

# Ancient TL

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"But, Sir, though I be very backward to admit strange things for truths, yet I am not very forward to reject them as impossibilities; and therefore I would not discourage any from making further enquiry, whether or no there be really in rerum natura any such thing as a true carbuncle or stone, that without rubbing will shine in the dark." Sir Robert Boyle, in a letter to Sir Robert Morray, to accompany his "Observations about Mr. Clayton's diamond.

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# THERMOLUMINESCENT DATING: APPARATUS AND PROCEDURE FOR MEASUREMENT OF THERMOLUMINESCENCE

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## Introduction

A study of thermoluminescent (TL) dating has recently commenced at Durham. The method of heating the sample of ceramic differs from the direct heating of a nichrome strip commonly employed in other laboratories, and the main purpose of this note is to outline the method and the results it is giving. Another point is that TL results are being obtained while heating the sample in vacuum rather than in a flow of nitrogen, which is the practice in most laboratories.

We have used indirect heating of the hot plate, requiring a current of little more than 3 amp. This results in an inexpensive control unit, as it avoids a heavy current transformer and heavy current control devices. Another advantage is that the thermocouple welded to the hot plate is isolated from the heating circuit. The use of vacuum rather than nitrogen started in the first place because access to this laboratory is rather difficult, and transport of nitrogen cylinders was to be avoided if possible.

## Experimental Arrangement

A nickel hot plate is used as in Figure 1, 0.1 mm sheet, 45 mm diameter, with a shallow central recess to locate the 10 mm nickel disc which contains the sample. Another advantage of this system is that the presence of such a recess does not lead to any non-uniformity of temperature, as may occur in a directly heated strip. An 8 ohm helical winding of 30 gauge Kanthal A wire (0.0124", 17 ohm per 36") provides the indirect heating, and is insulated from the hot plate by the pyrophyllite base disc below and a thin mica sheet above. The thermocouple wires are welded separately to the top of the hot plate, one each side of the recess. Three brackets of 0.1 mm nickel sheet support the plate from the central spindle, giving very low heat loss by conduction.

The heating circuit involves a variable ramp generator and comparator, based on a circuit designed by W. L. Paterson, (Rev. Sci. Instr. 46 No. 2, pp. 196-197). An integrator drives a high-gain control element consisting of a darlington pair, which controls the heater input power, derived from a 30 volt D. C. supply. The ramp setting 4 was normally used, giving a heating rate of 5° per second linear with time to about 400°C. Higher ramp settings gave non-linearity before 400° was reached. For example, setting 6 which was sometimes used gave a linear rise of 10°/sec. to 150°C, falling at higher temperatures. These were the highest rates obtainable with this heater winding and supply. Higher rates could no doubt be obtained by re-design, but there is no evidence so far that this is necessary. A temperature cut-off was provided in the circuit, which was set either at 450 or 500°C for pottery samples, or at 320°C when working with phosphors in teflon for TL dosimetry.

The hot plate was mounted in a brass cylinder which could be evacuated using a Speedivac single stage pump 1SC30A. This has produced pressures between 0.2 and 0.4 mm. The cylinder was enclosed in a lead castle so that irradiation of the sample could be carried out in situ when required. The lid to the cylinder, mounted via an o-ring seal, carried the photomultiplier (PM) type 9635 Q/B. The light from

the sample passed through a spectro-sil window, which also gave a vacuum seal via an O-ring; then through an OB14 blue filter, an HA3 infra-red absorbing filter, and finally a silica light-collecting cylinder 16 mm long and 35 mm diameter. The multiplier was normally operated at 1200V. A microswitch on the brass lid protected the PM in case it was lifted and exposed to light with the volts applied.

The signal from the PM passed through a pulse amplifier/photon ratemeter (Littlemore Sci. Eng.) to the Y-axis of a Bryans X-Y recorder 25000 A4. The thermocouple wires were connected to the control circuit which gave an output to the X-axis of the recorder.

The disadvantage of the above scheme is the slow cooling rate, particularly in vacuum. The time from 500° to 125°C is 5 minutes, and the total time to 30° is about 15 minutes. This can be accelerated a little by opening to air on falling to 80°, which seems to do no harm, or passing a flow of N<sub>2</sub> at any stage (4 litres/min., O<sub>2</sub> free). As explained, this is avoided if possible. It might be feasible to provide water-cooling for the hot-plate, but the structure is rather fragile, and the whole point of the design is to minimize heat loss, so that this possibility has not so far been seriously considered.

An artificial dose of  $\beta$ -radiation could be provided using a Sr90 1mCi foil source SIC12, originally from Harwell. This was mounted with Prespex, lead and brass protection on a circular brass plate the same size as the lid carrying the PM. This could be removed and replaced by the Sr90 source, which was then 0.6" above the Ni disc when it was in position in the recess in the hot plate. The source was calibrated by exposing phosphor test specimens to the source for various times, the specimens being in position on one of the Ni discs. The phosphors were provided and the calibration carried out by Dr. A. McKinlay of the National Radiological Protection Board at Glasgow. It has so far been assumed that the dose received by the ceramic samples is the same as that received by the phosphor when in the same position on the hot plate.

#### Comparison of vacuum and nitrogen atmospheres

(a) Wear-side sand. Samples of sand from the river-side at Willington gave a large and complex TL output above 250°C, either as received or after subsequent  $\beta$ -doses. Clear grains were prepared by washing in dilute HCl for 15 min., and etching in HF for 30 min. The geological TL was cleared by heating to 450°C, and standard artificial doses of 10 rad were given. Figure 2 shows the resultant TL in vacuum compared with that in O<sub>2</sub>-free nitrogen, flowing at 4 litres per min. The quartz peak is seen at 105°C, and peaks attributable to CaF<sub>2</sub> at 205 and 305°C.

It will be recalled that the thermocouple is welded to the hot plate, so that the sample will be at a lower temperature than that recorded. Figure 2 shows that the temperature lag in vacuum is greater than that in nitrogen, by about 20° at 100° and about 50° at 300°C. This would lead to some difficulty in interpreting conventional TL plots obtained in vacuum, though this could be overcome. There would, however, be no difficulty in interpreting predose results using quartz inclusions, and the height of the 105° quartz peak is the same in vacuum as in N<sub>2</sub>. Thus this result indicates that there is no objection to the use of vacuum. Of course, it is appreciated that the lag between vacuum and N<sub>2</sub> would be greater with better vacuum or higher heating rates.

Incidentally, the presence of CaF<sub>2</sub> in the sand had not been expected when the work started, but the conclusion from TL has been confirmed by X-ray analysis.

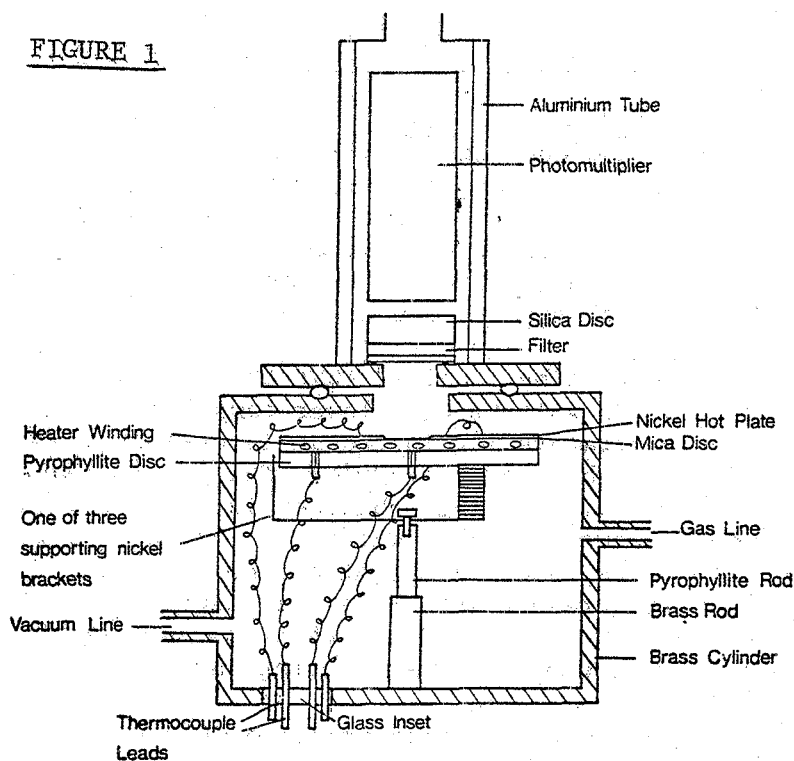
(b) North-east ceramics. Measurements are proceeding on pottery and tiles from two sites in Co. Durham, and on hearth tiles from the York Minster undercroft project. (D. Phillips, 1975, Friends of York Minster 46th Annual Report, pp. 19-27.) Figure 3 shows some typical plots of TL against thermocouple temperature in vacuum obtained from quartz grains from a York Minster sample of Roman tile. Our predose procedure follows Aitken and Murray (1976 Edinburgh Symposium Report), and it is hoped to publish the results of both predose and conventional TL when the self and soil dose-rates have been determined. In the meantime, Figure 3 indicates that the rather slow heating rate nevertheless leads to satisfactory TL plots. The poor vacuum may not be adequate for conventional TL, but is expected to be satisfactory for predose measurements. The archaeological doses so far determined for samples of medieval pottery from the two sites in Durham are in fact of the magnitude expected.

#### Acknowledgement

The ramp generator was designed and built by P. Bedall, final year undergraduate project in Applied Physics, 1976, aided by P. Friend, Electronics Technician in Applied Physics Department, University of Durham.

[Editor's note: As alluded to in the text, the dose rate from a beta source to a calibration phosphor such as  $\text{CaF}_2$  or  $\text{LiF}$  is not identical to that to a sample of quartz but differs by the ratio of their specific electron stopping powers. The specific electron stopping power is a function of sample composition and beta particle energy and is most conveniently obtained from tables (e. g. M. J. Berger and S. M. Seltzer, Tables of Energy Losses and Ranges of Electrons and Positrons, NASA Report SP-3012, 1964). The variation between most common phosphors is generally less than 10%.]

FIGURE 1



Hot Plate Assembly

Willington Sand:  
A Comparison of heating in N<sub>2</sub> and vacuum

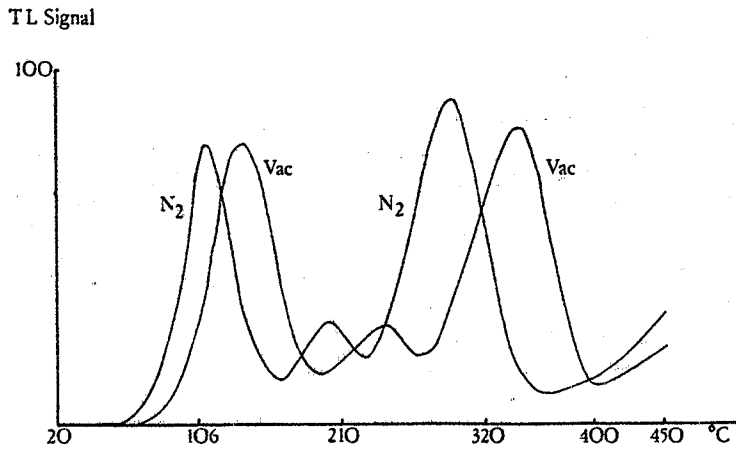


FIGURE 2

TL plots obtained in vacuum using 10 grains of quartz from "York Roman Tile"

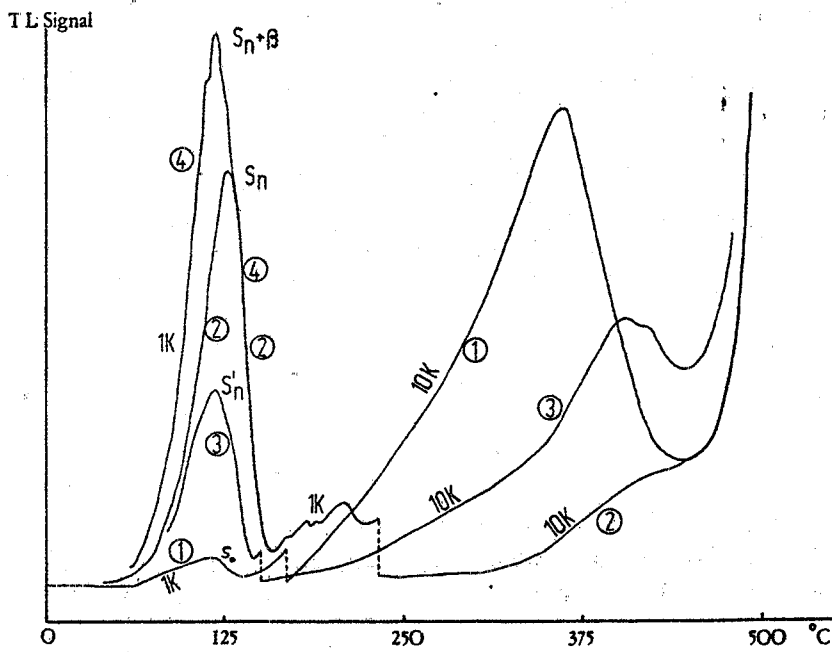


FIGURE 3

## TL COLOUR: HIGH VS LOW DOSE MEASUREMENTS AND THE PRE-DOSE MECHANISM

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The following spectra were recorded using a spinning interference spectrometer (to be published, J Phys:E) from a sample of quartz extracted from Egyptian medieval pottery (ref. 506cl) that has been dated by TL as being fired around 500 years ago. The spectra were recorded in the temperature range 350 - 400°C of the glow curve and were obtained in sequence from the same sample after various beta ( $^{90}\text{Sr}/^{90}\text{Y}$ ) irradiations. The spectra shown have been corrected for instrument response and have been normalized on the basis of total photon count. The sample was heated at  $10^\circ \text{sec}^{-1}$  in an atmosphere of oxygen-free nitrogen to a maximum of 500°C.

### Discussion

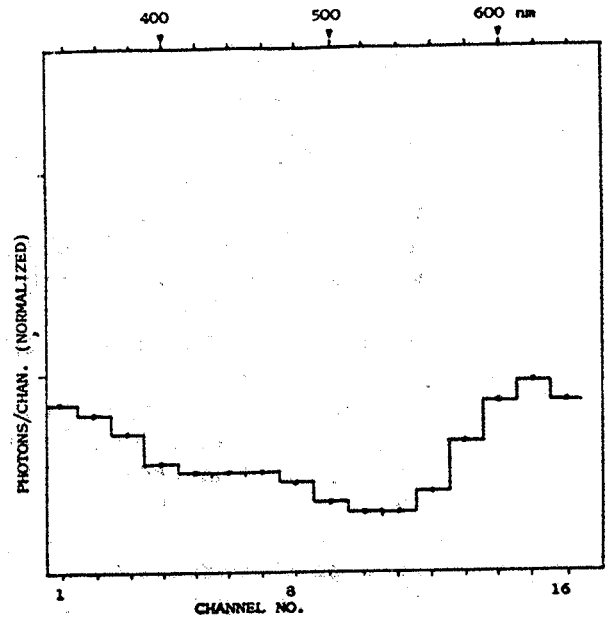
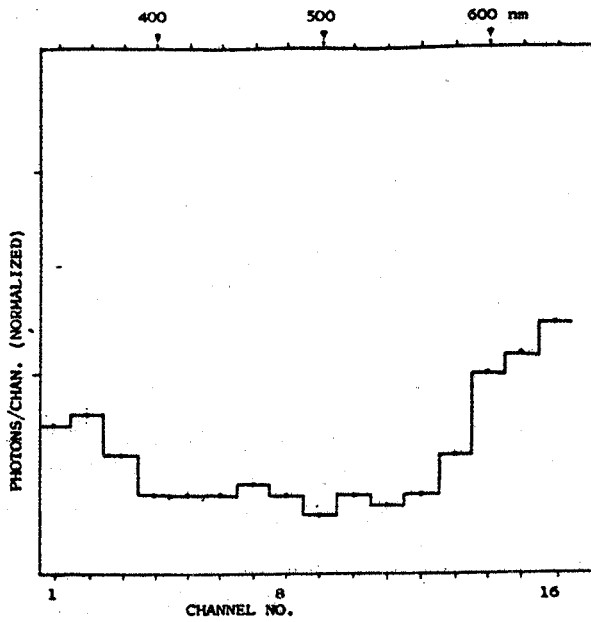
Although the test dose is large compared to the natural dose, the change in spectra shown in figs 1a and 1b is small. However, the high dose (46 krad) spectrum, fig 1c, is significantly different and would be a misleading guide to that to be expected after a dose of 5 krad. The effect of the pre-dose mechanism is shown clearly by the marked difference of fig. 1d in comparison with fig. 1b, which has given rise to a relatively higher enhancement in the blue (460 nm) region of the spectrum. The glow curve intensity after the administration of the third test dose had changed by a factor of four.

These results underline the necessity of making low dose spectral measurements and that spectra obtained at dose levels which are many hundreds of times higher than the natural dose, may be quite misleading.

### Acknowledgements

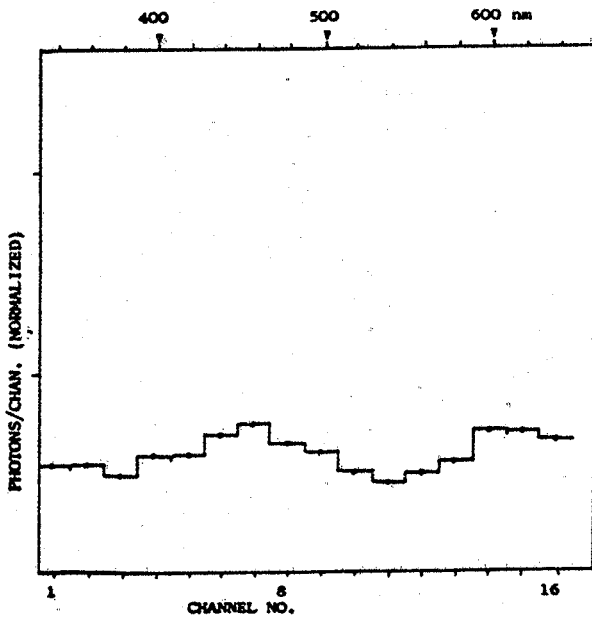
The age measurement on this sample was made by Joan Huxtable of this laboratory. The spectrometer was built with the aid of a grant from the Paul Instrument Fund of the Royal Society.

**FIGURE 1 : TL SPECTRA (reproducibility  $\pm$  5%)**

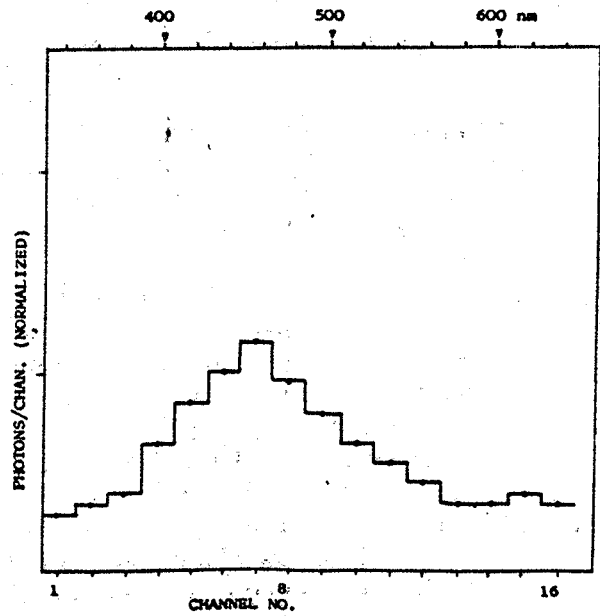


after a beta test dose of 5 krad in addition to the accrued archaeological dose equivalent to 150 rad.

b) after a beta test dose.



c) after a beta dose of 46 krad.



d) after a beta test dose.

# TL DATING: ERROR IMPLICATIONS IN CASE UNDETERMINED U-TH CONCENTRATION RATIO IN POTTERY SAMPLES

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## Introduction

Fleming (1976), while summarizing the present state of art of TL dating technique in archaeology, has put the error estimate of TL age determination at  $\pm 7$  to 10% contributed by uncertainties in factors such as spurious TL, alpha efficiency, supralinearity, anomalous fading, water uptake and radon escape. In routine work there is often a tendency to do away with the absolute determination of Th and U impurity contents in the pottery and measure only the gross alpha activity and calculate the dose rates assuming a Th/U weight ratio of about 3.16 (Aitken, 1976); this will be yet another factor contributing to the error limits for the TL age determinations. There is also a practice of assuming the entire alpha activity of the pottery as due to uranium and an error estimate of about 6% is often quoted for the final TL age obtained (Tite, 1968). Aitken and Aildred (1972) assumed that the fraction of total alpha counts which arises from the  $^{232}\text{Th}$  series is  $(0.35 \pm 0.1)$  and accordingly have given error limits for their dose rate conversion factors to take care of the uncertainty in Th/U ratio.

In this paper the error in the TL age is estimated when the Th/U ratio is not determined but only the gross alpha count rate is measured from an infinitely thick sample as has been suggested by Tite and Waine (1962); the best value to assume for the Th/U ratio is taken to be that for which the dose rate is the median value between the extreme limits  $\text{Th/U} = 0$  and  $\text{Th/U} = \infty$ .

## Dose rate conversions

Bell (1976, 1977) has calculated the conversion factors from gross alpha count rates to annual dose rates from alpha, beta and gamma radiation for a typical pottery containing Th and U in the ratio of 3.167. Making use of the same basic data provided by him, calculation of dose rate conversion factors for the gross alpha count rates are made for arbitrary Thorium and Uranium concentrations at Th/U weight ratios covering the entire range  $0 \leq \text{Th/U} \leq \infty$  and assuming secular equilibrium conditions (Table 1).

In practical applications when a particular gross alpha count rate is obtained on a pottery sample, one is interested to know the conversion factor to be used to obtain the dose rate and the uncertainty involved owing to the unknown relative concentrations of Th and U in the sample. This is best illustrated by a plot of the dose rate conversion factors against Th/U concentration ratio (Figure 1). All the three curves for  $\alpha$ ,  $\beta$ , and  $\gamma$  approach asymptotically the limiting values corresponding to  $0 \leq \text{Th/U} \leq \infty$  and the median values for the three components correspond to a Th/U concentration ratio of about 3.55 as shown in the figure. In the absence of a knowledge about the relative concentrations of Th and U when only the gross alpha surface emission rate  $C_\alpha$  is known, it then follows that the relevant dose rates ( $D_\alpha$ ,  $D_\beta$  and  $D_\gamma$ ) should be obtained as follows:

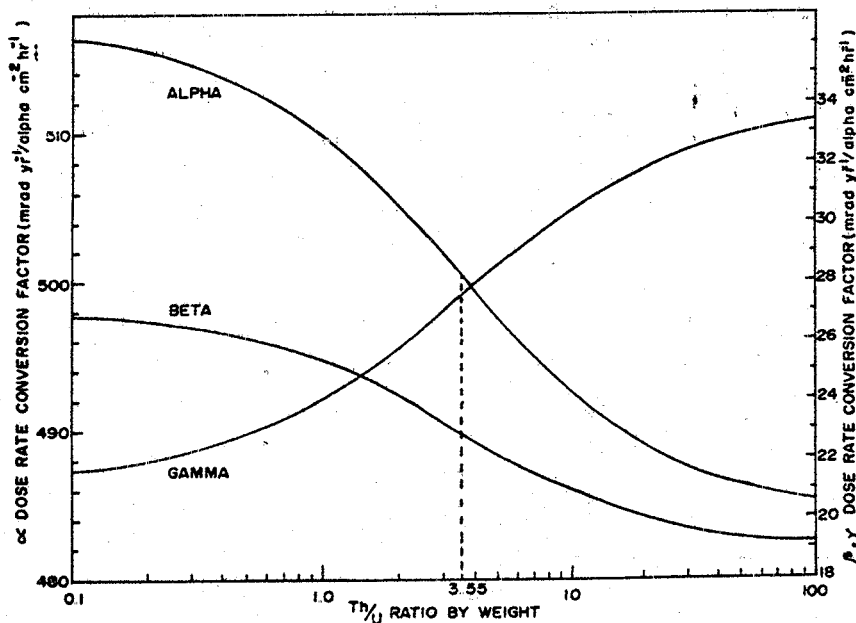
$$\begin{aligned} D_\alpha &= 500.6 C_\alpha \pm 3.3\% \text{ mrad. yr}^{-1} \dots \dots \dots (1) \\ D_\beta &= 23.0 C_\alpha \pm 18.3\% \text{ mrad. yr}^{-1} \dots \dots \dots (2) \\ D_\gamma &= 27.5 C_\alpha \pm 22.5\% \text{ mrad. yr}^{-1} \dots \dots \dots (3) \end{aligned}$$



Table 1

Dose rate conversion factors

U ppm	Th ppm	Th/U	Gross alpha surface emission rate $\text{cm}^{-2} \text{hr}^{-1}$ $C_{\alpha}$	Dose rate conversion factors $\text{mrad. yr.}^{-1}$ per alpha emitted per $\text{cm}^2 \text{hr}$		
				alpha $D_{\alpha}$	beta $D_{\beta}$	gamma $D_{\gamma}$
0.00	1.00	$\infty$	0.1525	483.93	18.75	33.70
0.01	0.30	30.0	0.0511	487.44	19.64	32.40
0.10	2.00	20.0	0.3588	488.92	20.02	31.85
0.10	1.50	15.0	0.2826	490.28	20.36	31.35
0.10	0.90	9.0	0.1916	493.33	21.13	30.22
1.00	5.00	5.0	1.3005	497.73	22.24	28.59
0.50	1.50	3.0	0.4978	501.96	23.30	27.02
1.50	3.00	2.0	1.2645	505.22	24.13	25.81
1.00	1.00	1.0	0.6905	509.92	25.31	24.07
0.50	0.30	0.6	0.3148	512.44	25.95	23.14
0.40	0.12	0.3	0.2335	514.67	26.51	22.31
1.00	0.00	0.0	0.5380	517.29	27.17	21.34



VARIATION IN DOSE RATE CONVERSION FACTORS FOR VARIOUS Th/U CONCENTRATION RATIOS IN POTTERIES. (THE MEDIAN VALUES FOR THE CONVERSION FACTORS OCCUR WHEN Th/U CONCENTRATION RATIO IS 3.55)

FIGURE 1

The constants in the above equations refer to conversion factors obtained at a Th/U ratio of 3.55 in Figure 1; the extent of variations possible in the conversion factors when the actual Th/U ratio lies anywhere between 0 and  $\infty$  are indicated by the percentage factors. At half the given error variations, the Th/U concentration ratio limits correspond to 1.2 and 10.5 as can be seen from the figure and these represent more or less the practical range in which most of the pottery samples can be found to possess the Th and U impurities. Hence for all practical purposes, the errors involved in the dose rate estimates due to uncertainty in the Th/U ratio will be only  $\pm 1.7\%$ ,  $9.2\%$ , and  $11.3\%$  respectively for the  $\alpha$ ,  $\beta$  and  $\gamma$  components.

The equations arrived at above are of most general applicability and the error limits are significantly different, compared to what can be surmised from the findings of Aitken and Alldred (1972):

$$\begin{aligned}
 D_{\alpha} &= 146.0 C_{\alpha}^{\dagger} \pm 0.7\% \text{ mrad. yr}^{-1} \dots\dots\dots (1) \\
 D_{\beta} &= 6.2 C_{\alpha}^{\dagger} \pm 3.9\% \text{ mrad. yr}^{-1} \dots\dots\dots (2) \\
 D_{\gamma} &= 8.8 C_{\alpha}^{\dagger} \pm 6.8\% \text{ mrad. yr}^{-1} \dots\dots\dots (3)
 \end{aligned}$$

where  $C_{\alpha}^{\dagger}$  is the gross alpha counts per kilosecond (for a thick source of diameter 42 mm and for 85% counting efficiency) and the constants refer to conversion factors obtained assuming the fraction of the total counts which arises from the  $^{232}\text{Th}$  series to be  $(0.35 \pm 0.1)$ .

Error in TL age estimates

To calculate the error component in the TL age estimates of pottery samples due to the above recommended dose rate conversion factors for gross  $\alpha$  count rate, the two usually adopted TL dating procedures have to be separately considered: (1) In the fine grain dating method, it can be assumed that the archaeologically significant equivalent dose is constituted by a 50% alpha component and a 10% beta component from Th and U chains in equilibrium; (2) In the quartz inclusion dating method, it can be assumed that the archaeologically significantly equivalent dose is constituted by a 25% beta component from the Th and U chains in equilibrium. The above assumptions are borne out of available published data on a large number of pottery samples (Aitken et al., 1968; Fleming, 1970; Zimmerman, 1971; Aitken et al., 1971; Sasidharan et al., 1975). Accordingly, the error components that will be reflected in the TL age estimate are given below in Table 2.

Table 2 Error component in TL age estimate

TL dating method	Error component involved in the age estimate if a nominal Th/U weight ratio of 3.55 is assumed for the gross alpha activity	
	when $0 \leq \text{Th/U} \leq \infty$	when $1.2 \leq \text{Th/U} \leq 10.5$
1. Fine grain method	$\pm 3.5\%$	$\pm 1.8\%$
2. Quartz inclusion method	$\pm 4.6\%$	$\pm 2.3\%$

It is obvious that in rare occasions when there is not much K in a pottery sample, the error component due to uncertainty in Th/U ratio will be substantially more.

### Conclusion

Thus, the calculations presented above lead to the following recommendations for TL age estimations using (Th + U) gross alpha count rates (under secular equilibrium): (1) the dose rate conversion factors to be used for  $\alpha$ ,  $\beta$  and  $\gamma$  components of (Th + U) present in pottery are respectively 500.6, 23.0 and 27.5  $\text{mrad. yr}^{-1}$  per alpha emitted per  $\text{cm}^2\text{hr}$ , and these correspond to a Th/U concentration ratio of 3.55 and (2) the error component appearing in the final TL age estimate due to the above assumption will be  $\pm 4\%$  to  $5\%$  for  $0 < \text{Th/U} < \infty$  and will be practically only about  $\pm 2\%$  (for  $1.2 \leq \text{Th/U} \leq 10.5$ ) in most of the samples.

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