# INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS TO DETERMINE THE ANNUAL RADIATION DOSE FOR THERMOLUMINESCENCE DATING OF POTTERY FROM CANINDÉ-SERGIPE, BRAZIL

**José O. SANTOS[1], Mauro. J. SANTOS[1], Casimiro S. MUNITA[2]**

[1]Instituto Federal de Educação, Ciência e Tecnologia de Sergipe, IFS, Av Lourival Baptista s/n, (79000-000), Lagarto, SE. Brasil. osmansantos@ig.com.br.
[2]Instituto de Pesquisas Energéticas e Nucleares (IPEN–CNEN/SP), Av Prof. Lineu Prestes, 2242 (05508-000) São Paulo, SP, Brasil.

Thermoluminescence (TL) dating is an important method for dating archaeological potteries, the method is based in the thermoluminescence emission of the quartz signal. The age calculation requires estimating two factors: the equivalent dose (*De*) which is the absorbed dose and the annual dose ($D_{an}$). The ratio between both doses, $D_e$ / $D_{an}$, provides the age. In order to obtain pure quartz grains from each ceramic fragment to estimate de $D_e$ a chemical procedure was used. The $D_{an}$ dose rate determination was performed by means of the determination of U, Th and K concentrations using INAA. This paper shows as the relation of thermoluminescence (TL) and radiochemistry techniques can help to solve chronological problems for areas with poorly stratified sites and few organics remains, such as archeological sites at Canindé - Sergipe, Brazil. This study uses TL to dating potteries that were collected during the excavation at Canindé, where the potteries is greatly expressed because many ceramics are associated to mortuary sites. The additive dose method was used to determine the paleodose in potteries samples in which the response at 320 ºC peak as a function of the added dose was linear. The ages determined resulted in a range between 457 and 3,716 BP. Considering the results, this work provide a contribution for chronological reconstruction of Brazilian Northeast ceramist population.

Keywords: thermoluminescence dating; Archaeometry; Annual Dose rate; INAA.

## 1. Introduction

Ancient potteries represent a sophisticated merging of previously separate domains of human knowledge and experience, these objects are intensely studied by means of archaeometric methods around the world [1, 2]. Visual properties such as shape and surface decoration are frequently used as cultural and chronological indicators. In addition, microscopic properties such as paste texture (i.e., the clay and temper combination) can be used to study preparation techniques. The chemical composition can be used to locate the source(s) of ingredients or to provide evidence of geographic displacement. Oxidation state of iron-bearing constituents can be used to reconstruct firing conditions. Trace elements present at concentrations below 1000 ppm usually provide the best information for provenance studies [3].

In the context, the radioanalytical science to develop the methodology for the investigation of properties and structure of matter at level of single nucleus and scientific analysis to determine either composition or elemental contents have been indispensable in archaeology application [4 – 8]. According Blackman & Bishop (2007), as a result of the dedication of nuclear and physical chemists the protocol for the application of INAA, the most radioanalytical technique to archaeological studies of potteries, to the study of archaeological ceramics has been well established [9]. Generally, a large proportion of archaeological and archaeometry investigations are oriented towards ancient culture, having as their main objectives: compositional identification and archaeological dating. One of the most questions in archaeometry concerns the age of the archeological objects. In this paper, particularly, the archaeometry studies from pottery samples collected at Canindé – Sergipe, Brazil, by means of Thermoluminescence (TL) dating have been carried out to establishing of chronology of archaeological sites in the area of Xingó.

The luminescence stimulated thermally (thermoluminescence – TL) has been applied in several archaeological studies to dating of inorganic materials [10]. The TL emission is the result of the light releases charged from light – sensitive traps in crystals of minerals such as quartz and feldspar. To understand the TL emission from material and its dosimetric properties for TL dating, the defect structure of an insulating and semiconductor has been studied for several authors [11, 12]. Archaeological ceramics contains polyminerals that it can receive ionizing radiation from radionuclei in surrounding soil and this natural irradiation causes ionization and creates electron/hole pairs, which can be trapped at lattice defects within structure of mineral [13]. Since these electrons and holes accumulate with time, and when excited by heating they can recombine and the photons are emitted, their amount and thus the thermoluminescence signal can be used to dating [14, 15].

In fact, the basic principle of TL dating is that clays and its temper of pottery lose their accumulated geological dose when the pot is fired during its manufacture. The newly formed pot is now subjected to natural radiation from its surrounding and the pottery accumulates an absolved dose which is proportional to its archaeological age [16]. The absolved dose is a result of radiation from all material surrounding which contains a small amount of naturally occurring radioactive materials such Uranium ($^{235}U$ and $^{238}U$), Thorium ($^{232}Th$), Potassium – 40 ($^{40}K$), a few Rubidium ($^{86}Rb$) and cosmic rays. For establishing of the chronology by TL method, it is require the measurement of the absorbed dose of ionizing radiation (paleodose) and the annual dose rate.

Potassium – 40 is radioactive and decay it emanates beta and gamma radiation. The various members of thorium and uranium series emit a variety of alpha, beta and gamma radiation and the amount of thermoluminescence induced depends both on the rate of emission and on the energy carried by radiation [15]. To determine the annual dose rate we need to know the rate at which energy is being deposited by the various radiations from radionuclides. In this work, the INAA has been used to determine the composition of soil surrounding of potteries and K, Th, Rb and U concentrations it has been converted in annual dose rate according [17].

In this work, a pilot study aims to demonstrate how the thermoluminescence and instrumental neutron activation analysis applications can be used to establish the chronology of archaeological sites at Canindé-Sergipe, Brazil, which rarely contain artefacts organics to dating by carbon-14. The TL method has been used to dating the pottery samples from four archaeological sites: Justino, São José, Saco da Onça and Curituba. The archaeological sites are situated in Canindé do São Francisco, a city in the area of São Francisco River, about 150 km from Aracaju, capital of Sergipe State, Brazil (Figure 1).

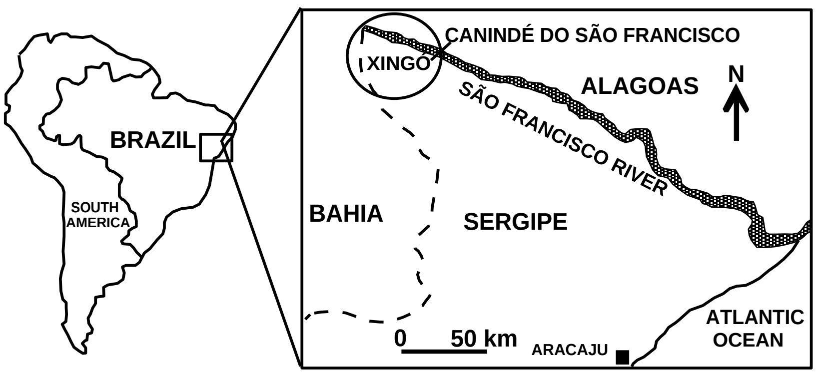



**Figure 1. Study area localization map**

The fragments used for dating in this work are from vessels excavated during a rescue archaeological project. This rescue occurred when a large alluvial terrain on the margins of São Francisco River, in the area of Canindé do São Francisco, Brazilian Northeast, was flooded due to the construction of the Hydroelectric Xingó Dan.

Archeological studies accomplished in the area have shown that the pottery form the studied sites have the same technical profile [18]. Recent studies carried out in the area have shown the existence of an independent ceramist group, with no relation to the ceramist group well established in the Brazilian Northeast, called Tupiguarani and Aratu [19]. Dating obtained by means of $^{14}C$ from skeletons has indicated that in the "Xingó" region there is evidence of the human occupation 9,000 years BP. Thus, this chronological study for thermoluminescence method aims to contribute to studies related to the establishment of a new ceramist culture at Brazilian Northeast.

## 2. Experimental Methodology

### 2.1 INAA Analysis

***Sample preparation and standard***

The annual natural dose rate was determined by means of INAA using U, Th, Rb and K content in the soil and in the sample. For INAA, the sample was powered and dried at 105°C for 24 h. The powder was weighed into a polyethylene bag, which was packed in aluminum foil and irradiated into the research reactor IEA-R1m with a thermal flux of about 5 $10^{12}$ n $cm^{-2}$ $s^{-1}$ for 8 h. The gamma spectrometry was carried out using Ge (hyperpure) detector, with 1.90 keV resolution at the 1332.49 keV gamma peak of $^{60}Co$, coupled with Canberra S – 100 MCA, constituted with 8192 channels. These measurements were divided in two, one realized after 7 days of cooling for K and U determination and after 30 cooling days for Th and Rb determination.

Constituent Elements in Coal Fly Ash - NIST-SRM-1633b, were used as standards in all analysis. The standard reference material Brick Clay - NIST-SRM-679 was used to check the analytical quality of the results. The standards and the samples were dried in an oven at 105$^{o}$C, the standards for 4 h and samples for 24 h and stored in a desiccator until weighing [5].

***Irradiation and radioactivity***

About 100 mg of ceramic samples, and NIST-SRM-1633b were weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 ceramic samples and two reference materials were packed in aluminum foil and irradiated in the swimming pool research reactor, IEA-R1m (IPEN/CNEN – SP) at a thermal neutron flux at about 5 x $10^{12}$ $n \cdot cm^{-2} \cdot s^{-1}$ for 8h.

Two measurement series were carried out using Ge (hyperpure) detector, model GX 2020 from Canberra, with a resolution of 1.90 keV at the 1332.49 keV gamma peaks of $^{60}Co$, with S-100 MCA of Canberra with 8192 channels. As, K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time and Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, and Zn after 25-30 days. Gamma ray spectra analysis was carried out using the software Genie 2000 NAA Procedure from Canberra.

## 2.2 **Sample preparation to Thermoluminescence dating**

The entire surfaces of the ceramics were polished and they were then gently crushed. After sieving, grains of diameter between 75 – 150 μm were chemically treated. Carbonate phases were removed by HCl (50%) for 2 h and organic matter was removed by washing for 4 h in NaOH (6M). During multiple rinsing in distilled water, the clayed fraction was consecutively removed. An additional treatment by immersion in dilute HF (20%) for 1 h was also performed to dissolve remaining clay materials that coated quartz and to eliminate the contribution of alpha radiation, carbonates and feldspars [20]. After being immersed in HF the sample was treated in HCl to eliminate fluorides. Throughout the procedure above the quartz fraction of 75 to 150 μm served as base material for thermoluminescence measurements.

The additive dose method was used to determine the equivalent dose (paleodose) in the samples [15]. The TL curves were recorded at room temperature to 400°C using a heating rate 4°C $s^{-1}$ in a home made TL reader, equipped with EMI photomultiplier, model 9789QB, with sample comportment and associated electronic. Prior to readout, the samples were preheated to 100 – 150°C on the planchet, to eliminate low temperature TL from laboratory irradiated samples.

For irradiation, a $^{90}Sr/^{90}Y$ source was used which delivered 0.415 Gy $min^{-1}$ to the quartz sample in the standard.

## 3. Results and Discussion

To evaluate the analytical process the elemental concentrations for reference material Brick Clay - NIST-SRM-679 were statistically compared with the data found in our laboratory. The elements (U, Th, K and Rb) presented RSD (Relative Standard Deviation) less than 10% and are similar to those from the literature [21].

An X-ray diffractometry analysis has been carried out to verify the crystallography obtained after sample preparation. The X - ray diffractogram in Figure 2 shows that the sample obtained was predominantly quartz and feldspar.

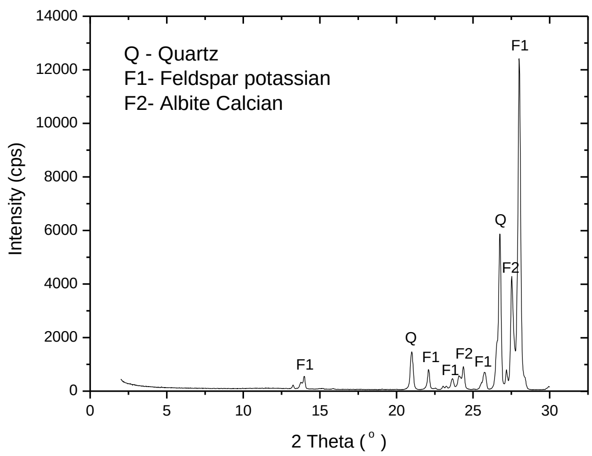



**Figure 2. X – ray diffractogram of sample prepared for TL dating.**

A protocol of Multiple Aliquots Additive Dose (MAAD) was used for paleodose determination. According [20], the advantage of the MAAD is that there is no change in TL reponse per unit of dose due to heat treatment utilized in the total in the Total Regenation method. Each points of growth curve is the average of 3 aliquots and the error bar means the standard desviation of the values. TL glow curves of natural and natural plus $^{90}Sr/^{90}Y$-dose of 10, 20, 30 and 40 Gy is recorded in the Figure 3 and provides a typical glow curve of the sample collected from Justino site. Peaks are seen at 200°C and 320°C. The plateau test not shown here indicates that 320°C TL peak can be used for dating.

The Figures 3 show the TL response of 320°C peak as function of the added dose. The TL response to additive dose for all samples, seen in the Figures 4 (a-d), could be fitted by linear equation. By extrapolating these curves to dose axis the paleodoses were obtained for the 4 pottery studied in this work. The results showed that the paleodoses are 10.9 ± 0.4 Gy, 1.48 ± 0.06 Gy, 3.11 ± 0.07 and 4.90 ±0.08 Gy for Justino, São José, Saco da Onça and Curituba, respectively.

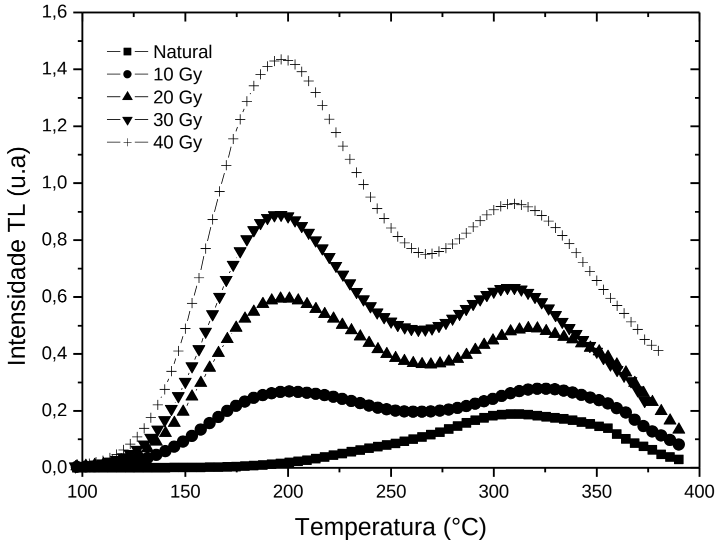
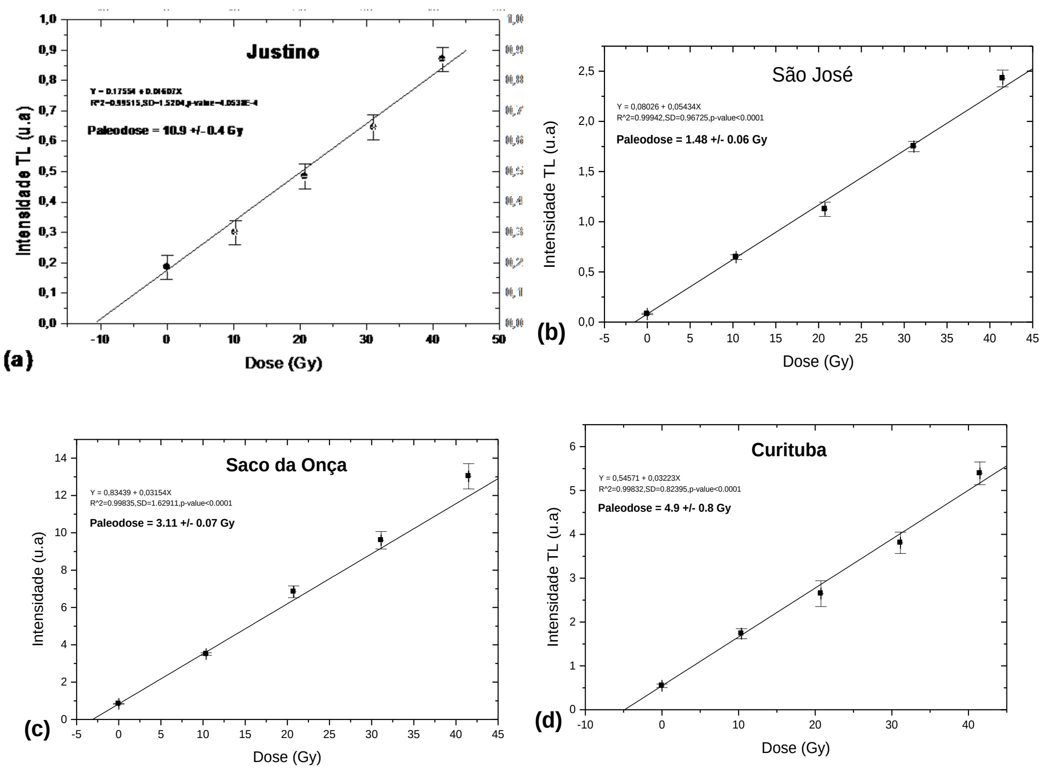



**Figure 3. Glow curve for natural and natural plus $^{90}Sr/^{90}Y$ doses of 10, 20, 30 and 40 Gy.**




**Figures 4. TL responses as function of additive dose for 320°C TL peaks for natural plus additional laboratory dose. The plots (a), (b), (c) and (d) correspond to Justino, São José, Saco da Onça and Curituba, respectively**

The INAA yielded an average of U, Th, Rb, and K are 3.71± 0.48 ppm, 12.83 ± 2.35 ppm, 77.82 ± 12.68 and 2.45 ± 0.29, respectively, where the error is a standard deviations. According to these values it can be observed that there is not a big difference in the values to determine the annual dose. From these values the annual dose rate was calculated using Ikeya's equation (Ikeya, 1993). Considering that cosmic rays contribution is of 250 μGy/yr, an average annual dose rate of 2.89 ± 0.33 $mGy.yr^{-1}$ was obtained. The age estimation was done by means of paleodoses and the dose rates cited above. The estimated ages are listed in the table 1.

**Table 1. TL dating of pottery fragments from Xingó sites. Total uncertainty was obtained by propagation of uncertainty from the uncertainty of the paleodose and annual dose rate.**

| Sample | Paleodose (Gy) | Estimated age (BP) |
|---|---|---|
| Justino (phase 15) | 10.9 ± 0.4 | 3716 ± 398 |
| São José (phase 08) | 1.48 ± 0.06 | 457 ± 35 |
| Saco da Onça (phase 06) | 3.11 ± 0.07 | 1021 ±190 |
| Curituba (phase 09) | 4.90 ±0.08 Gy | 1640 ± 140 |

## 4. Conclusions

In this work has shown that the 320°C TL peak the quartz exhibited a linear response as a function of the additive dose. The estimated ceramic age was done from the estimated paleodose and annual dose rate. It was found that samples from Justino, São José, Saco da onça, and Curituba sites presented ages 3716 ± 398, 457 ± 35, 1021 ±190 and 1640 ± 140, respectively. The burned charcoal sample collected from Justino site (phase 15) and dated by $^{14}C$ method indicated an age of about 3270 ± 135 BP (phase 13) and agrees with the result obtained by TL method in this work. Therefore, the TL dating can contributed significantly in establishing the chronology of the ancient community of the “Xingó” region.

**Acknowledgement**

The authors wish to thank the CAPES (Project PROCAD 0056/014) and PETROBRAS for financial support.

**References**

1. P. M. RICE. J. Archaeol. Method Theory, 1 (1999) 1.

2. M. T. STARK. J. Archaeol. Res., 11 (2003) 193.

3. P. WEIGAND, G. HARBOTTLE, E. V. SAYRE; Earle and J.E. Ericson (eds). Exchange Systems in Prehistory. Academic Press, New York, 1977, p.15.

4. SCHIMIDT, C., RUFER, D., PREUSSER, F., KRBETSCHEK, M., HILGERS, A. The assessment of radionuclide distribution in silex by autoradiography in the context of dose rate determination for thermoluminescence dating. Archaeometry, **55 (3)**, pp. 407 – 422, 2013.

5. SANTOS, J. O, MUNITA, C. S., VALERIO, M. E. G., VERGNE, M. C., SILVA, R. S., OLIVEIRA, P. M. S. The archaeometry study of the chemical and mineral composition of pottery from Brazil Northeast. Journal of Radioanalytical and Nuclear Chemistry, **281**, pp. 189 – 192, 2009.

6. BAXTER, M.J. Mathematics, statistics and archaeometry: the past 50 years or so. Archaeometry, **50 (6)**, pp. 968 – 982, 2008.

7. MARTINI, M., SIBILIA, E. Radiation in archaeometry: archaeological dating. Radiation Physics and Chemistry, **61**, pp. 241 – 246, 2001.

8. WALLIS, N. J., KAMENOV, G. D. Challenges in the analysis of heterogeneous pottery by LA – ICP – MS: a comparison with INAA. Archaeometry, **55 (5)**, 893 – 909, 2013.

9. BLACKMAN, M. J., BISHOP, R. L. The smithsonian – NIST partnership: the application of instrumental neutron activation analysis to archaeology. Archaeometry, **49 (2)**, pp. 321 – 341, 2007.

10. Wintle A.G., 1997. Luminescence Dating: Laboratoty procedure and protocols. Radiat. Meas. 27, 769 – 817.

11. MARTINI, M., FASOLI, M., MVILLA, I. Defects studies in quartz: composite nature of the blue and UV emission. Nuclear Instruments and Methods in Physics Research B, **325**, pp. 15 – 21, 2014.

12. BEERTEN, K., STESMANS, A. Some properties of Ti – related paramagnetic centers relevant for electron spin resonance dating of single sedimentary quartz grains. Applied Radiation and Isotopes, **64**, pp. 594 – 602, 2006.

13. Schmidt, C., Anghelinu, M., Chabai, V., Kels, H., Uthmeier, T., Hauck, T., Hilgers , A., Richter, J., Radtke, U. First chronometric dates (TL and OSL) for the Aurignacian open-air site of Românesti-Dumbravita I, Romania. Journal of Archaeological Science, **40**, pp. 3740 – 3753, 2013

14. Guibert P., Bechtel F., Schvoerer M., Müller P., Balescu S., 1998. A new method for gamma dose – rate estimation of heterogeneous media in the TL dating. Radiat. Meas. 29, 561 – 572.

15. Aitken, M.J., 1985. Thermoluminescence Dating. Academic Press, New York & EUA.

16. McKeever, S. W. S. 1985. Thermoluminescence of Solids. Cambridge Solid State Science Series. xiv + 376 pp.

17**.** Ikeya, M., 1993. New Applications of Electron Spin Resonance – Dating, Dosimetry and Microscopy. World Scientific, Singapore & China.

18. Luna S., Nascimento A., 1997. Os Grupos Ceramistas do Baixo São Francisco. Cadernos de Arqueologia, Universidade Federal de Sergipe, Aracaju, Brasil, doc.12.

19. Martin G., 2000. Pré-história do Nordeste do Brasil. Editora Universitária da Universidade Federal de Pernambuco, Recife, Brasil.

20. TUDELA, D. R .G., TATUMI, S. H., YEE, M., BRITO, S. L.M., MORAIS, J. L., MORAIS, D., PIEDADE, S. C., MUNITA, C. S., HAZENFRATZ, R. TL, OSL and C-14 Dating Results of the Sedimentsand Bricks from Mummified Nuns' Grave. Anais da Academia Brasileira de Ciências, **84(2)**, pp. 237-244, 2012.

21. C. S. MUNITA, R. P. PAIVA, M. A. ALVES, E. F. MOMOSE. J. Radioanal. and Nucl. Chem., 244 (2000) 244.