"Thermoluminescence dating laboratory improvements tested on an archaeological rescue site in Trino, Vercelli province, Italy"

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Thermoluminescence dating laboratory improvements tested on an archaeological rescue site in Trino, Vercelli province, Italy.

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***Abstract* – Thermoluminescence (TL) is a reliable radiation-based technique for the dating and authentication of ceramic objects, allowing the evaluation of the time elapsed since their last exposure to high temperatures (e.g. firing in kiln or later fire events). The TL laboratory developed in the last decade at the Physics Department of the University of Torino, currently operating within the INFN (National Institute of Nuclear Physics) CHNet network, is presented. The 10-years-long experience in the field resulted in the enhancement of the procedures, with the development of customised α and β irradiation systems and the optimisation of sampling approach and chemical pre-treatment. In collaboration with TecnArt S.r.l., the improved procedures were employed for dating two structures from a rescue archaeological site in the Vercelli province (Italy).**

Keywords: *Thermoluminescence, dating, customised instrumentation, rescue archaeological site*

I. INTRODUCTION

The dating process of an artefact or structure can be of uttermost importance for the deep understanding of ancient civilizations and their development. Given this need of a certain collocation in the temporal line, the absolute techniques have in time completely complemented the archaeological relative approach [1,2].

Luminescence is a very suitable parameter for characterizing cultural heritage objects, being directly proportional to some intrinsic characteristics of the material. Therefore, out-of-context objects can also be investigated. The team at University of Torino extensively applies in this field various luminescence-based techniques, such as ionoluminescence [3-5] and X-ray luminescence [6], always pursuing the development of customised instrumentation that could better meet the needs of the archaeological and artistic samples. Since 2007, a thermoluminescence (TL) dating laboratory has been developed at the Physics Department, in collaboration with the National Institute of Nuclear Physics (INFN). In the first years of activity it provided an excellent support to the archaeological surveys in the nearby Piedmont area [7,8]. The laboratory has been progressively expanded with new instruments and methods that are presented in this work.

The employment of the TL phenomena for dating purposes was introduced by Aitken and his group in the 60s of the last century [9]. The technique allows to obtain the age of a clay object by measuring the radiation dose absorbed since its last firing in some of its compositional minerals (e.g. quartz and feldspars); this is due to natural occurring radioactivity and it is proportional to the luminous signal emitted by the material when heated at a few hundred degrees Celsius in laboratory. This means that not only the absorbed dose (paleodose) is to be known, but also the dose rate at which the artefact has been subjected in time (annual dose), that depends from the conservation conditions and varies with the geographical area. The age can be consequently calculated by the simple ratio between the two quantities.

A lot of measurements are therefore required for a complete dating: first of all, the evaluation of the paleodose by TL signal acquisitions, obtained via increasing artificial irradiation of samples using α and β sources. The data needed for the calculation of the annual dose are then collected by the measure of the artefact α activity (caused by decay chain events of Uranium and Thorium atoms contained in the clay matrix), the

quantification of the environmental dose rate and the measure of ^{40}K isotope concentration in the material. In addition, further corrections for water absorption, supralinearity and anomalous fading are performed.

Thermoluminescence is an invasive technique, and needs the sampling of about 1-2 grams of powdered material for the preparation of samples by the fine grain method [9]. Clay material from archaeological objects is often contaminated by organic matter and carbonates (the latter enhanced by long time-spans spent in highly-humid burial grounds). This requires a chemical pre-treatment of the powder before the fine grain, to eliminate these sources of spurious luminescence.

In the following sections the equipment and procedures adopted are presented; the results of a recent case study for a complete dating will then be illustrated.

II. THE TL LABORATORY AT THE UNIVERSITY OF TORINO

For the setup of the TL laboratory in the Physics Department of the University of Torino it was decided not to use an all-in-one TL analyser, to be able to adapt the specific components (TL reader, irradiation systems, etc.) to the arising needs of analysis and samples.

The main instrumentations currently used in the laboratory are described in the next sections. All the equipment is operated under red light, as well as the sampling procedures. If necessary, sampling is followed by a chemical pre-treatment of the powder, that is outlined in section G.

A. TL measurement apparatus

The instrumental setup for thermoluminescence measurement consists in a sample holding chamber, a 9235QA Electron Tubes photomultiplier powered at -1100 V by an HiVo voltage supply and the IPSES-TL2000 control unit, regulated by its dedicated software. Between the sample and the phototube two filters are inserted: a KG5 filter that cuts the IR radiation and a BG25 filter that selects only photons in the blue range. The sample is put in the chamber on a heating metal stripe; a thermocouple allows to monitor the temperature and to control the heating rate (kept constant at usually 5-10 °C/s). During measurements, vacuum is generated in the chamber by a rotative pump and nitrogen is inserted up to a pressure of 0.4-0.6 bar, to avoid spurious luminescence and to obtain a homogeneous heating for the sample. The glow curves, as the TL signals are commonly called, are created registering the TL signal every 1 second between 50 and 450 °C.

B. Alpha irradiation system

A customised α irradiation system (fig. 1) was designed, realized and optimised to evaluate the α particles efficiency for each analysed object.

Fig. 1. On the left: α irradiation system with the view of inner sample holder wheel. On the right: β irradiation system and its internal structure scheme.

A steel chamber contains in the upper part a ^{241}Am source, with a 4 MBq activity and an active surface of 16 cm^2. The α source is shielded on the top and sides; the active surface, facing down towards the sample, is protected by a 2 μm Au-Pd layer. In addition, a steel and lead shield is situated between the source and the sample holding wheel, with an automated shutter that opens only during measurements. Since the penetration range of α particle in air is just a few centimetres, vacuum is needed to reach the samples. With an optimal pressure of 170 mbar the particles get to the sample with a mean energy of about 2.9 MeV, providing a dose of 2.0±0.1 mGy/s.

C. Beta irradiation system

For the determination of the paleodose, β irradiations are performed with a $^{90}Sr/^{90}Y$ source with nominal activity of 1.48 GBq and a dose rate of 13.2±0.1 mGy/s. The irradiation apparatus has been developed by INFN. The source is installed in a brass box irradiating downwards and facing the sample holder; this is a wheel with four slots that is accessible through the external brass case by a hole with screw top. Additional shielding is provided by lead plates contained in a plexiglass case. The whole system is fully automated and four irradiations in a row can be set up without reopening the case. Also, a quartz window with 8 mm thickness works as a shutter between the source and the sample wheel when no sample has to be irradiated.

The high repeatability of irradiations was tested and confirmed on (LiF:Mg,Ti) TLD-100 dosimeters with a 0.5 Gy dose.

D. Alpha activity measurements

Uranium and Thorium atoms contained in the clay matrix of the object decay with α particle emission and contribute to the annual dose. The total α activity can be easily determined by covering a ZnS scintillator with a

homogeneous layer of ceramic powder (at least 600 mg): the scintillator emits a photon each time it is struck by the α particle and these photons are collected by a photomultiplier powered at -1100 V. The generated electric signal is transferred to an Amptek MCA 8000A multichannel analyser and the real time spectrum of α counts is created. The system can also evaluate the U/Th ratio using the "pairs" technique [9]. This measurement usually lasts at least 7-10 days for suitable statistics, as the typical count rate *k* for ceramics usually varies between 10 and 20 counts/ks.

E. Environmental dose measurements

The dose provided to the artefact by the radioisotopes present in the surrounding environment can easily be evaluated using thermoluminescent dosimeters (TLDs). These are doped crystals, typically LiF or $CaSO_4/CaF_2$, which indistinctively accumulate energy from α, β and γ particles and their piled up dose can be measured by means of thermoluminescence. TLDs needs to be situated in the exact spot where the sample was collected, recreating the environment in which the sample was conserved before discovery, and kept in place for a very long time (approximately 1 month). If there is no possibility to place dosimeters *in situ*, a good alternative is performing γ spectroscopy measurements on the excavation terrain. TL laboratory users have access to the Biomedical Physics instrumentation at the University of Torino, that is equipped with a cooled cylindric HPGe detector with a diameter of 48.2 mm; special beckers with "Marinelli" geometry are used due to the cylindrical symmetry. The analysis supplies the activities of each radioisotope and allows to measure the annual dose provided by U and Th chains as well as by ^{40}K. Lastly, if it is not possible to acquire a sufficient amount of terrain for the analysis, it can be supposed an equality between the activities of the environment and the artefact itself.

F. Other measurements

If the sample is conserved in a high humidity environment, the open porosity of the ceramic material can be filled with water that partially absorbs the ionizing radiation. A correction to the annual dose is then needed, considering the ratio

$$W = \frac{w_{wet} - w_{dry}}{w_{dry}} \quad (1)$$

where *w* is the weight of the sample. For W evaluation, a small fragment of the archaeological sample is saturated with distilled water, then a Sartorius MA35 moisture analyzer is used to heat it for 15 minutes up to 150 °C. The weight is measured every second with an accuracy of 1 mg; when no further change in weight is detected, information on moisture content and W ratio is displayed.

The quantification of K content for the sample is obtained via ICP-OES analysis performed at the Chemistry Department of the University of Torino with a Perkin-Elmer Optima 2000 spectrometer. The resulting percentage by mass for K is then used to directly calculate the contribution to the annual dose of his radioisotope ^{40}K, up to some multiplicative constants [9].

G. Sample pre-treatment

Most often the sampled powder needs a chemical treatment for the elimination of carbonates and organic matter, main causes for spurious luminescence. At first the procedure finalised in the IRAMAT-CRP2A laboratory of Bordeaux was employed, using three different reagents: hydrochloric acid (HCl), hydrogen peroxide (H_2O_2) and hydrofluoric acid (HF) [10]. However, in the last years, our TL laboratory has customised this procedure on the basis of application experience. It was verified that the use of the same reagents in higher concentration but for a shorter time provides the same results, simultaneously speeding up the method. Moreover, it is not always necessary to use them all: depending on the sample and the knowledge of its composition and conservative environment one can choose to use HCl or H_2O_2 only. Acetic acid (CH_3COOH) in concentrations between 30 and 10% w/w is also an effective substitute for hydrogen peroxide in organic matter removal. Considering the shorter reaction time required for this preparation, it can result as more convenient when organic matter presence is prevalent.

It must also be stressed out that each step of the pre-treatment procedure causes the loss of a part of the material, small but significant in the cultural heritage field where availability is scarce from the beginning. To further limit these losses, a vacuum system coupled with a 1 μm pore size paper filter is used to retrieve and wash the powder in one single step.

After the chemical treatment, the powder is deposited on the analytical aluminium disks using the fine grain technique described in [9].

III. CASE STUDY: DATING OF BRICKS FROM AN EXCAVATION SITE IN TRINO (VC), ITALY

In 2016, the excavations for the construction of a new gas pipeline in the Vercelli province, Piedmont (Italy), revealed the presence of some ancient brick structures. The institution in charge of the rescue archaeological site (Soprintendenza Archeologia Belle Arti e Paesaggio delle Province di Biella, Novara, Verbano-Cusio-Ossola e Vercelli) requested some TL dating analyses for a sepulture and a building found outside the city of Trino, at geographical coordinates 45°11'30.5"N – 8°16'51.1"E. The analyses were performed in collaboration with TecnArt S.r.l., a company dedicated to scientific diagnostic for cultural heritage and founded as a spin-off of the University of Torino.

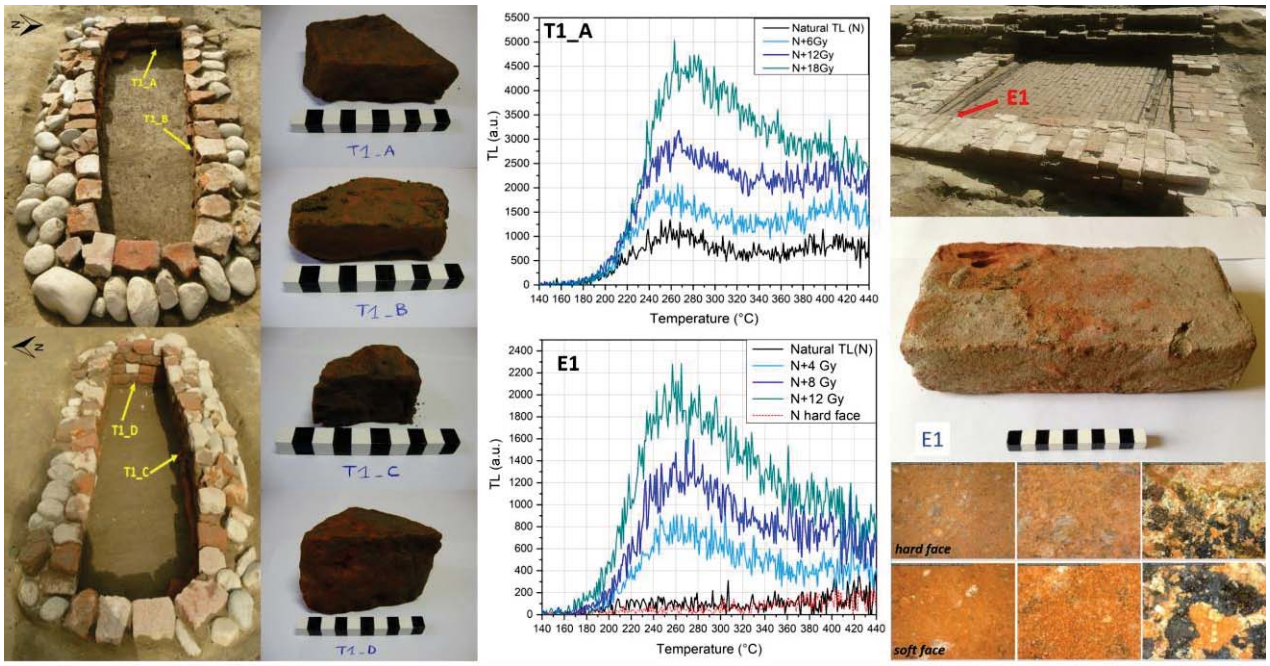

Fig. 2 Samples from Trino excavation site and TL glow curves. On the left: tomb T1, its four samples and their original position. On the right: the studied brick from the building (E1) and optical microscope images of its "hard" face (upper row) and soft face (lower row). In the center: an example of glow curves resulting from the additive method measurements: the natural TL signal for the hard face is also reported with a red dashed line.

A. Structures and in situ sampling

The first of the two structures chosen for TL analysis was a sepulture with W-E orientation, built with an outer stone wall and an inner brick one (fig. 2). Inside the tomb a brick curb was also present, applied at a later time to the main construction and creating a new space section where a smaller skeleton was conserved. Four bricks were sampled, one for each wall but all of them from the deepest level of the tomb. In particular, sample T1_C and T1_D were extracted from the main structure, whereas T1_A and T1_B were collected from the inner curb. TLDs were placed in the sampling spots, covered with excavation terrain and left *in situ* for 28 days.

A short distance away from the burial, a very well preserved brick flooring with two wooden beams was found (fig. 2). From the shape of the bricks and the type of the construction, this building was considered definitely more modern than the tomb by the archaeologists. Due to the closing of the rescue excavation, only one sample (E1) was retrieved; also, as it was impossible to leave dosimeter on site, the environmental dose was obtained in this case with γ spectrometry measurements on both the powdered brick and the surrounding terrain.

B. TL dating procedures

For each brick of the sepulture, at least three values of effective dose (ED) were calculated by additive dose method [9] with β irradiations; the effective dose is exactly equal to the paleodose when supralinearity is absent. The collected powder (about 1 g per sampling by drilling) was treated only with HCl 15% w/w for 45 minutes, but no evident effervescent reaction was observed.

The brick from the building presented a peculiar hardness on one of the larger faces, whereas the specular face had a soft ceramic body and was easy to sample with the drill. The comparison of microscopical observations did not highlight differences beyond a more intense reddish hue of the soft part; on the other hand, the TL natural signals were quite different, as the one from the harder side seemed to be bleached up to 300 °C (see fig. 2). Powder from the bulk was then also analysed, and the TL response was compatible with the soft side. It can be assumed that this brick was subjected to an inhomogeneous firing in kiln or that was reached by an high temperature blaze. On this hypothesis, only results from the soft face and the bulk were considered for statistical purposes on the effective dose determination. Powder from the surface was treated for 45 minutes with HCl 15% w/w; as in the bulk the organic component was high enough to alter the TL natural signal, in this case a 60 minutes treatment with CH_3COOH 10% w/w was preferred.

In addition, for all the samples, about 1 g per brick was destined to α spectroscopy and U-Th counts. Absence of

Table 1. Results of TL dating measurements for Trino samples. For sample E1, a distinction is reported for results obtained using γ spectroscopy on terrain (T) or on brick (B).

Sample	**T1_A**	**T1_B**	**T1_C**	**T1_D**	**E1**
Chemical pre-treatment	HCl 15%w/w	HCl 15% w/w	HCl 15% w/w	HCl 15% w/w	HCl 15% w/w (surface) CH_3COOH 10% w/w (bulk)
# ED evaluations	3	3	4	3	3
T integration interval from plateau test (C°)	320-380	350-390	330-370	350-400	350-380
Added β doses (Gy)	6-12-18 (x2) 12-24-36	4-8-12	4-8-12 (x3) 4-8-16	4-8-16	4-8-12 (surface) 2-4-8-12 (x2) (bulk)
ED β (Gy)	4.27±0.28	4.73±0.11	2.75±0.08	2.57±0.19	1.10±0.18
Supralinearity	none	none	none	none	none
Anomalous fading	none	none	none	none	none
Paleodose (Gy)	**4.27±0.28**	**4.73±0.11**	**2.75±0.08**	**2.57±0.19**	**1.10±0.18**
Counts α/ks	16.1±0.1	13.3±0.1	13.0±0.1	12.3±0.1	11.0±0.1
W%	16.65±0.01	13.65±0.01	11.48±0.01	15.29±0.01	13.52±0.01
K% w/w	1.26±0.08	1.16±0.08	1.30±0.09	1.27±0.09	1.19±0.08
ED α (Gy)	233±35	115±23	65.6±3.4	37±5	23.4±4.8
k coefficient	0.015±0.003	0.034±0.007	0.035±0.002	0.058±0.009	0.04±0.01
Environmental dose (μGy/yr)	1292±40	1459±56	1432±187	1213±246	***T*** 673±84 ***B*** 1038±103
Annual dose (μGy/yr)	**3470±230**	**3740±240**	**3840±270**	**3820±350**	***T*** **2800±240** ***B*** **3160±250**
Age (yrs AD)	**790±110**	**750±80**	**1300±50**	**1340±70**	***T*** **1620±60** ***B*** **1670±50**

supralinearity was verified with regenerative method, anomalous fading was checked and K quantifications were performed. Finally, effective dose via α irradiation was also obtained, in order to calculate the *k* coefficient. All the measured and calculated parameters resulting from the TL dating can be found in table 1.

C. TL dating results

The age determination for samples coming from tomb T1 led to a very interesting result: bricks T1_A and T1_B go back to VIII century AD (790±110 and 750±80 respectively), but the other two samples to XIV century AD (1300±50 for T1_C and 1340±70 for T1_D). In such a case, TL dating assigns the sepulture as contemporary to the more recent component, hence reuse material was employed for building the curb. It should be noted that the medieval bricks could have been reused as well: a comparison with radiocarbon dating on the skeletons could then be crucial but, unfortunately, bones and teeth were too deteriorated by the very acid soil.

The case of this tomb highlights how important the *in situ* sampling phase can be in the results interpretation: if only bricks near T1_A and T1_B were to be collected, they would have not been representative of the real age of the tomb and would have induced an inaccurate dating.

On the other hand, although the flooring appeared very homogeneous in material constitution, the analysis of only one brick from the building can not represent the whole structure. However, this case is an example of how γ spectroscopy can alternatively be used on the brick itself or on the surrounding terrain: the two calculated ages are compatible (1670±50 AD using the brick and 1620±60 AD using the soil) and confirm the archaeological hypothesis of a more recent construction.

IV. CONCLUSIONS

The improvements brought about in the thermoluminescence dating laboratory at the University of Torino allowed to perform faster and more automated measurements, but always tailored on the specific artefact under investigation. The approach starts with a representative sampling *in situ* and a more flexible chemical pre-treatment, if needed. The new irradiation systems consent to collect more data in the same amount of operating time, enhancing the statistics.

Our analyses of brick samples from the rescue excavation site in Trino led to a dating result with less than 15% error. The studied tomb resulted to be an interesting example of building material reuse and its realisation appears to go back to the XIV century AD.

The adjacent flooring allowed to test two different ways to measure the environmental dose, performing γ spectroscopy on both excavation terrain and the sample brick. The resulting two values for calculated age are compatible and correspond to the XVII century AD.

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