THERMOLUMINESCENCE DATING OF SOME HUNGARIAN MEDIEVAL CHURCHES

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Summary

Thermoluminescence (TL) dating of some hungarian historic buildings e.g. Churches of Kallósd, Nagykapornak and Türje were investigated. The quartz inclusion technique was applied. The quartz grains selected from the bricks of the Churches were used as samples to the measurement. According to the results achieved by the TL method, the age of the Church of Kallósd (707 years) was about 10%, and that of Nagykapornak about 30% less than that of estimated by some other ways. In the case of the Church of Türje the dating showed a good agreement with the estimated values.

Introduction

The elaboration of the exact methods for the dating of historical building materials, further the adaptation of the methods for the solving of practical tasks of archeology, history of art and protection of monuments are all over the world in the centre of interest [1].

In this field experiments were carried out in Hungary since more than ten years, aimed at the composition of the comparative chronology of historic mortars [2].

Of the physical methods applied in archeology thermoluminescence (TL) method plays an important role in the dating of fired clay (ceramics, terracotta, pottery, bricks, earthenware, tiles, etc.). The fired matrix and mineral inclusions contained reveal TL properties, and at the high temperature ($t > 1000$ °C) used in the preparation of these objects TL indication is erased, and from this time on the "archeological clock" measured the time.

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As contrary to the method based on the measurement of radiocarbon, TL indication increases with the age of the sample. The most simple form of age relationship is:

$$\text{age} = \frac{\text{natural TL}}{(\text{TL/unit dose}) \times (\text{dose/year})} \tag{1}$$

The age relationship (1) is deceptively simple, however, in practice many difficulties are met. These are mainly connected with the TL processes proceeding, and with the details of radiation dosimetry.

The structure of ceramics, earthenware and bricks is heterogenous. In the fired clay matrix mineral inclusions are embedded, which either were already originally present in the initial material, or were deliberately admixed to improve some property. The substance of these inclusions generally is quartz or feldspar, the TL sensitivity of which is considerably higher, than that of the clay matrix. On the basis of this several TL techniques were developed. Of these the quartz inclusion method [3], the fine-grain method [4], the feldspar inclusion method [5] and the radioactive inclusion method [6, 7] should be mentioned. In Hungary the application of the TL method for dating begun in the Seventies [7].

In our work brick was used for the TL dating of historical Hungarian churches. The advantage of this method is that the time of preparation of the

Fig. 1. Kallósd. Romanesque style round church, from the south-east

bricks yielding the samples is generally the same as the time of their building in. However, problems not to be disregarded may be caused by the possible reuse of older bricks, by damage caused by fire, and by younger bricks used at a later renovation. Therefore, samples must be taken with great care and circumspection.

From the aspect of research on the history of architecture one of the most important considerations is that TL dating can be also used in cases, where there are no stylistical characteristics, accompanying materials of finds datable within narrow time limits, or where there are no stylistic characteristics at all.

Fig. 2. Nagykapornak: Roman Catholic church, former Benedictine abbey, western facade

In such cases possibly this is the only mode of dating. The importance of the TL method is to be emphasized in the archeological research of town centers, building components.

The present paper reports on results obtained in the TL dating of the Roman Catholic church of Kallósd (Fig. 1), of the former Benedictine abbey of Nagykapornak (today Roman Catholic parish-church) (Fig. 2) and of the Roman Catholic provostal church in Türje (Fig. 3). Quartz inclusion technique was used in our investigations.

Fig. 3. Türje: Roman Catholic provostal church

Experimental part

Preparation of the samples

A surface layer of some mm of the piece of brick, taken at the findspot and stored in plastics film, was removed, the rest was crushed in a copper mortar and sieved. The fraction of 125–200 μm diameter was processed. The fraction below 125 μm diameter was used for the determination of the radioactivity of the matrix substance.

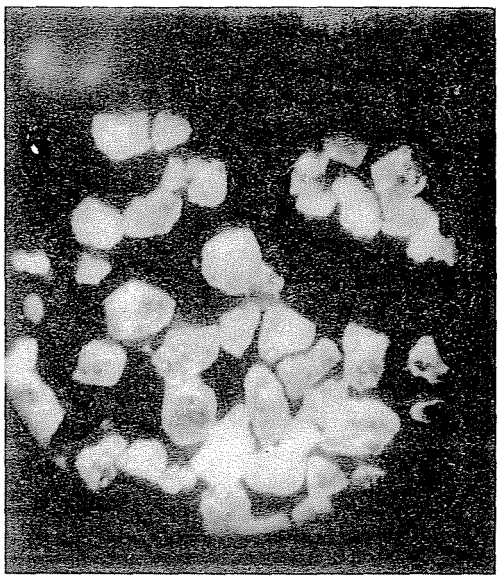

Fig. 4. Microscopic picture of quartz inclusions, obtained from the brick sample of Kallósd

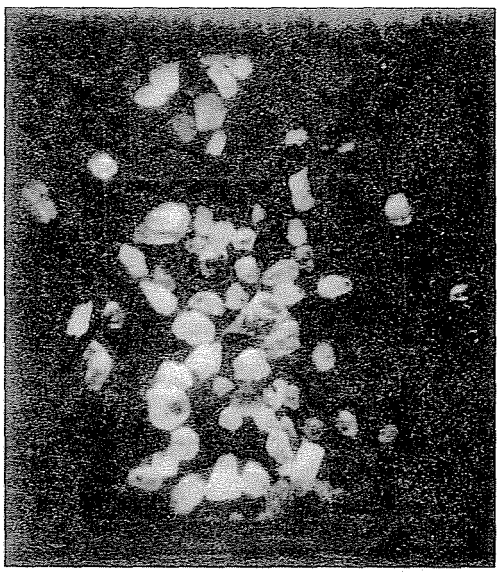

Fig. 5. Microscopic picture of quartz inclusions, obtained from the brick sample of Nagykapornak

Fig. 6. Microscopic picture of quartz inclusions, obtained from the brick sample of Türje

To remove calcium carbonate present in the brick matrix, the 125–200 μm fraction was soaked for a day in concentrated hydrochloric acid, then washed free of chloride ion with distilled water on a glass filter. The colour of the products obtained after washing with hydrochloric acid is generally red. The sample was then kept for an hour in concentrated hydrogen fluoride, washed with distilled water by decanting, while mildly stirring the particles with a glass rod. Decanting was continued until white transparent quartz particles were obtained (Figs 4–6). However, a few coloured particles could be observed among the colourless quartz particles.

Irradiation, measurement

Samples were irradiated with ^{60}Co-gamma rays in the State Office for Metrology. The irradiation dose was 2.5 and 5.0 Gy, respectively. A TLD reader Model TLD-04B, manufactured by MTA-KFKI was used for the measurement of the not irradiated and irradiated samples. Glow-curves were taken with an X—Y recorder, and measurement was carried out in nitrogen

atmosphere. For the evaluation of the measuring results the double heating method was used [9]. Evaluation parameters are contained in Table 1.

Table 1

Evaluation parameters

Heating rate	7.5 C/s
Maximal heating temperature	400 C
Time of keeping at maximal temperature	5 s
Gating	180 C
Termination of counting after keeping at temperature	250 C

Beta dose was measured with a $CaSO_4$: Dy TL dosimeter placed into the matrix substance. Yearly gamma radiation dose and cosmic radiation dose were measured with a $CaSO_4$: Dy TL-dosimeter, arranged and kept for a year at the place of sampling.

Results and their evaluation

The glow curves of the non-irradiated (natural TL : TL_N) samples and of the samples irradiated with 2.5 and 5.0 Gy doses ($TL_{N+2.5}$ and $TL_{N+5,resp.}$) are shown in Figs 7–9.

The integration method was used for the determination of the dose, at the parameters given in Table 1. Evaluation curves plotted from these are shown in

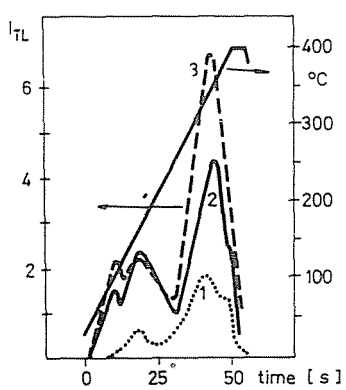

Fig. 7. Kállósd: glow-curves

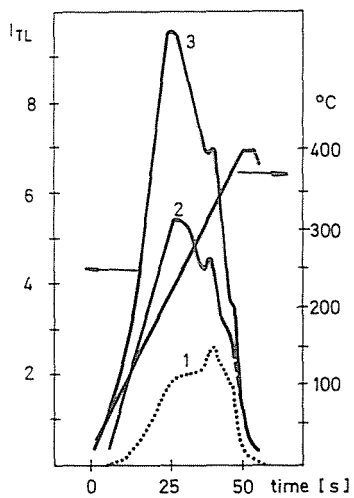

Fig. 8. Nagykapornak: glow-curves

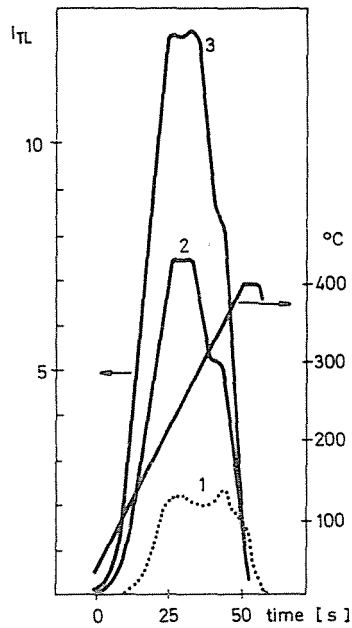

Fig. 9. Türje: glow-curves

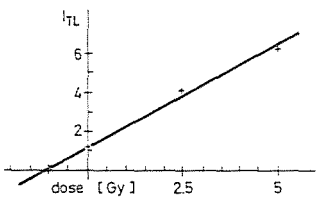

Fig. 10. Kallósd; determination of the equivalent dose (ED)

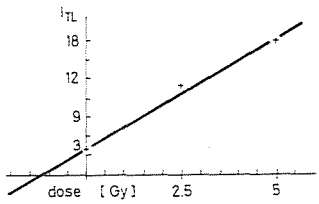

Fig. 11. Nagykapornak; determination of the equivalent dose (ED)

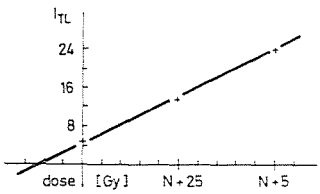

Fig. 12. Türje; determination of the equivalent dose (ED)

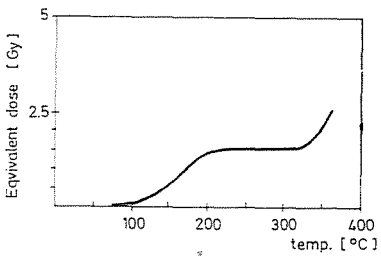

Fig. 13. Türje; the "plateau" test

Figs 10–12. Equivalent doses (ED) determined on the basis of the glow-curves are given in column 5 of Table 2. Table 2 contains the values of the yearly measured beta-dose (D_β), the yearly gamma and cosmic radiation dose ($D_{\gamma+C}$), and the sum of the two ($D_{\beta+\gamma+C}$), that is, the yearly total dose.

Table 2

D_β, $D_{\gamma+C}$, $D_{\beta+\gamma+C}$ and the ED values

	D_β μGy/year	$D_{\gamma+C}$ μGy/year	$D_{\beta+\gamma+C}$ mGy/year	ED mGy
Kallósd	604.2	1023.1	1.6273	1150
Nagykapornak	794	1389.4	2.1834	1250
Türje	629	856.3	1.4862	1100

From data in Table 2 age can be calculated with the following formula, if the archeological dose (AD) is the same as the equivalent dose (this is not always the case):

$$\text{age} = \frac{\text{ED}}{D_{\beta+\gamma+C}/\text{year}} \tag{2}$$

Age and dating calculated with formula (2) are contained in Table 3.

Table 3

Results of dating

Sample	Age (year)	Dating	Dating estimated with architectural-historical methods
Kallósd	707	1276	1180 – 1220
Nagykapornak	572	1411	1200 – 1250
Türje	740	1243	1250

Results obtained with the TL method gave in the case of Kallósd an age younger by about 60–80 years ($\sim 10\%$), in the case of Nagykapornak by about 160–200 years ($\sim 30\%$), than the age estimated with other methods, while in the case of Türje the result is rather good (Table 3). This is supported also by the fact that the sample of Türje showed a very good behaviour according to the plateau-test performed (Fig. 13).

In the TL dating method there are several possible sources of error, which must be taken into consideration and correction, to achieve more exact results. Moreover, in the quartz inclusion technique used it must be investigated, whether our substances show a supralinear behaviour (Δ). If so, its extent must

be determined and taken into correction in the value of the equivalent dose (ED), to obtain the archeological dose (AD), as $AD = ED + \Delta$ (3).

It is further important in the measurement of the beta-dose to refer the values measured by the TL-dosimeters, placed in a polyethylene tube into the substance matrix, to zero wall thickness, and to take into consideration possible radon escape. A further task in the measurement of the yearly gamma-dose is to take into exact correction fading, as the dosimeters are exposed a year at the site of sampling. In the case of the $CaSO_4$: Dy TL-dosimeter prepared and used by us, the expected value of yearly fading amounts to a few percents. Though our measuring results discussed were not corrected, or not with sufficient accuracy, for the above said possible errors, results obtained can be considered as good.

In summary, it can be established that the quartz inclusion TL dating method is applicable for the dating of the bricks of medieval buildings. By the refining of the measuring method the achievement of better results is to be expected.

In our next paper we will report on the possible application of the pre-dose technique and on results obtained with the method.

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