2020 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Trento, Italy, October 22-24, 2020

Thermoluminescence dating and microstructural characterization of archaeological ceramic samples from Corvins'Castle area

Rodica-Mariana ION[1,2*], Radu SETNESCU[3,4], Tanta SETNESCU[4], Anca Irina GHEBOIANU[5], Gabriel VASILIEVICI[1], Sorin TINCU[6]

[1] *ICECHIM, Group "Evaluation and Conservation of Cultural Heritage", Bucharest, Romania*
[2] *Valahia University, Materials Engineering Doctoral School, Targoviste, Romania*
[3] *National Institute on Electrical Engineering (INCDIE ICPE-CA), Bucharest, Romania*
[4] *Valahia University of Targoviste, Faculty of Sciences and Arts, Targoviste, Romania*
[5] *Institute of Multidisciplinary Research for Science and Technology, Valahia University of Targoviste, Targoviste, Romania*
[6] *Corvins' Castle, Hunedoara, Romania*

Abstract – Some ceramics samples from Corvins'Castle area – Coart Area, in different weathering stages, have been analyzed in this paper by different analytical techniques: XRD, thermal analysis (TG, DTG), porosity and thermoluminescence (TL) dating. For identification of the technology employed in the pottery production, the firing temperature could be determined through the presence of some minerals (evidenced by XRD), quartz and calcite being the most important ones. Crushed calcite is a good indicator, because it is present in the ceramics which have been tired up to 750° C (under oxidized atmosphere). By TL the nature of the crystalline network could be detected, ceramics consist of a number of crystalline inclusions (mainly quartz and feldspar) embedded in the ceramic matrix. The peak related to 343 °C is always found in quartz. The date obtained by TL technique was in good agreement with the date assigned by archaeologists.

I. INTRODUCTION

Pottery is the most abundant material found on various archaeological sites [1,2]. Pottery sherds can be dated by different methods, the luminescence dating and have become common current alternative methods for assessing the chronological information of archaeological sites it has the two major advantages: it offers the age in calendar years and also, the dates the ceramic object directly [1].

In the last few years, there have been major developments in both luminescence dating instrumentation and measurement methodology. Nevertheless, the application of luminescence to burnt pottery appears to have benefited only little from these advances in dating technology.

The thermoluminescence (TL) technique may provide complementary information to other techniques, describing the state and characteristics of crystalline defects and dating is based on the measurement of the amount of light that is released upon thermal or optical stimulation, by minerals such as quartz and feldspar [2]. The mechanism of this method consists in the interaction and effect of ionizing radiation on an irradiated solid, which depends both on the nature of the solid body, the nature of the crystalline network and the nature of the ionizing radiation. Some trace amounts of radioactive atoms, such as uranium and thorium, in rock, soil, and clay produce constant low amounts of background ionizing radiation. The atoms of crystalline solids, such as pottery and rock, can be altered by this radiation in these minerals through time. Specifically, the electrons of quartz, feldspar, diamond, or calcite crystals can become displaced from their normal positions in atoms and trapped in imperfections in the crystal lattice of the clay molecules. This energy charged electrons progressively accumulate over time [3].

The crushed calcite is a good indicator, because it is present in the fabrics which have been tired up to 750° C (under oxidized atmosphere) whereas at a higher temperature it disappears leaving a well-defined rhombohedral shape void. These electrons are released from the interaction of nuclear radiation with the crystal in the case, and their number is proportional to the absorbed dose, causing dose rate, an age can be calculated. The moment that is dated is one zero time when resetting this information. In the case of pottery, this moment is represented by the burning of the vessel, the distinct stage in the process production.

The luminiscence dating is relatively simple, can be summed up as follows:

Age (Archaeological) = Archaeological Dose/Annual Dose

In this paper, the thermoluminescence technique has been used to date some ceramics samples from Corvins'Castle – the Court Area. Except these measurements, XRD technique has been used to identi thermoluminescence measuring by the main minerals as calcite, quartz, present in the samples, porosity parameters, TGA/DTA thermal techniques in order to correlate the type of sample with TL measurements and EDS for identifying the main elements present in the samples.

2. EXPERIMENTAL PART
2.1 Materials

The pottery sherds have been collected from Court Area, Hunedoara. They have different colored from yellow to brown or even black, as could be shown in Figure 1.

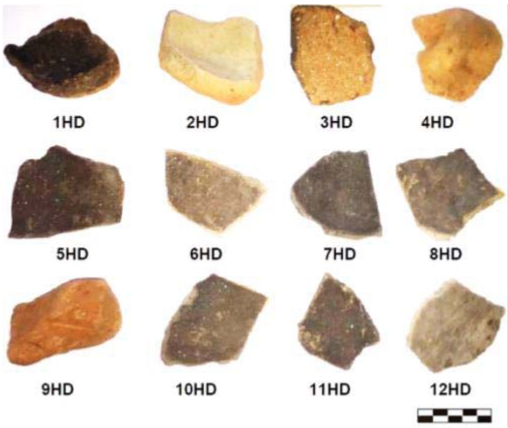

Figure 1. The photo of the investigated sample

2.2 Methods

Thermal analysis (DTA and TGA) was conducted on a Shimadzu derivatograph DTG-60H at a heating rate of 10°C/min, from room temperature up to 1100°C. Alumina open crucibles and α-alumina powder as reference material were used, and the measurements were performed in a dynamic nitrogen and air atmosphere at a flow rate of 70 ml/min.

The X-ray diffraction (XRD) investigations were conducted with a Shimadzu XRD-6000 diffractometer, using Cu-Kα radiation (λ = 1.5418 Å), with Ni–filter. The XRD patterns were recorded in the 2θ scan range 10-80°, with a scan speed of 2°/min, using quartz powder as calibrating material. The operating power of the X-ray source was 40 kV at 30 mA intensity.

The nitrogen adsorption/desorption isotherms were recorded at 77K in the relative pressure range p/po=0.005-1.0 using NOVA2200e Gas Sorption Analyzer (Quantachrome). Data processing was performed using NovaWin version 11.03 software. Prior to adsorption measurements, the samples were out gassed 4 hours at 300°C under vacuum. The specific surface area was determined by the standard Brunauer-Emmett-Teller (BET) equation. The total pore volume was estimated from the volume adsorbed at a relative pressure p/po close to unity. The pore size distribution and mesopores volume were obtained from desorption branch of the isotherm by applying the Barrett-Joyner-Halenda (BJH) model. The t-plot method was used to estimate micropore surface area and external surface area.

For thermoluminescence (TL) emission measurement, a FIMEL LTM type device with a high voltage source (HV) supplying the photo multiplier tube (PM), the sample furnace (F) placed under the window of the photomultiplier tube, the heating programmer (H) which ensures the increase of sample temperatures after a certain program; amplification stages and electronic signal processing photomultiplier tube. Measurement of TL emission was performed with the FIMEL LTM under the following conditions: sample mass: 5-6 mg powder; voltage applied to the photomultiplier tube: 850 W; heating rate: Different heating rates ranging between 0.5 and 5 ° C / min; the atmosphere around the sample: air; integration range: between 50 ° C and the TL peak offset. The pre-irradiation of the samples to record the signal was performed with gamma radiation using a Gammator M-38 (Radiation Machinery) equipped with 137 Cs radioisotope. The source activity was 22.9TBq, and the dose rate was 370 kGy / h. All irradiations were carried out at ambient temperature in the presence of air, the samples being placed in open glass tubes.

The recording of TL signals was done using a cryostat coupled with a photomultiplier EMI-9558 QA and a recorder ORION-EMG. The increase in temperature was measured with a thermocouple iron/constantan at a heating rate of 90 °C/min.

3. RESULTS AND DISCUSSION

The settlement from the Hunedoara – the Court area was discovered in the 70th by the priest Petre Govora, who, on the occasion of some public works, harvested a series of ceramic fragments that have been published [1]. The ceramics discovered in this area is mostly coarse and belong to the same the cultural horizon, with colours ranging from brick or orange to brown and black. Sporadically, ceramic fragments were burnt in the black-topped technique.

In the last century scientists worked to establish new methods for dating pottery, different relative techniques used to determine the chronological sequence of pottery artefacts [9]. Under such context, some authors suggested a new method of dating geological materials that depends on the luminescence energy released of minerals by heating or being subjected to light [10].

This method is applied to some categories of fired ceramics at temperatures above 500 ºC. The method is based on the principle according to which, for ceramics fired at temperatures around 500 degrees, the energy clock is erased. From that moment new recordings begin. The phenomenon is known as thermoluminescence. It is known that radiation (alpha, beta or gamma), caused by various radioactive sources (x-rays or cosmic rays), produces ionization. Crystals almost always contain traces of urmanium or thorium, which are radioactive metals. All this allows the recording and measurement of the radiation dose of the ceramic material in which the respective crystals are located.

The investigated samples show a firing treatment of the ceramic between 700 and 900 °C, where the sample underwent a series of phase transformations such as dehydration of hydroxides (gibbsite and goethite) and dehydroxylation of kaolinite to metakaolinite formation. This range of temperature is characterized by the decomposition of carbonates, which starts at around 650 °C and ends at around 800-850 °C. Calcite, the most common pure calcium carbonate ($CaCO_3$), decomposes in calcium oxide (CaO) and release CO_2 increasing the porosity. The presence of calcite in the spectrum indicates that the firing temperature is lower than 850°C, which is the approximate maximum temperature at which calcite may still exist. All these data are correlated with porosity experiments, Table 1.

The porosity has long been recognized as an important tool for study of ceramics: raw materials, clay processing and fabrication methods, firing regimes, and the deterioration factors [11]. During clay processing and fabrication, some air bubbles could form and the shrinkage during firing could led to larger pores, Table 1. There are two types of pores: long linear pores (with parallel alignment, which can appear from shrinkage of the clay and water release) and less interconnected linear pores (that appear at higher firing temperatures at lower firing temperatures. If firing temperatures are high enough, porosity can decline if vitrification occurs and bloated round pores could appear visible at overfiring. The bulk porosity analysis would not be as informative as being able to examine the variety in size, volume, and distribution of the pores (Table 1). In our case, the pore volume and diameter are quite similar, but the surface area are different, this last observation could be an evidence of nanometric size of the pores. Higher value of surface area, means smaller size of the pores.

Table 1. Porosity parameters for ceramic samples

Sample	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (nm)
1	17.392	0.026	4.287
2	8.710	0.015	2.959
3	16.955	0.026	4.259
4	17.615	0.026	4.275
5	22.68o	0.033	4.258
6	9.575	0.015	3.264
7	11.657	0.017	4.249
8	9.677	0.016	4.237
9	17.165	0.022	4.245
10	13.941	0.022	4.249
11	8.339	0.013	4.238
12	9.238	0.017	4.259

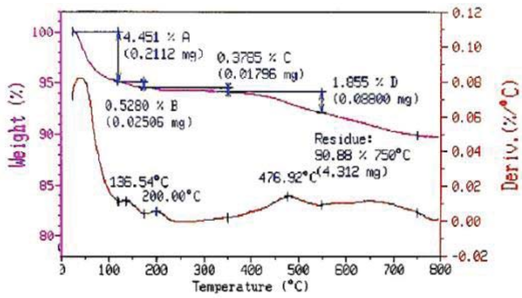

Figure 2. TG/DTA of the ceramic samples

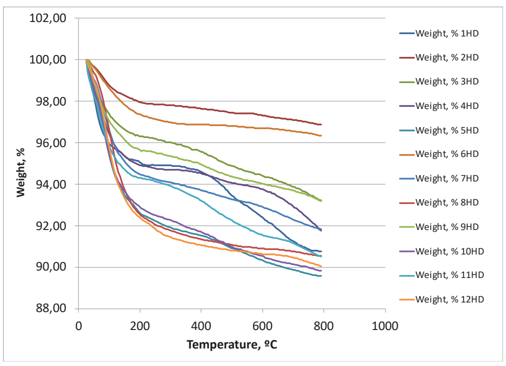

Figure 3. TGA analysis of the ceramic samples

From the XRD spectra, could be possible to identify the major phase as quartz at the following 2 theta values: 20.82 (1,0,0), 26.60 (0,1,1), 36.47 (1,1,0), 39.42 (1,0,2) and 40.23 (1,1,1). Except this phase, graphite have been identified at 27.85 (0,0,2) and niocalite at 23.736 (2,2,0), 25.38 (25.38(0,0,2), 27.85 (0,3,0) and 40.23 (3,3,1), microcline with the major peak at 65.64 (1,1,4) and a spinel phase at 31.25 (2,2,0).

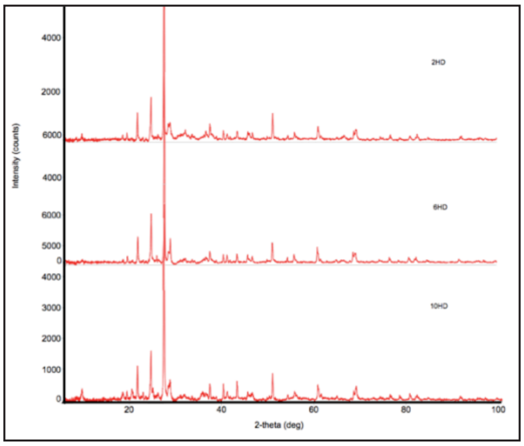

Figure 4. XRD for some ceramic samples

Many naturally occurring TL mineral constituents of ceramics, including quartz and most feldspars, are able to act as dosimeters for ionising radiation. This radiation comes from uranium, thorium and potassium present in the ceramics or in soil surrounding it, in the concentration of few ppm.
The colour of the cross section of the ceramic sherds was used to develop a hypothesis/model for the deduction of firing atmosphere [12]: red and brown colour caused by Fe^{3+} indicated the oxidizing atmosphere; black and grey colour caused by Fe^{2+} indicated the reducing atmosphere; combination of black/grey and brown/red indicated the change from a reducing atmosphere to an oxidizing atmosphere. The modal composition of the ceramics was calculated on the basis of the X-ray diffraction and EDS, correlated with thermal analysis [13]. The analysed oxides were attributed to minerals in the following way: Na_2O: plagioclase (albite); K_2O: K-feldspar (microcline), mica (biotite); CaO: plagioclase, apatite; MgO: mica (biotite); FeO/Fe_2O_3: biotite, goethite/hematite; Al_2O_3: feldspar, metakaolinite, mica (biotite); SiO_2: quartz, aluminosilicates; TiO_2: biotite, rutile. The elements responsible for these ceramics have been identified by EDS and will be reported in the future publications. An average chemical composition of the homogeneous group of ceramics fitted with the chemistry of the clays. It can be suggested that potters did not modify the clay paste during pottery manufacture. The lower content of silicon oxide and the higher contents of iron, magnesium, calcium and sodium oxides in this ceramic clearly revealed its different origin (probably from another place as a cultural exchange with near localities [14].
Finally, TL measurements were also performed on the sample to calculate the equivalent dose, De. TL characterization was carried out to study the thermal stability of this emission. This peak is probably related to 325 ^{O}C TL peak always found in quartz. The other peaks might be satellites, especially with high temperatures, which include the 375 ^{O}C TL peak of quartz, which in the sample presented low intensity and large noise. The mean value of the *De* values calculated from 325 to 375 ºC (343 ºC) was used to age determination, and it was estimated as *De* = (6.13±0.06) Gy. The parameters used in quantification were the maximum temperature (T_{max}), the height of the peak (I_{max}), and the area (integral) of the peak (S_{int}) between the range considered, Figure 5. It was observed that the TL signal increases with the radiation dose, both the peak height and the area of the RTL peak increasing with the dose.

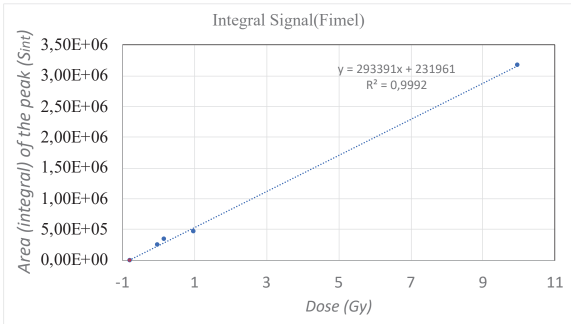

Figure 5. The relationship between S_{int} and Dose

Knowing that D_0 = 0,792 Gy, the final TL age is dating from 1727 ± 30 years. Conversion of a TL age (A = 227 ± 30 years) to a calendar date is achieved through the linear transformation g(t) = (2000 − t), knowing that in this period of time has been produced similar ceramic vessels. This age value of 1727 ± 30 years could also be explained to anomalous fading from constituent feldspars [15]. These ceramic pieces belong to the semifine category and are brick-coloured and brownish-brick-coloured, with traces of soot in the inferior side (visible by high residue concentration, as Fig.2 shows), most probably from a stove, possibly dated from the middle of the XVIth century and the beginning of the XVIIth century [16]. The ceramic belonging to this area is the most numerous category of medieval pottery, but it is also the least analyzed, as noticed P. L. Szöcs that made a brief analysis of the historiographic segment of the pottery in Transilvania, in the XVIth - XVIIth centuries [17].

4. CONCLUSIONS

Some ceramics samples from Corvins'Castle area – Coart Area, in different weathering stages, have been analyzed in this paper by different analytical techniques: XRD, thermal analysis (TG, DTG), porosity and thermoluminescence (TL) dating. Crushed calcite is a good indicator, because it is present in the ceramics which have been tired up to 750° C (under oxidized atmosphere). The ceramics consist of a number of crystalline inclusions (mainly quartz) embedded in the ceramic matrix, and through the peak related to 343 ºC found in quartz, was possible to determine the ceramic samples age. TL is recognized as the most proper dating method for ceramics and the age of the analyzed ceramic samples was from XVIth - XVIIth centuries, in good agreement with similar reports.

Acknowlwdgements: This work was supported by the project: PNIII 51 PCCDI/2018 and 5PS/2019.

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