Characterization of Italian Tile Samples Using Comparative Neutron Activation Analysis

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Introduction

Comparative neutron activation analysis (CNAA) is a technique used to determine trace element compositions of unknown samples by comparing them with samples containing known trace element concentrations. Both samples are activated with thermal neutrons and the resulting delayed gammarays are measured. There are three principal goals achieved from this research project: development of an irradiation fixture with suitable neutron fluxes and large sample capacity, characterization of the thermal neutron flux of the irradiation fixture, and the determination the trace element composition of 15 Italian tile samples. The Italian tiles come from two archeological sites, Tarquinia and Veii in Italy. By determining the trace element composition of the samples, the tiles can be separated into groups based on their composition. Archeologists then use the composition data to determine where material used to make these tiles and other similar artefacts originated from. Once the origins of these samples are determined other conclusions such as trade and technology transfer in the region can be drawn.

Neutron Activation Analysis Methods

Using neutron activation analysis (NAA) to determine the composition of a material has inherent advantages, including: NAA is a non-destructive technique, NAA can identify multiple elements simultaneously, and NAA can measure concentrations in the ppm and ppb ranges. NAA relies on the ability of neutrons to be absorbed by the trace materials, followed by measurement of the induced radioactivity. In general, the activity of a neutron-irradiated sample can be determined as shown in Equation 1. The measured activity is then correlated to the sample concentration.

\[ A = \sigma_{abs} \phi_{th} N (1 - e^{-\lambda t}) \]  

1

\( A \) is the induced activity, \( \sigma_{abs} \) is the absorption cross section of the target isotope, \( \phi_{th} \) is the thermal neutron flux, \( N \) is the number of atoms of a specific isotope in the material, \( \lambda \) is the decay constant of the daughter isotope, and \( t \) is the decay time.

CNAA, also known as the relative method, compares an unknown sample with a known standard. It uses the relationship between the induced radioactivity of the unknown sample and the induced radioactivity and known composition of the standard to determine the composition of the unknown sample. This method is useful when a suitable standard can be found that has a similar geometry, background matrix, and trace element composition as the unknown sample. By irradiating the standard and samples together, and then measuring their induced activities on the same measurement system, exact knowledge of the neutron flux and the efficiency and calibration of the detector system is unnecessary, making CNAA much simpler than other NAA methods. The concentration of an element in an unknown sample using CNAA is found by:

\[ w_s = \frac{w_s}{m_s \sigma_{th} D C \phi_s} \]  

2

The subscript \( s \) refers to the standard used in the comparison, \( w \) is the concentration of the target element (in either wt%, ppm, or ppb, as long as units are consistent), \( m \) is the mass of the sample, \( A \) is the decay rate of the product nuclide in Becquerels (Bq), \( D \) is the decay correction factor \( D = \exp(-\lambda t_d) \), where \( t_d \) is the decay time between the end of irradiation and the beginning of measurement, \( C \) is the measurement counting factor \( C = 1 - \exp(-\lambda t_c) \), where \( t_c \) is the counting time, and \( \phi \) is the relative flux correction based on the position of the sample in the sample holder [1, 2].

Experimental Setup

There are two important conditions that are considered for the irradiation of samples in this project. The first condition is finding an irradiation location in the reactor that maximizes the thermal neutron flux, allowing for a reasonable irradiation time of 10 hours or less. The second factor is finding a location where a large number of samples (>20) can be irradiated simultaneously without experiencing a significant neutron flux gradient across the samples.

There are a number of irradiation locations within the reactor core, including two dry tubes and a wet central
thimble, both of which are 1" in diameter. However, due to the geometries of the dry tubes, central thimble, and quartz encapsulation of the samples, the number of samples irradiated at one time would be limited to approximately five or six. This would increase the number of irradiations and irradiation time in the reactor fourfold.

Fortunately, the Penn State Breazeale Reactor (PSBR) has an irradiation tube with a 2" x 6" rectangular cross section that attaches to the PSBR core face via extra placeholders in the bottom reactor grid plate. Figure 1 gives an aerial view of the irradiation fixture position at the front of the core face. This tube allows for the irradiation of almost 30 pottery related samples at a time. The location of the 2" x 6" tube just off the core face is also helpful in that it provides for additional thermalization of fast neutrons that travel through the water between the core and the tube.

![Figure 1: A map of the PSBR core loading number 54, with the 2'' x 6'' irradiation fixture located at the front face.](image)

Thermal neutrons provide the vast majority of the neutron activation reactions that produce the radioactive species to be measured post-irradiation. In order to use CNAA, the neutron fluence experienced by the sample should be the same as that experienced by the comparator standard. Since the neutron fluence across the sample holder used in the 2" x 6" tube is similar, but not exactly the same, a correction factor needs to be applied. In order to apply this correction factor, the neutron flux profile across the sample holder was determined. The characterized flux profile was then normalized so that it could be used to adjust element concentrations between samples and their respective comparator standard that may have received different neutron fluences during irradiation.

The thermal neutron flux across the sample holder was characterized using gold-aluminum wires that are 0.112% gold by weight. The only naturally occurring gold isotope, $^{197}$Au, has a high thermal neutron cross-section for the $^{197}$Au(n, y) $^{198}$Au reaction, and $^{198}$Au has a 2.7 day half-life, making it an ideal thermal neutron monitor. A total of 28 wires were used, one in each tube in the holder. In order to determine the thermal and epithermal neutron flux and validate the assumption that the epithermal neutron flux is negligible, half of the wires were covered with cadmium, which shields the gold wires from neutrons with energies less than 0.55 eV, approximately the boundary between thermal and epithermal neutron energies.

The wires in the odd-numbered tubes were bare and the wires in the even-numbered tubes were cadmium covered (Figure 3). The relative neutron flux values were therefore determined in pairs; 14 pairs of bare and cadmium covered wires were irradiated and then analyzed to determine the flux profile in the sample holder. The epithermal flux is determined by Equation 3:

$$\phi_{\text{res}} = \frac{c_{cd} \exp(\lambda t_w)}{N_0 \epsilon \gamma I_0 G_{\text{res}} (1 - \exp(-\lambda t_i))} \tag{3}$$

Where $C_{cd}$ is net count rate of the cadmium covered wire, $\lambda$ is the half-life of $^{197}$Au, $t_w$ is the decay time between the end of irradiation and the start of counting, $N_0$ is the number of gold atoms in the gold-aluminum wire, $\epsilon$ is the detector efficiency, $\gamma$ is the gamma ray abundance factor, $I_0$ is the resonance integral of an ideal dilute detector, $G_{\text{res}}$ is the epithermal self-shielding factor, and $t_i$ is the irradiation time. The thermal flux is determined by Equation 4:

$$\phi_{\text{th}} = \frac{1}{G_{\text{th}} \ast t_i} \left[ C_b - C_{cd} \left( 1 + \frac{g \sigma_0 f_1}{G_{\text{res}} I_0} \right) \left( \exp(\lambda t_w) \right) \frac{1}{\lambda N_0 \epsilon \gamma} \right] \tag{4}$$

where $G_{\text{th}}$ is the thermal self-shielding factor, $C_b$ is the net count rate of the bare wire, $g$ is the Westcott factor which accounts for the departures from the ideal $1/v$ detector cross section in the thermal energy range, $\sigma_0$ is the absorption cross section of gold, and $f_1$ is a function, equal to 0.468 in this case, describing the epithermal activation of a $1/v$ detector in a specified energy range [3-6].

The pottery samples (Figure 3) have a complex composition comprised of many elements. The radioisotopes produced in these elements via neutron irradiation have a wide range of half-lives, varying from seconds to several hundred or even thousands of years. This wide variety of half-lives necessitates two distinct irradiation and counting times. Short-lived radioisotopes ($t_{1/2} < 15$ hours) require a short irradiation time (on the order of minutes) so that after a short decay period, the activated sample holder has a low enough radiation dose that the short-lived radioisotopes can be removed from the holder and measured before they decay away. The medium and long-lived isotopes require a longer irradiation because they need to be activated enough such that, after decaying for several days to allow short-lived isotopes to decay away, a sufficient number of the long-lived isotopes still remain that can be counted.
counting, all the samples are again placed in the sample holder, which is then placed back in the 2” x 6” tube on the core face.

The second irradiation was for eight hours at a reactor power of 900 kW, for a total neutron fluence of ~ 5.8 x 10^{17} neutrons/cm^2. After this long irradiation the sample holder remained in the 2” x 6” tube for seven days to allow many of the short-lived radioisotopes to decay and for the activation products in the sample holder to decay to safe levels. The samples were counted for 50 minutes eight days after the end of the long irradiation. The samples were then counted again, this time 23 days after irradiation for three hours each. The samples were counted for progressively longer periods of time to ensure that there were sufficient counts in each of the identifying gamma-ray photopeaks so that each element could be identified with a reliable statistical confidence.

Two comparator standard reference materials (SRMs) from the National Institute of Standards and Technology (NIST) were used to determine the trace element content of the Italian tiles (NIST SRM-98b Plastic Clay) and to act as a quality control (NIST SRM-679 Brick Clay). Both standards were chosen for their trace element content and background matrix, which closely resemble those of the tile samples.

Results

The sample holder characterization results are shown in Figure 4. The neutron flux is consistent across both rows (with a slight variation in the bottom row), and the neutron flux varies by about 20% between the two rows. Additionally, this sample holder is rugged and can be used for many future irradiations.

![FIGURE 2: The sample holder with the hinges closed. The first number represents the position number (1-28) in the sample holder. The second number is the sample (1398-1538), the plastic clay standard (S1-55) or brick clay quality control (B1-B5). The sample holder faces the reactor core from this position.](image)

![FIGURE 3: Fifteen Italian tile samples after being sealed in quartz ampoules.](image)

Using the information collected from an activity prediction program and from previous work [7] the following irradiation schedule was developed to identify short, medium, and long-lived radioisotopes in the samples. The first irradiation was for six minutes at a reactor power of 110 kW, for a total neutron fluence of ~ 6.1 x 10^{14} neutrons/cm^2. After irradiation, the sample holder remains in the 2” x 6” tube for two hours so that very short-lived isotopes can decay and the exposure rates from the activation of the aluminum sample holder decrease to safe levels. The hinge design of the sample holder greatly enhanced the ease with which the samples could be removed from the holder. Each sample is counted with a high purity germanium detector (HPGe) for 15 minutes. After irradiation, the sample holder faces the reactor core from this position.

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![FIGURE 4: The normalized thermal neutron flux in the sample holder.](image)

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rubidium (0.1-0.6 mg/g), antimony (0.15-5.7 ppm), barium (64 ppm-2.7 mg/g), hafnium (4.3-11 ppm), calcium (0.17-1.6 mg/g), and zirconium (0.2-3 mg/g).

The 15 samples were divided into two groups based on these trace element compositions. The first group is composed of samples 139B-148B and the provenance of that group is likely Tarquinia, based on comparison with previous work. The second group is composed of samples 149B-153B and the provenance of that group is likely Veii also based on comparison with previous work. These groupings were determined using multivariate analysis techniques such as Mean Character Difference (MCD) and Squared Mean Euclidean Distance and with scatter plots of concentrations of important trace elements found in the samples. The most useful scatter plots had either europium or chromium as one of the trace elements and an example is shown in Figure 5.

The MCD is given in Equation 5:

\[
MCD_{A,B} = \frac{1}{n} \sum_{i=1}^{n} |A_i - B_i|
\]

where \( n \) is the number of trace elements, \( A_i \) and \( B_i \) are the logarithmic concentrations of the \( i \)th element in pottery samples A and B respectively. The results of the MCD applied to the tile samples are found in Table 1.

Conclusions

This research analyzed the composition of 15 Italian tile samples whose trace element composition was unknown. A sample holder was designed and evaluated that allows for irradiation of up to 28 samples with a consistent neutron flux across each level of the holder. Up to 16 trace element concentrations could be found in each sample, and, through multivariate analysis techniques, the samples clearly indicated two distinct locations of origin.

TABLE 1: MCD grouping data for the Italian pottery samples

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<tr>
<th>Sample</th>
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References


Publications