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Research article

Annual Dose Analysis of Pottery from Thoud-Ta Thoud-Yai Archaeological Site in the Songkhla Province of Southern Thailand

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Abstract: Thoud-Ta Thoud-Yai is Thailand's oldest archaeological site. Identifying the age of artifacts helps link past and present in storytelling. Absolute dating techniques are used to estimate a sample's geological age. Calculating the annual dose is the essential step. The annual dose depends on samples' concentrations of natural radionuclides and the sediment surrounding them. This research performed the annual radiation dose analysis in pottery by quantifying the concentrations of natural radionuclides using Neutron Activation Analysis (NAA). According to the volume analysis, internal dose, external dose, and cosmic rays contribute 0.180 ± 0.027, 0.959 ± 0.110, and 0.177 ± 0.009 mGy/year, respectively. The annual dose was found to be 1.139 ± 0.113 mGy/year. Annual dose measurements are necessary for determining the age of pottery samples. Since the age is determined by dividing the equivalent dose by the annual dose, this result connects the past and present at the Thoud-Ta Thoud-Yai archaeological site.

Keywords: Annual Dose, Neutron Activation Analysis, Pottery, Thoud-Ta Thoud-Yai

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1. Introduction

There are several methods of dating material samples for their age. Each is appropriate for some restricted sample structure type. The sample's aging value is also a factor. It focuses on the proportional connection between the equivalent and annual doses. In other words, the annual dose is important for determining the age. The sample's age apparent from its radionuclides is affected by radiation from the surrounding environment, so a radiation level is needed to calculate the sample's age. Most naturally radioactive elements are the radioactive series (uranium, actinium, and thorium) and some non-series nuclides (mainly potassium). This naturally occurring alpha, beta, and gamma radiation sources expose minerals to radiation continuously [1-2]. Suppose a mineral is exposed to natural radiation. In that case, some paired electrons are ionized, and trapped by impurities, and unpaired electrons, also known as lattice defects, are also formed, leading to aging [3]. The annual radiation dose must thus constantly be assessed [4]. The concentrations of U-238, Th-232, and K-40 in archaeological and geological materials will be used to calculate the

annual dose, which is the most important factor in dating. Several methods are employed to determine the contents of U-238, Th-232, K-40, and the annual dose rates of geological and archaeological material. Each method has its own merits and conveniences [5]. The aforementioned include alpha, beta, and gamma-ray spectroscopy; track detection (fission tracks and alpha-tracks); mass spectrometry: secondary ion mass spectrometry (SIMS) or with an ion micro-analyzer (IMA); inductively coupled plasma-optical emission spectrometry (ICP-OES); inductively coupled plasma mass spectrometry (ICP-MS); and chemical analyses: X-ray Fluorescence: (XRF), liquid scintillation counting (LSC), and neutron activation analysis (NAA).

Ancient materials' age is determined through annual radiation dose assessments. It is established by examining the U-238, Th-232, and K-40 concentrations. The previously mentioned NAA is an interesting technique. Archaeological artifacts contain 1-10 ppm of naturally radioactive elements, requiring careful investigation. NAA estimates long-lived radioisotopes in the environment. NAA's sensitivity and isotope specificity identify radionuclides with 104-year half-lives. Neutron activation creates radionuclides with shorter half-lives and increased specific activity. The 1950s: S.A.A. (the first artificial radionuclide was produced in 1934). Activation analysis identifies and quantifies stable elements using artificial radionuclides. Only a few stable atoms in the sample turn into radionuclides [6]. Neutron energy influences elastic collision, radiative capture, charged particle reactions, neutron reactions, fission, and fissionable isotope reactions. NAA starts nuclear processes using neutrons. Quantify neutron capture radiation. The addition of radioactive nuclei causes radioactivity. The latter kind is typically NAA [7]. Nondestructive NAA detects low background gamma radiation. In recent decades, semiconductor detectors and digital technologies have helped it advance. Gamma-ray photons generate electron-hole pairs in photon detectors such as a Highly Pure Germanium (HPGe) detector, a Ge for low energy photon spectroscopy (Ge-LEPS), and a lithium-doped Ge [Ge (Li)] detector cooled by liquid nitrogen detectors for gamma radiation. Peak current caused by electrons and holes is proportional to gamma-ray spectra used to assess U-, Th-, and K-series elements. Electrons and holes create peak currents. Gamma-ray spectroscopy can be used to find NAA's gamma-ray peaks and figure out its parts [4, 6].

The annual radiation dose must be found by adding the samples' radiation doses and the radiation dose from the environment, including cosmic rays. This study investigates the annual radiation dose of pottery at the Thoud-Ta Thoud-Yai archaeological site to determine the concentrations of natural radionuclides. By employing NAA methods and gamma spectrometry with HPGe well-type detectors, we could estimate ancient materials' U-238, Th-232, and K-40 compositions. It is important to determine the pottery samples' age and annual exposure levels. The archeological site of Thoud-Ta Thoud-Yai should link the following sequence of past and present occurrences. The 13th Songkhla Fine Arts Department has investigated the archaeological site of Thoud-Ta Thoud-Yai. The examination found that the archaeological site had several objects from antiquity. The preliminary analysis suggested that they were objects from the ancient period [8]. The annual dose levels determined in this study may be utilized to examine ages and verify the accuracy of archaeological data.

2. Materials and Methods

As indicated in Figure 1, the Thoud-Ta Thoud-Yai archeological site is situated in the Kao Daeng, Saba Yoi district of Songkhla province. As seen in Figure 2, Songkhla's 13th Department of Fine Arts unit discovered the samples in 2010. This current study used pottery samples and the surrounding environment as its study materials. The cliffs are 60 m in length and 20 m in width. There is a natural headboard slicing through the cliff shed's front face. The current is thick with vegetation. Archaeological evidence has been uncovered at several damaged sites. These include remnants of pottery containers, human skeletal fragments, steel tool components, and animal bone fragments. The archaeological site goes back to ancient periods, according to estimates. The excavation site is shown in Figure 3. Two wells, TP1 and TP2, were excavated. TP1 was the pottery excavation employed in this study's annual radiation dose analysis. At the same time, TP2 was the excavation where human skeletons were discovered, as seen in Figures 4A and 4B, while Figure 4C shows an example of pottery used in the research [8].

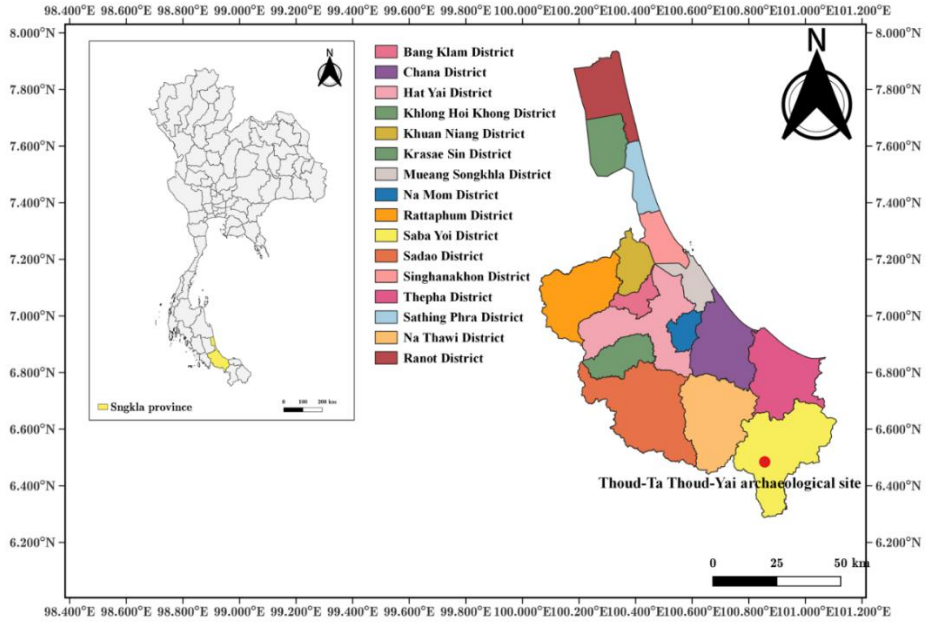

Figure 1. The Thoud-Ta Thoud-Yai archaeological site of Songkhla province.

Figure 2. The external area and the excavation site of the Thoud-Ta Thoud-Yai archaeological site [8].

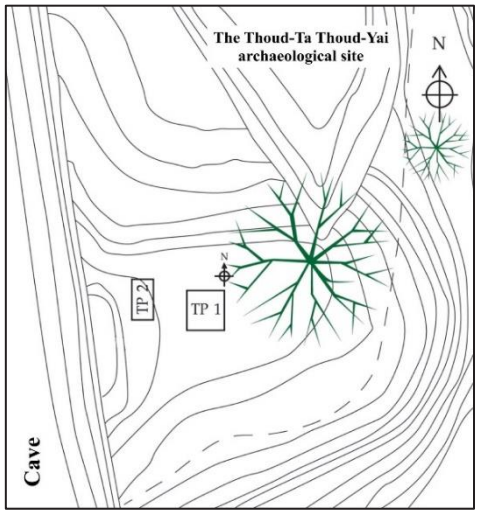

Figure 3. The excavation site. Two wells, TP1 and TP2, were excavated [8].

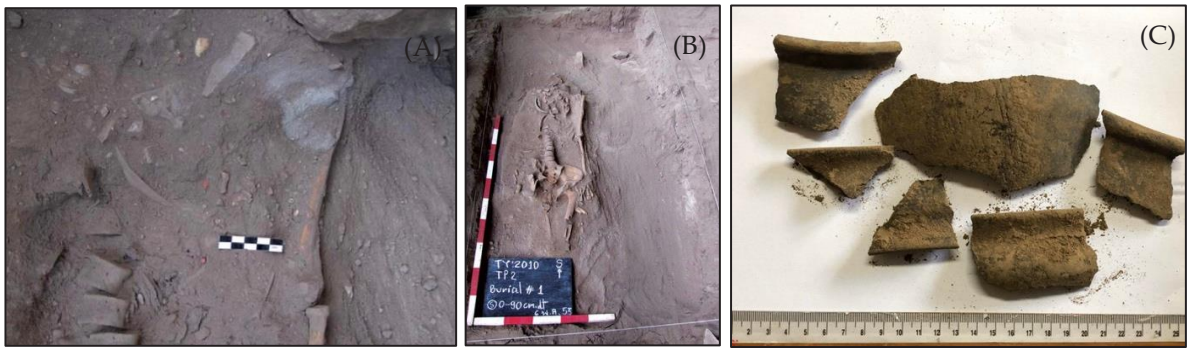

Figure 4. The excavation site (A) TP1 was the pottery excavation location used in this study's annual radiation dose analysis; (B) TP2 was the excavation where human skeletons were recovered; and (C) shows a sample of pottery used in the research [8].

The sediment and pottery samples were collected at 50–60 cm depth. All samples were dried in an oven at 60 °C for 24 h, then crushed, pulverized, and homogenized. Note that clean containers should be used for the preparation and handling stages to prevent contamination [9]. Each powdered sample was crushed to a 0-90 μm particle size and stored in polyethylene vials of the same shape and volume as those holding 150-250 mg of standard reference material. The lamp cap was heated to form a tight seal. Samples and standard references are stored in plastic cylinders in alternating order. All samples were radiation in two phases at the Thai Research Reactor-1/Modification (TTR-1/M1) at the Office of Atoms for Peace (OAP) facility. First, the concentration of U-238 and Th-232 were found by using long-term irradiation for 12 h and a cooling time of 5–6 d in the epithermal neutron flux of $2x10^9$ n/(cm^2.s). Using short-term irradiations of 10 minutes and 12 h of cooling with a thermal neutron flux of $2x10^{11}$ n/(cm^2.s), the concentration of K-40 was found [2]. The gamma-ray spectra were started. GWL series HPGe (High-purity Germanium) coaxial wells, installed in a vacuum-tight cryostat, make up the gamma spectrometer system. The aluminum absorbing layers (well wall) are 0.5 mm thick. For this purpose, we utilized the Gamma Vision-32 V 3.2 Gamma-Ray. Spectroscopy Software has a friendly graphical user interface and is great for working with and analyzing spectra on a home computer. The quantitative ratio of the gamma-ray spectrum would be altered as a consequence. A feasible method for measuring Np-239 and Pa-233 is U-238 and Th-232 because of their short half-lives, as indicated in Equation 1 (see Figure 1) [10]. Table 1 also includes important nuclear data from neutron activation studies on U-238, Th-232, and K-40. K is necessary for life. K-40 isotope abundance in nature is 0.01%, whereas K-41 is 6.7%. Hence K-40 contamination is computed from K-41. Despite its short half-life, K-42 is a common radiotracer. The only K isotope with a similar half-life is K-43, which is harder to generate than K-42. Neutron activation analysis uses K-42 to measure potassium content. [9-12]

$$\begin{aligned} &\text{U-238}(n,\gamma)\text{U-239} \xrightarrow{\beta^-} \text{Np-239}(2.55\text{d}) \\ &\text{Th-232}(n,\gamma)\text{Th-233} \xrightarrow{\beta^-} \text{Pa-233}\,(27.4\text{d}) \\ &\text{K - 41}(n,\gamma)\text{K - 42}\,(12.36\text{h}) \end{aligned} \tag{1}$$

Table 1. This study used important nuclear data from neutron activation of U-238, Th-232, and K-41 [9-10].

Element	Isotope	Half-lives	Energies of emitted Gamma ray (keV)	% of emission
U-238	Np-239	2.55 d	277.6	14.1
Th-232	Pa-233	27.4 d	311.9	33.7
K-41	K-42	12.36 h	1524.7	17.9

The annual radiation dose (D) consists of the internal dose (D_{in}), the external dose (D_{ex}), and the cosmic dose (D_{cos}). The cosmic rays were controlled by longitude, latitude, elevation, and the contributions lessened

with sample depth. Radiation from U, Th, and K in the pottery is responsible for the internal dose. Still, radiation from the same elements in the sediment around the pottery is responsible for the external dose. Radioactive element concentrations were used to analyze each contribution. U, Th, and K decay produce alpha, beta, and gamma radiation, in addition to the cosmic rays. Equation 2 may be used to determine the annual dose [6, 13].

$$D = D_{in} + D_{ex} + D_{cos} \quad (2)$$

Internal gamma radiation can be ignored since the pottery was too thin to absorb gamma rays. Due to our samples' coarse grain structure, we considered that the efficiency of the defect production (k-value) by alpha-particles in quartz remained minimal for the internal annual dose calculation. The k-value is a correction factor because an alpha particle's luminescence effects are limited to a small grain volume along the track [14]; hence, alpha particles induce less luminescence in each component of absorbed energy than beta particles and gamma radiation. Therefore, the internal dose would be exclusively determined by the beta dose rate. [6, 15]. Since the pottery surface was etched, alpha particles can be ignored when calculating the external annual dose [5]. The annual internal and external dose rates may therefore be expressed as,

$$D_{in} = kD_{\alpha} + D_{\beta} \quad (3)$$

$$D_{ex} = D_{\gamma} + D_{\beta} \quad (4)$$

In Equations 3 and 4 D_{α} , D_{β} , and D_{γ} can be determined using Equation 5. The following equation, for example, C_U is the U-238 concentration and $D_{U(\alpha)}$ a conversion factor is the alpha-particle emission rate U-238 [5, 15-16].

$$\begin{aligned} D_{\alpha} &= C_U D_{U(\alpha)} + C_{Th} D_{Th(\alpha)} \\ D_{\beta} &= C_U D_{U(\beta)} + C_{Th} D_{Th(\beta)} \\ D_{\gamma} &= C_U D_{U(\gamma)} + C_{Th} D_{Th(\gamma)} + C_K D_{K(\gamma)} \end{aligned} \quad (5)$$

The concentrations of those radioactive elements are used to estimate D_{in} and D_{ex} based on the online Dose Rate Calculator (DRAC) using the conversion factors from Guerin *et al.* [17], alpha and beta grain size attenuation factors respectively from Brennan *et al.* [18] and Guerin *et al.* [19]. Beta etch attenuation factors from Bell [20]. The cosmic dose rate, derived from the geographical location and elevation of the site, is nearly identical for each collecting site since these are in the same cosmic exposure area, with a mean square deviation of 1%. The combination of the three doses is the total annual dose of the samples [21].

3. Results and Discussion

Figure 5A shows the gamma spectra of U-238, Th-232, and their daughters, while Figure 5B shows the gamma spectrum of K-40. However, the results in Figure 5 are just an example of all the results for gamma spectra of U-238, Th-232, K-40, and daughters. Figure 5A shows a region of interest according to photopeaks at 277.60 keV and 311.90 keV for their associated radionuclides Np-239 and Pa-233, respectively. These photopeaks were used to calculate the concentrations of U-238 and Th-232, respectively. Furthermore, Figure 5B is based on photopeaks at 1524.7 keV, the associated radionuclide of K-42, and were used to calculate the concentration of K-40 [22].

The annual dose could be determined by analyzing the gamma spectra in Figure 5 for the concentrations of U-238, Th-232, and K-40 described in Table 2 (D). As indicated in Table 2, pottery samples do not contain potassium since ancient pottery was made from clay. Therefore, the majority of clays have

detectable levels of uranium and thorium. However, there is little to no potassium [23]. Using the correlation coefficients for D_{in}, D_{ex}, and D_{cos}, the Internal Dose (D_{in}), External Dose (D_{ex}), and Cosmic Dose (D_{cos}) were determined using DRAC [21]. Table 3 displays the results.

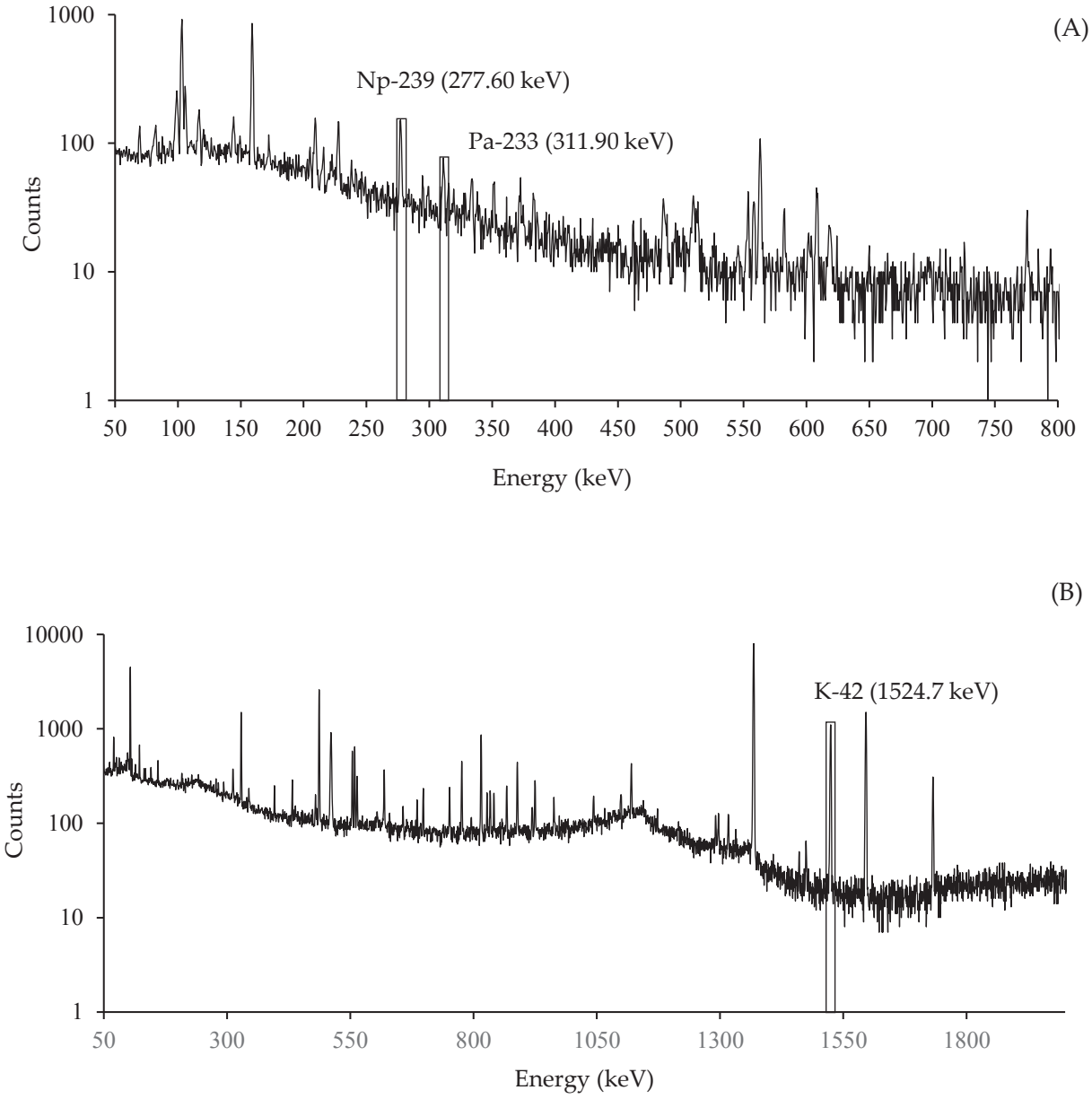

Figure 5. The significant photo peaks and associated radionuclides of sediment around the pottery are shown. (A) and (B) display gamma spectra for the radioactive elements U-238, Th-232, and K-40, respectively.

Table 2. The concentrations of U-238, Th-232 and K-40 in pottery samples and clay around pottery.

Sample	U-238 (ppm)	Th-232 (ppm)	K-40 (%)
pottery	5.61 ± 0.87	15.60 ± 1.20	-
Sediment around pottery	1.70 ± 0.66	3.27 ± 0.46	0.22 ± 0.01

Table 3. The annual levels of Internal Dose (D_{in}), External Dose (D_{ex}), Cosmic Rays Dose (D_{cos}), and the total Annual Dose (D).

Sample	D_{in} (mGy/year)	D_{ex} (mGy/year)	D_{cos} (mGy/year)	D (mGy/year)
Pottery	0.180 ± 0.027	0.959 ± 0.110	0.177 ± 0.009	1.139 ± 0.113

4. Conclusions

An annual dose assessment was performed based on the analysis of U-238, Th-232, and K-40 concentrations in pottery samples and sediment around pottery. The radiation levels of internal, external, and cosmic rays were determined. Calculated doses of radiation were 0.180 ± 0.027, 0.959 ± 0.110, and 0.177 ± 0.009 mGy/year, respectively. The annual radiation dose (D) estimate was then 1.139 ± 0.113 mGy/year. These annual dose levels can now be applied to quantify the ages of pottery samples. Such as trapping techniques (OSL, Tl, and ESR dating), [14-16, 20] age values can be used to connect historical events. The next stage is to connect to past events at the archaeological site of Thoud-Ta Thoud-Yai.

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Author Contributions: Tidarut Vichaidid participated in data analysis and drafted the manuscript. Piyawan Latam conceived the study, designed the study, coordinated the study, carried out data analysis, interpreted the results, and aided in drafting the manuscript. All authors gave final approval for publication.

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