td>Bi(^{214})</td>
<td>0.609</td>
<td>163</td>
<td>1333</td>
</tr>
<tr>
<td>Ac(^{228})</td>
<td>0.969</td>
<td>874</td>
<td>21634</td>
</tr>
<tr>
<td>Ac(^{228})</td>
<td>0.911</td>
<td>464</td>
<td>11980</td>
</tr>
<tr>
<td>Ra(^{224})</td>
<td>0.339</td>
<td>461</td>
<td>11411</td>
</tr>
<tr>
<td>Po(^{212})</td>
<td>0.239</td>
<td>78</td>
<td>1931</td>
</tr>
<tr>
<td>Bi(^{212})</td>
<td>0.727</td>
<td>1261</td>
<td>31213</td>
</tr>
<tr>
<td>Ti(^{208})</td>
<td>2.61</td>
<td>1984</td>
<td>44609</td>
</tr>
<tr>
<td>Ti(^{208})</td>
<td>1.583</td>
<td>212</td>
<td>5248</td>
</tr>
<tr>
<td>K(^{40})</td>
<td>1.461</td>
<td>2336</td>
<td>919</td>
</tr>
</tbody>
</table>

(c) Sodium iodide gamma spectrometer (3x3 inch)

The use of a NaI(Tl) scintillator as a gamma ray detector is essentially the same as the case for the Ge(Li) detector, although higher backgrounds are to be expected since the gamma peaks are so much wider. The constants to convert to minimum detectable concentration (ppm) are given below for 10g samples.

- Uranium (1.764MeV from Bi\(^{214}\)) \(-\frac{1}{E.f} = 141\), \(G = 1146\)
- Thorium (2.614MeV from Ti\(^{208}\)) \(-\frac{1}{E.f} = 86.8\), \(G = 2149\)
- Potassium (1.461MeV from K\(^{40}\)) \(-\frac{1}{E.f} = 173\), \(G = 68\)
  (N.B. 1% K is equivalent to 1.17ppm K\(^{40}\))

d) Coincidence gamma spectrometry

When calculating MDC for coincidence systems, the decay fraction leading to coincident photons must be determined. For U and Th, the
decay schemes of Bi\(^{214}\) and Tl\(^{208}\) produce gamma rays with a high coincidence decay fraction. See figures (7.2, 7.3).

These decay fractions are calculated to be:

- For Bi\(^{214}\)(U daughter) - 14.6%
- For Tl\(^{208}\)(Th daughter) - 32%

Hence G can be determined for 10g samples with which the MDC can be calculated using figures (7.10, 7.11).

\[
\text{Uranium} - \frac{1}{E.f} = 572, \quad G = 4284 \\
\text{Thorium} - \frac{1}{E.f} = 283, \quad G = 7004
\]

### 7.6.3 MDC Comparison of Detectors

Table (7.12) gives a comparison of MDC using the criterion of equation (7-7). Typical backgrounds have been determined for each spectrometer, although these values would be expected to vary with differing shielding arrangements and detectors.

It is evident in table (7.12) that alpha counting is the most sensitive technique for measuring uranium and thorium, although separate measurements must be made to determine the potassium content. However, it must be noted that in the conversion of alpha count-rate to parts per million concentration a typical Th/U ratio (3.16) for all samples is assumed. Variations in the Th/U ratio will have greatest effect on the beta and gamma contributions to the dose rate. For example—varying Th/U from 1.19 to 7.83 affects the dose rate as follows: Alpha contribution decreased by 5.4%, beta decreased by 17% and gamma contribution increased by 16.8% (Bowman, 1976). Thus for inclusion dating (no alpha contribution), alpha counting may not be suitable unless the Th/U ratio is known. With fine grain dating, where the alpha contribution to the dose rate is approximately 90% of the total dose rate, an assumed Th/U
Table (7.12) Comparison of MDC

<table>
<thead>
<tr>
<th>Detector</th>
<th>Parts per million concentration for T=10^5s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U  Th  K</td>
</tr>
<tr>
<td>α-counting</td>
<td>1.6  4.7  -</td>
</tr>
<tr>
<td>Ge(Li)</td>
<td>3.6  16.7  2.6</td>
</tr>
<tr>
<td>NaI(Tl)</td>
<td>12.6  18.8  .63</td>
</tr>
<tr>
<td>Coincidence</td>
<td>5.1  15.2  -</td>
</tr>
</tbody>
</table>

a- Background constant at 0.4 counts per ksec.
b- Analysis of .583MeV for Th^{232} (B= 4c.p.1000s)
    1.352MeV for U^{238} (B= 6c.p.1000s)
    1.461MeV for K^{40} (B= 8c.p.1000s)
c- Analysis of 2.614MeV for Th^{232} (B= 35c.p.1000s)
    1.764MeV for U^{238} (B= 50c.p.1000s)
    1.461MeV for K^{40} (B= 65c.p.1000s)
d- Thorium coincidence background = 0.3 c.p.1000s
    Uranium coincidence background = 0.1 c.p.1000s

value of 3.16 (equal U and Th activities) will not introduce large errors.

The single 3x3 inch NaI(Tl) detector shows the highest MDC and is therefore perhaps not the most suitable of the gamma spectrometers. However, NaI(Tl) does have the advantage of being cheap and simple to use, therefore allowing simultaneous measurements using multiple detectors over long counting times (>2 days), thus reducing the MDC. A particular cost constraint on a multiple NaI(Tl) system, would be the need to supply a separate ADC for each detector. Shielding arrangements could have been improved on the NaI(Tl) spectrometer, which would have produced a lower background and better MDC.

The coincidence system does show a slightly better sensitivity than the Ge(Li) detector for the thorium series, but is slightly worse for uranium. The inability of this coincidence spectrometer to measure the potassium content, and its added complexity, favours
the use of a Ge(Li) detector for routine use.

7.6.4 Comparison of Resulting Dose Rates

A comparison of the self-dose rates in four samples calculated from concentration values determined by the five techniques described in sections 7.1 to 7.5, is shown in table (7.13). The results of BELL(1979) were used to effect the conversion to dose rate.

Table (7.13) Comparison of Dose Rate Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alpha Counting</th>
<th>Gamma Spec(Ge(Li))</th>
<th>Gamma Spec(Equilibrium)</th>
<th>NAA&lt;sup)b&lt;/sup&gt;</th>
<th>Gamma Spec(Na1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Total&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Total&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Total&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Total&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>W</td>
<td>1.81</td>
<td>2.06</td>
<td>1.92</td>
<td>2.36</td>
<td>1.78</td>
</tr>
<tr>
<td>X</td>
<td>2.77</td>
<td>2.91</td>
<td>2.51</td>
<td>2.90</td>
<td>2.36</td>
</tr>
<tr>
<td>Y</td>
<td>1.79</td>
<td>1.89</td>
<td>1.61</td>
<td>1.87</td>
<td>-</td>
</tr>
<tr>
<td>Z</td>
<td>3.03</td>
<td>3.17</td>
<td>2.96</td>
<td>3.38</td>
<td>2.82</td>
</tr>
</tbody>
</table>

<sup>a</sup> Use K<sup>40</sup> values from Table(6.4)

<sup>b</sup> Includes Rb<sup>87</sup> contribution

The degree of agreement between the five methods shows that each is capable of determining the total self-dose rate in pottery. The range of variation between the results of a single sample are 9% for sample Z and 16% for sample Y. The choice of technique for use on a routine basis, depends on the dating method to be used.
As the fine-grain method relies most heavily on the alpha dose contribution, the ease of applying the alpha-counter recommends itself in this case, particularly as changes in the Th/U ratio have a small effect on the total dose acquired by the fine grains (see section 7.6.3), and its MDC has been shown to be the lowest of the cases reported.

For inclusion dating, the alpha dose is not significant, but the environmental gamma dose from the surroundings becomes important. The Ge(Li) detector provides the most flexible and cost effective technique in this case, being able to determine the U, Th and K concentrations simultaneously.

The neutron activation analysis technique proved to be rather time consuming, although the method leads to accurate results due to the high induced activity in the sample, and the absence of an interfering background signal from the environment.
8 CONCLUSIONS

The aim of this thesis has been to study some experimental techniques in thermoluminescence dating, with a view to producing a dating system with a well founded method of operation. A TL apparatus has been constructed for this purpose to measure low signal levels. Particular attention has been paid to the radio-isotope analysis of ceramics in order that accurate values for the absorbed dose received by the natural TL phosphors contained within them, may be calculated. Minimum detectable activities for the analytical techniques reviewed have been determined, and the results discussed.

A critique and discussion, including proposed further experimentation of the sections within this thesis, are presented below.

8.1 THE THERMOLUMINESCENCE APPARATUS

The apparatus as originally designed, has been used without major alterations since it was first constructed, apart from a detailed change in the heater construction (see section 2.1.2). Utilisation of the modular design philosophy has not yet been fully exploited, as time has not allowed the implementation of a proposed experiment, which would have required major changes in the optics stage. It had been intended to measure the TL signal using two photomultiplier tubes in time coincidence, in order to determine whether TL photons are emitted in pairs or groups during readout due to cascade transitions in the luminescent centres.

An alternative approach is to use the sum-coincidence method for determining the possible emission of multiple photons, by using a photomultiplier with a caesium activated gallium phosphide dynode.
structure. A photomultiplier of this type has been shown to be capable of resolving multiple photon events due to the emission of as many as five electrons from the photocathode (LeskovaR, 1972). Use of such coincident TL photons may be a method of reducing black-body interference at high temperatures, thus enabling much deeper traps to be explored.

A desirable change in the apparatus would have been to replace the present objective lens (f1, quartz) for an f0.6 Fresnel lens. In this way, the increase in the light collecting efficiency would be of the order of x3, which is a useful gain in any TL reader.

It was soon found that the focus of the objective lens was very critical, and that rough handling could cause a misalignment, and a consequent reduction in the light reaching the PMT. An improved control over focussing, and a more precise assembly of the optical components would therefore be desirable.

The shutter mechanism has been found to be extremely successful, and only a very small increase in the dark count is observed when the PMT is removed from the heating oven. The fitting of an automatic shutter, such that when the PMT housing and optics are lifted from the oven the shutter is closed, would be necessary if an operator, not familiar with the apparatus, is employed, as exposing the PMT to ambient light whilst connected to the high voltage supply, would cause permanent damage. Even exposure without an H.T. supply will raise the level of the dark current for a considerable period.

Temperature control by microprocessor has been found to be very reliable, and allows a greater flexibility than a dedicated analogue device could provide. For example, a continuous range of heating rates could be provided without the need to generate a lookup table, by a straightforward change in the controlling program. The flexibility of a microprocessor controlled TL heater can be illustrated by noting the chief disadvantage of the apparatus in the current form. At present,
the amplified output pulses from the PMT are recorded by a multi-channel analyser (MCA), operated in the multi-channel scaling mode. Two disadvantages of this method are: a) the waste of machine 'power', as most of the facilities of the MCA, in particular the pulse height analyser, are unused and, b) the difficulty of analysing the stored TL spectrum, as it is now recorded in a device in which only the most rudimentary glow curve analysis is permitted (i.e. measurement of peak heights for well resolved peaks).

At present the TL spectrum is analysed by transferring the MCA data onto paper tape, and then reading this tape into the university's main computer, where it may be stored and manipulated. This process is time consuming and prone to data corruption.

A proposed solution to this problem is to record the PMT output using a scaler with the facility to output its acquired counts when requested, and then continue from zero when this task is complete. Such a scaler (for example the CANBERRA 1476A or 1773) can be made to output its acquired count at timed intervals to the controlling microprocessor. With the data in this form, and a disk operated, high level language available, the microprocessor may be used for data acquisition and analysis, as well as temperature control. Such a system would therefore be independent of other supportive equipment and computers.

N.B. The CANBERRA 1773 is a 25MHz scaler, giving 1% dead time for a count rate of $2.5 \times 10^5$ cps.

An estimate of the minimum detectable beta-gamma dose in quartz for the TL reader, may be found by using the following assumptions. For a combined background of 100 c.p.s (PMT dark counts plus spurious counts from the sample), and a minimum acceptable signal to noise ratio of 2:1, the required signal from the quartz is 200 c.p.s. An average sensitivity for quartz to beta and gamma radiation has been found to be 15 c.p.s per rad for a 10mg sample, therefore the minimum detectable
dose will be 13 rads. For inclusion dating of a typical pottery matrix (3ppm U, 10ppm Th and 1% K), this figure indicated that the youngest pottery sample that may be dated is 50 years.

8.2 THE QUARTZ ANALYSIS

The results presented in section 5, comparing the trace element compositions of five quartz samples with their TL properties, has yielded inconclusive results. In retrospect, for the ceramic quartz samples, it is evident that the involved sample preparation procedure, and the possibility of significant levels of contamination diffusing into the small quartz crystals during firing (due to their large surface area), has lead to confusing results. The geological samples are from a pure source by comparison, and will not be affected so severely by these problems. This experiment would be best repeated using pure quartz samples (of geological origin), thus obviating contamination of the sample arising from the clay matrix in a ceramic, and the involved preparation procedure. The neutron activation analysis itself was easily accomplished, as the spectrometer at the University of London reactor centre is a fully automatic Ge(Li) detector system, using a 4000 channel pulse height analyser. However, it should be noted that neutron activation is not equally sensitive for all elements, and some may be overlooked.

The measurement of peak sensitivities was found to be straightforward, but the study of photo-transferred TL (PTTL) was lacking a suitable UV source of sufficient power. A useful extension to this part of the experiment would be to employ a powerful monochromated UV source in order that successive excitation energies could be used to produce the PTTL phenomena, thus determining whether the PTTL signal versus frequency response shows any evidence of deep levels, and if so,
whether there exists a correlation between these results, and the trace element composition. This may be an interesting application of the Daresbury synchrotron radiation source.

8.3 THE RADIO-ISOTOPE ANALYSIS

As can be seen in section 7.6.4, the comparison of the calculated dose rates of the four ceramics detailed in appendix (C), show good agreement between the five experimental techniques. However, it must be noted that great care was taken over these test case measurements, and therefore if used in routine work, the time taken for some of them may be prohibitive, if a large through-put is required.

For ease of use, simple data analysis and low cost, the alpha counter is a very useful method to employ. Reference to section 7.6.3 shows that this technique possesses the lowest minimum detectable activity (MDA) of all the counting methods investigated (excluding neutron activation analysis). When using alpha counting, an estimate of the Th/U ratio is required for accurate dose predictions, especially in the case of inclusion dating. By running many alpha counters simultaneously, a large number of samples may be analysed in a reasonably short period of time. A disadvantage of this method is the need for a separate determination of the potassium content of the sample.

Table (7.12) shows the simple NaI(Tl) spectrometer as the least sensitive of the analytical techniques. It should be noted that these figures were prepared for a counting period of $10^5$ seconds (approximately 1.2 days). A counting period of 3 days would yield an MDC figure for U, Th and K of 4.8 ppm, 7.6 ppm and 0.3 ppm respectively, for a 10% accuracy at one standard deviation. Even though these MDC values are not truly competitive, it must be noted that this
spectrometer was not well protected from the external background, therefore these values may be reduced with an improved shielding arrangement.

This gamma counting technique has a major advantage of being able to measure the U, Th and K content of a sample with one measurement, which may be important for routine work. The cost of a NaI crystal spectrometer is low compared to the Ge(Li) detector, and a multi detector system can make measurements on different samples simultaneously, particularly with modern multi-channel analysers, which are able to acquire spectra from many detectors running concurrently.

By using two NaI(Tl) detectors in coincidence, a very isotope selective detector is produced, with a sensitivity improvement over the single crystal system. The most marked difference is seen in the reduced MDC for uranium, whereas for thorium, the reduction is not as significant. The added complexity of the coincidence system, and the greater difficulty in setting up the device ready for use, results overall in an equivalent service to that provided by two single NaI crystals run over longer periods.

The Ge(Li) detector, although an expensive item to buy and run, and also requiring extensive shielding, is perhaps the most flexible of the spectrometers. Assuming secular equilibrium in the decay chains of U and Th, it may be used in a way similar to the NaI(Tl) spectrometer, but yielding a lower MDC (particularly in the case of uranium). If a more thorough analysis of the decay chain is required, longer counting periods should provide sufficient information to give the count rates of key isotopes, and hence determine whether a significant disequilibrium has occurred.

The neutron activation analysis scheme has been designed in order that actual measurements of the samples may be made on a local Ge(Li) spectrometer, some time after the sample irradiation. This method does have the disadvantage of it being necessary to remeasure the sample at
various times, in order to optimise the signal. Therefore careful planning is required for routine analysis, when many samples are to be measured.

8.4 THE TL THEORY

A review of some relevant TL theory has been included in section 3, mainly to provide a comparison to the non-linear heating mathematics presented in section 4. The linear heating method of CHEN (1969b) has been used to determine the trapping parameters in the green quartz sample. This may be compared to a similar analysis using the non-linear heating technique of section 4. The linear method suffers the major disadvantage of it being necessary to take measurements from the falling slope of the glow curve, which is prone to problems of interference from higher trapping levels. The non-linear technique avoids this problem by only requiring measurements to be made on the rising slope of the glow curve.

Using a peak stripping technique in the CHEN analysis, both methods result in trap depths which are in good agreement. The non-linear method also produces values for the glow curve order, however, the values derived predict a greater peak temperature shift than is observed when the heating constant is varied (see section 4.6).

An attempt has been made to predict the phenomena expected to arise from the simple band theory of TL phosphors, under conditions of varying irradiation rates, and trapping constants. This has been achieved by applying a numerical technique to solving the simultaneous equations describing this model, in two simple states (one trap and two trap). In the latter state, the solutions generated have been shown to agree with the approximated analytical solution of CHEN (1978), for predicting the conditions necessary for a supralinear TL dose response.
to occur. It has been shown to be straightforward to extend this technique to more complex models if so desired, in order that other hypotheses may be tested without resorting to approximate and lengthy analytical solutions.

Thermoluminescence dating has been shown capable of producing reliable dates (SHAPLIN, 1978, FLEMING, 1973, ZIMMERMAN, 1969). Although the physical processes involved in the TL mechanism are not yet fully understood, the responses of many naturally occurring TL phosphors to radiation are becoming increasingly well known, and with adequate safeguards against undesired responses, good accuracy (certainly better than 10%) can be achieved.

The abundance of pottery fragments associated with most archaeologically interesting sites, gives this absolute age measuring technique a usefulness which should not be overlooked, and its continuous refinement will enable it to play a useful complementary role alongside other well established dating techniques.
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I would like to acknowledge the help afforded to me by my supervisor, Dr. Walter Gilboy, as our discussions throughout the last three years have gently lead my thoughts to the more fruitful areas of my work. I must also thank his liaison with Dr. A. Clark of the Ancient Monuments Laboratory, whose initial work together, made this project a reality, thus making it worthy of a much appreciated S.R.C grant.

Thanks must also go to my fellow research students for their frequent conversations upon the complete spectrum of physical knowledge, as some of their more 'down to earth' suggestions have often been useful.

I also wish to acknowledge all of the teaching and technical staff with whom I have worked, for their assistance, and a special thanks to my fiancée, Sue, for proof-reading my manuscripts, and always having ready some moral support when necessary.


APPENDIX (A)

Infinite Matrix Dose-rate (mrad/yr) (Bell, 1979)

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<tr>
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<td>1.03</td>
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</tr>
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<td>Uranium (U$^{238}$)</td>
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<tr>
<td>No Radon Loss</td>
<td>278.3</td>
<td>14.62</td>
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<td>126.2</td>
<td>6.09</td>
<td>0.56</td>
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<td></td>
<td></td>
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<tr>
<td>1% K$_2$O</td>
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<tr>
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<td></td>
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<tr>
<td>100 ppm Rubidium</td>
<td>-</td>
<td>4.64</td>
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* 1 ppm by weight of parent isotope
APPENDIX B

Segment ECU Page 1

50 ; **** VARIABLE STORE ****
100 ; **** SEGMENT... ECU ****
200 ; ORG OCH

0010 CO 300 COUNTU FCB C
0011 CO 400 COUNTL FCB C
0013 CO 550 AU FCB O
0015 CO 600 AN FCB O
0017 CO 700 AL FCB O
0019 CO 800 K FCB O
001B CC 900 MOUNT FCB C
001D CC 1000 CUTU FCB C
001F DF 1100 CUTL FCB C
0021 CO 1200 CUTUZ FCB DAGH
0023 CO 1300 TMTNL FCB D
0025 CO 1400 TMTNL FCB D
0027 CO 1500 TMTNL FCB D
0029 CO 1600 VOLTL FCB D
002B CO 1700 T7F1FL FCB D
002D CO 1800 T7F1FL FCB D
002F CO 1900 T7F1FL FCB D
0031 CO 2000 T7F1FL FCB D
0033 CO 2100 T7F1FL FCB D
0035 CO 2200 T7F1FL FCB D
0037 CO 2300 POWER FCB C
0039 CO 2400 SWF FCB D
003B CO 2500 TBHU FCB C
003D CO 2600 T6H C
003F DD 2700 INITU FCB DAH
0041 DD 2800 T7TL FCB 09H
0043 DD 2900 CYCLE FCB III
0045 DD 3000 HEMU FCB 9
0047 DD 3100 HDMH FCB O
0049 DD 3200 HDMH FCB O
004B DD 3300 KI FCB O
004D DD 3400 K< FCB O
004F DD 3500 CU FCB O
0051 DD 3600 CL FCB C
0053 DD 3700 LOCUS FCB C
0055 DD 3800 LOCUS FCB C
0057 DD 3900 FLAG FCB C

Segment INIT Page 1

20 ; **** SEGMENT... INIT ****
40 ; **** PURPOSE... INITIALIZATION ****
60 ; ORG CONH
80 ; ORG CONH

0040 CE0000 100 ; LDX F0400
0042 FE0000 120 ; STX G010H
0044 CE000A 200 ; LDX @TEXT
0046 CE0000 140 ; SET SUI VECTOR ****
0049 FE0012 160 ; STX G010H
004C CE000A 200 ; LDX @TEXT
004F CE0000 220 ; JSR START.DAT
0052 01 260 ; FCE 1
0053 CE0026 300 ; LDX TEXT7
0056 CE0029 240 ; JSR START.DAT
0059 01 300 ; FCE 1
005A CE0023 320 ; LDX TEXT8
005D CE002A 340 ; JSR START.DAT
005E 01 340 ; FCE 1
005F 01 400 ; FCE 1
0060 01 420 ; LDX A 03H

80 ; **** INIT ****

0067 2F 460 ; CLA E
006E FE0048 500 ; STA A 040H
006F FE0049 500 ; STA A 040H
006E 7E0071 520 ; JPF START2
0071 BD*** 560 ; **** DINERABLE POWER SUPPLY ****
0074 01 580 ; FCE 1
0075 860 600 ; LDA A 0AH
0077 7A*** 620 ; STA A TUTLE.QEU
007A CE0050 640 ; LDA E 01H
007C FF*** 660 ; STA B TUTLE.QEU

60 ; **** PRINT TEXT... (LINEAR OR NON-LINEAR) ****

007F CE0211 700 ; LDX @TEXT
0082 BD*** 720 ; JSR START.DAT
0085 01 740 ; FCE 1
0086 60*** 760 ; JSR START.DAT
0089 01 780 ; FCE 1
008A FE*** 600 ; CMP A Y.EQU
008D CE027C 620 ; JSR TBLN
0091 CE0800 640 ; **** SET LINEAR INTERRUPT VECTOR AND FLAG ****

008F CE0290 850 ; LDX W500H
0092 FF0000 850 ; STX G010H
0095 79*** 900 ; CLA FLAG.EQU
0096 7E00B0 920 ; JMP START
0099 01 940 ; **** SET NON-LINEAR INTERRUPT VECTOR AND CUT-OFF MAX ****
009B CE0400 9600 ; HLNX LDX W000H
009D FF0000 9500 ; STX G010H
009F 01 CE0000 10000 ; LDX 00000H
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</table>

**MICROPROCESSOR CONTROLLED HEATER**

*G. C. COLEIN 1981*
SEGMENT FETCH PAGE 1

0464 80FF 2500 LDA #0FFH
0466 BF77 2550 STA A FLAG.EQU
0466 CE9000 3000 LDX #0900H
046C FFAC00 3050 STX GAS00H
046F 77FF 3100 CLR CONTU.EQU
0472 77FF 3150 CLR CONTL.EQU
0475 7FF7 3200 JMP START.T1
0478 7FF7 3250 OUT 3 JMP TEXTE.INIT

SEGMENT T1 PAGE 1

03C7 2703 1650 BNE CON ;IF K=ZERO ACTION TO BE TAKEN
03C8 7F7F 1700 JMP START.SHAKE
03C9 E600 1750 CON HDA D,0X
03CA 06 1800 INX
03CB 06 1800 LDA A,0X
03CD 06 1800 ROL K,EQU
03CE 04 1850 ROL K,EQU
03CF 56 1850 ROL K,EQU
03D8 96 1900 ROL K.EQU
03D9 2703 1950 BNE CON ;IF K=ZERO ACTION TO BE TAKEN
03DA E600 1970 CON HDA D,0X
03DB 06 1970 INX
03DC 06 1970 LDA A,0X
03DD 06 1970 ROL K.EQU
03DE 04 1970 ROL K,EQU
03DF 56 1970 ROL K.EQU
03E0 96 2000 ROL K.EQU
03E1 2730 2050 BNE CON ;IF K=ZERO ACTION TO BE TAKEN
03E2 DT77 2100 STA A CUTF.EQU
03E4 17 2200 TIA
03E4 E4OF 2250 ADD A,0FFH
03E4 B77F 2300 STA A CUTF.EQU
03E4 DT77 2350 STA A CUTF.EQU
03E5 7F7F 2400 ;DETERMINE HEATING RATE FOR LIN PORTION
03E6 38E0 2450 CLR K,EQU
03E6 46C00 3100 LDA #06C0H
03E8 3800 3150 LDA #03800H
03E8 C800 3200 ADC A #00
03E9 7F7F 3250 CLSR SEC.SEG
03EA 9200 3300 LDA #09200H
03EB 7F7F 3350 JMP START.T1
03EC 7F7F 3400 ;SET FLAG HIGH TO SHOW LIN PORTION
03ED 7F7F 3450 ;SEGMENT..... T1 ****
03EE 7F7F 3500 ;PURPOSE..... UPDATE TIMER
03EF 7F7F 3550 ;SEGMENT..... T1 ****
03F0 7F7F 3600 ;SEGMENT..... T1 ****
SEGMENT Z0D

100 : **** SEGMENT ... Z0D ****
200 : **** PURPOSE ... CALCULATE REQUIRED LINEAR TEMPERATURE
0410 01 200 START FCB 1
2404 04 START A PULDU, ECU
04CF 04 START D PULDU, ECU
04DA 04 START A LK, ECU
04DD 04 START A D, ECU
04DC 04 800 JRP START, MULT
04EE 04 1000 ADD TEN TIMES ROOM TEMP ****
04EC 04 1100 LDA A AL, ECU
04E3 04 1200 ADD A T闹, ECU
04E4 04 1300 STA A AL, ECU
04E5 04 1400 LDA A AI, ECU
04E6 04 1500 ADD A T闹, ECU
04E7 04 1600 STA A AL, ECU "AU WILL NOT BE ALTERED"
04E8 04 1700 ; **** REQUIRED TEMP = T闹10 IN AL, AI
04E9 04 1800 JRP START, SHAKE

SEGMENT SHAKE

100 : **** SEGMENT ... SHAKE ****
200 : **** PURPOSE ... HARD SHAKE WITH ADC ****
0400 01 200 START FCB 1
0403 03 500 LDA A #3
0404 04 600 STA A APID, PIA
0405 05 700 FCB 1
0406 06 800 FCB 1
0407 07 900 FCB 1
0408 08 1000 LDA A #2
0409 09 1100 ADD A APID, PIA
040A 0A 1200 LDA A APID, PIA
040B 0B 1300 STA A APID, PIA
040C 0C 1400 LDA A APID, PIA
040D 0D 1500 LDA A APID, PIA
040E 0E 1600 LDA A APID, PIA
040F 0F 1700 JRP START, T3
**** SUBROUTINE... MUL ****

200 ; PURPOSE... MULTIPLY 16 BIT BY 16 BIT NUMBERS ****
400 ; RESULT
500 ; AU = AL = AL = RESULT
600 ; START

066A CC 0
066B 6606
066C 77****
066D 7F****
066E FF****
0670 FC****
0671 54
0672 FF****
0673 2400
0674 BF****
0675 58
0676 46
0677 FF****
0678 2200
0679 7F****
067A FF****
067B 2300
067C 2F00
067D 2700
067E 2510
067F 2900
0680 2700
0681 3300
0682 3900
0683 3800
0684 3700
0685 3600
0686 3900
0687 4000
0688 4100
0689 4200
068A 4300
068B 4400
068C 4500
068D 4600
068E 4700
068F 4800
0690 4900
0691 4A00
0692 4B00
0693 4C00
0694 4D00
0695 4E00
0696 4F00
0697 5000
0698 5100
0699 5200
069A 5300
069B 5400
069C 5500
069D 5600
069E 5700
069F 5800

**** SUBROUTINE... DIV ****

100 ; PURPOSE... DIVIDE 16 BIT NUMBERS ****
120 ; (DEN0 + DEN1) / (DIV0 + DIV1) ****

0700 CC 0
0701 6600
0702 2100
0703 3100
0704 4100
0705 5100
0706 6100
0707 7100
0708 8100
0709 9100
070A 1000
070B 1100
070C 1200
070D 1300
070E 1400
070F 1500
0710 1600
0711 1700
0712 1800
0713 1900
0714 1A00
0715 1B00
0716 1C00
0717 1D00
0718 1E00
0719 1F00
071A 2000
071B 2100
071C 2200
071D 2300
071E 2400
071F 2500
0720 2600
0721 2700
0722 2800
0723 2900
0724 2A00
0725 2B00
0726 2C00
0727 2D00
0728 2E00
0729 2F00
072A 3000
072B 3100
072C 3200
072D 3300
072E 3400
072F 3500
0730 3600
0731 3700
0732 3800
0733 3900
0734 3A00
0735 3B00
0736 3C00
0737 3D00
0738 3E00
0739 3F00
073A 4000
073B 4100
073C 4200
073D 4300
073E 4400
073F 4500
0740 4600
0741 4700
0742 4800
0743 4900
0744 4A00
0745 4B00
0746 4C00
0747 4D00
0748 4E00
0749 4F00
074A 5000
074B 5100
074C 5200
074D 5300
074E 5400
074F 5500
0750 5600
0751 5700
0752 5800
0753 5900
0754 5A00
0755 5B00
0756 5C00
0757 5D00
0758 5E00
0759 5F00
075A 6000
075B 6100
075C 6200
075D 6300
075E 6400
075F 6500
0760 6600
0761 6700
0762 6800
0763 6900
0764 6A00
0765 6B00
0766 6C00
0767 6D00
0768 6E00
0769 6F00
076A 7000
076B 7100
076C 7200
076D 7300
076E 7400
076F 7500
0770 7600
0771 7700
0772 7800
0773 7900
0774 7A00
0775 7B00
0776 7C00
0777 7D00
0778 7E00
0779 7F00
077A 8000
077B 8100
077C 8200
077D 8300
077E 8400
077F 8500
0780 8600
0781 8700
0782 8800
0783 8900
0784 8A00
0785 8B00
0786 8C00
0787 8D00
0788 8E00
0789 8F00
078A 9000
078B 9100
078C 9200
078D 9300
078E 9400
078F 9500
0790 9600
0791 9700
0792 9800
0793 9900
0794 9A00
0795 9B00
0796 9C00
0797 9D00
0798 9E00
0799 9F00
079A AF00
079B AF00
079C AF00
079D AF00
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<td>; *** PURPOSE... SET G VECTOR ****</td>
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</table>
### Provenance of Quartz Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Provenance</th>
</tr>
</thead>
</table>
| R      | Rose quartz - Madagascar.  
Translucent, rose pink, massive.  
Supplied by: R.F.D. Parkinson & Co.,  
Doulting, Somerset. |
| G      | Green quartz (Jasper) - Cornwall.  
Green massive.  
Supplied by: (as above) |
| W      | Ceramic quartz - Grove Priory  
nr. Leighton Buzzard.  
Mediaeval tile. |
| X      | Ceramic quartz - Beverly  
nr. Humberside.  
Mediaeval tile. |
| Y      | Ceramic quartz - London.  
12th - 13th century hearth tile. |
| Z      | Ceramic quartz - Newbury, Berks.  
Mediaeval tile. |
### Simplified Decay Scheme for U, Th, K, and Rb

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Decay Const. ($\times 10^{-9}$)</th>
<th>Emitted Radiation</th>
<th>Gamma Energy (MeV)</th>
<th>Gamma Fraction ($\times 10^{-9}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{232}$Th</td>
<td>1.6 $\times 10^{-18}$</td>
<td>$\alpha, \gamma$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^{228}$Ra</td>
<td>3.1 $\times 10^{-9}$</td>
<td>$\beta$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^{228}$Ac</td>
<td>6.1 $\times 10^{-7}$</td>
<td>$\beta, \gamma$</td>
<td>1.91</td>
<td>9.3</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>1.2 $\times 10^{-8}$</td>
<td>$\alpha, \gamma$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^{234}$Ra</td>
<td>2.3 $\times 10^{-5}$</td>
<td>$\beta, \gamma$</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>$^{218}$Po</td>
<td>4.5 $\times 10^{-9}$</td>
<td>$\alpha$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^{212}$Po</td>
<td>1.8 $\times 10^{-5}$</td>
<td>$\beta, \gamma$</td>
<td>0.075</td>
<td>9.6</td>
</tr>
<tr>
<td>$^{212}$Bi</td>
<td>1.9 $\times 10^{-4}$</td>
<td>$\alpha, \beta, \gamma$</td>
<td>0.727</td>
<td>6.5</td>
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<tr>
<td>$^{212}$Pb</td>
<td>2.3 $\times 10^{-6}$</td>
<td>$\alpha, \gamma$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^{208}$Tl</td>
<td>3.7 $\times 10^{-3}$</td>
<td>$\beta, \gamma$</td>
<td>2.01</td>
<td>36.0</td>
</tr>
<tr>
<td>$^{13}$Al</td>
<td>1.7 $\times 10^{-17}$</td>
<td>$\beta, \gamma$</td>
<td>1.46</td>
<td>10.7</td>
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</table>

Note: The table continues with similar entries for other isotopes and decay constants.
APPENDIX E

Infinite Matrix Dose-rate (mrad/s/y) of the Equilibrium Groups
(CARRIVEAU, 1978)

<table>
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<tr>
<th>Group No. &amp; Parent</th>
<th>$\alpha$-Dose rate</th>
<th>$\beta$-Dose rate</th>
<th>$\gamma$-Dose rate</th>
<th>Total Dose rate</th>
<th>Series Parent</th>
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</thead>
<tbody>
<tr>
<td>Th$_1$, Th$^{232}$</td>
<td>8.203</td>
<td>.915</td>
<td>1.437</td>
<td>10.56</td>
<td>Th$^{232}$</td>
</tr>
<tr>
<td>Th$_2$, Th$^{228}$</td>
<td>22.68</td>
<td>.041</td>
<td>.027</td>
<td>22.75</td>
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</tr>
<tr>
<td>Th$_3$, Rn$^{220}$</td>
<td>42.76</td>
<td>1.796</td>
<td>2.998</td>
<td>47.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equilibrium Total Series Dose = 80.86</td>
<td></td>
</tr>
<tr>
<td>U$_1$, U$^{238}$</td>
<td>26.47</td>
<td>5.608</td>
<td>.130</td>
<td>32.21</td>
<td>U$^{238}$</td>
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<tr>
<td>U$_2$, U$^{234}$</td>
<td>30.02</td>
<td>.071</td>
<td>.004</td>
<td>30.10</td>
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<td>U$_3$, Th$^{230}$</td>
<td>29.39</td>
<td>.077</td>
<td>.013</td>
<td>29.48</td>
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<td>U$_4$, Ra$^{226}$</td>
<td>30.10</td>
<td>.022</td>
<td>.052</td>
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<tr>
<td>U$_5$, Rn$^{222}$</td>
<td>120.77</td>
<td>5.917</td>
<td>12.110</td>
<td>138.80</td>
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<tr>
<td>U$_6$, Pb$^{210}$</td>
<td>33.46</td>
<td>2.671</td>
<td>.001</td>
<td>36.14</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equilibrium Total Series Dose = 296.9</td>
<td></td>
</tr>
<tr>
<td>U$^{235}$</td>
<td>11.61</td>
<td>.361</td>
<td>.120</td>
<td>12.09</td>
<td>U$^{235}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1/138 ppm)</td>
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</tr>
<tr>
<td>K$^{40}$</td>
<td>-</td>
<td>82.3</td>
<td>24.7</td>
<td>107.0</td>
<td>K$^{40}$</td>
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<td></td>
<td></td>
<td>(1% Nat. K)</td>
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</tr>
<tr>
<td>Rb$^{87}$</td>
<td>-</td>
<td>.19</td>
<td>-</td>
<td>.19</td>
<td>Rb$^{87}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1 ppm Rb$^{87}$)</td>
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APPENDIX F

Graph of 'k' - Values

\[ \text{Probability (\%)} \]

[Graph showing a curve with axes labeled 'y' and 'x', depicting the relationship between probability and values of 'k'.]
A Separation Technique for the Inclusion Dating Method

An essential step in the inclusion dating technique, is the extraction from the sample of the TL mineral fraction. For the most typical case, this requires the separation of quartz, although other minerals, for example feldspars, zircon and calcite, are of interest in TL dating.

The techniques most applicable to TL dating are based on: 1) Floating the crushed sample in a 'heavy' liquid, and adjusting the liquid's density to permit the required mineral to sink, and thus be removed, or 2) Magnetic separation, whereby the magnetic fractions of a crushed sample are removed at varying field strengths, depending on the magnetic susceptibility of the TL fraction. The latter technique is generally found to be more sensitive to the samples provenance. The magnetic separator has been used successfully in recovering quartz fractions of up to 90% of the total (GAULIN, 1981).

The heavy liquid separation technique requires simple apparatus, and is quick and easy to use. The description below, shows the use of only one heavy liquid (bromoform), although other more dense liquids may be employed. See table (G1). It was found that bromoform has an advantage in being simple to recover to its original specific gravity after dilution.

The description below gives a successful method for the separation of quartz from a typical shard, whilst table (G2) presents the ranges of specific gravity for some minerals of possible interest in TL dating.

1) The sample is crushed in a mortar, and the required size fraction extracted by sieving (usually in the range 50-150μm).
2) The separated size fraction is washed in distilled water to remove dust sized particles, and subsequently placed into a hot acid bath to encourage any further disaggregation (hydrochloric acid, 80°C). This last treatment also removes any acid soluble minerals (e.g. calcite and apatite).

3) After re-sieving, the sample is dried before being poured into a separating funnel containing the undiluted bromoform. Any minerals which do not float at this stage are discarded.

4) Acetone is added dropwise with careful stirring of the mixture. When it becomes apparent that a large percentage of the sample does not immediately float after the stirring has stopped, the mixture should be left to settle for approximately 10 minutes.

5) The quartz (heavy fraction) will be evident by the predominantly white crystals at the neck of the separating funnel, whilst the brown/red light fraction still floats upon the bromoform. The quartz fraction may now be removed.

6) After filtering the light fraction, the bromoform may be recovered to its maximum specific gravity by mixing with distilled water (acetone is soluble in water, whilst bromoform is not), and separating the two immiscible liquids.

7) The quartz fraction may now be etched in 48% hydrofluoric acid before being thoroughly washed (distilled water and acetone) and dried.

N.B. An alternative technique to be used when time is short, is to slowly add hydrofluoric acid to the unseparated sample (after crushing), and when all reaction appears to have stopped, dilute the mixture with excess water, and remove the remaining non-soluble fraction. Quartz is found to predominate this fraction, which may now be etched further.
Table (G1)

Heavy Liquids for Mineral Separation (ALLMAN, 1972)

<table>
<thead>
<tr>
<th>Heavy liquid</th>
<th>Max. sp.gr. (20°C)</th>
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<tr>
<td>Bromoform</td>
<td>2.87</td>
</tr>
<tr>
<td>Tetrabromoethane</td>
<td>2.96</td>
</tr>
<tr>
<td>Methylene iodide solution</td>
<td>3.30</td>
</tr>
<tr>
<td>Clerici's solution</td>
<td>4.25</td>
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</table>

Table (G2)

The Specific Gravity of some useful Minerals (ALLMAN, 1972)

<table>
<thead>
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<th>Mineral</th>
<th>Range of sp. gr.</th>
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<tr>
<td>Apatite</td>
<td>3.17 - 3.23</td>
</tr>
<tr>
<td>Calcite</td>
<td>2.71</td>
</tr>
<tr>
<td>Corundum</td>
<td>3.90 - 4.10</td>
</tr>
<tr>
<td>Feldspar</td>
<td>2.50 - 3.20</td>
</tr>
<tr>
<td>Fluorite</td>
<td>3.00 - 3.25</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.65</td>
</tr>
<tr>
<td>Zircon</td>
<td>4.70</td>
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APPENDIX H

Uranium / Thorium Standard Spectrum
(19.2mg U$^{238}$, 47.2mg Th$^{232}$ in 10g SiO$_2$ - 63 hour count)

Detector Resolution

Peak Energy = 1.764MeV (from Bi$^{214}$)
FWHM = 2.9keV
Peak Counts = 26481 (64hours)
Background = 4619 (64hours)