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Nuclear Forensics: An important tool to verify unknown nuclear sources

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Declaration of Originality

Except where reference is made in the text of this diploma thesis, this diploma thesis contains no material published elsewhere or extracted in whole or in part from a thesis presented by me for another degree or diploma. No other person's work has been used without due acknowledgement in the main text of the diploma thesis. This thesis has not been submitted for the award of any other degree or diploma in any other tertiary institution.

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Abstract

Orphan or stolen sources, illicitly transported material and nuclear or radioactive weapon devices pose a great risk for people in their surroundings. Nuclear Forensics are investigations to identify nuclear or radioactive materials and determine where they came from and what the original intended usage was. The collection, securing, transport, preparation and measurements of samples as well the drawn conclusions about measurement results constitute the process of a forensic investigation.

The International Atomic Energy Agency (IAEA) provides guidelines for a Master of Science programme in nuclear security with an elective course which focusses on Nuclear Forensics - the NS19. In 32 hours students are introduced to the basics of investigations, the variety of nuclear forensic techniques and some practical exercises.

The aim of this thesis is the preparation of slide show presentations with guides for future lecturers of the NS19 course. Additionally three practical exercises are selected to represent the process of a nuclear forensic investigation which can be realised beside the theoretical course to clarify the principles of Nuclear Forensics.

Kurzfassung

Nukleare oder radioaktive Waffentechnologie, gestohlenes und geschmuggeltes Material und unbekannte, gefundene Quellen stellen eine potentielle Gefahr für Menschen in deren näheren Umgebung dar. Das Ziel von (nuklear) forensischen Untersuchungen ist die Identifikation und Herkunftsbestimmung von nuklearem oder radioaktivem Material sowie die Bestimmung der ursprünglichen Nutzung. Der Verlauf einer forensischen Untersuchung lässt sich im Wesentlichen auf Sicherstellung, Transport, Aufbereitung, die diversen Messungen des Materials und die anschließende Auswertung der Ergebnisse reduzieren.

Die Internationale Atomenergie Organisation (IAEO, englisch IAEA) schlägt Inhalte für einen Master-Studiengang im Bereich Nuklearer Sicherheit vor, welcher ein Wahlfach beinhaltet, das sich mit Nuclear Forensics auseinandersetzt, der NS19. In dem 32-stündigen Kurs werden die Grundlagen forensischer Untersuchungen und die Vielfalt an Messmethoden präsentiert sowie einige praktische Übungen durchgeführt.

Das Ziel dieser Arbeit ist die Zusammenstellung des Präsentationsmaterials mit einem Leitfaden für zukünftige Vortragende des NS19-Kurses. Des Weiteren werden drei praktische Übungen, welche den wesentlichen Vorgang von forensischen Untersuchungen repräsentieren, ausgewählt, durchgeführt und beschrieben, sodass diese parallel zur Verdeutlichung der Theorie praktiziert werden können.

Contents

Glossary

$(NH_4)_2CrO_4$	Ammonium chromate.
Al	Aluminium.
Bi	Bismuth.
Br	Bromine.
Cl	Chlorine.
Co	Cobalt.
Cr	Chromium.
DIAMEX	Diamide Extraction.
ENEN	European Nuclear Education Network.
Fe	Iron.
HNO_3	Nitric acid.
IAEA	International Atomic Energy Agency.
ICP-MS	Inductively coupled plasma mass spectroscopy.
In	Indium.
INSEN	International Nuclear Security Education Network.
ITWG	Nuclear Forensics International Technical Working Group.
LLE	Liquid-Liquid-Extraction.
Mo	Molybdenum.
MSc	Master of Science.
N	Nitrogen.

Na_2CrO_4	Sodium chromate.
NDA	Non Destructive Assay.
Ni	Nickel.
NS	Nuclear Security.
Pa	Protactinium.
Po	Polonium.
PUREX	Plutonium Uranium Redox Extraction.
SANEX	Selective Actinide Extraction.
Sn	Tin.
Sr	Strontium.
TBP	Tributyl Phosphate.
Tc	Technetium.
Ti	Titanium.
TRUEX	Transuranic Extraction.
U_3O_8	Triuranium Octoxide.
UF_6	Uranium Hexafluoride.
UNEX	Universal Extraction.
$UO_2(NO_3)_2$	Uranyl Nitrate.
UREX	Uranium Extraction.

1. Introduction

1.1. Motivation

"I feel impelled to speak today in a language that in a sense is new – one, which I, who have spent so much of my life in the military profession, would have preferred never to use. That new language is the language of atomic warfare" (December 8, 1953, Press Release: "Atoms for Peace" Speech, Page 2) is one of the most incisive statements of U.S. President Dwight David Eisenhower during his famous speech "Atoms for Peace" to the UN General Assembly in New York City on December 8, 1953. This speech adressed the rising popularity of nuclear technology to raise awareness on the risks and hopes of that new trend. The essence of that speech was to accomplish and maintain peaceful usage of nuclear power.

The International Atomic Energy Agency was founded four years later in 1957 shaped by the ideals of Eisenhower. The "Atoms for Peace" organization was approved unanimously by 81 member nations of the UN in October 1956. The two major objectives of the IAEA are the promotion and the control of peaceful usage of nuclear power. The headquarter of the IAEA has been established in Vienna, Austria in the Vienna International Center in 1979. Additionally two regional offices in Toronto, Canada and Tokyo, Japan have been built up together with liaison offices in New York, USA and Geneva, Switzerland [1].

Since April 2018 there are a total of 170 member states of the International Atomic Energy Agency which is currently led by Yukiya Amano [2]. Today the organization supports research and development of nuclear technology in all member states and nuclear newcomer states as well as the training and education of professionals in all nuclear fields. The increasing development and expansion of nuclear power programs and the application of nuclear or radioactive material in industry, medicine and research lead to a simultaneously growing issue: The threat of vicious acts involving nuclear or radioactive material out of regulatory control. The prevention of said illegal activities requires qualified personnel in nuclear security. For that purpose the Board of Governors of the IAEA decided to set up a Nuclear Security Plan in September 2005 as a guideline for the development of a MSc programme and a certificate programme in nuclear security. In cooperation with experts from all Member States and the European Nuclear Education Network (ENEN) prerequisites and a schedule of the MSc programme have been established to be used in participating universities. Teaching materials for all courses of the programme are developed under the guidance of the International Nuclear Security Education Network (INSEN) [3]

The schedule contains obligatory subjects and a list of elective courses with one being NS19: Nuclear Forensics and Attribution. The aim of nuclear forensic investigations and subsequent nuclear attribution is the identification of nuclear material or radioactive sources out of regulatory control and to determine the origin and history of seized material [4]. After attending the NS19 course, students should have a clear understanding of nuclear forensic investigation and the analytical tools used to identify seized samples.

The following topics are covered in the lectures of the NS19 as listed in [3]:

- NS19.1 Physical basis for nuclear forensic science
    - Nuclear and other radioactive material
    - Nuclear material and criticality
    - Effects of production and treatment of nuclear and other radioactive material on specific signatures
- NS19.2 Radioanalytical chemistry principles and practices
    - Dissolution of solids
    - Carriers and tracers in inorganic analysis
    - Relevant chemical and physical properties
    - Techniques for forensic signatures
    - Collateral forensic indicators
    - Radionuclide separation and purification
    - Standard methods in radioanalytical chemistry
- NS19.3 Incident response
    - Securing the incident site
    - On-site measurements
    - Collection of traditional forensic evidence
    - Collection of evidence in radiological incidents
- NS19.4 Nuclear forensic laboratory sampling and distribution
    - Nuclear forensic laboratory
    - Forensic management team
    - Sampling in the nuclear forensics laboratory
- NS19.5 Nuclear forensic analysis
    - Characterization goals
    - Presentation of available analytical tools for nuclear forensics

  - Sequence of analysis techniques and methods

- NS19.6 Nuclear forensic interpretation
  - Nuclear dating methods and forensic signatures
  - Cooperation with other nuclear forensics laboratories
  - Knowledge bases of nuclear processes
  - Iterative nuclear forensics process
- NS19.7 Confidence in conclusions
  - Analytical data quality objectives control
  - Precision and accuracy
  - Sensitivity
  - Reporting of results
  - Source and route attribution

In addition to the lectures, students will participate in three practical exercises, which represent the process of nuclear forensic investigations [3].

1.2. Goals

The aim of this diploma thesis is the preparation of said practical exercises to represent three major parts of the nuclear forensic process: On-site investigations with sample collection, sample preparation and the evaluation of analytic results for nuclear attribution. The main task is to structure exercises that may be either conducted practically but also function as realistic scenarios in case of limited access to the required equipment or material.

1.3. Content

This thesis is divided into five chapters. The first chapter contains the introduction and defines the goals. The following chapter presents the first practical exercise of the NS19 course. A nuclear forensic team performs investigations on-site to find and collect samples of a hidden radiation source. This part discusses the role of each investigator, a list of the required equipment and a detailed description of the procedure.

The third chapter deals with sample preparation in laboratories and handling of radioactive samples. Liquid-liquid extraction is used to separate chromates based on their oxidation states. The separation technique, the execution, its results and its uses in nuclear industry are shown in this part.

The next chapter introduces the process of nuclear attribution. Unknown nuclear material is identified based on the results of inductively coupled plasma mass spectrometry and gamma spectroscopy. The chapter includes the explanation of both measurement techniques, the processing and interpretation of results as well as the attribution to identify the analyzed source. This thesis concludes with a summary of all exercises and a guideline how to integrate them in the NS19 course.

2. On-Site Investigations

2.1. Overview

The first exercise, a preset scenario of a hidden radiation source in a defined area to be found and collected by the team of investigators, is a simplified model based on the actions required during real cases. For that purpose the officialy suggested on-site actions for investigations of incidents involving nuclear or radioactive material are explained and compared with the simplified scenario for students of the NS19 course.

2.2. Incident Response

2.2.1. Tactical Command Structure

Before any actions are taken, a command structure with internal reporting procedures is formed. Decisions about public safety and the safety of involved staff, protection of the environment and handling of evidence are made by the incident commander. The incident commander assembles a team of required experts of multiple disciplines based on the a priori knowledge of the incident. An example of the tactical command structure is shown in Figure 1.

The role of the response personnel is to supervise the area to prevent entry to the incident site of unauthorized individuals. They also maintain a list of each registered member of the incident-response team. Additionally, traffic and public media are managed by the on-scene control.

The duty of the **radiological advisor** is to conduct radiation surveys, to prevent unwanted contamination and to assist the response personnel. The **incident investigation staff** is composed of two major groups. One group is specialized in traditional forensics, collecting evidence like trace evidence and impressions. The other group is responsible for the localisation, identification and collection of radiation sources and potentially contaminated samples. The command structure is adjusted depending on the type of incident [5].

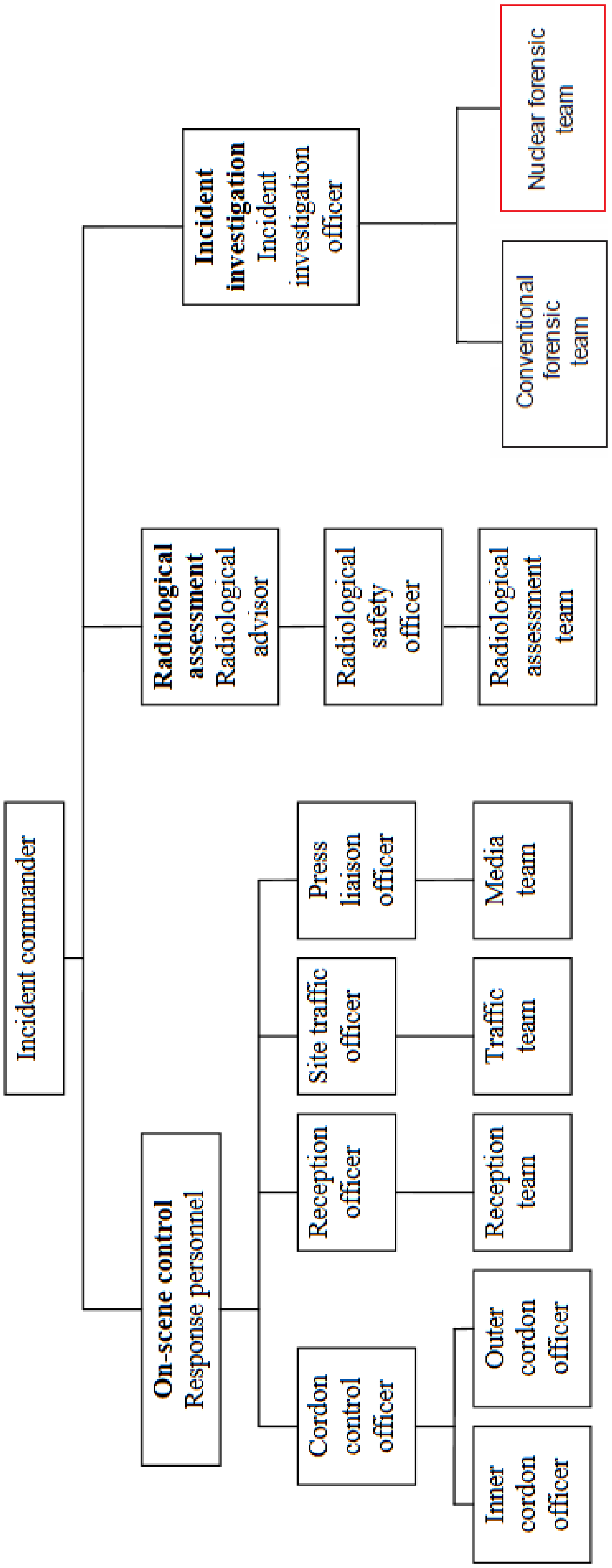


Figure 1: An example command structure [5, 6]

2.2.2. Nuclear Forensic Plan of Action

After the determination of the investigation team, an action plan is established as a guideline of nuclear forensic investigations in cooperation with the traditional forensic group, law enforcement and national nuclear forensic laboratories for the actions on-site and for sample processing. The following sequence is the suggested Nuclear Forensic Plan of Action of the ITWG as shown in [7].

1. Detection, cordoning off and guarding of the site by the law enforcement service.
2. The competent service must confirm the nuclear or radioactive nature of the material and determine whether a nuclear or radiation hazard exists.
3. The central authority which is authorized to initiate the action plan must be informed.
4. On-site, the following actions should take place:
    - Law enforcement actions to check for booby traps and preservation of evidence, chain of custody.
    - Health Physics examination for occupational and public radiation hazard.
    - On-site categorisation of seized material by mobile NDA instrumentation.
    - Safe storage of material until transport.
5. The following investigations are to be foreseen at the specialised national laboratory:
    - checking for booby traps before unpacking.
    - Preservation of evidence and classical forensic analysis of non radioactive material.
    - detailed investigation according to laboratories capabilities (visual, quantity, sampling, nuclear properties etc).
    - first query with nuclear materials database to guide in-depth investigations.
    - in-depth analysis of material in a specialised laboratory to characterise the material to such an extent that the identification of the origin, intended use and last legal owner becomes possible.

6. If the national laboratory is not in a position to carry out certain analysis a sample of the material could be shipped to an external specialised laboratory.
7. The results are compared with an appropriate database, possibly resulting in further investigations.
8. An analytical “expert opinion” of the analyzed seized material is to be written for the national law enforcement authorities where the seizure occurred.
9. A synopsis and evaluation of all evidence is to be made by the national legal authority.
10. The case will be treated by the national courts.
11. The material should be returned to the last legal owner in accordance with an international agreement and existing non-proliferation legislation.
12. If the material’s owner cannot be determined or the material cannot be returned because of the international situation a use or disposal of the material is decided according to relevant legislation.

2.2.3. Securing the incident site

Once the action plan is defined, the incident response team begins with the classification of the area and the preparation of individual working zones. Additionally outer and inner cordoned areas are defined to confine the actual incident site and a safe area around that location. Figure 2 shows a diagram of the control areas [5].

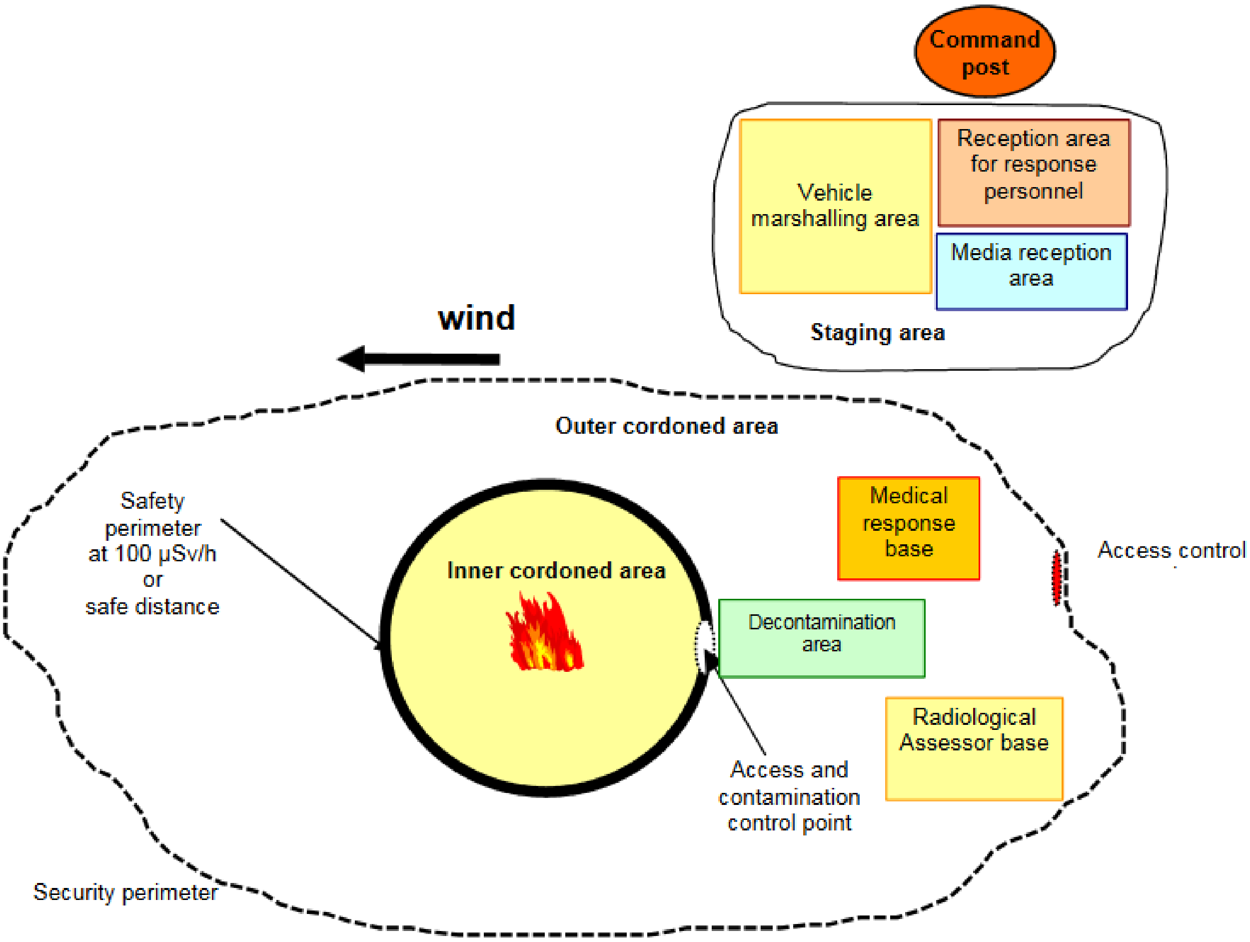


Figure 2: The cordon controlled areas of the incident site [5]

Securing the incident site aims to fulfill three major objectives [6]:

- The prevention of radiation hazards at the incident location
- The control of radiation sources
- The preservation of evidence

2.2.4. On-Site Analysis

After the incident area is secured and weapon- and explosives experts confirmed that there is no threat of explosive devices, the location is released and the investigation teams may enter the area via the access point. The goal is to find involved nuclear or radioactive material which is identified and categorized on-site. Depending on the condition of the radiation source further steps must be taken.

The following equipment is required for on-site investigations:

- Portable dosimeters
- Portable neutron detector
- Portable gamma ray detector
- Forceps
- Zipper bags
- Spatula or shovel
- Plastic bottles
- Syringes or pipettes
- Wet vacuum
- Plastic containers
- Lead containers
- Camera
- Swipes or sticky tapes

Before approaching the incident site, an accurate diagram of the location with an overlayed grid-system is drawn to support the radiological survey. Size and shape of the grid-system is chosen based on the knowledge of the incident and expected types of radiation sources. A square- and triangular grid system are shown in Figure 3 [6].

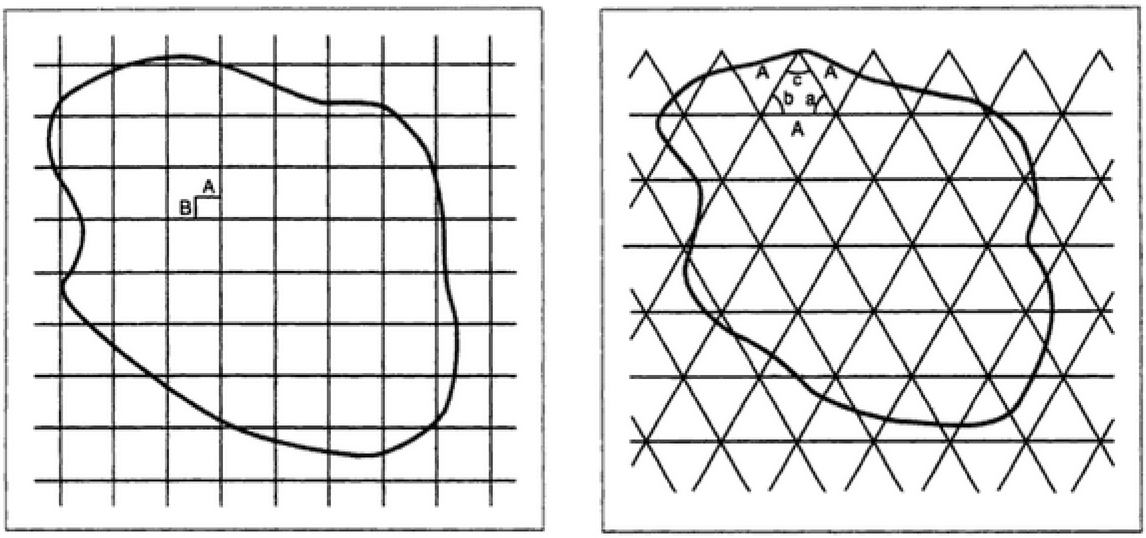


Figure 3: Example grid-systems [8]

When entering the incident-site, it is important to make sure that radiological safety practices are applied. Therefore everyone who enters the incident is equipped with a portable dosimeter for the monitoring of received dose rates. Risks of radiation hazards may be reduced by minimizing the retention time at potentially contaminated areas and by increasing the distance and shielding between investigators and the radiation source. The highest possible time for individuals at the incident site is determined based on type and level of radioactivity and in extreme cases either shiftwork or even remote-controlled robots are used [9].

Each section of the grid is examined with the help of radiation survey instrumentation to locate radiation sources. Once detected, the source can be categorized with non-destructive assay by using neutron detectors and gamma ray detectors. Activity measurements and the identification of constituents support the categorization and determine the appropriate shielding for the transportation of the source. If the source is just an alpha- or beta emitter, plastic containers are sufficient but in case of strong beta or gamma radiation, lead containers must be used. Ideally photographs of the source are taken before distance-tools like forceps are used to put it inside a transportation container. The container must be labelled with the content, activity and categorization.

If the source is found in an intact container or shielding, it may be collected and transported outside the incident site immediately. Additional samples around the location of the source are taken to exclude contamination of that area. In case of scattered nuclear or radioactive material at the incident location, multiple samples must be taken to secure valuable information of the source and to detect contaminated items and areas. Solid samples are taken with the help of spatulas or shovels and put in zipper bags while syringes or pipettes are used to take liquid samples which are collected in plastic bottles. Larger volumes are collected with a wet vacuum. If large and immobile objects are possibly contaminated, swipe-tests are performed with sticky tapes or swipes made of filter material. Each sample must be taken with clean or different instruments to avoid cross-contamination and the equipment must be decontaminated after usage.

To maintain the chain of custody, each sample has to be added to the evidence recovery log. Date and time as well as the exact location where the sample has been taken are recorded and each bottle or plastic bag must be labelled according to its content.

The nuclear forensic team collaborates with the conventional forensic experts to avoid the destruction of traditional evidence, for example fingerprints, which may be destroyed by swipe-tests. Furthermore traditional evidence in close proximity to the radiation source might be contaminated and therefore must be collected by the nuclear forensic personnel.

Before releasing the scene, the forensic teams must ensure that all investigations are completed and no errors were made during the collection and recording of collected evidence. Accounting of samples and photographs of the final condition of the incident site are made before leaving the area [6].

2.2.5. The Nuclear Forensic Group

The exercise is reduced to the nuclear forensic tasks of the incident investigation team. After the instructions and objectives of the practical lesson have been introduced, students form groups of five and define roles for each member.

The following list shows each individual role and its task for the exercise:

- **Incident investigation officer**:
  The incident investigation officer is the leader of the group and acting from the entrance of the incident site. His role is to communicate with investigating units via radio sets to give clear instructions and to receive information and requests for specific equipment. As the head of the investigation group, he is supposed to know the duties of all members and to know all details about the event and its location.

- **"Clean guy":**
  The "clean guy" and the incident investigation officer form the observation group outside of the incident area. His duty is the preparation and examination of equipment, which is then handed to the "dirty guy" at the entrance of the incident site. Additionally any evidence and used equipment is received and monitored for contamination.

- **"Dirty guy":**
  The "dirty guy" is the first member of the actual investigation group on-site. He interacts with the "clean guy" by taking prepared equipment and handing seized material and used equipment to the entrance of the incident site. He is the "person of interaction".

- **Reporter:**
  The reporter takes photographs of the incident site, suspicious items and found material. He is always in contact with the incident investigation officer to provide information and to redirect requests for equipment. Further if any radioactive or nuclear material is found, the reporter is supposed to record details with the help of an evidence collection form. Before departure from the incident location, a final check must be made to assure that no errors were made during the collection of the sample.

- **Evidence collector:**
  The evidence collector is the first to enter the site with a radiation counter for the detection of contaminated material and radiation sources. After subsequent identification of detected radiation sources with the help of a gamma detector the material is collected and put in an appropriate case and labelled accordingly.

2.3. The Exercise

2.3.1. The Scenario

The starting point of the scenario is a report of an unknown radiation source hidden in a specific area. The nuclear forensic investigation team is supposed to find, identify and secure the nuclear or radioactive material at the target location.

Both, radiation source and incident area are chosen and prepared by the course instructor. The radiation source must be in a sealed container, for example a vial or bottle to avoid accidental spread of the material. Suitable sources are alpha- or beta emitters with detectable activities that do not pose a risk to the health of participants like natural or low-enriched Uranium. The training location may either be inside a building, for example office-rooms or outdoors. In both cases the location must be cordoned off to avoid unauthorized entrance. The exact position of the source is chosen individually for each investigation group. Optionally multiple sources or "dummy-material" may be hidden prior to the investigation of each team depending on the size of the area and designated time for the exercise.

2.3.2. List of Equipment

The following equipment is required for each group of students:

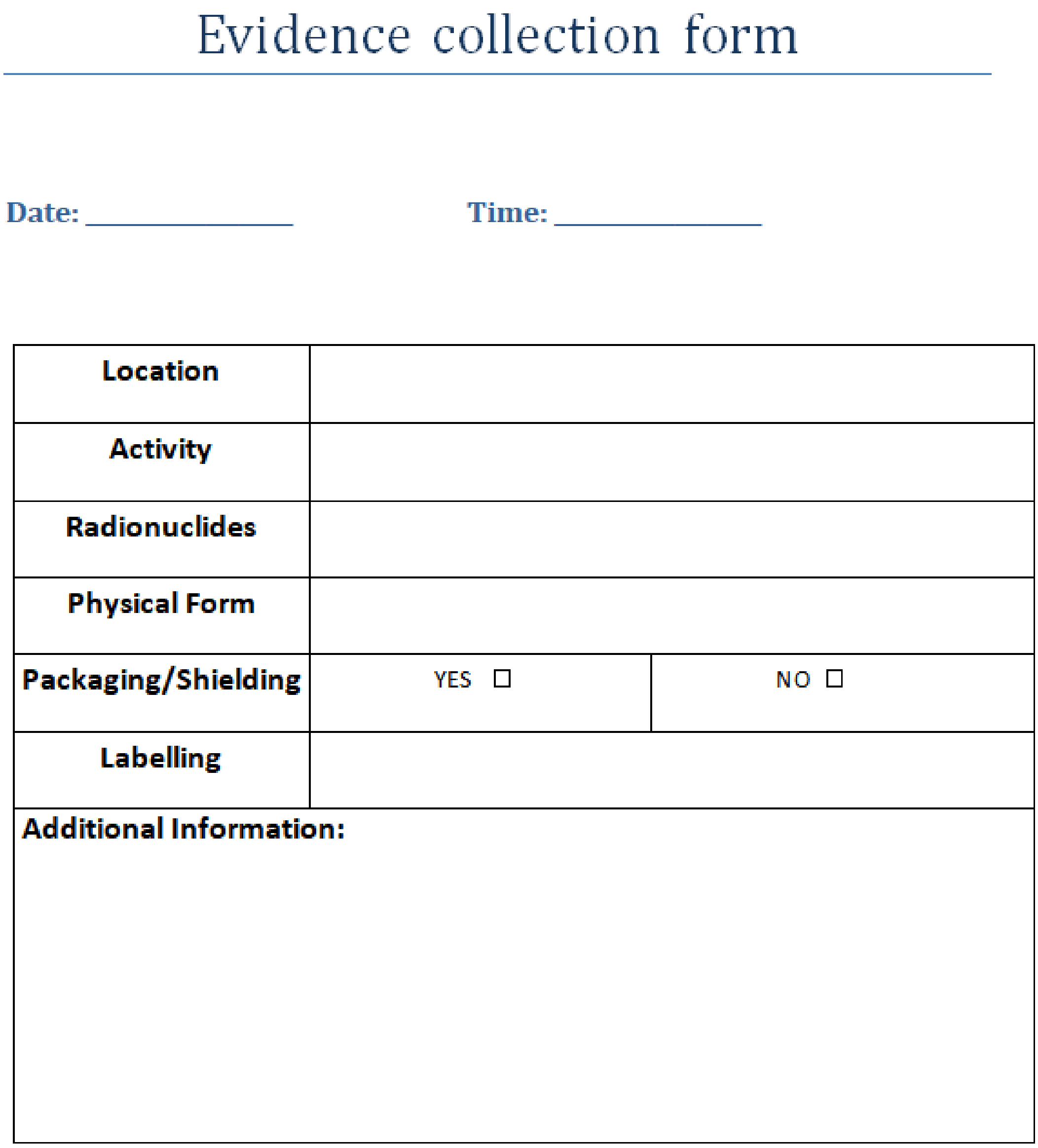
- Portable dosimeters
- Portable radiation counter
- Portable gamma ray detector
- Radio sets

- Camera
- Evidence collection form
- Sample collection kit with:
  - Latex gloves
  - Forceps
  - Zipper bags
  - Sample cases

After the team formation, students are introduced to the radiological safety practices and to the measurement devices.

2.3.3. Training Analysis

The execution of the on-site investigation and its objectives are identical with the procedures of a real case as explained in Chapter 2.2.4 On-Site Analysis. The goal is to search the training area for the hidden source with the help of a predetermined square-grid-system using a portable radiation counter. The source will then be identified with a gamma ray detector and put in a zipper bag and appropriate sample case. Additionally, photographs are taken and an evidence collection form is filled in to record the attributes of the source. An example-template of the evidence collection form is shown in Figure 4. Other groups will observe the performance of the investigating team and after the last iteration, the exercises and results are discussed.



Evidence collection form

Date: ______________ **Time:** ______________

Location		
Activity		
Radionuclides		
Physical Form		
Packaging/Shielding	YES ☐	NO ☐
Labelling		
Additional Information:		

Figure 4: Example-template for an evidence collection form

3. Laboratory Work

3.1. Overview

Nuclear or radioactive material seized during on-site investigations is subsequently analyzed in a nuclear forensic laboratory. Before certain measurements are achievable, samples must be prepared according to the type of measurement. Parts of the sample need to be separated for measurements with different techniques.

A commonly used separation technique used for the purification of uranium during fuel production and for the reprocessing of spent nuclear fuel is the liquid-liquid-extraction. The second exercise represents such separation processes and explains the handling and preparation of radioactive samples. Because of legal restrictions, it is not possible to perform that exercise with uranium as an example of the PUREX process. Instead, neutron activation of chromates with thermal neutrons is performed. That leads to Szilard-Chalmers reactions and to different oxidation states of the chromates. Then two consecutive iterations of liquid-liquid-extraction separate the sample based on different oxidation states.

3.2. LLE of the Nuclear Fuel Cycle

Szilard-Chalmers-Reactions are just one example, where liquid-liquid-extraction is performed to achieve high specific activities of certain radionuclides for industrial or medical uses. LLE is also an important part of the nuclear fuel cycle. It is a mandatory step for the processing of uranium before enrichment but also used as a separation method during reprocessing of spent nuclear fuel. In this chapter both applications of LLE are explained in detail.

Conversion of yellowcake

Once uranium ores are mined and refined, the product, triuranium octoxide (U_3O_8) with thorium, tungsten and decay products of uranium has to be purified and converted to uranium hexafluoride (UF_6). The steps of purfication and conversion are shown in Figure 5.

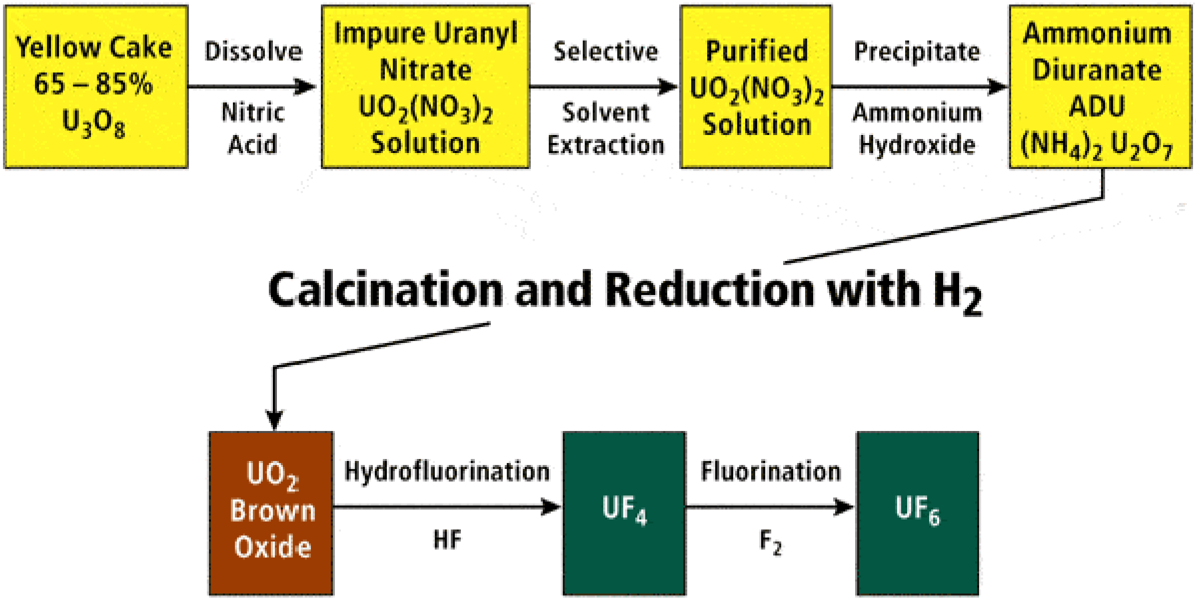


Figure 5: Purification and conversion of yellowcake [10]

Yellowcake is dissolved in nitric acid (HNO_3) to form the aqueous phase of the liquid-liquid-extraction. Tributyl phosphate (TBP) is used to separate the uranyl nitrates ($UO_2(NO_3)_2$) with uranium in a hexavalent oxidation state from undesired components like the decay products of uranium in the aqueous solution. The second step of LLE is the transition of the uranyl nitrates into another aqueous phase with clean water for the next steps of conversion. The clean TBP is used again for step one of the purification process [11]. The liquid-liquid-extraction of uranyl nitrate is shown in Figure 6.

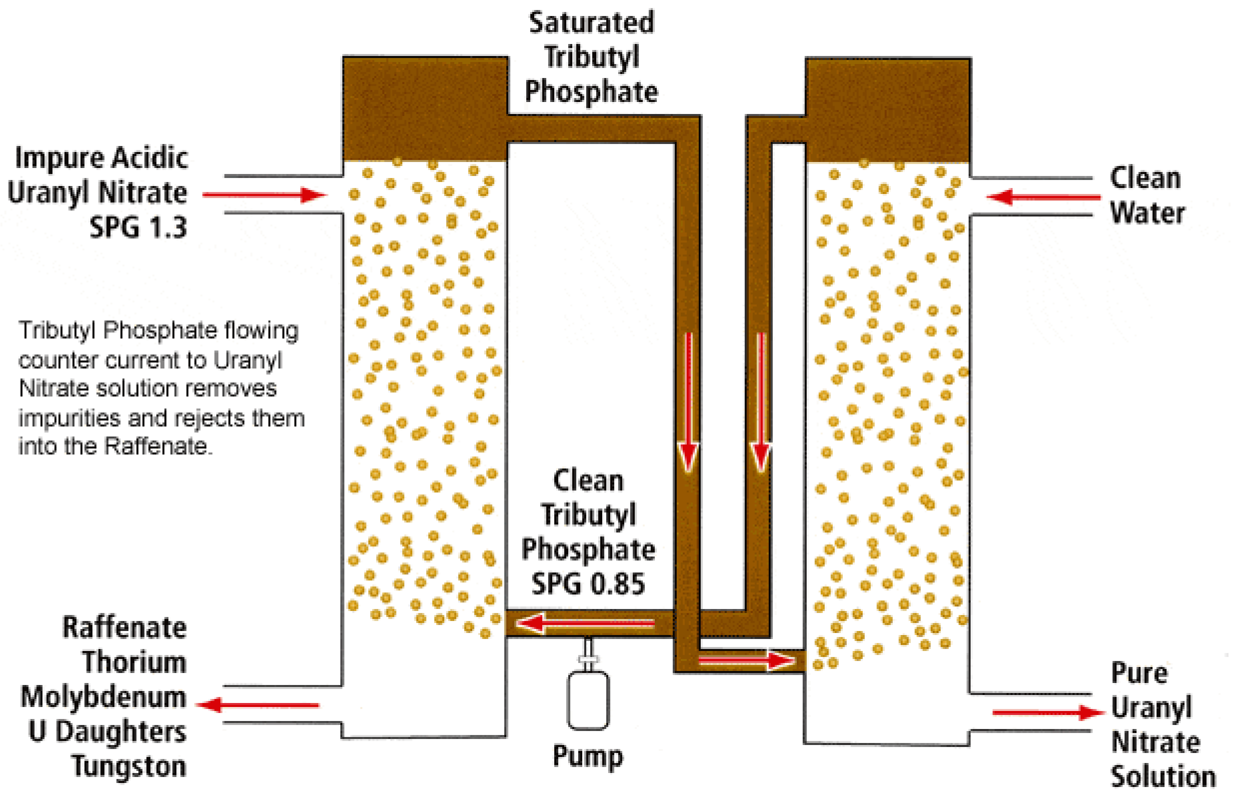


Figure 6: LLE of uranyl nitrate for yellowcake conversion [11]

Reprocessing of spent nuclear fuel

After a few years of usage and irradiation in nuclear reactors, the fuel assemblies have to be removed and replaced. Compared to fresh nuclear fuel, the composition changes over the period of irradiation. Unused uranium with highly radioactive fission products and long-lived, transuranic isotopes are the remains after years of irradiation while in use. Figure 7 shows the change of the fuel composition over time.

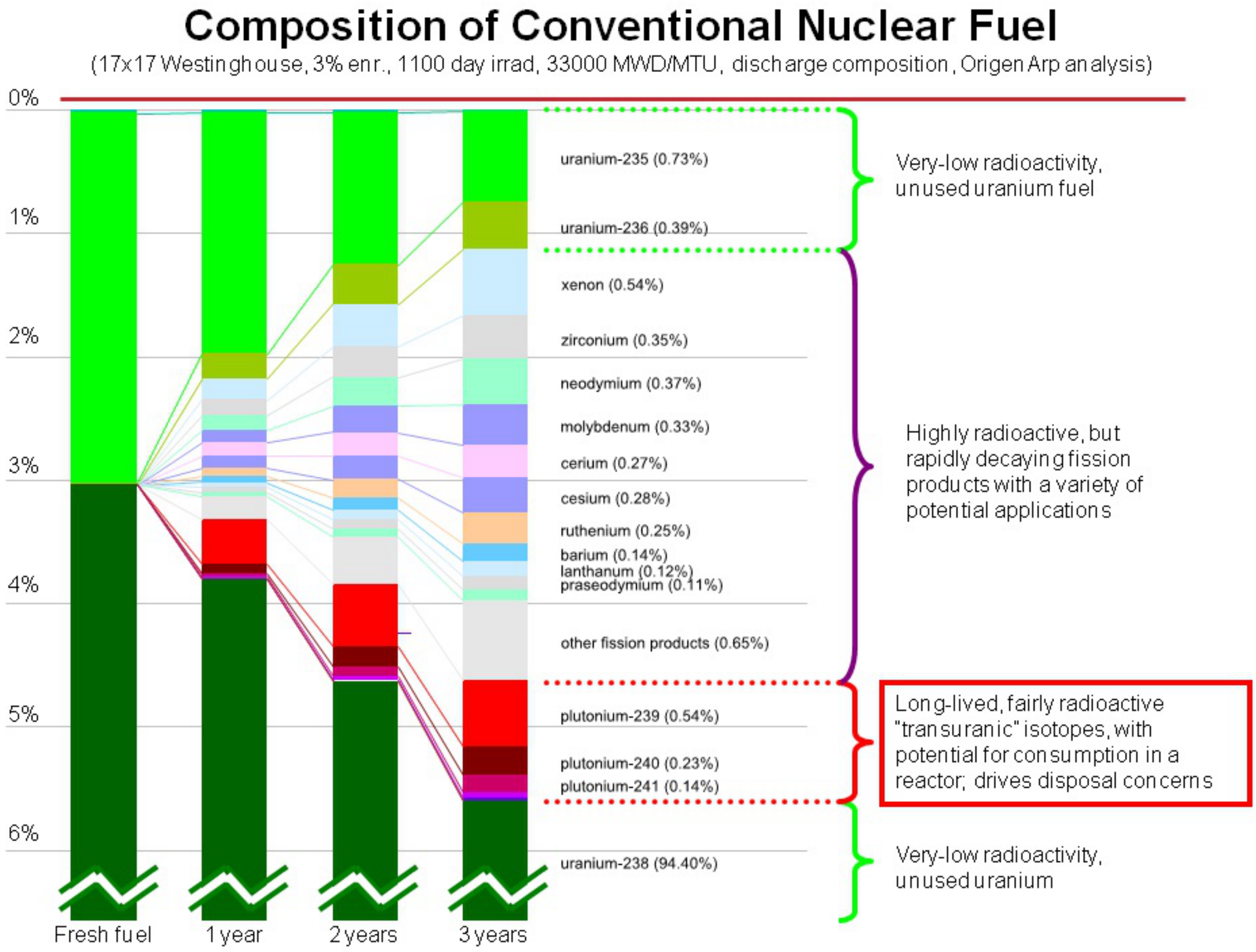


Figure 7: The composition of nuclear fuel after few years of usage [12]

After removal from the nuclear reactor, spent fuel is usually stored in spent fuel pools at the reactor site for a certain period of time. Afterwards there are two options about the further processing of spent nuclear fuel: the open nuclear fuel cycle and the closed nuclear fuel cycle.

In case of an open nuclear fuel cycle, the next step after on-site storage is the transportation to storage facilities away from the reactor. Those depend on type and decay heat of the fuel, either wet type with pools or dry type in special containers. A storage period of several decades ensures that radionuclides with very high activities have decayed, leaving behind radioactive isotopes with lower activities. Nevertheless the material still poses a great risk for the environment and therefore the last step is final disposal in accordance with national nuclear waste disposal programs.

The next step of the closed nuclear fuel cycle after long-term storage away from the reactor is not final disposal but the reprocessing of used nuclear fuel. The goal of reprocessing is to separate and recover reusable nuclear material - uranium and plutonium - from high-level decay-products with chemical separation techniques. The most commonly used process for reprocessing is the Plutonium Uranium Redox Extraction (PUREX). Uranium and plutonium are separated from fission products with liquid-liquid-extraction [13].

The PUREX process is a separation technique in two stages. In the first stage, uranium and plutonium are separated from fission products and minor actinides and the second stage finally separates uranium from plutonium in form of oxides. First spent fuel is sheared and dissolved in concentrated nitric acid. Using LLE, uranium and plutonium in the aqueous nitric acid solution enter an organic phase of TBP dissolved in kerosene or dodecane. Fission products and other elements remain in the aqueous solution - the raffinate.

In the second stage, uranium is separated from plutonium with an aqueous stream of nitric acid and hexavalent uranium added as a reductant. Plutonium is transferred to the aqueous phase while uranium remains in the organic TBP-kerosene solution. Uranium is stripped from the organic phase with diluted nitric acid. Plutonium nitrates and uranium nitrates are finally converted to oxides which can be utilized again for nuclear fuel prduction [14]. A flowchart of the PUREX process is shown in Figure 8.

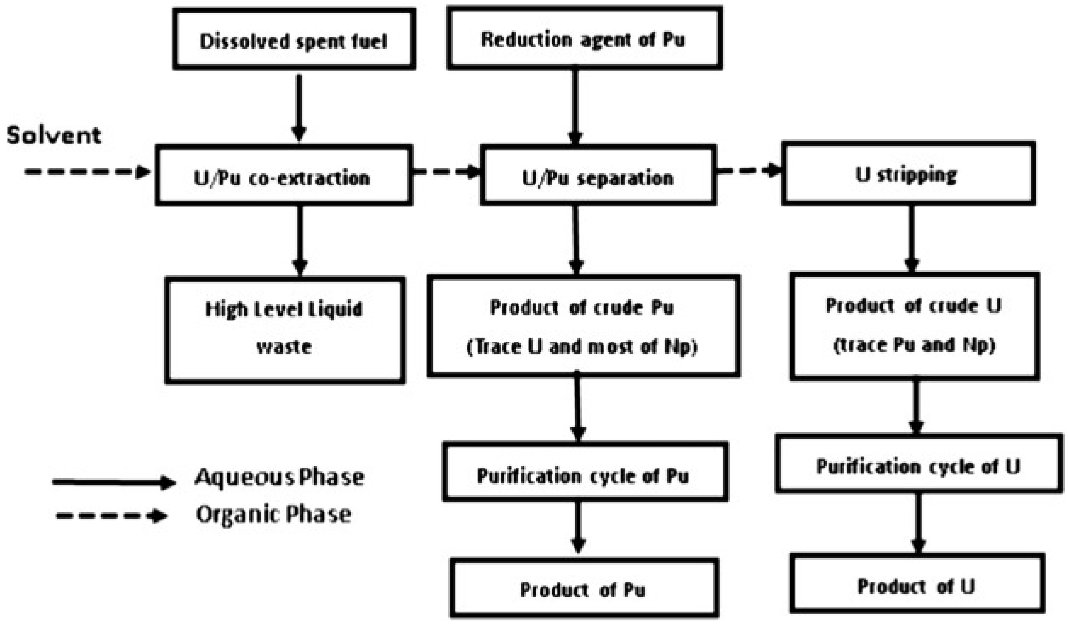


Figure 8: Flowchart of the PUREX process [15]

There are modification of the PUREX for the separation of uranium and plutonium of spent nuclear fuel. One example is the Uranium Extraction (UREX), which prevents plutonium from being separated and solely uranium is extracted.

The Transuranic Extracton (TRUEX) is an enhancement to remove transuranic metals like americium and curium from waste of PUREX to reduce the alpha activity. An alternative process is the Diamide Extraction (DIAMEX) with improvements of the production of organic waste. After TRUEX or DIAMEX actinides like americium could be further utilized in industry. For that purpose lanthanides have to be removed with another separation process, which is currently still being researched - the Selective Actinide Extraction (SANEX).

The removal of the most troublesome components of reprocessing waste is achieved with Universal Extraction (UNEX), where strontium, caesium and minor actinides are separated [16].

3.3. Neutron Activation

Irradiation of samples with a neutron beam leads to the capture of neutrons in sample-nuclei and to the activation of the material. Neutron activation is usually perfomed either with nuclear reactors or other neutron sources. An important value for neutron activation is the reaction cross-section σ of the irradiated target. The cross-section is a measure of the reaction probability and specific for each nuclide and dependent on the energy of the incident neutron. It has the dimension of area and is usually stated in units of barns with the following conversion [17].

$$1\ barn \ = \ 10^{-24}\ cm^2 \tag{3.1}$$

Figure 9 shows the activation cross-section of ^{59}Co versus the neutron energy.

The rate of activations per unit of time is given as:

$$R \ = \ \Phi_n \ * \ \sigma \ * \ \rho_A \tag{3.2}$$

Where

Φ_n ... Neutron flux density
ρ_A ... Density of atoms in the target
σ ... Reaction cross-section

Neutron activation is used for example in research for the NDA of elemental- or isotopic composition of sample material. For that purpose the sample is activated and released energies of subsequent radioactive decays are measured to identify the material [17].

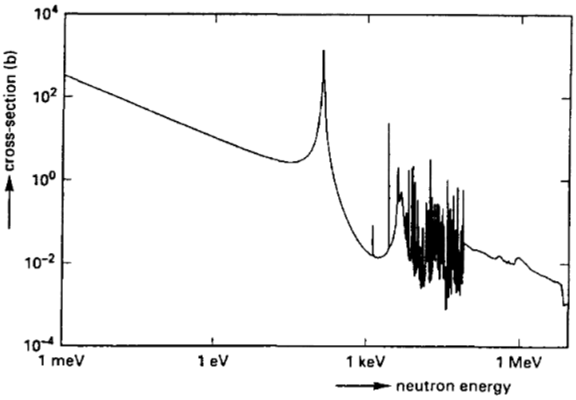


Figure 9: Activation cross-section of ^{59}Co [18]

3.4. Szilard-Chalmers Reactions

The binding energies between atoms in molecules are between approximately 0.4 to 4 eV. Released energies of nuclear reactions are on the order of MeV. Therefore nuclear reactions may lead to consecutive chemical reactions caused by a partial transfer of the energies to involved atoms in form of recoil.

The resulting chemical effects may be divided in primary and secondary effects. Primary effects concern effects that are caused directly by recoil: Recoil of the nucleus, ionization or change of the atomic number in case of an atomic reaction . Secondary effects depend on chemical bonds and state of the material. Chemical bonds in molecules may be broken by recoil.

Assuming that the velocity of emitted particles in nuclear reactions is approaching the velocity of light c, the energy of the recoiling atom E_1 with mass m_1 is calculated with energy and mass E_2 and m_2 of the particle and the relativistic conservation of momentum.

$$E_1 = \frac{m_2}{m_1}E_2 + \frac{E_2^2}{2m_1c^2} \tag{3.3}$$

Replacing the mass of the recoiling atom m_1 and the mass of the emitted particle m_2 with the nuclide masses M_1 and M_2 , wich is transfered to the recoiling atom.

$$E_1 = \frac{E_2}{M_1}(M_2 + \frac{E_2}{2c^2}) \tag{3.4}$$

The second term of Equation 3.4 may be neglected in case of $M_2 \geq 1$ u.

In case of a β decay the emitted particle is either an electron or a positron the mass of the emitted particle M_2 is $5.49 * 10^{-4}$ u.

For gamma emissions the conservation of momentum is

$$m_1 v_1 = \frac{E_\gamma}{c} \tag{3.5}$$

with the velocity v_1 of the recoiling atom and the energy E_γ of the emitted photon. The resulting energy of the recoil becomes

$$E_1 = \frac{E_\gamma^2}{2M_1c^2} \tag{3.6}$$

Released energies, the magnitude of the recoil and the resulting chemical effect vary depending on the type of nuclear reaction. The following list shows examples of nuclear reactions and their possible effect on chemical bonds in atoms and molecules.

1. α **decay**
   The energy of α particles emitted in the decay of Po-212 have an energy of $E_2 = 8.785$ MeV. With Equation 3.4 the recoil energy is $E_1 = 0.169$ MeV. As mentioned previously the binding energies are between approximately 0.4 and 4 eV, which means that the recoil energy is sufficient to break chemical bonds. In case of an α decay, recoil energy transferred to the atom is always in the magnitude of MeV. Therefore α decays will always lead to the break of chemical bonds.

2. β^- **decay**
   The released energy of β^- decays is shared between the emitted electron and anti-neutrino. The energy of the particles depends on the angle under which they are emitted. During decay of Sr-90 the shared energy between the emitted particles is 0.546 MeV. The maximum recoil energy $E_1 = 5.11$ eV is calculated with Equation 3.4 assuming that the electron has got the full energy of that

decay. Because of the share of the energy with the anti-neutrino the recoil energy frequently has only a portion of that energy. This means that the probability to break chemical bonds increases with the energy of the electron.

3. **Isomeric transition**
   After beta emission or neutron capture, positron emission or electron capture, the radioactive nucleus remains in an excited state. By emission of excess energy in form of gamma photons they relax into the ground state. During the most common isomeric transition of ^{53m}Fe photons with an energy of 0.701 MeV, 1.012 MeV and 1.328 MeV are emitted [19]. With Equation 3.6 the recoil energy caused by photons with 0.701 MeV is $E_1 = 4.725$ eV and is therefore sufficient to break chemical bonds. Isometric transition of ^{80m}Br, where photons with an energy of 0.049 MeV and 0.037 MeV are emitted, leads to a recoil energy of $E_1 = 0.016$ eV. This means, that the resulting recoil energy of low-energy photons may be lower than the binding energies between atoms.

4. **Binuclear reactions with subsequent emission of protons, neutrons or α particles**
   Binuclear reactions, for example the absorption of thermal neutrons, may lead to the emission of protons, neutrons or α particles. Excess energy after a binuclear reaction is shared among all reaction products. As an example the irradiation of ^{14}N with thermal neutrons leads to the reaction ^{14}N(n,p)^{14}C with the release of an energy of 0.626 MeV which is shared among the reaction products. If the kinetic energy of the thermal neutron is neglected the recoil energy $\mathrm{E}_1 =$ 0.042 MeV is calculated using Equation 3.4. The recoil energy during emission of protons, neutrons or α particles is generally higher than the binding energies between atoms.

5. **Binuclear reactions with subsequent emission of γ photons**
   Binuclear reactions may also lead to the emission of one or several γ photons. For example,the maximum energy of the characteristic photons from the reaction ^{37}Cl(n,γ)^{38}Cl equals 6.11 MeV which is shared among one or more photons, thus the maximum recoil energy delivered to the remaining nucleus of $E_1 = 528$ eV is calculated with Equation 3.6. This energy and even fractions resulting from the emission of several photons are sufficient to break chemical bonds. In general, most (n,γ) reactions lead to the break of chemical bonds.

Szilard-Chalmers reactions are binuclear reactions with emission of γ photons, which are used for the separation of isotopic product nuclides. Followed by chemical separation techniques based on oxidation state or chemical bonds, the production of material with high specific activities is possible.

Despite the sufficient magnitude of γ-energies, there are some products of the (n,γ)-reaction that remain in their original chemical compound, which is called primary retention. Secondary retention is caused by recombination after chemical bonds have been broken [20]. Examples of irradiated compounds and their retention are listed in Table 2.

Irradiated compound	Nuclear reaction	Yield (%)	Retention (%)
CH_3CH_2I	$^{127}I(n,\gamma)^{128}I$	54	46
$LiIO_3$		34	66
$NaIO_3$		33	67
KIO_3		33	67
NH_4IO_3		78	22
CH_2Br_2	$^{81}Br(n,\gamma)^{82}Br$	57	43
$CHBr_3$		53	47
$NaBrO_3$		90	10
$KBrO_3$		91	9
C_6H_5Cl	$^{37}Cl(n,\gamma)^{38}Cl$	65	35
$NAClO_3$		98	2
Li_2CrO_4	$^{50}Cr(n,\gamma)^{51}Cr$	34	66
Na_2CrO_4		26	74
$Na_2Cr_2O_7$		20	80
K_2CrO_4		39	61
$K_2Cr_2O_7$		10	90
$(NH_4)_2CrO_4$		82	18
$(NH_4)_2Cr_2O_7$		68	32
$LiMnO_4$	$^{55}Mn(n,\gamma)^{56}Mn$	91	9
$NaMnO_4$		91	9
$KMnO_4$		77	23
Na_3PO_4	$^{31}P(n,\gamma)^{32}P$	50	50
Na_2HPO_4		55	45
$Na_4P_2O_7$		42	58
Na_3AsO_3	$^{75}As(n,\gamma)^{76}As$	10	90
Na_2HAsO_4		40	60

Table 2: Szilard-Chalmers Reactions [21]

3.5. Liquid-Liquid-Extraction

Liquid-Liquid-Extraction is a chemical separation process used for the extraction of components disolved in a liquid based on chemical properties like polarity and hydrophobic or hydrophilic character. Prior to the extraction the samples to be separated are dissolved, usually in an aqueous liquid. The resulting feed solution is then put together with an organic solvent. Both liquids are stirred and form immiscible phases afterwards. Components of the feed solution are transferred to the organic solvent to achieve a thermodynamic equilibrium state, which depends on the interactions between the dissolved sample and the solvent phase.

The two liquid phases may be separated with separation funnels resulting in a solvent-rich solution, the extract and the raffinate with the extracted feed. Figure 10 shows the principle of LLE.

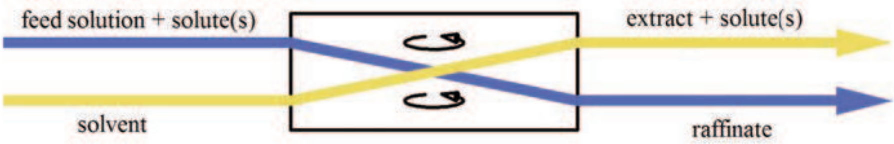


Figure 10: Liquid-Liquid-Extraction [22]

3.6. The Exercise

3.6.1. List of Equipment

Following equipment is used for the second exercise:

- Separation funnel
- Forceps
- Pipettes
- Beakers
- Sample vials
- Ammonium chromate

- Sodium chromate
- Unimolar hydrochloric acid
- Methyl isobutyl ketone
- Distilled water
- Latex gloves
- Laboratory coat
- Safety goggles

3.6.2. The Sequence of the Exercise

For the preparation of the exercise, both ammonium chromate and sodium chromate are irradiated with thermal neutrons, which leads to following nuclear reaction:

$$^{50}\mathrm{Cr}\ (n,\gamma)\ ^{51}\mathrm{Cr} \tag{3.7}$$

Subsequent Szilard-Chalmers Reactions break the bond of an oxygen-atom in both ammonium chromate $(NH_4)_2CrO_4$ and sodium chromate Na_2CrO_4 which results in the change of the oxidation states of both molecules. The hexavalent oxidation state of both chromates is changed to a trivalent oxidation state.

After irradiation of the chromates they are put in a sample vial which is then filled with 20 ml of unimolar hydrochloric acid to dissolve the irradiated chromate-samples. After emptying the sample vial into the separation funnel, inactive chromium nitrate $Cr(NO_3)_3$ is added as a carrier for trivalent chromates. Further 10 ml hydrochloric acid are used to rinse out the sample vial to dissolve potential residues, which is then added to the separatory funnel.

Afterwards liquid-liquid-extraction is conducted to separate trivalent chromates in an aqueous solvent. For that purpose the following steps are repeated three times:

1. 10 ml of an organic solvent - methyl isobutyl ketone $C_6H_{12}O$ - is put in the separation funnel. Hexavalent chromates are transferred to the organic solvent while trivalent chromates remain in the aqueous phase.

2. The separation funnel is closed, shaken and its stopper is lifted carefully for ventilation
3. After a short period, a clear line between the organic and the aqueous phase is visible as seen in Figure 11. Because of the difference in densities the aqueous phase is below the organic phase.
4. Both the aqueous phase with trivalent chromates and the organic phase with hexavalent chromates are filled in two separate beakers.

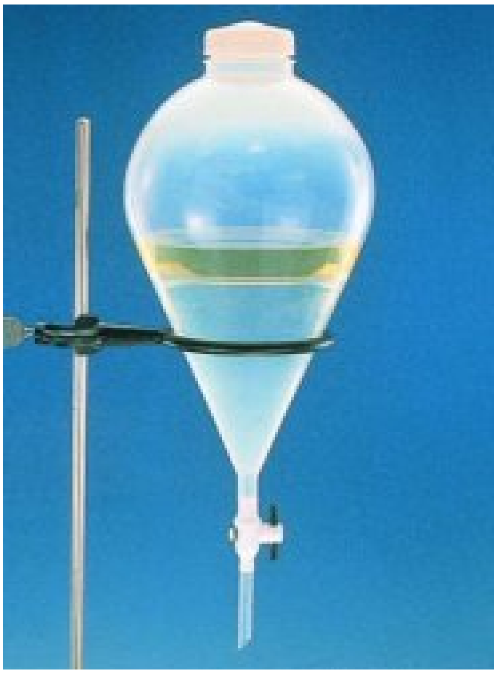


Figure 11: The organic and aqueous phase of liquid-liquid-extraction

After the first liquid-liquid-extraction the aqueous phase with dissolved trivalent chromates is filled into a sample vial and triple distilled water is added. Afterwards another liquid-liquid-extraction is performed to transfer the hexavalent chromates from the organic phase to an aqueous phase using triple distilled water.

The following steps are repeated three times:

1. The organic phase and 10 ml distilled water are filled into the separatory funnel.

2. The separation funnel is again closed, shaken and the stopper is removed carefully for ventilation.

3. Once the two phases are clearly visible, the aqueous phase and the organic phase are filled in two separate beakers.

Subsequent activity measurements with gamma spectroscopy are conducted to evaluate the amount of chromates in all sample vials. Activity measurements of the sample vial with methyl isobutyl ketone ideally results in a very low activity because no chromates should remain in the organic phase. Gamma spectroscopy is discussed in detail in Chapter 4.3.

3.6.3. Results and Interpretation

Cr-51 which is the result of neutron activation of Cr-50, has a γ-peak at 320 keV. The counts of the samples have been measured for 300 seconds, leading to the following results.

Sample	Na_2CrO_4	$(NH_4)_2CrO_4$
Cr(III)	$4109\ cts \pm 1.58\%$	$9856\ cts \pm 1.02\%$
Cr(VI)	$7862\ cts \pm 1.14\%$	$2445\ cts \pm 2.05\%$
$C_6H_{12}O$	$73\ cts \pm 11.70\%$	$20\ cts \pm 22.38\%$

Table 3: Measurement Results of LLE

In case of this exercise the retention equals the percentage of chromates that remain in the hexavalent oxidation state as well as chromates that recombine to the original hexavalent state. The retention is calculated with the following equation.

$$R = \frac{A_0}{A} \tag{3.8}$$

Where

R = Retention

A_0 = Activity of Cr(VI)

A = Total activity of Cr(VI) and Cr(III)

The measurement results lead to 65.68 % retention for Na_2CrO_4 and 19.88 % retention for $(NH_4)_2CrO_4$. Comparing the retentions with the table in Figure 2 shows good conformity with the literature values.

Because of its low retention, ammonium-chromate is more efficient to achieve higher specific activities compared to sodium-chromate.

3.6.4. Execution of the Exercise

The exercise starts with a brief introduction of liquid-liquid-extraction and Szilard-Chalmers reactions. Students are then informed about the sequence of this exercise in Chapter 3.6.2.

Before starting the exercise with radioactive material, students perform a "dry run", where all steps of the exercise are performed with chromates that have not been irradiated. The "dry run" is an opportunity to become familiar with each step of the exercise while no radioactive material is present. This enables a better routine for the second iteration of the exercise with radioactive material.

Once the dry run is completed, prepared chromates are irradiated for the actual exercise, where students repeat the sequence of the exercise with activated material. After finishing the two stages of liquid-liquid-extraction, three sample vials, one with hexavalent chromates in an aqueous solution, one with tetravalent chromates in an aqueous soluton and a vial with methyl isobutyl ketone are prepared for activity measurements with gamma spectrometry. The measured activities are then used to determine the retention of both chromates. Optionally, an activity-measurement of the methyl isobutyl ketone can be performed to determine if any residues of the chromates are left in the organic phase.

4. Nuclear Attribution

4.1. Overview

The last exercise represents the final step after nuclear forensic analysis: Nuclear attribution.

The objective of nuclear attribution is the identification of the origin of nuclear or radioactive material out of regulatory control which has been involved in illicit activities like nuclear smuggling and discovery of abandoned radiation sources. To achieve accurate results, multiple resources of information have to be utilized. On the one hand, measurement results of nuclear forensic analysis have to be evaluated and on the other hand, research about environmental signatures, methodology for different production techniques of industrial and medical radiation sources and nuclear material combined with information from intelligence sources and law enforcement is carried out.

Each individual case of illicit activities raises different questions, which have to be answered with nuclear attribution. For example in case of smuggled nuclear or radioactive material the identification of the origin of the material and involved individuals are just two major goals of nuclear attribution [9].

This exercise explains the evaluation of measurement results of an "unknown" nuclear material that has been measured with Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and gamma spectroscopy. Goal of the exercise is the identification of the nuclear material with an interpretation of measurement results. The analytical methods used for that are explained in Section 4.2.

4.2. Inductively Coupled Plasma Mass Spectrometry

The ICP-MS is an analytical tool to determine elemental and isotopic composition of samples with very low detection limits. The ICP-MS consists of three parts: The sample injection system, the ionizer and the mass analyzer system.

The ionization of samples is conducted in a plasma, which is produced by inductively heating with an electromagnetic coil. The plasma is generated and sustained in the torch, which is made of three concentric tubes, usually made of quartz, within the induction coil. While in a radio-frequency magnetic field, argon gas is introduced in the middle tube of the torch and an electric spark is applied to introduce free electrons into the gas stream. Because of the magnetic field, free electrons are accelerated in alternating directions with a high frequency. Collisions between free electrons and argon atoms may lead to the release of further electrons which may lead to additional ionizations of argon atoms. Once a balance between the rate of ionizations and the rate of recombinations of free electrons with argon ions is achieved, inductively coupled plasma is generated. Another stream of gas of the outer tube retains the inductively coupled plasma and prevents the contact of the plasma with the walls of the torch. The concentric tubes are cooled with an additional tangential flow of gas.

The central tube of the plasma torch introduces another flow of argon gas which is the carrier of the sample. As a preparation for measurements the sample has to be dissolved so that the liquid sample passes a vaporizer and is then transferred to the carrier gas stream. To ensure stability, the introduction should be with least possible liquid and a consistent size of droplets. Usually a spray chamber after the vaporizer is used to remove larger droplets before entering the plasma torch. Another option is the use of laser ablation in case of solid samples. The target sample is irradiated with a pulsed laser beam and heated by the absorbed energy and evaporized. Ions produced by thermal ionization, absorption of laser energy or collissions with electrons are finally introduced into the plasma torch. Figure 12 shows the schematic of a plasma torch [23, 24].

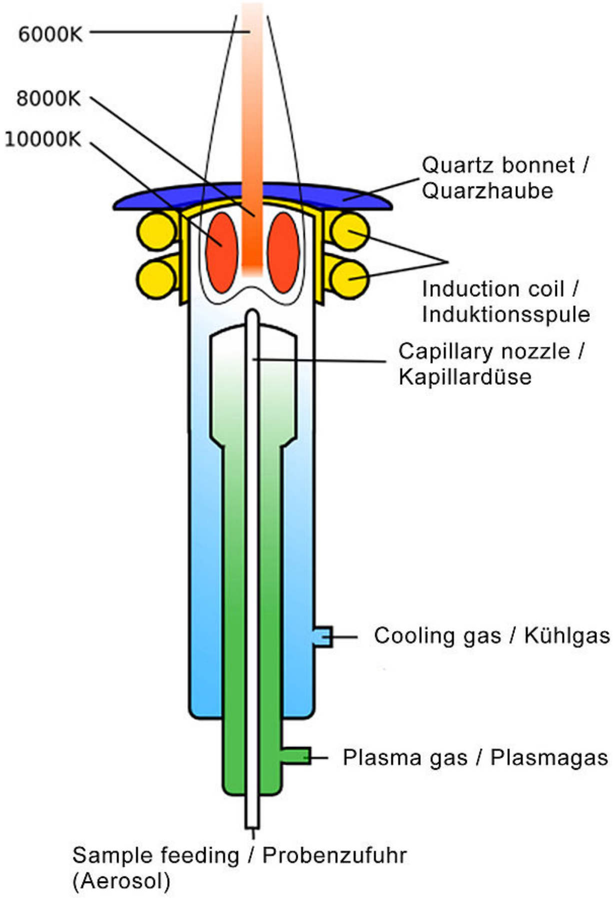


Figure 12: The inductively coupled plasma torch [25]

Before entering the mass spectrometer, sample ions in the plasma have to be transferred into high vacuum. This is achieved with a differentially pumped atomspheric-pressure-to-vacuum interface. A fraction of the ions created in the plasma pass a sampler cone with 1 mm diameter and enter the first vacuum chamber. The vacuum is generated with a series of pumps. Usually a rotary vane pump removes most of the gas in the first vacuum chamber and reaches a pressure of 133 Pa. The ions in the plasma pass a second aperture with a temperature-resistant skimmer cone and enter a high vacuum stage which is generated by high capacity vacuum pumps. A beam of sample ions is formed and accelerated with optical elements and an applied voltage.

After being transfered from plasma into vacuum, the sample particles enter the mass spectrometer to be analyzed. There are multiple different mass analyzer systems, for example magnetic sensor fields, time-of flight, Pauli ion trap and ion detection systems [26].

One of the most commonly used types of mass analyzer systems is the quadrupole mass filter. The quadrupole mass filter is made of four parallel cylindrical rods arranged in a square. The opposite rods have the same charge and are connected to each other. Figure 13 shows the structure of a quadrupole mass filter.

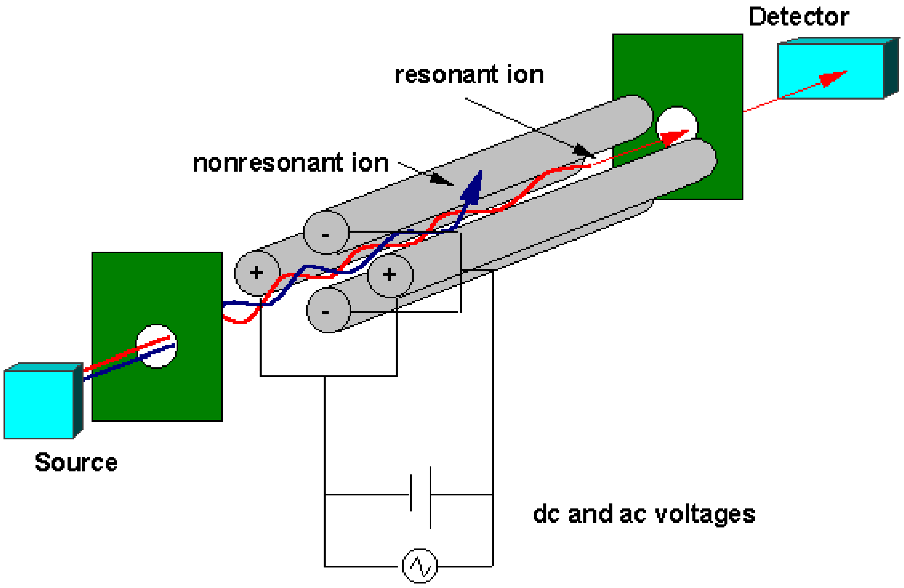


Figure 13: The sheme of a quadrupole mass filter [27]

An electrical voltage is applied, which has a portion of direct current and a portion of alternating current. The resulting electric field excerts a force on charged particles inside the mass filter that influences their trajectory. Only particles with a stable trajectory can reach the detector, while others will not pass the mass filter and hit one of the mass filter rods. The stability of the trajectory only depends on the mass-charge ratio and the applied voltage, which means that particles with certain mass-charge ratios can be selected by adjusting the applied voltage.

4.3. Gamma Spectroscopy

After radioactive decay, the daughter nucleus usually remains in an excited state with excess energy. During relaxation, the nucleus releases that energy in form of emitted photons. It is notable that the energy of emitted photons varies depending on the energy levels of the daughter nucleus. Excess energy may be released in form of one or more photons with characteristic energies that can be measured and used to identify the nucleus. For that purpose, interactions of gamma radiation with matter are used to detect and measure the energy of those photons. In general, there are three different interactions that can be measured in gamma spectroscopy: photoelectric absorption, compton scattering and pair production.

In case of photoelectric absorption, the emitted photon interacts with one of the shell electrons of an atom. As a result the full energy of the photon is absorbed, leading to the ejection of the electron from its shell. The kinetic energy of the released electron equals the difference between the energy of the gamma-ray and the binding energy that has to be overcome.

The ionized atom remains in an excited state with an excess energy equal to the binding energy of the released electron. The relaxation of the excited atom may be conducted in two different ways. On the one hand, the excess energy may be split between remaining electrons of the atom which may lead to the release of further electrons in a so-called Auger cascade. On the other hand, an electron in a higher energy-state may take the place of the previously released electron while emitting energy in form of a characteristic X-ray photon. The shell from which the electron is ejected depends solely on the energy of the absorbed photon. It is most likely that the ejected electron is in the K shell of the atom but if the energy of the gamma-ray is not enough an electron of the L or M shell is released instead.

Compton scattering is the partial transfer of the gamma-photon energy to an interacting electron of the atom. A recoil electron is released while the gamma-photon is scattered at a specific angle. The kinetic energy E_e of the electron depends on the scattering angle Θ of the photon and its energy E_γ and is given as

$$E_e = E_\gamma \left\{ 1 - \frac{1}{[1 + \frac{E_\gamma(1 - cos\Theta)}{m_0 c^2}]} \right\} \tag{4.1}$$

Compton scattering is most common between gamma-rays and the outer electrons with lower binding energies which means that the probability of a released recoil electron is quite high.

Pair production is not an interaction with bound electrons of the atom but with the core of the atom itself. If the photon is near the nucleus of an atom it may interact with the coulomb field leading to the conversion into an electron-positron pair. The energy of the interacting gamma-ray must be higher than the rest-mass of the electron and positron which means that the energy has to be at least 1022 keV. Excess energy of the gamma-ray is shared between the electron and the positron.

Collision with another electron leads to the annihilation of both. During that process two annihilation photons with 511 keV each are emitted.

After conducting gamma spectroscopy, all those events significantly influence the measurement results. Figure 14 shows an example of a gamma spectrum.

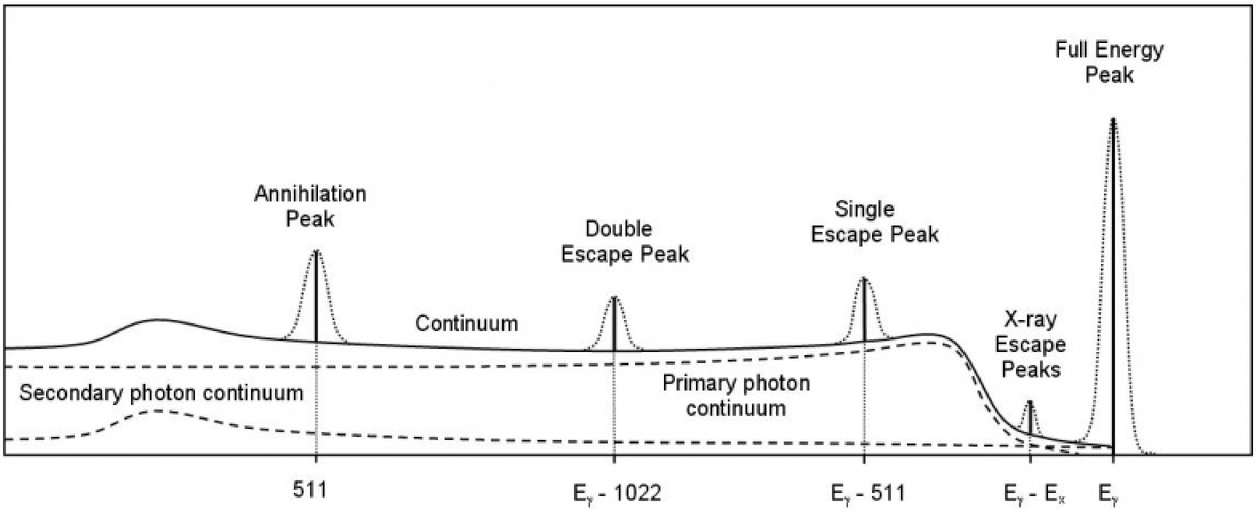


Figure 14: An example gamma spectrum [28]

The spectrum shows all interactions previously mentioned. The Full Energy Peak corresponds to the photoelectric absorption, where the whole energy of the photon E_γ is absorbed. The Full Energy Peaks in a gamma spectrum are utilized to identify the components of the radiation source. Compton scattering is shown as a continuum edge at lower energies than the Full Energy Peak. The transferred energy from the initial photon to the recoiled electron depends on the scattering angle which leads to the continuum edge in the spectrum.

The annihilation peak is always at 511 keV and equals the measurement of the released photons after an electron and a positron annihilate. Additionally if one of those photons leaves the detector without being measured, another peak occurs in the spectrum: The Single Escape Peak at the energy of the difference between E_γ and 511 keV. If both photons remain undetected, they contribute to the Double Escape Peak, with an energy of the difference between E_γ and 1022 keV [29].

Such gamma spectra are made by recording the interactions between the photons with matter. Those interactions lead to the ionization of interacting atoms which is used in detectors to measure gamma radiation. Released electrons are accelerated in an electric field and collide with further atoms transferring energy to bound electrons which again leads to ionization and to an avalanche of ionized electrons. As a result an electrical pulse is measured with a current proportional to the energy of the initial photon. Non destructive assay may be conducted with different types of detectors to register the charge of the ionized electrons either directly with proportional counters (gas-filled detectors) and solid state detectors (semiconductor detectors) or indirectly with secondary reactions in scintillator detectors.

For the exercise, a solid state semiconductor detector has been used. The volume of interaction with gamma rays in such detectors is the depleted region of a semiconductor crystal in a reverse-biased n-p or p-n junction. Gamma rays lift electrons from the valence band to the conduction band, generating electron-hole-pairs which may move freely in the depleted region. An applied voltage produces a high electric field in the semiconductor, which accelerates the ionization charge towards the electrodes where an electric pulse is measured in an outer circuit. The number of electron-hole-pairs that are set free only depends on the semiconductor material and is proportional to the energy of the incident radiation. Commonly used semiconductor materials are silicon and Hyperpure germanium crystals.

The reverse-biased n-p or p-n junction in solid state semiconductor detectors usually results in very low currents in the detector. Therefore interferences by natural, thermally generated electrical noise in the semiconductor crystal has to be reduced with cryogenic cooling which is mandatory for semiconductor detectors [30]. The components of a semiconductor detector are shown in Figure 15.

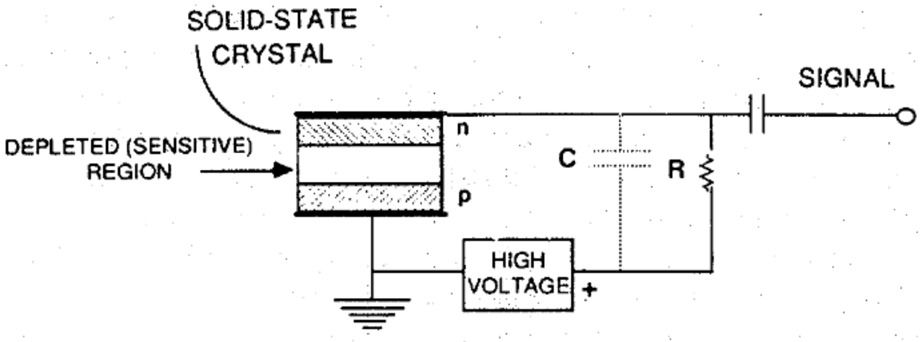


Figure 15: The simplified diagram of a semiconductor detector [30]

4.4. Nuclear Chronometry

For further use, natural or spent nuclear material usually has to be purified, which means that undesired decay products are removed. The time elapsed since the purification is called the "age" of the material. The age of nuclear material may provide important information about when the material has been produced, and eventually where with knowledge of other signatures and knowledge of potential processing locations. In nuclear chronometry the relative composition of radioisotopes that are linked through radioactive decay are measured to determine the age of the nuclear material. Depending on the half-life of a parent and its daughter isotopes an equilibrium may be reached. A disturbance of that equilibrium is an indicator for the age of the corresponding material [31].

A radioactive decay chain can be described with the Bateman equations. The decay of a parent radioisotope with N_m nuclei and half-life T_p into a daughter radioisotope with N_d nuclei and half-life T_d is given by following differential equations

$$\frac{dN_p}{dt} = -\lambda_p N_p \tag{4.2}$$

$$\frac{dN_d}{dt} = \lambda_p N_p - \lambda_d N_d \tag{4.3}$$

with

$$\lambda = \frac{ln(2)}{T} \tag{4.4}$$

This system of linear differential equations leads to

$$N_d(t) = N_{p,0}\ \frac{\lambda_p}{\lambda_d - \lambda_p}(e^{-\lambda_p t} - e^{-\lambda_d t}) + N_{d,0}\ e^{-\lambda_d t} \tag{4.5}$$

$N_{p,0}$ and $N_{d,0}$ are the initial amount of parent and daughter nuclei. In case of purification of nuclear material, all decay products are removed prior to further processing and therefore $N_{d,0}$ equals zero and the last part of equation 4.5 may be neglected.

The activity A of parent and daughter radionuclides is given as

$$A = \lambda N \tag{4.6}$$

which allows to rewrite equation 4.5

$$A_d(t) = A_{p,0}\ \frac{\lambda_d}{\lambda_d - \lambda_p}(e^{-\lambda_p t} - e^{-\lambda_d t}) \tag{4.7}$$

From this, one can infer that, with the measurement of the activity of both parent and daughter nuclide and the decay-constant or half-life, the age of the nuclear material may be determined [32].

As mentioned previously, the decay from parent nuclide to daughter nuclide may reach an equilibrium, depending on the magnitude of the difference between their half-lifes.

If $T_d < T_p$ and therefore $\lambda_d > \lambda_p$ and when $t > \ 10 * T_d$, Equation 4.5 becomes

$$A_d(t) = A_{p,0}\ \frac{\lambda_d}{\lambda_d - \lambda_p} e^{-\lambda_p t} = A_p(t)\ \frac{\lambda_d}{\lambda_d - \lambda_p} \tag{4.8}$$

This means that the activity of the daughter nuclide is initially growing and reaches a maximum, followed by an equilibrium where it further decays but with the half-life of its parent nuclide. This equilibrium is called transient. A diagram with the logarithmic activities of Molybdenum-99 and Technetium-99m is shown in Figure 16.

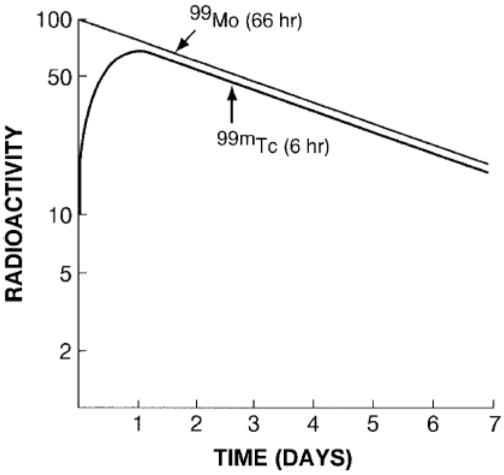


Figure 16: Transient equilibrium between Mo-99 and Tc-99m [33]

When $T_d << T_p$ and therefore $\lambda_d >> \lambda_p$, secular equilibrium is established. λ_p may be neglected compared to λ_d which means that equation 4.5 transforms to

$$A_d(t) = A_p(t) \tag{4.9}$$

The activity of the daughter nuclide becomes equal to its parent and both decay with the half-life of the parent nuclide [33]. Figure 17 shows the logarithmic activities of the parent isotope tin-113 and its daughter isotope indium-113m.

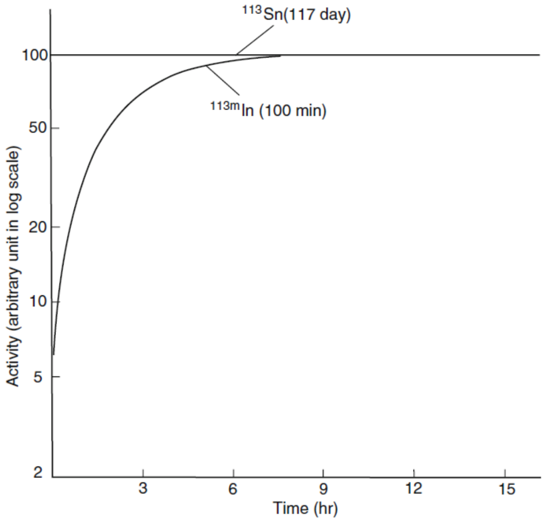


Figure 17: Secular equilibrium between Sn-113 and In-113m [33]

Assuming that perfect purification was performed and no initial decay products are left, the age of a nuclear or radioactive material can be determined after measuring the activities of the decay products. If an equilibrium between a parent isotope and its daughter isotope has not yet been reached. The age of the material may then be calculated with Equation 4.7.

With the current activity of the parent isotope

$$A_p(t) = A_{p,0}\ e^{\lambda_p t} \tag{4.10}$$

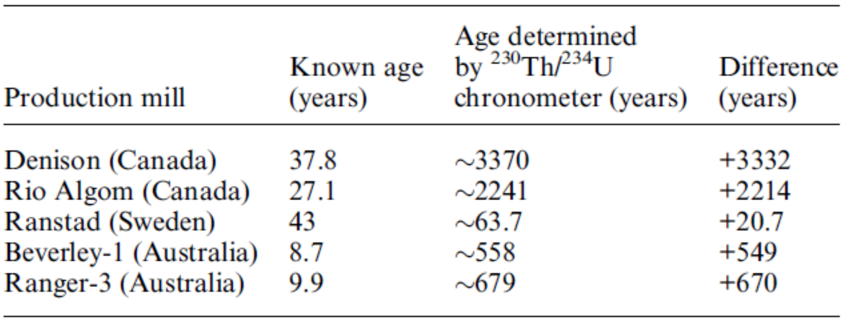
it can be rewritten to

$$A_d(t) = \frac{\lambda_d}{\lambda_d - \lambda_p}\ A_p(t)(1 - e^{(\lambda_p - \lambda_d)t}) \tag{4.11}$$

after mathematical transformations the age of the material is given as

$$t = \frac{ln(1 - \frac{A_d(t)}{A_p(t)} \frac{\lambda_d - \lambda_p}{\lambda_d})}{\lambda_p - \lambda_d} \tag{4.12}$$

Nevertheless, the accuracy of chronometric calculations is limited by multiple factors. The calculations assume a perfect purification process, which is not valid for many materials. Leftovers of decay products, that could not be removed successfully during purification, heavily influence the results of nuclear chronometry. In that case, the age determined with chronometry may become impossibly large. Additionally environmental conditions may also influence the results of nuclear chronometry. The age-dating methods assume a closed system behaviour, which means that all decay products produced after purification are retained. If the material is exposed to certain conditions, decay products may be transported out of or into the material, leading to inaccurate chronometric results. Another reason for differences between the real age and the determined age is the presence of radionuclides that decay into radionuclides, which are considered for calculations. As an example, the presence of plutonium in the material influences chronometric calculations with decay products of uranium. Besides of deviations caused by assumtions related to the material, uncertainties depending on the type of sample preparation and the technique used for activity measurements have to be considered. A possible way to improve the accuracy of chronometric calculations is the use of validated reference material, which is hardly available. Therefore, a more common option is the chronometric calculation of multiple nuclides in the decay chain of the measured material. Comparison of calculations with different nuclides may improve the accuracy of the resulting age of the material [34]. Figure 18 shows the known age of nuclear material with their respective production mill in comparison with the calculated age.



Production mill	Known age (years)	Age determined by ^{230}Th/^{234}U chronometer (years)	Difference (years)
Denison (Canada)	37.8	~3370	+3332
Rio Algom (Canada)	27.1	~2241	+2214
Ranstad (Sweden)	43	~63.7	+20.7
Beverley-1 (Australia)	8.7	~558	+549
Ranger-3 (Australia)	9.9	~679	+670

Figure 18: The comparison of known ages and calculated ages with Thorium-Uranium-chronometry [34]

It is notable, that the ratio of the known age and the age determined by nuclear chronometry is between approximately 1.2-1.5% for all production mills except Ranstad (Sweden).

4.5. The Exercise

4.5.1. The Material

The goal of this exercise is to determine the age of reactor fuel microspheres using the results of gamma spectrometry and the ratio of uranium isotopes. Together with residues of different metals measured with mass spectrometry, the nuclear material should be identified.

The reactor fuel microspheres were originally in a metallic container with a label that states the producer "Minnesota Mining and Manufacturing Company" and its content. The container is shown in Figure 19. The inside of the metallic container is filled with foam material where a small vial made of metal is enclosed. The dark gray powder in the vial and a sample taken with the tip of a syringe are shown in Figures 20 and 21.

Figure 19: The container labelled with "reactor fuel microspheres"

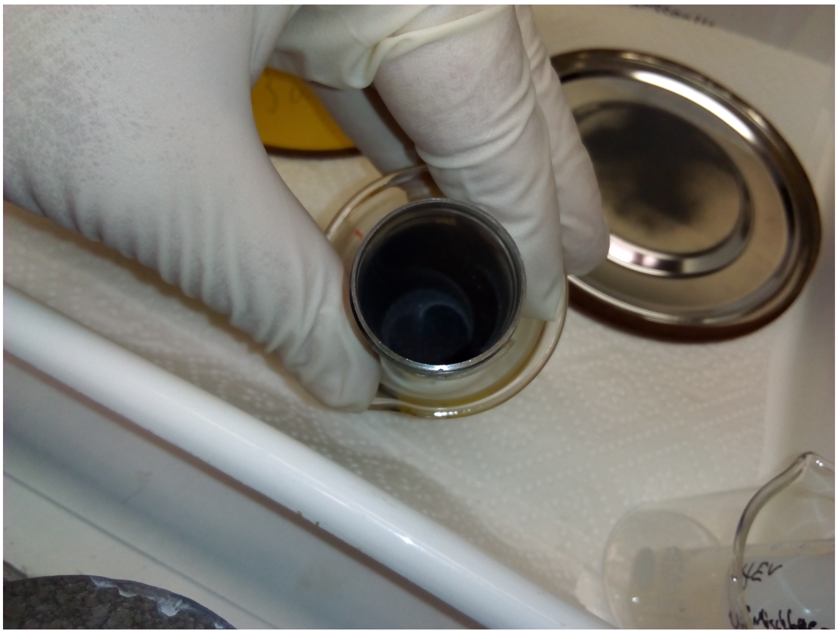


Figure 20: The microspheres in the metallic vial

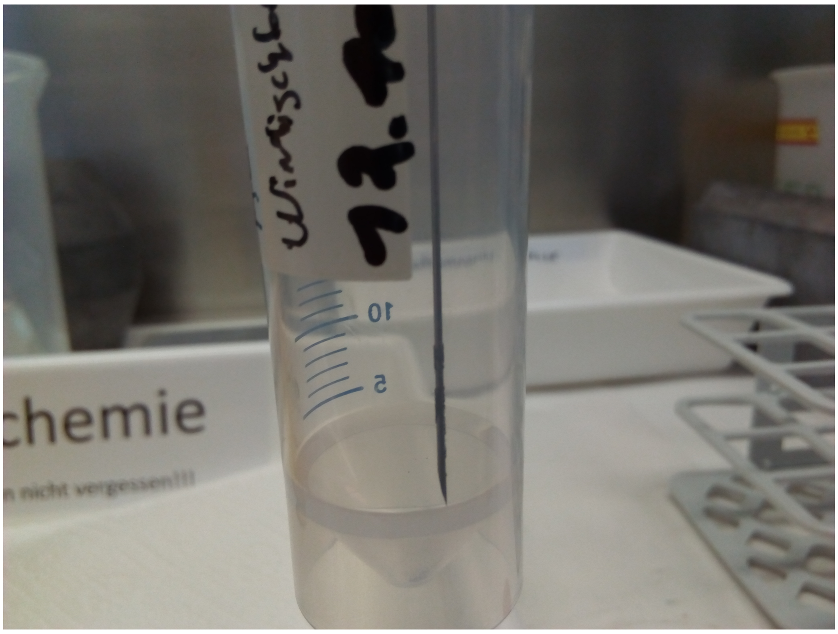


Figure 21: A sample of the reactor fuel microspheres

4.5.2. ICP-MS

For ICP-MS the sample has to be prepared in a liquid form before conducting measurements, which means that the reactor fuel microspheres have to be dissolved. For that purpose, a sample of the nuclear material is taken with the tip of a syringe and is dissolved with 1.5 ml of 8-molar nitric acid. Afterwards the solution is diluted with 40 ml distilled water. Additionally a blank sample is prepared. Measurements are then conducted with an ELAN DRC II ICP-MS from Perkin Elmer SCIEX.

The first measurement is about metallic residues in the nuclear material that could be potential indicators of tools used during processing of the reactor fuel microspheres. The traces of nickel, cobalt, titanium, chromium, aluminium and iron are measured. The relative amounts in the sample and the blank are in Table 4.

Metal	Powder	Blank	Difference
Ni	12459	1122	11337
Co	814	92	722
Ti	3391	2720	671
Cr	128964	17274	111690
Al	66206	61720	4486
Fe	44744	16068	28676

Table 4: Metallic residues measured with ICP-MS

In subsequent measurements the ratio of the uranium-isotopes U-234, U-235 and U-238 are measured to determine the degree of enrichment of the nuclear material. With the concentration of the solution used for the analysis of metallic residues the saturation quantity of U-238 of the mass spectrometer detectors is exceeded. Therefore the solution with the sample has to be further diluted.

Two diluted solutions are prepared. One solution with 100 μl of the sample and 10 ml of distilled water, which equals a 1:100 ratio. The other sample is diluted in a 1:1000 ratio with 20 μl of the sample and 20 ml distilled water. The results of subsequent measurements of both solutions are shown in Table 5.

Uranium Isotope	Mass Fraction (1:100)	Mass Fraction (1:1000)
U-234	0.000 %	0.003 %
U-235	0.018 %	0.462 %
U-238	99.982 %	99.535 %

Table 5: The measured uranium ratios of the 1:100 and 1:1000 Solution

4.5.3. Gamma Spectrometry

Gamma Spectrometry is conducted to determine the relative activities of the radionuclides in the reactor fuel microspheres. Knowledge of the activity of multiple radioisotopes in a decay-chain can be utilized to determine the age of the material, which is the goal of this measurement. The nuclear material is measured with a High-Purity Germanium semiconductor detector. The measurement results are shown in Appendix A.1.

4.5.4. Measurement Data Processing

The results of ICP-MS and gamma spectrometry support the identification of the reactor fuel microspheres, which is the goal of the last exercise. Students receive the measurement data and are supposed to utilize them to identify the nuclear material. Before approaching the last step of nuclear forensic analysis, the nuclear attribution, they are left with the task to process measurement data for the subsequent identification. The photo-peak gamma spectrum needs to undergo some corrections before being used for nuclear attribution.

First of all the efficiency calibration of the gamma spectrometer has to be taken into account. The efficiency is defined as the ratio of the number of measured gamma photons in the detector and the number of gamma photons emitted by the radiation source. If a radiation source with an unknown composition of radioisotopes is measured, the efficiency of the detector varies depending on the measured energy but also depending on the shape and size of the sample. This means that an energy-dependent correction factor has to be evaluated.

There are different ways to determine the efficiency calibration of a gamma detector. A commonly used method is the comparative measurement between the unknown sample and a standard material with similar attributes as the unknown source. Apart from the experimental method a virtual energy calibration may also be determined with Monte-Carlo calculations or modeling [35].

In case of the exercise a virtual, logarithmic efficiency calibration ε as a function of the gamma energy E is given as

$$log(\varepsilon) = -0.0001374E - 2.207 + \frac{251.9}{E} - \frac{32940}{E^2} + \frac{1810000}{E^3} - \frac{44560000}{E^4} \qquad (4.13)$$

The plot of the efficiency calibration for the energies where photo-peaks have been measured during gamma spectrometry is shown in Figure 22.

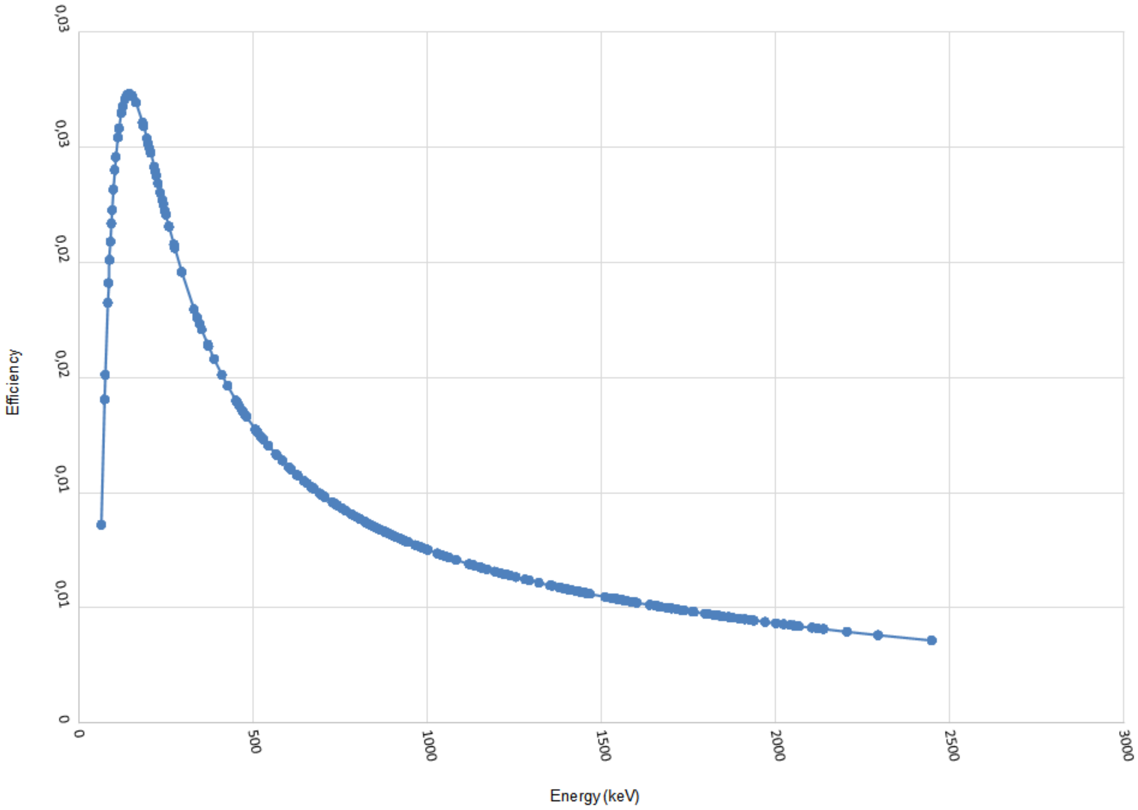
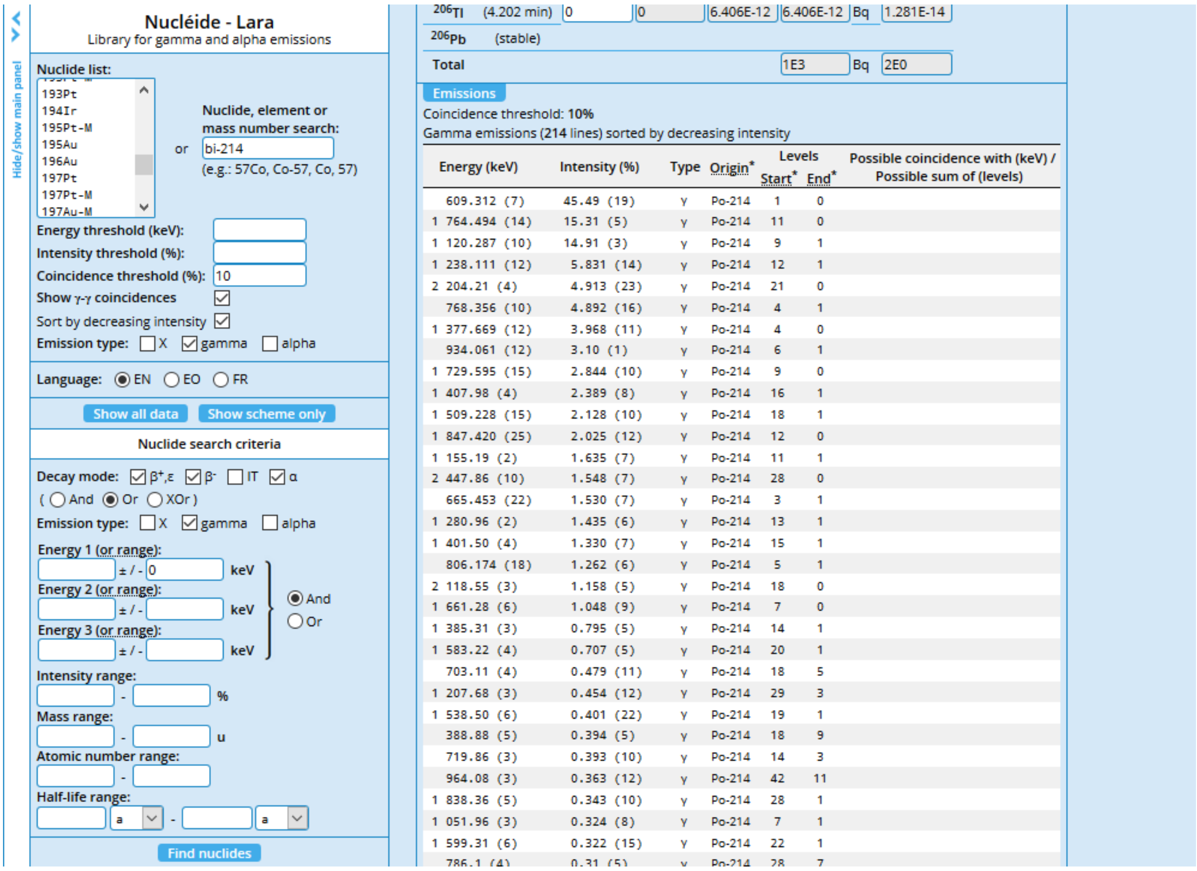


Figure 22: The efficiency calibration curve

Besides the efficiency calibration, there is another important correction in the gamma spectrum. The number of measured counts of peaks at lower energies need to be modified due to self-absorption within the measured material.

Gamma photons with low energies might be absorbed by the atoms of the sample material before being detected, which results in a loss of low energy counts in the gamma spectrum. The self-absorption is usually determined together with the efficiency calibration correction by using a standard sample or alternatively caluclated or modelled. The correction factor is a function of the gamma energy which can be approximated with a linear function. For that purpose the counts of peaks with higher energies are used to interpolate that function.

The first step is the identification of radioisotopes that have been measured during gamma spectrometry. Therefore photo-peaks with higher energies are compared with a database to match the peaks with possible radionuclides. Further emission probabilities have to be included for the calculation of relative activities. The identification and determination of emission probabilities is conducted with "NUCLÉIDE-LARA", an online library for gamma and alpha emissions. The type of decay and either the energy or potential radionuclides are entered in the search panel of the left leading to a list of all full-energy peaks with their respective escape probabilities (or intensities) for that radioisotope. The interface of the website is shown in Figure 23.



Nucléide - Lara
Library for gamma and alpha emissions

Nuclide list:
193Pt
194Ir
195Pt-M
195Au
196Au
197Pt
197Pt-M
197Au-M

or Nuclide, element or mass number search: bi-214
(e.g.: 57Co, Co-57, Co, 57)

Energy threshold (keV):
Intensity threshold (%):
Coincidence threshold (%): 10
Show γ-γ coincidences ☑
Sort by decreasing intensity ☑
Emission type: ☐ X ☑ gamma ☐ alpha

Language: ● EN ○ EO ○ FR

Nuclide search criteria

Decay mode: ☑ β+,ε ☑ β- ☐ IT ☑ α
(○ And ● Or ○ XOr)
Emission type: ☐ X ☑ gamma ☐ alpha
Energy 1 (or range): ± / - 0 keV
Energy 2 (or range): ± / - keV
Energy 3 (or range): ± / - keV
● And ○ Or
Intensity range: - %
Mass range: - u
Atomic number range: -
Half-life range: a - a

^{206}Tl (4.202 min) 0 0 6.406E-12 6.406E-12 Bq 1.281E-14
^{206}Pb (stable)
Total 1E3 Bq 2E0

Coincidence threshold: 10%
Gamma emissions (214 lines) sorted by decreasing intensity

Energy (keV)	Intensity (%)	Type	Origin*	Levels		Possible coincidence with (keV) / Possible sum of (levels)
				Start*	End*	
609.312 (7)	45.49 (19)	γ	Po-214	1	0	
1 764.494 (14)	15.31 (5)	γ	Po-214	11	0	
1 120.287 (10)	14.91 (3)	γ	Po-214	9	1	
1 238.111 (12)	5.831 (14)	γ	Po-214	12	1	
2 204.21 (4)	4.913 (23)	γ	Po-214	21	0	
768.356 (10)	4.892 (16)	γ	Po-214	4	1	
1 377.669 (12)	3.968 (11)	γ	Po-214	4	0	
934.061 (12)	3.10 (1)	γ	Po-214	6	1	
1 729.595 (15)	2.844 (10)	γ	Po-214	9	0	
1 407.98 (4)	2.389 (8)	γ	Po-214	16	1	
1 509.228 (15)	2.128 (10)	γ	Po-214	18	1	
1 847.420 (25)	2.025 (12)	γ	Po-214	12	0	
1 155.19 (2)	1.635 (7)	γ	Po-214	11	1	
2 447.86 (10)	1.548 (7)	γ	Po-214	28	0	
665.453 (22)	1.530 (7)	γ	Po-214	3	1	
1 280.96 (2)	1.435 (6)	γ	Po-214	13	1	
1 401.50 (4)	1.330 (7)	γ	Po-214	15	1	
806.174 (18)	1.262 (6)	γ	Po-214	5	1	
2 118.55 (3)	1.158 (5)	γ	Po-214	18	0	
1 661.28 (6)	1.048 (9)	γ	Po-214	7	0	
1 385.31 (3)	0.795 (5)	γ	Po-214	14	1	
1 583.22 (4)	0.707 (5)	γ	Po-214	20	1	
703.11 (4)	0.479 (11)	γ	Po-214	18	5	
1 207.68 (3)	0.454 (12)	γ	Po-214	29	3	
1 538.50 (6)	0.401 (22)	γ	Po-214	19	1	
388.88 (5)	0.394 (5)	γ	Po-214	18	9	
719.86 (3)	0.393 (10)	γ	Po-214	14	3	
964.08 (3)	0.363 (12)	γ	Po-214	42	11	
1 838.36 (5)	0.343 (10)	γ	Po-214	28	1	
1 051.96 (3)	0.324 (8)	γ	Po-214	7	1	
1 599.31 (6)	0.322 (15)	γ	Po-214	22	1	
786.1 (4)	0.31 (5)	γ	Po-214	28	7	

Figure 23: The interface of "NUCLÈIDE-LARA" with all photo-peaks of Bi-214 [36]

For the correction factor of self-absorption, it is important that only photo-peaks with higher energies are used for the linear interpolation. Besides many peaks are interfering photo-peaks of different radiosiotopes.

Considering the relative uranium-composition measured with ICP-MS allows to assume that the majority of gamma photons were emitted from decay products of Uranium-238. Especially Bi-214 has many full-energy peaks with high energies that do not interfere with other decay products of any measured uranium-isotopes. The following photo-peaks have been used for the linear interpolation of the self-absorption correction factor.

Energy (keV)	Net Peak Area (cts)	Efficiency	Intensity (%)	Corrected Counts
933.94	18654	0.00792123	3.1	75965682
1280.99	7430	0.00622884	1.435	83124596
1155.05	9544	0.00674282	1.635	86570768
1661.55	4910	0.00506717	1.048	92460143
1729.79	13994	0.00490103	2.844	100397941

Table 6: The Bi-214 photo-peaks for linear interpolation

Subsequent linear interpolation, shown in Figure 24, results in the energy-dependent correction factor for self-absorption C_{SA}

$$C_{SA} = 0.0002554322E + 0.5281502335 \tag{4.14}$$

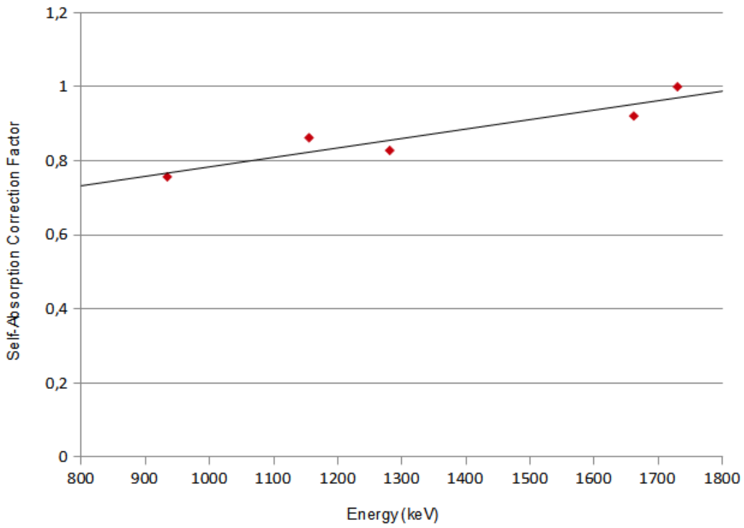


Figure 24: The linear interpolation of the self-absorption correction factor

Applying the correction factors for efficiency calibration and self-absorption results in a gamma spectrum that can be utilized for nuclear attribution. The corrected measurement results are shown in Appendix A.2.

4.5.5. Nuclear Attribution

Nucler attribution is the very last step of nuclear forensic analysis. Results of measurements combined with databases of nuclear material and their processing methods are used to identify unknown sources and their origin. After all measurements are finished and the correction factors of gamma spectrometry are applied, nuclear attribution may finally be conducted.

Metallic residues in the reactor fuel microspheres are an indicator of the tools used for processing techniques. The measurement results in Table 4 show that the number of counts for aluminium are almost equal in the solution with the nuclear material and the blank sample. It is also notable that the counts of cobalt and titanium are relatively low compared to the other countrates. Therefore it may be assumed that the metallic residues only consist of nickel, chromium and iron. The relative composition of those residues is shown in Table 7.

Metal	Counts	%
Ni	11337	7.47
Cr	111690	73.62
Fe	28676	18.90
Total	151703	

Table 7: The relative composition of metallic residues in the nuclear material

Alloys with iron and the majority chromium are called Ferrochrome. Most of the alloy is used in the manufacturing of stainless steel. Ferrochrome is characterized by its temperature and corrosion resistance. The addition of nickel further increases the resistance to corrosion and heat [37, 38]. Measurements of the uranium-isotope ratio of the reactor fuel microspheres show that the material used for the production is depleted uranium with lower amounts of Uranium-235 compared to natural uranium [39]. Therefore it may be excluded that the metallic residues originate in tools for enrichment. It is rather possible that the final step of processing was the grinding of the material to produce particles of that small size.

The corrected gamma-spectrum in Table 10 can be used to determine the age of the reactor fuel microspheres. The uranium-isotope ratio is an indicator that the majority of measured radionuclides in the gamma spectrum are decay products of Uranium-238. The first step to approach nuclear dating is to consider the decay chain of Uranium-238. The age of nuclear material is defined as the latest conducted purification to remove undesired decay products before further processing and it will take a certain time until an equilibrium between parent and daughter nuclides in the decay chain is restored. A disequilibrium may be utilized to calculate the age of the material. The decay chain of Uranium-238 is shown in Figure 25.

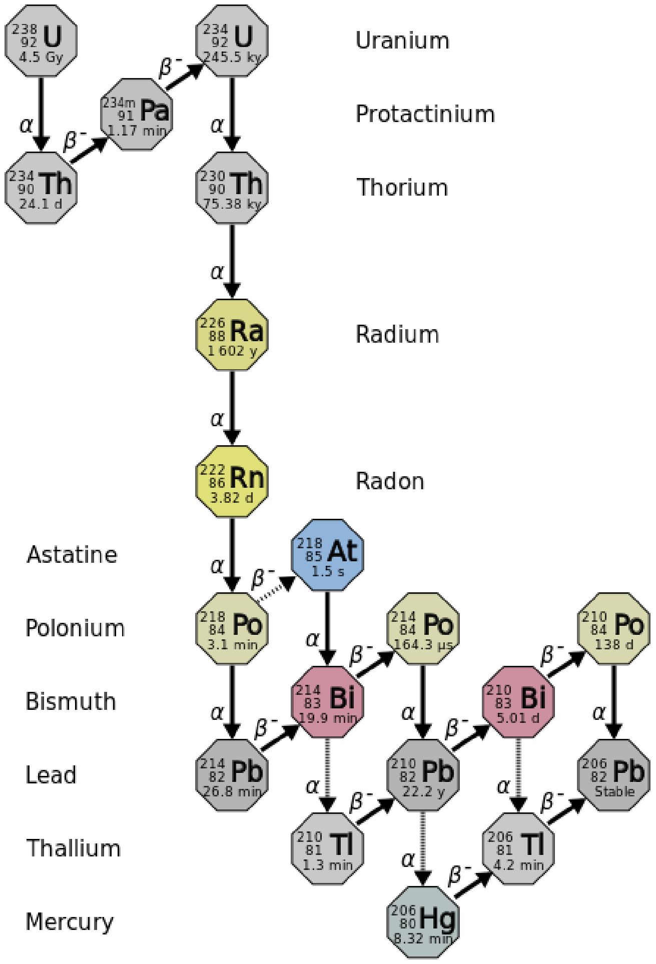


Figure 25: The decay chain of Uranium-238 [40]

It is assumed that the age of the material is about 50 years. That means the equilibrium should be restored until Uranium-234. It is also certain that Bi-214 is in equilibrium with its parent nuclides until Radium-226. The activity of any radionuclide in those parts of the decay chain may be used as a proxy for Uranium-234 and Radium-226. The age of the reactor fuel microspheres may then be calculated with Equation 4.12.

Bi-214 is a suitable proxy for Radium-226 while either Thorium-234 or Protactinium-234 are potential substitutes for Uranium-234. With the help of "NUCLÈIDE-LARA" multiple Pa-234 peaks can be identified. Table 8 shows the full-energy peaks of Pa-234 and Bi-214 used for the calculation.

Energy (keV)	Radionuclide	Activity (Bq)
506.8	Pa-234	1324
669.71	Pa-234	1128
880.35	Pa-234	1250
883.12	Pa-234	1369
898.54	Pa-234	1066
1638.24	Pa-234	1045
1700.7	Pa-234	1346
933.94	Bi-214	384
1155.05	Bi-214	404
1280.99	Bi-214	372
1661.55	Bi-214	377
1729.79	Bi-214	410

Table 8: The photo peaks used for nuclear dating

The average values of both radionuclides result in an activity of 1219 Bq for Pa-234 and 389 Bq for Bi-214. Both radionuclides are used as a proxy for Uranium-234 and Radium-226 and therefore those activities are used instead. The half-life of Uranium-234 is 245500 years and the half-life of Radium-226 is 1602 years.

With the values above, the age of the material is approximately 894 years, which is impossible. A potential reason for that error could be the wrong assumption of a perfect purification, as mentioned in Chapter 4.4. Residues of decay products can lead to unrealistically high results of chronometric calculations. Considering the ratios between the real age and the calculated age of the material in Figure 18, leads to an age of approximately 20 years.

Online research leads to multiple patents of the "Minnesota Mining and Manufacturing Company" with one US-patent (US3331783A) that has been submitted in 1964 which is about the production of "Microspheres containing colloidal carbon" [41]. The measured photo-peaks have been adjusted for the IAEA NS19 course to result in an appropriate age to exclude other potential patents.

For that purpose, the ratio between the activities of Pa-234 and Bi-214 has to be modified to adjust the calculated age of the reactor fuel microspheres. The wanted age of the material should match with the patent mentioned above, which means that a measurement in 2018 has to result in an age of at least 50 years to exclude newer patents than the US3331783A.

Inserting that age in Equation 4.11 leads to a new activity ratio

$$r_{new} = 0.02140 \tag{4.15}$$

which means that the measured activity ratio

$$r_{meas} = \frac{389}{1219} = 0.31953 \tag{4.16}$$

has to be adjusted by a modification factor of

$$f_{mod} = 0.06697 \tag{4.17}$$

The Bi-214 peaks have been utilized for the self-absorption correction factor, which means that a modification of the Pa-234 will not affect any previous corrections and leads to the desired age of approximately 50 years.

4.5.6. Execution of the Exercise

The exercise starts with an introduction to the process of nuclear attribution and a briefing on the material used during the exercise. Students receive pictures of the material (Chapter 4.5.1), information on the preparation of the samples and measurement results of ICP-MS (Chapter 4.5.2) and gamma spectrometry (Chapter 4.5.3).

The first step of the exercise is the analysis of measurement data combined with data processing. With an explanation of the corrections of the gamma spectrum to be performed and the energy calibration curve, students should evaluate correction factors and learn how to identify radioisotopes based on measured full-energy peaks. Once all correction factors are applied, the gamma-spectrum and results of ICP-MS are analyzed and interpreted. The focus is on the determination of the composition of the uranium isotopes in the material, the identification of metallic residues and their characteristics and the age of the reactor fuel microspheres.

Once the analysis is completed, students should attempt to interpret the results with the help of open sources (e.g. the internet). That way, students will see that nuclear attribution is an excluding process, where possible interpretations are eliminated with the help of measurement results, which leads to a final conclusion based on correct interpretations.

5. Conclusion

The NS19 course of the International Atomic Energy Agency is an elective course for a Nuclear Security Master's programme. The course is an opportunity for insights on the complex process of nuclear forensic analysis and subsequent nuclear attribution. The NS19 course consists of a theoretical part with lecture material for more than 20 hours combined with the three practical exercises introduced in this thesis. It provides a good overview of the tasks to be completed during nuclear forensic analysis but also what kind of problems may occur during nuclear attribution.

The main goal of this diploma thesis was the preparation of exercises that may be conducted without the requirement of difficult to access equipment and material. Furthermore if equipment is unavailable they should be viable as a theoretical scenario for students to work through. This has been achieved with exercises that include the collection of evidence material, collection on incident sites, the preparation of samples for measurements and the evaluation and interpretation of measurement results. These exercises have been designed to be integrated in the course after their specific topic has been discussed in the lectures. This supports a better understanding of the procedures during nuclear forensic analysis and nuclear attribution.

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A. Appendix

A.1. The measurement results of gamma spectrometry

Energy (keV)	Net Peak Area (cts)	Bkgnd (cts)	FWHM (keV)	Counts/sec
64.24	2993192	5028062	1.158	12.22
75.85	2653924	5802937	1.217	10.83
85.22	2722573	7139418	1.512	11.11
88.09	993650	7533842	1.518	4.056
90.54	1093032	7369405	1.522	4.462
93.28	11249508	6852182	1.528	45.92
95.41	6877352	6287445	1.532	28.08
106.22	2579779	5123534	1.552	10.53
121.53	61493	2990010	1.038	0.251
125.73	4072	3018050	1.045	0.01663
136.42	41887	3733910	1.226	0.171
141.3	118545	3414996	1.234	0.4839
144.31	2824489	3777250	1.239	11.53
163.85	1652648	4592444	1.245	6.747
183.17	214469	3507114	1.262	0.8755
186.17	22558998	3563764	1.267	92.09
199.58	30222	3162445	1.291	0.1234
205.74	2233636	3091559	1.3	9.119
215.7	7691	2964993	1.605	0.0314
218.31	13009	3465559	1.609	0.05311
221.81	39385	3673696	1.613	0.1608
227.36	64110	3319432	1.62	0.2617
233.88	10907	3466221	1.628	0.04453
239.11	17082	3139006	1.635	0.06973
247.04	32657	3252173	1.645	0.1333
275.49	9421	1846271	1.017	0.03846
330.73	14323	1764375	1.308	0.05847
338.89	14241	1861853	2.031	0.05814
346.23	17729	1663179	1.407	0.07238

Energy (keV)	Net Peak Area (cts)	Bkgnd (cts)	FWHM (keV)	Counts/sec
410.25	10548	1400249	1.554	0.04306
427.18	17614	1869310	2.209	0.07191
451.13	33431	1220318	1.352	0.1365
468.62	28451	1252328	1.591	0.1161
472.63	7554	1330224	1.594	0.03084
475.9	33986	1221418	1.597	0.1387
481.07	12217	1200719	1.602	0.04988
513.26	36959	1365470	1.951	0.1509
521.19	19678	1425725	2.398	0.08033
528.45	11815	1487108	2.404	0.04823
544.08	43130	1119260	1.595	0.1761
569.37	239194	1030310	1.761	0.9765
583.36	26335	942837	1.602	0.1075
602.6	7128	748078	1.629	0.0291
609.39	370500	785677	1.634	1.513
624.59	7891	797421	2.247	0.03221
628.67	13131	900592	2.25	0.05361
647.13	5921	639478	1.657	0.02417
654.34	23407	686273	1.663	0.09556
666.12	31029	817630	1.994	0.1267
674.07	10085	793036	2	0.04117
727.31	6856	690471	1.792	0.02799
739.89	140087	688829	1.8	0.5719
781.63	93334	642280	1.811	0.381
786.22	596968	635003	1.814	2.437
805.72	113658	448049	1.882	0.464
808.18	32979	501052	1.884	0.1346
824.94	105384	411960	1.895	0.4302
839.05	8675	389830	1.904	0.03541
844.26	19601	375073	1.908	0.08002
851.5	6497	352771	1.912	0.02652
860.33	1749	307898	1.918	0.007142
866.49	8718	313466	1.922	0.03559

Energy (keV)	Net Peak Area (cts)	Bkgnd (cts)	FWHM (keV)	Counts/sec
887.19	73711	237919	1.859	0.3009
904.11	6153	213272	1.862	0.02512
911.06	20203	203923	1.867	0.08247
921.7	133822	247478	2.32	0.5463
925.89	293423	241963	2.322	1.198
936.31	7434	234000	2.329	0.03035
941.69	24864	231188	2.332	0.1015
945.89	355464	226362	2.335	1.451
968.84	10448	186701	2.005	0.04265
983.98	28224	180767	2.13	0.1152
1000.9	7909981	140434	1.968	32.29
1028.56	6303	78501	1.597	0.02573
1041.9	12679	107338	2.693	0.05176
1051.78	2191	63001	1.752	0.008943
1061.71	20975	116846	2.278	0.08563
1083.34	12662	100225	2.491	0.05169
1124.94	39545	78726	2.18	0.1614
1150.79	2728	74924	2.032	0.01114
1171.04	2491	92008	3.194	0.01017
1193.69	114820	85781	2.117	0.4687
1220.18	8684	70926	2.424	0.03545
1226.67	3089	71906	2.427	0.01261
1254.49	4151	60021	4.016	0.01695
1292.72	6319	49336	2.074	0.02579
1320.39	3580	65332	3.489	0.01462
1358.23	2224	52741	2.678	0.009079
1414.06	19074	47013	2.553	0.07787
1426.58	3478	50293	2.925	0.0142
1434.32	73675	50391	2.928	0.3008
1445.46	4083	45847	2.561	0.01667
1452.81	9360	45460	2.564	0.03821
1460.56	5966	45047	2.568	0.02436
1466.65	1777	38371	2.571	0.007254

Energy (keV)	Net Peak Area (cts)	Bkgnd (cts)	FWHM (keV)	Counts/sec
1527.35	17567	45242	2.444	0.07172
1548.41	10606	35062	2.435	0.0433
1553.93	60151	35745	2.438	0.2456
1558.51	5809	29607	2.44	0.02372
1570.91	7944	36799	2.458	0.03243
1601.38	4590	41922	4.146	0.01874
1638.24	2730	24667	2.76	0.01114
1654.65	2511	19402	2.546	0.01025
1668.58	8330	20140	2.553	0.03401
1694.34	11027	19043	2.981	0.04502
1700.7	1705	17433	2.984	0.006961
1716.84	1658	12236	2.768	0.006768
1737.94	139136	11683	2.596	0.568
1760.2	10566	10413	2.884	0.04314
1796.93	3531	6630	2.951	0.01442
1809.3	23163	5806	2.813	0.09456
1820.01	6731	5855	2.818	0.02748
1831.67	95042	5208	2.823	0.388
1863.52	7307	4733	2.964	0.02983
1867.95	56996	4437	2.967	0.2327
1875.4	57138	4240	2.97	0.2333
1893.84	14453	4784	3.52	0.059
1911.51	36487	3996	2.735	0.149
1926.03	3461	3244	2.789	0.01413
1937.37	17971	3047	2.794	0.07337
1969.23	2367	2932	2.89	0.009664
2000.55	369	2211	2.44	0.001507
2022.59	991	2240	2.715	0.004047
2041.47	590	1669	2.429	0.002409
2053.37	278	1401	2.434	0.001134
2066.29	372	1470	2.312	0.001518
2103.59	1937	1603	3.668	0.007907
2137.16	472	1165	2.897	0.001925

Energy (keV)	Net Peak Area (cts)	Bkgnd (cts)	FWHM (keV)	Counts/sec
2615.25	13080	327	3.248	0.0534

Table 9: Measurement results of gamma spectrometry

A.2. The corrected measurement results

Energy (keV)	Net Peak Area (cts)	Efficiency	C_{SA}	Corrected Counts
64.24	2993192	0.00859769	0.544559198	639304431
75.85	2653924	0.015122423	0.547524766	320526045
85.22	2722573	0.019106281	0.549918166	259122602
88.09	993650	0.020110097	0.550651256	89731027
90.54	1093032	0.020894866	0.551277065	94890639
93.28	11249508	0.021698684	0.551976949	939245658
95.41	6877352	0.022272776	0.55252102	558853655
106.22	2579779	0.024582575	0.555282242	188991095
121.53	61493	0.026478367	0.559192909	4153104
125.73	4072	0.026781169	0.560265724	271384
136.42	41887	0.027230268	0.562996294	2732259
141.3	118545	0.027307727	0.564242803	7693636
144.31	2824489	0.02732235	0.565011654	182963487
163.85	1652648	0.026949741	0.570002799	107584270
183.17	214469	0.026074247	0.57493775	14306452
186.17	22558998	0.025912304	0.575704046	1512218337
199.58	30222	0.025139394	0.579129392	2075835
205.74	2233636	0.024766714	0.580702854	155306649
215.7	7691	0.024153218	0.583246959	545953
218.31	13009	0.023991482	0.583913637	928620
221.81	39385	0.023774549	0.58480765	2832732
227.36	64110	0.023431282	0.586225298	4667294
233.88	10907	0.023030654	0.587890716	805568
239.11	17082	0.022712428	0.589226627	1276418
247.04	32657	0.022236896	0.591252204	2483873
275.49	9421	0.02062191	0.59851925	763291

Energy (keV)	Net Peak Area (cts)	Efficiency	C_{SA}	Corrected Counts
330.73	14323	0.01796261	0.612629325	1301568
338.89	14241	0.017621978	0.614713652	1314659
346.23	17729	0.017326157	0.616588524	1659536
410.25	10548	0.015120716	0.632941294	1102134
427.18	17614	0.01463381	0.637265761	1888774
451.13	33431	0.014001537	0.643383362	3711110
468.62	28451	0.013577336	0.647850871	3234506
472.63	7554	0.013484178	0.648875154	863359
475.9	33986	0.013409292	0.649710417	3900986
481.07	12217	0.01329283	0.651031002	1411710
513.26	36959	0.012617314	0.659253364	4443252
521.19	19678	0.012462996	0.661278942	2387667
528.45	11815	0.012325564	0.66313338	1445526
544.08	43130	0.012041517	0.667125785	5368964
569.37	239194	0.011613414	0.673585665	30577187
583.36	26335	0.011391826	0.677159162	3413888
602.6	7128	0.011103151	0.682073677	941218
609.39	370500	0.011005434	0.683808062	49231925
624.59	7891	0.010794048	0.687690631	1063052
628.67	13131	0.010738969	0.688732795	1775352
647.13	5921	0.010498053	0.693448073	813340
654.34	23407	0.010407478	0.695289739	3234703
666.12	31029	0.010263512	0.698298731	4329428
674.07	10085	0.010169059	0.700329417	1416096
727.31	6856	0.009587092	0.713928627	1001680
739.89	140087	0.009461148	0.717141964	20646616
781.63	93334	0.009070553	0.727803704	14138126
786.22	596968	0.009029966	0.728976138	90688376
805.72	113658	0.008862328	0.733957066	17473566
808.18	32979	0.008841712	0.734585429	5077604
824.94	105384	0.008704282	0.738866473	16386106
839.05	8675	0.008592506	0.742470621	1359785
844.26	19601	0.008552101	0.743801423	3081402

Energy (keV)	Net Peak Area (cts)	Efficiency	C_{SA}	Corrected Counts
851.5	6497	0.008496705	0.745650752	1025479
860.33	1749	0.008430298	0.747906218	277396
866.49	8718	0.008384702	0.74947968	1387297
887.19	73711	0.008235705	0.754767127	11858194
904.11	6153	0.008118513	0.75908904	998430
911.06	20203	0.008071514	0.760864294	3289680
921.7	133822	0.008000797	0.763582092	21904761
925.89	293423	0.007973349	0.764652353	48127061
936.31	7434	0.007906043	0.767313957	1225435
941.69	24864	0.007871813	0.768688182	4109093
945.89	355464	0.007845332	0.769760997	58861102
968.84	10448	0.007704241	0.775623166	1748447
983.98	28224	0.007614358	0.77949041	4755262
1000.9	7909981	0.007516744	0.783812322	1342559635
1028.56	6303	0.007363237	0.790877577	1082354
1041.9	12679	0.007291743	0.794285043	2189159
1051.78	2191	0.007239805	0.796808713	379806
1061.71	20975	0.007188446	0.799345155	3650334
1083.34	12662	0.007079378	0.804870153	2222191
1124.94	39545	0.006879715	0.815496133	7048541
1150.79	2728	0.00676182	0.822099055	490746
1171.04	2491	0.006672523	0.827271557	451269
1193.69	114820	0.00657564	0.833057096	20960650
1220.18	8684	0.006466121	0.839823495	1599145
1226.67	3089	0.006439884	0.84148125	570027
1254.49	4151	0.006329941	0.848587374	772781
1292.72	6319	0.006185166	0.858352547	1190231
1320.39	3580	0.006084616	0.865420356	679865
1358.23	2224	0.005952436	0.875085911	426962
1414.06	19074	0.005767706	0.88934669	3718498
1426.58	3478	0.005727842	0.892544701	680313
1434.32	73675	0.005703469	0.894521747	14440763
1445.46	4083	0.005668747	0.897367261	802642

Energy (keV)	Net Peak Area (cts)	Efficiency	C_{SA}	Corrected Counts
1452.81	9360	0.005646064	0.899244688	1843538
1460.56	5966	0.005622338	0.901224288	1177425
1466.65	1777	0.00560383	0.90277987	351253
1527.35	17567	0.005425599	0.918284604	3525921
1548.41	10606	0.005366268	0.923664006	2139761
1553.93	60151	0.005350919	0.925073992	12151726
1558.51	5809	0.005338247	0.926243872	1174836
1570.91	7944	0.005304217	0.929411231	1611425
1601.38	4590	0.005222292	0.93719425	937825
1638.24	2730	0.005126257	0.946609481	562589
1654.65	2511	0.005084533	0.950801123	519405
1668.58	8330	0.005049594	0.954359294	1728529
1694.34	11027	0.004986108	0.960939227	2301441
1700.7	1705	0.004970652	0.962563776	356354
1716.84	1658	0.00493181	0.966686452	347770
1737.94	139136	0.004881834	0.972076071	29319482
1760.2	10566	0.004830064	0.977761992	2237302
1796.93	3531	0.004746698	0.987144017	753573
1809.3	23163	0.004719177	0.990303713	4956329
1820.01	6731	0.00469557	0.993039392	1443527
1831.67	95042	0.004670095	0.996017731	20432558
1863.52	7307	0.004601689		1587895
1867.95	56996	0.004592308		12411189
1875.4	57138	0.004576603		12484805
1893.84	14453	0.004538115		3184803
1911.51	36487	0.004501734		8105098
1926.03	3461	0.004472198		773892
1937.37	17971	0.004449351		4039016
1969.23	2367	0.004386171		539651
2000.55	369	0.004325463		85309
2022.59	991	0.004283546		231350
2041.47	590	0.00424815		138884
2053.37	278	0.004226077		65782

Energy (keV)	Net Peak Area (cts)	Efficiency	C_{SA}	Corrected Counts
2066.29	372	0.004202316		88523
2103.59	1937	0.004134878		468454
2137.16	472	0.004075607		115811
2615.25	13080	0.003351725		3902468

Table 10: The gamma spectrum with all correction factors