

THERMOLUMINESCENCE DATING OF ARCHAEOLOGICAL MATERIALS RICH IN CALCIUM CARBONATE: A NEW APPROACH

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Abstract

A new thermoluminescence approach for dating archaeological samples is described in this paper. Calcium carbonate-rich samples can be dated if TL emission is filtered through a OG-550 Newport filter. Using this technique we have dated three archaeological sites which were previously dated by the TL standard fine grain method. We found a good concordance between both methods, though noted some systematic minor values for TL ages in calcite samples.

Resumen

Este artículo es un nuevo aporte a la datación arqueológica por termoluminiscencia para fechar muestras arqueológicas. Las muestras de carbonatos, ricas en calcio, pueden ser datadas si la emisión de TL es filtrada a través de un filtro de OG-550 Newport. Usando esta técnica hemos fechado tres yacimientos arqueológicos que fueron datados previamente por el método TL de grano fino estándar. Encontramos una buena concordancia entre ambos métodos, aunque se observaron algunos valores sistemáticos menores en las dataciones sobre muestras de calcita en TL.

INTRODUCTION:

From a general point of view, it seems widely accepted that referring to both experimental work conditions (e.g. the use of a EMI 5265 QB two-alkaline photo-cathode and blue-coloured filter) and methodologies (fine grain, zircon inclusion etc...), the absolute dating by thermoluminescence (TL) have arrived to establish some relevant working conditions completely accepted. Nevertheless, as it was recognised a long time ago (Martini y col. 1997), a relevant percentage of ceramics rich in calcium carbonate cannot be dated by this technique. That is why studies using calcium carbonate in geological dating are being developed in order to solve this kind of

problems (Wintle 1978; Henning y col. 1994; Debenham 1983; Debenham and Aitken 1984; Skimmer y Wieker 1992; Ninagawa y col. 1994) by introducing some innovations to such a technique, although with variable success. By doing so, it seems that calcium carbonate would become eligible as a dosimeter mineral, at least for low doses. This paper examines the potential use of the calcite (calcium carbonate) as a natural dosimeter in ceramics, and propose a new strategy for dating of in calcium carbonate rich ceramics using thermoluminescence technique.

EXPERIMENTAL:

Thermoluminescence (TL-2D) measurements were performed in Riso TLDA-10 according to the established methodology for the fine grain (Zimmerman 1971). Experimental conditions for these measures may be considered as the usual ones, that is, previous vacuum, high-quality gas and the presence of HA-3 colour filter between the gas-fired furnace and the photo-multiplier (EMI-9652 QB). The heating rate was 5°C/s from room temperature to 500°C in a nitrogen atmosphere after preheating at 90 C for 3 min. Equivalent Dose (ED) were estimated using Additive Dose method and TL intensities were determined by integration of glow curves in the range 300-400C after preheating . A second set of TL measures was achieved from the proportional samples, with the aim to calculate a new ED in carbonate rich samples. In this time an optical filter (OG-550 Newport)was interpolated between the sample and the corresponding photo-multiplier tube. This filter's main advantage is the capacity of isolating only the corresponding wavelength of carbonate emission, that is, 610-630 nm (Calderón y col,1996).

Alpha particles' effectiveness for producing TL (in relation to beta ones),that is to say, the -k value, was determined through the supply of increasing alpha doses, coming from an Am241, with a Dose Rate of 0.0297 mGy/sec. The calculation for the -k value was obtained in the temperatures region corresponding to the "plateau" of the curve resulting from the natural Thermoluminescence representation (nTL)/inductive Thermoluminescence by beta irradiation (Tli) versus temperature (Aitken 1985).

The calculation of the Annual Dose (AD), for each sample, was determined by combining two types of measures. On the one hand, the determination of the beta radioactivity coming from K40, present on the samples, through the Geiger-Muller counting system; on the other, the alpha activity measure coming from Uranium and Thorium, also present on the samples, through the counting system of solid scintillation (SZn). In the latter method, loss of radioactivity was not found as a result of possibly Radon escape. Gamma activity coming from cosmic radiation was measured "in situ" when taking samples through the INa (TL) solid scintillation counting system. Speed conversions of alpha, beta gamma and cosmic counting, have been achieved on the basis of the works developed by Nambi.et al. 1986).

Different samples of standard powdered calcite were irradiated with gamma doses between 500 Gy and 30 kGy at the NAYADE unit of the C.I.E.M.A.T (Centre for Environmental Energetic and Technological Research ,Madrid).The samples were then suspended in acetone and this suspension was pipetted on to steel disks and allowed to evaporate to dryness at room temperature (RT),ready for TL measurement. The calcite samples, used as referent pattern in this paper, were acquired from a supplier and later on, characterised by X-Ray diffraction (XRD).

For the achievement of the corresponding ceramics emission spectra here studied a three dimensional TL system (TL-3D) was used (Luff & Townsend ,1993). Two spectrometers with position-sensitive photomultiplier tubes are used to detect emissions simultaneously over the spectral range of 200-800 nm and over a temperature range 30-400 °C at a heating rate of 2,5 °C/s, under vacuum.

Characterisation of minerals compounding the ceramics was carried out through the X-ray diffraction method in a Philips 2000 machine.

RESULTS AND DISCUSSION:

Table I

Arch. Site	Sample Ref Lab.	Mineral 1 Quarz	Mineral 2 Feldspar	Mineral 3 Calcium carbonate	Mineral 4 Others
Los Villares	Mad-1	xx	^{xix}	x	
	Mad-2	xx	x	x	
	Mad-3	xxx	x	xx	
	Mad-4	xx	xx	x	
	Mad-5	xx	xxx	
	Mad-6	xx	xx	detc	
	Mad-7	xx	xxx	xx	
Guadalajara (Yunta)	Mad-31	xx	x	xxx	
	Mad-32	xxx	x	x	
	Mad-33	xxx	xx	rmoscov/biot
	Mad-34	xxx	xx	moscov.
Alicante	Mad-431	x		xxx	moscov.
	Mad-432	xx		xxx	
	Mad-433	x		xxx	

(Table 1) represents mineralogical characterisations of the major compounds detected through the samples and corresponding to the archaeological sites studied: Los Villares (Albacete), La Yunta (Guadalajara), and Alicante.

The minerals contained in these samples correspond to those considered as usual, that is, feldspars, quartz and, sometimes, calcite; all of them included within a clay matrix. According to the results shown on table 1, samples can be divided in two groups: 1) rich in calcite or containing it and, 2) samples without calcite.

Table I.a) Characterisation of samples by XRD : xxx: very abundant; xx: abundant; x: minority.

b) Mad1-7: samples coming from the archaeological site Los Villares (Albacete) (Blázquez-Pérez, 1991*, b).

Suggested period IV-II BC.

Mad 31-34: samples coming from the archaeological site La Yunta (Cerdeño et al. 1990). Chronology: II-IV BC

Mad 431-433: samples coming from private collection. XX-XXX BC.

As previously mentioned, it is widely accepted formal working conditions established for the TL dating, by using the fine grain methodology, require at least two conditions to be assumed: a) the polymineral sample coming from the ceramic behaves as a dosimeter regarding time and radiation; b) emission of thermoluminescence of the samples after the beta irradiation in laboratory -according to the additive dose- is located within the blue-visible region (300-500) of electromagnetic wavelength spectrum which is, precisely, the region where most of the photo-multipliers used, are more sensitive. As far as we know,, this is only a practical consideration. It is obvious that the interposition of a blue filter (e.g. Corning blue 7-59) at the detector entrance reduces the red sign coming from the furnace. By doing so we improve the sample sign quality, which will give evidence of the existence of emission in this region of the spectrum.

However, whether or not this option may be the best or the only one available has not been tested. On the other hand, the existence of certain ceramics which show difficulty to be dated by TL technique (Martini et al., 1988) has been proved.

Following this theory, the spectrum of thermoluminescent emission (TL-3D) has been obtained from archaeological samples. The most significant example is presented through figure 1 a,b. Here, a three-dimensional representation is shown regarding thermoluminescence intensity versus temperature and wavelength corresponding to two samples (Mad-5 and Mad-431). The first one represents non-calcite ceramics and the second one, those rich in this material (see table 1). As we can see from this figure (fig1.a), the spectrum of the emission of this kind of samples is made up by a group of TL peaks whose most intensive emission is located at the spectrum 400-410 nm blue part. These can be related to the presence of important natural dosimeters (quartz, feldspars), which are present in the original sample composition. As it is seen from the results obtained historic-practical considerations on the relations between filters and photo-multipliers selection, on one hand, and TL dating, on the other, seem to be correct. Nevertheless, fig.1.b shows the emission corresponding to a ceramic sample, rich in calcite, irradiated by beta radiation. As shown on the figure, the main TL peak detected is now presenting the maximum emission in the orange-red area of the spectrum (600-630 nm). This emission is directly related to the presence of Mn 2+ ion in calcites (Medlin, 1968; Calderón et al., 1996). Under such circumstances, with this type of samples, rich in calcite, any commercial equipment, which is supposed to be prepared to detect light in the spectrum blue region, would not detect light from TL and, therefore, the sample would be classified as "unable to be dated by TL".

Notwithstanding, the problem does not seem to be on the sample but rather on the bad selection performed of the experimental conditions. After these revealing results, the procedure described above needs to be rectified by achieving a previous characterisation of the mineral composition in order to help when selecting the strategy to be developed. Another fact determined from the fig.1b is that the characteristic emission of the calcite

(610-620) can be isolated through the use of a red filter (e.g. Newport OG-550). It was also determined that the emission observed for this type of samples is, at least, similar to the one observed for the rest of the minerals compounding ceramics. The final conclusion deduced from the information given above (fig 1^a and 1b), may be the urgent need to change the equipment developed to TL dating, according, precisely, to the mineral composition of the ceramic sample or change the set-up in the commercial ones.

This conclusion is important since our activity requires the quantification of the luminescent sign coming from mineral dosimeters contained in ceramics and, thus, this quantification is directly used for dating purposes. It is very difficult to determine signs within the orange-red region (coming from the carbonates) with a blue filter or with sensitive photo-multipliers in this area .

A further question to be faced is whether to change the whole system of detection (basically the photo-multiplier) or simply to isolate the length of the desired wave through the use of optical filters. The first option is desirable but, it might not be justified due to the high expenses involved.

The second one, a loss of sign around 90% is expected (the EMI9235QA photo-multiplier quantity efficacy -QE- reaches the 3% at 600 nm), although it may be compensated with both high-intensity signs and the simplicity of the methodology. With the aim of studying this method's potential, based on the use of carbonates as dosimeter minerals, we should carry out research work on the dosimeter possibilities by isolating this mineral (using a mineral calcium carbonate sample). From this calcite sample -prepared according to the process described within the experimental section-, several samples were obtained, which were irradiated by gamma radiation. Several doses were applied (from 0.5 at 30 kGy). All TL the measures on the calcite were carried out with the support of a OG-550 filter, whose main transmission is shown on fig. 2. The reason of this election is clearly related to the emission of calcite (610-630 nm) we want to isolate. Data from fig.3^a, represent the TL curves for different samples of calcite and they show the TL curves evolution with a gamma dose of irradiation. As we can see, the TL curves of this mineral are characterised by the presence of two peaks, one at low temperature (316 °C) and the other at high temperature (360°C). The behaviour of both peaks with the dose (fig3.b) is similar and they experiment a super-linear growth at very low doses and, afterwards, they behave as linear (at least until 7 kGy), where saturation began. Another compulsory requirement for this material to be use as dosimeter in archaeological samples, is that the sign, stored after certain period of time, remain stable, that is to say, that they should not present decay. In order to explore the sign stability regarding the time, additional measures of TL were taken for irradiated samples in the darkness. Such measures gave as a result stability of the sign regarding the time, for both peaks at 316°C and 360°C. More precisely, we can establish the non existence of variations concerning TL sign intensity of major to 3 % for the two-month period in which the samples were stored.

In view of the results we suggest that:

i) It seems reasonable to measure the calcite's (or carbonates') main emission which is produced within the electromagnetic spectrum red-orange region with the help of a red filter (such as Newport OG-550 or similar) and not within the blue zone, where works have been doing until now (Debenham, 1983).

ii) Calcite is a good dosimeter to be used for archaeological and geological dating purpose.

Once the possibility of dating from calcite samples, this hypothesis was tested on ceramic samples from several historic contexts and different content of calcite, coming from archaeological sites, which were previously dated by TL, according to the classic methodology of fine grain. The samples, previously characterised, appear identified on table I. Thus, we have dated the same samples in two different ways: a) fine grain with blue filter (process no. 1) and b) fine grain with Newport OG-550 orange filter (process b). In both cases, and for the calculation of the corresponding Equivalent Dose, the Additive Dose method was used.

The results obtained by using both proceedings (either a or b) are shown on Tables II, III and IV.

Table II .-

Sherds	ED (Gy)	AD (mGy/a)	K (value)	Date (B.P) (with blue filter)	Date (B.P) (OG filter)	CO ₃ Ca
Mad-1 a) b)	14.3 ∓ 0.1 18.2 ∓ 2.7	6.1 ∓ 0.2 8.1 ∓ 0.4	0.14 0.30	2368 ∓ 156	2242 ∓ 237	YES
Mad-2 a) b)	14.1 ∓ 0.7 15.7 ∓ 2.7	5.5 ∓ 0.3 6.5 ∓ 0.4	0.15 0.23	2577 ∓ 191	2427 ∓ 289	YES
Mad-3 a) b)	12.8 ∓ 0.4 16.5 ∓ 6.3	5.2 ∓ 0.3 6.9 ∓ 0.2	0.07 0.23	2449 ∓ 132	2387 ∓ 602	YES
Mad-4 a) b)	scattering 34.8 ∓ 6.4	----- 14.14 ∓ 0.6	----- 0.43	----- -----	----- 2464 ∓ 194	YES

Mad-5 a) b)	25.59 \forall 3 -----	10.1 \forall 0.4 -----	0.17	2519 \forall 247	-----	NO
Mad-6 a) b)	25.94 \forall 2 -----	8.4 \forall 0.3 -----	0.14	3085 \forall 243	-----	NO
Mad-7 a) b)	23.1 \forall 0 39.4 \forall 0	8.2 \forall 9.8 16.51 \forall 0.8	0.14 0.51	2810 \forall 167	2385 \forall 176	YES

Table II.-Sherds Mad.1-7: samples coming from the archaeological site Los Villares (Albacete, Spain ;Blázquez-Pérez, 1991 a, b). Suggested period IV-II BC.

Table III

Sample (lab. reference)	ED (Gy)	AD (mGy/year)	K value	Age (BP) With Blue filter	Age (BP) With orange (OG)filter	Calcium Carbonate
Mad.-31 a) b)	27,31 \forall 2,0 30.98 \forall 1 1	1 1,2 \forall 0,4 12,91 \forall 0,6	0,44 0,71	2448 \forall 184	2397 \forall 220	yes
Mad.-32 a) b)	30,36 \forall 2 46,45 \forall 8	12,51 \forall 0,5 19,5 \forall 0,9	0,40 0,74	2421 \forall 172	2380 \forall 209	yes
Mad.-33 a) b)	20,94 \forall 1 scattering	8,9 \forall 0,3	0,15	2355 \forall 173	-----	no
Mad.-34 a) b)	23,48 \forall 3 scattering	9,6 \forall 0,4	0,15	2547E 237		no

Table III.-Sherds Mad 31-34: samples coming from the archaeological site La Yunta (Albacete, Spain ;Cerdeño et al. 1990). Suggested chronology: II-IV BC

Table IV.-

Sample (Ref.lah)	ED (Gy)	AD (mGy/year)	k value	Age (BP) With blue filter	Age (BP) With orange (OG) filter	Calcium carbonate
Mad.- 431						medium
a)	53,99 ∇ 9	13,41 ∇ 0,9	0,91	4011 ∇ 406		
b)	37,97 ∇ 3	10,9 ∇ 0,7	0,67		3478 ∇ 317	
Mad.- 432						yes
a)	40,8 ∇ 6	9,8 ∇ 0,7	0,63	4101 ∇ 350		
b)	37,4 ∇ 3	11,4 ∇ 0,7	0,82		3357 ∇ 317	
Mad.-433						yes
a)	36,86 ∇ 6	9,2 ∇ 0,5	0,55	4002 ∇ 402		
b)	43,65 ∇ 6,	13,11 ∇ 0,8	0,91		3357 339	

Table IV.- Sherds Mad 431-433: samples coming from private collection (Alicante, Spain).
Suggested chronology XX-XXV BC.

The results obtained seems also suggest:

a) The Equivalent Dose (EQ) values attained by both proceedings are different, remarking that the energy (spectral colour) where the corresponding values were obtained from is also different.

b) k values (correction factors used in dating in order to compensate the different effect from alpha and beta radiation in ceramics), for calcite rich samples, are also higher than the theoretical ones expected, although similar to those obtained for similar materials, such as stalactite or mollusk (Debenham 1983; Lyons and Brennan 1991; Ninagawa et al. 1994).

c) The ages obtained for the samples containing carbonate are systematically lower than those using "all in one" dosimeter material.

d) It is evident that the method, based on the presence of concrete mineral (calcite), is limited and, therefore, an instrumental modification of commercial equipment existing in dating laboratories seems to be unjustified (e.g. change of photo-multiplier). Nevertheless, this methodology may be useful in all those cases in which other ones have not achieved successful results (see Tables II and III) or, whenever the calcium carbonate is an evident mineral in the sample's mineralogical composition.

CONCLUSIONS:

1) Ceramic samples rich in calcium carbonate can be dated whether the luminescent emission is detected within the proper region of the electromagnetic spectrum by using an orange-red filter (Newport OG-550 or similar).

2) As far as we know, the values of ages obtained through this strategy are systematically lower than those resulting from the use of "all in one" as a dosimeter material. Although further research work has to be done so as to achieve more accurate results, this new strategy widens the dating possibilities, both in the field of archaeology and geology.

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REFERENCES:

- (1) Aitken, M.J. (1985) Thermoluminescence Dating. Academic Press. London.UK.
- (2) Blázquez Pérez, J. (1991a) Las necropolis ibéricas en el Suroeste de la Meseta. Special Publication.U.A.M. (Madrid,Spain) .Serie Varia. 1 .235-278
- (3) Blázquez Pérez, J. (1991 b) Iberos y griegos : Lecturas desde la diversidad. Hueh,aArqueologica. XIII, 1, 321-354.
- (4) Calderón, T.; Townsend, P.D.; Beneitez, P.; García-Guinea, J.; Millán, A.; Rendell, H.M.; Tookey, A.; Urbina and Wood, R.A. (1996) . Crystal field effects on the Thermoluminescence of Manganese in carbonate lattices. Radiation Measurements, Vol. 26. N° 5, pp. 719-731.
- (5) Cerdeño, M.L.; Garcia Huerta, R. (1990) Las necropolis de incineracion de Alto Jalon y Alto Tajo. in "Las Necropolis Ibericas." .Ed.
- (6) Debenham, N.C. (1983) Reliability of thermoluminescence dating of stalagmitic calcite . Nature 304,154-156.
- (7) Debenham, N.C. and Aitken, M.J. (1984) Thermoluminescence dating of stalagmitic calcite Archaeometry 26,2,155-170.
- (8) Luff, B.J.; Townsend, P.D. (1993) High sensitivity thermoluminescence spectrometer. Meas. Sci. Technol.4,65-71.
- (9) Henning, G.J.; Bangert, U.; Herr,W.; and Poulianos, A. (1980) Uranium series dating and thermoluminescence ages of spelaeothem from Petralona Cave. Anthropos 7,174-214.
- (10) Lyons, R.G.; Brennan, B.J. (1991). Alpha/gamma effectiveness ratios of calcite speleothems. Nucl. Tracks Radiat. Meas., 18,1 /2,223-227.
- (11) Martini, M.; Sibila, M.; Calderon,T.; Renzo, F. (1988) Spurious TL in archaeological ceramics : a study of affecting factors. Nuclear Tracks. Radiat.Meas.,14,1/2,339-342.
- (12) Medlin, W.L. (1964). Trapping centers in thermoluminescent calcite. Phys. Rev. 135, 1770-1779.
- (13) Nambi, K.; Aitken, MI (1986) Thermoluminescence dating. Refinement of quartz inclusion method. Archaeometry. 28,202-205.
- (14) Ninagawa, K.; Matsukuma, Y.; Fukuda, T.; Sato, A.; Hoshino, N.; Nakagawa, M.; Yamamoto, I. alada, T.; Yamashita,Y.;Sekimoto,K.; Komura,K. (1994) Thermoluminescence dating of calcite shell, crassostrea gigas (thunberg) in the ostreidae family. Quaternary Science Rev.13,589-594.
- (15) Skimmer, A.F.; Weiker, N. (1992) ESR dating of Chione cancellata and Chama sinuosa Quaternary Science Rev.11,225-230.

(16) Zimmerman, D. W. (1971)Thermoluminescence dating using fine grains from pottery Archaeometry. 13,29-52

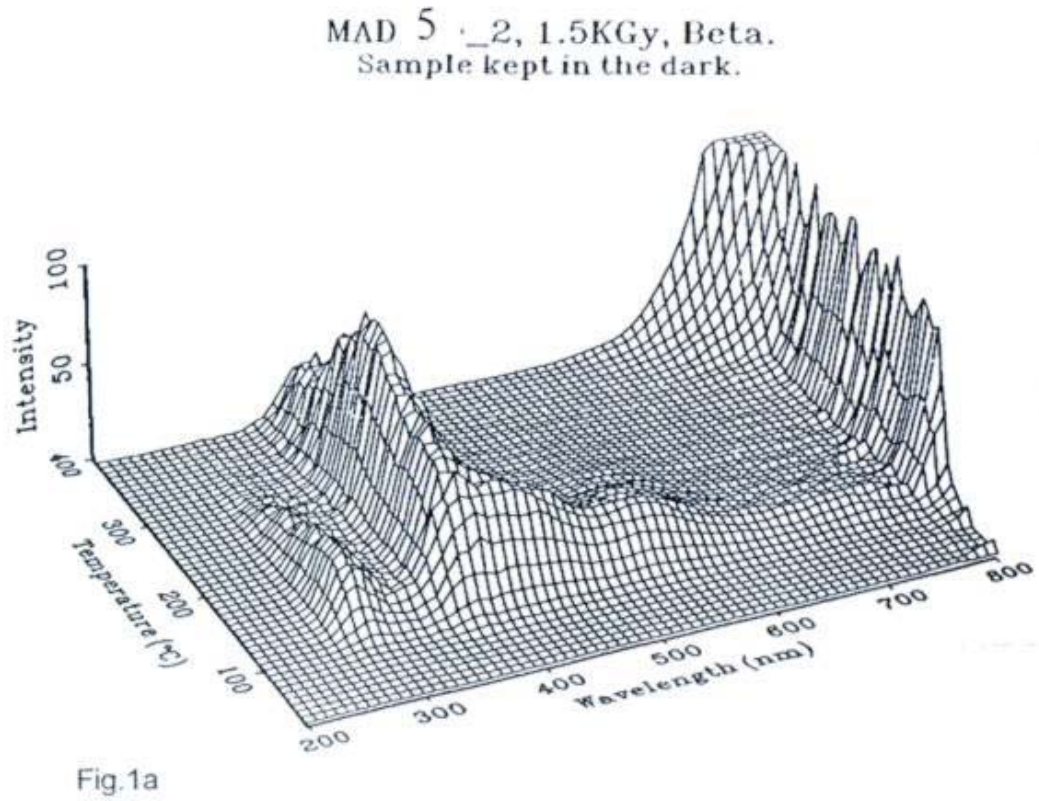


Fig. 1a. Three-dimensional representation of a 1.5 kGy b radiated Mad-5 sample (calcite ,non detected)

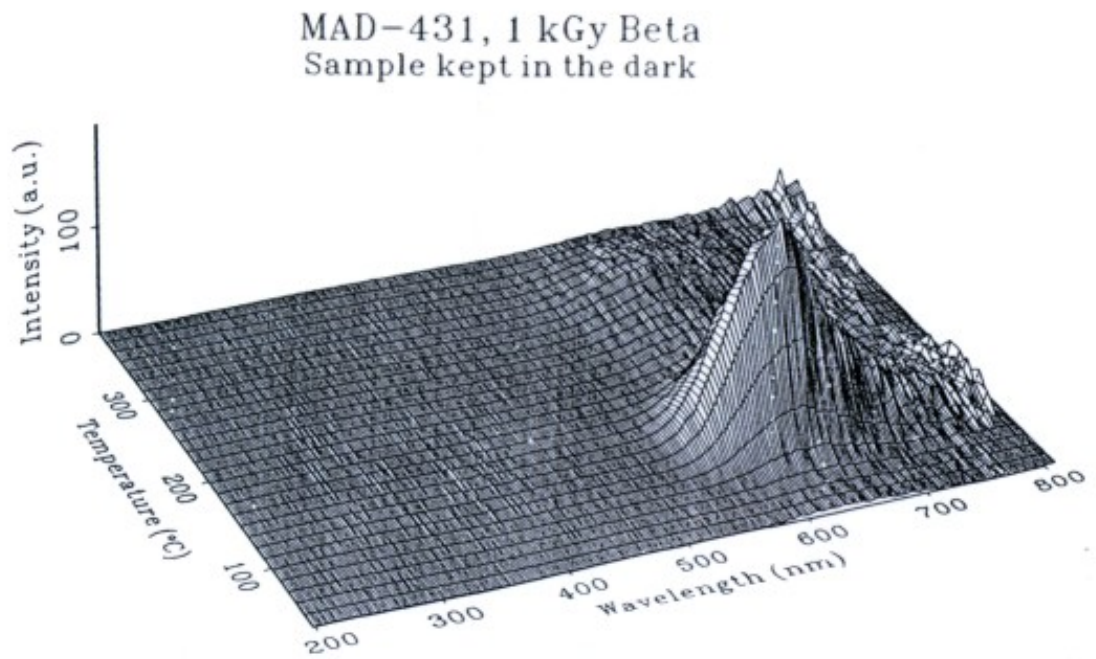


Fig. 1b. Three-dimensional representation of a 1 kGy b radiated Mad-431 sample

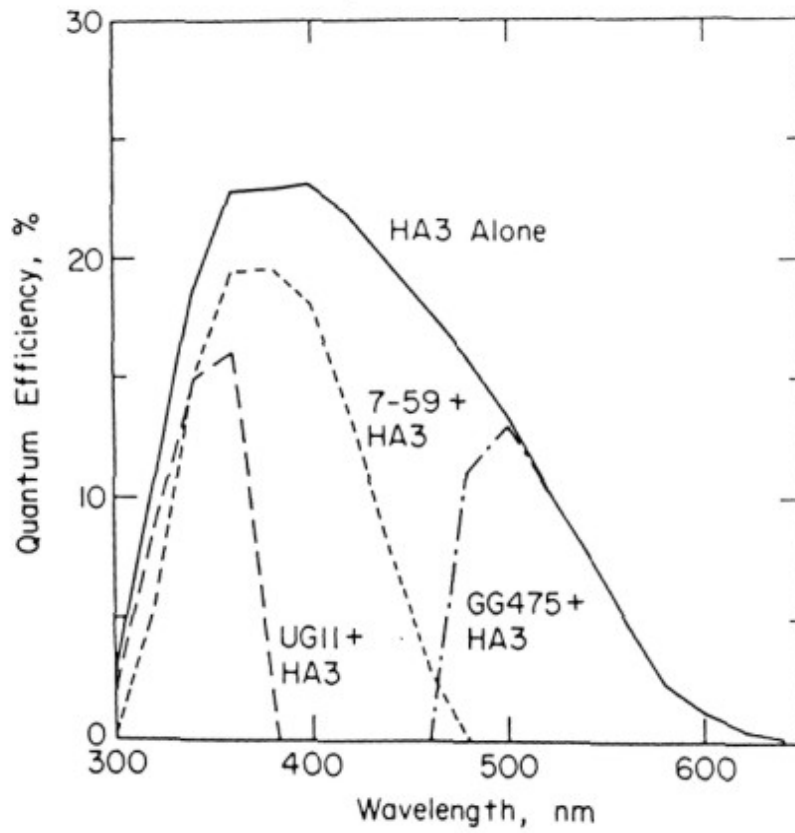


Fig. 2. Quantum efficiency of EMI-9635Q photo-multiplier tube.

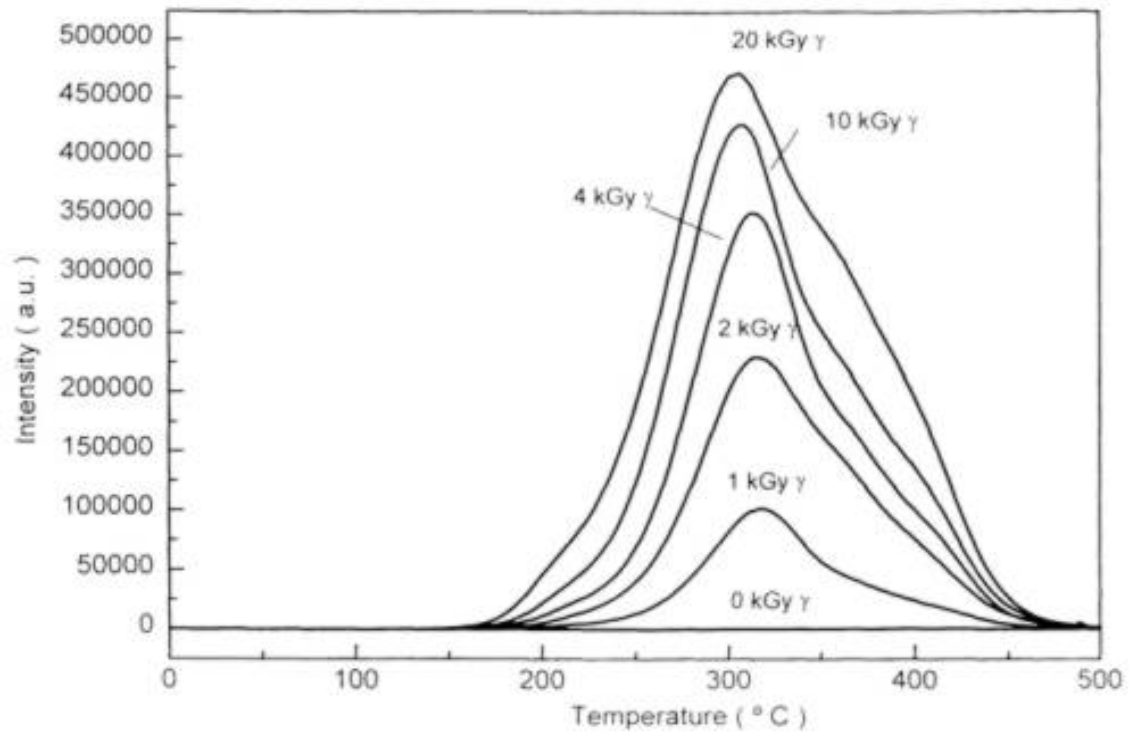


Fig. 3a

Fig. 3a. TL curves of calcite-10 after subsequent g-irradiation.

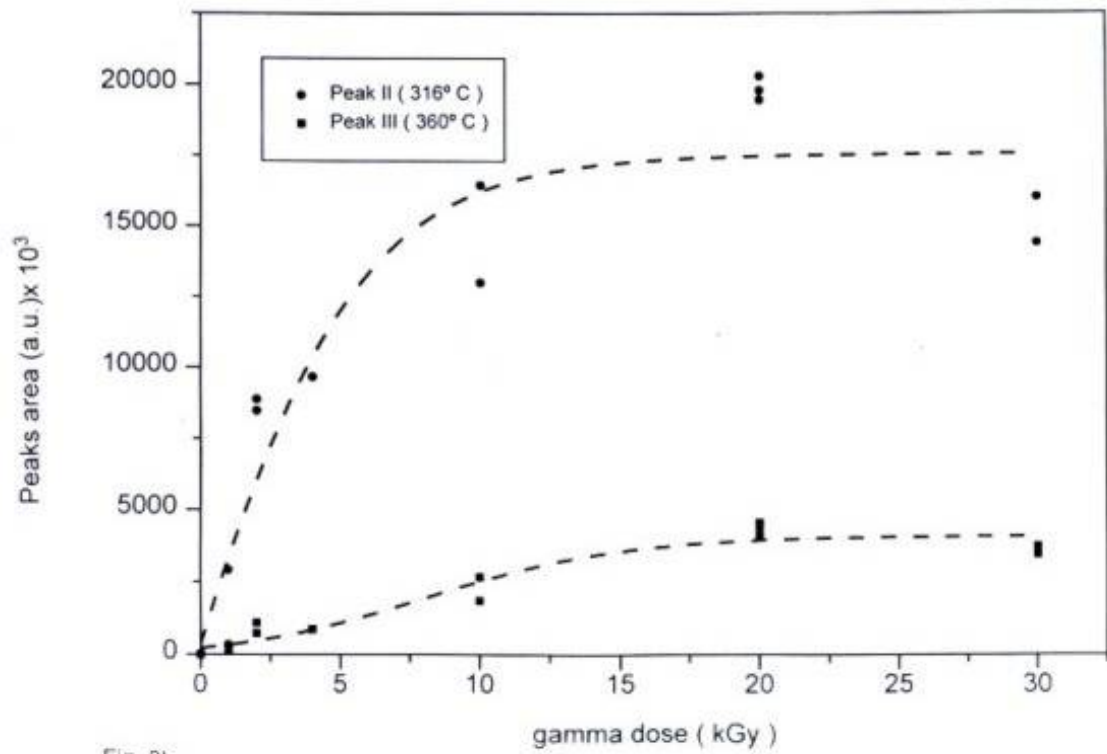


Fig. 3b

Fig. 3b. Saturation curves by peaks of calcite-10 g- radiated.