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Ancient TL

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"May: 'Oh. Have the crystals faults like us?'

Old Lecturer: 'Certainly, May. Their best virtues are shown in fighting their faults. And some have a great many faults; and some are very naughty crystals indeed.' "

(John Ruskin, "The Ethics of the Dust, Ten Lectures to Little Housewives on the Elements of Crystallisation", 1866).

IN THIS ISSUE . . . . .

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A STUDY OF PHOTOTRANSFER IN ZIRCON, APRIL - JULY, 1978

An internal report by D. W. Zimmerman on his work during a visit to the Oxford Research Laboratory, edited by M. J. Aitken.

PURPOSES OF RESEARCH

1. To try to confirm I. K. Bailiff's finding that very deep traps in zircon do not fade (Nature 264, 531).

2. To try to improve sensitivity and to reduce the residual level in the transfer technique.

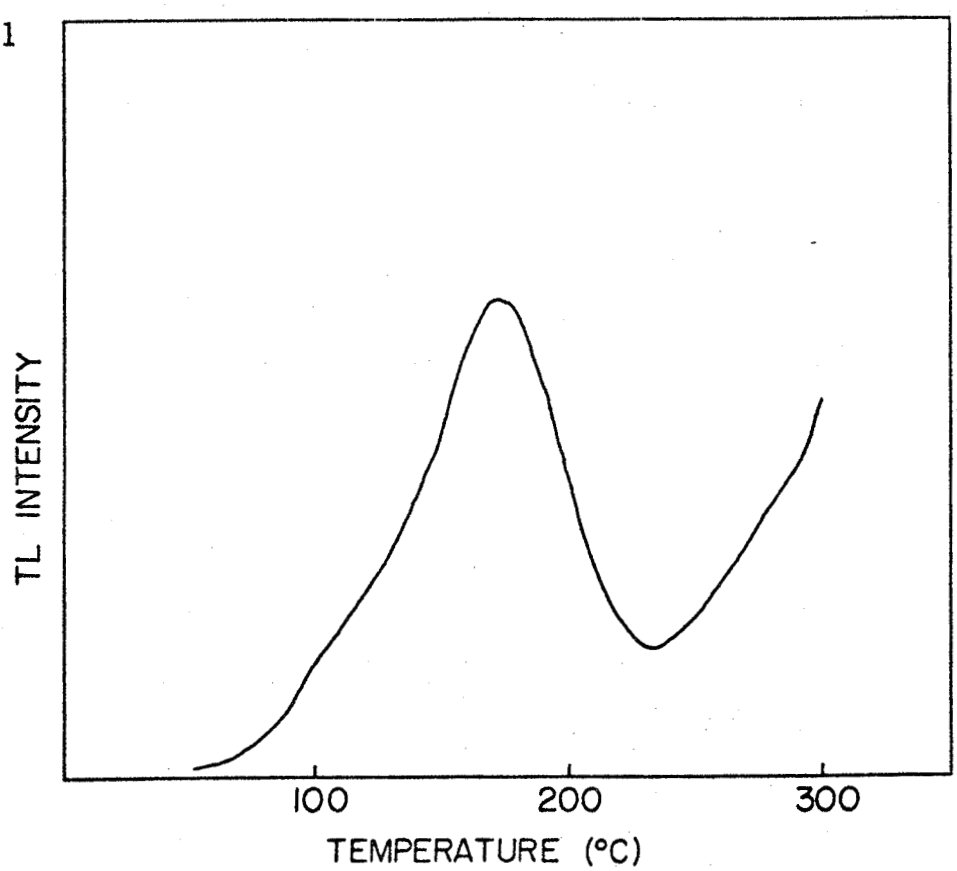
3. If 1 and 2 successful, to try transfer on zircon grains from archaeological ceramics, especially in the zircon 'natural' method (Sutton and Zimmerman, 1976, Archaeometry 18, 125).

RESULTS

A. Apparatus

Figure 1 shows a typical glow curve of transfer TL. The light was detected in all experiments using an EMI photomultiplier type 9635 without filters. Unless stated otherwise the illumination used for transfer was at a wavelength of 365 nm, and for 1 minute; this was using a 150-watt mercury lamp with a DGO Metrospec mono-chromator having an f number of 4. The set-up was that developed by S. G. E. Bowman with the sample at room temperature during transfer, except in section F.

FIG. 1

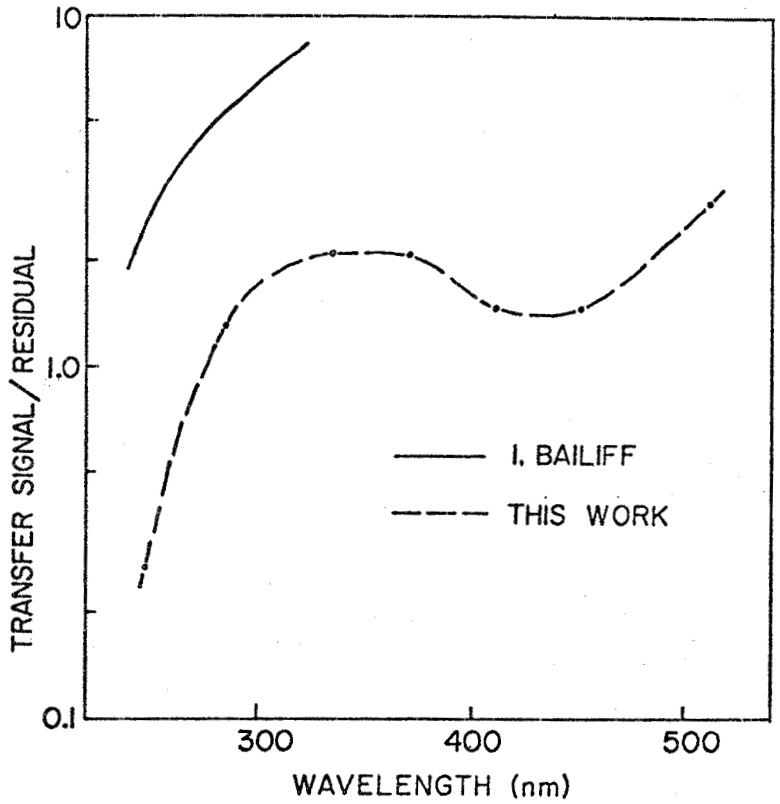


B. Wavelength dependence of transfer

(i) Instrument checks: by using various filters, it was determined that the monochromator output below 310 nm is deminated by stray light. Above 310 nm stray light is apparently unimportant, but all subeequent measurements were made with appropriate Corning color glass filter(s) in the beam to reduce stray light.

(ii) The ratio of transfer signal to residual signal was measured for Washington University (WU) sample Z-2 (geologic zircon) as a function of wavelength (Figure 2). As the quantum efficiency fell as the wavelength increased above 400 nm, the best region seemed to be about 320 to 380 nm. The intense 365 Hg line was subsequently used for most experiments.

FIG. 2



C. Fading of deep traps

WU samples Z-1 and Z-2 were beta irradiated (10 krads), heated to 475°C, the transfer signal measured 6 minutes after irradiation, and 2 days later. Corrections for bleaching during transfer were necessary. (Fading of 375°C TL = 25% (Z1) and 15% (Z2) in 2 days.)

Results:

Z-1	Fading + bleach	= 10.0 ± 0.7%
	Bleach alone	= 8.9 ± 0.3%
	Fading (2 days)	= 1.1 ± 0.8%
Z-2	Fading + bleach	= 3 ± 2%
	Bleach alone	= 3 ± 1%
	Fading (2 days)	= 0 ± 3%

(Bailiff result = 0 ± 3%, 6 months).

D. Residual signal

Bailiff (1976) reported a residual signal (annealed, unirradiated zircon) equivalent to about 10 krads. In the present work the levels were:-

Z-2, annealed 700°C, residual = 3000 rads
" " 900°C, " = 600 rads
" " 1200°C, " = 150 rads

Comparable residual levels were found (700° anneal) for Z-1, Z-12 and zircons from an Idaho baked soil. Archaeological firing may not exceed 700°C, so that is the relevant level.

(i) Optical bleaching

A wide variety of optical bleaches using various wavelengths from the monochromator and with a Hanovia germicidal lamp (Model 16) + filters. Most rapid bleaching was obtained with the Hanovia lamp plus Corning 0-52 filter (> 360 nm). Any light less than 320 nm was disastrous - it greatly increased the subsequent residual level.

Typical results with the Hanovia plus 0-52 filter were:-

700° annealed sample: residual = 3000 rads
after 1 hr bleach, " = 1500 rads
after 65 hr bleach, " = 460 rads

1220°C annealed sample: 150 rad residual not reduced by 1½ hr bleach.

(ii) Bleaching at elevated temperature

Bleaching for 5 min at 400°C was tried with three wavelengths; Hanovia plus 0-52, Hanovia plus 7-59, and Hanovia with no filters. All produced a small (about 50%) increase in the residual. Also, bleaching for 5 min at 700°C was tried with the Hanovia lamp plus 0-52 filter. It increased residual by x 3.

E. Sensitivity

The intensity of the transferred TL (from above 500°C) was compared to the direct TL (350°C) for three geologic zircon samples (annealed 700°C, then irradiated).

	transfer		direct		transfer
Sample	Dose (rads)	Peak ht. (cps)	Dose (rads)	Peak ht. (cps)	direct
Z-1	12K	11K	100	30K	1/300
Z-2	"	6K	"	80K	1/1600
Z-12	"	12K	"	35K	1/350

The sensitivity can be increased by x 20 using longer or more intense illumination.

F. Transfer at low temperature

Measurements on Z-2 were made in co-operation with S. Mobbs using her apparatus at about 20° above liquid nitrogen temperature. No significant change (compared to room temperature) was seen in the transfer signal intensity either of the residual or of a 2.3 Krad signal.

G. Alpha efficiency

All measurements above were made with beta irradiation (for convenience). One measurement on Z-2, annealed 700°C, 100 μm dia. grains in monolayer, was irradiated with a curium -242 source. The estimated dose was 8000 rads (one-fifth of the dose to fine-grains), within a factor of two. The alpha efficiency of the transfer TL and the direct 300° TL were found to be approximately the same, namely about 0.2.

H. Idaho Soil Zircons

Measurements were made on zircons from a 'pseudo' archaeologic sample - a lava baked soil from Idaho having an age of about 2300 years according to C-14 and quartz TL. The sample was about 1 mg of zircon in the size range 10 to 100 μm.

Results:

		Peak ht.
1.	Natural TL to 450°C	196 k cps
2.	Transfer (1 min, 365 nm)	45 k cps
3.	Beta irradiation, 5 krads	
4.	TL to 450°C	152 k cps
5.	Transfer	55 k cps
6.	Heat to 700°C	
7.	Transfer (residual)	2.0 k cps
8.	beta 5 krads	
9.	TL to 450°	133 k cps
10.	Transfer	2.2 k cps

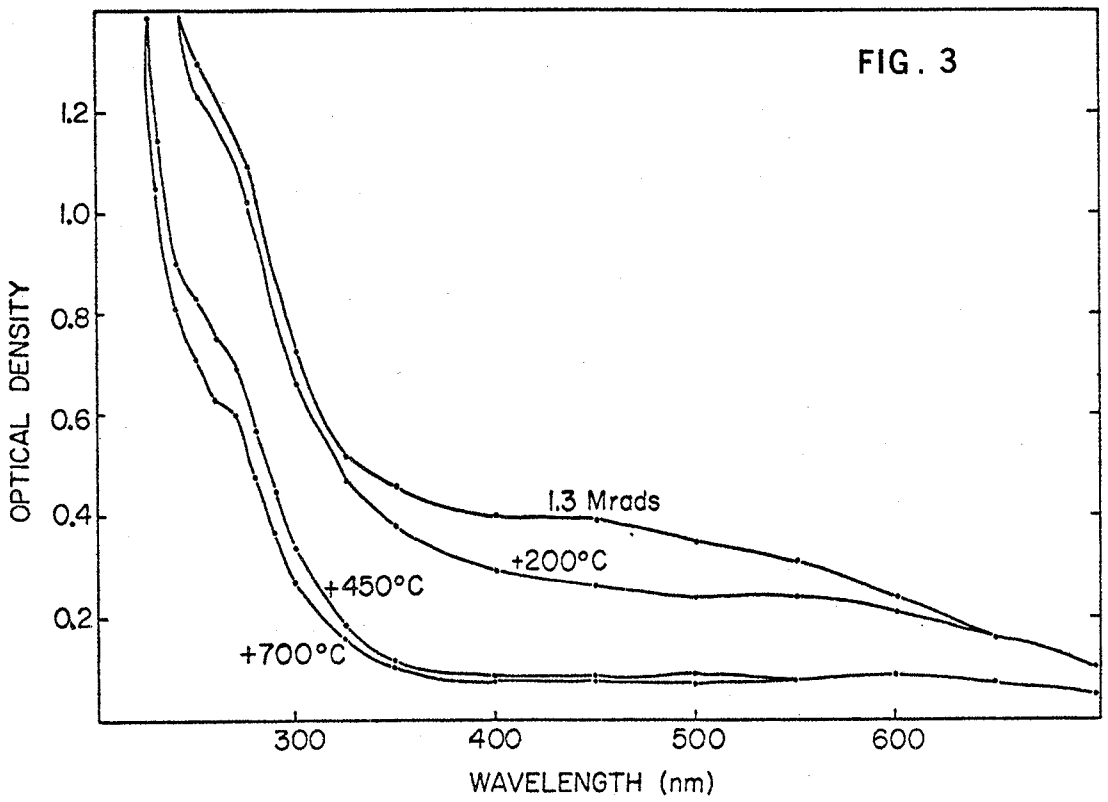
Comment:

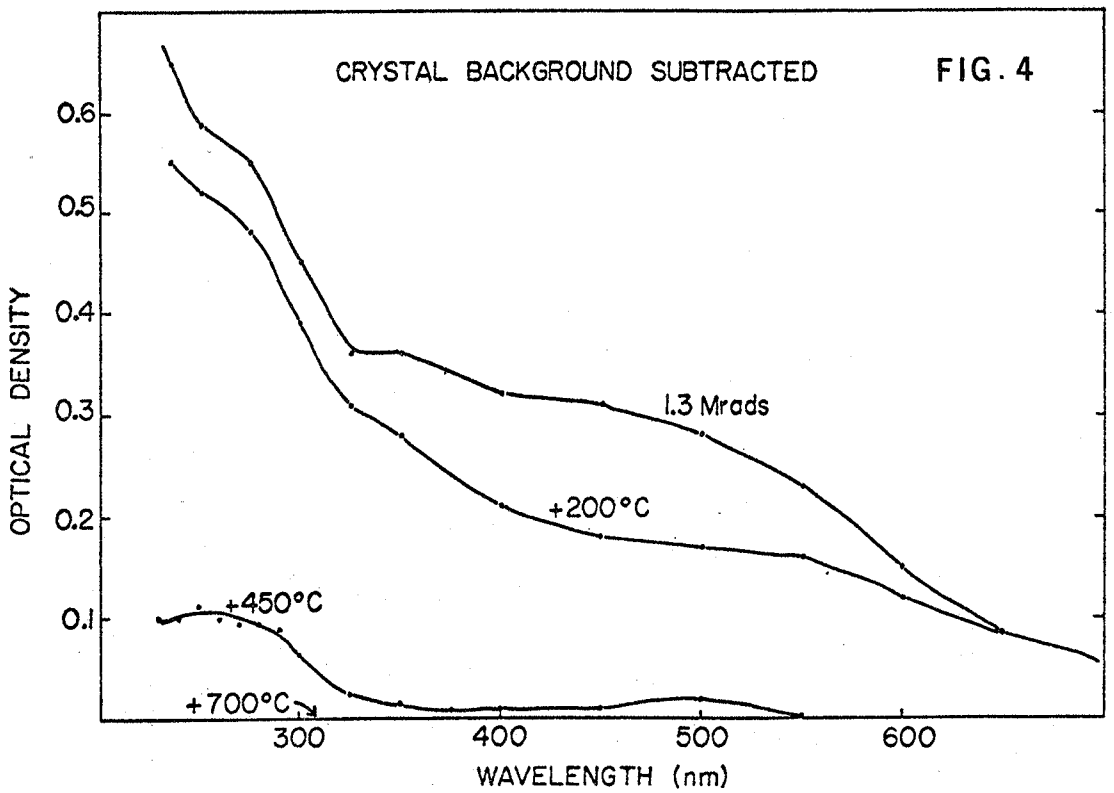
Transfer (from 5 krads) = 0.2 k cts/sec, direct TL (from 5 krads) = 125 k cts/sec. Therefore direct TL is at least 500 times more sensitive than transfer (in agreement with studies of geologic zircons, section E). The large transfer signal from the natural (step 2 above) was presumably from the geological dose, suggesting that the sample had not been heated high enough by the lava for resetting. If it had been, it appears that the sensitivity would have been marginal for measuring even the natural.

I. Optical Absorption Measurements

To obtain a better idea of what is happening, optical absorption measurements were made on a large single crystal of Z-12 (about 10 x 5 x 4 mm). The crystal was annealed for 1 hr at 700°C, mounted in araldite, and then ground on coarse sandpaper to expose two parallel faces. These were given a smoother grinding (600 grit on glass) and then polished (by R. Holland, Dept. of Geology, in charge of thin-section preparation). The sample (now 10 x 5 x 2 mm) was then removed from the araldite.

The sample was then run on a Cary 14 recording spectrophotometer (in Inorganic Chemistry, thanks to the co-operation of Dr Peter Day and Dave Woodwark). Figures 3 and 4 show the absorption curves obtained for a 1.3 megarad dose with annealling at the temperatures indicated.





Results:

(i) Irradiation produces absorption bands over the entire region 240 to 700 nm but the bands are extremely broad and unresolved.

(ii) As a function of temperature the bands are also very broad.

R.T. to 200°C	325 to 575 nm
200 to 450°C	240 to 650 nm
450 to 700°C	240 to 325 nm
700°C	240 to 300 nm

(iii) The 1.3 mega rad (no annealing) sample was also run at liquid nitrogen temperature - no measurable change.

Comment:

The results are in reasonable agreement with the transfer characteristics. The greatest efficiency for transfer from the 500 to 700° traps is around 250-300 nm. However, the well annealed crystal (700°C) also has a large absorption there giving rise to the large residual transfer. The rapid rise in absorption at 250 nm is presumably the fundamental absorption edge. The shoulder at 270 nm could be either from structural defects and impurities, or from still higher temperature traps filled by previous irradiation.

The broad nature of the bands and lack of structure implies that there is no gain to be found in measuring the transfer characteristics in smaller wavelength increments.

The overlap of the different temperature regions may explain some non-linearities and the saturation observed in transfer as a function of bleaching time.

J. High Temperature TL

An attempt was made to measure the 500-700° TL directly using Z-2, Z-3, Z-8 and Z-12. The normal TL equipment was used, heating rate 10°C/sec and an EMI type 9635 photomultiplier with two corning 5-58 and two HA3 filters.

Of these samples, Z-12 was the best, giving 5 k cts/sec at 550°C for a 5000 rad dose. The blackbody background was 1 k cts/sec. However the TL at 550° was 20 times less that the TL at 350°C. The TL from the other samples fell more rapidly still at high temperatures. That, combined with the loss in intensity from the extra filters, results in too low a signal to be useful for dating.

General conclusions

(i) There do seem to be non-fading deep (500-700°) traps.

(ii) They are probably in significant numbers - around 10^8/mg at 100 rads.

(iii) Optical transfer is not the way to measure them. The residual is 3 orders of magnitude too large for the 'natural' method. This appears to be a fundamental limitation arising from the impurity of the crystals. The sensitivity is also low, though that may not be a fundamental limitation.

Acknowledgement

This work was supported by a Senior Visiting Fellowship from the UK Science Research Council.

REDUCTION OF SPURIOUS TL IN ATMOSPHERES

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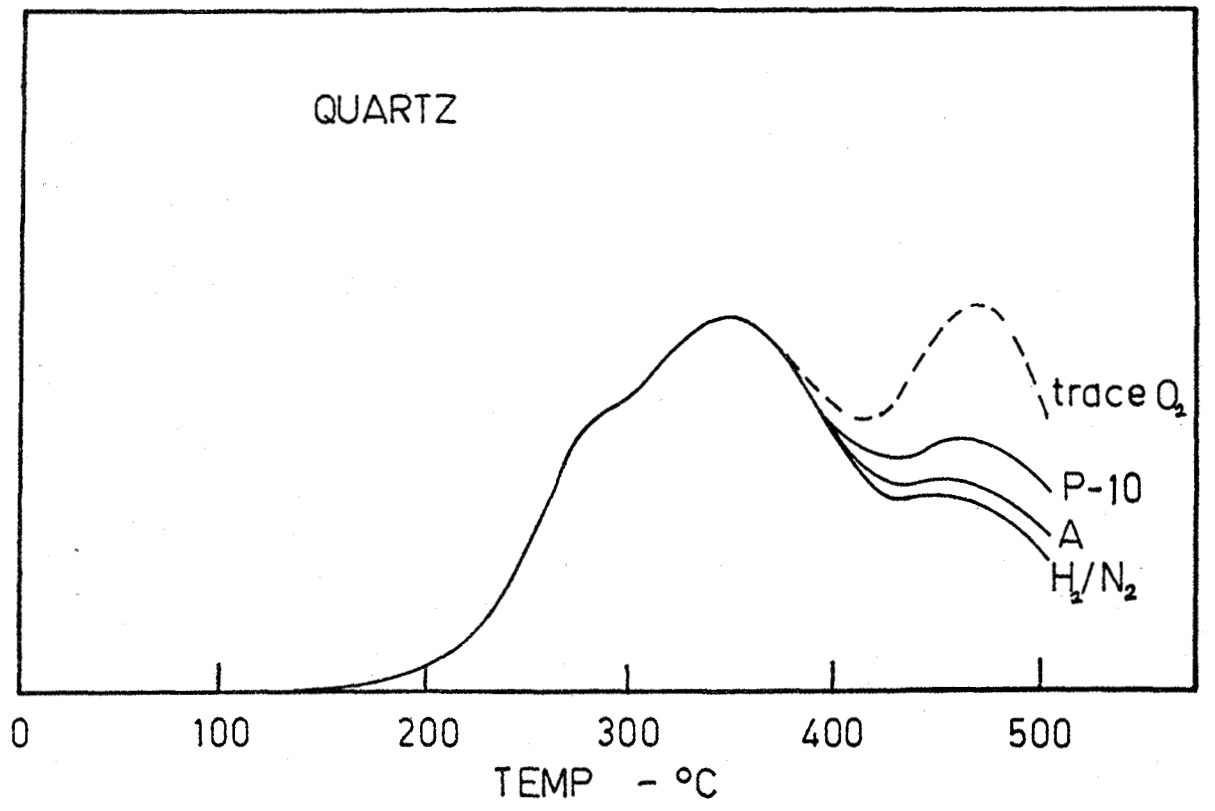
It is well-known that the so-called "Spurious TL" component of a glow curve can be reduced by heating samples in inert atmospheres having very low oxygen and moisture concentrations. The exact reasons for this have so far defied detailed explanation but it is quite clear that the lower the oxygen content of the gas in the TL system, the less likely is spurious TL to occur (see e.g. Sutton and Zimmerman, 1977). This suggests that some further improvement might be achieved with the use of chemically reducing atmospheres. Additionally, as an economic factor, the need for the use of high-purity gases might be avoided, or at least one might be able to tolerate a somewhat greater oxygen content in the gas used. A range of samples of archaeological and geological interest has been tested in a mixture of 5% hydrogen plus 95% nitrogen. (Manufacturer's specifications state: less than 10 ppm oxygen, less than 25 ppm moisture). Comparison was made with commercial high purity argon (less than 6 ppm oxygen, 12 ppm water). The samples tested included aboriginal hearthstones, baked clay, apatite, calcite, fluorite, zircon, pottery samples, various quartzes, as well as a variety of TLD phosphors. No great improvement was noted but in no case was the result worse than that obtained with the high purity argon. A mixture of 10% methane plus 90% argon, called P-10 and commonly used for filling gas counters (15 ppm oxygen 25 ppm moisture) did not give improved performance for any sample.

Fig. 1 shows glow curves obtained on a sample of powdered quartz using the above-mentioned heating atmospheres. This example was chosen as showing "average" behaviour rather than "typical" behaviour, since there were differences from sample to sample. In this particular case the hydrogen/nitrogen mixture is slightly better than argon in the region of the "Spurious TL" component but the improvement is not great.

From the point of view of economics (at least in this country) there is little to choose between the nitrogen/hydrogen mixture and high purity argon. However, it does have a price advantage by a factor of about 2.5 over ultra high purity nitrogen (less than 2 ppm oxygen, less than 1 ppm water).

Sutton, S.R. and Zimmerman, D.W., Ancient TL 1, 7 (1977)

FIG. 1



MORE ON FILTERS FOR LABORATORY IL LUMINATION

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The idea of using blue-UV filters on white fluorescent tubes for laboratory lighting was discussed recently by Sutton and Zimmerman (Ancient TL, No. 5, p 5, 1978). We are writing to give details of another suitable filter, which was suggested to us by J.R. Prescott after he visited Zimmerman in 1977.

A wide range of non-inflammable colour filters for theatrical lighting is manufactured by RANK STRAND ELECTRIC, P.O. BOX 70, Great West Road, BRENTFORD, MIDDLESEX TW8 9HR, U.K. and distributed worldwide. Many filters transmit all colours with a slight or modest spectral bias; they are obviously unsuitable for a TL laboratory. However, two of the "Cinemoid" filters do have very suitable spectral characteristics with sharp cut-off values (Fig 1). We use "Cinemoid" No. 1 (yellow) with a minimum of two thicknesses wrapped around each fluorescent tube, the ends of which we seal with black plastic sheet and adhesive tape. The cost of materials (through local agents) is about $4. for a 1.2m long tube.

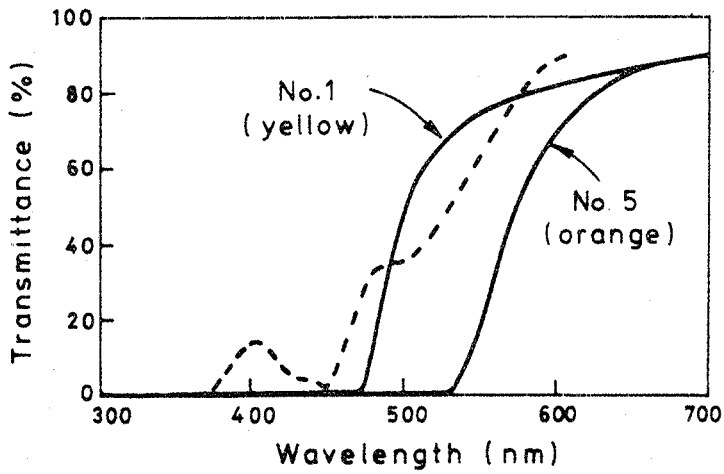

Fig 1. *Light transmission through single thicknesses of "Cinemoid" No. 1 and No. 5 colour filters (measured on Perkin Elmer and Pye Unicam spectrophotometers, Dept. of Physical and Inorganic Chemistry Adelaide University). Transmittance between 300 nm and the cut-off value (475 nm for No. 1, 530 nm for No. 5) is less than 0.5%. The dashed-line is the amber filter described by Sutton and Zimmerman (op.cit). Photons with wavelengths shorter than ~ 300 nm are not transmitted through the glass in fluorescent tubes.*

SHERD WATER UPTAKE MEASUREMENTS

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The effect of water uptake on the sherd dose rate has been known for some time (Zimmerman 1970) and dose rate corrections have been introduced (Zimmerman 1971). These corrections use the measured value of the maximum water uptake and assumed values for the fraction of total uptake, related to burial and climatic conditions at the site. The purpose of this short note is to introduce results of water uptake experiments so that an accurate measure of maximum water uptake may be made.

The questions asked were: a) what is an efficient method in which to introduce the water for maximum saturation and b) how long must the sherd be in the water for an effective measurement to be made? Measurements were performed on a total of eleven sherds covering a wide range of total water uptake values (5 to 35% water by weight). The sherds were wet using three techniques: a) simply plunging the dry sherd into a beaker of distilled water, b) placing the sherd in a dry beaker (in a vertical position) and slowly (over 24 hours) dripping distilled water into the beaker until the sherd was covered, c) placing the sherd in water and bringing the water to a boil, then allowing the water and sherd to cool to room temperature. In all cases, before wetting, the sherds were dried for 24 hours at 70°C. They were then weighed to determine their dry weight (sherds stored under normal room conditions can easily contain water up to a few percent of their dry weight). Subsequent wet measurements were made by removing the sherd from water, blotting dry with a tissue and weighing. The fractional water uptake is simply the wet weight minus the dry weight divided by the dry weight.

Figure 1 shows representative results from two sherds, illustrating the fractional water uptake as a function of time after the sherds were covered with water. Note that dripping has a greater wetting effect than simply plunging (in most cases, 5% to 15% increase in the total water uptake). Boiling the sherds was less effective than plunging or dripping. For the eleven sherds tested, the increase in water uptake measured after four days wetting compared to only one day wetting is relatively large (7.5% to 15% of total uptake). However, the increase from the third to fourth day is relatively small (from 2% to 5% of the total).

The results of these tests suggest a technique to be used to most accurately measure the total water uptake in ceramic sherds in a reasonable amount of time. The material should be wet slowly (over 24 hours) by dripping water, the sherd in a vertical position and a broken or unglazed edge at top and bottom. This ensures that the water is most effectively drawn into the pores by capillary action. Reasonable results should be expected at the end of three to four days wetting time.

We wish to thank Dr. Garmon Harbottle for his helpful comments.

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* Visiting Scientists, Chemistry Department, Brookhaven National Laboratory, Work at Brookhaven under contract with the U.S. Department of Energy and supported by its Division of Basic Energy Sciences.

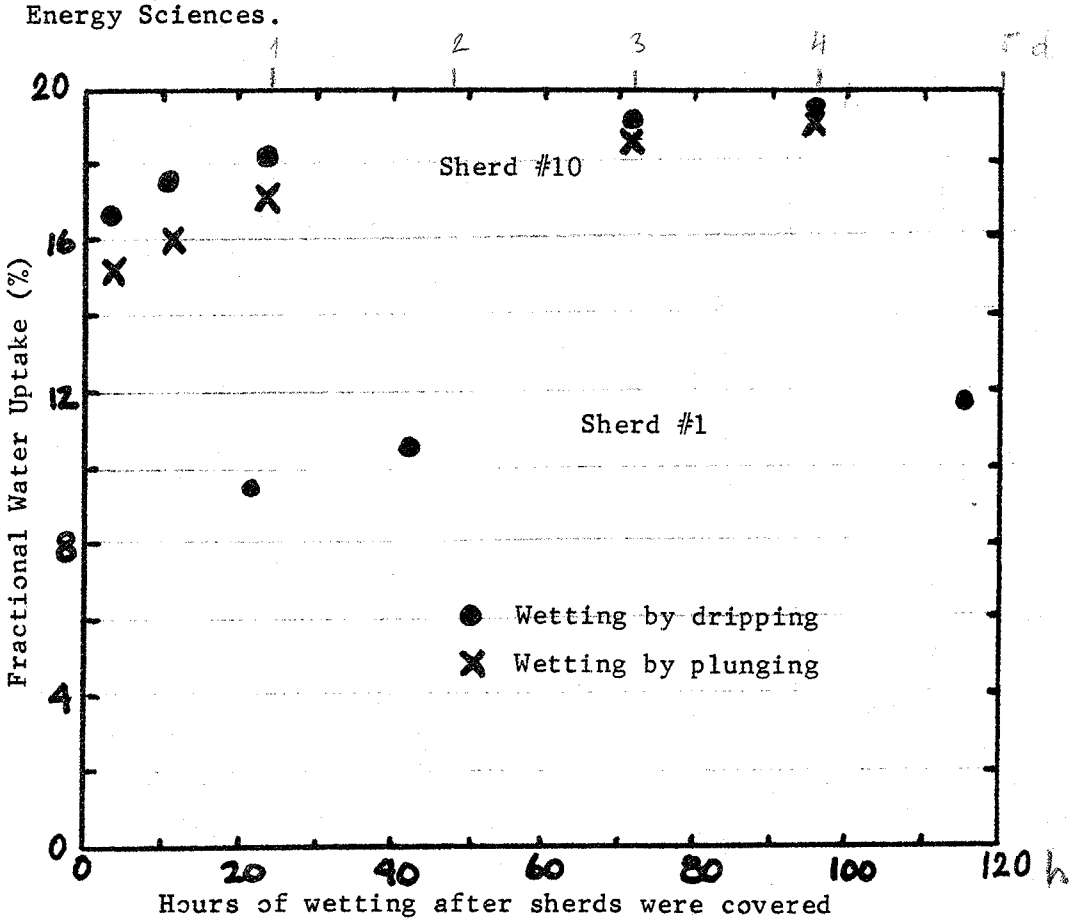

Figure 1.

THE 1979 ARCHAEOMETRY SYMPOSIUM - LONDON

by
Gary Carriveau

Two thermoluminescence sessions in this years Archaeometry Symposium were held on Wednesday, 28 March. Fourteen TL papers were given, with two papers represented only by abstracts.

Topics included: authenticity and dating using high temperature and pre-dose techniques, studies of quartz-feldspar subtraction dating, investigations into dose rate evaluations with special emphasis on beta and gamma contributions, measurements of deviations from secular equilibrium, and the dose rate dependence of flint and quartz TL response.

Texts of the abstracts are available from the British Museum Research Laboratory. There was discussion about publishing some papers presented during the TL sessions in the PACT Journal (the TL papers will not be published in the Proceedings of the Symposium). No decision was made at the end of the meeting; contact Dr. Vagn Mejdahl for further details.

An announcement of the Specialists Seminar on TL Dating was made by Dr. Martin Aitken. This will be held 1-6 September 1980, in Oxford.

ARCHAEOMETRY CONFERENCE - NEW ZEALAND, 1980

There will be an international conference held in Christchurch, New Zealand in August, 1980, on:

PHYSICS APPLIED TO PROBLEMS IN ARCHAEOLOGY

This is one of nine specialist conferences which will follow the two day New Zealand National Physics Conference (August 25-26). The Archaeometry Conference will begin August 27, and run for several days depending on the number of papers offered. If you wish to present a paper or attend without participating, please write to the convenor at the address below as soon as possible. Your name will be entered on a mailing list for future circulars. Contributors should nominate the title of their paper at this stage.

The Convenor Archaeometry Conference
Dr. Foss Leach
Anthropology Department
University of Otago
PO Box 56, Dunedin, New Zealand

SOME RECENT BIBLIOGRAPHY

The list of recent bibliography in each issue is kindly coordinated by Gary Carriveau. Please send references that have come to your attention to him at the Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, New York 11973, USA. Items of interest include journal publications, available theses and meeting proceedings.

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