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CORRELATION BETWEEN DELAY TIME AND MEASURED CONCENTRATION AND CONCENTRATION UNCERTAINTY BY NEUTRON ACTIVATION ANALYSIS

by

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ABSTRACT

For the last several decades, it has been apparent that new methods of identifying explosives can help investigators trace their origins. One way to identify an explosive is through the use of taggants: materials added to a product that encodes information about the product such as when it was manufactured.

This research investigates the survivability of a new identification taggant called the Nuclear Barcode that overcomes some of the downfalls that have been identified in prior taggants. The Nuclear Barcode encodes information as a unique combination of concentrations of rare earths (Ho, Eu, Sm, Lu, and Dy) and precious metals (Ir, Rh, and Re) that is then identified using Neutron Activation Analysis (NAA). The concept of "survivability" was tested through a series of experiments on aqueous solutions and post-blast residues containing three rare earths (Ho, Eu, and Sm).

The tests have shown that the three candidate taggant elements can be identified by NAA in an aqueous solution at concentrations as low as 100 parts per billion (ppb) with uncertainties in the concentration measurement as low as 5 ppb. These elements can be identified in post-blast residue produced by a detonating explosive at higher concentrations of 1,000 ppb. Being able to identify the taggant elements at these concentrations is critical for the practical implementation of the Nuclear Barcode, which requires uncertainties below 50 ppb. Five parameters were identified as contributing to the uncertainty and the effect of the delay time was investigated. After a period of 2.5 half-lives, the uncertainty in the concentration was found to be higher than the uncertainty immediately afterward, suggesting that samples be measured as soon as possible and eliminating some candidates.

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This research would not have been possible without the aid of the staff at the Missouri S&T Reactor, and especially Craig Reisner and Anthony Alchin. I greatly appreciate their support that allowed me to use the full capabilities of the MSTR. The post-blast tests that were critical to this research could not have been carried out without the support of Jeff Heniff, and my fellow graduate students Jay Schafler, Barbara Rutter, Martin Langenderfer, Jacob Brinkman, and Kelly Williams. Many thanks also to Phil Mulligan for his assistance in structuring much of the writing you see here.

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1. INTRODUCTION

This research investigated the detectability and measurability of three rare earth elements: holmium, samarium, and europium, in post-blast residue by neutron activation analysis (NAA). NAA provides an advantage over chemical techniques in that it detects the presence of elements by properties of their nucleus, which is not destroyed during the detonation process, as opposed to interatomic bonds that are probed by chemical and physical techniques such as infra-red spectroscopy. The detectability and measurability of these three elements was also evaluated when dissolved in aqueous solutions, which serve as simulants for undetonated explosives. Aqueous solutions can stand in for undetonated explosives because the major constituents of explosives (carbon, nitrogen, oxygen, and hydrogen) are effectively inert under NAA due to their low atomic numbers. Comparing these tests allows for understanding of the performance of NAA as a method for measuring concentrations of the three rare earth elements in post-blast residue. This will enable further research into additional identification taggants that can be used in explosives.

While performing this research, an observation was made about the effect of the delay time between irradiating and counting the samples during the process of performing NAA. This observation prompted further experiments that were performed to investigate the relationship between the delay time and the measured concentration and its uncertainty, which is defined mathematically in Section 2.2.2. These tests provide information about methods of optimizing testing of post-blast residue samples by NAA. These results provide additional information about the performance and suitability of NAA as an analytical method for further identification taggant research.

1.1. RESEARCH MOTIVATION FOR AN IDENTIFICATION TAGGANT

Terrorist attacks involving explosives have long been a challenge for investigators [1, 2]. The use of explosives often destroys items that might be used as evidence, and often makes identification of the type of explosive used difficult [3]. Additionally, this type of crime has resulted in some of the highest numbers of casualties of any crime, such as the bombing of the Edgar Murrah Building in 1995, which killed or injured approximately 850 people [2]. Developing a technology that provides critical information about the explosive, post detonation, could speed up investigations, or provide leads that may not be otherwise followed up on by providing novel methods of tracing back to purchase orders or other methods of determining the perpetrators.

One technology that could be used to provide this type of identification is a taggant. A taggant is a foreign material that is added to a product that provides information about that material. A taggant can be a physical object such as a particle, or it can be a chemical additive [1, 4]. Taggants can fall under two classifications: detection taggants and identification taggants. As the name suggests, detection taggants are something that is added to a material to enhance the detectability of that material. A common example is the small quantity of sulfur containing chemical compounds that are added to natural gas or propane at part per million levels. The addition of these sulfur compounds gives these normally odorless hydrocarbons "their" distinctive scent.

Identification taggants are the second class of taggants, and the one relevant to this dissertation. An identification taggant is something that is added to a product that provides information about that product. This information could include things like the manufacturer, what the material is, or when the material was manufactured. Identification taggants have been used in several places to encode this type of information to prevent theft or counterfeiting of goods such as currency, clothing, or pharmaceuticals [4, 5].

An explosive identification taggant can encode information about the manufacturer, the type of explosive, and the batch number of the explosive material. If that tagged explosive is used in a terrorist attack, or in another criminal act, investigators could then use the taggant to “read” this information assuming that the taggant survived detonation. Knowing this information would then enable the investigation to focus tracing that particular batch of explosives. This could speed up investigations by reducing the amount of work, or prevent further attacks if more explosives are discovered to be missing.

Identification taggants for explosives are not a new concept. Federal proposals for their inclusion in manufactured explosives were drafted 40 years ago, but were not ultimately acted upon [1, 2]. However, studies on introducing identification taggants have identified a number of criteria that a successful identification taggant must satisfy: survivability, recoverability, utility, compatibility with explosives, safety in manufacture and use, no effect on explosive performance or use, compatibility with mined products, environmental acceptability, and cost [1, 2]. These criteria are described in Table 1.1. A full discussion of these criteria is available throughout Section 2. Should an identification taggant technology satisfy these criteria, there is a high likelihood that such a technology can be practically implemented.

Identification taggants have been used in Switzerland since 1980. All explosives produced in Switzerland or imported for use in Switzerland must contain a taggant. Swiss authorities have credited the taggant program with improving the rate at which crimes involving explosives were solved.

Table 1.1. Successful Explosives Identification Taggant Criteria. adapted from [1, 2]

Criterion	Description
Survivability	Taggant must not be destroyed (rendered unreadable) by the detonation of the explosive
Recoverability	Taggant must be able to be found in post-blast environment
Utility	Taggant must encode information useful for law enforcement investigations
Compatibility with Explosives	Addition of taggant must not cause instability in the explosive that makes handling and storing the explosive unsafe or effect shelf life
Safety in manufacture and use	Taggant must not pose a health hazard to manufacturers of and users of tagged explosives
No effect on explosive performance	Taggant must not reduce explosive performance nor significantly increase or decrease sensitivity of tagged explosive material
Compatibility with mined products	Taggant must not contaminate any mined resources to the extent that the resource cannot be extracted
Environmental acceptability	Taggant must be non-toxic, and non-polluting
Cost	Taggant must be cheap relative to the cost of explosives and also cheap enough that analyzing tagged explosives is feasible in all cases

In the first 14 years of the taggant program, 44% of crimes involving explosives were solved when a taggant was recovered. Only 16% of crimes involving explosives were solved when no taggant was recovered. In total, a crime where explosives were used was 2.8 times more likely to be solved when taggants were used [2].

1.2. THE NUCLEAR BARCODE: A NOVEL IDENTIFICATION TAGGANT

This dissertation discusses the early development of a new identification taggant candidate, called the Nuclear Barcode. The Nuclear Barcode encodes information about the explosives as a unique combination of concentrations of certain rare metals. In 2014, 3.1 million metric tons of explosives (including blasting agents such as ANFO) were consumed in the United States [6]. Therefore, the Nuclear Barcode must be able to produce a very large number of unique codes.

Since several of the metals used in the proposed Nuclear Barcode are expensive, very low concentrations of these metals must be used to keep the cost low enough to be viable as an identification taggant. The most expensive metal used is iridium, with a cost of $1,200 per troy ounce in 2018. Concentrations ranging from 100 parts per billion (ppb) to 4,000 ppb are proposed, with concentration levels separated by 100 ppb. This produces, for eight taggant elements, a total of 6.56 trillion unique combinations. To utilize the Nuclear Barcode, the concentrations of the taggant elements must be able to be read with sufficient precision to place the concentration within one concentration level. With the 100 ppb separation between levels, this would require that the measurement technique has a precision of 50 ppb. One such technique, for the elements under consideration, is NAA which is described further in Section 2.2.

NAA works by bombarding a sample with neutrons. The nuclei of the atoms in the sample occasionally absorb one of these neutrons and convert to a radioactive isotope of the same element. When this radioactive nucleus decays, it emits a number of gamma photons at different energies that is characteristic of that particular isotope. These gamma photons can be counted using a detector, and the quantity of the radioactive isotope can be determined. Using this information, it is possible to determine the elemental composition of the original sample.

Neutron activation analysis provides a similar level of metrological certainty to Isotope Dilution Mass Spectroscopy, which is a primary method of measurement according to the Comité Consultatif pour la Quantité de Matière — Métrologie en Chimie (CCQM)

[7]. Metrological certainty as a principal means that the measured quantity is both accurately and precisely determined by the method chosen. By the CCQM's definition, a primary method of measurement "A primary method of measurement is a method having the highest metrological properties [that is, a method that is extremely precise], whose operation can be completely described and understood, for which a complete uncertainty statement [the uncertainty in the measured quantity is completely determined by the test method and any preparation steps, and there is no random component that contributes to uncertainty] can be written down in terms of SI units" [7]. The use of primary methods of measurement provides certainty that the results are both accurate and precise. The individual elements in the Nuclear Barcode will have different limits of detectability and also different levels of uncertainty. An explanation for these can be found in Section 2.2.

Using the nuclear barcode involves several steps. The first step is creating the identification taggant. For the nuclear barcode, the identification taggant is the unique combination of concentration levels of each of the eight elements used. This taggant is added to explosives during manufacturing in such a way that the taggant is well dispersed among the final product. When the explosive is detonated, the taggant elements remain behind in the solid phase as post-blast residue, which can be recovered by swabbing surfaces that collect post-blast residue with a cotton ball or another sampling implement. Finally, post-blast samples are subjected to NAA. NAA allows the concentrations of the taggant elements to be determined and reads the barcode. This dissertation investigated the scientific feasibility of this identification taggant.

1.3. RESEARCH OBJECTIVES

This research focuses on investigating the survivability of the Nuclear Barcode concept over other components listed in Table 1.1. Survivability of the Nuclear Barcode is the most important aspect, as without survivability, the other components listed in Table 1.1 do not matter. Due to the nature of testing for survivability, as well as the exact method of encoding information chosen in the Nuclear Barcode, there is an unavoidable overlap between the concept of survivability and the concept of recoverability. In doing so, the concept of survivability was broken down into a series of four objectives, such that if the Nuclear Barcode can satisfy these objectives, then it can be considered a survivable identification taggant. The four objectives are:

1. Determine if the taggant elements can be detected and quantified via NAA at the desired concentrations.

2. Determine if the different concentration levels of the taggant elements can be distinguished via NAA with sufficient precision that the measured concentration lies within only one concentration level (50 ppb precision to use the Nuclear Barcode as designed).

3. Determine the distinguishability of the taggant elements from background signals, including other taggant elements and common elements in the environment such as sodium, potassium, chlorine, etc.

4. Identify concentrations of the taggant elements in the post blast residues and verify them to be the same as in the undetonated sample.

These four objectives address both the qualitative and quantitative use of NAA. The qualitative use of NAA allows for the identification of different elements that are present in a single sample. Quantitative use of NAA determines the mass of at least one element that is present in the sample. Both qualitative and quantitative analysis can often be performed using the same test data but it is possible in some cases that only qualitative data can be obtained. Of the four objectives listed, only objective three is purely qualitative. Objectives one, two, and four combine both qualitative use of NAA by evaluating if the taggant element(s) can be identified and quantitative use of NAA by evaluating how much of the taggant element(s) is present in the sample. A series of eight tests was designed based on these four objectives. These tests were designed to build off of one another, while still providing information should the Nuclear Barcode fail a specific test. These tests are extensively described in Sections 4 and 5. While analyzing the results of these tests, five parameters involved in the calculation of the mass of an element by NAA were determined to be significant contributors to the results. Due to this, an additional series of tests on one of these, the delay time, was carried out. The delay time is the time between exposing the sample to neutrons and the counting the sample on a detector capable of detecting gamma photons. The five parameters identified by this testing are described in Section 5.10, and the delay time tests are described in detail in Section 6.

1.4. CONTRIBUTION TO SCIENCE

This dissertation discusses the survivability of three rare earth elements: holmium, samarium, and europium in post-blast residues produced by explosives using NAA. This research identifies these elements, measures their concentrations, and determines the effects of delay time on the uncertainty in their measured concentrations. Detectability of these elements is a crucial component towards the implementation of an identification taggant scheme, the Nuclear Barcode, that has been developed based off of this work. Detectability of these elements by NAA was found to be dependent on a total of five parameters: the neutron flux that the samples are exposed to; the efficiency of the detector used; the length of time the sample is irradiated; the length of time the sample is counted; and the delay time, the length of time between the irradiation and counting of the sample. This last parameter was the most varied during testing due to scheduling needs and safety concerns. These parameters are discussed more fully in Section 2.2 and Section 5.10.

Additionally, this dissertation examines the effects of the delay time between irradiating and counting the samples on the measured concentration and concentration uncertainties in aqueous solutions of holmium when analyzed using NAA. The delay time arises from necessity for some samples, which become too active after irradiation to safely handle until enough time passes. The measurements of the concentrations of holmium and the measured concentration uncertainties were compared based on the number of half-lives of holmium-166 that elapsed between irradiation and the start of the measurement. Based on these tests, the uncertainty in the measured concentration is minimized by measuring the sample before 2.5 half-lives have elapsed. In real time, this means that samples containing holmium should be measured within 67 hours of irradiating, samples containing europium should be measured within 23 hours of irradiating, and samples containing samarium should be measured within 115 hours of irradiating. These results will have consequences for optimizing the use of NAA as an analytical method with post-blast residues.

1.5. ORGANIZATION OF THIS DOCUMENT

This dissertation discusses the history and development of identification taggants in Section 2.1. This discussion is then followed by a review of the literature required to understand the foundational technology of NAA in Section 2.2, and a review of the basic properties of explosives in Section 2.3. Section 3 describes the concept of the nuclear barcode, an identification taggant that is read by NAA. Section 4 describes a series of eight tests that were performed to evaluate the four research objectives outlined in Section 1.3. Section 5 presents the results with an analysis of the tests outlined in Section 4, ultimately identifying five parameters important for controlling the uncertainty of NAA. The effects of one of them, the time delay between irradiating a sample and counting it, is presented in Section 6. Section 7 presents a discussion of the consequences of the results shown in Sections 5 and 6 and provides a cost estimate of the materials involved in the Nuclear Barcode. Conclusions regarding this research are presented in Section 8, and an overview of future work to enable the use of the Nuclear Barcode is presented in Section 9. Appendices A and B cover details of the calculation of the concentration of the taggant elements identified by NAA and the method by which one parameter was determined respectively. Appendix C breaks up Figure 5.1, adds additional figures according to individual element, and presents additional information about the data used to create Figure 5.1.

2. LITERATURE REVIEW

This section discusses prior research into identification taggants and NAA. A review of identification taggants research is presented in Section 2.1 and describes previously developed identification taggants and the circumstances under which they were developed. This review provides the context in which the taggant evaluation criteria in Table 1.1 were developed. Additionally, Section 2.1.3 compares previously developed taggants to a key subset of those criteria, foremost of which is survivability.

A review of the process of NAA is presented in Section 2.2. This review describes the mechanism by which NAA operates and how this can be used to determine the composition of a sample. Additionally, Section 2.2.2 includes disciplines where NAA is used to analyze low concentrations of rare earth elements in a bulk sample, which is the same use case that will be presented in Sections 3 through 6.

A review of explosives is presented in Section 2.3. Section 2.3.1 discusses the chemistry of detonation and predicts the formation of post-blast residue that remains after detonation. Section 2.3.2 discusses the characterization of explosives as low or high explosives; and as primary, secondary, or tertiary explosives. Section 2.3.3 discusses the performance of explosives and identifies key parameters for predicting this performance.

2.1. TAGGANTS LITERATURE REVIEW

Regulations governing explosives have often included requirements to provide information about the manufacturer, type, and batch of a commercially produced explosive. The first method of encoding information about an explosive was simply writing the desired information on the explosive’s packaging. Marking explosives in this way can be considered the first identification taggant. Identification taggants that encode this information have evolved over the course of over 100 years in the United States. The United States is being used as a general example of how taggant developments have been reactive, but developments have also occurred in other countries such as Switzerland. Identification taggants are particularly useful as they allow explosives to be tracked back to the manufacturer and purchaser. Correlations can be seen in the evolutional advances in identification taggants and events (wars and terrorist activities) that lead to regulations governing explosives. The information presented in this section walks through the evolution of identification taggants, since 1917, and attempts to identify the corresponding event that led to increased regulations governing explosives. The section illustrates that the efforts in identification taggants have been primarily reactionary and highlights the need for a more proactive approach in taggant research and implementation. Understanding the previously developed identification taggants has led to successive generations of taggant candidates. These taggant candidates each improve on some of the shortcomings of the previously developed identification taggants.

2.1.1. Overview. Commercial explosives are a valuable resource used in industries such as mining and construction. Throughout history, terrorist attacks and accidents have demonstrated the potential for misuse of commercial explosive materials to cause harm to both people and property [2]. Balancing the economic value of explosives while minimizing the destructive risks has been a topic of both scientific interest and government policy for over one hundred years in the United States [1, 2].

Regulations exist to reduce the misuse of explosives by addressing aspects such as the use, transport, and storage of these materials. These regulations have been historically enacted in response to new external circumstances such as war, increased concerns over terrorism, new technology, and new uses for explosives. This reactive approach means that there are inevitable loopholes that can be found by a motivated party that will only be closed after an unfortunate event. Regulations governing explosives have often included requirements to provide information about the manufacturer, type, and batch of a commercially produced explosive. Taggants are one technology that has been developed to identify explosives. This section will discuss those developments occurring in the United States specifically, but other taggant developments have occurred in other countries as well; the United States here is being used as a representative example.

There are two categories of taggants used with explosives: detection taggants and identification taggants. Detection taggants are designed to make explosives easier to detect and enable a sensor to produce a signal when explosives are present. One implementation of detection taggants is adding volatile chemicals to certain types of plasticized explosives. Unlike untagged explosives, bomb-sniffing dogs (for example) can detect these volatile chemicals by smell [2]. Additional technologies designed to detect either these volatile chemicals or other components of the explosive itself are used in the equipment present at airports or government buildings. Detection taggants and their attendant technologies will not be further discussed in this dissertation. Identification taggants provide information about the explosive when they are recovered. The key distinction between detection taggants and identification taggants is that identification taggants cannot be used until the explosive has been located. Once found, either detonated or undetonated, the identification taggant can be read, and the information about the explosive can be retrieved. This information may contain the manufacturer of the explosive, the type of the explosive, or other information such as batch or lot number.

Identification taggants are used in many fields such as pharmaceuticals and automotive manufacturing to provide information about materials [4]. For example, to prove the source or manufacturer of a product to safeguard against counterfeits [5], or for tracing materials that are then used to produce unlicensed copies or illegal goods [5].

The technology used to create and encode identification taggants has changed over time, and many different approaches have been developed such as: small particles, biological sensors, radionuclides, and combinations of chemical compounds. Additionally, simply writing information such as the manufacturer or batch on a casing around an explosive can be considered an identification taggant, since it encodes information about the explosive. Tagging explosives in some way that provides information about the explosive has been pursued for more than 100 years [8]. This review shows the progression of taggant technology and how it relates to specific events. Taggant technologies have progressed over the course of the 100 years of development and have identified key characteristics of a successful taggant.

2.1.2. Historic Events and Their Relation to Taggant Development. To have a clear understanding and proactive look at the development of new identification taggants, it is important to know the history that has shaped explosives regulations and requirements for manufacturers over time. A timeline of events and laws passed within the United States that surround identification taggants for explosives is shown in Figure 2.1.

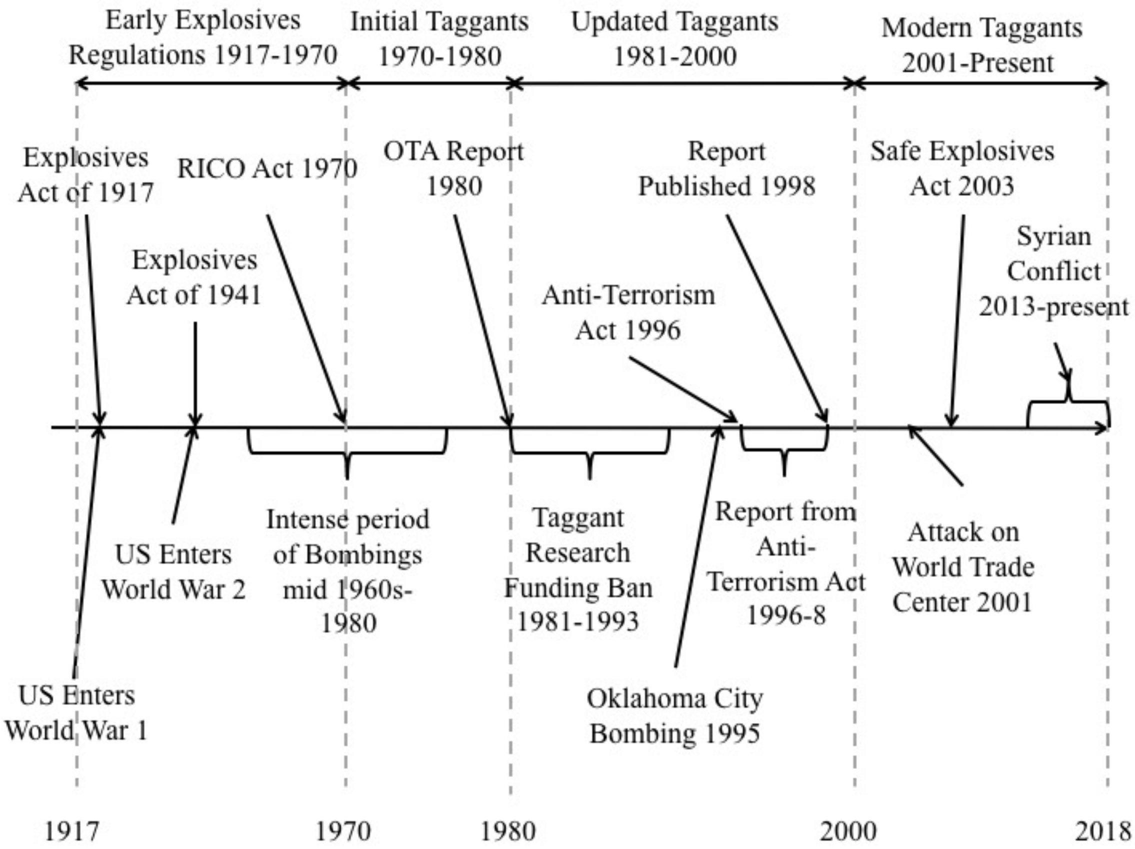


Figure 2.1. History of Identification Taggants Timeline in the US

From the events and laws shown in Figure 2.1, there have been four eras of identification taggant development: the early explosives regulations era, the initial taggants era, the updated taggants era, and the modern taggants era.

2.1.2.1 Early explosives regulations (1917-1970). Identification taggants are an additive to an explosive that provides information about the explosive. The earliest method used to provide this information was to encase the explosive in some wrapper that had information such as the manufacturer or type of explosive printed on it. The Explosives Act of 1917 standardized requirements for: licensing, manufacturing, storing, and distributing explosives and explosive ingredients in the United States upon the nation's entry into World War 1. One of the main concerns was over the availability of explosives for acts of sabotage or “bomb outrages”; acts that would be called terrorism today. This measure was intended to be a temporary one, applying only during the war, and its provisions expired in 1919 [8]. An almost identical law, the Federal Explosives Act, was passed upon the United States’ entry into World War 2 in 1941, with updated language and an updated list of explosive ingredients. This law, like the 1917 version, also was explicitly a wartime measure and expired at the end of World War 2. The passage of the Organized Crime Control Act of 1970 introduced permanent federal regulations for explosives in Title IX for the first time.

- *Explosives Act of 1917.* Due to the exceptional circumstance of the United States entering into World War 1, a uniform set of rules and regulations surrounding explosives was deemed necessary [8, 9]. The Explosives Act of 1917 was the first federal law passed regulating explosives. Prior to the passage of this act, explosives regulations were left to the states and municipalities. Some states and cities had significant regulations on explosives that were used as a template for the regulations coming from this act, while other states had no regulations on explosives, and these new regulations were the first to apply in these localities [8].

To reduce the possibility of misuse, the Explosives Act of 1917 required users and manufacturers of explosives to obtain a license. This license could only be issued by a designated authority and would include information about the licensee and required certification that the licensee was a loyal citizen of the United States [8]. Strictly following the wording of the Explosives Act of 1917 would require purchasers of approximately

1,500 materials, including things such as cotton or starch, to hold an explosives license [8]. As this would be impractical, the list of materials that would require licensure was reduced to oxidizers commonly used in explosives such as ammonium nitrate, as well as commercially produced explosives like nitroglycerin [8]. Additionally, sellers of explosives were required to verify that purchasers had the proper license and issue receipts that contained a description of the intended use for the explosives [8].

The increased burden on law-abiding citizens placed by the Explosives Act of 1917 was justified, due to the extraordinary circumstances of World War 1 [8, 9]. With the war's end, the law expired, and its provisions were no longer enforced. The Explosives Act of 1917 was credited with significant reductions in the availability of explosives for crimes or terrorism, as well as, injuries and damage from unintentional detonations caused by improper storage [8]. Due to the efficacy of this program, permanently implementing this act was discussed to resolve issues stemming from anarchists and other movements that were engaging in domestic terrorism [8]. Ultimately, no provision was made to adopt the Explosives Act of 1917 as a permanent law.

- *Federal Explosives Act (1941).* With the entry of the United States in World War 2, the same concerns arose surrounding the use of explosives that were present before the passage of the Explosives Act of 1917. Despite the lack of an official declaration of war, the provisions of the Explosives Act of 1917 were revived sometime between the beginning of World War Two and the end of 1940 [10]. After declaring war, the Federal Explosives Act was passed on December 26, 1941 [11]. This act amended and renamed the Explosives Act of 1917 [11]. The amendments were small details such as changing the list of explosives ingredients, not significantly altering the original 1917 act [11]. Notably, at the end of the war and thus the expiration of the act, the regulations stayed in place with the Federal Explosives Act. Additionally, the new Federal Explosives Act also implemented similar regulations to the ones drafted for the 1917 act, with expanded sections on storage and transport [11]. Overall, the changes to the Explosives Act of 1917 by the Federal Explosives Act were not substantial. The primary purpose was the same with both acts: prevent the use of explosives during wartime by those intending on using them against the United States' government.

- *Organized Crime Control Act (1970).* By 1970, there had been sufficient change in society to require a more extensive set of regulations outside of a formally declared state of war. The additional requirement of marking explosives with a manufacturer, type of explosive, and a date or batch code also shows the change in societal opinion of the necessity of explosives regulations. Domestic bombings by groups such as the bombing of the State Department Building in Washington, DC by Weather Underground in 1975, as well as other bombings throughout the 1960s and 1970s presented new challenges for investigators [12]. In the period between 1917 and 1970, federal explosives regulations evolved from an emergency proposal implemented due to the World Wars to a fully-fledged regulatory regime recognizable today in the modern Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF). This new regulatory regime stands in contrast to the ones created under the original Explosives Act passed in 1917, and the refreshed 1941 version. These two acts created regulations specifically applicable only during wartime that: "The operation of this law will doubtless cause inconvenience to persons engaged in legitimate business; it may embarrass worthy citizens in the pursuit of their livelihood…" [9].

With the passage of the Organized Crime Control Act in 1970, federal explosives law continued to evolve. Title IX of the act permanently enacted updated requirements in the same style as the earlier Explosives Act of 1917 and the Federal Explosives Act of 1941. The Organized Crime Control Act effected regulations of every aspect of explosives, though with less effect on transportation. It also implemented, for the first time, federal explosives regulations while the country was not at war [13]. Many of these regulations have been updated in the 48 years since the passage of the Organized Crime Control Act, but they all originated from this law [13]. Additionally, the act also gave the ATF federal regulatory responsibility for all explosives, where it remains today [13].

The Organized Crime Control Act required that all explosives manufactured after February 12, 1971, were to bear a label with the manufacturer, type of explosive, and a date or batch code [13]. These markings were required to be on the wrappings immediately around the explosives (identification taggant), such as a cartridge or bag [13]. Requiring a manufacturer label on the packaging of the explosive enables undetonated explosives to be identified and tracked with every sale. However, this method of tagging explosives is easily defeated by simply removing the markings or by detonating the explosives, although parts of the wrappings may survive, it is unlikely that enough of the identifying information will survive to be useful. Table 2.1 summarizes the different events and reactions prompted between 1917 and 1970.

2.1.2.2 Initial taggants (1971-1980). Manufacturer information included on the wrappings, labels, or receipts can be lost by simply removing this labeling, or by

Table 2.1. Summary of Events and Reactions between 1917 and 1970

Event	Reaction
US involvement in World War 1	• Passage of Explosives Act of 1917 – First federal regulation governing explosives
US involvement in World War 2	• Passage of Federal Explosives Act of 1941
Increased Domestic Bombings	• Passage of Organized Crime Control Act in 1970 • Initial taggant research efforts begin

detonation, which will destroy any wrappings around the explosive. This deficiency was recognized almost immediately by the ATF and others in government who began investigating better methods in 1972 [14]. In 1974, the Advisory Committee on Explosives Tagging, consisting of eleven government agencies and three external groups, was formed to investigate methods of implementing identification taggants. A study began in 1976 on the most promising candidates run by Aerospace Corporation [14].

In 1978, the Senate Judiciary Committee began hearings on the bill, ‘S. 2013’, that would require the use of identification taggants and detection taggants in explosives manufactured for use in the United States [14]. Approximately a year later in 1979, the Senate Committee on Government Affairs was considering a separate bill, ‘S. 333’ that would impose the same tagging requirements as part of a larger anti-terrorism bill [1]. The first bill, under consideration by the Judiciary Committee, held hearings for approximately a year and a half that included testimony from many sources, including the ATF and the company running the taggant study that had begun in 1976 [14]. The Congressional Office of Technology Assessment (OTA) was enlisted to provide a report, entitled *Taggants in Explosives* to the Committee on Government Affairs, and also used the information gleaned from the same taggant study [1].

The research conducted for the ATF by Aerospace Corporation and reported on in *Taggants in Explosives* was the first large-scale test program developed for identification taggants in the United States [1, 14]. As such, an important objective was first to define the evaluation criteria for a successful identification taggant. Five taggant evaluation areas were decided upon as the most important areas to determine if a particular taggant method would be effective:

1. *Taggant recoverability* – the ability of the taggant to be collected in the field despite the debris and other material present in a post-blast environment.

2. *Survivability of the taggant* – the ability to read the information encoded from the recovered taggant even after being in the explosion.

3. *Utility* – the amount of additional information the taggant could provide for investigations after the taggant was recovered and the information read.

4. *Compatibility of the taggant with explosives* – any change to the properties of the explosive such as its sensitivity, the amount of energy released, stability in storage, or other properties because of the introduction of an identification taggant.

5. *Cost of a taggant program* – the cost of the taggant itself, and additional costs to manufacturers, sellers, and regulators for tracking the new taggants, and any other costs a taggant program might impose [1].

Three categories of explosives taggants had been developed by the writing of *Taggants in Explosives* in 1980 and could be evaluated using these criteria: radiological, chemical, and physical taggants [1].

Radiological taggants were the first category of identification taggant under consideration, where one or more radioactive isotopes are added to the explosive to serve as an identifier. Detection of radioactive materials has been well developed, thus allowing radiological taggants to be recovered rapidly [1]. Since radiological taggants depend on the presence of particular isotopes, they are unchanged during the process of detonation. Recovering and reading taggants based on them does, however, require specialized lab equipment and procedures unlikely to be available for police work [1]. Radiological taggants provide two advantages. First, there are a large number of available radioactive isotopes that can potentially be used, which provides the potential for many unique identifiers or including more information [1]. Additionally, radiological taggants emit radiation, which enables them to serve as detection taggants as well as identification taggants. While this behavior makes detecting radiological taggants easy, it also poses a potential health hazard by exposing people who work with explosives, such as blasters and manufacturers, to radiation. This might also cause additional regulatory costs to manufacturers since workers exposed to radiation as part of their job fall under additional regulations [1]. There are also potential issues of public backlash with anything that potentially could expose the public to radiation [1].

Chemical taggants were the second category. One chemical taggant was discussed, but not tested, in *Taggants in Explosives* that was based on combinations of different concentrations of ethanol solutions of rare earth salts [1]. This taggant could then be recovered from the post-blast residue. This proposed chemical taggant system relied on identifying the rare earth elements and their concentrations, which would survive detonation. Other proposed chemical taggants might not survive detonation due to the high-temperature environment created during the detonation process. This chemical taggant provided a sufficient number of unique combinations of rare earth elements and concentrations that would provide many potential codes [1]. The reason this taggant was not tested was that the ethanol solutions could cause sensitization of the explosives, which would make handling more difficult. Unlike radiological taggants, there was no handheld, portable technology developed to detect the presence of a chemical taggant rapidly; so complex laboratory analysis would be needed [1]. The identification procedure and equipment for reading the identification taggant are complicated and require specialized equipment, which increases the cost of reading the taggant, and would not be available for forensics work in 1980 [1].

Physical taggants were the third category discussed, and the only category to undergo significant testing as part of the research conducted by Aerospace Corporation. Initially, two physical taggants were to be tested, one developed by 3M Corporation that was composed of small particles made from stacked colored layers of plastic, and one developed by Westinghouse composed of small ceramic particles doped with fluorescent rare earth compounds. These particles were small and designed to be introduced in relatively large numbers such that removing each of the individual particles would not be humanly possible. Due to concerns over liability, the Westinghouse taggant was not tested during this research program [1]. The physical taggant developed by 3M can be both recovered and read with simple equipment in the field on a theoretical basis, but it was determined that performing both of these tasks in the lab would be necessary in practice. In order to read the code, the taggant particles must be separated from the debris present at the blast site; these separation procedures were, however, determined to be simple, and can be performed with a small amount of training [1]. Testing of the 3M taggant showed that a number of particles would survive and be readable using a microscope [1]. The sequence of colors in the taggant particle encodes information, and a ten-layer particle with ten different colors produces a large number of codes. Theoretically, only one particle would need to be recovered, but increased accuracy could be obtained when additional particles were found [1]. The 3M taggant was tested with a range of different commercial explosive products and found to be compatible with all but one booster material, and one variety of smokeless powder [1]. The cost of tagging an explosive with 0.05% by weight using the 3M taggant was calculated as being a 2.3% to 23.5% increase depending on the type of explosive being considered, with the largest percentage increase coming from detonating cord which had the lowest cost basis [1].

The testing performed by Aerospace Corporation and the cost analysis performed in *Taggants in Explosives* show that the 3M physical taggant was a viable identification taggant, assuming the few material incompatibilities could be resolved [1]. This made the 3M taggant a very promising candidate. In 1978, two bills were under consideration in the

United States Senate, though ultimately, neither Senate Bill #2013 nor Senate Bill #333 became law. Senate Bill #2013, under consideration by the Senate Judiciary Committee, raised concerns by the committee members about whether the proposal included black and smokeless powders used in ammunition [14]. If these two materials were covered, additional concerns over the compatibility and cost were raised [14]. This uncertainty appears to have caused discussion on this bill to stop. Senate bill 333, which prompted the writing of *Taggants in Explosives,* required additional study [1]. As written, the bill would involve tagging any explosive material, including blasting agents such as ammonium nitrate, as well as black and smokeless powders [1]. The costs of implementing a taggant program while covering these materials increased the total program cost to an estimated 268 million dollars a year in the most comprehensive program [1]. The cost estimate was likely the reason for the failure of this second bill. Table 2.2 summarizes the events that occurred between 1971 and 1980, and reactions into investigating identification taggants.

2.1.2.3 Updated taggants (1981-1998). After the publication of *Taggants in Explosives*, identification taggant research continued in both government and industry [2, 15]. *Taggants in Explosives* recommended one of three courses of action:

1. Enact legislation requiring the addition of identification taggants contingent on the technical feasibility

2. Do not pass legislation but recommend research into identification taggants

3. Take no legislative action and encourage the executive branch to enhance alternative methods of investigating taggants [1].

Table 2.2. Summary of Events and Reactions between 1971 and 1980

Event	Reaction
Passage of Organized Crime Control Act (1970)	• Initial taggants created
Senate Bill 2013 (1978)	• Considered taggant requirements for all explosives • Raises concerns over compatibility with taggant in black powder and smokeless powder used for sport shooting
Senate Bill 333 (1978)	• Considered taggant requirements for all explosives • Commissioned *Taggants in Explosives*
Taggants In Explosives (1980)	• Identified evaluation criteria for successful identification taggant • Identified cost, survivability, and compatibility with explosives as major areas • Provided three recommended courses of action

Congress opted to specifically ban appropriations for taggant programs by the ATF from 1981 to 1993 [2].

As a direct result of the bombing of the Alfred P. Murrah Building in Oklahoma City in 1995, also influenced by the World Trade Center bombing in 1993, another reactive investigation into the state of identification taggants began [2]. The 1996 Antiterrorism and Effective Death Penalty Act required the compilation of a report of the effectiveness of taggants for explosives [2]. This report was published by the National Research Council in 1998 under the name *Containing the Threat from Illegal Bombings: An Integrated National Strategy for Marking, Tagging, Rendering Inert, and Licensing Explosives and Their Precursors*. This report henceforth referred to as *Marking and Rendering Inert*, provided a second comprehensive look at the state of taggant technologies, their utility, and the potential for future legislation requiring identification taggants and other technologies to guard against explosives [2].

This report defined three types of identification taggants that were developed or under development in between the publication of *Taggants in Explosives* and 1998. The first type of identification taggant that *Marking and Rendering Inert* identified was a particulate taggant. This is another name for a physical taggant and was so named due to the fact that the physical taggants developed at the time were mostly small particles [2]. The second type of identification taggant that was named was an isotopic taggant. This is similar to a chemical taggant where various chemical compounds are added to the material to be tagged. However isotopic taggants also introduce specific isotopes of atoms at some of the sites in the chemical compound to encode information [2]. The third type of identification taggant that was named was biological taggants. These taggants used some biologically produced chemicals as a chemical taggant such as DNA or used conventional chemical taggants that were detected using biologically derived detection methods such as immunoassays [2].

Particulate or physical taggants continued to be the most fully studied identification taggant due to the 18 years of required use in Switzerland [2]. The Swiss experience with physical taggants has shown that they can be recovered and that when recovered, they can increase the rate at which crimes are solved [2]. Different types of physical taggants have the potential to sensitize some or all explosives, due to the "gritty" nature of small particles. The added particles may create areas with higher than usual friction, which could sensitize or cause detonation of the explosive [2]. Additionally, physical identification taggants that can be used in explosives must be durable and unreactive in order to survive the detonation process. This means, however, that they are likely to survive in the environment indefinitely and thus present a contamination risk both in the environment and any raw materials produced via the use of explosives such as mining or quarrying [2].

Almost simultaneously with the publication of *Taggants in Explosives*, the country of Switzerland enacted a federal statute that required taggants to be added to explosives [2]. This legislation was enacted as a result of an increase in bombings that occurred during the late 1970s [2]. This statute requires that all explosives (dynamites, slurries, water gels, ammonium nitrate/fuel oil (ANFO), black powder) manufactured for consumption in the Swiss market must have a unique taggant per manufacturer that is changed twice a year [2], and a sample of the taggant is maintained by the Swiss federal government. Three taggants are approved: the Microtaggant® a commercially produced version of the 3M taggant tested in *Taggants for Explosives*; HF6, which is a Swiss developed version of the Microtaggant®; and one called "…Explotracer that consists of orange polyethylene chunks permeated with fluorescent markers, embedded iron particles, and rare-earth oxides" [2].

According to Swiss authorities, the addition of identification taggants into explosives has helped law enforcement track explosives that were used, or attempted to be used, in terrorist or criminal acts [2]. In Switzerland, 254 incidents where explosives, were used in either improvised explosive devices or safecracking, occurred between 1984 and 1994. Of these, 44.4% were successfully solved when taggants were recovered in 63 cases. Of the remaining 191 cases where taggants were not recovered, only 16.2% were solved [2]. Therefore, the Swiss experience shows that when identification taggants are used and recovered, the case is twice as likely to be solved under their taggant program [2].

Isotopic taggants were also evaluated, although limited experience and testing meant that such evaluations were mostly preliminary. The compatibility of isotopic taggants was judged to likely be acceptable since the proposed methods used parts per million of the additives. Explosives manufacturing processes of the time did not require this level of control, so it was deemed unlikely that the addition of such a low concentration of another material would materially affect the properties [2]. Incomplete testing prevented a full assessment of the survivability and recoverability of isotopic taggants in post-blast residue, as only small-scale tests had been performed [2]. Due to their low concentrations and the necessity of identifying the different isotopes used, analysis requires more specialized equipment and techniques such as mass spectroscopy, which reduces the number of facilities capable of performing the analysis [2, 4, 5]. The low concentrations of the isotopic taggants were thought to significantly reduce the chances of environmental risks or cause many issues with contamination of mined raw materials by the taggants, although not enough data was available at the time to fully assess their impact [2]. The cost of isotopic taggants is relatively high, though the low concentrations required make them useful on an overall cost basis [2, 4].

Biological taggants were also limited by the same lack of experience and testing that had hampered isotopic taggants. The compatibility of a biological taggant was hard to assess given the preliminary nature of the research, though it is generally expected that low concentrations would lower the risk of incompatibility [2]. The survivability and recoverability of biologically based chemicals are uncertain due to the heat generated by detonation and the harsh environment present during the manufacturing of some types of explosives. An example of a harsh environment for biologically derived materials or chemicals is the manufacture of ammonium nitrate prills, which takes place at high temperatures (145 to 155 ºC) and is strongly oxidizing as well [2]. A full evaluation of environmental acceptability and contamination of mined raw materials was not available at the time, but it was thought that the relatively low concentrations required would minimize the risk of biological taggants having a negative effect on these criteria. The cost of biological taggants depends on the production cost of the biological components. While not fully developed, it is expected that the low concentrations required would result in an acceptable cost for the benefits provided [2].

This extensive report was commissioned as a direct reaction to a terrorist attack on the Alfred P. Murrah Building that used explosives. At the time of publication in 1998, *Marking and Rendering Inert* evaluated a comprehensive identification taggant program as too expensive for the current bombing risk environment. It proposed further investigation into identification taggants so that in the event that the risk of bombings increased, at least one type of identification taggant would be evaluated and the costs and benefits of such a program could be evaluated again [2]. An additional conclusion of the report was that based on the Swiss experience with identification taggants, a taggant program has been shown to aid in solving crimes such as bombings [2].

The Oklahoma City bombing in 1995 caused Congress to reconsider a requirement to use identification taggants in explosives. As a component of the 1996 Antiterrorism and Effective Death Penalty Act, the second report on the feasibility of using identification taggants in explosives was commissioned and published in 1998 [2]. In the 18 years since the OTA report, three major developments in explosives tagging had occurred. The first was the passage in July of 1980, of the Swiss act requiring all explosives manufactured for the Swiss market to utilize an identification taggant program. The second development was that despite an appropriations committee ban on the ATF investigating identification taggants, additional identification taggant concepts had been invented based on the new technologies that became available between the mid-1970s and the late 1990s [2]. The final development was the International Civil Aviation Organization's Convention on Plastic Explosives from 1991 that required all signatories to adopt detection taggants in certain plastic explosives by the end of 1996. The 1998 report mostly reiterated the results of the 1980 OTA report: using identification taggants was technically feasible, but the cost of the taggant program and concerns for safety still needed to be addressed [1, 2]. An additional consideration from this new report was that many of the proposed taggant methods were underdeveloped and required live testing before they could be fully evaluated [2]. Table 2.3 summarizes the developments that occurred between 1981 and 1999.

Table 2.3. Summary of Events and Reactions between 1981 and 1999

Event	Reaction
Appropriations Ban (1981-1993)	• ATF not permitted to research taggants
Bombing of Alfred P. Murrah Building (1995)	• Passage of Antiterrorism and Effective Death Penalty Act
Antiterrorism and Effective Death Penalty Act (1996)	• Commissioned *Marking and Rendering Inert*
Marking and Rendering Inert (1998)	• Provided updated evaluation criteria for identification taggants • Summarized status of research performed between 1980 and publication (approximately 1998) • Emphasized importance of cost, compatibility, and survivability as the major evaluation areas

2.1.2.4 Modern taggants (2000- present). The deadliest terrorist attack ever in the United States occurred on September 11, 2001 with the attack on the World Trade Center and the Pentagon buildings. This prompted the passage of several laws, including the Safe Explosive Act of 2002, which was part of Public Law 107-296, a larger bill that created the Department of Homeland Security [16]. The major component of this act was to restrict the unlicensed handling of explosives further than the Organized Crime Control Act with the introduction of additional sitipulations for authorized users of explosives. As concerns over terrorism continued, research into identification taggants has continued as well. Most new technologies such as nanotechnology or DNA sequencing have been proposed as potential identification taggant methods. Older methods have also been adapted.

The Safe Explosives Act was passed as part of a larger bill that reorganized components of the federal government. The explosives components of the law included the most significant changes to explosive licenses and eligibility since the passage of the 1941 Federal Explosives Act. Under this new law, all purchasers and users of explosives must hold a license or permit, whereas previously only purchasers or users of explosives across state lines were required to hold a license or permit [17]. Additional changes were made to categories of people prohibited from handling explosives [17].

Research into taggants has continued to the modern day [4, 5, 18, 19], though available testing information and data remain scarce [5]. No new categories of identification taggants have been identified; however, improvements and refinements to the categories of physical, chemical, and biological taggants have occurred. Physical taggants remain an active area of research [4, 5, 18, 20, 21]. One type of physical taggants that have been proposed are particles containing quantum dots that emit light at specific frequencies, and the combination of frequencies can be used to encode information [4, 5]. Physical taggants where rare earths or other fluorescent materials such as dyes are introduced to a carrier particle have been developed as well [4, 5, 18, 19]. These particles encode information in the colors and intensities of the light they emit [4, 5, 18]. These approaches are similar to the first taggants, which use different concentrations of various elements contained within a particle [22, 23] but exploit the fluorescence of the dyes or rare earths to also increase recoverability of the particles [5, 18]. Unique codes based on a sequence of nucleotides can encode information that would be needed for an identification taggant.

Due to the rapid development in the area of biology, DNA based identification taggants continue to be proposed and developed [2, 4, 5]. Only low concentrations of taggant are needed due to the amplification that can be obtained using polymerase chain reaction (PCR) techniques [4, 5]. DNA sequences have been used commercially to tag pharmaceutical products like cancer drugs [4] as well as other anti-counterfeiting uses [5]. DNA sequences can theoretically be of any length, which allows for a practically unlimited number of codes [4, 5]. Reading these sequences using a technique such as PCR is well understood, but the reagents, equipment, and expertise needed are a significant cost [4, 5]. Additionally, the stability of a DNA sequence when subjected to the heat created by detonation is unknown and might preclude the use of DNA based identification taggants with explosives [2].

Small ceramic or metal oxide particles that contain fluorescent rare earth materials have been proposed as a taggant that can be used to identify if a particular type of material has been used [19, 20, 21]. The combination of rare earths used and the intensity of the fluorescence can create a way of encoding information [4, 5, 20]. These particles can be recovered in the field using a UV lamp [21]. Analysis of the particle requires the use of sophisticated laboratory equipment and is correspondingly expensive [20, 21].

Similar glass particles have also been proposed as an identification taggant, where the concentration of the different fluorescent rare earth elements is used to encode information, unfortunately large charges that might be used in mining or other legal uses (>500 lbs.) do not allow the glass microspheres to survive detonation [18, 19]. The taggant elements can be added to the liquid glass, thus allowing for an even distribution of the elements that make up the identification taggant in the final particle [18, 19]. Small spherical glass particles, called microspheres, are already used in commercially produced explosives [18]. This identification taggant changes the composition of the microspheres that are added [18, 19]. As with other physical taggants such as the Microtaggant®, recovery of the taggant is the major concern [2, 19]. Tests were performed to judge the recoverability of these microsphere taggants, and showed mixed results for recoverability and survivability of this taggant, where the taggant could be recovered for small charges, but not for larger charges, and not in all cases [18, 19].

Recent taggant developments utilizing DNA or nanoparticles have occurred because of the increased interest in technologies that counteract terrorism. This is a notable change from previous cycles in the United States where government efforts lead to research in identification taggants. The shift in priority from crime to terrorism and the use of explosives in asymmetric warfare has caused the development of identification taggants to shift its priorities as well. Current technologies are suited for commercially manufactured explosives but are of limited use for homemade explosive materials. The modern experience shows that a universal identification taggant that can be used effectively in identifying both commercially manufactured explosives and also homemade ones will be necessary for an effective identification taggant program.

An older technique, neutron activation analysis, has become more capable with modern computing power, software, and semiconductor manufacturing technology. This technique can be used on samples regardless of their physical state and is thus well suited to analyzing post-blast residue to find chemical taggants. Table 2.4 summarizes the events between 2000 and their reactions.

Table 2.4. Summary of Events and Reactions between 2000 and the Current Day

Event	Reaction
September 11th Terrorist Attacks (2001)	• Passage of Safe Explosives Act of 2002 • Creation of Department of Homeland Security
US involvement in conflicts in the Middle East (2003-current)	• Renewed interest in identification taggants for antiterrorism

2.1.3. Summary of Taggants Literature. Throughout the one hundred years of taggant development, the same cycle has repeated several times. The cycle begins with a triggering event such as a terrorist attack involving explosives or a major war. This event prompts the government to consider changes to law or regulations that would provide more identifying information about the explosives. During the drafting of these laws or regulations, studies are performed into mechanisms that can provide the type of information desired, such as identification taggants. The proposed mechanisms are then evaluated, and laws and regulations are finalized or ultimately rejected. Additional mechanisms are proposed and investigated, and the cycle begins again when the next triggering event occurs.

The implementation of a modern identification taggant would quickly provide useful information for criminal forensic investigations and aid in investigations of terrorist attacks involving explosives. Studies conducted in 1980 and 1998 have both shown that while technology existed that could be used as an identification taggant, the cost of a program and safety concerns were issues that would need to be resolved prior to implementation. Additionally, any identification taggant must be rigorously tested before being utilized. The 1998 report *Marking and Rendering Inert* identified other promising candidates, but concluded that the lack of full-scale testing meant that a more thorough evaluation would be needed.

The effectiveness of the different taggant technologies in meeting the identified evaluation criteria is described qualitatively with a score on a scale from one to five based on prior studies of taggants. A score of five means the taggant technology performs extremely well in that category, and a score of one meaning the opposite. Cost is also ranked on the same one to five scale, but with higher scores corresponding to lower taggant cost and cheaper analysis costs. Therefore, the most effective taggant technologies will have the highest total score. A comparison of the different identification taggant technologies is shown in Table 2.5.

By total score, biological taggants are in last place due to concerns with recoverability and survivability of the taggant as well as the relatively high cost of taggants, and analysis of any recovered taggants [2]. Isotopic taggants meet all the criteria except for the high cost of production [2]. Chemical taggants are tied with isotopic, due to some

Table 2.5. Comparison of Identification Taggant Categories

Taggant	Recoverability	Survivability	Utility	Compatibility with Explosives	Cost	Total Score
Radiological [1]	5	5	3	5	4	22
Chemical [2, 1]	3	3	5	4	3	21
Physical (or Particulate) [2, 1]	5	5	4	4	4	22
Isotopic [2]	5	5	5	5	1	21
Biological [2]	3	3	5	5	2	18

concerns over their recoverability and survivability [2]. Radiological taggants are tied for the highest score, with concerns over the total number of potential codes, as well as their cost [1]. Physical or particulate taggants share first place with radiological taggants. Due to the low cost of physical or particulate taggants that also meeting most of the other criteria, research focus has focused on producing a cheap physical taggant that is compatible with explosives [1, 2].

2.2. NEUTRON ACTIVATION ANALYSIS LITERATURE REVIEW

Several methods are capable of determining the composition of a chemical identification taggant. An ideal method for use with chemical taggants for explosives must be able to detect concentrations with ppb precision to enable extremely low taggant concentrations to be used, be used with minimal sample processing to reduce losses of recovered taggant, and be able to determine the composition of the bulk material to measure the concentration of the taggant in undetonated explosives [1]. Mass spectroscopy is a commonly used method to determine composition. Many forms of mass spectroscopy have the requisite precision, but require significant processing of the material to create the ions that are analyzed and can only work on extremely small samples of material which precludes most samples of undetonated explosives [24]. An alternative to mass spectroscopy would be a technique such as inductively coupled plasma optical emission spectroscopy (ICP-OES or ICP-AES). This technique introduces small quantities of a liquid sample into a high temperature plasma and measures the photons emitted as the sample atoms become ionized. While highly precise, this technique also requires processing that would result in loses of recovered taggant material [25]. NAA is a technique that matches the ideal method: it has the requisite precision to measure concentrations down to the ppb level, it requires no additional processing of samples, and it measures the composition of the bulk sample [7]. As a result of these advantages, NAA was the chosen analytical technique used for all analysis and is discussed further in the following sections.

2.2.1. Overview of NAA. In its most basic form, NAA is a simple technique where a specimen of interest is exposed to a large neutron flux for a period of time. While exposed to the neutron flux, the nuclei of the atoms making up the sample will be struck by neutrons and on occasion absorb them and convert from one isotope to a different one with an additional neutron. These isotopes may later decay and produce characteristic gamma rays while doing so. Using a specialized detector, the energy of the released gamma rays can be measured, allowing the isotope to be identified [26]. A schematic diagram of the process is shown in Figure 2.2.

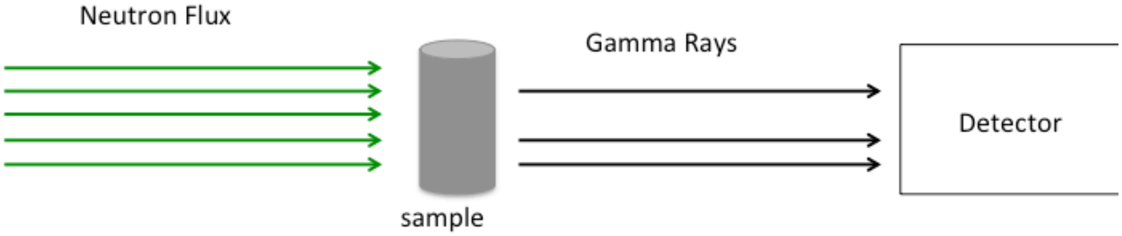


Figure 2.2. Schematic Diagram of Neutron Activation Analysis (NAA)

To calculate the NAA spectrum from a sample, it is necessary to consider all the isotopes of all the elements present in the sample. Fortunately, many of the common, low Z (low atomic number) elements like O, N, etc. have very low capture cross sections and do not contribute to the resulting spectrum to any real extent [27]. Many heavier elements, and some of the taggant elements of interest have multiple stable isotopes that are present in appreciable amounts in nature and convert to active nuclei, which can be detected by NAA. Therefore, it is necessary to track the conversion of each isotope of each of the taggant elements to determine what they convert to, and determine if that resulting, transmuted isotope is active and can be identified with NAA.

With the set of taggant elements chosen for the nuclear barcode, there are 23 naturally occurring isotopes that are present in less than 0.9% concentration [27]. They are organized in Table 2.6 into two columns: the first column contains isotopes that convert into active nuclei that can be detected by NAA [27], and the second column contains isotopes that convert into stable nuclei that cannot be detected by NAA [27]. The 17 isotopes in column 1 are ideal isotopes to detect using NAA. They have widely varying half-lives [27], which gives them each widely varying activities for a given irradiation time.

Modern NAA detectors can be run in multi-channel mode where they count the number of gamma rays that fall within a specific energy range as one channel and can

Table 2.6. Active and Stable Taggant Nuclei under NAA

Column 1: Active Transmuted Nuclei						Column 2: Stable Nuclei	
Eu-151	Eu-153	Dy-159	Dy-164	Ho-165	Lu-175	Dy-160	Dy-161
Lu-176	Sm-144	Sm-147	Sm-150	Sm-152	Sm-154	Dy-162	Dy-163
Ir-191	Ir-193	Re-185	Re-187	Rh-103		Sm-148	Sm-149

output the counts of all of the channels. Each active isotope has a characteristic gamma spectrum that it emits as it decays. Therefore, each active isotope will give a peak on the channel(s) that are closest in energy to their characteristic gamma rays [7]. This allows the experimenter to identify which elements are present, as long as they can emit enough of a signal to not be lost in background noise. A good spectrum will resemble the results in Figure 2.3.

The spike at about 662 keV is the signal from ^{60}Co, and is immediately apparent on the graph. The green line at the top of the peak is the cursor used by the display program, and is not of any analytical significance. A bad spectrum where the noise overwhelms the signal will lack any distinct peaks, as in Figure 2.3 between about 50 keV and 300 keV. Since the nuclear barcode uses such low concentrations of taggants, multi-channel NAA experiments can only be used when the background will not overwhelm the signal. When these difficulties are overcome, the taggant elements can be identified very easily, as each element has a distinct spectrum, and can be readily identified by the peaks present on the plot.

2.2.2. Mathematical Analysis. With the software support available, even very faint peaks can be identified. However, this sensitivity can also cause problems in some

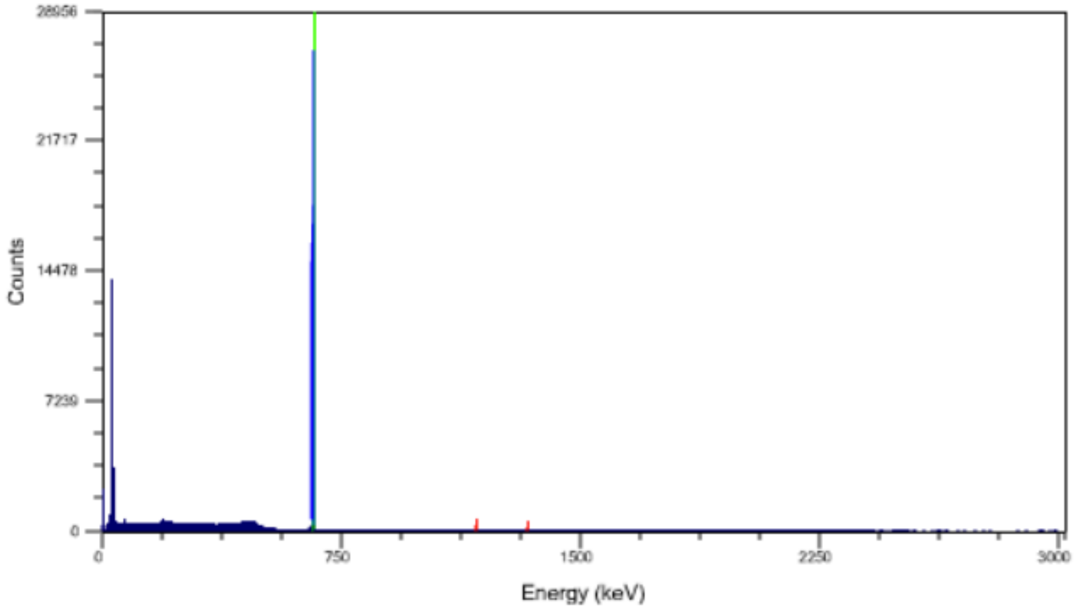


Figure 2.3. Example Multi-Channel NAA Plot (^{60}Co and ^{137}Cs calibration sample)

instances where "peaks" are identified that are not actually present in the sample. One criterion used to determine if a give peak is a real peak, or if it is statistical noise, is the ratio of the uncertainty in the net area under the peak and the net area under the peak itself (the number of counts for that particular peak). If the uncertainty in the net number of counts is less than the number of counts under a particular peak, then that peak is classified as real. In the opposite case, the peak is classified as noise, and not an actual peak.

NAA can also be used quantitatively [7]. When each active isotope emits its own characteristic gamma spectrum while irradiated, the detector identifies the energy of the emitted gamma ray and counts them. However, even the best gamma ray detectors can only keep track of a limited number of different energy bins. As a result, an active isotope's peak is broadened into something resembling a bell curve. Integrating the number of counts under the broadened peak gives the total activity associated with the active isotope responsible for that peak. This allows the amount of the active isotopes to individually be calculated, and thus give the concentrations associated with the nuclear barcode [7].

The usefulness of NAA is governed by the activity of the irradiated sample. The activity of any material is governed by Equation 1:

$$A_i = \lambda N_{trans,i} \tag{1}$$

where A is the activity of the sample from isotope i, λ is the decay constant of the transmuted isotope, and $N_{trans,i}$ is the number of atoms of the specific isotope i.

The number of transmuted atoms of isotope i can be calculated from the number of atoms of isotope $i - 1$ in Equation 2:

$$N_{trans,i} = N_{i-1}\sigma_{i-1}\phi t \tag{2}$$

where $N_{trans,i}$ is the number of transmuted atoms of isotope i; N_{i-1} is the number of atoms of isotope $i - 1$; σ_{i-1} is the neutron capture cross section of isotope $i - 1$; ϕ is the neutron flux; and t is the irradiation time of the sample. Equation 2 provides the way to calculate the number of atoms that capture a neutron from the incident flux, which converts it from one isotope to another. Since both the flux ϕ and the neutron capture cross section $\sigma_{c,i-1}$ are functions of the energy of the incident neutrons, the one group approximation will be used where these quantities are averaged to a single number [28].

The calculations carried out in Equations 1 and 2 describe the capture of one neutron from the flux by an isotope i. In general, for normal neutron fluxes and irradiation times, a nucleus will capture only one neutron, so there is no need to track transmutation from $i-2$ to $i-1$ for example. As such, any of these secondary conversions can be ignored, as they are extremely unlikely to occur. For the remaining analysis, the effects of these additional reactions will be ignored, and it will be assumed that the only reaction possible is the capture of a single neutron, after which the activated nucleus will simply decay.

The measured activity of a radioactive sample comes from the decay of the nuclei, which decay at a constant rate given by λ. Combining this information allows the quantity of an element to be identified by NAA using Equation 3 [7].

$$m = C\frac{\lambda}{((1-e^{-\lambda t_i})e^{-\lambda t_d}(1-e^{-\lambda t_m})} * \frac{M_a}{\Phi_{th}\sigma_{eff}\Gamma\varepsilon\theta N_A} \tag{3}$$

where m is the mass of the mass of the element, C is the net counts under the peak, t_i is the time the sample was irradiated for, t_d is the time between the irradiation of the sample and beginning to count the sample, t_m is the duration of the measurement, M_a is the atomic mass of the element, Φ_{th} is the one group approximation of the flux the sample was exposed to, σ_{eff} is the one group approximation of the neutron capture cross section, Γ is the probability of a gamma photon being emitted by a decay event, ε is the probability that an emitted photon will trigger a count in the detector, θ is the isotopic abundance of the target isotope, and N_A is Avogadro's number. Since all of these quantities can be found in reference materials, or are experimentally determined, the mass of the elements can be calculated.

The uncertainty in the measured mass of the element can also be determined [7]. The uncertainty in the calculated mass, u_m, of the element can be calculated by summing the product of the derivative of equation 3 with respect to each variable by the uncertainty in the value of each variable in equation 3 in quadrature. This is shown in equation 4.

$$u_m{}^2 = \sum_i \left[\left(\frac{\partial m}{\partial x_i} \right)^2 * u_i{}^2 \right] \tag{4}$$

2.2.3. Uses of NAA. NAA is particularly well suited for determining the composition of materials that are a) hard to dissolve into solution, b) easy to contaminate while trying to dissolve them, c) are unique and should not be destroyed or dissolved, or d) have a surface composition different from the bulk [7]. Many diverse disciplines and experiments can make use of this technique, including archeology [26] and semiconductor manufacturing [7].

NAA has been used in many fields since its invention to identify the composition of materials. In archeology, it has been used to investigate so called "trace" and "ultra-trace" elements present in clays used to make ceramics. These "trace" elements are present at parts per million level and "ultra-trace" at the parts per billion levels [29], which is the range of concentrations that the nuclear barcode uses. In fact, archeology uses these elements to identify what some researchers call a "fingerprint" of the clay, since these elements, present at such low concentrations, are incredibly unlikely to be added to the clay. The use of these "fingerprints" allows archeologists to identify the origin of the clay used in ceramics, which can reveal trade routes and contact between different groups if the clay is from a significant distance from where the ceramics were discovered [29].

Semiconductor manufacturing requires extremely pure materials, as any impurities can affect the electrical properties of the resulting device. In the manufacture of gallium arsenide (GaAs) based semiconductors, one important impurity is zinc (Zn), which acts as an electron acceptor and as such alters the electrical properties of the material [30]. Due to the sensitivity of GaAs based semiconductors to Zn impurities, accurately measuring the Zn concentration down to parts per billion level is crucial [30]. NAA and its derivatives are used to determine the concentration due to the accuracy and precision that is only possible with NAA, and not comparable techniques [30].

2.2.4. Summary of NAA. NAA is an analytical technique that is well suited for use in identifying a taggant in post-blast residue. The technique has strong theoretical underpinnings that allow for detailed analysis of the composition of the material. Additionally, the technique of NAA is well understood and an expression for the total uncertainty in the measurement of the composition of the material can be developed. NAA can be used on any sample regardless of the physical form, and is capable of probing not just the surface composition of the material, but providing measurements of the bulk. These advantages have been realized in fields such as the semiconductor industry when analyzing contaminant concentrations in wafers down to parts per billion [30]. Additionally, NAA is a nondestructive technique and this advantage has been used to great effect in archeology to identify the origins of ceramics by matching their compositions to clays [29]. These characteristics make NAA a good candidate technique for identifying an identification taggant in post-blast residue.

2.3. EXPLOSIVES LITERATURE REVIEW

An explosive is a material that undergoes a reaction known as detonation. Detonation produces a shockwave trailed by an extremely exothermic chemical reaction. Knowing the composition of the explosive allows the products of the reaction that occurs during detonation to be predicted. Parameters such as the detonation velocity and detonation pressure that describe the performance of the explosive can be predicted based on this knowledge of the detonation products as well [31].

2.3.1. Explosives Chemistry. Explosives react in an oxidation reaction, similar to the burning of a fuel. During this reaction, different elements are "burned" with the oxygen present in the explosive to produce highly oxidized products such as CO_2 or H_2O that maximize the sharing of electrons between atoms, since this produces the most thermodynamically stable products. Most explosives currently used are composed of four elements: carbon, hydrogen, oxygen, and nitrogen, which can be written as $C_xH_yN_wO_z$. It is generally assumed that the reaction occurs in two steps: first the explosive molecule separates into individual atoms due to the heat and energy, second the individual atoms react to form molecules and release energy that sustains the explosion. Additionally, there is a hierarchy or ordering in which the products are produced: first, nitrogen atoms combine to make nitrogen gas, second hydrogen and oxygen react to form water vapor, third carbon and oxygen react to form carbon monoxide, fourth carbon monoxide and oxygen react to form carbon dioxide, and fifth any remaining oxygen atoms react to form oxygen gas. While the exact mechanism by which this system of reactions occurs is unknown, the ordering of these reactions is a good "rule of thumb". If the explosive molecule has too little oxygen, then the reactions will stop when all of the oxygen is consumed, since this series of reactions occurs much faster than the products could mix with air from the environment [31].

Explosives that contain too little oxygen to fully convert carbon into carbon dioxide are called under oxidized explosives, explosives that produce oxygen gas are called overoxidized explosives, and explosives that fully convert carbon into carbon dioxide but do not produce any excess oxygen gas are called oxygen balanced explosives [31]. If an explosive is under oxidized, then incomplete reaction of carbon can occur, which produces solid carbon. This solid carbon is then dispersed throughout the environment and deposited on surfaces from which it can be recovered as post-blast residue. In real detonations, it is common to have pockets of overoxidation and under oxidation, so real detonations almost always produce post-blast residues. Additional post-blast residue can be produced by small particles of the undetonated explosive that do not detonate [32]. Figure 2.4 shows post-blast residue from a binary explosive that condensed onto a steel cylinder and was collected onto a cotton ball.

2.3.2. Explosive Characterization. Explosives can be characterized based on their reaction mechanism or their sensitivity. Detonation is a process where the explosive material reacts and produces a shockwave with a velocity higher than the speed of sound in the material that contains the reaction zone. Explosives that undergo detonation are called high explosives, and include materials such as trinitrotoluene (TNT) or nitroglycerine [31]. Low explosives do not produce a shock wave with a velocity that exceeds the speed of sound in the material and therefore do not undergo detonation. Instead low explosives undergo deflagration, where the reaction zone moves through the material slower than the speed of sound [31]. A common low explosive is black powder.

Figure 2.4. Post-blast Residue from Binary Explosive Collected onto a Cotton Ball

Explosives are also characterized by their sensitivity to stimuli such as friction or impact. The most sensitive explosives are referred to as primary explosives. Primary explosives require minimal stimulus to detonate. This characteristic makes them well suited for the use as initiators such as a blasting cap. Secondary explosives are less sensitive than primary explosives but produce more energy per unit mass than primary explosives. Most can be detonated with a blasting cap. This category contains common commercial and military explosives such as TNT and nitroglycerine. Tertiary explosives are less sensitive than secondary explosives, and typically require a relatively large quantity of secondary explosive be detonated in order for tertiary explosives to detonate. The most common example of a tertiary explosive is a mixture of ammonium nitrate with mass fuel oil (ANFO), which requires a booster charge composed of a secondary explosive when used in commercial blasting.

2.3.3. Explosive Performance. The explosive performance is dependent on several factors including the explosive used, the density of the explosive, and the degree of confinement of the explosive. Each explosive has a characteristic detonation velocity, which is the rate at which the reaction zone moves through the explosive at the maximum density of the explosive that permits detonation. In most explosives, if an explosive is too dense from being packed too tightly, detonation cannot sustain itself, and the explosive will not detonate [31]. The detonation velocity at densities other than the maximum density is typically linear and can be estimated. The detonation pressure produced by an explosive is the product of the explosive density and the square of the detonation velocity divided by the ratio of specific heats of the detonation product gases plus one [31]. The detonation velocity and detonation pressure are measures of the power of an explosive. The brisance or shattering strength of an explosive is also related to the detonation velocity [33].

The detonation of explosives destroys containers and produces fragments. The distance these fragments travel can be estimated by several methods. The most basic is through quantity-distance (QD), which takes the quantity of explosive and the distance from the explosive into account, and states that for a given quantity of explosives buildings, roads, etc. must be located beyond a certain distance [34]. In general, the further away from the explosive the fewer fragments. QD methods often assume that anything within the distance is unsafe and anywhere outside of this radius is perfectly safe, even if it is one inch beyond this distance [34]. Modeling such as IMESAFR includes more factors than just the quantity and distance by introducing simulations of the fragment dispersion [35]. These simulations produce probabilistic assessments of damage or injury at different distances based on the quantity and type of explosive [35, 34]. At the lab scale, it is possible to approximate the fragment production and distribution. The Gurney equation is used to determine the initial velocity of a fragment, the Mott equation to determine the number of fragments below a certain mass, and ballistics to determine the trajectory and time of flight of these fragments [31].

2.3.4. Summary of Explosives. When a material explodes, it produces large quantities of gaseous products and large amounts of energy. If the explosive, or part of the explosive, is under oxidized, then the detonation process will not result in the complete oxidation of carbon. This carbon can then be deposited on surfaces and collected as post-blast residue. Depending on the performance of the explosive, materials near it may be fragmented and scattered about. These fragments may contain traces of post-blast residue that can be sampled to collect an identification taggant, and their locations can be predicted by simulation or approximation.

3. NUCLEAR BARCODE CONCEPT

The taggant developments described in Section 2.1 have prompted the creation of a new identification taggant, the Nuclear Barcode, that is proposed to satisfy the key characteristics of a successful identification taggant better than previously developed taggants. The nuclear barcode focuses on allowing identification taggant to survive the detonation process intact, prevent counterfeiting or obscuration, as well as providing a sufficiently large number of potential codes to enable labeling individual batches of product. The nuclear barcode is designed to accomplish these goals inexpensively while also not affecting the properties or sensitivity of the tagged explosive.

3.1. NUCLEAR BARCODE CONCEPT DESCRIPTION

The nuclear barcode is a proposed identification taggant. It falls between a physical taggant and a chemical taggant that uses the combination of concentrations of rare earth and other elements to encode information. This provides a large number of possible codes. The present design of the nuclear barcode would use 40 different concentrations of eight elements, giving a total of 40^8 or 6.56 trillion unique combinations. This number can be increased further by using a larger number of elements or by using a larger number of concentration levels. The number of codes allows for a relatively large amount of information to be included in the codes such as the type of explosive, manufacturer, and enable identifying individual batches of the explosive products. This capability would represent a notable improvement compared to the system mandated in Switzerland [2]. A schematic of the Nuclear Barcode is shown in Figure 3.1.

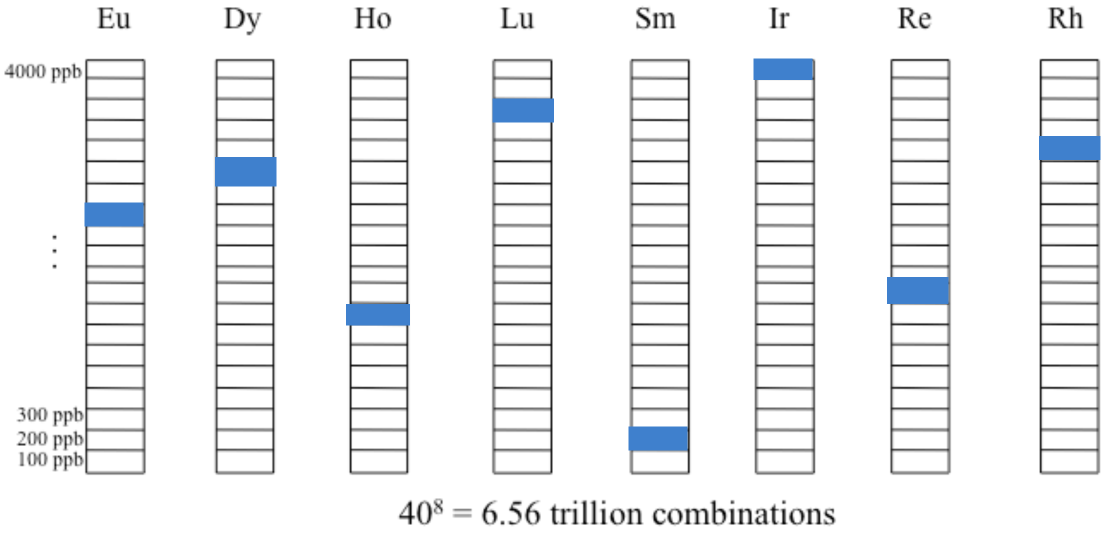


Figure 3.1. Nuclear Barcode Schematic

Additionally, recovery of the nuclear barcode taggant is simple, requiring only a sample of the post-blast residue that can be recovered with minimal training. Unlike most chemical taggants, the exact chemicals that are added to the explosive do not influence the recoverability or survivability of the taggant, as long as the elements are added in the correct concentrations. The nuclear barcode uses neutron activation analysis (NAA) to identify the concentration levels, which identifies the elements present in a sample by their nuclei and not their chemistry.

The elements used to create the nuclear barcode taggant are relatively expensive, being rare earth elements or precious metals, but they only need to be added in small concentrations (ppb to a few ppm). The use of NAA allows for the higher cost taggant elements to be used in concentrations down to 100 parts per billion (ppb), thus decreasing the cost of the taggant materials. This represents a tradeoff that reduces the cost of the taggant materials but increases the cost of the analysis, however, this tradeoff is economically favorable overall. Preliminary studies have been performed using the rare earth elements holmium (Ho), samarium (Sm), and europium (Eu) [36]. These elements were introduced into explosives as sulfates, and the most expensive of these materials cost approximately $15 per gram. At the average concentration of 1 ppm, this would be a sufficient quantity to tag one metric ton of explosives, and add about 1.5¢ per kilogram of explosives in material costs. This low material cost enables the tagging of any explosive material and may be suitable for use with some explosive precursors used in improvised explosive devices (IEDs) as well. A schematic illustrating the use of the nuclear barcode is shown in Figure 3.2.

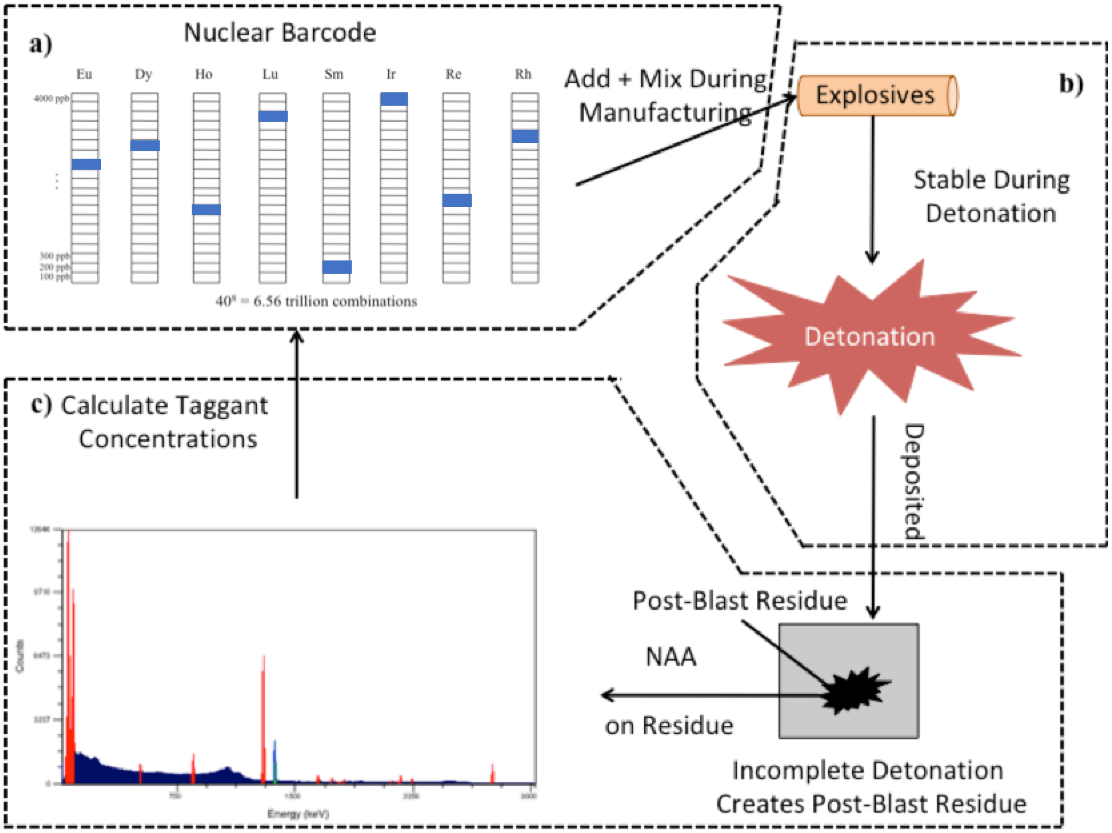


Figure 3.2. Creating (a), Using (b), and Reading the Nuclear Barcode (c) in an Explosive

As a taggant that is introduced at low concentrations, the effect of the nuclear barcode on the reactivity of energetic materials is minimal. Concentrations of components in manufacturing of explosives are not controlled with ppm tolerances, and the addition of these materials will not pose any problems to long-term stability either. Additionally, since the nuclear barcode taggant relies on the elements present and not on physical particles, there is no additional material that might be rough and cause increased sensitivity. Preliminary testing has shown no notable reactivity of two types of explosives with the rare earth elements holmium, samarium, and europium, although no long-term stability tests have been performed. Charges of a commercial binary explosive as well as composition B have been tagged with one or three rare earth elements at concentrations from 1 ppm to 14 ppm, with no apparent change in explosive properties.

The nuclear barcode provides solutions to the two largest issues raised in both the 1980 OTA report and the 1998 report: the cost of taggant and the potential for an identification taggant to sensitize the explosive to which it was added. The quantity of the higher cost taggant elements is controlled through the use of low concentrations, which is enabled by NAA. Since NAA is used to analyze the low concentrations, the cost of analyzing a sample will be high, since research reactors and neutron sources that can be used for NAA are few in number. This higher cost can be minimized by analyzing fewer samples; under ideal circumstances, only one sample would be required. Sensitization of explosives is also controlled through the use of low concentrations of taggant elements. The nuclear barcode also retains the advantages of modern identification taggants: survivability of the taggant in the post-blast residue, and forensic utility of the taggant.

These traits make the nuclear barcode a promising candidate as an identification taggant for explosives.

3.2. NUCLEAR BARCODE CONCEPT EVALUATION

The nuclear barcode taggant takes the higher compatibility with explosives from chemical taggants and combines it with the other properties of a physical taggant to produce a hybrid that performs better than previously developed taggant technologies. The nuclear barcode accomplishes forensic goals while also being relatively cheap to implement and having a minimal safety impact. Although the price of the materials used to tag explosives using the nuclear barcode is high, the use of neutron activation analysis for analyzing the results means the added cost from the taggant itself is low. Additionally, the low concentrations used also ameliorate the safety concerns, as manufacturing of explosives is not affected by concentrations at these low levels.

The survivability of the nuclear barcode must be established, since it enjoys a relative advantage in comparison to other physical and chemical taggants other areas. If the nuclear barcode proves survivable, then it would represent an improved taggant over previously developed ones. Section 1.3 presents four research objectives that assess the survivability of an identification taggant that are reproduced here:

1. Determine if the taggant elements can be detected and quantified via NAA at the desired concentrations.

2. Determine if the different concentration levels of the taggant elements can be distinguished via NAA with sufficient precision that the measured concentration lies within only one concentration level (50 ppb precision to use the Nuclear Barcode as designed).

3. Determine the distinguishability of the taggant elements from background signals, including other taggant elements and common elements in the environment such as sodium, potassium, chlorine, etc.

4. Identify concentrations of the taggant elements in the post blast residues and verify them to be the same as in the undetonated sample.

To test these objectives, a series of eight tests was developed. For each taggant element, these tests must determine the lowest concentration of the taggant element that can be measured, determine the survivability of the taggant element in post-blast residue, determine the effect of the type of explosive on the survivability of the taggant element, and determine the repeatability of measuring the concentration of the taggant element in post-blast residue. All of these must be determined simultaneously when multiple elements are included, and the different elements must not prevent one another from being measured. These tests are further described in Section 4. A summary of these tests and the research objectives they address are shown in Table 3.1.

Table 3.1. Summary of Tests Performed and Which Objectives they Address

Test Series	Test Objective	Research Objectives
Single Element Standard Solutions	Best case detectability of elements at low concentration	1,2
Single Element Binary Post-Blast	Survivability of elements in post-blast residue	3,4
Single Element Composition B Post-Blast	Effect of explosive type on survivability	3,4
Multi-Element Standard Solutions	Best case simultaneous survivability of elements	1,2,3
Multi-Element Binary Post-Blast	Simultaneous survivability of elements in post-blast residue	1,3,4
Multi-Element Composition B Post-Blast	Effect of explosive type on simultaneous survivability of elements in post-blast residue	1,3,4
Multi-Element Binary Repeatability	Repeatability of simultaneous survivability of elements in post-blast residue	1,2,3,4
Multi-Element Composition B Repeatability	Effect of explosive type on repeatability of simultaneous survivability of elements in post-blast residue	1,2,3,4

4. RESEARCH METHODS

The four research objectives stated in Section 1.3 led to the development of a series of eight tests to address the issue of the survivability of the nuclear barcode. This section describes the NAA procedure that was used to measure the samples from the eight test series in Section 4.1. Sections 4.2 through 4.9 describe the procedures for each test series, the objectives the test evaluates, and what a successful or unsuccessful test for each objective would entail.

4.1. NEUTRON ACTIVATION ANALYSIS USING MISSOURI S&T REACTOR

The sample preparation for each test is described in Sections 4.2 to 4.9. This section describes the preparation of a sample for NAA, the process of NAA as performed at the MSTR, and the process of counting a sample.

Samples are prepared before undergoing NAA to prevent the sample from breaking in the pneumatic tube system that transfers samples to and from the core. Samples were first placed in two small, one inch by two inch plastic bags. These plastic bags were then placed in a 20 mm diameter by two inch long plastic vial that snaps closed at the top. Once the vial is closed, any plastic that extends beyond the diameter of the vial is cut using scissors. The top of the vial is then sealed using a heat gun to ensure that the vial remains closed during transfers to and from the core. When a liquid sample was used, a small vial approximately five mm by ½ inch long that contained 0.5 mL (for single element standard solution tests) or 0.495 mL (for multi-element standard solution tests) of liquid was sealed in the same manner as a larger vial.

The pneumatic system that transfers the sealed samples to the core is called the rabbit system, since it takes approximately one second to travel the full length. Outside of the core, the sealed sample is loaded into a glove box that contains one end of the rabbit system. The sealed sample is inserted into a tube, and when the system is pressurized, transferred into a similar tube that is located in the reactor core. All irradiations used the bare rabbit tube; where the sealed samples were transferred to a tube that was not shielded by a sheet of cadmium, which exposed the samples to the thermal and fast flux produced by the reactor. A cadmium shielded rabbit tube was also available. Cadmium shields samples from thermal neutrons, so the only neutrons that would interact would have higher energies. After ten minutes, the sealed sample was transferred from the tube in the reactor core back to the tube in the glove box where it could be retrieved and the next sample could be irradiated.

When a sample was measured, it was first removed from the sealed vial that carried it through the rabbit system to the core. The sample was placed in a new plastic bag, and was then placed on the end cap of one of two HPGe detectors. After the first detector failed during measuring one sample of 500 ppb samarium solution, later samples used only the second detector that did not fail. Canberra's ProSpect software was used to control the detector and to collect the data. All samples were counted for one hour of counting time. This meant that longer than one hour of real time elapsed per sample due to the detector phenomenon of deadtime. When a critical number of photons hit the detector, the detector briefly loses the ability to measure any additional photons; the amount of time a detector stays in this state is called deadtime since the detector is not doing any work. Deadtime is usually expressed as a percent of the total time the detector was active, and deadtimes of

5% were typically observed. Deadtime can be reduced either through less active samples or better detectors, but cannot be completely eliminated.

After the data was collected for one hour of counting time, the resulting NAA spectrum was analyzed. The spectrum was gone through manually to identify peaks or potential peaks. The ProSpect software was used to match the shape of the peaks and calculate the total area under the curve of the manually fitted peaks. Additionally, the ProSpect software was used to estimate the net area (counts) under the peak and the background counts under the peak. After manual fitting, the software's built in peak search routine was run with a sensitivity of 2 to identify any additional peaks. In most circumstances, this process "identified" additional peaks that were determined to be not present after manually inspecting them, so the sensitivity settings were overly aggressive. In almost all circumstances, the peak search routine identified the manually identified peaks with good agreement with the shape of the peak, confirming that they were present. The net number of counts from the best fit of manual or software peak search routine was used as judged by the calculated gaussian ratio fit to the NAA spectrum. This number of counts, along with the amount of real time the detector operated for, the length of the irradiation time, and the delay time were then used to calculate the concentration of the taggant elements in the sample using Equation 3.

4.2. SINGLE ELEMENT STANDARD SOLUTIONS

The first series of tests was performed on solutions of three representative elements: holmium (Ho), samarium (Sm), and europium (Eu). The three elements were dissolved in deionized (DI) water and made into five solutions, each of a different concentration of one taggant element. The five concentrations used were 100, 500, 1,000, 2,000, and 4,000 parts per billion (ppb) on an atom basis, and measured using NAA. These concentrations cover the proposed range for the nuclear barcode and extend to higher concentrations. These solution tests were performed first to judge the effectiveness of the NAA parameters chosen and the suitability of the candidate elements for analysis with NAA.

4.2.1. Determine if the Taggant Elements can be Detected and Quantified via NAA at the Desired Concentration. This test series represents a best-case scenario for detecting and determining the concentrations of these elements; the test samples contain only the taggant element and DI water, which does not show up under these test conditions. Using these samples, it is possible to determine the minimum concentration of these taggant elements that can be detected using the MSTR and the detectors available there. To meet this objective, it must be possible to accurate measure the concentration of the taggant elements contained in the solutions. Any other result would mean the test fails to meet this objective.

4.2.2. Determine if the Different Concentration Levels of the Taggant Elements can be Distinguished and Quantified via NAA. The single element standard Solutions also offer the best-case scenario for determining the uncertainty in calculating the concentration of the taggant elements. The measurements of the uncertainty will depend only on the limits of the technique of NAA itself and not on any other conditions. This series of tests determines the minimum spacing between the concentration levels that can be used with the nuclear barcode. For the nuclear barcode to work, the concentration must be able to be put into one and only one of the concentration levels. Since the concentration levels are separated by 100 ppb, the maximum uncertainty in the concentration should be half of that or 50 ppb to make sure that the concentration would stay within one concentration level. This test meets this objective by having the uncertainty in the concentration of the taggant element below 50 ppb.

4.3. MULTI-ELEMENT STANDARD SOLUTIONS

The multi-element standard solutions build on the single element standard solution tests by adding an additional complicating factor. Instead of the samples containing only one taggant element, samples were prepared that contained all three of the taggant elements tested. Six total combinations of the three elements at three different concentrations (500 ppb, 1,000 ppb, and 2,000 ppb) were prepared, all of which are concentrations the nuclear barcode was designed to use.

4.3.1. Determine if the Taggant Elements can be Detected and Quantified via NAA at the Desired Concentration. The additional activity caused by the presence of multiple of these elements produces additional noise in the measured NAA spectrum. This noise reduces the prominence of the peaks that are detected. This objective is met if the added noise in the NAA spectrum does not prevent accurately measuring the concentration of the taggant elements in the prepared solutions.

4.3.2. Determine if the Different Concentration Levels of the Taggant Elements can be Distinguished and Quantified via NAA. This series of tests allows for the determination of the magnitude of this effect for combinations of these three elements. The higher noise in the NAA spectrum mentioned in the previous objective should increase the uncertainty in the calculated concentration of the taggant elements present. Otherwise, this is still close to a best-case scenario for the detection of the taggant elements and measuring their concentrations. The concentration levels determined by this series of experiments should be much more in line with what can be expected to be used for undetonated explosives or for other materials, since the most common components in explosives (carbon, hydrogen, oxygen, and nitrogen) also are not detectable using NAA like the DI water used in these solutions. Similar to the single element standard solutions, this test series requires that the concentrations of the different taggant elements be simultaneously resolved to within 50 ppb to meet this objective.

4.3.3. Determine the Distinguishability of the Taggant Elements from Background Signal, such as other Taggant Elements and Common Elements in the Environment such as Sodium, Potassium, Chlorine, etc. The multi-element standard solution test series directly tests the ability of NAA to differentiate between the different taggant elements used. This is one component of this third objective addressing the survivability of the nuclear barcode. In general, elements that are close in atomic number and are chemically similar, like rare earth elements, are harder to separate using NAA than elements that are not chemically similar. This test series directly evaluates if the three taggant elements are able to be separated using NAA. The number of codes the nuclear barcode can create is a function of the number of distinct elements used. Interference where the presence of one element prevents the identification of a second element would reduce this number and be detrimental to the nuclear barcode. This test meets this objective if each element has at least one peak in the NAA spectrum that does not overlap with any other peak.

4.4. SINGLE ELEMENT BINARY POST-BLAST

The most basic test to determine the detectability of holmium and samarium in the post-blast residue introduces these taggant elements into the undetonated explosives at higher concentration than would be used in the finished nuclear barcode. The explosive charges were a commercially manufactured, cap sensitive binary explosive: ammonium nitrate and nitromethane, which separately will not detonate, but when combined will detonate. The binary used has a maximum velocity of detonation (VOD) of 6,300 m/s [37].

Due to the difficulties first encountered when measuring out quantities of taggant material on the small charges used in these experiments (160 grams for binary explosive charges), larger concentrations than proposed for the nuclear barcode were added to the charges in this initial demonstration. For the holmium tests, the binary charges were each tagged with 0.00685 grams of holmium sulfate, giving a holmium mass concentration of 19,000 ppb to 20,000 ppb based on the manufacturing tolerances of the binary explosive. Similar concentrations were used for the samarium binary tests, but used 0.00789 grams of samarium sulfate per charge. Terrorist attacks would use significantly higher amounts of explosive and produce a larger amount of post-blast residue. Once the tagging process is scaled up to a commercial manufacturing level, the whole process would be scaled up and the quantities of taggant materials for a typical batch of explosives would be easier to measure.

Five charges were prepared: two were tagged with holmium, two with samarium, and the fifth was untagged to provide a control. The tagged, undetonated explosive charges were put in a steel cylinder to provide a surface from which post-blast residue could be collected. A new steel cylinder was used for each test to eliminate cross-contamination between different tests. A steel cylinder acts as a stand in for a trashcan or a piece of debris where post-blast residue from a real terrorist attack might be deposited. Figure 4.1 shows the setup of the charge within the cylinder (Figure 4.1a) and the same cylinder after detonation (Figure 4.1b).

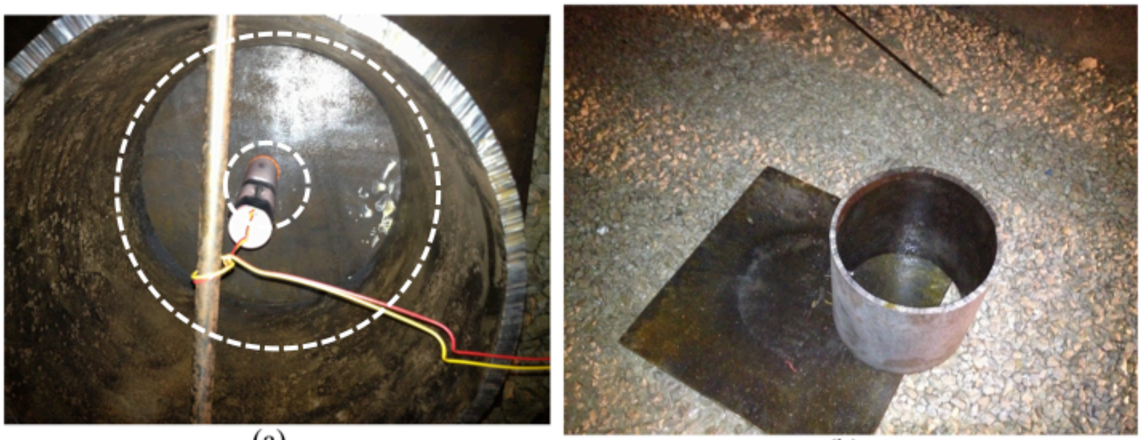

(a) (b)

Figure 4.1. Single Element Binary Post-Blast Test Showing the Charge Contained within the Steel Cylinder. Denoted (a) and the Same Cylinder after Detonation, with Post-Blast Residue Apparent at the Center (b). A Representative Sampling Path is Indicated by the Dashed Circles in Figure 4.1a

The single element binary post-blast test series was chronologically the first test series performed on post-blast residues. The testing methodology of all post-blast tests was based on the method developed for this series. After the explosive was detonated, a pre-weighed cotton ball was used to collect the post-blast residue. The cotton ball was dabbed along the dotted lines shown in Figure 4.1a to collect post blast residue deposited on the steel cylinder by the top, center, and bottom of the charge. After collecting the post-blast residue, the cotton ball was weighed again. The quantity of post-blast residue that was recovered is therefore the difference between the mass of the cotton ball before swabbing and after swabbing. Before detonation, a separate pre-weighed cotton ball was used to sample the same path that was used post-blast to provide a control and determine if the taggant elements were present in the steel cylinder itself. A third, clean, cotton ball was used as an additional control to ensure that no taggant elements were present on the cotton ball initially. Each post-blast test produced three samples: a cotton ball with post-blast residue, a cotton ball without post-blast residue, and a clean cotton ball.

4.4.1. Determine the Distinguishability of the Taggant Elements from Background Signal, such as other Taggant Elements and Common Elements in the Environment such as Sodium, Potassium, Chlorine, etc. This series of tests establishes a best-case scenario for detecting the taggant elements in the post-blast residue by using concentrations higher than specified by the nuclear barcode. This test series also establishes if the individual taggant elements will encounter any interference from the other elements present in the post blast residue. This test meets this objective if at least one peak from the taggant element can be identified in the NAA spectrum of the post-blast residue.

4.4.2. Identify Concentrations of the Taggant Elements in the Post-Blast Residues and Verify them to be the Same as in the Undetonated Sample. This series of tests on holmium and samarium tagged explosives provides the simplest test for identifying the taggant element in the post-blast residue, determining its concentration, and comparing its composition to the undetonated explosive. Only one taggant element is present in each explosive charge, so there should be no interferences from the other taggant elements. Additionally, the binary explosive produces the largest quantity of post-blast residue of the two types of explosive tested. Further enhancing the detectability of the taggant element is that the concentrations used are higher than prescribed by the nuclear barcode. This test meets this objective if the measured concentration of the taggant element in the post-blast residue is equal to the concentration of the taggant element in the undetonated explosive.

4.5. SINGLE ELEMENT COMPOSITION B POST-BLAST

The explosives charges used in these tests were two 60 gram charges of cast Composition B manufactured as a 50/50 mixture of TNT and RDX on site and tagged with holmium. Composition B has a maximum VOD ranging from 7600 to 8000 m/s [31]. Two tagged holmium charges were used to compare to the binary explosive charges tagged with holmium. Larger concentrations than proposed for the nuclear barcode were added to the charges in this initial demonstration, due to the relatively small size of the charges. For these tests, 0.00170 grams of holmium sulfate was added giving a concentration of 2,000 ppb to 3,000 ppb for each charge. Unlike the binary post-blast series of tests, no charges were tagged with samarium. This is because holmium is a monoisotopic element, which simplifies detection in the post-blast residue. Therefore, any differences in the survivability of the taggant that are observed are due to the use of Composition B.

The single element Composition B post-blast series of tests adds an additional layer of complexity to the single element binary post-blast test series due to the reduced quantity of post-blast residue produced by Composition B. This is likely due to a combination of factors such as Composition B’s higher velocity of detonation, and the binary explosive’s requirement for even mixing for maximum performance which was not always practical to achieve. While the lower quantity of post-blast residue means that a smaller quantity of other elements will be present in the sample, it also means that less of the taggant elements will be present as well.

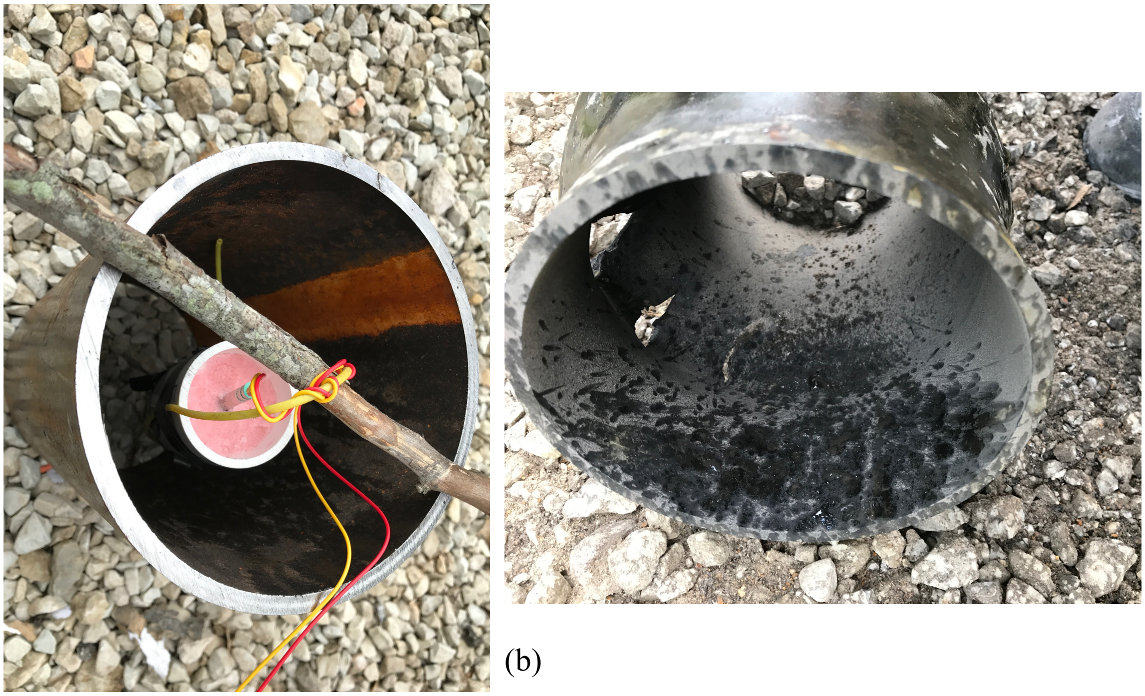
4.5.1. Determine the Distinguishability of the Taggant Elements from Background Signal, such as other Taggant Elements and Common Elements in the Environment such as Sodium, Potassium, Chlorine, etc. This test series is designed to determine if the reduced amount of taggant elements in the post-blast residue make identifying the taggant element harder than in the single element binary post-blast test series. Like the single element binary post-blast test series, a real-world terrorist attack would likely involve much larger quantities of explosives that would produce correspondingly larger quantities of post-blast residue, so the reduced quantity of residue produced by Composition B represent a low end estimate for the post-blast residue recovered. Like the single element binary post-blast test series, this test meets the objective if at least one peak from the taggant element can be identified in the NAA spectrum of the post-blast residue.

4.5.2. Identify Concentrations of the Taggant Elements in the Post-Blast Residues and Verify them to be the Same as in the Undetonated Sample. This series of single element Composition B post-blast tests also attempts to directly answer this last objective under worse conditions than the single element binary post-blast test series. The reduced quantity of post-blast residue produced by the detonation of composition B also reduces the amount of recovered taggant. This makes detecting the taggant element harder and thus makes quantifying the concentration of the taggant element in the post-blast residue more difficult than in the residue produced from the binary explosive. This test meets this objective under the same conditions as the single element binary post-blast residue test series.

4.6. MULTI-ELEMENT BINARY POST-BLAST

The multi-element binary post-blast test series adds the complication of recovering the taggant elements in the post-blast residue. A total of six combinations of the three elements were each added to an undetonated explosive like the previous multi-element standard solution test series. The concentrations used were doubled to 1,000 ppb, 2,000 ppb, or 4,000 ppb. These concentrations were used due to limits on measuring out the required quantities of salts containing the taggant elements when used with changes that were either approximately 150 grams or 50 grams. This would not be a problem when scaled up to the volume that manufacturers of explosives produce. Each element was tested twice each of the three concentrations. These charges used the same commercially available binary explosive as used in the single element post-blast test. The same test procedure was used as in the single element binary post-blast tests. Figure 4.2 shows the setup of the tagged explosive in the steel cylinder before detonation (Figure 4.2a) and the deposited post-blast residue after detonation (Figure 4.2b).

4.6.1. Determine if the Taggant Elements can be Detected and Quantified via NAA at the Desired Concentration. This series of tests essentially used a cut down version of the nuclear barcode with fewer total combinations. This represents a real world test on detecting the taggant elements and determining their concentrations from the post-blast residue using concentrations proposed by the nuclear barcode. Additionally, the concentrations used in this series of tests are lower than the concentrations used in the single element binary post-blast series. This objective is met if the concentration of the taggant elements can be measured in the post-blast residue.



(b)

(a)

Figure 4.2. Multi-Element Binary Post-Blast Charge and Witness Plate. Before Detonation (a) and Deposited Post-Blast Residue after Detonation (b)

4.6.2. Determine the Distinguishability of the Taggant Elements from Background Signal, such as other Taggant Elements and Common Elements in the Environment such as Sodium, Potassium, Chlorine, etc. The multi-element binary post-blast test series combines a test for the interference between different taggant elements like the multi-element standard solution test series with a test for interference between the taggant element and the post-blast residue like the single element binary post-blast test series. This series performs the first real-world tests designed to determine if the taggant elements can simultaneously be found in the post-blast residue, which meets this objective it this test series is able to do so.

4.6.3. Identify Concentrations of the Taggant Elements in the Post-Blast Residues and Verify them to be the Same as in the Undetonated Sample. The multi-element binary post-blast test series introduces two complications to the single-element binary post-blast test series. First, the concentrations of two of the three taggant elements in each test in the series fall within the range prescribed by the nuclear barcode. Additionally, this test series introduces multiple taggant elements to the post-blast residue. These concentrations need to be calculated simultaneously for the nuclear barcode concept to prove functional. This test also will determine if the interference from the different elements prevents the identification of the taggant elements or the determination of their concentrations. If the concentrations of the taggant elements can be measured simultaneously and determined to be the same as the concentrations of the taggant elements in the undetonated explosive, then this test series meets this objective.

4.7. MULTI-ELEMENT COMPOSITION B POST-BLAST

Not all explosives are equal. The multi-element composition B post-blast test series used the same combinations of taggant elements and their concentrations that were used in the multi-element binary post-blast test series but changed the type of explosive used from a commercially produced binary explosive to the same composition B formulation used in the single element Composition B post-blast tests. The single element Composition B post-blast testing showed that Composition B produces much less post-residue than the binary explosive, which reduces the amount of taggant recovered in the post-blast residue compared to the binary explosive.

4.7.1. Determine if the Taggant Elements can be Detected and Quantified via NAA at the Desired Concentration. This series of tests was designed to determine if the smaller quantity of post-blast residue gathered from these tests still permits the simultaneous identification of the taggant elements and their concentrations. This test series meets the objective under the same conditions as the multi-element binary post-blast test series.

4.7.2. Determine the Distinguishability of the Taggant Elements from Background Signal, such as other Taggant Elements and Common Elements in the Environment such as Sodium, Potassium, Chlorine, etc. As with the single element version of this test series, the multi-element composition B post-blast test series is designed to show the effect of the reduced recovery of post-blast residue on the ability to distinguish the different taggant elements in the post-blast residue. This test series meets this objective under the same conditions as the multi-element binary post-blast test series.

4.7.3. Identify Concentrations of the Taggant Elements in the Post-Blast Residues and Verify them to be the Same as in the Undetonated Sample. This test compares the ability of NAA to accurately measure the concentration of the taggant elements in the lower quantity of post-blast residue produced by the detonation of Composition B compared to the binary used. This test series meets this objective if it is possible to simultaneously measure the concentration of the taggant elements in the lower amount of post-blast residue produced from Composition B and determine these concentrations to be the same as in the undetonated explosive.

4.8. MULTI-ELEMENT BINARY REPEATABILITY POST-BLAST

A series of repeatability tests where the same combination of taggant elements and their concentrations were added to five separate charges of a commercially produced binary explosive. 2,000 ppb of holmium, 1,000 ppb of samarium, and 4,000 ppb of europium were added to five identical charges of each type of explosive. This test series followed the same procedure described in the multi-element binary post-blast test series.

4.8.1. Determine if the Taggant Elements can be Detected and Quantified via NAA at the Desired Concentration. This series of tests investigates how frequently the taggant elements holmium, samarium, and europium can be expected to be recovered from the post-blast residue when introduced at concentrations suggested by the nuclear barcode. This has real-world implications by showing how many samples of the post-blast residue will need to be obtained from the site of an actual detonation to definitively show the presence and concentrations of the taggant elements. This test series successfully meets this objective if the taggant elements can be simultaneously resolved and their concentrations measured in each sample.

4.8.2. Determine if the Different Concentration Levels of the Taggant Elements can be Distinguished and Quantified via NAA. While the uncertainty in the concentrations can be obtained from any post-blast residue test series; the multi-element binary repeatability series of tests represents the first series where a fuller determination of the degree of concentration level separation that is feasible can occur. The uncertainties in the measured concentrations of each element in the post-blast residue are determined five times in this test series. This allows for the determination of the average uncertainty in the concentration, as well as permitting more advanced statistical analysis of the uncertainties than would be possible with only one test. This series of tests produces a lower limit on the separation between concentration levels that can be determined from measurements of the post-blast residue for low explosives such as the ammonium nitrate based binary explosive used in this series of experiments. This series of tests meets this objective if the uncertainty in the concentrations, on average, is less than 50 ppb. This would permit the nuclear barcode to use concentration levels separated by 100 ppb as designed.

4.8.3. Determine the Distinguishability of the Taggant Elements from Background Signal, such as other Taggant Elements and Common Elements in the Environment such as Sodium, Potassium, Chlorine, etc. The multi-element binary repeatability test series is designed to determine if the taggant elements can consistently be distinguished from other elements in the post-blast residue. Since the prepared explosive charges are the same, the only variation will come from the process of depositing the post-blast residue for each detonation. Establishing the consistent ability to distinguish the taggant elements in the post-blast residue means that in a real usage scenario, fewer samples of the post-blast residue will be needed to determine the presence or absence of the nuclear barcode. This objective is met if at least one peak from each of the taggant elements can be simultaneously identified in the NAA spectrum of the post-blast residue.

4.8.4. Identify Concentrations of the Taggant Elements in the Post-Blast Residues and Verify them to be the Same as in the Undetonated Sample. The multi-element binary repeatability test series should behave identically to the specific test from the multi-element binary post-blast test that uses the same combination of concentrations. This series of tests gathers more data about the performance of this one combination of taggant elements and concentrations, which enables statistical analysis of the results for the particular combination used. This test meets this objective by accurately measuring the concentration of the three taggant elements simultaneous and determining them to be equal to the concentration in the undetonated explosive.

4.9. MULTI-ELEMENT COMPOSITION B REPEATABILITY POST-BLAST

A series of repeatability tests was also performed using composition B based charges, that were otherwise the same as the tests in the multi-element binary repeatability test series. This series of tests is necessary to show that this higher variance still permits accurate determination of the concentration of the taggant elements used. Like the multi-element binary repeatability tests, this series of tests also has real world implications on the number of post-blast residue samples that will need to be collected.

4.9.1. Determine if the Taggant Elements can be Detected and Quantified via NAA at the Desired Concentration. Since Composition B produces less post-blast residue than the binary explosive used in the previous test, it presents a more challenging test of determining the concentrations. Whether this test series meets this objective is determined in the same method as the multi-element binary repeatability post-blast test series.

4.9.2. Determine if the Different Concentration Levels of the Taggant Elements can be Distinguished and Quantified via NAA. As with the multi-element binary repeatability test, the multi-element composition B repeatability test yields more information than would be offered by just a single test. Since composition B produces less post-blast residue, and since the calculation of the concentration of the taggant elements and their uncertainties depend in part on the mass of the post-blast residue that is recovered, this test series presents the most challenging situation for the nuclear barcode. The small quantities of post-blast residue obtained must contain enough of the taggant elements to determine the concentration levels. Additionally, this test series is necessary to determine if the explosive used has some effect on the concentrations of the elements found in the post-blast residue. This test series meets this objective in the same manner as the multi-element binary repeatability test series.

4.9.3. Determine the Distinguishability of the Taggant Elements from Background Signal, such as other Taggant Elements and Common Elements in the Environment such as Sodium, Potassium, Chlorine, etc. Like the multi-element binary repeatability test, the multi-element composition B repeatability test will allow the determination of the consistency with which the taggant elements can be distinguished from the remainder of the post-blast residue. The lower quantity of post-blast residue available increases the variability in determining the concentrations of the taggant elements. Using composition B could potentially increase the variability in distinguishing the taggant elements in the post-blast residue due to the lower quantity of post-blast residue and thus taggant elements collected. This test series meets this objective under the same conditions as the multi-element binary repeatability post-blast test series.

4.9.4. Identify Concentrations of the Taggant Elements in the Post-Blast Residues and Verify them to be the Same as in the Undetonated Sample. Like the multi-element binary repeatability test, the multi-element composition B repeatability test provides additional data points of the concentrations of the taggant elements collected from post-blast residues of explosives tagged with a particular combination of taggant elements and concentrations. The additional data also allows for statistical analysis of the concentrations. Beyond this additional level of analysis, this test meets this objective under the same conditions as the multi-element binary repeatability post-blast test series.

5. RESULTS AND ANALYSIS

Section 5 presents the results of performing NAA as described in Section 4.1 on the samples from the tests described in Section 4.2 through 4.9. Additionally, at the end of each test, a table is included that evaluates if the test meets or fails to meet each objective that it was designed to evaluate. Section 5.9 provides an evaluation of each of the four research objectives based on all of the tests that addressed them. Finally, Section 5.10 summarizes the test results.

5.1. SINGLE ELEMENT STANDARD SOLUTIONS

Identifying the taggant element is the first step towards being able to calculate the concentration. The results of performing NAA on five samples of five different concentrations of the three elements are shown in Table 5.1, which shows the number of times the taggant element was detected.

Table 5.1. Number of Completed Tests Where Taggant Element was Detected in Solution

Element	100 ppb	500 ppb	1000 ppb	2000 ppb	4000 ppb
Holmium	Yes – 5/5	Yes – 5/5	Yes – 5/5	Yes – 5/5	Yes – 5/5
Samarium	Yes – 5/5	Yes* – 4/4	Yes – 5/5	Yes – 5/5	Yes – 5/5
Europium	Yes – 5/5	Yes – 5/5	Yes – 5/5	Yes – 5/5	Yes – 5/5

* One of the tests failed due to detector malfunction.

The taggant element was identified in all of the completed tests. One of the samarium 500 ppb samples suffered a detector failure during counting, so data was not gathered for this sample. The failure of this detector delayed measurements of the remaining 500 ppb samarium samples, as well as all 1,000 ppb, 2,000 ppb, and 4,000 ppb samples, which were all irradiated on the same day, by several days due to the time needed for repairs. This led to a long delay between irradiating and counting samples that partially inspired testing in Section 6, and that impacted the quality of the samarium results. All samples were counted for 1 hour.

Calculating the concentration depends on identifying the peaks in the NAA spectrum that correspond to the taggant elements and determining the number of counts under that peak and subtracting the number of counts caused by background noise under the peak. Appendix A presents a fully worked calculation of the concentration by this method. This difference is the net number of counts under a given peak, and is the number of counts associated with the taggant element. The average of the concentrations measured in each test is followed by the average uncertainty in the concentration measured, and is shown in Table 5.2.

Table 5.2. Averaged Measured Concentration and Concentration Uncertainty (in ppb)

Element	100 ppb	500 ppb	1000 ppb	2000 ppb	4000 ppb
Holmium	93.77 ± 12.40	498.49 ± 6.58	5,538.96 ± 13.35	11,311.11 ± 22.37	22,176.36 ± 37.76
Samarium	610.13 ± 16.33	3,163.34 ± 216.62	4,367.03 ± 82.45	7,489.04 ± 67.25	29,977.74 ± 158.16
Europium	148.52 ± 0.71	816.31 ± 3.29	1,546.19 ± 5.68	2,708.40 ± 9.80	6,466.16 ± 23.71

Except for the two lowest concentration holmium solutions, the measured concentrations of the taggant elements in solution are much higher than what they should be. These two tests utilized a different HPGe detector than the subsequent tests due to an equipment failure. Figure 5.1 plots the relationship between the measured concentration on the y-axis and the concentration that was prepared by sequential dilution on the x-axis, and excludes the two lowest concentration holmium solutions to keep the detector used consistent. The error bars show the standard deviation of the measured concentration of the samples at each nominal concentration. Results for each species individually are presented in Appendix C.

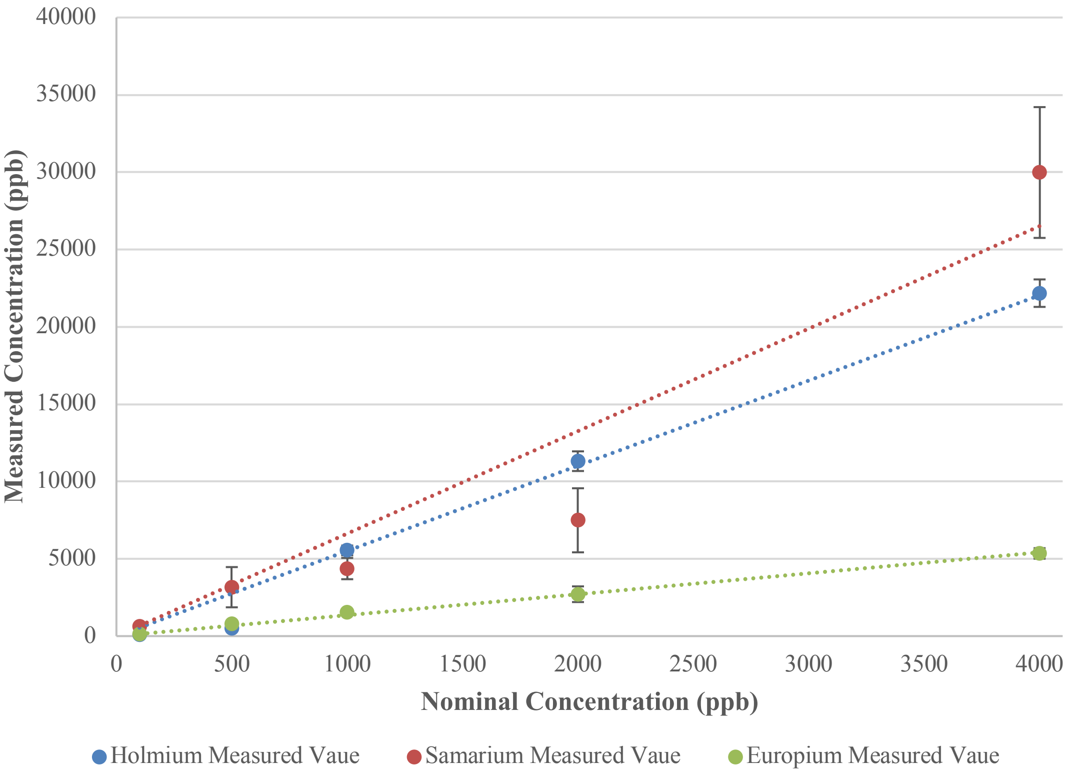


Figure 5.1. Comparison of Added Concentrations of Single Taggant Elements to Measured Concentrations in Solution

As shown in Figure 5.1, the measured concentrations that are derived using Equation 1 are substantially different from the actual concentration of the solutions. A linear regression with a y intercept of zero was run on the averages for each concentration of one particular element to produce the lines shown. This regression shows that the results for the europium (green) and holmium (blue) test series are very highly correlated with one another, with an R^2 value of 0.996 for the europium tests and an R^2 value of 0.984 for the holmium tests. The correlation coefficient for the samarium (red) tests is a lower 0.911. A high correlation coefficient in a linear regression implies that there exists a constant factor that is causing the difference. The parameters for the linear regression are summarized below in Table 5.3.

Table 5.3. Linearity of Measured Concentrations Showing Scale Factor (ratio) between Measured Concentration and Added Concentration

Element	Scale Factor	R^2 value
Holmium	5.51	0.984
Samarium	6.63	0.911
Europium	1.56	0.996

In Equation 3 there are two factors, in addition to the number of counts, that need to be determined by experiment: the neutron flux, which under the test conditions should be the thermal neutron flux of the MSTR Φ_{th}, and the probability that the detector will count a given emitted gamma photon ε. The calculated mass of the element, and thus the concentration of the element is inversely related to these parameters.

The slope given by performing a linear regression shows the magnitude of the constant error. For example, it shows that the error in one or both of these parameters is a constant factor of 6.6274 for the samarium samples. This factor decreases for holmium to 5.5092 and further decreases for europium to 1.564. This trend matches the trend with the parameter ε, as HPGe detectors are much more efficient for lower energy gamma photons than higher energy gamma photons. The samarium concentrations are calculated from the peak in the spectrum at 69.673 keV, the holmium concentrations from an 80.576 keV peak, and the europium concentrations from a 344.29 keV peak. An error solely in the thermal neutron flux parameter would be constant across the different taggant elements.

Despite the error in calculating the concentrations, most of the uncertainties in the calculated concentration are less than 50 ppb. Therefore, utilizing concentration levels separated by 100 ppb is feasible under these best-case scenarios for most tests. Resolving the issue with the concentrations is expected to reduce the uncertainties but it is unknown if the other uncertainties will be reduced to less than 50 ppb. Table 5.4 summarizes the objectives the single element standard solutions test addresses and whether the test met each objective.

Table 5.4. Single Element Standard Solutions Test Objectives Summary

Objective	Objective met or failed
Objective 1: Taggant Elements Measured?	Failed
Objective 2: Concentration ± 50 ppb?	11/15 Met 4/15 Failed

5.2. SINGLE ELEMENT BINARY POST-BLAST

The presence or absence of an element in the post-blast residue can be determined by the presence or absence of a peak at the characteristic energy corresponding to the element. Any other elements that were present in the post-blast residue did not interfere with identifying what, if any, taggant elements were present. Results for the post-blast tests using the different tagged binary charge are shown in Table 5.5 [36].

For tests one and two, holmium was added to the undetonated explosive. In both of these tests, the net number of counts under the peak is greater than the uncertainty in the number of counts, and therefore holmium was found to be present in these tests.

Table 5.5. Taggant Elements Present, Net Counts, and Uncertainties of Holmium and Samarium Tagged Binary Post-Blast Residues. (Bold Indicating Taggant Element was Detected)

Test	Taggant Element Added	Holmium Net Counts (80.6 keV peak)	Samarium Net Counts (69.6 keV peak)
1	Holmium	**2,236 ± 668**	290 ± 1,306
2	Holmium	**98,026 ±1,744**	-
3	Samarium	63 ± 1,490	**10,872 ± 1,299**
4	Samarium	**3,372 ± 1,762**	**66,381 ± 2,589**
5	Control	766 ± 1,802	849 ± 988

The results for samarium in these tests are shown as well, and indicate that samarium was not found in the first test, and a measurement of the peak in the second test was not able to be made due to a technical error where the software used failed to measure the area under the peak [36].

For tests three and four, samarium was added to the undetonated explosive. In both of these tests, the number of net counts under the peak is once again larger than the uncertainty in the number of counts, indicating that samarium was present in the samples. Test three shows no presence of holmium in the sample. Test four shows a spurious holmium presence, as an additional peak near, but not at, the energy corresponding to holmium and can be disregarded [36].

Figure 5.2 shows the NAA spectrum measured from each test between gamma energies of 30 keV and 120 keV. The spectra are scaled to percent of the maximum value in the time span so that all of them can be presented on a single chart.

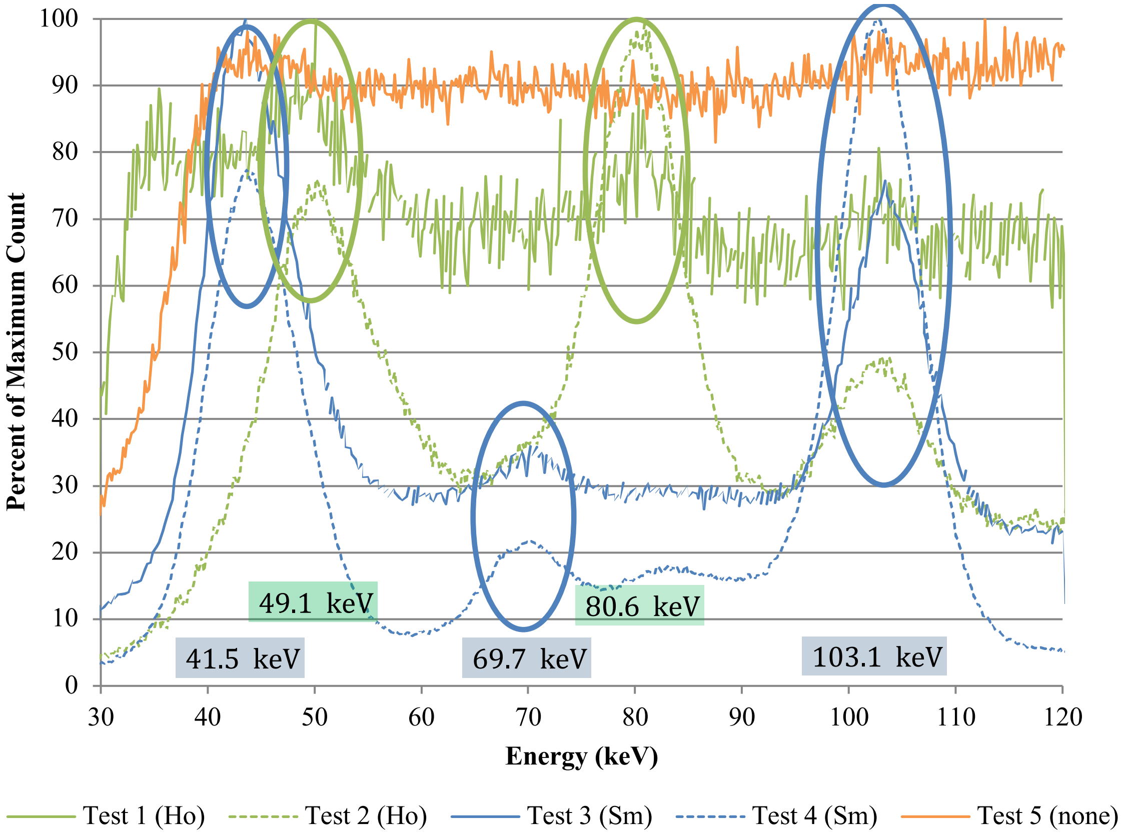


Figure 5.2. Comparison of NAA Spectra of Post-Blast Residues Containing Holmium (green), Samarium (blue) or no Taggants (orange)

The number of net counts listed in Table 5.5 is the net number of counts under the peak at 80.6 keV and 69.7 keV for the holmium counts and the samarium counts respectively. The single element standard solutions test series identified these peaks in particular to be the most specific for these two elements. In test 4, the only test where a non-taggant element was found in the post-blast residue, there is a small peak at 82.5 keV.

The range of energies covered by the 82.5 keV peak in test 4, and the range of energies around 80.6 keV from holmium in tests 1 and 2 partially overlap. When this area is counted for the test 4 results, this small peak at 82.5 keV contributes to the counts shown under the "Holmium Net Counts", but is not actually from the presence of holmium. While the net counts for test 4 technically meet the criteria to say that holmium is present, the asterisk in the table denotes that holmium was not truly detected.

These tests also used the same irradiation parameters as the solution tests in the previous subsections. One change between them though was the addition of a delay period between counting and irradiating the samples. Due to the presence of additional elements in the post-blast residue that were not found in the solution based tests, the total activity of the irradiated samples was too high to accurately obtain an NAA spectrum. As a result, a 48 hour delay time was implemented. The tests are summarized in Table 5.6, and show the taggant element, the concentration of the taggant element in the undetonated explosive, and the measured concentration of the taggant element in the post-blast residue.

Table 5.6. Single Element Binary Post-Blast Test Undetonated Concentrations and Measured Post-Blast Residue Concentrations (in ppb)

Test	Taggant Element	Taggant Undetonated Concentration	Measured Post-Blast Residue Concentration
1	Holmium	19,600	5,289 ± 30
2	Holmium	19,600	79,230 ± 1,410
3	Samarium	19,700	13,690 ± 560
4	Samarium	20,100	1,320 ±160

The measured concentrations of taggant elements in these tests is scattered, but none of them match the undetonated concentration. Tests 1 and 3 are of the same order of magnitude as the concentration in the undetonated explosive. Tests 2 and 4 are both very far off from the concentration in the undetonated explosive, though in different directions. Table 5.7 summarizes the objectives the single element binary post-blast test addresses and whether the test met each objective.

Table 5.7. Single Element Binary Post-Blast Test Objectives Summary

Objective	Objective met or failed
Objective 3: Taggant found above Background?	Met
Objective 4: Concentration same in post-blast residue and undetonated?	Failed

5.3. SINGLE ELEMENT COMPOSITION B POST-BLAST

The series of tests performed using a Composition B focused on identifying the taggant element holmium, when added to the undetonated explosive, in the post-blast residue. Since post-blast residues contain many elements, the primary concern is determining if the taggant elements can be found. Results for the post-blast tests using a tagged composition B charge are shown in Table 5.8.

Table 5.8. Taggant Elements Present, Net Counts, and Uncertainties of Holmium Tagged Composition B Post-Blast Residue. (Bold Indicating Taggant Element was Detected)

Test	Taggant Element	Holmium Net Counts
1	Holmium	**54,523 ± 820**
2	Holmium	5,384 ± 42,206*

* Denotes that although this test fails the objective criterion used, further analysis shows that holmium is present in this test sample

Test 1 clearly shows the presence of holmium in the post-blast residue. Test 2 does not. However, on inspecting the NAA spectrum from Test 2, which is shown in Figure 5.3, there is a clear peak at the 80.6 keV that is expected for holmium. The additional peak around 49 keV is also indicative of holmium, but is not used to definitively identify holmium due to other elements having peaks that interfere with this holmium peak. The asterisk in the table denotes that although the number of net counts does not show the presence of the taggant element, the spectrum clearly does. While the software can be helpful, it is necessary to make sure that the results are examined closely.

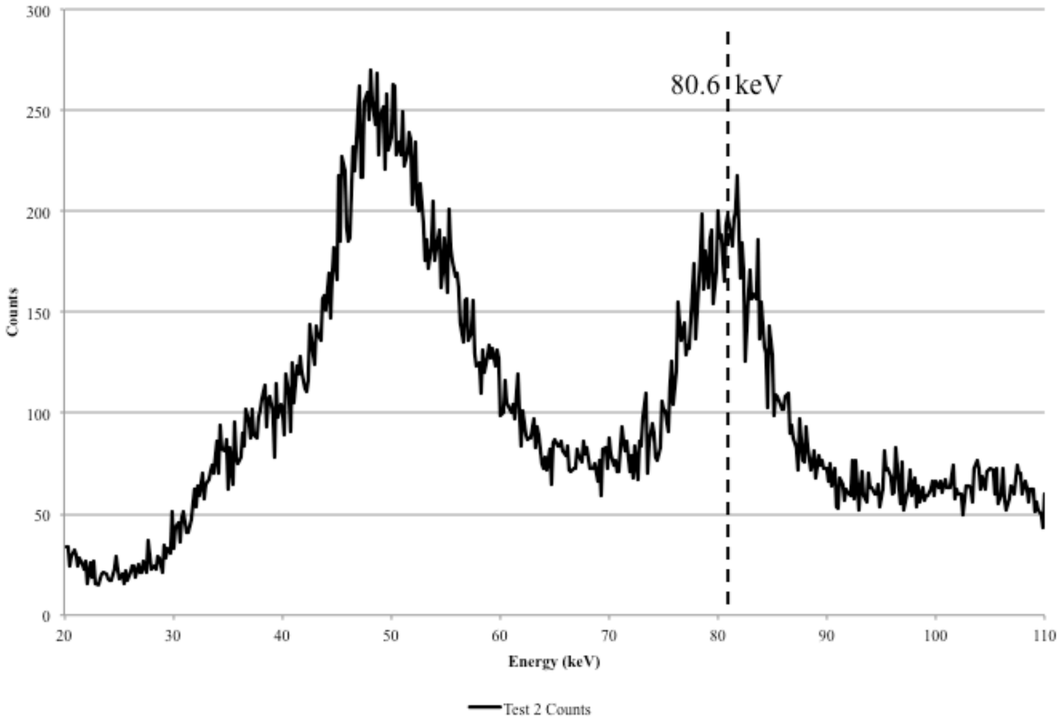


Figure 5.3. NAA Spectrum from Test 2 of Single Element Composition B Post-Blast Series Showing the Presence of Holmium at 80.6 keV

The goal of this series of tests was to determine if the taggant elements can be identified in the post-blast residue. These tests were carried out like the single element binary post-blast tests and included a delay time of 48 hours. These results are shown in Table 5.9.

Table 5.9. Single Element Composition B Post-Blast Test Undetonated Concentrations and Measured Post-Blast Residue Concentrations (in ppb)

Test	Taggant Element	Taggant Undetonated Concentration	Measured Post-Blast Residue Concentration
1	Holmium	14,300	29,970,000 ± 3,561,000
2	Holmium	13,900	882,100 ± 6,915,000

The concentration of the taggant element is higher in the post-blast residue than in the undetonated explosive. Combing these results and the results from the single element of the explosive is converted to gaseous products while some small fraction of the mass of binary post blast tests imply that it is unlikely that the concentration of the taggant element in the post-blast residue remains the same as in the undetonated explosive, and is instead higher in the post-blast residue than the undetonated explosive. The likely explanation for this is that during detonation, some fraction of the undetonated explosive is only partially reacted and becomes post-blast residue. The taggant elements used do not form gaseous products, and would remain behind in the solid phase. This process increases the concentration of the taggant elements relative to their concentration in the undetonated explosive.

The uncertainties in the concentrations here are also extremely high and seem to show that, for these tests at least, the uncertainty is too high to use concentration levels separated by 100 ppb. Since the measurement is of the mass concentration of the taggant element in the post-blast residue, it is necessary to convert the mass that can be calculated using Equation 4 to find the concentration. The markedly higher concentration uncertainties are due to the small quantity of post-blast residue recovered as well as how close these quantities are to the precision of the balance used for the measurement. The quantity of post-blast residue recovered from these two tests is approximately two orders of magnitude smaller than the quantities recovered from the single element binary post-blast tests. Table 5.10 summarizes the objectives the single element Composition B post-blast test addresses and whether the test met each objective.

Table 5.10. Single Element Composition B Post-Blast Test Objectives Summary

Objective	Objective met or failed
Objective 3: Taggant found above Background?	Met
Objective 4: Concentration same in post-blast residue and undetonated?	Failed

5.4. MULTI-ELEMENT STANDARD SOLUTIONS

The multi-element standard solutions build on the single element standard solution tests by preparing samples that contained all three of the taggant elements in various concentrations. The presence of multiple elements produces more gammas, which could create either too much noise or overlapping peaks in the NAA spectrum and prevent accurately identifying the individual taggant elements. Six total combinations of the three elements at three different concentrations (500 ppb, 1,000 ppb, and 2,000 ppb) were prepared. For each mixture, five samples were prepared and tested. The different mixtures that were prepared, the concentrations of the three taggant elements used in each mixture, and the number of tests out of five where the elements were detected are shown in Table 5.11.

Table 5.11. Multi Element Standard Solutions Table; Number of Tests out of Five where Taggant Elements in Multi-Element Standard Solutions were Detected. Each Combination in Parentheses

Mixture #	Holmium	Samarium	Europium
1	500 ppb (5)	1,000 ppb (5)	2,000 ppb (5)
2	500 ppb (5)	2,000 ppb (5)	1,000 ppb (5)
3	1,000 ppb (5)	500 ppb (5)	2,000 ppb (5)
4	1,000 ppb (5)	2,000 ppb (5)	500 ppb (5)
5	2,000 ppb (5)	500 ppb (5)	1,000 ppb (5)
6	2,000 ppb (5)	1,000 ppb (5)	500 ppb (5)

The taggant elements could be identified as separate elements in every test at these concentrations. This experiment indicates that these taggant elements will be able to be identified at all the concentration levels of the nuclear barcode. The multi-element standard solution series of tests was able to answer whether or not the three taggant elements would interfere with identifying one another.

A representative spectrum showing a sample of the low energy peaks created by each element is shown in Figure 5.4, which shows that the peaks do not overlap and are easily identified. Five samples of each combination of concentrations were prepared and NAA was performed. The average measured concentrations of the taggant elements in these tests are shown in Table 5.12.

Table 5.12. Averaged Measured Concentrations of Multi Element Standard Solutions in Parts per Billion. (Abbreviated as Concentration of Holmium: Concentration of Samarium: Concentration of Europium)

Element	500:1000:2000	500:2000:1000	1000:500:2000	1000:2000:500	2000:500:1000	2000:1000:500
Holmium	3,378.56 ± 49.25	3,348.21 ± 48.57	4,894.96 ± 54.18	3,322.31 ± 30.22	6,827.21 ± 28.82	4,665.52 ± 44.29
Samarium	4,125.91 ± 42.18	3,772.04 ± 95.70	926.37 ± 66.90	3,635.08 ± 45.55	473.63 ± 56.95	2,112.78 ± 32.13
Europium	13,735.85 ± 131.09	1,218.92 ± 7.95	2,663.69 ± 11.77	628.67 ± 3.22	1,010.37 ± 5.23	578.77 ± 3.07

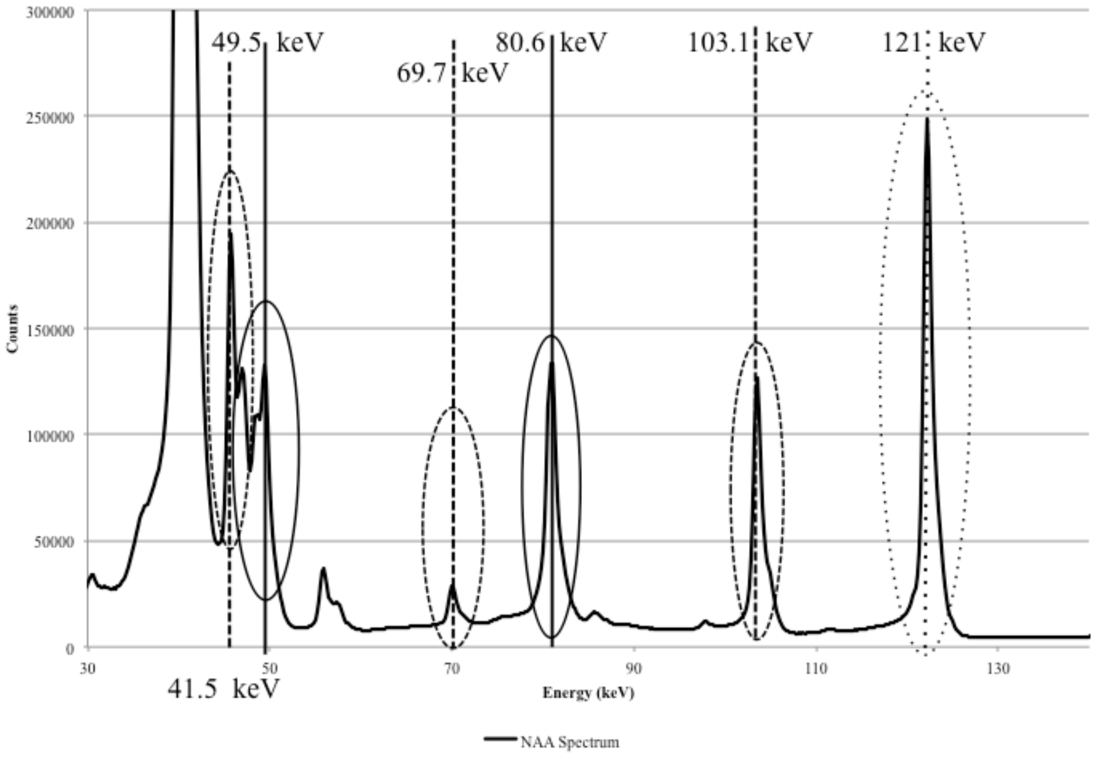


Figure 5.4. NAA Spectrum of a Representative Multi-Element Standard Solution. Containing 2000 ppb Holmium, 1000 ppb Samarium, and 500 ppb Europium. Peaks (circled) Correspond to Holmium (solid), Samarium (dashed), and Europium (dotted)

The same problem appears in these calculations for the concentration as in the calculations for the single element standard solution concentrations. As such, the calculated concentrations measured do not match up with the nominal concentrations. Plotting the average measured concentration against the nominal concentration produces Figure 5.5. A total of six combinations of the three taggant elements at three different concentrations were created and measured. Therefore, each element is present at each concentration twice, and error bars show the standard deviation in the measured concentration.

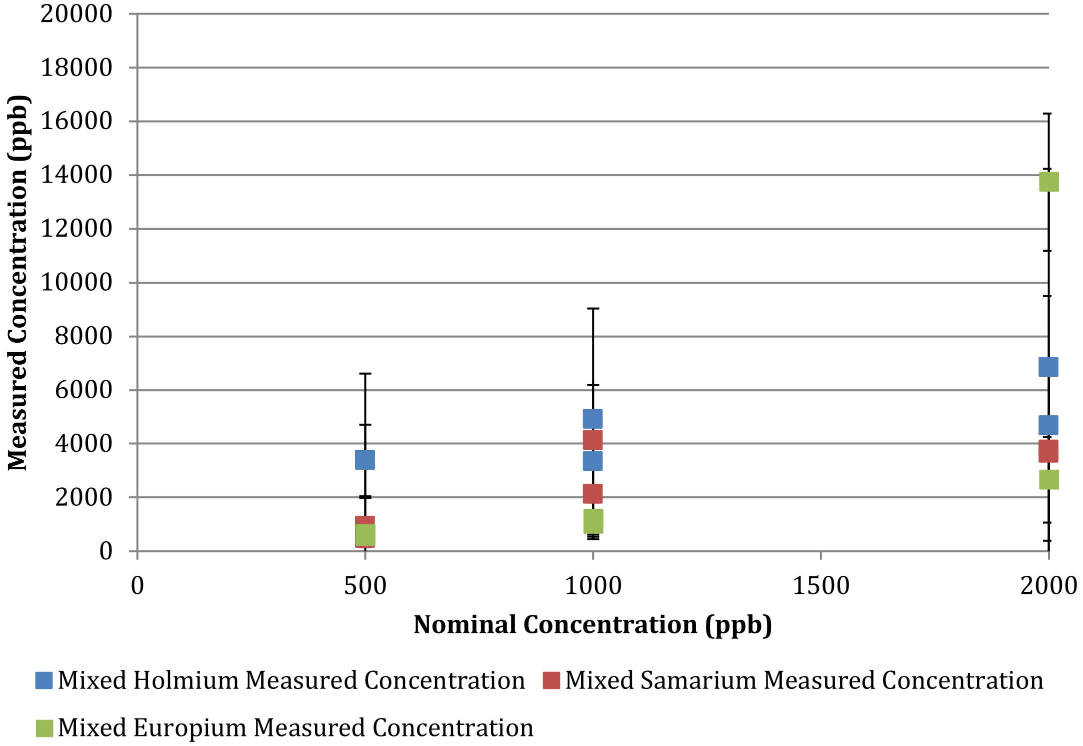


Figure 5.5. Comparison of Added Concentrations of Multiple Taggant Elements to Measured Concentrations in Solution

Unlike the single element standard solution concentrations, the results from this series of tests are less conclusive about the reason for the measured concentrations being much higher than what the concentrations should be. The parameters for the linear regression are summarized below in Table 5.13.

Table 5.13. Linearity of Measured Concentrations showing Scale Factor between Measured Concentration and Added Concentration

Element	Scale Factor	R^2 value
Holmium	3.29	0.306
Samarium	2.07	0.597
Europium	3.39	0.415

Unlike the single element solution tests, instead of R^2 values of at least 0.9, the absolute value of the R^2 values falls within the range of 0.3 to 0.59. This range is generally considered to be insufficient to say that there exists a correlation. However, this range of correlation coefficients also does not imply the lack of a correlation either.

In addition to the R^2 values being different from the single element case, the scale factor between the measured concentration and the actual concentration is different. Notably, these scale factors are closer together than the ones seen with the single element case. The cause for this is uncertain, but would imply the opposite of the single element solution tests. These results imply that there is a constant error factor, possibly in the reactor flux. Table 5.14 summarizes the objectives the multi-element standard solutions test addresses and whether the test met each objective.

Table 5.14. Multi-Element Standard Solution Test Objectives Summary

Objective	Objective met or failed
Objective 1: Taggant Elements Measured?	Failed
Objective 2: Concentration ± 50 ppb?	13/18 Met 5/18 Failed
Objective 3: Taggant found above Background?	Met

5.5. MULTI-ELEMENT BINARY POST-BLAST

As with the single element post-blast tests, the presence and absence of elements can be assessed by determining the net number of counts under the peaks, and the uncertainties in the net counts, corresponding to that element in the NAA spectrum obtained from the sample. The net counts and the uncertainties for each of the three taggant elements used for tests one through six in this series are shown in Table 5.15.

Table 5.15. Taggant Elements Present, Net Counts, and Uncertainties in Multi-Element Binary Post-Blast Residues. (Bold Indicating Taggant Element was Detected)

Test	Holmium Net Counts	Holmium Present	Samarium Net Counts	Samarium Present	Europium Net Counts	Europium Present
1	**377.27 ± 172.55**	Yes	**744.72 ± 294.59**	Yes	0	No
2	**551.95 ± 273.78**	Yes	0	No	0	No
3	147.09 ± 325.00	No	**2,383.53 ± 359.49**	Yes	0	No
4	122.32 ± 194.84	No	0	No	0	No
5	**216.11 ± 200.87**	Yes	180.80 ± 243.56	No	0	No
6	118.49 ± 148.10	No	**774.50 ± 163.65**	Yes	0	No

In each of these tests, europium could not be identified. There are two possible reasons for this. Europium has two stable, naturally occurring isotopes, ^{151}Eu and ^{153}Eu [38]. During NAA, these elements produce isotopes that have relatively long half-lives on the order of several years. This long half-life, however, makes these elements relatively inactive, and thus they require longer counting times, making their use not feasible for this experiment. Activation also produces the europium isotope ^{152m1}Eu, a metastable isotope with a half-life of 9.29 hours [38]. This more active isotope is the one that has been used to specifically identify the presence of europium. The post-blast residue sample from the first test in this series began counting 70 hours after irradiation. This delay was necessary to allow safe handling of the samples due to the activity of some shorter lived isotopes including manganese, silicon, and aluminum that were picked up from the environment. This period of time is approximately 7.5 half-lives, so the amount of the active isotope being measured has been reduced by a factor of $2^{7.5}$, or approximately 1/186th of its original concentration. Therefore, the activated europium allows for a considerably shorter counting time, but it may be too unstable to be seen after the required delay period.

The second possible reason for the absence of europium in the post-blast samples is that none of the added europium taggant was collected. While the elements added to the explosive cannot be destroyed during the detonation process, it could be that the europium partitions in the cloud of particulate material generated by the detonating explosive differently than holmium and samarium due to either physical characteristics such as atomic weight or density, or due to chemical characteristics such as reactivity with the detonation products. This possibility will need further study. However, since all three elements are rare earth elements, they should be chemically similar, which suggests they should act similarly during detonation. Additionally, rare earths commonly have similar physical characteristics as well. While the data collected cannot discriminate between the two possible reasons, we consider it more likely that the time delay between irradiating the samples and counting them is responsible for the lack of any measurable quantity of europium in the samples.

The results for holmium are positive. All samples showed traces of holmium, however tests three, four, and six did not show more net counts than the uncertainty in the measurement. A peak at the correct energy for holmium was observable for each test, similar to the results for test two of the single element composition B test series, but the measured net counts do not meet our criteria for stating that holmium is present in those tests.

The results for samarium are mixed. In two samples, no trace of a samarium peak at 69.6 keV was found. From the single and multi-element standard solutions tests, this peak was found to be the most specific peak indicating the presence of samarium, despite larger peaks present at 41.5 and 103.1 keV which had other peaks close enough to interfere with measurement. Of the remaining tests, three showed net counts well in excess of the uncertainty, and one does not meet that criteria. The results from test five, like the holmium results from tests three, four, and six; have noticeable peaks, but do not meet the criterion to say that samarium is present.

In the end, this test did not provide a clear answer to determining if the taggant elements interfere with one another. In all the tests where the taggant elements can be shown to be present, their peaks are distinct from those from other elements present in the sample. However, due to the presence of other environmental material, the post-blast residue becomes highly active when irradiated under the test conditions, and a period of time is needed to allow the samples to "cool" sufficiently so that they can be handled safely. This period of time was too long for the 9.29 hour half-life of metastable ^{152m1}Eu isotope. More tests will need to be performed in future work to fully evaluate the suitability of europium for use in the Nuclear Barcode. Both holmium and samarium are recommended as successful candidates for the Nuclear barcode and with the increased knowledge from this study, additional taggant options will be selected with similar half-lives for ease of reading the barcode post detonation.

As with the single element post-blast tests, a delay time between irradiating and counting the samples was added, however this period varied between the different tests in this series. Table 5.16 shows the measured concentrations of the taggant elements in the post-blast residue created by the binary charges.

Table 5.16. Multi-Element Binary Post-Blast Series Concentration and Their Uncertainties (in ppb)

Test	Holmium Concentrations	Samarium Concentrations	Europium Concentrations
1	4,544.33 ± 9,305.14	13,487.41 ± 2,7617.31	-
2	17,080.33 ± 254,950.59	-	-
3	1,567.97 ± 2,494.45	5,072.96 ± 8,070.45	-
4	3,222.75 ± 29,804.05	-	-
5	n/a	n/a	n/a
6	4,105.55 ± 32,607.88	32.00 ± 254,144.73	-

It is immediately obvious that these concentrations are inconsistent. One contributor to this might be that concentration uncertainties are all higher than the calculated concentrations. This is mostly because of the uncertainty from the quantity of post-blast residue that was recovered. The in all cases, not much post-blast residue was recovered, which likely also contributed to the issue with test five where the measured mass was less than zero, and no concentrations were calculated for this sample. These concentrations do not match up well to the concentrations of the undetonated explosive except for the holmium concentration in test 6 which should be 4,000 ppb and was measured at 4,105.55 ppb. That the uncertainty is eight times larger than the measured value makes this result unreliable, however.

Additionally, only holmium was detectable in all tests. Europium was not detected in any of the tests that were performed, and samarium was only detected some of the time. It is not surprising that europium was not found: almost 7.5 half-lives had elapsed, and therefore the activated europium decayed away. On the other hand, holmium has a half-life of 26.8 hours, and so some holmium should still be present. The fact that samarium was not detected, despite the longer half-life of the activated samarium isotope used (Sm-154), of 46 hours makes analysis difficult. No trace of samarium was found in tests 2 and 4, even though samarium should be comparatively long lived; it can only be concluded that samarium was not present in the post-blast residues from these samples. Table 5.17 summarizes the objectives the multi-element binary post-blast test addresses and whether the test met each objective.

5.6. MULTI-ELEMENT COMPOSITION B POST-BLAST

This series of tests on tagged composition B uses the same combination of three elements at three concentration levels to create six unique combinations of taggants that

Table 5.17. Multi-Element Binary Post-Blast Test Objectives Summary

Objective	Objective met or failed
Objective 1: Taggant Elements Measured?	Failed
Objective 3: Taggant found above Background?	6/18 Met 12/18 Failed
Objective 4: Concentration same in post-blast residue and undetonated?	Failed

was used in the multi-element binary post-blast test series described previously in Section 5.5. Comparing the number of net counts to the uncertainty in the net counts provides a good method of identifying if the taggant element is present in the sample. These are presented below in Table 5.18.

Table 5.18. Taggant Elements Present, Net Counts, and Uncertainties in Multi-Element Composition B Post-Blast Residues. (Bold Indicating Taggant Element was Detected)

Test	Holmium Net Counts	Holmium Present	Samarium Net Counts	Samarium Present	Europium Net Counts	Europium Present
1	91.107 ± 236.34	No	124.90 ± 211.64	No	0	No
2	312.68 ± 198.07	No	**705.81 ± 259.58**	Yes	96.14 ± 235.48	No
3	99.40 ± 351.30	No	**445.28 ± 183.78**	Yes	0	No
4	**352.03 ± 203.59**	Yes	**1,466.35 ± 254.15**	Yes	141.91 ± 529.62	No
5	0	No	**223.20 ± 159.70**	Yes	0	No
6	91.66 ± 96.99	No	**537.86 ± 208.04**	Yes	0	No

Results are similar to the binary post-blast tests. Samarium and holmium can be found in most tests, while europium cannot be definitively located. Unlike the tests on binary post-blast samples, europium peaks can be noticed in the spectra of some tests, but insufficient counts are available for adequate quantification in others. The amount of europium measured here is small and considered “not detected”. These samples were counted approximately 20 hours sooner than the samples from the mixed element binary post-blast test series. This additional data supports the hypothesis that the problem locating europium is radioactive decay.

The peaks of the three taggant elements are all well separated from the peaks coming from other elements present in the sample. However, not all samples showed peaks for all three taggant elements. This partially addresses the objective of determining if the taggant elements interfere with one another or are lost in the background. Taggant peaks are located at distinct energies from the background, but the peaks can be lost due to the time needed to allow the samples to be handled after activation.

The same six mixtures of the three taggant elements were added to composition B charges prepared the same way as in the single element tests. All other parameters of the test were identical between this test series and the previous test series. The measured concentrations are presented in Table 5.19.

Table 5.19. Multi-Element Composition B Post-Blast Series Concentration and Uncertainties (in ppb)

Test	Holmium Concentration	Samarium Concentration	Europium Concentration
1	5,593.31 ± 154,939.27	9,413.34 ± 260,757.29	-
2	1,245.23 ± 123.14	3,744.33 ± 379.27	656.19 ± 64.91
3	765.29 ± 274.40	4,097.66 ± 1,469.27	-
4	845.15 ± 24.42	4,154.91 ± 119.79	654.98 ± 20.70
5	-	6,530.26 ± 5,496.39	-
6	589.72 ± 126.40	3,973.96 ± 851.76	-

The measured concentrations from this series of tests, like the binary tests in Table 5.16, are mixed. This implies that the results are not directly dependent on the type of explosive used. The concentrations measured from the post-blast residue are not close to the prepared concentrations of the tagged charges. The uncertainties in the concentrations are generally better than expected, in general being at least the same magnitude of the concentration, and often better. The exception is test one. Test one was the lightest sample, weighing one order of magnitude less than the other samples. This shows the effect that the collected mass of post-blast residue has on the measured concentration uncertainties of the taggant elements. Recovering more of the post-blast residue will lead to lower uncertainties in the measured concentrations.

This series of tests behaves more sensibly than the binary ones. Samarium is always detected, holmium sometimes, and europium less frequently. This follows the relationship between the half-lives of the isotopes used to measure the presence of these elements. Additionally, the delay between irradiating and counting these samples was shorter than the previous test series by 20 hours, for a time delay of approximately 48 hours. These tests also have smaller uncertainties in the concentration than the previous test series, excluding test one which has high uncertainty because less post-blast residue was collected. Table 5.20 summarizes the objectives the multi-element Composition B post-blast test addresses and whether the test met each objective.

5.7. MULTI-ELEMENT BINARY REPEATABILITY

Variation between samples is expected, so by using identical charges, information about the repeatability of the nuclear barcode can be obtained. This series of tests can

Table 5.20. Multi-Element Composition B Post-Blast Test Objectives Summary

Objective	Objective met or failed
Objective 1: Taggant Elements Measured?	Failed
Objective 3: Taggant found above Background?	5/18 Met 13/18 Failed
Objective 4: Concentration same in post-blast residue and undetonated?	Failed

provide additional information about the recoverability of the individual elements. Like previous tests, comparing the net counts to the uncertainty in the net counts is a straightforward test for the presence of the taggant elements. These data are shown in Table 5.21.

Table 5.21. Taggant Elements Present, Net counts, and Uncertainties in Multi-Element Binary Repeatability Post-Blast Residues. (Bold Indicating Taggant Element was Detected)

Test	Holmium Net Counts	Holmium Present	Samarium Net Counts	Samarium Present	Europium Net Counts	Europium Present
1	**538.71 ± 197.90**	Yes	**1,815.94 ± 389.52**	Yes	**521.29 ± 280.97**	Yes
2	**394.81 ± 170.12**	Yes	**290.30 ± 120.63**	Yes	227.79 ± 291.55	No
3	**2,709.14 ± 224.31**	Yes	**1,162.77 ± 226.54**	Yes	**286.42 ± 250.78**	Yes
4	176.38 ± 484.80	No	**1,381.30 ± 204.16**	Yes	201.56 ± 272.21	No
5	**382.73 ± 244.62**	Yes	**1,773.01 ± 255.60**	Yes	**439.94 ± 299.55**	Yes

There were three instances where an element was not found in the post-blast residue: europium in the second test, and both holmium and europium in the fourth test. The advantage of this series of tests is the same concentrations of taggant elements were added to undetonated explosive. Despite the noisy environment produced during detonation and seen in NAA, the taggant elements could be identified in 12 of 15 cases in this series of tests. An example of the NAA spectrum of a post-blast residue sample is included in Figure 5.6.

Additional elements in the sample produce their own gammas and due to scattering and reflection produce extra background in the NAA spectrum. This is a normal process and happens with all samples that undergo NAA, however searching for trace elements such as the taggant elements used in the nuclear barcode exacerbates the issue. This process of losing energy produces a broad spectrum of photons from the narrow peaks emitted by a radioactive species, and multiple species all increase this broad spectrum noise. There were three occasions where the taggant elements could not be positively identified because the number of net counts was lower than the uncertainty: holmium in test 4, and europium in tests 2 and 4. In those cases, the peak was not present.

A key component to the workings of the Nuclear Barcode is the repeatability of the measurement of the taggant. Measurements of the same batch of explosive must all produce the same results. The concentrations for each element across each of the five samples should be the same, since the charges were prepared identically. The measured concentrations for each of the five charges, as well as the average across all five measurements, are shown in Table 5.22.

Uniquely among all of the post-blast tests performed, all three taggant elements were detected in every test. This test series required a delay of 48 hours between irradiating and counting the samples of these post-blast tests for the samples to become sufficiently cool to handle. Because this delay was small, measurements of each of the taggant

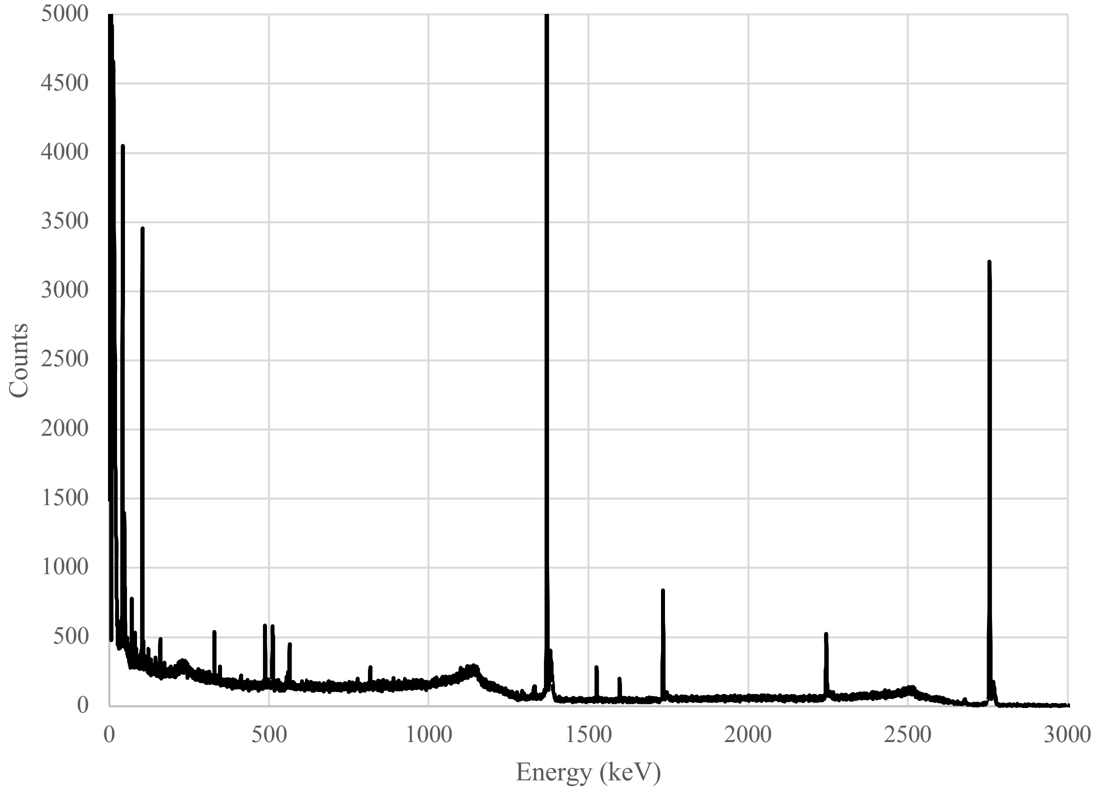


Figure 5.6. Example NAA Spectrum of Post-Blast Residue. (note: This is a Zoomed in Figure and Cuts off a Peak at Approximately 5 keV Reaching 90,000 Counts and the Peak in the Center at 1293 keV Reaching 10,000 Counts to Show more of the Peaks that are Present in the Spectrum)

Table 5.22. Multi-Element Binary Repeatability Post-Blast Series Concentrations and Uncertainties (in ppb)

Test	Holmium Concentrations	Samarium Concentrations	Europium Concentrations
1	1,869.02 ± 686.62	7,331.87 ± 1,572.70	3,703.48 ± 1,996.12
2	7,304.70 ± 3,147.48	6,315.29 ± 2,624.15	8,239.27 ± 10,545.35
3	16,696.67 ± 1,382.48	8,536.70 ± 1,663.18	3,255.58 ± 2,850.56
4	747.11 ± 2,053.52	7,057.98 ± 1,043.17	1,488.50 ± 2,010.25
5	697.99 ± 446.10	3,949.62 ± 569.37	1,322.72 ± 900.633
Average	5,463.10 ± 1,543.24	6,638.29 ± 1,494.51	3,601.91 ± 3,480.46

elements were able to be obtained. Looking first at the average concentrations, the measured concentrations are off, but at least of the correct order of magnitude. The uncertainties are high, with holmium and samarium having very similar average uncertainties, and europium having an uncertainty nearly identical to the measured concentration.

Going through the tests individually provides some additional information. Europium has two pairs of measurements that are close to one another in tests 1 and 3 as well as tests 4 and 5. Test 2 however, shows much higher amounts of europium than any of the previous tests, and also has the highest uncertainty by far. Samarium is more consistent, with only test 5 particularly far from any of the others. Tests 1 through 4 have samarium measurements that are the same, taking the uncertainties into account. Holmium has an outlier in test 3, and unpredictable behavior in the other tests. Why this particular sample has so much holmium compared to the other ones is unknown.

For these tests, the uncertainty is predominantly a function of the quantity of post-blast residue recovered. The concentration of the taggant element is measured by dividing the mass of the taggant element calculated using Equation 3 by this mass, and multiplying by 10^9 to give parts per billion. When the mass of the post-blast residue is small, the uncertainty then becomes a larger fraction of the total mass, and thus contributes more than under other circumstances.

The concentration and uncertainty in each element across each test are shown in Figure 5.7.

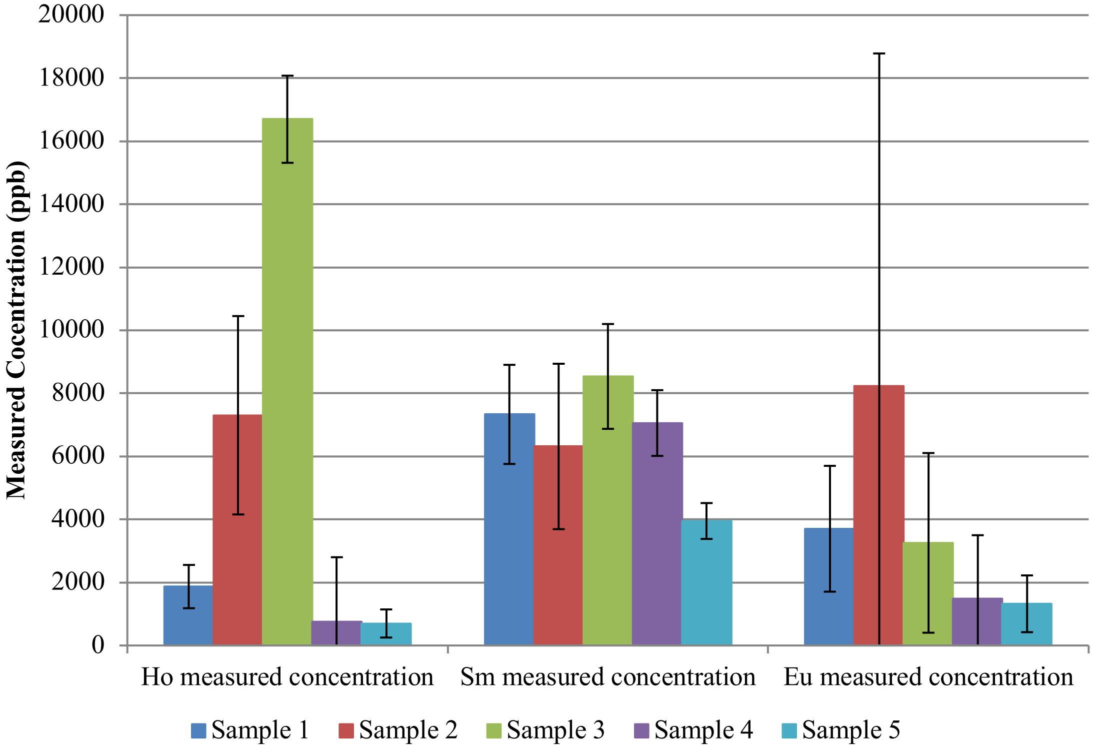


Figure 5.7. Repeatability of Measured Concentration of the Three Taggant Elements across Five Tests and Their Uncertainties. All Measured Concentrations should be the same for each Element

The measured concentrations and their uncertainties vary depending on the test. This suggests that using the nuclear barcode in the field will require obtaining multiple samples to read it. The concentrations for each element across each sample should be the same, since the charges were prepared identically.

The concentrations of the taggant elements can be determined. However, these concentrations are suspect due to the issue shown with both the single element standard solution series and the multi-element standard solution series. The calculated concentrations do not match the concentrations of the taggant elements that were added to the undetonated explosive. Table 5.23 summarizes the objectives the multi-element binary post-blast repeatability test addresses and whether the test met each objective.

Table 5.23. Multi-Element Binary Post-Blast Repeatability Test Objectives Summary

Objective	Objective met or failed
Objective 1: Taggant Elements Measured?	Failed
Objective 2: Concentration ± 50 ppb?	Failed
Objective 3: Taggant found above Background?	15/18 Met 3/18 Failed
Objective 4: Concentration same in post-blast residue and undetonated?	Failed

5.8. MULTI-ELEMENT COMPOSITION B REPEATABILITY

This series of tests used the same concentrations of each of the three taggant elements that were used in the previous section. To show the detectability of these elements, the net counts and the uncertainties in the net counts that were obtained from the post-blast residues from this series of tests are shown below in Table 5.24.

Table 5.24. Taggant Elements Present, Net Counts, and Uncertainties in Multi-Element Composition B Repeatability Post-Blast Residues. (Bold Indicating Taggant Element was Detected)

Test	Holmium Net Counts	Holmium Present	Samarium Net Counts	Samarium Present	Europium Net Counts	Europium Present
1	**197.37 ± 97.90**	Yes	30.65 ± 631.94	No	0	No
2	0	No	**328.98 ± 155.69**	Yes	0	No
3	**231.31 ± 217.42**	Yes	110.01 ± 156.95	No	0	No
4	165.45 ± 207.91	No	**126.14 ± 89.52**	Yes	0	No
5	138.68 ± 161.62	No	0	No	0	No

Peaks corresponding to holmium and samarium can be seen in all but one test each, however these elements can only be definitively said to be present in a couple tests. Holmium can only be said to be present in tests one and three, while samarium can only be said to be present in tests two and four. Once again, the time between irradiation and counting appears to have allowed for any activated europium to decay away. The composition B repeatability post-blast residue tests had a roughly 12.5% higher delay time (54 hours vs. 48 hours) between irradiating the sample and counting them compared to the binary repeatability post-blast residue tests. This additional time could account for the difference in the detectability of europium in the two test series.

The taggant element peaks can be readily distinguished from peaks resulting from other background elements present in the sample. However, not all samples showed notable peaks for the taggant elements. Taking additional samples of the post-blast residue would provide additional data points to determine if the elements are truly not present in the post-blast residue for those tests, or if they were not identifiable in that particular sample of the post-blast residue.

This series of tests, like the previous series of multi-element binary repeatability post-blast series, added the same concentration of taggant elements to the explosive charges used. This should allow for a test of the repeatability of this experiment. The calculated uncertainty in the measured concentration of the taggant elements does not fall within the 50 ppb needed to have concentration levels separated by 100 ppb as the nuclear barcode is designed for. The measured concentrations of each taggant element and the averaged concentration across each of the five tests are shown in Table 5.25.

Table 5.25. Multi-Element Composition B Repeatability Post-Blast Series Concentrations and Uncertainties (in ppb)

Test	Holmium Concentration	Samarium Concentration	Europium Concentration
1	11,789.27 ± 23,000.32	2,062.15 ± 4,023.16	-
2	-	1,546.49 ± 13.56	-
3	14,216.78 ± 30,461.49	7,836.76 ± 16,890.60	-
4	20,793.77 ± 206,284.12	18,620.15 ± 184,720.76	-
5	5,117.26 ± 4,659.43	-	-
Average	10,383.42 ± 44,097.56	6,013.11 ± 41,129.61	-

This test series required a delay time of 54 hours for the samples to decay enough to be safely measured. As a result, sufficient time elapsed for the activated europium to decay. An additional difference between these tests and the tests involving binary explosives is that the quantity of post-blast residue collected from the Composition B tests is much lower. As a result, the effects of the uncertainty in the measurement of the quantity of post-blast residue begin to dominate the calculation for the total uncertainty in the measured concentration of the taggant elements.

The measured concentrations of both holmium and samarium are not close to the quantity that were added to the explosive charges. The measured quantities are incorrect by a similar factor (5x for holmium vs. 6x for samarium). This seems to be more of a coincidence based on the size of the uncertainties. In tests 1, 3, and 4 where both elements were detected, the uncertainty in the concentration is larger than the measured concentration. This indicates that these measurements are unreliable.

The concentrations of holmium and samarium found in the samples from this test are included in Figure 5.8. Note that in an ideal case, the concentrations across each test would be the same.

The uncertainty in the measured concentration for the fourth sample is this series of tests is cut off to better show the measurements of the concentrations. Europium concentrations are not included in this figure because no europium peaks were found during testing. The shown concentrations are not similar to one another. Additionally, the uncertainties in each test are much larger than the necessary 50 ppb. Obtaining multiple samples, and acquiring large individual samples of the post-blast residue should increase the accuracy of the concentration measurement of the post-blast residue and reduce the magnitude of the uncertainty of the measured concentration.

As with previous samples, the taggant element peaks can be readily distinguished from peaks resulting from other background elements present in the sample. However, not all samples showed notable peaks for the taggant elements. Taking additional samples of the post-blast residue would provide additional data points to determine if the elements are truly not present in the post-blast residue for those tests, or if they were not identifiable in that particular sample of the post-blast residue.

These concentrations do not match the concentrations of the taggant elements that were present in the undetonated explosive. Additionally, there is still the unresolved difficulty with calculating the concentrations of the elements that was initially shown in the first series of single element standard solutions. Once this error is resolved, a better determination of the accuracy of these results should be possible. Table 5.26 summarizes the objectives the multi-element Composition B post-blast repeatability test addresses and whether the test met each objective.

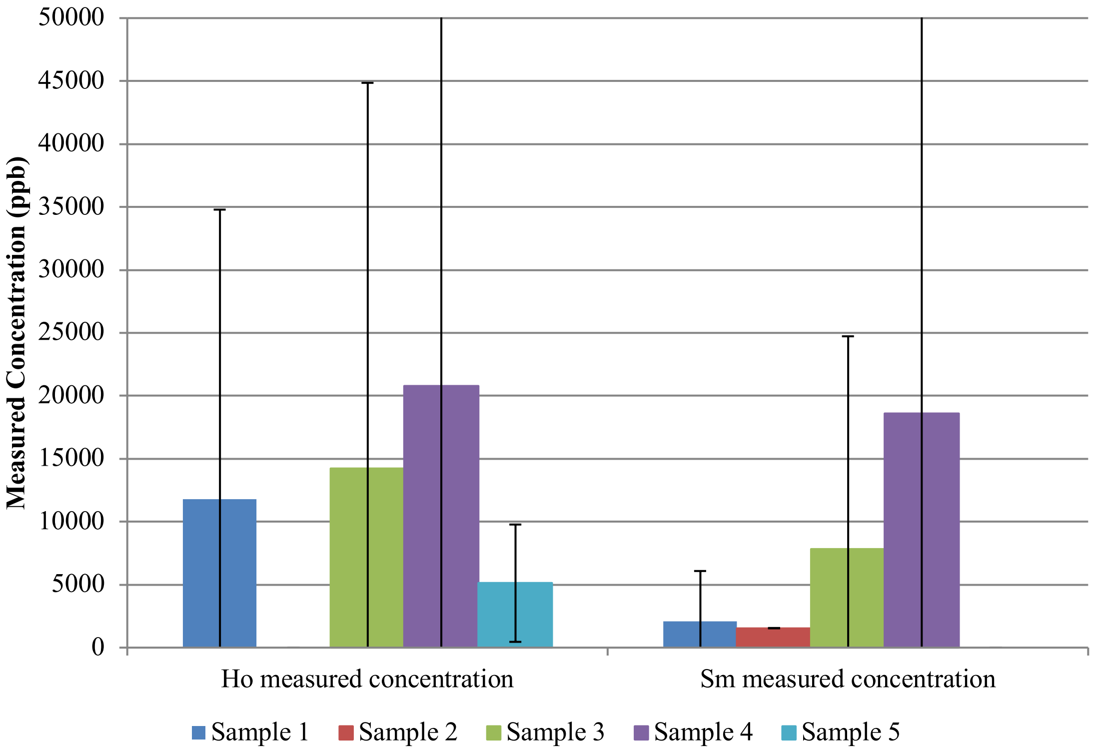


Figure 5.8. Repeatability of Measured Concentration of the Two Detected Elements across Five Tests and Their Uncertainties. Each Concentration Should be the Same. Europium was used as a Taggant, but was not Detected in any of the Samples, so it was not Included in this Figure

Table 5.26. Multi-Element Composition B Post-Blast Repeatability Test Objectives Summary

Objective	Objective met or failed
Objective 1: Taggant Elements Measured?	Failed
Objective 2: Concentration ± 50 ppb?	Failed
Objective 3: Taggant found above Background?	4/18 Met 14/18 Failed
Objective 4: Concentration same in post-blast residue and undetonated?	Failed

5.9. EVALUATION OF POST-BLAST SURVIVABILITY OBJECTIVES

The objective of this research has been to evaluate the survivability of the Nuclear Barcode identification taggant concept. To evaluate this property, the concept of survivability was broken down into a series of four objectives that the Nuclear Barcode must satisfy in order to meet the definition of a survivable taggant. These four objectives then informed the design of a series of eight experiments.

1. Determine if the taggant elements can be detected and quantified via NAA at the desired concentrations.

2. Determine if the different concentration levels of the taggant elements can be distinguished via NAA with sufficient precision that the measured concentration lies within only one concentration level (50 ppb precision to use the Nuclear Barcode as designed).

3. Determine the distinguishability of the taggant elements from the background, such as other taggant elements and other common elements in the environment such as sodium, potassium, chlorine, etc.

4. Identify concentrations of the taggant elements in the post blast residues and verify them to be the same as in the undetonated sample.

5.9.1. Research Objective One. The results of the experiments described in the previous sections show that NAA performs well in identifying the presence or absence of three taggant elements: holmium, samarium, and europium. The technique is sound, and is now considered a reference technique for the measurement of composition of a material [7]. The current results for using the technique on the equipment at the MSTR are more mixed.

Currently, the concentrations of solutions of taggant elements dissolved in water cannot be correctly measured. However, these results show high correlation coefficients for single element solutions that are greater than 0.9. This indicates that for these solutions, there is a systematic reason. Calculating the concentration uses Equation 3. Two components of this equation are not experimental parameters and need to be determined by other experiments. The first component, the thermal flux Φ_{th}, is not likely to be the cause of the disparity. If an error in the thermal flux were the cause of this disparity, then the magnitude of this disparity would be the same for each element that was measured. However, the measured disparity is not constant. In fact, the measured disparity decreases as the peak energy increases. This is what would be expected if this disparity were caused by an error in determining the probability that a photon released by the sample interacts with the detector.

This factor, ε, is a function of the energy of the incident photon and decreases as the energy of the incident photon increases. For the multi-element solutions, the correlation coefficient is notably smaller. This indicates that the results for the multi-element standard solution test series does not support or go against the possible causes shown by the single element test series. It is possible that both factors are incorrect; the results from the single element standard solutions and multi-element standard solutions do not rule out this possibility. Currently, it is possible to detect the presence of the taggant elements, but it is not possible to correctly measure the concentration of the taggant elements.

5.9.2. Research Objective Two. The issue from objective one with accurately determining the concentration of elements using NAA prevents any solid conclusions from being drawn about the ability of the technique to resolve the concentration levels necessary for the nuclear barcode to work. However, one conclusion that can be drawn from the results is that obtaining many samples will produce a better measurement than only obtaining one. For the nuclear barcode, this means that the post-blast residue should be sampled from as many different locations as possible in order to accurately determine the concentrations. The resolved concentrations for some tests hint that if the concentrations can be accurately resolved, then NAA will be able to determine the different concentration levels to the necessary degree of precision. The uncertainty in the measured concentration for the single element solutions, which represents the best case scenario for these measurements, is less than 100 ppb for 11 out of the 15 combinations of the three elements at 5 concentrations. However, until this issue with correctly measuring the concentrations is resolved, no conclusion can be accurately reached.

5.9.3. Research Objective Three. It was initially proposed that measurements of the concentration of taggant elements would be taken from materials that might be present in a post-detonation environment. This was proposed to ensure that the presence of the taggant element and the concentration of the taggant element that was measured using NAA would result only from the actual taggant, and not be from a naturally occurring source. Initial tests on both binary and composition B explosives that were tagged with a single element showed no sign of the proposed taggant elements in the post-detonation environment. Thus, this proposed series of tests was considered to be unnecessary since performing NAA on the post-blast residue would collect the same information. In no tests were the taggant elements interfering with reading one another, nor was there any interference from peaks caused by an element present in the environment. The "noise" caused by the presence of other peaks might be responsible for some of the measured uncertainty in the concentrations, since this would increase the amount of background noise and decrease the prominence of any peaks. Additionally, detector dead time is a factor to consider as well, and a higher amount of other active isotopes will increase this dead time. This dead time arises from the limit of the detector in counting and determining the energy of many gammas simultaneously and is an inherent limit of the detector.

5.9.4. Research Objective Four. Despite the issue preventing accurate calculation of the concentration of the taggant elements, it is likely the case that the concentration of the taggant elements in the post-blast residue does not match the concentration of the elements in the undetonated explosive. This is reasonable, since only a fraction of the mass of the undetonated explosive ends up being deposited as post-blast residue. An altered version of objective four then becomes "determine if the concentrations of the taggant elements in the post-blast residue are a predictable function of the concentrations of the taggant elements in the undetonated explosive". This altered objective requires that the concentrations of the taggant elements in the post-blast residue be accurately measured, which has not yet been demonstrated.

In many tests, the taggant elements have been able to be identified in the post-blast residues. However, in some of the tests, the taggant elements have not been able to be identified in the post-blast residues. A key parameter, then, is the delay between when the sample is irradiated and when the sample is counted. This delay is necessary for the post-blast residue containing samples as the detonation results in the deposition of other elements onto the witness plates. Some of these elements become highly active after the ten minute irradiation used, and become too active to safely handle the sample. This delay allows for the samples to decay to a safer level of activity. The delay time requirement was especially problematic for measurements of the comparatively short lived europium-151m1 isotope. As a result, europium was rarely measured in the post-blast residue, despite providing the best results in solutions. An analysis of the effect of this delay time on the measured concentration and the uncertainty in the concentration measurement is presented in Section 6.

These tests also observed much higher uncertainties in the calculated concentrations that results from the low mass of post-blast residue that is collected. Quantities of post-blast residue from the binary tests were approximately two orders of magnitude larger than the amount of post-blast residue recovered from the tests using Comp B. Lower uncertainties would be achieved when larger quantities of post-blast residue have been obtained. This is another result in favor of requiring many samples of post-blast residue in order to use the nuclear barcode as an identification taggant for explosives. Multiple samples would permit averaging of the concentration of taggants based on the total weight of post-blast residue recovered, which in theory could reduce the contribution to uncertainty from the mass of post-blast residue. The low quantity of post-blast residue recovered also means that correspondingly small amounts of taggant elements are recovered, which may not be found due to being overwhelmed by background noise.

The low quantity of post-blast residue recovered certainly did not help when trying to identify the presence of the short lived europium-152m1 isotope in many samples.

5.10. SECTION SUMMARY

While performing the series of tests described in this section to evaluate the survivability of the Nuclear Barcode in the post-blast residue, the critical parameters for performing NAA were identified. A total of five key parameters that can be controlled experimentally were identified. Each must be optimized to fully evaluate the performance of NAA in this application in determining the concentration of the taggant elements. The parameters are listed in Table 5.27, and use the notation for each variable from Equation 3.

Table 5.27. Five Key Parameters for Optimizing NAA

Variable	Variable Description	How is it controlled/determined
Φ_{th}	Flux	Controlled by reactor used, and power
ε	Efficiency	Inherent to detector and sample geometry
t_i	Irradiation time	By experiment
t_d	Delay time	By sequencing
t_m	Counting time	By experiment

The effect of the delay time t_d on the measured concentration and the uncertainty in the measured was selected for further study. This parameter varied the most across and within each test series. In the middle of testing the second of the five replicate samples of the 500 ppb solution of samarium (described in Section 5.1), the detector being used failed, and was not repaired for several days. This led to measurements of the remaining replicates being delayed, and they produced the highest measured uncertainty of any of the tested solutions containing samarium. In comparison, holmium and europium tests, as well as samarium tests excluding the 500 ppb samples, showed a trend of increased uncertainty with increased concentrations.

Additionally, the variable delay time between irradiating and counting the samples is the most likely cause of the inability to detect europium in almost all of the post-blast residue samples. Since the presence of europium is indicated by measuring a greater number of net counts than the uncertainty in the measurement of the number of net counts, the delay time might have an effect. The uncertainty in the mass and therefore concentration of the taggant elements is also dependent on this relationship and should be evaluated as well.

Finally, the delay time was permitted to vary so that samples could be handled safely after being irradiated. The length of time where the sample was too active to measure varied from sample to sample, and detector availability also played a role in this. For these three reasons, an additional series of tests on the effect of delay time on measured concentrations and measured concentration uncertainty was performed.

6. DELAY TIME EFFECTS ON UNCERTAINTY

The delay time between irradiating and counting the sample was shown to be a key determining factor in identifying the presence or absence of elements, as well as possibly having an effect on the measured concentration or the uncertainty of the concentration measurement. Based on these prior results, a series of experiments was performed to evaluate the effect of the delay time on the measured concentration and the uncertainty. To truly optimize NAA, the experimenter must optimize five of the quantities in Equation 3 (reproduced here from Section 2): t_i, t_m, t_d, Φ_{th}, and ε.

$$m = C\frac{\lambda}{((1-e^{-\lambda t_i})e^{-\lambda t_d}(1-e^{-\lambda t_m})} * \frac{M_a}{\Phi_{th}\sigma_{eff}\Gamma\varepsilon\theta N_A}$$

6.1. EXPERIMENTAL METHOD

Five identical samples of 1,000 ppb holmium solution were prepared at the same time by successive dilution. The samples were placed into plastic vials and transferred by the unshielded pneumatic or “rabbit” system to the core of the MSTR for 10 minutes when operating at 200 kW. The samples were then retrieved using the same pneumatic system and removed from the plastic vial once it was safe. Although these are the same power and irradiation time parameters that were used for the tests in Section 5, the reactor core configuration was changed between the end of the testing in Section 5 and the beginning of the testing in Section 6. The reactor core configuration is the specific arrangement of fuel rods, control rods, and other components in the reactor core. Changing the core configuration could change the flux profile, and would make direct comparisons of the measured concentrations incorrect since the new flux profile was not known. These samples were then counted 5 times for one hour each time over a 96 hour period. The sample was counted 10 minutes after being irradiated, and the sample was also counted at 24 hour intervals after irradiation to observe the effect on the delay between irradiating and counting the sample on the measured concentration. The detector used was an HPGe detector operated at a voltage of 4500 V, and measurements were recorded using Canberra's ProSpect software.

The method for calculating the concentration of holmium in the samples used Equation 3 from Section 2.2, the same as the tests in Section 5. The uncertainties in the measured concentration were calculated in the same way as tests in Section 5 as well. Uncertainties in the measured concentrations were derived by summing the partial derivative of Equation 3 with respect to each variable, multiplied by the uncertainty in that variable in quadrature to yield the uncertainty in the mass of the taggant element. The same method for estimating the uncertainty was used for the equation to calculate the mass concentration of the taggant element. Specifically, this means that the presented uncertainties are not the same as the standard deviation in measured concentration. The calculated uncertainties presented here give the minimum uncertainty in concentration that can be obtained, while taking all variables into account. This analysis was used on the raw spectrum obtained by NAA for each of the samples of the test series.

Holmium was used because it is a monoisotopic element, and prior experience has shown that it produces only a few distinct gammas. This simplifies the subsequent analysis and should mean that any observed effects are directly a result of the imposed delay time. Holmium was dissolved in DI water to provide a clean background to identify the peaks.

Another benefit of using holmium is that the half-life of the activated holmium is 26.8 hours, close to the 24 hour delay between irradiations. A 24 hour delay was used due to scheduling and access limitations to the detector and reactor facilities at the MSTR. Therefore, each of the 24 hour periods was approximately one half-life.

6.2. RESULTS AND ANALYSIS

The measured concentrations of each sample across each of the five measurements are shown in Figure 6.1.

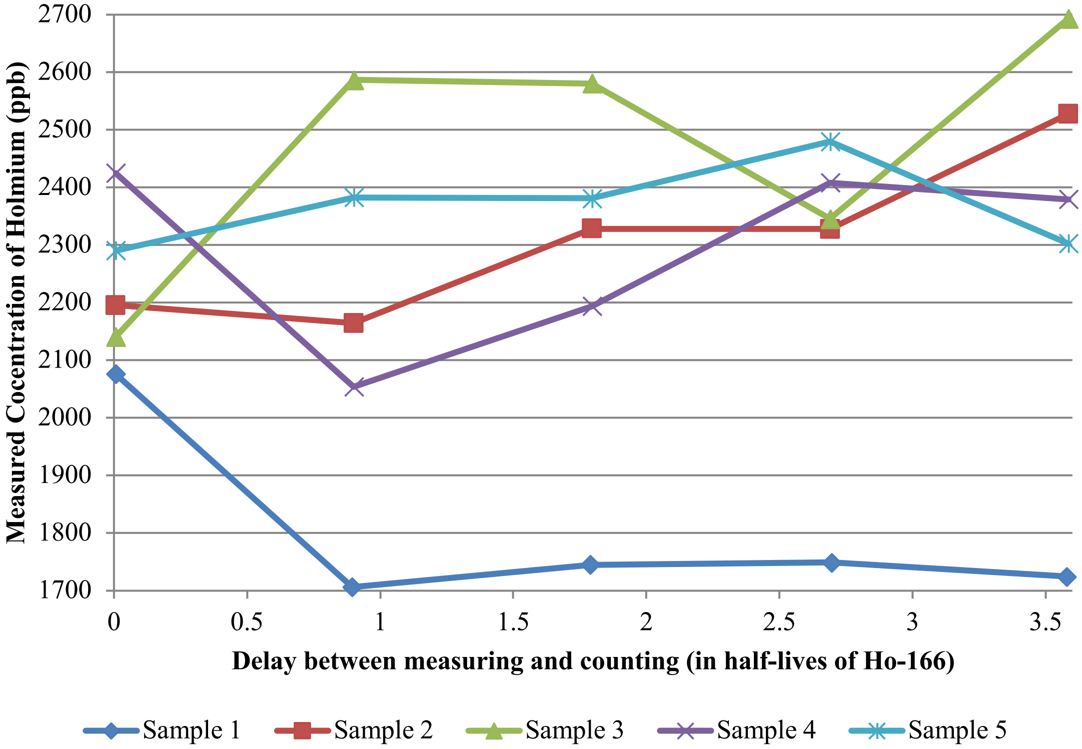


Figure 6.1. Delay Time Measured Concentrations (in ppb) of 1000 ppb Holmium Dissolved in DI Water

The samples were prepared with the same concentration. Sample 2 was measured 10 minutes earlier than all the other samples, due to experimenter error. This time difference is much shorter than both the 24 hour period between measurements and also the 28.6 hour half-life of activated holmium-166. Therefore, despite this difference in when sample 2 was measured compared to the others, any errors from this should be negligible, and sample 2's measured concentrations can be directly compared to the other samples. Samples 2 through 5 are all consistent with one another, having a measured concentration between 2,100 ppb and 2,700 ppb. Sample 1 appears to be an outlier, as it consistently has a lower concentration than any of the other samples after one day had elapsed, despite the fact that all samples were prepared in such a manner that their concentrations should be identical. On average, these five samples have a measured concentration of holmium of 2,247 ppb, compared to 5,538 ppb from the previous 1,000 ppb holmium solutions. Since the detector and measurement methodology remained the same, while the reactor configuration changed, the change in measured concentration must come from the contribution from flux. This result supports the explanation that both the thermal neutron flux parameter and the detector efficiency parameter are contributing to the discrepancy in the measured concentrations seen in the previous section. There is no consistent trend in the measured concentration as a function of the time delay across these samples, as expected from the delay term that accounts for time in Equation 3.

The previous test results indicate that there might be some component to uncertainty as a function of delay time, particularly the notably higher uncertainty found in the 1,000 ppb samarium test. Uncertainty results are shown in Figure 6.2. Figure 6.2 shows a trend in the uncertainty in the concentration measurement as a function of delay time. Somewhere between 2.5 and 3 half-lives after irradiating the samples, the uncertainty increased beyond its value when measured immediately after irradiating with no time delay.

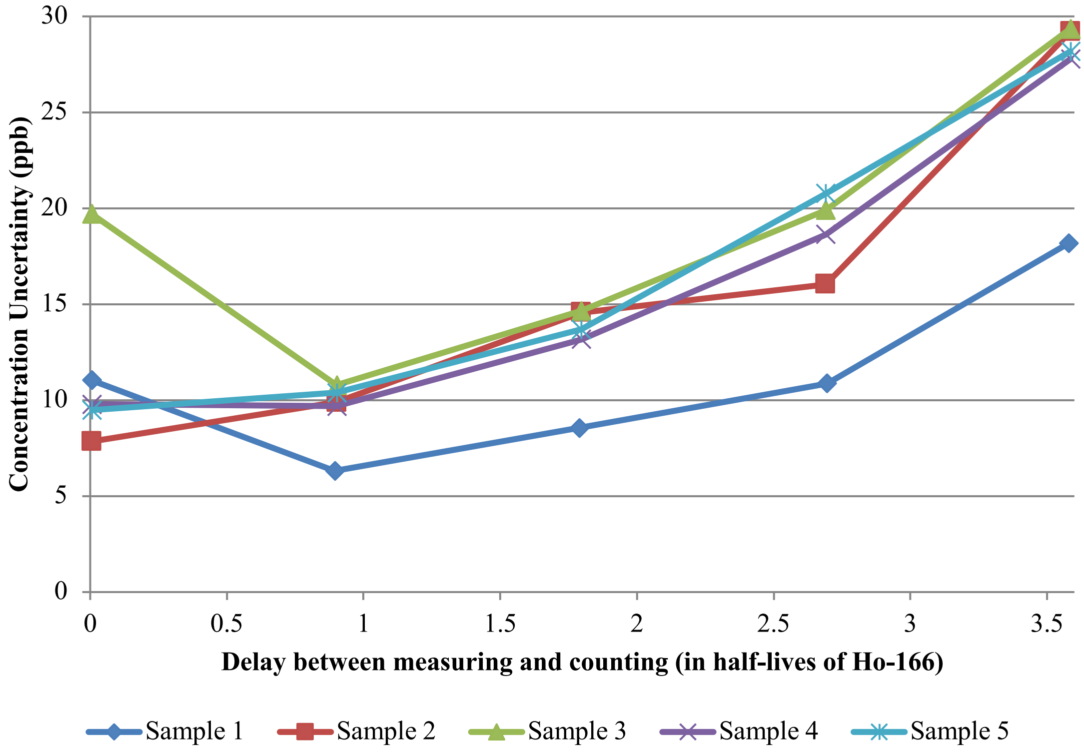


Figure 6.2. Delay Time Measured Uncertainty (in ppb) of 1000 ppb Holmium Solution

Sodium was the only other element found in solution other than holmium, in the form of Na-24. It is suspected that the presence of sodium-24 is what is responsible for the noticeable dip in uncertainty for samples 1 and 3 after approximately one half-life. The activated sodium also produces gammas while it decays, like holmium, which produces additional background noise. Since Na-24 has a half-life of 14.99 hours compared to the 28.6 hour half-life of Ho-166, more sodium will decay than holmium in the given time period. This should reduce the amount of background gammas produced by sodium compared to the quantity of gammas produced by holmium that is of interest, which would produce lower uncertainties in the measured holmium concentration. If the contaminant isotope has a longer half-life than the isotope being measured, this would not occur, and measurements should be made as soon as possible.

The shape of the uncertainty curve appears to change over time. At low delay times, below the critical 2.5 to 3 half-lives value, the uncertainty appears to increase at the same rate with an average increase of 3.9 ppb from just under 1 half-life to over 1.5 half-lives and 4.8 ppb from over 1.5 half-lives to just over 2.5 half-lives. At delay times above 2.5 half-lives, the slope increases to an average of 10.4 ppb. The method used to calculate the uncertainty in the concentration sums the product of the derivative of Equation 3 with respect to a variable and the uncertainty in that variable in quadrature. The different slopes imply that above approximately 2.5 half-lives, the delay time component of this calculation dominates the results, whereas below this time, another or multiple parameters from equation 3 dominate the result for this particular test.

6.3. SECTION SUMMARY

The need for a delay between irradiating and measuring the samples due to scheduling constraints led to unexpected results while evaluating objectives 1 through 4. The uncertainty of the sample with the longest delay time was approximately double that of the next highest uncertainty measurement. It was found that the uncertainty increases as the concentration of the solution increases from 1,000 ppb to 4,000 ppb. However, the highest uncertainty was found with 1,000 ppb solutions of samarium. This uncertainty is also approximately 6 times that of the uncertainty measured in 1,000 ppb holmium which has a similar error in concentration measurements. The added delay time raised a question of what effect this delay had on both the measured concentration of the taggant elements, as well as the uncertainty of the concentration and prompted further testing using holmium solutions at 1,000 ppb. Tests show that there is no noticeable trend in the measured concentration as a function of delay time out to 3.5 half-lives for holmium but there was for the uncertainly calculation. This testing supports the hypothesis that an error in the thermal neutron flux combined with an error in the detector efficiency is the cause of the inaccurate concentration measurements.

An increase in the uncertainty of the holmium concentration was observed when comparing measurements made immediately after irradiating to measurements made after 2.5 to 3 half-lives. The uncertainty increased from a range between 7.8 ppb to 19.7 ppb at 10 minutes or approximately 0 half-lives after irradiation to a range of 10.8 ppb to 20.8 ppb after approximately 2.5 half-lives. The behavior of the uncertainty in the period between 0 and 2.5 half-lives is less certain, due to the presence of sodium in the samples. Sodium (14.997 hours) [39] has a shorter half-life than the holmium (28.6 hours) [39] that was being measured, and would decay more rapidly. This effect would reduce the amount of noise in the NAA spectrum, and also reduce the comparative uncertainty in measured holmium concentration. In samples where this did not occur, there appears to be an increase in the slope of the lines connecting adjacent measurements after approximately 2.5 to 3 half-lives from an average of 3.9 ppb (from just under 1 half-life to 1.7 half-lives) to 10.4 ppb between 2.5 half-lives and 3.5 half-lives. This means that the relative contributions of the factors in the equation used to determine the uncertainty change when entering this region.

These results show that after this period of approximately 2.5 half-lives, the measured uncertainty in the concentration becomes dominated by the delay time. Therefore, to minimize the uncertainty in the concentration for holmium solutions, they should be counted within 67 hours of irradiating the samples. This same 2.5 half-lives criteria can be applied to the two other elements that were tested in Section 5. Europium concentrations, specifically Eu-152m1 should be counted within 23 hours and samarium concentrations should be counted within 115 hours.

Combining the results from the testing in Section 5 with this result, it can be concluded that elements with a half-life of below 19.2 hours are unsuitable for use with the nuclear barcode. This eliminates the use of europium from consideration for use with the nuclear barcode. A 19.2 hour half-life means that the expected 48 hour delay time between measuring and counting the samples from Section 5 is already greater than 2.5 half-lives. As such, even if the element can be identified after this length of time, unlike europium, the uncertainty will already start to be dominated by the delay time. If this occurs, it will be extremely unlikely that the uncertainty in the concentration will remain below 50 ppb.

7. DISCUSSION

7.1. TAGGANT SURVIVABILITY

Historically, taggants have been investigated as a response to proposed laws which are themselves responses to crimes and terrorist actions. Regrettably, since terrorism is inevitable, further legal restrictions on explosives will occur. Previously, proposed laws have required the implementation of identification taggants in explosives. These would provide information that would aid law enforcement in investigating crimes involving these explosives. This idea appears to be attractive and has been proposed for a period of 40 years [1, 2]. After the next or the subsequent major terrorist attack in the United States, this pattern suggests that identification taggants will become required in the United States. As such, having a fully developed and characterized identification taggant ready to be deployed would prove to be a great advantage when that occurs. Figure 7.1 shows the position of the nuclear barcode on the timeline of explosive legislation and taggant efforts.

The Nuclear Barcode is an identification taggant that gets its name from nature of the technique of neutron activation analysis. This nuclear technique has been used in the semiconductor industry to analyze the impurities in the ultrapure wafers down to the parts per billion level to ensure that they can be used to manufacture the chips modern technology relies on [30]. Archeologists use this technique to analyze the composition of pottery and match the combinations of trace elements, typically rare earths, to determine where the clay that was used came from. This information can be used to determine ancient trade routes and cultural spheres of influence [40].

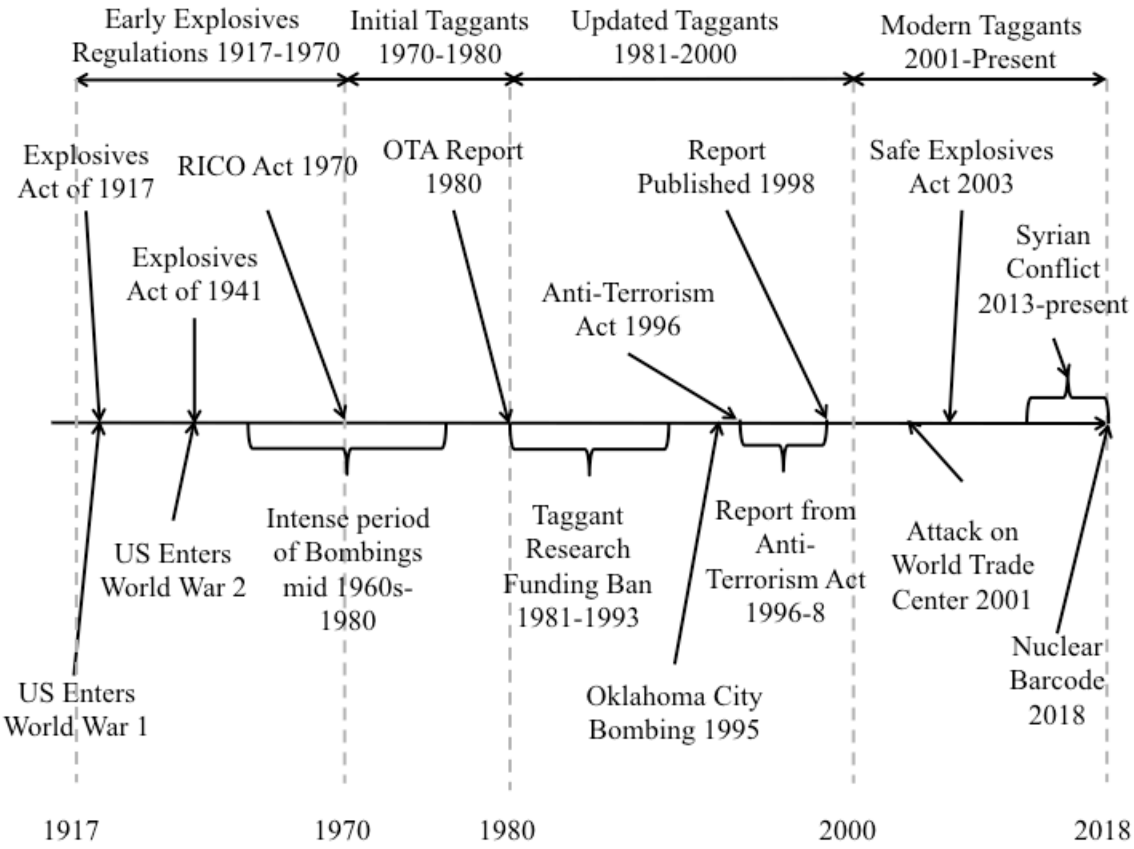


Figure 7.1. Nuclear Barcode's Position on Timeline of Explosive Legislation and Taggant Efforts

These two uses of NAA suggest a good candidate identification taggant for explosives: introduce very small, parts per billion level quantities of trace elements during manufacture. Utilizing a unique combination of these elements would create a way of tracing manufactured explosives.

The nuclear barcode's performance is compared to the performance of other taggant technologies in Table 7.1, which adds the nuclear barcode to Table 2.5 on the same one to five scale, with a score of five meaning the taggant technology performs extremely well in that category or is incredibly cheap, and a score of one meaning the opposite. The nuclear barcode scores highly across all criteria. Post-blast residues are produced by every

Table 7.1. Comparison of Different Taggant Technologies with Nuclear Barcode

Taggant	Recoverability	Survivability	Utility	Compatibility with Explosives	Cost	Total Score
Radiological [1]	5	5	3	5	4	22
Chemical [2, 1]	3	3	5	4	3	21
Physical (or Particulate) [2, 1]	5	5	4	4	4	22
Isotopic [2]	5	5	5	5	1	21
Biological [2]	3	3	5	5	2	18
Nuclear Barcode	5	5	5	5	4	24

detonation, and can be collected with a cotton ball, giving the nuclear barcode a high recoverability score. The taggant elements are not destroyed during detonation, giving it a high score in the survivability category. The ability to produce many unique codes gives the nuclear barcode its high utility score. At the low concentrations used, the taggant elements that make up the nuclear barcode are compatible with explosives. And the high cost of taggant materials is mitigated by the extremely low concentrations enabled by the accuracy of NAA. In total, the nuclear barcode exceeds, on a design basis, the scores of all earlier taggant categories.

Testing of aqueous solutions containing three candidate taggant elements (holmium, samarium, and europium) as well as post-blast residues of explosives that had these elements introduced was performed. It was found that the mass of the post-blast residue that was recovered from tests using Composition B as an explosive was approximately two orders of magnitude less than the quantity of post-blast residue that was recovered from tests using binary explosive. This testing at the MSTR produced inaccurate measurements of the concentrations of the taggant elements. The sources of this inaccuracy were reduced to five possible NAA parameters: the neutron flux that the samples are exposed to; the efficiency of the detector used; the length of time the sample is irradiated; the length of time the sample is counted; and the delay time, the length of time between the irradiation and counting of the sample.

This prompted an experiment to be carried out on the effect of the delay time between irradiating and counting the sample on the uncertainty in the measurement. This experiment was performed based on interesting results in the uncertainties that occurred when scheduling at the MSTR, equipment malfunction, or the variable time needed for an irradiated sample to cool sufficiently to be safely handled caused longer than expected delays. For these experiments it was assumed that although the measurements of the absolute concentration and concentration uncertainty were incorrect, any trends in the observed measurements were real. It was further assumed that the magnitude of these effects would likely change when correct measurements of the concentration could be taken, but they would not disappear.

Using these assumptions, it was observed that the uncertainty in the measured concentration increases once the delay time exceeds a critical value of approximately 2.5 or 3 half-lives. Additionally, the increase in uncertainty as delay time increases appears to be constant for most samples from immediately after irradiating until the critical value. However, after the critical value, the uncertainty appears to increase faster. This implies that there are two regions in the measured uncertainty: after the critical delay time the measured uncertainty is dominated only by the delay time, whereas before the critical delay time, the measured uncertainty is dominated by at least one factor that is not the delay time.

7.2. NUCLEAR BARCODE MATERIALS COSTS

The Nuclear Barcode uses low concentrations of taggant elements for two purposes. The first is to make the Nuclear Barcode stealthy, or difficult to detect without specialized equipment and knowledge. It is expected that this difficulty will make the Nuclear Barcode extremely difficult to fake by most groups. The second purpose is to reduce the material cost. Rare earth and platinum group metals are used because of their superior properties when it comes to NAA, however these metals are also expensive. Iridium is the most expensive metal, with a price of approximately $1,200 per troy ounce in 2018. This puts iridium metal at approximately $40 per gram. Assuming that the average concentration of iridium used in a unique tag is 2,000 ppb, then one gram of iridium could be used to tag 500 kg of explosives, and would add a cost of $0.08 per kg of explosive, or $0.036 per pound. The other elements used are not nearly expensive, so the major materials cost driver of the Nuclear Barcode will be iridium in normal economic circumstances. This is a small increase in the total price, and can be further mitigated by reducing the concentrations of relatively expensive metals like iridium, rhenium, and europium, and increasing the concentrations of relatively cheap metals such as holmium or samarium.

8. CONCLUSIONS AND RECOMMMENDATIONS

8.1. CONCLUSIONS

8.1.1. Taggant Survivability. The survivability of the Nuclear Barcode was assessed by the tests described in Section 4. The conclusions listed below are directly shown by the results presented in Section 5.

- All three taggant elements tested (holmium, samarium, europium) can be identified by NAA
- All three taggant elements tested can be identified in aqueous solutions at concentrations of 100 ppb and above
- All three taggant elements have distinct peaks that are separated from the peaks produced by the other taggant elements
- All three taggant elements have been identified in the post-blast residue.
- Other elements present in the post-blast residue do not interfere with identifying the peaks of the three taggant elements or measuring the number of counts under these peaks.

- Short half-life of europium makes it hard to detect in the post-blast residue due to the length of the delay time required to safely handle and measure the samples.

- The introduction of the taggants, either as aqueous solutions or solid salts did not affect the performance of the explosives which detonated in every test.

8.1.2. Delay Time Effects on Uncertainty. The effects of delay time on the uncertainty in the measured concentration were tested in Section 6. The conclusions listed below follow from these results.

- Concentration measurements stay approximately constant.

- Equation 3 is verified to be accurately compensating for the delay time.

- Uncertainty in the measured concentration increases as delay time increases.

- After approximately 2.5 half-lives, the uncertainty in the measured concentration is greater than when measured immediately after irradiating.

- The change in uncertainty in the measured concentration increases as the delay time increases.

- Uncertainty in the measured concentration increases faster from 2.5 half-lives to 3.5 half-lives than at any other times measured.

- The effect of the delay time dominates uncertainty in measured concentration after 2.5 half-lives.

8.2. NUCLEAR BARCODE RECOMMENDATIONS

This research has shown that explosives tagged with holmium, samarium, and europium have some potential for use as an identification taggant. These elements can be detected by NAA in the post-blast residue produced by detonation of the tagged explosive, and collected by sampling a piece of material where these detonation products settle. Neutron activation analysis is a proven method for analyzing concentrations, but the method used in this research is not able to accurately determine the concentrations. While using NAA, it is important to understand the contribution of the delay time to the overall uncertainty. Although it is not always possible due to safety concerns, samples should ideally be counted within one half-life of the activated isotopes after irradiation to obtain the results with the lowest uncertainty, and to ensure that all of the taggant elements are identified, and no later than 2.5 half-lives after irradiating. Table 8.1 lists the maximum delay time corresponding to 2.5 half-lives after irradiating the eight elements identified as possible candidates (Eu, Dy, Ho, Lu, Sm, Ir, Re, and Rh), assuming they behave similarly to holmium [27]. Due to the problems observed with detecting the activated form of europium in the post-blast residue, any element used in the Nuclear Barcode should have a half-life of longer than 10 hours. It has been observed from the post-blast tests that an approximately 48 hour delay is the minimum required to safely handle the samples when irradiated under the test conditions used. This would eliminate any elements that have a maximum delay time of less than 48 hours.

Table 8.1. Maximum Delay Time for Candidate Elements

Element	Active Isotope	Half-Life	Maximum Delay Time
Europium	Eu-152m1	9.2 hours	23.1 hours
Dysprosium	Dy-159	144.4 days	361 days
Holmium	Ho-166	26.8 hours	67 hours
Lutetium	Lu-177	6.6 days	16.6 days
Samarium	Sm-153	46.3 hours	115.7 hours
Iridium	Ir-194	19.3 hours	48.2 hours
Rhenium	Re-186	3.7 days	9.3 days
Rhodium	Rh-104	42.3 seconds	105.8 seconds

As Table 8.1 shows, this eliminates the use of Eu-152m1 and Rh-104, with Ir-194 falling just beyond this cutoff. Europium produces other isotopes as well, but these were not found during testing of aqueous solutions of europium. The significantly longer half-lives of Eu-152 and Eu-154 (13.5 and 8.6 years respectively) would require that the sample be measured soon after irradiation for shorter lived isotopes such as holmium and samarium, and then would need to be measured again after several weeks or months have elapsed to identify the concentration of europium in the sample. This would drastically increase the time required for testing and therefore slow down any criminal investigation.

Rhodium produces no other isotopes during irradiation. Due to their short half-lives, europium and rhodium should not be used in the Nuclear Barcode unless that limitation can be overcome.

Of the remaining six elements, the only concern is the particularly long lived Dy-159 isotope. Longer lived isotopes produce fewer gammas per unit of time, and thus would require longer counting times. A solution that might overcome this issue would be to perform a 1 hour count as soon as possible to identify the five elements that are not eliminated. After this count, a longer 8, 16, or 24 hour count might yield enough gammas from Dy-159 to accurately identify the concentration. Assuming this is the case, and that no other elements are introduced, this reduces the maximum, theoretical, total number of unique combinations from 40^8 to 40^6. This results in a total of 4.1 billion potential combinations for use with the Nuclear Barcode.

Utilizing some assumptions, the utility of the 4.1 billion codes can be estimated. In the US, 3.1 million metric tons of explosives were sold for use in 2014 [6]. Assuming that the US represents approximately 20 to 25% of the world explosive market, the global production and sale of explosives in one year is 15.5 million metric tons. Assuming that the average size of a batch of explosives is 5000 kg, or just over 10,000 pounds, then for an identification taggant scheme that uses a unique code per batch of explosives a total of 3.1 million unique codes will be used to tag one year of production. Not all explosive products are produced in the same size batch, with specialist products such as boosters or dynamite produced in much smaller quantities than ANFO. To account for these variations, it will be assumed that 10 times more codes are required than estimated based on the batch size of 5000 kg, meaning that 31 million unique codes must be used each year. At this rate, the 4.1 billion codes produced by the nuclear barcode will last for 132 years before having to repeat codes. This should be a sufficient length of time, as most companies do not survive for 130 years, let alone retain consumables for this length of time.

9. FUTURE WORK

The research presented here was performed in the greater context of developing an identification taggant for explosives that encodes information about the explosive in a unique combination of concentrations of several uncommon elements. The results of this research show that while the presence of these elements can be identified in many circumstances, it is not currently possible to accurately measure the concentration of the three candidate taggant elements at the MSTR. This must be corrected before any further research on a taggant like the Nuclear Barcode is performed.

This research suggests two explanations for the inability to measure the concentrations. First, the efficiency of the detector as a function of the energy of the incident gamma ray needs to be well characterized. A factor complicating this characterization is that there is a geometric component to this efficiency. The detector is relatively small (2 inch by 2 inch), and therefore only some gammas will be encountered by the detector and potentially be measured. A method to ensure that the geometric component is consistent will be needed. Secondly, more recent tests suggest that the reactor flux profile has changed since it was last measured. Characterizing the reactor flux profile can be done using the ASTM E262 standard method. An alternative method would be to perform future irradiations simultaneously with a reference standard. Once these two parameters are determined, it will be possible to determine if the concentration measurement problems that this research has encountered are due solely to the aforementioned factors, or a product of the Nuclear Barcode taggant method.

In addition to characterizing the detector efficiency and the reactor flux, to truly optimize NAA results, it is necessary to optimize the irradiation time, the counting time, and the delay time. This research presents results on the effect of increasing the delay time on the uncertainty in the concentration measurement. The effects of the other four parameters must be resolved as well to optimize the effectiveness of NAA.

The measured uncertainty in the concentration of the taggant elements was most dependent on two factors. For the single and multi-element standard solutions, approximately 80 to 90% of the uncertainty was from the uncertainty in the number of counts under the peak used. Future work to improve this by counting for a longer time, or using some other means to reduce this contribution would vastly reduce the uncertainties in these measurements. For post-blast samples, and especially the Composition B post-blast samples, the mass of post-blast residue recovered was often a significant contribution to the measured uncertainty. In order to calculate the uncertainty of the post-blast samples, the mass of the element measured using NAA is calculated using Equation 3. This mass is then divided by the mass of the collected post-blast residue. The measured uncertainty takes the total derivative of this equation with respect to both masses. Therefore, when the mass of the post-blast residue is approximately equal to the minimum that the balance can measure, the measured uncertainty becomes completely dominated by the total mass of post-blast residue and the uncertainty in the measurement of the mass of post-blast residue that is recovered.

This work utilized the one group approximation for neutron flux in the derivation of Equation 3, and assumed that all neutrons were thermalized in the reactor and reduced to low energies. Future work should include the resonance integral contribution in this derivation, since the resonance integral for the elements holmium, samarium, and europium is large, and therefore any intermediate energy neutrons will have a high probability of being captured. Adding this term will reduce the measured concentration of the taggant elements in all measurements. The magnitude of this effect will depend on both the resonance integrals of the taggant elements and the intermediate flux of the MSTR.

Utilizing taggants on a research scale presented special challenges. Ways to optimally introduce the taggant elements into the explosives and to ensure that they are evenly mixed throughout the undetonated explosive need to be investigated. This research introduced the taggant elements as aqueous solutions of sulfate salts into the liquid phase of the binary explosive (nitromethane) or to liquid Composition B before casting. Some experiments also introduced the salts directly into either of these two phases. Regardless of how the taggant was introduced, the liquid phase was stirred thoroughly before being mixed with the solid phase (in the case of the binary explosive) or cast and allowed to cool (in the case of Composition B). The small quantities of taggants needed to tag the explosives at the concentrations desired made it impossible to verify that the salts or solutions were evenly mixed throughout the explosive, and it was hoped that any poor mixing would be compensated by additional mixing that would occur during detonation. Ethanol based solutions containing rare earth elements were tested previously and would likely have higher miscibility with the liquid phases, but prior research noted that the use of ethanol sensitized tagged explosives [1].

Further research will also need to be performed on the effect of the delay time between irradiating and counting a sample. It is assumed that the results presented in this accurately show the presence or absence of the different elements by measuring a total number of net counts greater than the uncertainty in this number. Tests on solutions of holmium show that the ratio of uncertainty to net counts sometimes decreases after a short number of half-lives when an element with a shorter half-life than the taggant element is present. This might allow for future variations of the Nuclear Barcode to use lower concentrations or have more concentration levels if the effect persists.

Further experiments on the delay time and the measured uncertainty should also be carried out and extended to longer delay times. Short delay times showed a critical delay time of approximately 2.5 to 3 half-lives was when the uncertainty in the measured concentration became dominated by delay time effects. Assuming this result can be reproduced, carrying out tests beyond 4 half-lives would prove useful as the isotope of europium used in the post-blast tests had a delay time between 7 and 10 half-lives. Any change of behavior in this range would strengthen the observation made in Section 6 that a change in the rate at which the uncertainty in the measured concentration is increasing indicates a change in the relative magnitudes of the delay time contribution.

Future testing of the Nuclear Barcode should be performed before determining if it is a viable identification taggant. The tests below are ordered based on the current state of the Nuclear Barcode and where the most significant improvements can be found, with the first five being more important than the final two.

- Calibrate the HPGe detector so that accurate measurements by NAA can be obtained.

- Accurately determine the flux profile of the MSTR.

- Determine optimal counting time for each taggant element and reduce the uncertainty in the number of counts under a peak by an order of magnitude.

- Methods of adding and evenly mixing the taggant with the explosive during the manufacturing process.

- Determine feasibility of utilizing longer-lived isotopes such as Eu-152 and Dy-159 in the Nuclear Barcode.

- Effect of sample geometry and orientation on measurement of concentrations.

- Effect of distance from site of the blast to the sampling area on the measured concentration of taggant elements.

Assuming these extra tests are successful, then the Nuclear Barcode is most likely a survivable identification taggant. *Taggants in Explosives* and *Marking and Rendering Inert* identified other characteristics in addition to survivability necessary for the widespread adoption of identification taggants: recoverability, utility for law enforcement, compatibility with explosives, safety in manufacture and use, no effect on explosive performance, compatibility with mined products, environmental acceptability, and cost of a taggant program. A future, full evaluation of an identification taggant program should test the performance of an identification taggant in these areas.

APPENDIX A.

DETAILED CALCULATION OF CONCENTRATIONS BY NEUTRON ACTIVATION ANALYSIS

This appendix provides a detailed, step-by-step calculation of the concentration of the taggant elements found in one sample. All concentrations in the previous sections were calculated using this method. Equation 3, first presented in Section 2.2, describes how to calculate the mass of any element found in a sample when performing NAA. This equation was used to determine the mass of the taggant elements used in the course of the experiments described in the previous sections: holmium, samarium, and europium. From these masses, concentrations of these taggant elements could then be obtained by dividing the mass of the taggant element(s) found by the total mass of the analyzed sample. Equation 3 is reproduced below for ease of reference.

$$m = C\frac{\lambda}{((1-e^{-\lambda t_i})e^{-\lambda t_d}(1-e^{-\lambda t_m})} * \frac{M_a}{\Phi_{th}\sigma_{eff}\Gamma\varepsilon\theta N_A}$$

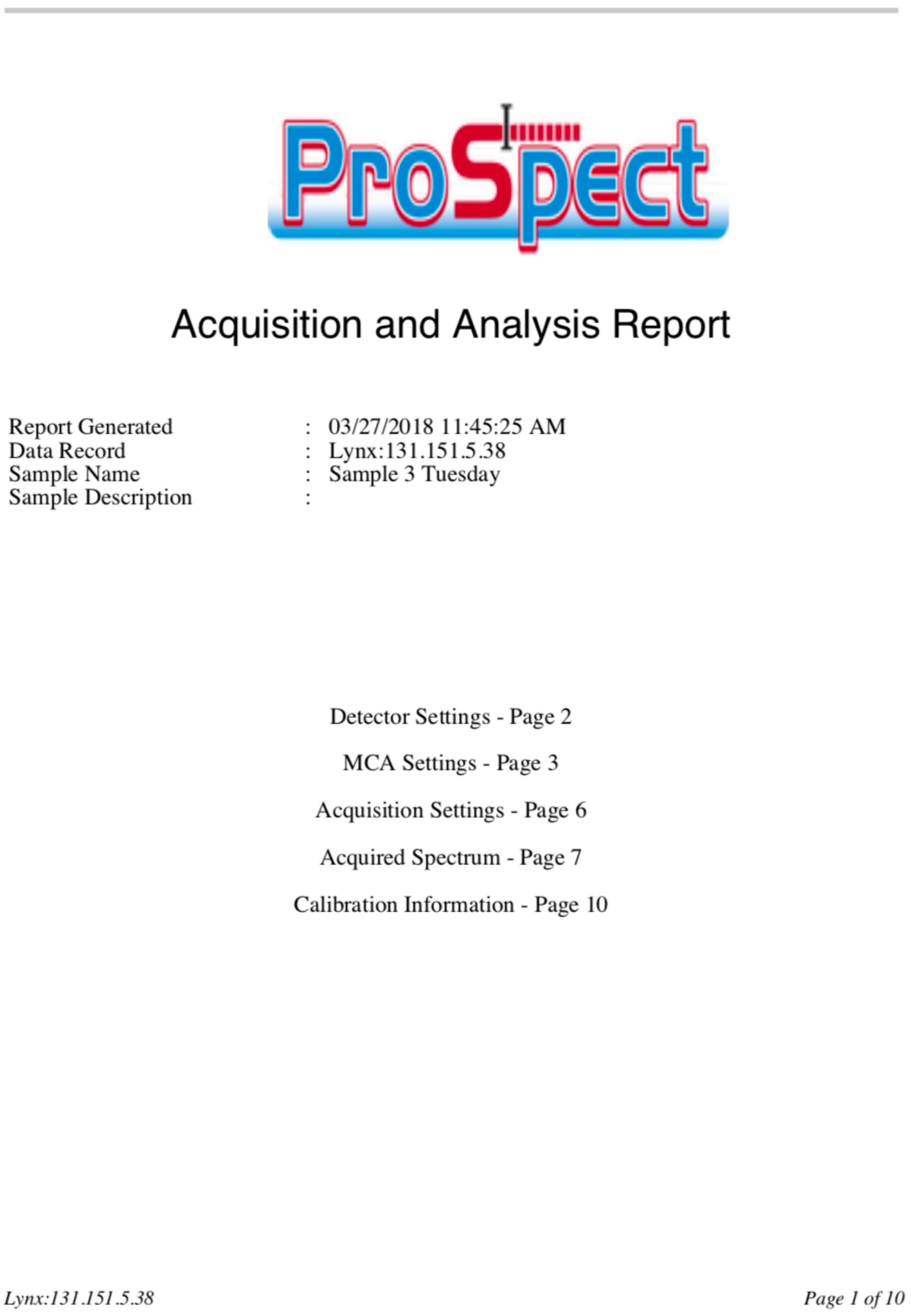
Of the 13 terms used in equation 3 to calculate the mass, two are universal constants: e, the base of the natural logarithm; and N_A, Avogadro's number, and can be obtained from any number of references. Five of these quantities are constants that depend on the element that is being investigated: λ, the decay constant for the activated isotope of the element (that is, the isotope of the element that has captured a neutron during irradiation, and calculated by dividing ln(2) by the half-life of the isotope in seconds) under investigation; M_a, the molecular weight of the nonactivated isotope of the element; σ_{eff}, the probability that a neutron is absorbed by the nucleus of the nonactivated isotope (under a one group assumption where it is assumed that all neutrons can be assumed to be thermalized, the value used is the thermal capture cross section); Γ, the fraction of all radioactive decays by an activated isotope that produce a gamma ray of the energy being investigated; and θ, the natural abundance of the nonactivated isotope of the element (the fraction of all atoms of this element that are the specific isotope that's activation is being investigated). These four values can be obtained from reference sources such as the IAEA's Nuclear Data Service.

Three parameters are set by the experimenter: t_i, the time that the sample is irradiated; t_m, the time that gamma rays are counted by the detector, and t_d, the delay time between irradiating and counting the sample. The first two time parameters are set in advance by the experimenter, the third parameter is often set by scheduling constraints. The MSTR takes approximately 60-90 minutes to start up and reach the power used by these experiments. As the irradiation time used is only 10 minutes, and samples are being counted for one hour, it is inefficient to start up the reactor to irradiate only one sample, and operating the reactor with no sample in it for 50 minutes between samples is not practically feasible either. As a result, several samples were typically irradiated at the same time, and then counted over the course of a day or several days. This resulted in a range of delay times used, and prompted an investigation of the effects of the delay time that is shown in Section 6.

Ten of the thirteen parameters are therefore set by the experimenter or are standard values that can be found in references. The next parameter, C, is the number of counts in the peak at the gamma energy corresponding to the element being investigated that is measured by the detector. Modern detectors are generally made from high purity germanium (HPGe) that is cooled by liquid nitrogen.

These detectors are intrinsic semiconductors and when a gamma photon hits the detector, it triggers a cascade of physical reactions by electrons that produce a signal that can be measured. This signal can be separated using microprocessors based on the energy of the gamma photon that hit the detector. HPGe detectors are sensitive to photons in the range of approximately 10 keV to approximately 3000 keV depending on the exact model of detector used. This energy range is broken down into a number of different 'channels' or 'bins' with a typical number being 16384 unique energies (2^{14}). The second last parameter, ε, is the efficiency of the detector. This efficiency is a measurement of the probability that a gamma photon emitted by an activated isotope interacts with the detector and produces a signal in the electronics that is then recorded. The last parameter, Φ_{th} is the neutron flux that the sample is exposed to during irradiation. At the MSTR, this parameter was assumed to be the thermal flux produced by the reactor while operating at its full, 200 kW power limit. It is assumed, for the purposes of these calculations, that the flux is described only by neutrons that have been thermalized (that is, have a kinetic energy between 0 eV and 0.0273 eV) by interacting with the water used to cool the core. Prior measurements by Dr. Castano and others established that the overwhelming proportion of the flux produced by the MSTR falls within the range of thermal neutrons. These last two parameters must be determined by experiment before they can be used to calculate the mass using NAA.

The measured counts from the detector are fed into a software program called ProSpect. One component of this software produces a report which summarizes the spectrum and provides counts and uncertainties in the counts for the number of gamma photons at certain peaks. A full report is shown below as Figure A.1.



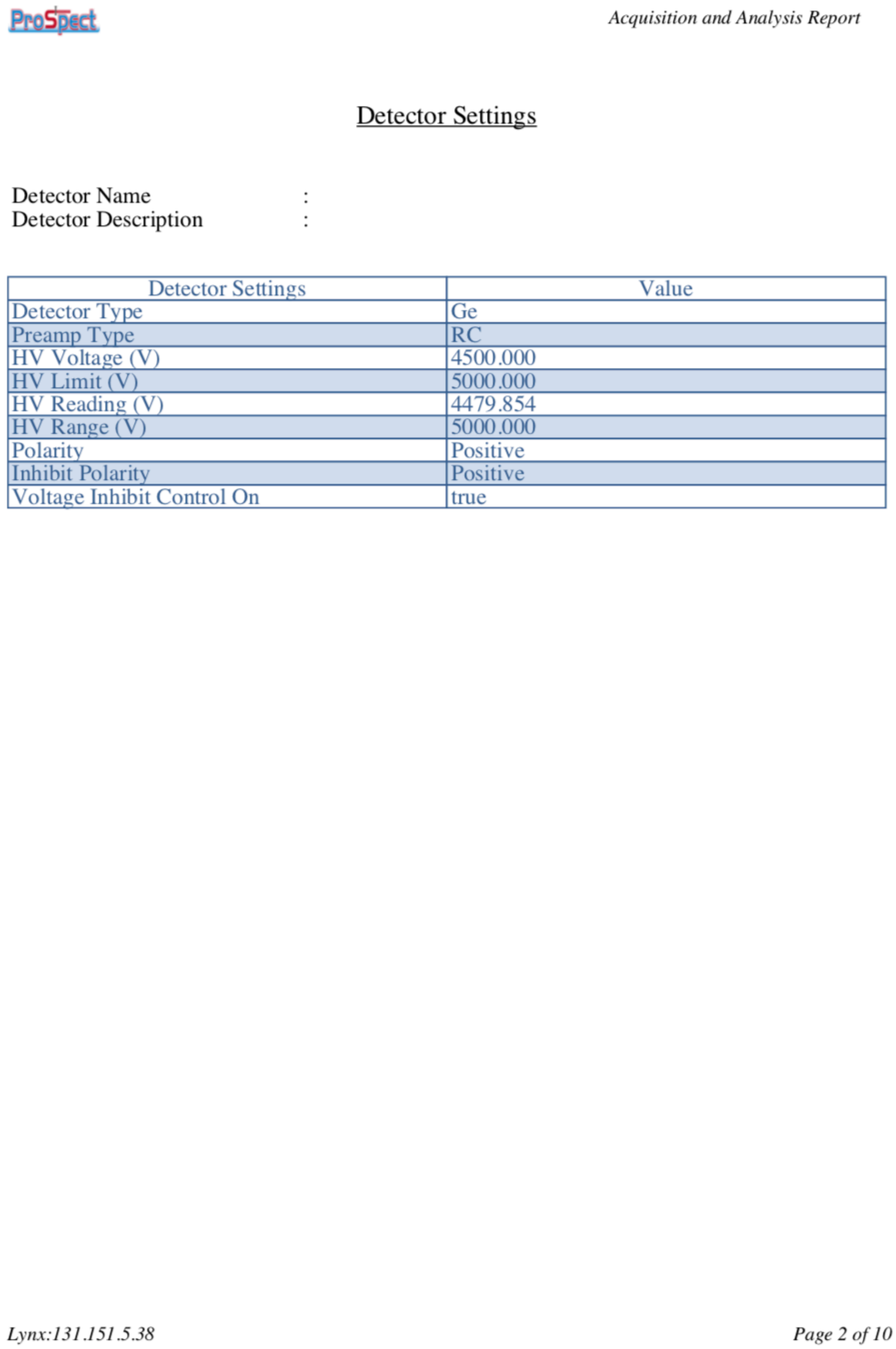
ProSpect

Acquisition and Analysis Report

Report Generated : 03/27/2018 11:45:25 AM
Data Record : Lynx:131.151.5.38
Sample Name : Sample 3 Tuesday
Sample Description :

Lynx:131.151.5.38 *Page 1 of 10*

Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life)

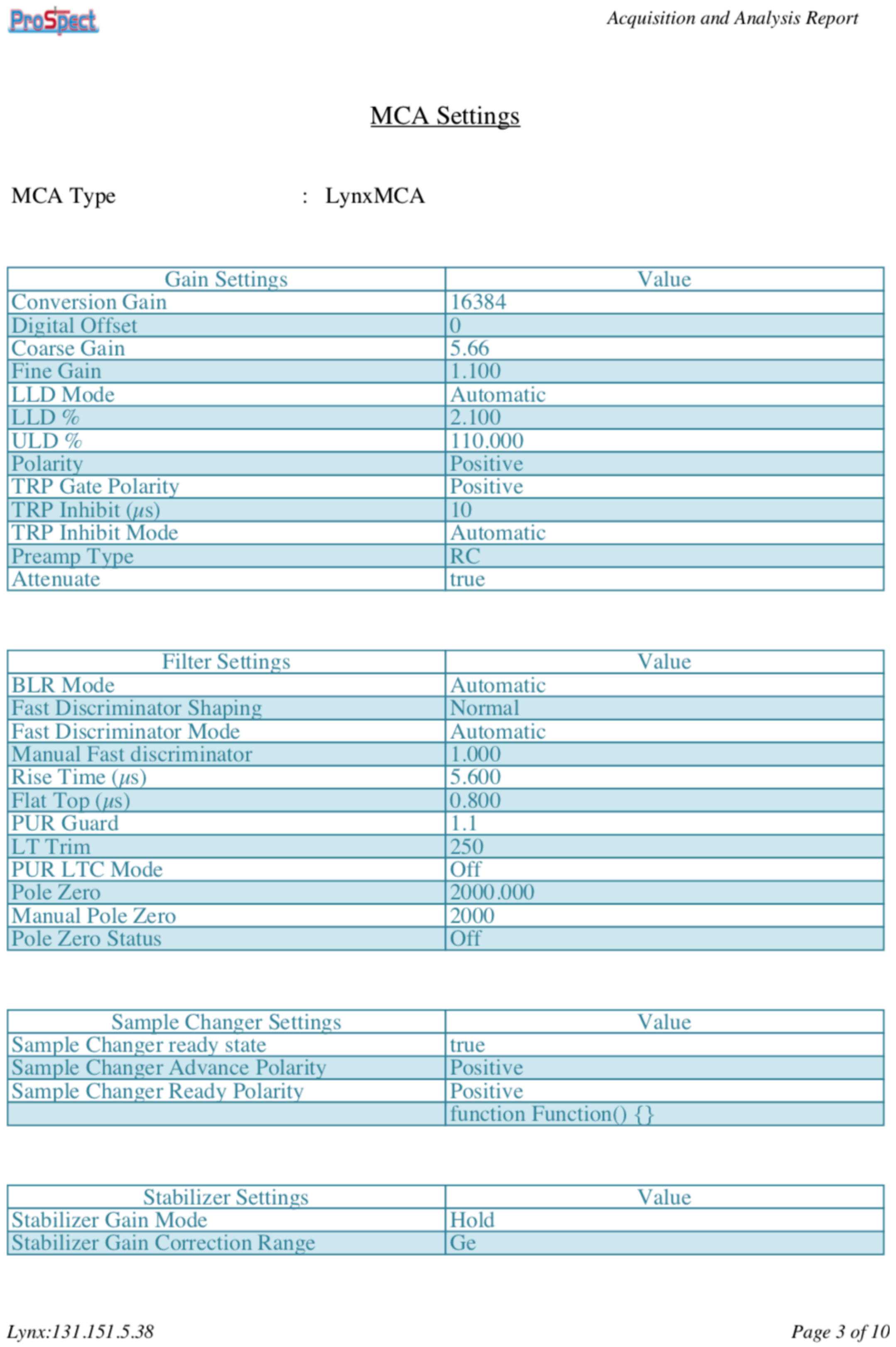


Detector Settings

Detector Name :
Detector Description :

Detector Settings	Value
Detector Type	Ge
Preamp Type	RC
HV Voltage (V)	4500.000
HV Limit (V)	5000.000
HV Reading (V)	4479.854
HV Range (V)	5000.000
Polarity	Positive
Inhibit Polarity	Positive
Voltage Inhibit Control On	true

Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)



ProSpect

Acquisition and Analysis Report

MCA Settings

MCA Type : LynxMCA

Gain Settings	Value
Conversion Gain	16384
Digital Offset	0
Coarse Gain	5.66
Fine Gain	1.100
LLD Mode	Automatic
LLD %	2.100
ULD %	110.000
Polarity	Positive
TRP Gate Polarity	Positive
TRP Inhibit (μs)	10
TRP Inhibit Mode	Automatic
Preamp Type	RC
Attenuate	true

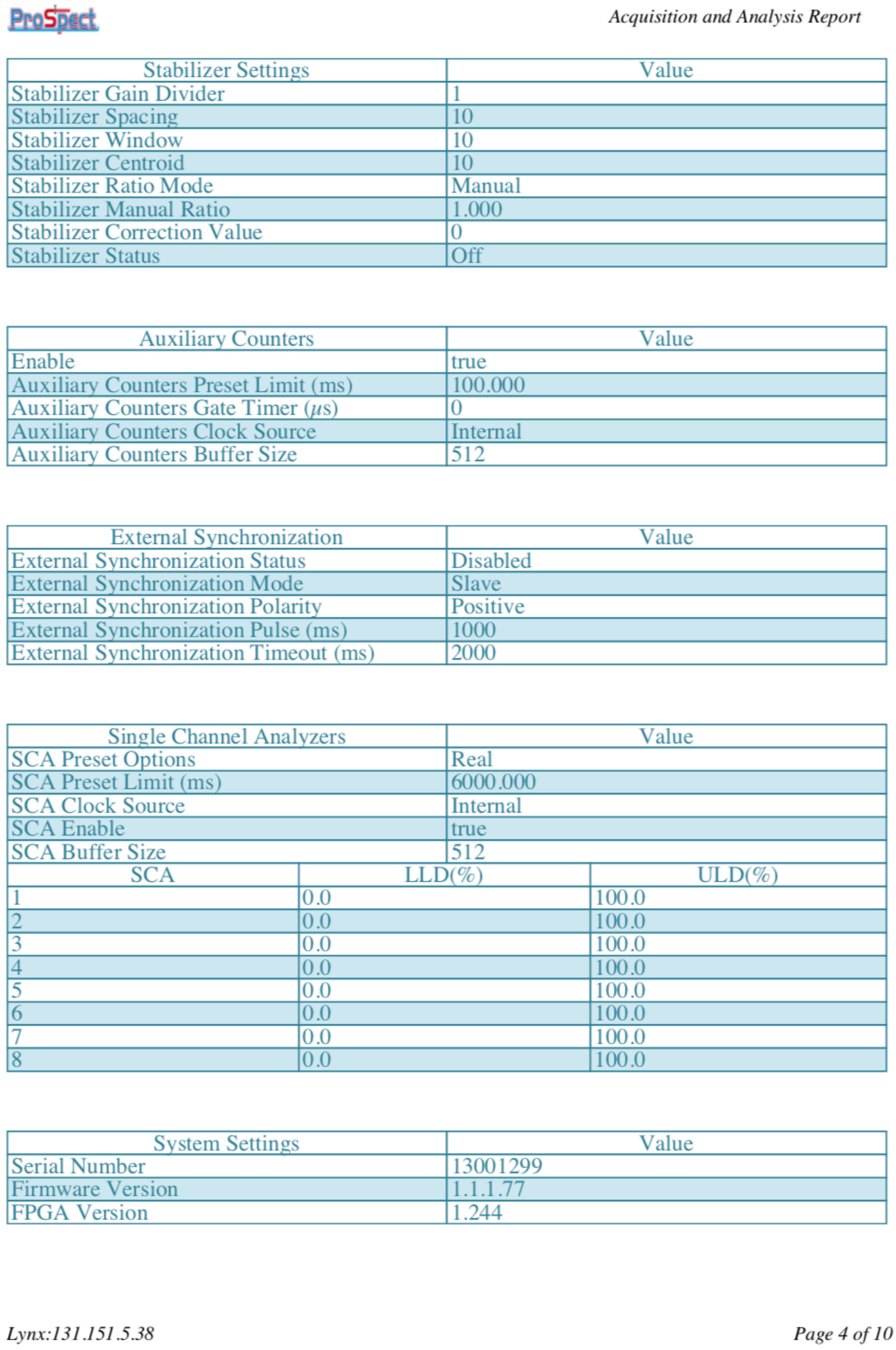
Filter Settings	Value
BLR Mode	Automatic
Fast Discriminator Shaping	Normal
Fast Discriminator Mode	Automatic
Manual Fast discriminator	1.000
Rise Time (μs)	5.600
Flat Top (μs)	0.800
PUR Guard	1.1
LT Trim	250
PUR LTC Mode	Off
Pole Zero	2000.000
Manual Pole Zero	2000
Pole Zero Status	Off

Sample Changer Settings	Value
Sample Changer ready state	true
Sample Changer Advance Polarity	Positive
Sample Changer Ready Polarity	Positive
	function Function() {}

Stabilizer Settings	Value
Stabilizer Gain Mode	Hold
Stabilizer Gain Correction Range	Ge

Lynx:131.151.5.38 *Page 3 of 10*

Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)



ProSpect

Acquisition and Analysis Report

Stabilizer Settings	Value
Stabilizer Gain Divider	1
Stabilizer Spacing	10
Stabilizer Window	10
Stabilizer Centroid	10
Stabilizer Ratio Mode	Manual
Stabilizer Manual Ratio	1.000
Stabilizer Correction Value	0
Stabilizer Status	Off

Auxiliary Counters	Value
Enable	true
Auxiliary Counters Preset Limit (ms)	100.000
Auxiliary Counters Gate Timer (μs)	0
Auxiliary Counters Clock Source	Internal
Auxiliary Counters Buffer Size	512

External Synchronization	Value
External Synchronization Status	Disabled
External Synchronization Mode	Slave
External Synchronization Polarity	Positive
External Synchronization Pulse (ms)	1000
External Synchronization Timeout (ms)	2000

Single Channel Analyzers	Value
SCA Preset Options	Real
SCA Preset Limit (ms)	6000.000
SCA Clock Source	Internal
SCA Enable	true
SCA Buffer Size	512

SCA	LLD(%)	ULD(%)
1	0.0	100.0
2	0.0	100.0
3	0.0	100.0
4	0.0	100.0
5	0.0	100.0
6	0.0	100.0
7	0.0	100.0
8	0.0	100.0

System Settings	Value
Serial Number	13001299
Firmware Version	1.1.1.77
FPGA Version	1.244

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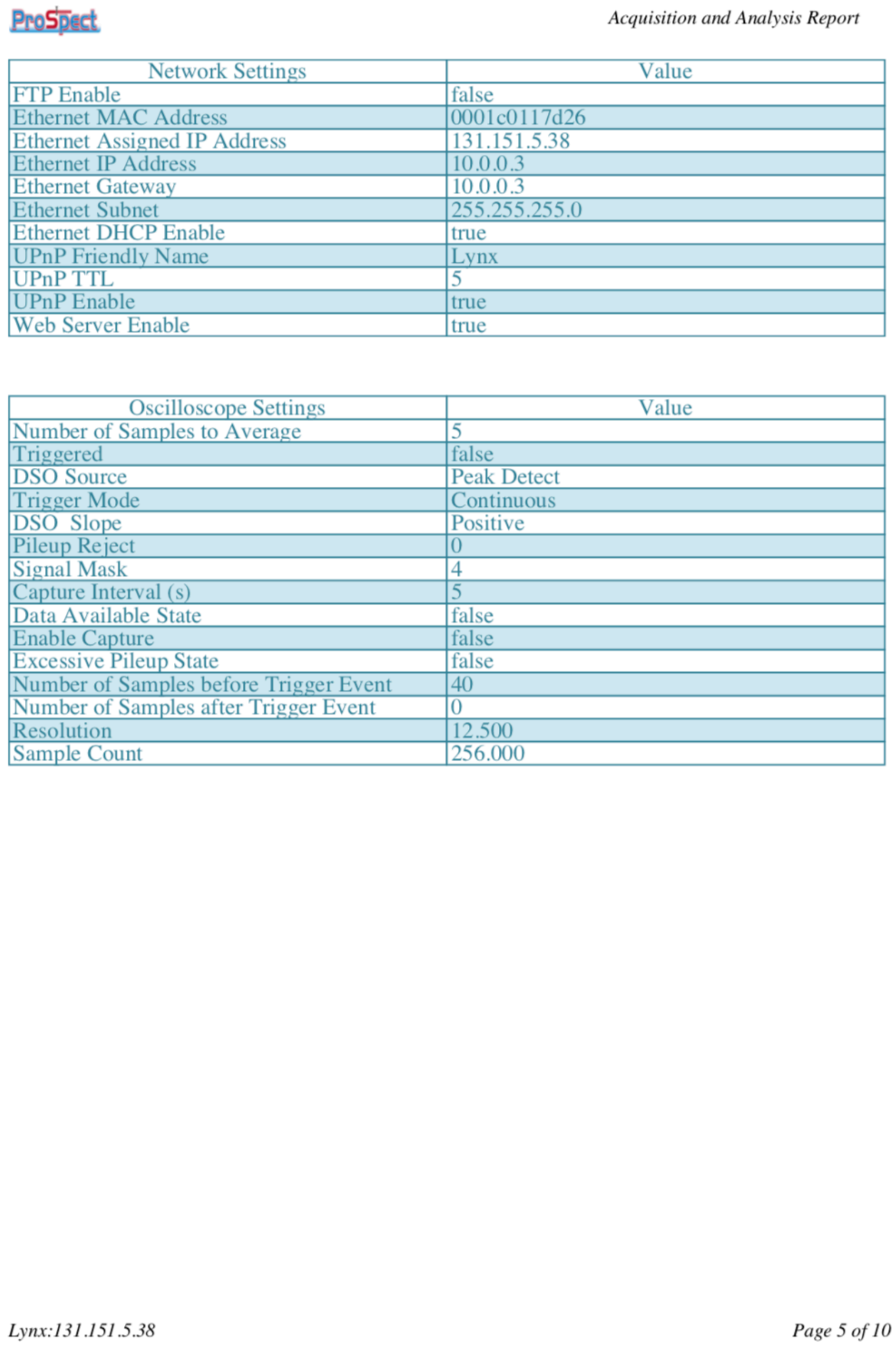
Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)



Acquisition and Analysis Report

Network Settings	Value
FTP Enable	false
Ethernet MAC Address	0001c0117d26
Ethernet Assigned IP Address	131.151.5.38
Ethernet IP Address	10.0.0.3
Ethernet Gateway	10.0.0.3
Ethernet Subnet	255.255.255.0
Ethernet DHCP Enable	true
UPnP Friendly Name	Lynx
UPnP TTL	5
UPnP Enable	true
Web Server Enable	true

Oscilloscope Settings	Value
Number of Samples to Average	5
Triggered	false
DSO Source	Peak Detect
Trigger Mode	Continuous
DSO Slope	Positive
Pileup Reject	0
Signal Mask	4
Capture Interval (s)	5
Data Available State	false
Enable Capture	false
Excessive Pileup State	false
Number of Samples before Trigger Event	40
Number of Samples after Trigger Event	0
Resolution	12.500
Sample Count	256.000

Lynx:131.151.5.38

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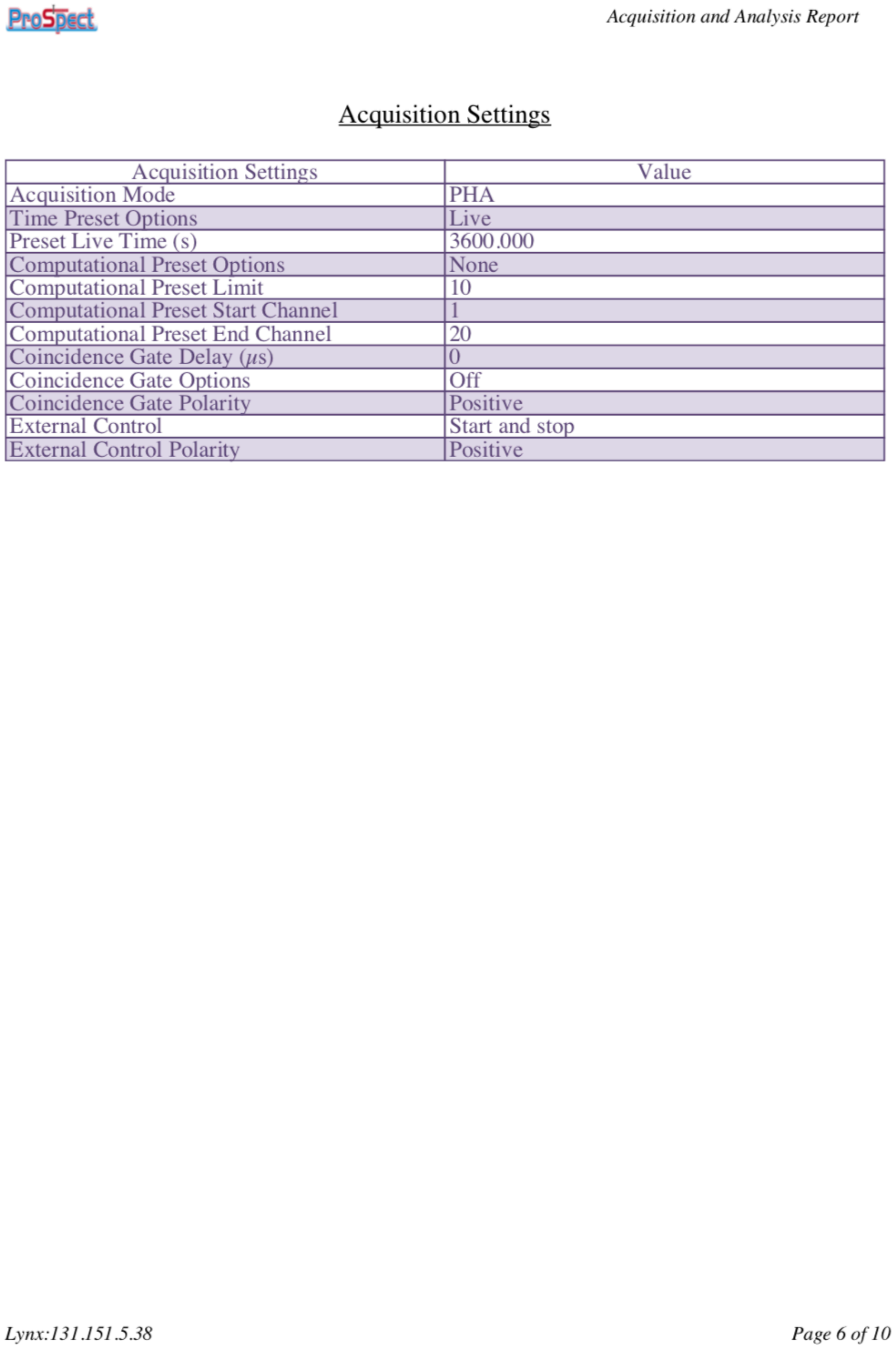
Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)



Acquisition and Analysis Report

Acquisition Settings

Acquisition Settings	Value
Acquisition Mode	PHA
Time Preset Options	Live
Preset Live Time (s)	3600.000
Computational Preset Options	None
Computational Preset Limit	10
Computational Preset Start Channel	1
Computational Preset End Channel	20
Coincidence Gate Delay (μs)	0
Coincidence Gate Options	Off
Coincidence Gate Polarity	Positive
External Control	Start and stop
External Control Polarity	Positive

Lynx:131.151.5.38

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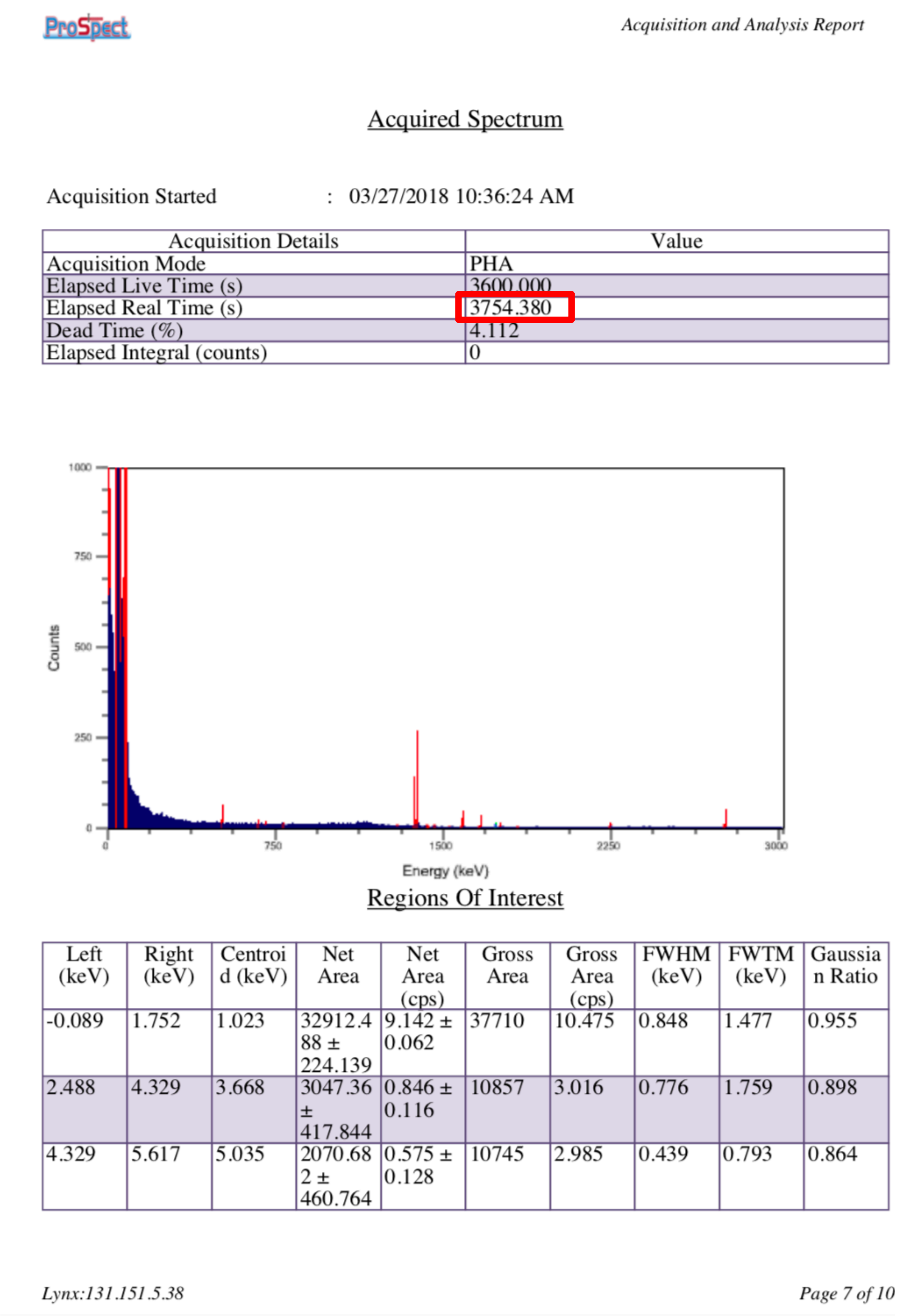
Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)



ProSpect *Acquisition and Analysis Report*

Acquired Spectrum

Acquisition Started : 03/27/2018 10:36:24 AM

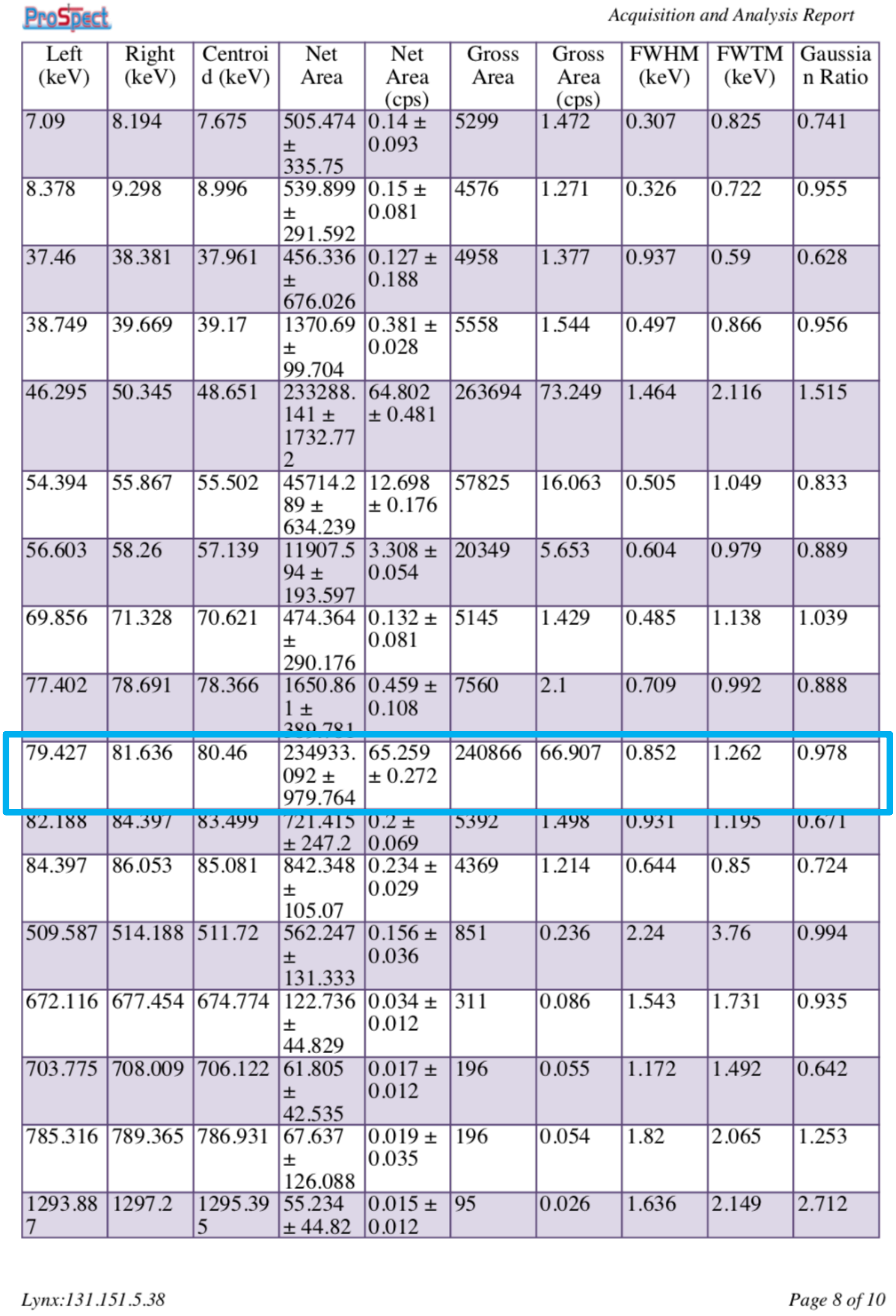
Acquisition Details	Value
Acquisition Mode	PHA
Elapsed Live Time (s)	3600.000
Elapsed Real Time (s)	3754.380
Dead Time (%)	4.112
Elapsed Integral (counts)	0

Regions Of Interest

Left (keV)	Right (keV)	Centroid (keV)	Net Area	Net Area (cps)	Gross Area	Gross Area (cps)	FWHM (keV)	FWTM (keV)	Gaussian Ratio
-0.089	1.752	1.023	32912.488 ± 224.139	9.142 ± 0.062	37710	10.475	0.848	1.477	0.955
2.488	4.329	3.668	3047.36 ± 417.844	0.846 ± 0.116	10857	3.016	0.776	1.759	0.898
4.329	5.617	5.035	2070.682 ± 460.764	0.575 ± 0.128	10745	2.985	0.439	0.793	0.864

Lynx:131.151.5.38 *Page 7 of 10*

Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)

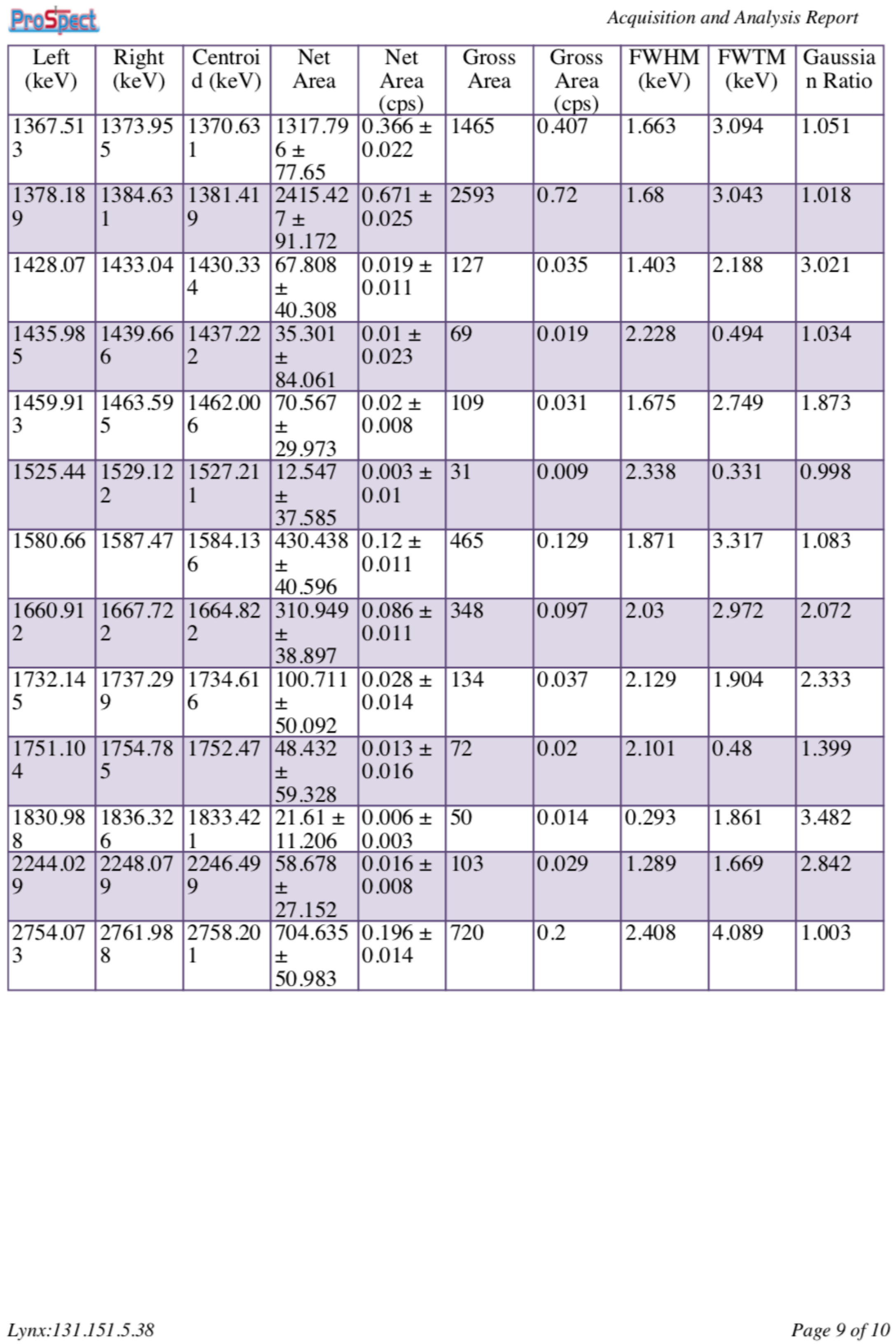


ProSpect *Acquisition and Analysis Report*

Left (keV)	Right (keV)	Centroid (keV)	Net Area	Net Area (cps)	Gross Area	Gross Area (cps)	FWHM (keV)	FWTM (keV)	Gaussian Ratio
7.09	8.194	7.675	505.474 ± 335.75	0.14 ± 0.093	5299	1.472	0.307	0.825	0.741
8.378	9.298	8.996	539.899 ± 291.592	0.15 ± 0.081	4576	1.271	0.326	0.722	0.955
37.46	38.381	37.961	456.336 ± 676.026	0.127 ± 0.188	4958	1.377	0.937	0.59	0.628
38.749	39.669	39.17	1370.69 ± 99.704	0.381 ± 0.028	5558	1.544	0.497	0.866	0.956
46.295	50.345	48.651	233288.141 ± 1732.772	64.802 ± 0.481	263694	73.249	1.464	2.116	1.515
54.394	55.867	55.502	45714.289 ± 634.239	12.698 ± 0.176	57825	16.063	0.505	1.049	0.833
56.603	58.26	57.139	11907.594 ± 193.597	3.308 ± 0.054	20349	5.653	0.604	0.979	0.889
69.856	71.328	70.621	474.364 ± 290.176	0.132 ± 0.081	5145	1.429	0.485	1.138	1.039
77.402	78.691	78.366	1650.861 ± 389.781	0.459 ± 0.108	7560	2.1	0.709	0.992	0.888
79.427	81.636	80.46	234933.092 ± 979.764	65.259 ± 0.272	240866	66.907	0.852	1.262	0.978
82.188	84.397	83.499	721.415 ± 247.2	0.2 ± 0.069	5392	1.498	0.931	1.195	0.671
84.397	86.053	85.081	842.348 ± 105.07	0.234 ± 0.029	4369	1.214	0.644	0.85	0.724
509.587	514.188	511.72	562.247 ± 131.333	0.156 ± 0.036	851	0.236	2.24	3.76	0.994
672.116	677.454	674.774	122.736 ± 44.829	0.034 ± 0.012	311	0.086	1.543	1.731	0.935
703.775	708.009	706.122	61.805 ± 42.535	0.017 ± 0.012	196	0.055	1.172	1.492	0.642
785.316	789.365	786.931	67.637 ± 126.088	0.019 ± 0.035	196	0.054	1.82	2.065	1.253
1293.887	1297.2	1295.395	55.234 ± 44.82	0.015 ± 0.012	95	0.026	1.636	2.149	2.712

Lynx:131.151.5.38 *Page 8 of 10*

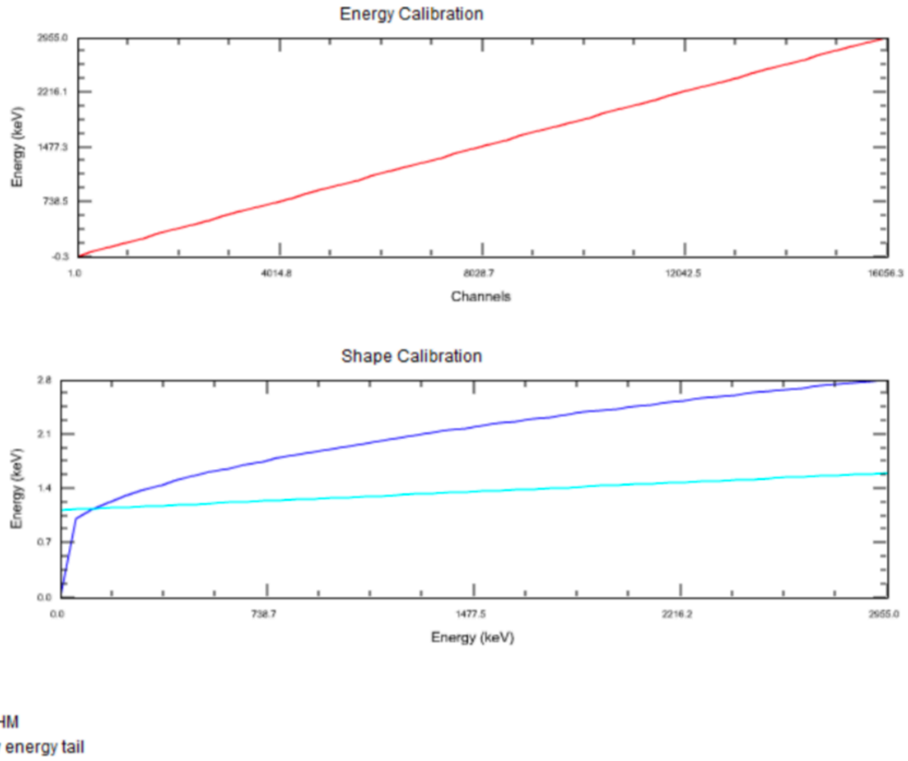
Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)



Left (keV)	Right (keV)	Centroid (keV)	Net Area	Net Area (cps)	Gross Area	Gross Area (cps)	FWHM (keV)	FWTM (keV)	Gaussian Ratio
1367.513	1373.955	1370.631	1317.796 ± 77.65	0.366 ± 0.022	1465	0.407	1.663	3.094	1.051
1378.189	1384.631	1381.419	2415.427 ± 91.172	0.671 ± 0.025	2593	0.72	1.68	3.043	1.018
1428.07	1433.04	1430.334	67.808 ± 40.308	0.019 ± 0.011	127	0.035	1.403	2.188	3.021
1435.985	1439.666	1437.222	35.301 ± 84.061	0.01 ± 0.023	69	0.019	2.228	0.494	1.034
1459.913	1463.595	1462.006	70.567 ± 29.973	0.02 ± 0.008	109	0.031	1.675	2.749	1.873
1525.44	1529.122	1527.211	12.547 ± 37.585	0.003 ± 0.01	31	0.009	2.338	0.331	0.998
1580.66	1587.47	1584.136	430.438 ± 40.596	0.12 ± 0.011	465	0.129	1.871	3.317	1.083
1660.912	1667.722	1664.822	310.949 ± 38.897	0.086 ± 0.011	348	0.097	2.03	2.972	2.072
1732.145	1737.299	1734.616	100.711 ± 50.092	0.028 ± 0.014	134	0.037	2.129	1.904	2.333
1751.104	1754.785	1752.47	48.432 ± 59.328	0.013 ± 0.016	72	0.02	2.101	0.48	1.399
1830.988	1836.326	1833.421	21.61 ± 11.206	0.006 ± 0.003	50	0.014	0.293	1.861	3.482
2244.029	2248.079	2246.499	58.678 ± 27.152	0.016 ± 0.008	103	0.029	1.289	1.669	2.842
2754.073	2761.988	2758.201	704.635 ± 50.983	0.196 ± 0.014	720	0.2	2.408	4.089	1.003

Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)

Calibration Information



	a		b	c	χ^2
Energy:	-0.457	+	0.184 Ch		Indeterminable
FWHM:	0.703	+	3.797e-2 $E^{.5}$		Indeterminable
Low Tail:	1.103	+	1.597e-4 E		Indeterminable

Continuum Type	Step
Continuum	8
Units	Chans

Figure A.1. ProSpect Report Holmium Delay Time Sample 3, (~1 half-life) (cont.)

Of the ten pages of the report, only two numbers are relevant to calculating the mass of the taggant element holmium [the sample was a 0.5 mL sample of 1 ppm holmium dissolved in DI water]. They are the total counting time shown in the red box on page 7 (3753.380 seconds), and the net area under the peak with a centroid at 80.46 keV which is the number in the fourth column of the row surrounded by a blue square on page 8 of the report (234933.092 ± 979.764 counts). It should be noted that in reality, it is impossible to have a fraction of a count, and therefore there should only be a whole number of counts. The fraction of a count arises from the method by which the net area under the peak is determined. First, the total area under the peak is measured by summing the counts for all of the channels that are part of the peak. Then, the average counts of the channels near but outside the peak are taken. These counts are assumed to represent the background, counts that arise from reflections or reemissions of gamma photons and do not correspond to any particular element. The average number of counts multiplied by the number of channels that make up the peak is then subtracted from the total area under the peak. This produces the net number of counts under a peak, and will almost always result in some fractional number of counts. For most peaks, the number of counts is very high, so rounding the counts to the nearest whole number will have no effect. The values for the parameters used to calculate the concentration of holmium in this example are shown in Table A.1 along with the uncertainties in these values.

Table A.1. Holmium mass calculation parameters

Parameter	Value	Units	Uncertainty in value (u_i)
e	2.71828	-	n/a
N_A	$6.022*10^{23}$	atoms/mol	$7.4*10^{15}$
λ	$7.17793*10^{-6}$	1/s	$3.21111*10^{-9}$
M_a	164.930328	g/mol	$2.7*10^{-6}$
σ_{eff}	$6.47*10^{-23}$	cm^2	$1.2*10^{-24}$
Γ	0.0656	-	0.0013
θ	1	-	n/a
t_i	600	s	5
t_m	3,753.380	s	1
t_d	87,000	s	8
C	234,933.092	counts	979.764
ε	0.051	-	0.0024
Φ_{th}	$2.94*10^{12}$	$1/(cm^2*s)$	$1.9*10^{10}$

These parameters are then inserted into equation 3 from the main body to produce equation 1.

$$m = 234{,}933.092 * \frac{(7.17793 * 10^{-6})}{((1 - e^{-(7.17793*10^{-6})*600})e^{-(7.17793*10^{-6})*87000}(1 - e^{-(7.17793*10^{-6})*3{,}753.380})} * \frac{164.930328}{(2.94 * 10^{12}) * (6.47 * 10^{-23}) * 0.0656 * 0.051 * 1 * (6.022 * 10^{22})} \quad (1)$$

This calculates a mass of $1.182*10^{-5}$ grams of holmium in the sample. In 0.5 mL of water at room temperature, the number of molecules of water is given by:

$$\frac{0.5\,mL * 0.9984\frac{g}{mL} * 6.022 * 10^{23}\,\frac{molecules}{mol}}{18.0098\,g/mol} = 1.6689 * 10^{22} \qquad (2)$$

Therefore, the concentration of holmium atoms in the water in parts per billion is equal to:

$$\frac{10^{9}\ \text{ppb} *\ 1.182 * 10^{-5}\ \text{g Ho}\ * \dfrac{6.022 * \frac{10^{23}\text{atoms}}{\text{mol}}\text{Ho}}{164.930328\ \text{g}\frac{\text{Ho}}{\text{mol}}\text{Ho}}}{1.6689 * 10^{22}\ \text{molecules}\ water +\ 1.182 * 10^{-5}\ \text{g Ho}\ * 6.022 * \frac{10^{23}\text{atoms}}{\text{mol}}\text{Ho}} \qquad (3)$$
$$= 2586.80\ parts\ Ho\ per\ billion$$

The uncertainty in the measured concentration can also be calculated using neutron activation analysis, assuming that all of the measurement errors are normally distributed and that the uncertainty values, u_i listed in Table A.1 are acceptable estimates of the standard deviation of the measured quantity. Under these assumptions, the uncertainty in the calculated mass, u_m, of the taggant holmium in this sample can be calculated by summing the product of the derivative of equation 3 with respect to each variable by the uncertainty in the value of each variable in equation 3 in quadrature, which is expressed below in equations 4 (reproduced from Section 2) and 4.

$${u_m}^2 = \sum_i \left[\left(\frac{\partial m}{\partial x_i}\right)^2 * {u_i}^2\right]$$

$$u_m{}^2 = \sum_i \left[\left(\frac{\partial}{\partial x_i} \left(C \frac{\lambda}{((1-e^{-\lambda t_i})e^{-\lambda t_d}(1-e^{-\lambda t_m})} * \frac{M_a}{\Phi_{th}\sigma_{eff}\Gamma\varepsilon\theta N_A} \right) \right)^2 u_i{}^2 \right] \quad (4)$$

Taking the necessary derivatives and inserting the correct values into equation 6 gives a calculated uncertainty in the mass of the taggant of 4.93*10^{-9} grams. The uncertainty in the concentration of the taggant element can be calculated using the same method. The derivative of each component of the equation is multiplied by the uncertainty in the measurements, and then summed in quadrature. Performing this calculation produces an uncertainty in the concentration measurement equal to 10.79 ppb. This process was carried out for each test where concentrations were determined.

Of these parameters, many remain the same across all the elements tested. The individual parameters that change when Equation 3 is used to calculate concentrations of samarium and europium are shown below in Table A.2, along with the corresponding values for holmium. The listed value for the parameter θ is the natural abundance of the isotope Eu-151 (0.5219) multiplied by the probability that an atom of Eu-151 becomes the metastable isotope Eu-152m1 (0.3176712) when it captures a neutron during irradiation.

Table A.2 Comparison of variable parameters in Equation 3 when used with various elements

Parameter [unit]	Holmium	Samarium	Europium
λ [1/s]	7.17793*10^{-6}	4.15999*10^{-6}	2.06775*10^{-5}
M_a [amu]	164.930328	152.9220974	151.9217445
σ_{eff} [cm^2]	6.47*10^{-23}	2.06*10^{-22}	9.2*10^{-21}
Γ	0.0656	0.0473	0.024
θ	1	0.2675	0.1658
ε	0.051	0.051	0.033

APPENDIX B.

CALCULATION OF DETECTOR EFFICIENCY AT 69.9 KEV, 80.6 KEV, AND 344.3 KEV

The procedure used to calculate the efficiency of the detector used for the three key energies corresponding to samarium, holmium, and europium is described here. A NIST traceable, multi-element standard is available at the reactor manufactured by Eckert and Ziegler (certificate of calibration 91818). The standard consisted of a 3 mm thick disk of material suspended half way up a 20 mm diameter by 2 inch long plastic NAA vial. This standard was then placed in the middle of the same HPGe detector used in Section 5 and 6, and counted for 1 hour using Canberra's ProSpect software to collect the data. Any identifiable peaks were measured, and the net counts per second of these peaks were divided by the calibration results after correcting for the time between calibration and measurement to give the detector efficiency. The uncertainty was obtained by dividing the uncertainty in the measured net counts per second of the peaks by the expected counts per second. This process was performed for both detectors used. Table B.1 shows the energy of the peaks identified, the corresponding isotopes, the expected number of counts per second based on the time between certification and when the measurements were performed, the measured number of counts per second, and detector efficiency in %, and the uncertainty in the detector efficiency in % for the second detector that was used for the vast majority of the testing (>90% of tests). This detector efficiency is the product of the geometric efficiency (how many gammas emitted by the sample end up interacting with the detector) and the inherent detector efficiency (the probability that an interaction between a gamma photon and the detector produces a signal in the detector that is amplified and measured). As none of the taggant elements used in this research were used in the standard, both the efficiency of the detector at the desired energies, and the uncertainty in the efficiency were obtained by linear interpolation.

Table B.1. Detector Efficiency Measurements for Second Detector used

Peak Energy (keV)	Isotope	Expected Counts per Second	Measured Counts per Second	Detector efficiency (%)	Efficiency Uncertainty (%)
59.5	Am-241	1999.0	115.5	5.8	0.02
88.0	Cd-109	219.6	12.4	5.6	0.07
122.1	Co-57	19.4	0.9	4.8	0.50
661.7	Cs-137	1738.8	19.5	1.1	0.01
1173.2	Co-60	1964.6	12.7	0.6	0.01
1332.5	Co-60	1965.1	11.3	0.6	0.00

Table B.2 presents the interpolated detector efficiencies of the 80.6 keV peak for holmium, the 69.9 keV peak for samarium, and the 344.3 keV peak for europium 152m1.

Table B.2. Detector Efficiencies for Holmium, Samarium, and Europium Peaks

Element	Peak Energy (keV)	Interpolated Efficiency (%)	Interpolated Uncertainty (%)
Samarium	69.6	5.1	0.22
Holmium	80.6	5.2	0.24
Europium	344.3	3.3	0.07

APPENDIX C.

EXPANDED FIGURE 5.1

Figure 5.1 includes multiple elements in the same diagram. The error bars represent the standard deviation in the measured concentrations of the taggant element. Figures C.1 through C.3 show the individual elements that comprise Figure 5.1 on the same vertical scale. Figure C.4 shows the data for europium on a more natural scale, and is zoomed in compared to Figure 5.1.

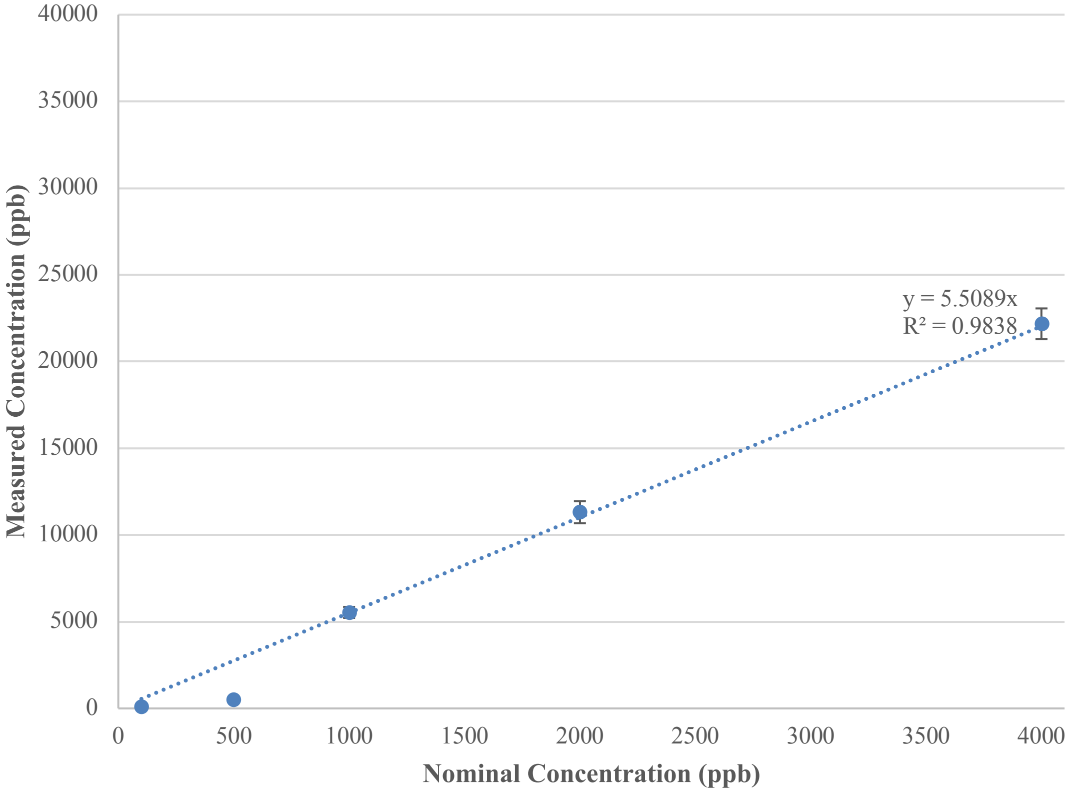


Figure C.1. Holmium Data in Figure 5.1

The measurements for 100 ppb and 500 ppb holmium are not comparable to the rest of the measurements. These measurements were used to determine the detector efficiency by assuming that they were measured correctly. The data for samarium are also questionable. The detector broke after measuring all five of the 100 ppb samples, and one of the 500 ppb samples. All samples were irradiated at the same time, since counting was expected to take only a couple days. When the detector broke, this introduced a delay time of up to a week in the case of the 4,000 ppb samples, which is responsible for the substantial error bars seen in Figure C.2. As such, these data are being presented for the sake of completeness.

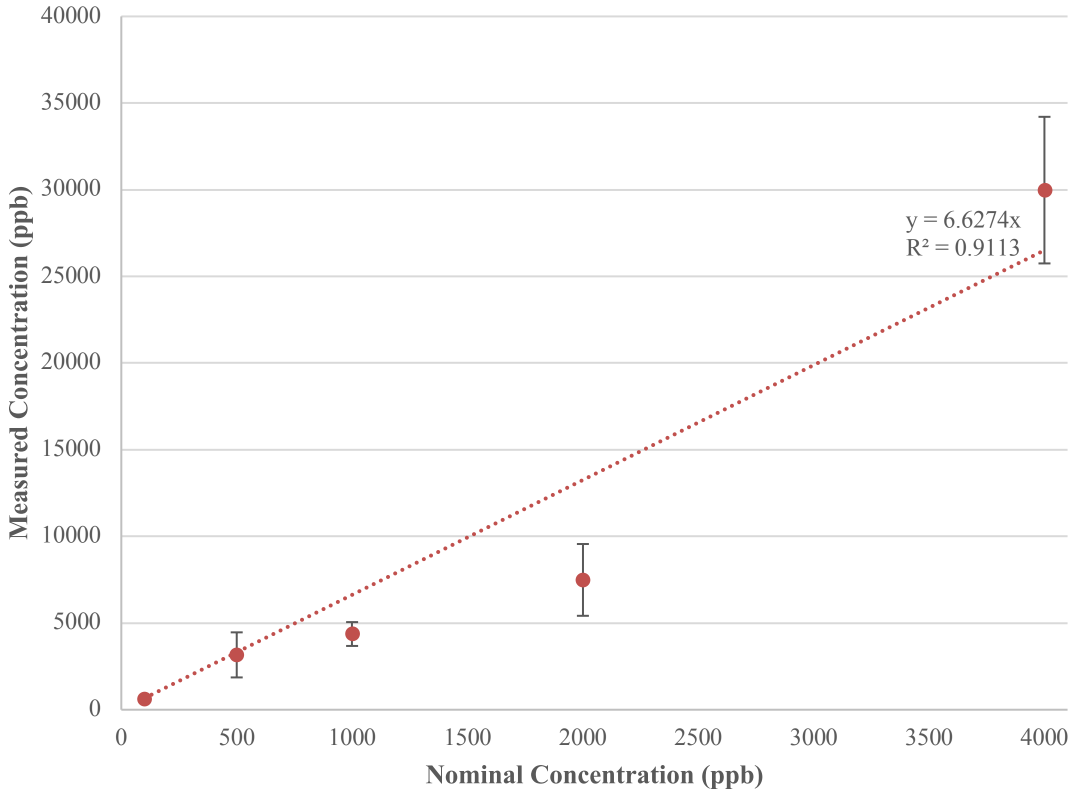


Figure C.2. Samarium Data in Figure 5.1

Figure C.3 shows europium, and the data here look far more linear than either the holmium or samarium samples. Figure C.4 confirms this, as the data still appear highly linear when zoomed in. A strange result is that the standard deviation of the europium 2,000 ppb samples are larger than those of the 4,000 ppb samples. Additionally, these two test series each have one outlier result, which was discarded when calculating the standard deviation. The reason for this is unknown, but since both outliers were the fifth of five samples at the same concentration, it is possible there was insufficient mixing of the original solutions that the samples were drawn from. This would create a concentration gradient and therefore produce outliers.

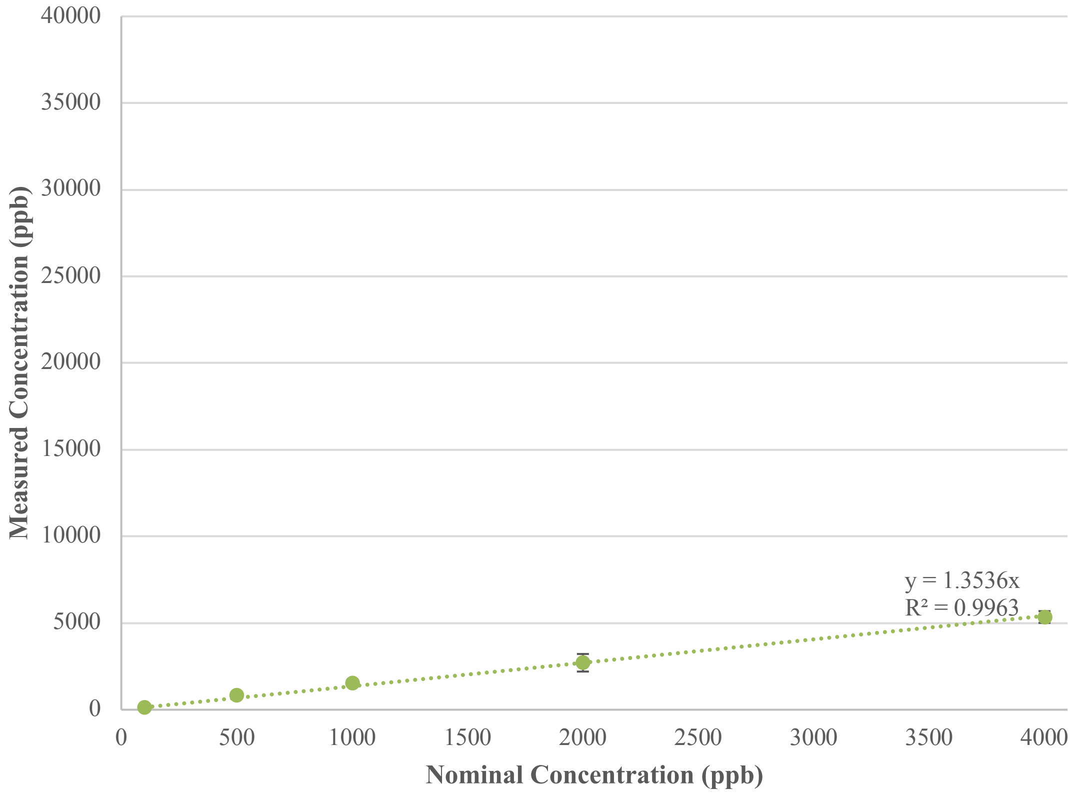


Figure C.3. Europium Data in Figure 5.1

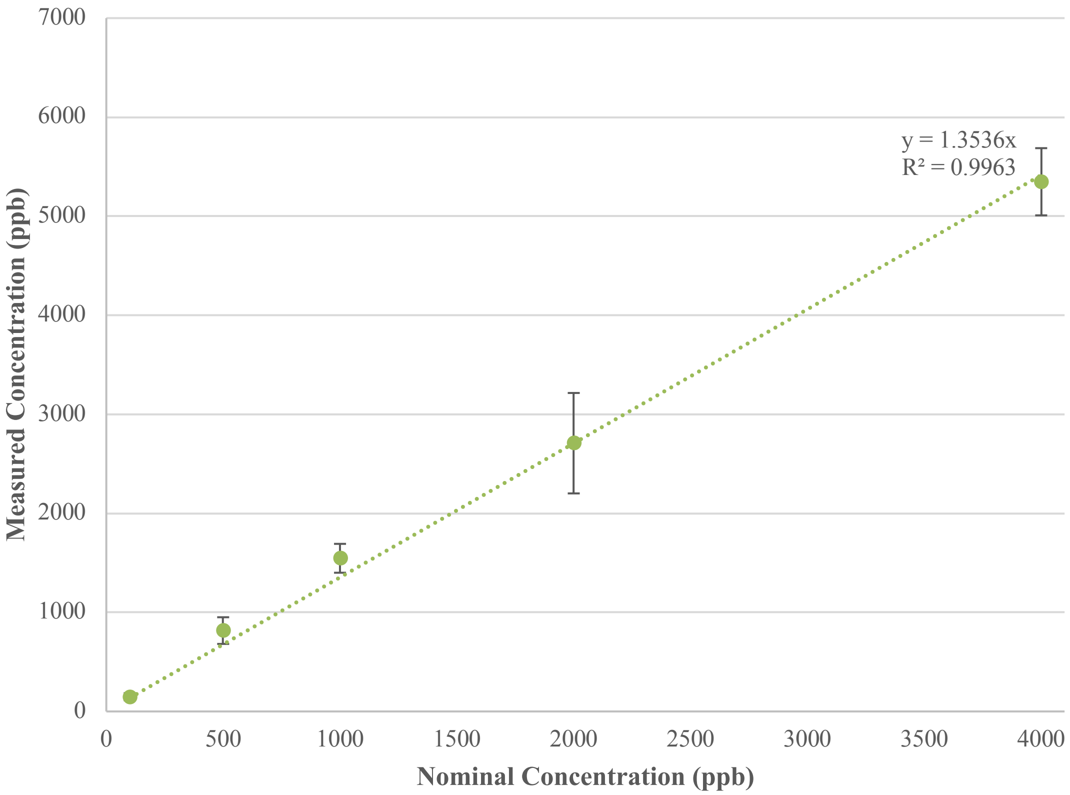


Figure C.4. Europium Data in Figure 5.1 (Zoomed)

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