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Neutron activation analysis capabilities and applications at the Penn State Radiation Science and Engineering Center

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ABSTRACT

The Penn State Breazeale Reactor has a long history of neutron activation analysis research and development, including applications for forensic applications. Our current experimental capabilities, including a 1 MW TRIGA reactor with a movable core and multiple irradiation locations, a pneumatic sample transfer system, multiple HPGe detectors, and a Compton suppression system, have enabled the development of an active NAA program investigating trace-element concentrations in environmental samples, archaeological samples, and industrial materials. Three NAA projects concerning tree-ring trace element analysis for correlation with large volcanic eruptions, ancient Italian tile element analysis to investigate Roman-era construction materials, and the implementation of k_0-standardization method, are highlighted to demonstrate how our facilities and our current NAA research experience make the Penn State RSEC readily available for high-precision trace element analysis for forensics applications.

1. Introduction

The Penn State Breazeale Reactor (PSBR), the United States' longest continuously operating university research reactor, has a long history of innovation regarding the use of neutron activation analysis (NAA) methods for forensic applications. Previous forensic work by researchers using the PSBR from the 1970s through the 1990s includes the analysis of the content and distribution patterns of airborne gunshot residues [1,2], activatable tracers in the environment used to determine pollution sources [3,4], and arsenic content in archaeological hair samples [5].

Building on these previous innovations, the PSBR currently has an active NAA program investigating trace-element concentrations in environmental samples, archaeological samples, and industrial materials. This paper highlights three of the NAA projects conducted at the PSBR in the last several years: NAA of absolutely dated tree rings, NAA of ancient Italian tile samples, and the implementation of the k_0-standardization method at the PSBR. Each of these projects is also relevant to the use of NAA for forensic applications, and positions the PSBR as a capable research partner within the forensic NAA community.

2. Background

2.1. NAA of absolutely dated tree rings

Tree rings can provide an interesting historical record of large-scale environmental effects, such as volcanic eruptions, climate variations, and anthropogenic pollution. Trees add a new growth ring on an annual basis, and each of these growth rings can provide a wealth of information. For example, the thickness of the annual ring is driven by the temperature and precipitation during that year. Because trees in the same region are likely to have the same growth patterns as their neighboring trees from year to year, trees of different but overlapping ages can be cross-matched to accurately date successively older trees. This technique is referred to as *dendrochronology* [6].

Within dendrochronology there are several subfields, including *dendrochemistry*, the study of the elemental concentrations found within the tree rings in order to make inferences about the chemical environment surrounding the tree over time. Natural phenomena, such as volcanic activity, or anthropogenic activity, such as pollution from ore smelters, can be registered in tree rings when the polluting elements are expelled into the atmosphere and then carried by precipitation to the earth's surface, where they can be absorbed through the tree's root system or they can change the soil chemistry to allow an increase or decrease in the tree's ability to absorb particular elements [7].

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One of the more interesting trace elements for environmental investigations using tree rings is gold. Trees require copper as an essential nutrient, but because of their similar chemistry, the other two naturally occurring Group 11 elements, silver and gold, are also taken up by trees along with copper. However, while the tree metabolizes the copper, the gold is more or less permanently deposited in the tree ring. Thus, changes in gold concentrations in tree rings can serve as an indicator of environmental changes over the lifetime of the tree.

Gold is also well-suited for analysis via NAA. Naturally occurring gold has a 100% isotopic abundance of the ^{197}Au isotope, which readily captures a neutron to form radioactive ^{198}Au, which has a 2.695 day half-life and emits a 411.8 keV gamma ray with 100% intensity [8]. Depending on the sample contents, the relatively low-energy 411.8 keV gamma ray emission can be overwhelmed by the signal from other isotopes, necessitating the use of the Compton suppression technique detailed in Section 3.2.

Both INAA (Section 5.2) and the k_o-standardization method (Sections 2.3 and 5.3), along with the Compton suppression technique (Section 3.2), have been used at the PSBR to determine the concentration of gold in absolutely dated tree rings and assess their correlation with major atmospheric events.

2.2. NAA of ancient Italian tile samples

Archaeology is the study of previous human societies and civilizations by analyzing artifacts, such as tools, pottery, or structural materials, and using multi-disciplinary sources and techniques, such historical records and chemical analysis, together to form hypotheses regarding those civilizations. Historically, archaeological analyses depended on evaluations of physical attributes available to the human eye, like color, shape, decorative styles, and iconography [9–11]. Current archaeological research combines the previous visual classification schemes with modern analytical science techniques, of which NAA has been an important contributor since the 1960s [12]. Indeed, NAA has been the preferred technique for trace element analysis in archaeology because of its sensitivity and because it does not require the extensive and destructive sample preparations that chemical analysis methods do.

In this work, we examine samples of tiles from archaeological digs in Tarquinia and Veii, Italy, from the 7th and 6th centuries B.C. Roman society at that time in history is of great interest to archaeologists, as it marks an era of relatively rapid technological development and technology transfer over significant geographical areas. In particular, the technological advances in construction techniques, and specifically in tile making, are thought to have made possible significant urban growth. Archaeologists are particularly interested in questions concerning the origins of the clays used to manufacture the tiles, and whether the tile-making technologies and clay materials were shared or transported in areas around Rome. Trace element quantification techniques like NAA can help answer these and other important archaeological questions.

Research at the PSBR on the trace element content of ancient Italian pottery used the CNAA technique (Section 5.1) and a custom sample holder to accommodate samples and standard reference materials.

2.3. Implementation of the k_0-standardization method at the PSBR

There are a number of NAA techniques in use today, including the classic methods of comparative neutron activation analysis (CNAA; Section 5.1) and instrumental neutron activation analysis (INAA; Section 5.2). Each of these NAA techniques has attributes that make it more or less suitable for specific applications of NAA. For example, INAA allows for the absolute determination of any activatable element of sufficient concentration, but is very sensitive to small changes in the neutron flux, sample self-shielding, and changes in sample geometries and detector efficiencies. CNAA is a simpler technique that eliminates the sensitivities of INAA, but requires a comparator standard of similar matrix that has standardized amounts of the elements under analysis.

The single-comparator method was developed as a way to simplify multi-element analysis without the need for the complex standards necessary for CNAA. A single element standard, frequently gold, is irradiated directly alongside the sample. Experimentally determined variables, called k-factors, are then used to assist in the determination of each desired element in the sample, based on the measured activity in the single comparator wire. An improvement on this single comparator method known as the *k_0-standardization method* has been implemented at the PSBR.

3. Penn State RSEC NAA facilities

3.1. The Penn State Breazeale nuclear reactor

The PSBR, which first reached criticality in 1955 and is now part of the Penn State Radiation Science and Engineering Center (RSEC), is a 1 MW TRIGA (Training, Research, Isotopes, General Atomics) reactor with pulsing capability. The reactor core resides in a 24 ft deep pool with approximately 71,000 gallons of demineralized water and is movable in several directions. This flexibility of movement allows for a variety of irradiation fixtures outside of the core, in addition to the near- and in-core irradiation locations (Fig. 1). A pneumatic transfer system is also available for thermal neutron irradiation of samples. In steady state operation at 1 MW, the PSBR's thermal neutron flux is approximately 10^{13} n/cm^{2}s at the edge of the core and 3×10^{13} n/cm^{2}s in the central thimble. The PSBR maximum pulse provides a neutron flux of approximately 6×10^{16} n/cm^{2}s with a pulse half width of about 10 ms. The available neutron flux and the flexibility offered by numerous irradiation locations makes the PSBR an excellent source of neutrons for NAA applications.

3.2. The Penn State Radionuclear Applications Laboratory

The Penn State Radionuclear Applications Laboratory (RAL) provides the measurement capabilities necessary for NAA research. The RAL includes the PSBR pneumatic transfer system terminus, sample preparation and post-irradiation handling facilities, four shielded HPGe detectors with state of the art counting systems and software (including two DSA-2000 Digital Spectrum Analyzers and Canberra's Genie-2000 software), two Automatic Sample Handling Systems (ASHS), and a Compton Suppression System.

The primary ASHS (Scalacs, Inc.; Fig. 2) is used for nearly all NAA sample counting. This ASHS has a capacity of over 90 samples, moves each sample one at a time to the face of the HPGe detector, and can be programmed for counting times ranging from seconds to days. The automation of this counting system provides sample measurement consistency and reliability by minimizing the decay time between samples, thus minimizing the measurement errors associated with counting statistics. Once the ASHS moves a sample into place, it is measured with a Canberra GC1518 High Purity Germanium (HPGe) detector, a DSA-2000 analyzer, and Canberra's Genie-2000 software for gamma ray spectrum analysis.

PSBR NAA research may also use a measurement technique called Compton suppression. When a gamma ray interacts with matter, it can undergo one of three significant processes, depending on the energy of the gamma ray: photoelectric absorption, Compton scattering, and pair production. For the germanium

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