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ΠΡΟΕΔΡΙΑ ΔΙΟΝ. Α. ΖΑΚΥΘΗΝΟΥ

ΦΥΣΙΚΗ.—**Putting together of statues from fragments with the help of thermoluminescence,** *by George N. Afordakos* *. Ἀνεκοινώθη ὑπὸ τοῦ Ἀκαδημαϊκοῦ κ. Καίσαρος Ἀλεξοπούλου.

### INTRODUCTION

Putting together of statues from fragments is usually routine work in archaeology. If however the pieces must be selected from a large number of fragments their joining becomes difficult and the archaeologist in many cases would like to have additional information. This in certain cases can be supplied by determining physical qualities of the fragments involved [**1**]. In an extensive investigation of the thermoluminescence of marble samples from a large number of quarries in Greece [**2**] it was found that these thermoluminescence qualities might be of help in solving the archaeological problem mentioned above.

Under the term «Thermoluminescence» natural sciences describe the emission of faint light by certain materials when heated. This light is produced at certain sites of the solid material where, either a disturbance of the regularity of the crystal lattice occurs or foreign atoms happen to be present. These points of disturbance which are called centers, can become excited by a number of agents as cosmic radiation, radioactive inclusions etc. Upon heating, the excited centers loose their

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excitation energy by emitting light. Thus if the material is gradually heated then at a certain temperature the light emitted becomes intense but only for so long until all centers have become de-excited. If the sample contains a variety of types of centers, then light is emitted at various temperatures each of which is characteristic of the type of center involved [3, 4, 5]. The results of such experiments are called glow curves.

When the effect is investigated on a sample of marble as obtained directly from a quarry, the emission is described as natural thermoluminescence (NTL), because the excitation is due to the natural causes mentioned above. It is clear that, after heating the sample for the first time, all centers become de-excited, so that upon a second heating no light is emitted.

After the first heating the centers can be subsequently excited by an artificial exciting agent (as for example X-rays) so that the luminescence can be repeated. This type of luminescence can be named artificial thermoluminescence (ATL) and can be reproduced as often as desired.

A third method of investigation is also possible, called mixed thermoluminescence (MTL). In this case the material is irradiated with X-rays before any heating. Upon heating a glow curve appears with the peaks of the NTL and ATL. Usually the NTL peaks are enhanced.

As mentioned, each type of center becomes de-excited at a certain temperature. The investigation [2] showed that samples from different quarries contain different types of centers. This led, initially, to the idea that it would be possible to determine the quarry from which a sample came. However it was noticed that the quality and the distribution of the centers was not uniform over the whole area of the quarry so that such a determination would not always be secure.

On the other hand if the sample were taken from adjacent points of the same block of marble, no such differences arose.

This observation leeds to the possibility of determining, if two fragments of an object of archaeological value belong together. As will appear from the following presentation, an answer can only be given in a negative sense i. e. when the two fragments display different TL - qua-

lities one can definitely state that they not belong to the same piece. If, on the other hand, they d o have the same qualities one cannot exclude the possibility of their belonging to different articles (statues etc.) but both of them having provenience from the same quarry. Even this information can, in some cases, be of help to the archaeologist.

In order to evaluate practically the extent of such help, a number

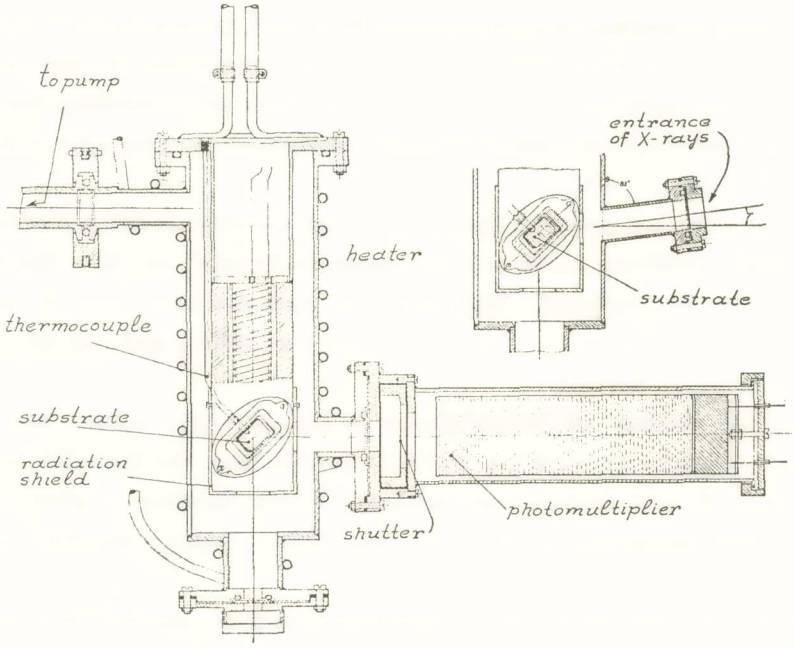


Fig. 1. Thermostat.

of samples from Archaeological Museum of Athens was investigated and the results are described in the present paper. Before giving these results, a short description is given of the experimental apparatus.

## EXPERIMENTAL

The material was initialy investigated in the form of a small block. Later, it was found that a small quantity of powder (about 0,1 gr) was sufficiant. Such powder can be obtained from the drilling to which archaeological fragments are subjected in order for them to be held

together. This powder was wetted with water, so that it adhered to the surface of a thin metal substrate.

This substrate was placed in a thermostat (Fig. 1) that could be heated under vacuum up to 250°C. The heater of the thermostat could be regulated so as to heat the sample at a rate up to 20°C per minute.

Before the main experiment the sample was subjected to a temperature of 250°C in order for NTL to be expelled. After bringing it back to normal temperature it was irradiated, with X-rays for 10 minutes, through a window covered with a thin Al foil. The X-ray tube (Fe anode, 35 KV, 10 mA) was held at a distance of about 20 cm from the sample.

Upon heating the light emitted was detected with a photomultiplier EMI 6255 S which could detect any radiation from the extreme red (0,65 μ) to the UV (0,2 μ). The current was amplified in a d.c.—amplifier (Keithley picoameter No 410) and recorded on a paper chart.

The temperature of the sample was measured with a iron - constantan thermocouple which was in contact the surface of the powder layer. The vacuum of the thermostat was better than $10^{-3}$ Torr.

In Fig. 2 we show the glow curve of the MTL from a sample of Arachova marble and in Fig. 2b the corresponding ATL. The temperature gradually increases from right to left.

During the experiment the chart advanced at a velocity of 30 cm/hour. The temperature was constantly measured so that a temperature curve could subsequently be drawn on the chart by hand. In this way the temperature at each point of the experiment can be easily determined. The ordinates of the figure correspond to the current of the photomultiplier. (The autografic recorder produced rectangular ordinates and not curvilinear as the printed lines on the chart might suggest). As the temperature increased, thermoluminescence appeared showing peaks at temperatures depending on the type of the experiment. The material was not heated beyond 300°C, because the photomultiplier was sensitive to infrared black — body radiation that is emitted at higher temperatures. This is the reason of the increasing background on the left end of the figures.

The initial step on the right which appears upon opening the optical shutter shows a faint phosphorescence of this material.

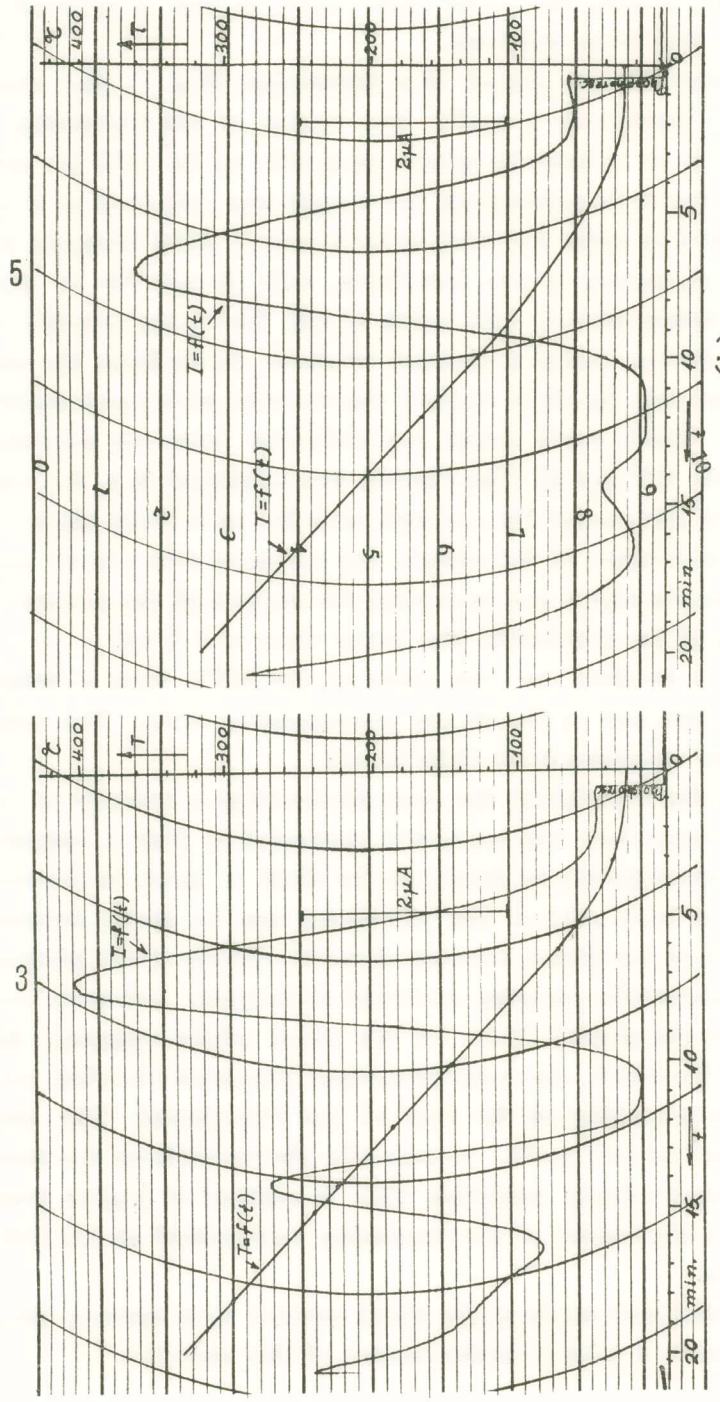


Fig. 2. Comparison of the glow curves of the mixed TL (a) and the artificial TL (b).

## RESULTS

In order to determine the amount of credibility that can be given to the method, powders were compared obtained by drilling holes in a block at two adjacent points. At this stage of the investigation we want to draw attention to the fact that the NTL, which would be the simplest type of experiment, as it would not need the help of X-rays, might not always give idendical results when comparing two powders from the same block. Such differences must appear when the heating of the powder during the drilling procedure is not exactly the same. If the pressure of the drill is different in the two cases, the results will be different as the samples will have been heated to different temperatures and thus they will have emitted part of their NTL during the drilling process. This same objection holds for MTL. The above reason necessitates the comparison to be made with ATL measurements. All checks showed that ATL results from adjacent drillings of a block give the same results within a few percent. They have furthermore the advantage that the ATL experiment of a given powder can be repeated as often was desired.

In Fig. 3 a and b we reproduce two ATL glow curves taken in sequense from the same powder obtained from the torso of an Antikythera statue. In table I we give the temperatures of the first and the second peak. We notice that they differ only by 2 resp 7 degrees. In the fifth column we give the ratio of the intesities of the two peaks. We notice that they differ only by 5%.

TABLE I.

**Results of ATL glow curves.**

| Fragment | $T_{1oC}$ | $T_{2oC}$ | $I_1$ | $I_2$ | $I_1 / I_2$ | Fluorescence |
|---|---|---|---|---|---|---|
| Torso from Antikythera | 97 | 225 | 49 | 25,5 | 1,90 | 18 |
| Second experiment of above sample . . . . . | 95 | 219 | 44 | 24,5 | 1,80 | 18,5 |
| Leg from Antikythera . | 99 | 226 | 33,5 | 17,5 | 1,91 | 15 |
| Arm from Delos . . . . | 153 | 222 | 4,8 | 1,0 | 4,8 | 3,4 |

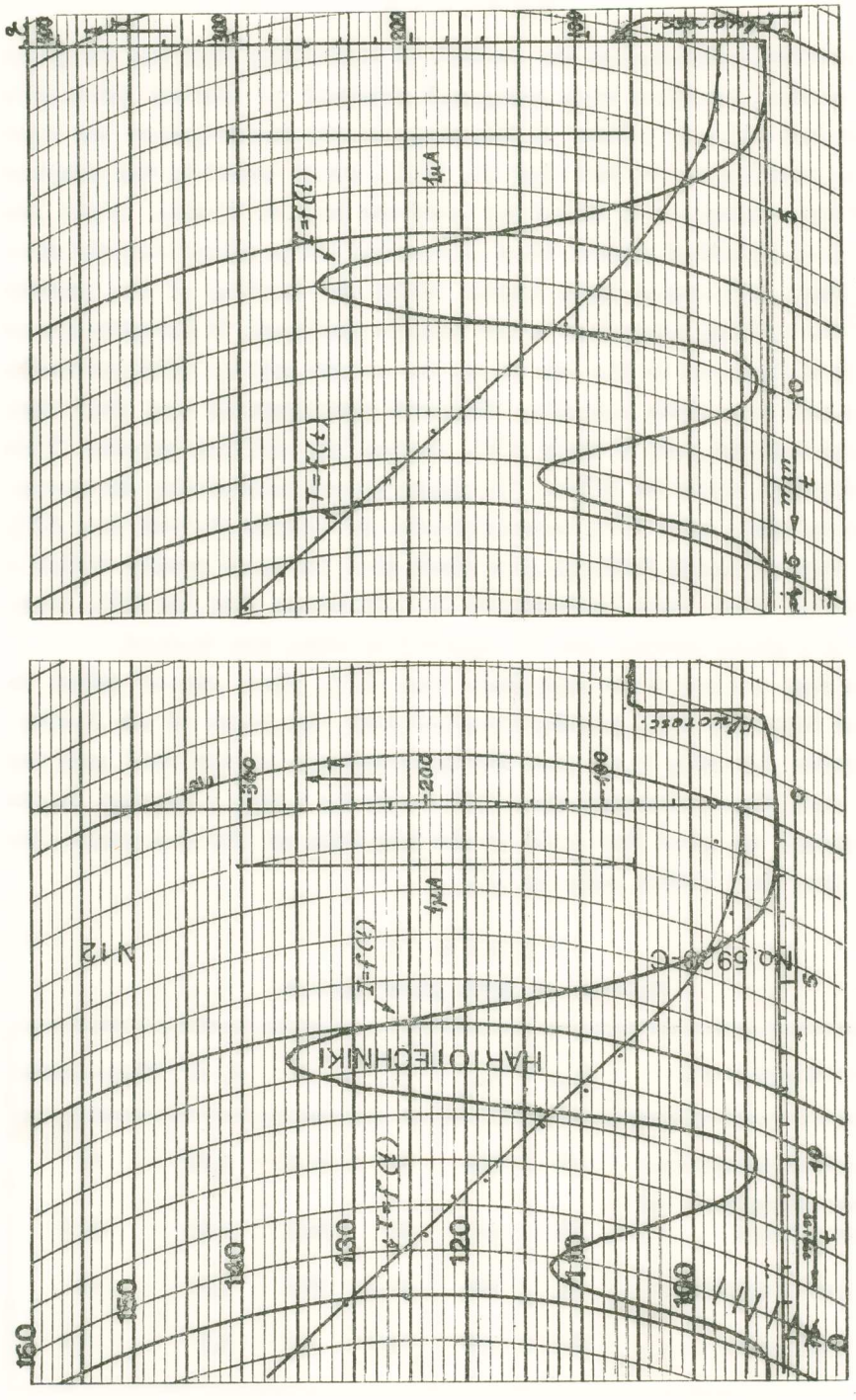


Fig. 3. ATL glow curves taken in sequence from the same powder (torso from Antikythera).

In Fig. 4 we reproduce the ATL glow curve of a piece of marble belonging to the leg of a statue found at Antikythera. Its results are given in the third line of table I. We notice that the values of $T_1$, $T_2$ and $I_1/I_2$ coincide very well, within the accuracy of the method, with the values obtained for the torso of Antikythera, thus indicating that the two marble fragments came from the same quarry.

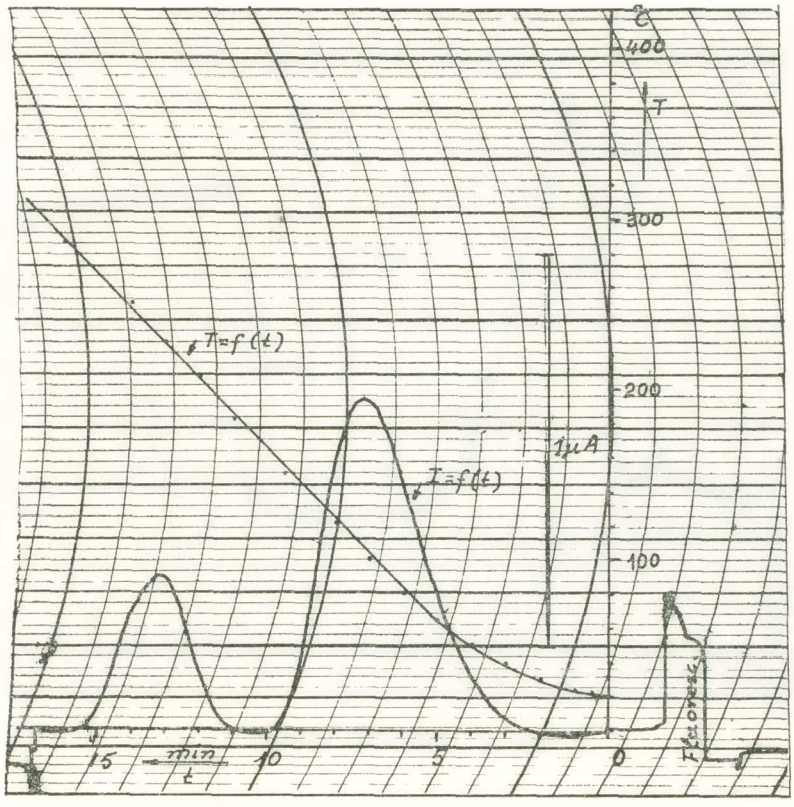


Fig. 4. Leg from Antikythera.

The intensities of the peaks are given in columns 3 and 4. These values should only be considered as giving a qualitative indication of the intesities of the peak and must not be used as a criterion for the comparison with data of other samples. This is due to the difficulty to insert the powder samples to exactly the same position in the thermostat with exactly the same dose of X-rays. The ratio $I_1/I_2$ of the intensities is found to be a more reliable criterion.

A further qualitative means of judjement is the fluorescence i. e. the light emitted from the sample at room temperature during the excitation with X-rays.

On Fig. 5 we reproduce the ATL curve from the arm of a statue found at Delos. By comparing the Delos sample to those from Antikythera we notice that the first peaks appear at different temperatures,

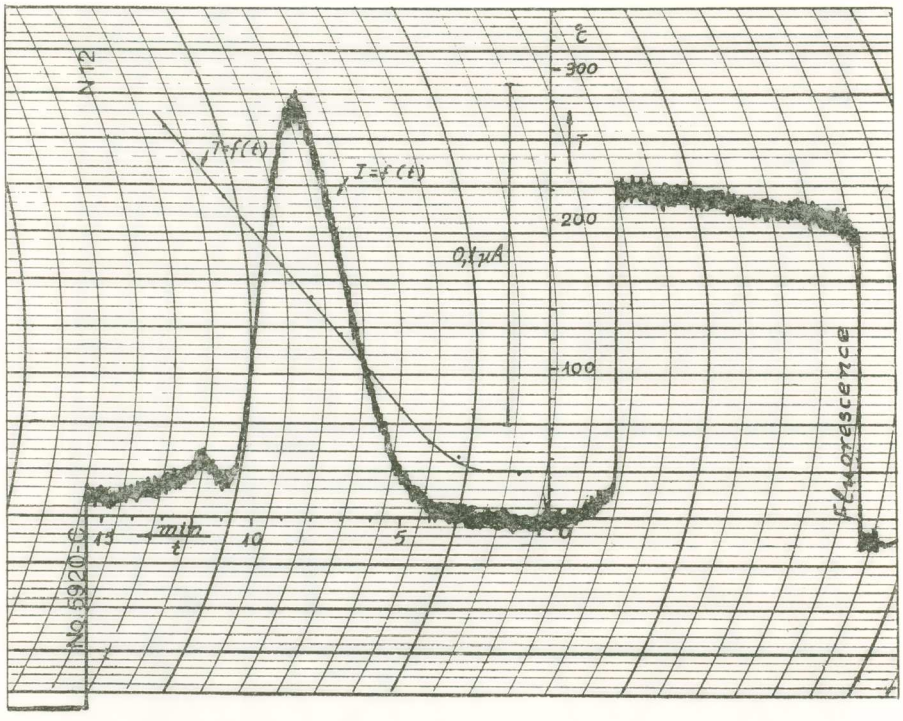


Fig. 5. Arm from Delos.

clearly beyond the error margin, thus indicating difinitely the difference in the two materials. The second peaks happen to appear near each other, so that they cannot be considered as an indicator of different provenience. However the ratio $I_1 / I_2$ also gives a completely different result. Also the fluorescence intensity, although only a qualitative criterion, is very different.

The above presentation describes the results of single glow curves Actually the ATL of each sample was repeatedly determined. The verdict for the comparison of two fragments depended on the comparison of

the mean values and fluctuation of $T_1$, $T_2$ and $I_1 / I_2$ of each fragment.

Some of the results given above have been qualitatively described in a letter to Nature [6].

## SUMMARY

The thermoluminescence of marble samples was investigated in order to determine the possibility of ascertaining if two samples belong to the same block.

About 0,1 gr of powder from each block was sufficiant to determine the temperature at which the glow peaks appeared. Reliable results cannot be obtained from samples upon their first heating. This is due to the fact that the marble powder is heated to an unknown extent by the drilling process. Powder samples from the same marble block give idendical results if the «artificial thermoluminescence» is investigated. To this purpose the material must first be heated until all thermoluminescence has been expelled and then irradiated, for a given time, with X-rays. The subsequent heatings then give results that do not depent on the drilling procedure.

The method is of value to archaelogists, because in certain cases it can exclude the possibility of two fragments belonging to the same block.

The degree of the accuracy of the method can be evaluated from the data on three powder samples.

## ACKNOWLEDGEMENTS

This work was initiated under the guidance of professor K. Alexopoulos to which I express my thanks. I wish also to thank Mr Naoum Bakalis for his help in the measurements.

The problems investigated in the present work were selected from restoration work going on at the National Archaeological Museum of Athens by Dr N. Gialouris and St. Triantis. At this point I would like to thank them for the preparation of the samples and their cooperation.

## Π Ε Ρ Ι Α Η Ψ Ι Σ

Εἰς τὴν παροῦσαν ἐργασίαν ἐμελετήθη ἡ θερμοφωταύγεια μαρμαρικῶν δοκιμίων μὲ σκοπὸν νὰ προσδιορισθῇ κατὰ πόσον δύο μαρμαρικὰ δείγματα προέρχονται ἐκ τοῦ αὐτοῦ τεμάχους.

Πρὸς τοῦτο παρεσκευάσθησαν δείγματα ἐκ κόνεως (περίπου 0,1 gr ἕκαστον) καὶ ἐλήφθησαν αἱ «καμπύλαι λάμψεως» αὐτῶν. Ἡ λαμβανομένη καμπύλη κατὰ τὴν πρώτην θέρμανσιν τοῦ δοκιμίου ἀποτελεῖ τὴν φ υ σ ι κ ὴ ν θ ε ρ μ ο φ ω τ α ύ γ ε ι α ν (ΦΘΦ), ἐνῷ ἡ λαμβανομένη μετὰ τὴν πρώτην θέρμανσιν καὶ κατόπιν ἐνδιαμέσου ἀκτινοβολήσεως μὲ ἀκτῖνας Χ, ἀποτελεῖ τὴν τ ε χ ν η τ ὴ ν θ ε ρ μ ο φ ω τ α ύ γ ε ι α ν (ΤΘΦ). Προσφορωτέρα κρίνεται ἡ μελέτη τῆς ΤΘΦ, καθ' ὅσον ἡ ΦΘΦ πιθανῶς νὰ ἔχῃ ἐπηρεασθῇ λόγῳ θερμάνσεως τοῦ δοκιμίου κατὰ τὴν διαδικασίαν λήψεως αὐτοῦ (τρύπημα, κόψιμο κ.λ.π.). Ἐπιπροσθέτως ἡ ΤΘΦ ἑνὸς δοκιμίου εἶναι φαινόμενον ἐπιδεχόμενον ἐπανάληψιν κατὰ βούλησιν, ὥστε νὰ εὑρίσκωνται μέσαι τιμαὶ τῶν μετρουμένων μεγεθῶν ηὐξημένης ἀκριβείας.

Ἡ μέθοδος δύναται νὰ χρησιμοποιηθῇ εἰς τὴν Ἀρχαιολογίαν, παρέχουσα μίαν πρόσθετον ἔνδειξιν, ὡς πρὸς τὴν δυνατότητα δύο δοκιμίων νὰ συνανήκουν εἰς τὸ αὐτὸ τέμαχος.

Ἐκ τῶν διαφόρων ἐπιδεικνυομένων καμπυλῶν λάμψεως εἶναι δυνατὸν νὰ κριθοῦν τὰ σφάλματα μιᾶς ἑκάστης μετρήσεως, ὡς καὶ ὁ μέσος ὅρος αὐτῶν. Ἐκ τῆς συγκρίσεως τῶν μέσων ὅρων ἐδόθη ἀπάντησις εἰς ἐρώτημα τοῦ Ἐθνικοῦ Ἀρχαιολογικοῦ Μουσείου περὶ τοῦ ἐὰν συνανήκουν 2 θραύσματα μηροῦ καὶ κορμοῦ εὑρεθέντα εἰς ναυάγιον πλησίον τῶν Ἀντικυθήρων.


## R E F E R E N C E S


1. D. McDougall, Thermoluminescence of Geological Materials, Academic Press, 1968.
2. G. Afordakos, Thermoluminescence of greek marbles and calcites, (Thesis). Athens, 1972 (in Greek).
3. D. Curie, Luminescence Cristalline, Dunod. Paris, 1960.
4. Paul Goldberg, Luminescence of inorganic solids, Academic Press, 1966.
5. G. Bonfiglioli, P. Brovetto and C. Cortese, Thermoluminescence and F-centers (Theory) Phys. Rew. 114/951/1959.
6. G. Afordakos, K. Alexopoulos and D. Miliotis, Nature, July 5, 1974.