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ESTABLISHING A NUCLEAR FORENSIC CAPABILITY: APPLICATION OF ANALYTICAL TECHNIQUES

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ESTABLISHING A NUCLEAR FORENSIC CAPABILITY: APPLICATION OF ANALYTICAL TECHNIQUES

INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

Nuclear forensics supports national nuclear security measures and criminal investigations by providing information on the identity, origin and history of nuclear or other radioactive material found outside of regulatory control. A nuclear forensic examination uses analytical techniques to generate data in the context of a criminal investigation. A nuclear forensic capability can enhance national nuclear security programmes and can support the enforcement of a State's laws that prohibit the possession and use of nuclear or other radioactive material out of regulatory control.

Since 2005, Member States have acknowledged and supported the further development of nuclear forensics at the IAEA in General Conference resolutions. The IAEA programme of assistance in nuclear forensics has grown significantly over the past decade and includes training, coordinated research, technical advisory activities and published guidance. IAEA Nuclear Security Series No. 2-G (Rev. 1), Nuclear Forensics in Support of Investigations, provides guidance to States on implementing a nuclear forensic capability, conducting a nuclear forensic examination and the role of nuclear forensics in criminal investigations and national nuclear security programmes.

This publication takes guidance provided in IAEA Nuclear Security Series No. 2-G (Rev. 1) and provides technical information, including details of analytical techniques and methodologies used in nuclear forensic examinations to support investigations of criminal or other unauthorized acts involving nuclear or other radioactive material.

The preparation of this publication would not have been possible without the contributions of Member States. The IAEA is grateful to all who contributed to the drafting and review of this publication. The IAEA officers responsible for this publication were G. Eppich, D. Smith and E. Széles of the Division of Nuclear Security.

CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

Nuclear forensic science (hereafter referred to as 'nuclear forensics') is a component of nuclear security and, in particular, of investigations of criminal or other unauthorized acts involving nuclear or other radioactive material. Along with other methods of investigation, nuclear forensics can provide information that may assist investigators in enforcing laws and regulations that prohibit the possession and use of nuclear or other radioactive material out of regulatory control. Nuclear forensics can help identify linkages between nuclear or other radioactive material out of regulatory control and people, places and events subject to the investigation, as well as between disparate criminal activities involving nuclear or other radioactive material. Nuclear forensics may also be used to assist in determining when, where and how the nuclear or other radioactive material was lost from regulatory control. It can aid investigators in the identification of deficiencies and weaknesses in nuclear material accountancy and control systems, as well as vulnerabilities in physical protection systems at nuclear facilities and radiation detection systems at borders, ports and other national points of entry.

A State may perform a nuclear forensic examination, as a component of a broader investigation led by an investigative authority of the State, of the circumstances and criminal aspects of nuclear or other radioactive material encountered out of regulatory control. In a nuclear forensic examination, nuclear or other radioactive material is analysed using scientific instruments and analytical techniques capable of measuring the physical, chemical, elemental and isotopic properties of the material. A nuclear forensic examination results in the generation of technical data that support the needs and requirements of the investigative authority relating to the criminal circumstances of the event. A nuclear forensic examination may utilize one or several analytical techniques to examine the material, resulting in the generation of data that can be used in the investigation. While the instruments and analytical techniques themselves are an inherent aspect of nuclear forensic analysis, many States utilize subject matter experts with experience in using these instruments to perform the analyses. Subject matter expertise may aid the interpretation and reporting of nuclear forensic data to the investigative authority.

The development of an analytical plan for nuclear forensic examination is good practice for the generation of credible and reliable nuclear forensic data in support of investigations. The International Atomic Energy Agency (IAEA), in its Nuclear Security Series (NSS) No. 2-G (Rev. 1), Nuclear Forensics in Support of Investigations [1], provides guidance on the role of nuclear forensics in the context of investigating various types of criminal or other unauthorized act involving nuclear or other radioactive material. The publication also describes the development of a nuclear forensic capability, the role of nuclear forensics in a national nuclear security regime (including the investigation of criminal or other unauthorized acts involving nuclear or other radioactive material) and mechanisms for international cooperation and assistance in nuclear forensics.

1.2. OBJECTIVE

The purpose of this publication is to provide information for Member States on the use of nuclear forensics in response to criminal or other unauthorized acts involving nuclear or other radioactive material, based on the guidance provided in Ref. [1]. This publication is intended for technical and non-technical personnel responsible for developing and implementing nuclear

forensic analytical capabilities within the context of a broader national nuclear forensic programme stemming from national legislation.

1.3. SCOPE

This publication covers the conduct of a nuclear forensic examination in the context of commonly used techniques for analysing the physical, chemical, elemental and isotopic properties of nuclear or other radioactive material found out of regulatory control. It provides technical information that describes the application of specific methods, analytical techniques and technical expertise used for nuclear forensic analysis in support of investigations of criminal or other unauthorized acts involving nuclear or other radioactive material, the conduct of which may differ in each State. It also provides an understanding of the role of nuclear forensics within the broader investigation of criminal or other unauthorized acts involving nuclear or other radioactive material. Information contained in this publication can be adapted within the context of national legislative requirements relating to criminal investigations to the extent relevant to the needs of an individual State. Not all States may need the full extent of analytical instrumentation described in this publication.

1.4. STRUCTURE

Following this introductory section, Section 2 reviews how nuclear forensics supports investigations of criminal or other unauthorized acts involving nuclear or other radioactive material. Section 3 describes activities that may occur at a radiological crime scene, including categorization and initial characterization of nuclear or other radioactive material. Section 4 considers the handling of nuclear or other radioactive material upon receipt by a nuclear forensic laboratory. Section 5 addresses the characterization of nuclear or other radioactive material using non-destructive analytical (NDA) methods. Section 6 describes the characterization of nuclear or other radioactive material using destructive analytical methods. Section 7 describes some quality assurance measures that may be taken during nuclear forensic examinations. Section 8 discusses good practice in the reporting of results from nuclear forensic examinations. Section 9 describes some mechanisms for international cooperation and assistance. Annexes I and II contain additional information regarding the handling of the types of nuclear or other radioactive material that may be the subject of a nuclear forensic examination, as well as detailed descriptions of analytical techniques that can be used during a nuclear forensic examination.

2. NUCLEAR FORENSICS IN SUPPORT OF INVESTIGATIONS OF CRIMINAL OR OTHER UNAUTHORIZED ACTS INVOLVING NUCLEAR OR OTHER RADIOACTIVE MATERIAL

A nuclear forensic examination, conducted in support of a criminal investigation related to an occurrence of nuclear or other radioactive material out of regulatory control, involves the use of analytical techniques to determine the physical, chemical, elemental and/or isotopic properties of the material. Data generated in the nuclear forensic examination can then be used, in consultation with subject matter experts, by the State investigative authority in furtherance of the investigation. The types of data needed by the investigative authority may vary significantly due to the wide variety of nuclear or other radioactive material in use around the world, as well as the different types of criminal or other unauthorized act involving nuclear or other radioactive material, specific circumstances of each case and differences in national laws.

Nuclear forensics is typically conducted in a laboratory setting by technical personnel with training and experience in the handling and analysis of nuclear or other radioactive material. During an investigation, the State investigative authority may ask a State nuclear forensic laboratory to perform a nuclear forensic examination in order to generate data on the physical, chemical, elemental and/or isotopic properties of the interdicted nuclear or other radioactive material, or of associated non-radioactive material. In some investigations, the use of relatively straightforward methods and instrumentation to identify and quantify the presence of specific radioactive isotopes in the material is sufficient to aid the investigation. However, in other investigations, additional, more sensitive and/or more precise analyses could be required to generate the types of data needed to support the investigation. In some cases, nuclear forensics can provide the data necessary for investigators to clearly identify the producer or last legal owner of the nuclear or other radioactive material, as well as its history outside of regulatory control. In other cases, nuclear forensics can be used to exclude possible origins or proliferation pathways.

Nuclear forensic analyses are typically performed at a laboratory that has been authorized by the State to receive and analyse nuclear or other radioactive material. This laboratory is often designated for nuclear forensic examination in the State's legal framework. If the legal framework has not yet been established in a State, it is possible for a State to task a non-designated laboratory to conduct nuclear forensic analyses. However, the designation of a national nuclear forensic laboratory helps ensure that the designated laboratory is legally empowered to perform nuclear forensic analyses in a safe and secure environment, and that the data produced by the laboratory are authorized for use in the context of legal proceedings.

States may be able to use analytical techniques and subject matter expertise already present in the State to establish a nuclear forensic capability and conduct a nuclear forensic examination. The types of instrument useful in nuclear forensics, when operated by subject matter experts, can be found in nuclear research institutes, national or private laboratories, academic institutions, regulatory bodies, nuclear and radioactive material production plants, nuclear facilities, medical facilities, industrial facilities and other entities. If the investigation necessitates additional techniques that are not available in the State, international assistance from regional or international partners can be sought. For example, if a high-precision isotope ratio measurement capability is necessary to aid a specific investigation, and if the State does not currently have the capability to perform this type of measurement, other States may be able to assist.

When a criminal or other unauthorized act involving nuclear or other radioactive material occurs that results in an investigation that the State deems necessary for nuclear forensic analysis, many laboratories first develop a nuclear forensic analytical plan. Ref. [1] describes a model action plan for nuclear forensic analysis, which may be adapted for use by State nuclear forensic laboratories. Because the needs of the investigation may vary considerably due to the type of nuclear or other radioactive material under examination, many laboratories develop a unique analytical plan for each examination. Furthermore, the analytical plan may be adaptable in the event of the discovery of new information during the nuclear forensic examination.

A nuclear forensic examination often begins at the radiological crime scene or at the site of the discovery of the material if the event is not criminal in nature. Upon discovery, the nuclear or other radioactive material is often handled as evidence by many States, and chain of custody is maintained and documented from this point onward. Nuclear forensic analysis may also commence at this point, through in-field analysis of the physical, chemical, elemental and/or

isotopic properties of the material using field-deployable instruments operated by personnel trained on their use. Because of this, a State's nuclear forensic capability is intrinsically linked with its capability for managing crime scenes where nuclear or other radioactive material is known or suspected to be present. IAEA NSS No. 22-G, Radiological Crime Scene Management [2] provides guidance on radiological crime scene management.

A State's nuclear forensic capability is also linked with its ability to collect and analyse the types of traditional forensic evidence typically encountered in a criminal forensic examination, such as fingerprints, hair, fibres and many other types of evidence. The nuclear forensic model action plan describes the complementary role that nuclear forensics plays alongside traditional criminal forensics in the investigation [1]. If a State's nuclear forensic capability can function cooperatively and collaboratively with its criminal forensic capability, the State can ensure that all forms of nuclear and traditional forensic evidence are identified, retained and examined during the investigation.

Because each State has unique nuclear security needs and considerations, many States have chosen to develop nuclear forensic capabilities commensurate with their specific needs. A State may choose to possess a nuclear forensic capability sufficient to perform analyses of the types of nuclear or other radioactive material within regulatory control and current legal use by the State. For example, a State with a nuclear power plant or research reactor may possess the nuclear forensic capability to analyse pre- and post-irradiation nuclear fuels, as well as radioactive waste products and other radioactive material associated with reactor operation. Many States consider other factors as well, such as the history of smuggling and trafficking of specific types of nuclear or other radioactive material within or through the State, if known. For example, a State that has a history of interdicting nuclear or other radioactive material may develop a nuclear forensic capability that can analyse the specific types of material interdicted, even if the material does not originate from within the State's nuclear or other radioactive material holdings.

Confidence in nuclear forensic data can be demonstrated through a programme of quality assurance and quality control, achieved through laboratory accreditation, written and validated procedures, the employment of trained and experienced personnel, the use of standard reference materials and good practice in nuclear forensic analysis. Concise and clear technical reports resulting from nuclear forensic examination are ideal for addressing the needs and requirements of the investigative authority. Technical reports are used for establishing, clarifying and/or assessing data, facts and circumstances that are important for advancing investigations involving nuclear or other radioactive material. Data generated during the nuclear forensic examination may be used in legal proceedings. Many nuclear forensic laboratories take into consideration any requirements by the State to retain evidence and supporting information that may be later requested by a court if nuclear forensic findings are used in legal proceedings.

Many States have worked to ensure that their nuclear forensic capabilities are sustainable, regularly exercised and are available to respond to a variety of possible nuclear security incidents. Sustainability can be ensured by using instrumentation and subject matter expertise that exists within the State. Although a State might have little experience in nuclear forensics in the early stages of establishing a nuclear forensic capability, for most analytical techniques, experience can be gained through workshops, trainings and exercises in nuclear forensics. Some States have organized internal nuclear forensic exercises and have participated in bilateral, regional or international exercises.

3. ACTIVITIES AT A RADIOLOGICAL CRIME SCENE INCLUDING CATEGORIZATION AND INITIAL CHARACTERIZATION OF NUCLEAR OR OTHER RADIOACTIVE MATERIAL

For many States, nuclear forensic examination begins at a radiological crime scene after the scene has been secured, all hazards have been identified and managed and all threats to life and property have been addressed. Decisions made and actions taken at a radiological crime scene can affect the conduct of a nuclear forensic examination, the quality of laboratory measurements and the legal defensibility of findings. In some cases, nuclear or other radioactive material out of regulatory control can be detected passively using radiation detection equipment (e.g. radiation portal monitors) installed at designated points of entry (e.g. border crossings, seaports, airports). In other cases, law enforcement personnel may detect the presence of radiation at a crime scene using handheld devices capable of informing the responding officers of the presence of gamma or neutron radiation above background levels. In the context of broader efforts to combat nuclear smuggling and trafficking, law enforcement personnel may also receive information from other sources regarding specific types of nuclear or other radioactive material out of regulatory control that might be in the possession of smugglers. In all cases, responding personnel typically utilize special procedures when dealing with radioactive hazards as they work to identify and secure nuclear or other radioactive material out of regulatory control.

Reference [2] describes radiological crime scene management as "the process used to ensure safe, secure, effective and efficient operations at a crime scene where nuclear or other radioactive material is known, or suspected, to be present." It describes in detail the framework and functional elements for managing a radiological crime scene, with particular emphasis on responding to radiological hazards and securing nuclear or other radioactive material for eventual examination by the nuclear forensic laboratory. The actions taken at the radiological crime scene by responding law enforcement personnel may impact, positively or negatively, the conduct of a nuclear forensic examination, the quality of the data generated and the confidence in conclusions based on the data. It is good practice to ensure that all responders to a criminal or other unauthorized act involving nuclear or other radioactive material remain aware of the needs of a subsequent nuclear forensic examination and understand how their actions can affect the legal defensibility of findings. Nuclear or other radioactive material out of regulatory control may constitute both traditional and nuclear forensic evidence, and it is good practice for the laboratory to ensure that the integrity of both types of evidence is maintained. Good communication between the investigative authority, in-field responders and the nuclear forensic laboratory can help to ensure that all evidence is handled and examined properly.

According to Ref. [1], "[c]ategorization is performed to identify nuclear security implications and the risk of the seized material to first responders, law enforcement personnel and the public". In contrast, "[c]haracterization is performed to determine the nature of the radioactive material and associated evidence" [1]. In the context of nuclear forensics, the physical, chemical, elemental and isotopic properties of nuclear or other radioactive material are often referred to collectively as nuclear forensic signatures.

Categorization measurements are often performed in the field, at the site of the interdiction or discovery of nuclear or other radioactive material out of regulatory control. Initial characterization measurements can also be performed in the field if the necessary field-deployable analytical instrumentation is available. Initial in-field characterization

measurements can provide preliminary data to assist the nuclear forensic laboratory in the development of an analytical plan. More precise, accurate and sensitive categorization measurements are usually performed when nuclear or other radioactive material is received at the nuclear forensic laboratory. Categorization and characterization measurements can also provide valuable information that may assist the investigative authority in maintaining the integrity of evidence, in preserving items of evidentiary value and in informing the State of the appropriate response to the criminal or other unauthorized act involving nuclear or other radioactive material.

In-field categorization measurements are often performed using handheld or field-deployable gamma and neutron analytical equipment by personnel familiar with their operation and use [3]. In some cases, law enforcement personnel work in partnership with gamma spectrometry experts and other relevant subject matter experts for in-field analysis. Some States choose to deploy gamma spectrometry experts to the field, under the guidance and supervision of law enforcement personnel, to conduct measurements. In other cases, measurements may be performed by law enforcement personnel or other responders trained in the operation and use of field-deployable gamma spectrometry equipment. In either case, the personnel performing in-field categorization and characterization measurements often remain in communication with laboratory-based subject matter experts, who can provide expert guidance on interpretation of gamma spectra and additional guidance on the handling of various types of nuclear or other radioactive material.

Low resolution handheld gamma spectrometers are useful for performing initial dose rate measurements and preliminary isotope identification and can also be used to locate additional nuclear or other radioactive material through secondary inspections of items at a radiological crime scene. These initial measurements can guide law enforcement personnel in the handling, collection, packaging and shielding of nuclear and other radioactive material, ensuring the continued safety of responding personnel and maintenance of evidence integrity.

More precise measurements can be performed using field-deployable high resolution gamma spectrometers. These instruments can reveal the presence and abundance of radionuclides that are challenging to identify using low resolution instruments. However, high resolution gamma spectra may be difficult to interpret without expert guidance, and in-field analysts may choose to consult gamma spectrometry experts and other relevant subject matter experts during and after data collection.

If gamma spectral data are consistent with the identification of nuclear material such as uranium or plutonium, in-field neutron detectors can be used for additional categorization measurements and can provide useful information regarding the hazard presented by the nuclear material. The Convention on the Physical Protection of Nuclear Material, as amended, provides a categorization of nuclear material into Categories I, II and III, in descending order of risk, and includes provisions on the physical protection of this material [4]. Radioactive sources can be categorized following the recommendations provided in IAEA Safety Standards Series No. RS-G-1.9, Categorization of Radioactive Sources [5], from Category 1 (high risk) to Category 5 (low risk).

Completion of in-field categorization and characterization measurements may result in a more complete understanding as to the nature of, and hazards presented by, the nuclear or other radioactive material. Categorization data may be shared with personnel responsible for material storage and transport, as well as other stakeholders involved in the investigation. In some cases,

in-field categorization and characterization measurements may be sufficient to address the needs and requirements of the investigative authority. However, in many cases, in-field measurements might not meet the evidentiary standards of the State and might lack the accuracy, precision or sensitivity of comparable measurements performed in a laboratory setting.

4. RECEIPT AND HANDLING OF SAMPLES AT THE NUCLEAR FORENSIC LABORATORY

The activities of the nuclear forensic laboratory may often follow the steps outlined below:

1. Receipt of a request for nuclear forensic analysis from the State investigative authority alongside relevant in-field categorization and initial characterization data;
2. Development of a nuclear forensic analytical plan for the specific type of nuclear or other radioactive material;
3. Receipt of material while maintaining chain of custody (this step is often performed in parallel with step 2);
4. Analysis of material upon receipt to confirm accuracy of in-field categorization;
5. Unpacking of the material, and documenting the status of the material upon receipt using photography and/or videography, alongside preservation of packaging, documentation and preservation of any associated traditional evidence;
6. If necessary, aliquoting (subsampling the material into smaller portions for analysis) for subsequent nuclear forensic examination.

4.1. RECEIPT OF REQUEST FOR NUCLEAR FORENSIC ANALYSIS FROM THE INVESTIGATIVE AUTHORITY ALONGSIDE RELEVANT IN-FIELD CATEGORIZATION AND CHARACTERIZATION DATA

A nuclear forensic examination is driven by the needs and requirements of the investigative authority. The role of the nuclear forensic laboratory is to support the investigation through the measurement of nuclear forensic signatures in nuclear or other radioactive material and associated non-radioactive material that is the subject of the investigation. At the start of the investigation, the investigative authority may communicate a preliminary list of questions to the laboratory, for which the laboratory can generate data to address. Some examples of the types of question the investigative authority might seek nuclear forensic data to answer include the following:

— What are the most abundant radionuclides present in the material?
— What is the total specific activity of the material?
— What is the isotopic composition of the material (for special nuclear material)?
— What is the category of radioactive source (for a radioactive source)?
— What is the origin of the material (or can any possible origins be ruled out)?
— Is the material consistent with a particular segment of the nuclear fuel cycle?
— What is the probable method of production in the nuclear fuel cycle?
— What pathway did the material take after loss from regulatory control?
— Are the physical, chemical, elemental and isotopic properties of the material consistent or inconsistent with nuclear or other radioactive material from a particular facility within the State?
— Is there more material like it out of regulatory control?

To assist in laboratory preparation for the arrival of the material, the investigative authority may share the results of in-field measurements, such as the dose rate and preliminary measurements of radioactive isotopes. The investigative authority may also provide any additional relevant information to assist the laboratory in the handling and analysis of the material, such as the presence of dispersible radioactive material, traditional forensic evidence that may need preservation and other considerations. This information can aid the laboratory in the development of an analytical plan and can help ensure that laboratory personnel are prepared to unpack and handle the material [6].

Communication between the laboratory and the investigative authority can be facilitated if a laboratory point of contact is established. The point of contact, often the manager of the nuclear forensic laboratory or another associated expert in nuclear forensics, is often the person with the most comprehensive understanding of the capabilities of the laboratory as well as legal considerations related to nuclear forensic examination. It is possible that a representative or representatives of the laboratory may be invited to provide expert witness testimony in legal proceedings related to the investigation. The point of contact therefore typically has the knowledge and experience required to explain key technical aspects of nuclear forensics to non-technical audiences.

4.2. DEVELOPMENT OF A NUCLEAR FORENSIC ANALYTICAL PLAN FOR THE SPECIFIC TYPE OF NUCLEAR OR OTHER RADIOACTIVE MATERIAL

A nuclear forensic analytical plan, developed through coordination and communication between the laboratory and the investigative authority, specifies the analytical technique or techniques to be performed in the nuclear forensic examination and describes the sequence in which they may be performed. The analytical plan may also describe which laboratory personnel will perform each measurement, as well as the quantity of the sample that is needed for measurement, how long each analysis will take and other considerations relevant to the examination. A nuclear forensic analytical plan is typically designed to ensure that nuclear forensic signature data that meet the needs and requirements of the investigative authority are generated during the examination. Development of the nuclear forensic analytical plan is typically also informed by the results of in-field categorization measurements and by the circumstances of the material interdiction or discovery.

Some laboratories aim to produce a series of analytical reports that may be provided to the investigative authority at intervals of 24 hours, one week and two months after receipt of the material by the laboratory. These timelines may be modified to meet the needs and requirements of the investigative authority. Clear understanding and communication of expected reporting timescales as part of the analytical plan development and modification process can help ensure that all parties remain aware of the expected progression of the nuclear forensic examination. Reporting timescales may account for not only the time needed for completion of measurements and data analysis, but also the time needed to compile, interpret and document the findings. Depending on the complexity of the nuclear forensic examination, the compilation and interpretation of data may take longer than the measurements themselves.

Once the investigative authority and the nuclear forensic laboratory concur on the analytical plan, laboratory analysis can commence. The analytical plan may be modified during the course of the examination for various reasons, such as in response to developments in the investigation or as a result of laboratory findings. For example, the discovery of the presence of a specific radionuclide may lead the investigative authority to request a more precise analysis of the

abundance of that radionuclide. Through regular reporting to the investigative authority during the course of the examination, all stakeholders can remain aware of developments that may necessitate adjustments to the analytical plan.

4.3. RECEIPT OF MATERIAL WHILE MAINTAINING CHAIN OF CUSTODY

It is good practice for the nuclear forensic laboratory to follow policies and procedures consistent with national evidentiary requirements for use in a criminal investigation to ensure that integrity of evidence is maintained throughout. Chain of custody is often initiated at the scene of nuclear or other radioactive material interdiction or discovery and maintained during transport and upon receipt by the laboratory. Many States use photography to document the initial status of nuclear or other radioactive material alongside packaging and shipping materials. It is good practice to ensure that chain of custody is also maintained within the nuclear forensic laboratory. A laboratory information management system can be used to track the material within the laboratory following similar procedures consistent with national laws and regulations on evidence handling within criminal forensic laboratories.

4.4. ANALYSIS OF MATERIAL UPON RECEIPT TO CONFIRM ACCURACY OF IN-FIELD CATEGORIZATION

Material unpacking is typically performed only after the nuclear forensic analytical plan has been developed, and after the material has been transferred to a secure, controlled area authorized for the handling of nuclear or other radioactive material. In most cases, laboratory personnel will have some information as to the nature of the material, as well as possible hazards presented by the unpacking and handling of the material, as a result of in-field categorization and characterization measurements. However, owing to the challenge of analysing nuclear or other radioactive material in suboptimal field conditions, categorization and characterization measurements performed in the field are often less precise and accurate than characterization measurements performed in the laboratory. Many laboratories choose to replicate in-field categorization measurements in the laboratory before and during the unpacking process [7]. Because of the radiation shielding effect caused by packaging materials, confirmation of categorization measurements might not be possible until some or all layers of packaging have been removed. Failure to perform these measurements may result in the development of an analytical plan that fails to call for the analysis of key nuclear forensic signatures and the exposure of laboratory personnel to unexpected radiation hazards. Of particular concern is the release of dispersible radioactive material within the workspace, which might contaminate the laboratory, compromise the integrity of ongoing work and injure laboratory personnel [8].

Prior to the arrival of the material, in order to ensure the safety of laboratory personnel and to minimize the possibility of cross contamination, the nuclear forensic laboratory may have already identified a workspace for the unpacking and initial handling of the material. An ideal workspace for unpacking and handling is one that has been cleaned thoroughly prior to the arrival of the material and is capable of receiving material with potentially high levels of radioactivity and/or dispersible radioactive material. Many nuclear forensic laboratories make use of a dedicated fume hood, which is cleaned and prepared for use in a nuclear forensic examination upon notification by the investigative authority of the imminent arrival of nuclear or other radioactive material out of regulatory control. The handling of nuclear or other radioactive material is typically performed in the laboratory using engineering controls such as glove boxes or glove bags, as well as personal protective equipment such as laboratory-grade

single use gloves, laboratory coats, masks and safety glasses. Dosimetry equipment can be employed by laboratory personnel throughout the unpacking and handling process to continually assess the radiation hazard.

4.5. UNPACKING AND DOCUMENTATION OF MATERIAL, AND PRESERVATION AND DOCUMENTATION OF ANY ASSOCIATED TRADITIONAL FORENSIC EVIDENCE

It is good practice to thoroughly document the unpacking process, including the characteristics of the packaging material itself, as well as the key features and relationships of packaging layers separating different material. Photography and videography are useful tools for recording details that might be difficult to document in written notes. Many laboratories include a sample identification number in photographs and videos of each material, as well as some form of visual scale, such as a ruler and colour scale. When unpacking is complete, the laboratory may verify the received evidence inventory before proceeding, ensuring that all nuclear and radioactive material, and associated non-nuclear material have been received. Along with the nuclear or other radioactive material itself, the inventory could include packaging materials, traditional evidence, swipes taken to assess radioactive contamination, non-radioactive material associated with nuclear or other radioactive material and other items. Discrepancies between the expected and received material may be communicated to the investigative authority prior to proceeding with the nuclear forensic examination.

At this point of the nuclear forensic examination, the nuclear or other radioactive material under examination is typically treated by the laboratory as one or more nuclear forensic samples to be subjected to analysis, in whole or in part. Hereafter, this publication will use the terms 'sample' or 'samples' to refer to the nuclear or other radioactive material under nuclear forensic examination in the laboratory setting. Many laboratories assign a unique identifier to each sample at this stage of the examination.

During unpacking, the laboratory may identify traditional forensic evidence associated with the material. It is good practice to avoid alteration or destruction of traditional forensic evidence as much as possible. For example, swiping the samples to monitor for dispersible radioactive material may be performed in a location of the sample where fingerprints are least likely to be encountered. If traditional forensic evidence is encountered during the unpacking process, it can be documented for assessment by the investigative authority and assessed for appropriate follow-on analysis by a criminal forensic laboratory. If possible, it is good practice for unpacking to be supported by experts who can assist in identifying and preserving traditional forensic evidence.

Many States choose to designate for nuclear forensic examination a laboratory that routinely performs other analytical work involving nuclear or other radioactive material for other applications (e.g. environmental radioactivity measurements, characterization of nuclear fuels for the nuclear power industry or for analysis of post-irradiation research reactor targets). This can be challenging for laboratory personnel, as the needs of a nuclear forensic examination may be different than those of routine laboratory work. Many laboratories take steps to ensure that samples are not contaminated by other samples that may be present in the laboratory. Conversely, because nuclear forensic samples may be far more radioactive than the types of sample handled for routine laboratory analysis, many laboratories take additional steps to ensure that routine laboratory work is not compromised upon completion of nuclear forensic examination. Furthermore, nuclear forensic samples may contain radionuclides, such as

plutonium, with which the laboratory may be unfamiliar and/or not licensed to work. For these reasons, it is often beneficial for a State to identify and designate a nuclear forensic laboratory that is licensed to handle a wide variety of radioactive and nuclear material types.

4.6. ALIQUOTING FOR SUBSEQUENT NUCLEAR FORENSIC EXAMINATION, IF NECESSARY

Depending on the needs and requirements of the investigative authority, a nuclear forensic examination may involve the use of several analytical techniques including destructive analytical techniques, necessitating sample aliquoting. If aliquoting is necessary, consideration may be given to the physical form of the samples and the available amount of mass in each sample. The extent of physical, chemical, elemental and isotopic heterogeneity may also be considered, which can occur at the microscale and might not be visibly apparent. Characterization measurements may reveal the presence of heterogeneity that can be further examined in subsequent analyses, especially using spatially resolved techniques [9].

In bulk solid samples, heterogeneity may manifest as structural features or localized inclusions, and the aliquoting of the material may be performed in such a way as to reveal, emphasize or at least preserve such features, or to highlight bulk characteristics. In powder samples, it is possible that individual grains may be representative of one or more populations of grains. Grain populations may be characterized as distinctive in terms of physical, chemical, elemental and/or isotopic properties, and powder samples may contain two or more grain populations that can be distinguished and characterized using a variety of analytical techniques [10]. Alternatively, grain composition may vary over a wide range, representing a continuum of compositions [11]. Because of the inherent complexity of powder samples, laboratory personnel may attempt to characterize such samples at bulk and at single particle scales using spatially resolved analytical techniques, if available [12]. For slurries or liquid samples, it may be possible to separate solid or colloidal components from the bulk liquid, as the composition of these features may be distinct from the liquid component. In all cases, laboratory personnel can work to ensure that enough sample material remains after aliquoting so that all techniques called for in the analytical plan can be performed. If available, the remaining sample mass can be archived at the laboratory or kept in the custody of the investigative authority.

A more detailed review of sample handling and analysis considerations for nuclear or other radioactive material for nuclear forensic examination can be found in Annex I of this publication.

5. CHARACTERIZATION THROUGH NON-DESTRUCTIVE ANALYSIS

NDA is the analysis of a nuclear forensic sample in a manner that does not involve the physical alteration or consumption of the sample. For this reason, NDA methods are among the first analyses performed in a typical nuclear forensic examination. Depending on the needs and requirements of the investigative authority, NDA techniques alone might or might not be sufficient to generate nuclear forensic data to aid the investigation. In other cases, data obtained using NDA techniques can guide aliquoting and enable laboratory personnel to perform higher precision and more sensitive analyses using other analytical techniques.

A wide variety of NDA techniques may be used to perform measurements of the physical, chemical, elemental and/or isotopic properties of nuclear or other radioactive material. The selection and application of any given NDA technique is dependent on the needs and

requirements of the investigative authority, the nature of the samples and other considerations. NDA techniques are outlined in this section and discussed in more detail in Annex II of this publication. These techniques can provide data to assess the following:

— The physical characteristics of sample material;
— The identity and quantity of radionuclides present (including isotopic composition);
— The elemental composition;
— The chemical form (e.g. metal, oxide, alloy, ceramic, glass) and the identity and abundance of its crystalline constituents;
— The physical, chemical, elemental and isotopic heterogeneity at the micro- to macroscale.

For many NDA techniques, it may be possible to collect and report data to the investigative authority within 24 hours. For additional information on reporting timelines, which may be modified to fit the needs of the individual investigation and nuclear forensic analytical plan, see Ref. [1].

5.1. RADIOMETRIC NON-DESTRUCTIVE ANALYTICAL TECHNIQUES

Radiometric NDA techniques, especially gamma spectrometry techniques, are the foundation of a State's nuclear forensic capability. Because nuclear forensic examinations are primarily concerned with the radioactive properties of nuclear or other radioactive material out of regulatory control, gamma spectrometry is effective for rapid and precise measurements of these properties [13]. Gamma spectrometry can be performed using a range of instruments, from field-portable spectrometers capable of radioactive isotope identification at low energy resolution (e.g. scintillator detectors) to spectrometers capable of determining several radioactive isotopes present in a sample with high energy resolution (e.g. semiconductor detectors, such as high purity germanium detectors). When calibrated using standard reference materials, high resolution gamma spectrometry instruments are also capable of determining the specific activity of individual radioactive isotopes present in the sample (a measure of their overall abundance in the sample), as well as the isotopic composition of some elements with multiple gamma emitting isotopes.

Gamma spectrometry instruments, when operated by trained and experienced personnel, can provide a wealth of data to aid investigations. However, gamma spectral data can be complex to interpret, and misinterpretation can lead to erroneous conclusions. Gamma spectrometry specialists typically utilize spectral interpretation software to assist in interpretation of gamma spectrometry data, and most gamma spectrometry instrument manufacturers include or make available for purchase software for spectral analysis. Specialized gamma spectrometry software may be used for specific applications, such as the accurate determination of uranium and plutonium isotope ratios in nuclear material. Free, open-source software packages for gamma spectrum analysis are also available from several sources.

Commercially available gamma spectrometers vary in terms of resolution (broadly defined as low resolution, medium resolution and high resolution), cooling system (electrical or liquid nitrogen cooling), portability (field-portable or fixed) and other parameters. The choice of gamma spectrometer to use for a specific application in nuclear forensics depends on several variables, including the type of nuclear or other radioactive material, sample size and total specific activity. High resolution instruments, such as high purity germanium spectrometers used by many nuclear forensic laboratories around the world, are capable of resolving small

differences in gamma radiation energies, enabling identification and quantification the radionuclides present with a higher degree of confidence [7]. Field-deployable high purity germanium spectrometers may also be used at a radiological crime scene for in-field characterization of material, enabling in-field radionuclide identification with a higher degree of confidence. However, high resolution gamma spectrometers may involve significantly longer analytical times than low resolution instruments, especially if samples are only weakly radioactive. Ease of use is also a consideration, as many field-portable low resolution gamma spectrometers are simpler to use, and spectral interpretation can be handled by the pre-installed software with minimal operator involvement [3]. However, confidence in radionuclide identification might be significantly lower than with high resolution instruments. In most cases, a sequential approach can be taken, beginning with initial low resolution analysis in the field using handheld, low resolution instruments, followed by confirmation using higher resolution instruments in the field or in the laboratory. Additional analyses using high resolution instruments with longer count times can confirm the detection of isotopes identified in the field with high confidence and may reveal the presence and abundance of other gamma emitting radionuclides [14]. High resolution instruments are useful for additional measurements, such as accurate and precise isotope ratio determination [15].

Gamma spectrometry has many specific applications in a nuclear forensic examination. For example, gamma spectrometry may be used to determine the presence and abundance of fission and activation products in an irradiated uranium fuel material [16–18], which may then be used alongside other data to determine the type of reactor (or rule out possible reactor types) in which the material was irradiated [19]. Gamma spectrometry may also be used to characterize the radioactive properties of industrial or medical radiation sources encountered out of regulatory control [20, 21]. In some cases, the age of relatively pure radioactive material can be determined by calculating its radiochronometric age (a practice known as radiochronometry), based on the abundance of daughter nuclides relative to parent nuclides [22, 23]. Gamma spectrometry is particularly suited to the determination of the age of plutonium, using the ^{241}Pu–^{241}Am parent–daughter system [24].

5.2. PHYSICAL NON-DESTRUCTIVE MEASUREMENTS

Characterization of the physical nuclear forensic signatures of nuclear forensic samples includes analysis of features such as physical form (e.g. solid, powder, liquid), colour, morphological features, surface textures, dimensions (e.g. length, width, thickness, height and dimensions of specific features), mass, density and distinctive physical features. Physical characterization also includes microscale features, such as grain size, grain shape and other morphological features measurable using microscopy techniques. Physical measurements typically do not need advanced instrumentation to be performed, and useful data can be collected using instrumentation such as an optical microscope and high resolution digital camera. In some cases, physical NDA measurements may be sufficient to address the needs and requirements of the investigative authority [25, 26]. In cases where sealed radioactive sources are the subject of nuclear forensic examination, labels, serial numbers or other unique identifiers may be present and may be of high diagnostic value for the determination of the material origin [27]. In other cases, images of distinctive physical features, such as imperfections or evidence of damage (e.g. scratches, chips), can provide insight into the history of the material after loss from regulatory control. These features may suggest, for example, the manner in which the material was handled and whether pieces or fragments of the material might still remain out of regulatory control [28].

Prior to other measurements, nuclear forensic samples can be photographed from a variety of angles and at various magnifications. Clear labelling of photographs ensures that each individual sample can be identified by an assigned unique identifier. Inclusion of a scale in each photograph ensures that dimensional data are captured at this stage of the examination. The colour of a nuclear forensic sample can be characterized using digital photography with certified colour charts, which may be purchased at low cost. It is useful to include some kind of colour reference because human perception of colour can vary significantly, and colour blindness is common in the general population. For more precise colour measurements, an ultraviolet/visible light spectrometer may be utilized. Colour is a diagnostic property of certain uranium-rich fuel cycle material, such as uranium ore concentrate, and can be indicative of the elemental and chemical composition of the material [29].

Mass is an inherently useful property of the nuclear or other radioactive material under nuclear forensic examination, and a precise and accurate determination of material mass is likely to be required by the investigative authority in most nuclear forensic examinations [28]. Mass can be determined with high accuracy and precision using a laboratory-grade analytical balance. Sample mass data are necessary for determining sample density, as well as for accurate calculation of elemental concentration following measurement using other instruments. If the sample is aliquoted, the mass of each aliquot is typically measured prior to subsequent analyses. Before determination of sample mass, the accuracy of the analytical balance can be assessed using calibration weights, which are commercially available from analytical balance manufacturers. Some sample matrices, such as plastic materials, may be susceptible to electrostatic effects that can result in erroneous laboratory balance measurements. In this case, anti-static devices may be employed to minimize this effect during the weighing process. The masses of liquids, slurries and other non-solid samples can be determined by massing within clean, pre-weighed beakers. Powder samples can be massed within pre-weighed beakers, or by using weighing paper, while taking precautions to ensure that dispersible radioactive material is not released during measurement.

The size of nuclear forensic samples may vary widely, from individual microscale radioactive particles present on the surface of another material to bulk nuclear or other radioactive material, such as uranium fuel pellets or bulk uranium metals of centimetre scale or larger. Sample size and shape (hereafter referred to as 'sample geometry') can be measured using an optical microscope and digital camera with a ruler, calliper or other measuring equipment. For more precise measurements, a three-dimensional (3D) scanner may be used to reconstruct the sample as a 3D model. Sample geometry data are particularly useful for investigations of uranium fuel pellets out of regulatory control because pellets are manufactured to meet the narrow specifications of specific reactor types [30]. Therefore, their masses and geometries can be diagnostic of the type of nuclear reactor for which they were intended, and these data may be used by the investigative authority to determine, or exclude, the identity of the producer or the last legal owner of the material [31]. Furthermore, sample mass and sample geometry data may be used to inform other analyses, such as the calibration of the full energy peak efficiency of a high purity germanium gamma spectrometer, allowing for the calculation of more precise radionuclide abundances and isotope ratios [7].

If the mass of a sample is known, its density can be calculated following a measurement of its volume. In the case of a solid sample with a simple 3D shape, such as a cylinder, its volume can be calculated using measurements of key dimensions, such as height and radius. A 3D scanner may be used to determine the volume of irregularly shaped samples. Alternatively, a gas or liquid pycnometer may be employed to determine sample volume using the displacement

method [28]. Two advantages of gas pycnometry over liquid pycnometry are its applicability to samples containing significant pore space, such as powders, and its lower likelihood of sample contamination. Density measurements can be useful as diagnostic nuclear forensic signatures of metallic alloys and ceramics used in the nuclear fuel cycle, among other applications.

Because optical microscopes are only capable of magnification up to ~1500×, techniques such as scanning electron microscopy (SEM) are useful for obtaining physical data at higher magnifications. Commercially available SEM instruments are capable of magnification up to ~100 000×, revealing physical features as small as 10^{-9} m. Utilizing SEM, it is possible to make qualitative observations and quantitative measurements (such as the physical dimensions of individual grains) on the microscale [19, 32]. Most SEM instruments have two modes, enabling the collection of high resolution two-dimensional (2D) images of micro- to nanoscale structural sample features and the determination of elemental composition, also at the micro- to nanoscale [33]. SEM is especially useful for assessing sample heterogeneity, which can guide additional aliquoting and analysis [34].

While SEM is nominally non-destructive, in most cases, the sample is prepared for analysis in some respect [35]. Most samples need mounting in the SEM sample chamber, which is often performed using electrically conductive tape which may contaminate the surface of the sample with metallic elements. As SEM measurements are performed at high vacuum, loose radioactive powders can be dispersed within the sample chamber, contaminating and potentially damaging the instrument as well as jeopardizing the safety of laboratory personnel. Accurate elemental measurements are usually obtained on a flat sample surface, which can be achieved by polishing prior to analysis but results in the destruction of sample surface morphology. In most cases, physical characterization using standard photographic and optical microscopic techniques is completed before SEM analysis is performed.

As some physical characteristics are qualitative in nature (e.g. involving physical descriptions of the material and its features that cannot be directly quantified), interpretation of physical nuclear forensic signatures is aided by subject matter experts [36]. Many States utilize laboratory personnel familiar with the types of nuclear or other radioactive material in their material holdings and their physical, chemical, elemental and isotopic properties. Inclusion of these experienced and knowledgeable personnel can significantly improve the interpretation of physical nuclear forensic signature data.

5.3. ELEMENTAL AND CHEMICAL NON-DESTRUCTIVE MEASUREMENTS

Gamma emitting radionuclides present in nuclear or other radioactive material may be measured using gamma spectrometry techniques. The remaining elements can be measured using other analytical techniques. In many types of nuclear or other radioactive material, the bulk of the sample mass consists of non-radioactive isotopes, and the presence and abundance of these elements may be measured using a variety of techniques. The most commonly used technique for non-destructive elemental analysis is X ray fluorescence spectroscopy (XRF), which can be used to measure the concentration of most elements that might be present in the sample. Because an XRF analysis can be performed in minutes, it is often the first technique used for elemental measurements in a nuclear forensic examination [37]. Most XRF instruments can be run without calibration for a specific nuclear or radioactive material type, instead relying on the fundamental parameters of X ray generation to enable calculation of the elemental concentration [38]. However, irregularly shaped samples and coarse-grained powder

samples benefit from geometric correction or the use of standard reference materials to ensure accurate measurement. Furthermore, some sample matrices present unique challenges for XRF. For example, the uranium in uranium-rich samples may generate spectral interferences via XRF that prohibit the determination of certain elements, such as molybdenum and zirconium.

Many SEM instruments are equipped with an XRF capability, enabling spatially resolved elemental analysis of nuclear forensic samples on the microscale (this capability is sometimes referred to as 'energy dispersive spectroscopy'). Using a SEM equipped with an energy dispersive spectroscopy capability, it is possible to measure the elemental composition of 'points' on the surface of a sample (on the scale of 10^{-6} m) and to generate elemental 'maps' of the surface of a sample, revealing elemental heterogeneity that might not be visible using optical microscopy [39]. Elemental heterogeneity may be correlated with physical heterogeneity also measured using SEM. This powerful approach has many applications for nuclear forensics. For example, it is possible to observe the locations of uranium within a glass sample or differences in elemental composition between various grains and grain populations in a powder sample [40].

X ray diffraction spectroscopy (XRD) is an NDA technique used for determination of the chemical composition (arrangement of atoms in crystalline or polycrystalline materials such as ores, metals, ceramics and oxides) of a nuclear forensic sample [41]. Nuclear or other radioactive material can consist of one or a mixture of several crystalline solids (sometimes referred to as 'phases') or non-crystalline constituents (such as glass), and XRD can measure the presence of, and in some cases the abundance of, the crystalline components [42]. Although the XRD analysis is itself non-destructive, the sample is typically loaded into the instrument in such a manner as to ensure a flat surface for analysis [43]. Therefore, this technique is ideally suited for analysis of fine-grained powder samples, which can be loaded in the spectrometer to produce a flat surface. Other types of sample can be analysed using XRD, but may involve some alteration, such as the crushing of a sample aliquot to a fine-grained powder prior to loading. Due to the inherently disordered arrangement of atoms in glass and other non-crystalline materials, XRD is incapable of quantifying these constituents.

6. CHARACTERIZATION THROUGH DESTRUCTIVE ANALYSIS

In some nuclear forensic examinations, NDA techniques might not be sufficient to generate the data necessary to support the needs and requirements of the investigative authority. In these cases, characterization through destructive analysis may be necessary. Destructive analysis techniques are often capable of providing more precise data on the physical, chemical, elemental and isotopic properties of nuclear or other radioactive material than NDA techniques. Furthermore, destructive analysis techniques tend to be more sensitive than NDA techniques. However, destructive analysis techniques often take longer to perform than NDA techniques and need greater expertise in the instrumentation, which is usually more expensive to procure and operate. Moreover, destructive analysis techniques necessitate sample aliquoting and sample preparation prior to analysis, and usually result in the consumption of the aliquot during analysis.

A wide variety of destructive analysis techniques may be used to perform measurements of the physical, chemical, elemental and isotopic properties of nuclear or other radioactive material. These techniques are discussed in more detail in Annex II. Selection and application of a specific destructive analysis technique or techniques typically depends on the needs and

requirements of the investigative authority. Several considerations are important when deciding which destructive analysis technique to use, if any. These include the following:

— The quantity and type of sample available and needed for the measurement;
— The sample preparation needs for the measurement;
— The amount of sample to be consumed during the course of the measurement;
— The possibility of heterogeneity in the physical, chemical, elemental and/or isotopic composition of the sample, which may result in the analysis of a non-representative aliquot.

Because the use of destructive analysis techniques necessitates consumption of a sample aliquot, it is impossible to replicate the measurement on a given aliquot. The production of multiple aliquots, and, in some cases, the transfer and reuse of aliquots from NDA techniques to destructive analysis techniques, is a good strategy for maximizing the data generated from a minimum amount of available sample. These considerations are particularly important when only a limited amount of sample mass is available for analysis.

6.1. ELEMENTAL AND CHEMICAL COMPOSITION MEASUREMENTS

An elemental composition dataset consists of the concentration of a set of elements that constitute the mass of the sample, along with corresponding measurement uncertainty for each element. A wide variety of analytical techniques can be used to measure elemental composition, though not all techniques are well suited for every type of nuclear or other radioactive material or for every element. For example, mass spectrometry techniques are ideal for metallic and semi-metallic elements but are poorly suited to non-metallic elements such as fluorine or chlorine. XRF can be used to quantify virtually every element that might be present in a sample, but it might lack the measurement precision, accuracy and sensitivity (especially for the lightest elements) to meet the needs and requirements of the investigative authority. Single element quantification methods, such as titration methods, can provide high precision elemental concentration data for one or a few important element(s), but might involve consumption of a significant amount of sample. The choice of technique is ultimately driven by factors such as the needs and requirements of the investigative authority, the type of sample under examination and the amount of sample available.

Mass spectrometry is a destructive analysis technique commonly used in nuclear forensics for determination of the elemental composition of many types of nuclear or other radioactive material. Although the field of mass spectrometry encompasses a wide range of techniques, including those used for the analysis of organic compounds, applications in nuclear forensics generally focus on quantification of the metallic and semi-metallic elements. Because of this, inductively coupled plasma mass spectrometry (ICP-MS) has gained widespread popularity in nuclear forensics [44]. This technique, which typically involves the dissolution of an aliquot of the sample in an acid matrix, makes use of a high temperature plasma to atomize and ionize the elements present within the sample. Ions are then accelerated under vacuum in a magnetic field, forming a beam of ions. The ions are separated on the basis of their mass-to-charge ratio using a mass analyser. The intensities of the separated ion beams are measured by one or more detectors within the instrument.

For elemental concentration measurements in a nuclear forensic examination, the use of a mass spectrometer with a quadrupole mass analyser is often useful. This type of mass spectrometer can accurately and precisely measure the metallic and semi-metallic elements in a sample

within minutes to hours, excluding sample preparation time. Quadrupole ICP-MS instruments can determine the concentration of most metallic elements with a sensitivity of four to six orders of magnitude higher than XRF [45]. However, quadrupole ICP-MS involves optimization and calibration of each set of elements to be measured, and a new calibration is typically performed once or more per day. In addition, sample preparation and dissolution for mass spectrometry usually involves laboratory personnel working within a clean workspace or laboratory. Moreover, for this method, purified acids and single use disposable laboratory equipment are useful to ensure that the background for the measurements is kept as low as possible. The establishment of liquid radioactive waste streams ensures that waste generated during measurement is collected and properly disposed of. For these reasons, quadrupole ICP-MS necessitates considerable training and experience on the part of laboratory personnel, as well as significant laboratory infrastructure.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an alternative method for elemental composition measurements, with some specific applications to nuclear forensics [46]. ICP-AES functions similarly to ICP-MS, but instead of measuring the ion beams generated during atomization and ionization in the plasma, the instrument measures the characteristic electromagnetic radiation (usually around the visible light spectrum) produced during sample ionization. Although ICP-AES is less sensitive than ICP-MS for most of the elements that both can analyse, it can accurately and precisely measure the concentration of many elements that may of be of interest to the investigative authority. However, ICP-AES retains many of the limitations of ICP-MS, including the need for a clean preparation space and a radioactive waste stream.

XRF can also be performed as a destructive analysis technique. Powder samples can be converted into pressed pellets using a pellet press and binding material to minimize pore space and increase particle density, resulting in more accurate and precise concentration measurements [47]. Alternatively, solid samples can be melted using a furnace and fluxing compound, then quenched to produce a glass disc or bead, which can then be analysed by XRF. This approach minimizes sample heterogeneity effects by ensuring an even distribution of atoms within a glass matrix, resulting in more accurate elemental concentration data [48]. However, the production of glass discs and beads consumes a large amount of the sample, and the quality of the resultant glass is somewhat dependent on the composition of the sample and the speed at which the melt is quenched. Moreover, the melting and quenching of radioactive samples might present a dispersible radioactive material hazard.

There are several titration methods that can be used to determine single element concentrations in nuclear forensic samples [49, 50]. One titration method frequently used in nuclear forensics is the modified Davies-Gray technique, which is capable of accurate and precise measurements of uranium concentration [51]. This technique is ideally suited to uranium-rich material, such as uranium ore concentrate and uranium fuel pellets. Although this technique can be performed manually, a more reliable and reproducible approach is to utilize an auto-titration system, which can analyse eight or more samples in sequence, with reliability superior to that achievable by a human operator [52]. Although the application of this technique necessitates experience in benchtop chemistry, it is significantly less expensive than mass spectrometry, while still capable of producing high precision uranium concentration data comparable to some mass spectrometry techniques [53].

There are two primary options for determining the presence and abundance of chemical compounds using destructive analysis: XRD and Fourier transform infrared spectrometry

(FTIR). Preparation for XRD can involve the aliquoting and crushing of the sample into a fine-grained powder prior to analysis, and this transformation of the aliquot can be considered destruction of the sample. This aliquot can then be used for other non-destructive or destructive analytical techniques, since the XRD measurement itself does not consume the sample [54]. Similarly, FTIR is in principle an NDA technique, but in most cases, the technique involves the grinding of an aliquot into a powder, followed by the formation of a pellet using a pellet press and binding material. The FTIR technique involves bombardment of the sample with infrared photons, resulting in the production of spectra that are characteristic of the molecular compounds present in the sample [55, 56]. The spectra can then be compared against the spectral patterns of known chemical compounds, allowing for identification of the compounds present.

Elemental and chemical composition data have many uses in investigations of nuclear or other radioactive material out of regulatory control, and the involvement of subject matter experts can aid interpretation [57]. In some cases, a suite of elemental data may be useful for determining the geological origin of the material. Many uranium ore and uranium ore concentrate materials have distinctive elemental profiles [58–64], in particular the lanthanide elements, which can be indicative of the type of ore deposit from which the material originated [65]. Linking these materials to geological and geographic origins may provide insight into the last legal owner of the material and may aid determination of where it was lost from regulatory control [66]. High concentrations of anionic groups such as fluoride, chloride, sulphate and phosphate are often found in trace levels in uranium-rich fuel cycle material originating from the use of mineral acids and other reagents during uranium extraction and purification [67, 68]. For instance, sulphuric and nitric acids are commonly used for the leaching and dissolution of uranium ore [69]. Although fluoride is often used in the nuclear fuel cycle for the storage of purified uranium-rich products (uranium tetrafluoride) or in enrichment processes (uranium hexafluoride), fluorine is not usually added intentionally during the production of uranium ore concentrate. For this reason, the likely sources of fluoride anionic groups in uranium ore concentrate are uranium bearing minerals, the presence of which can aid determination of geological origin [70]. Similarly, in cases where the uranium is recovered as a by-product from phosphate-based ores, an elevated level of phosphate in the uranium product may be expected.

Many other elements are indicative of nuclear fuel cycle processes. For example, the presence of elevated boron or gadolinium concentrations in a uranium fuel pellet may indicate that the addition of these elements was intentional during manufacture, as a neutron poison, and may be indicative of the type of nuclear reactor for which it was intended [71]. In another example, some fuel manufacturers use aluminium stearate as a mould release agent, which can result in elevated aluminium concentration in fuel pellets [72]. Contaminants on the surface of fuel pellets may also be present, which may provide information about pellet fabrication techniques used in production, such as sintering and grinding [52]. For example, trace amounts of molybdenum may be deposited on pellets from molybdenum trays used to hold the pellets during the sintering process.

6.2. ISOTOPIC COMPOSITION MEASUREMENTS

The ability to measure the isotopic composition of uranium and plutonium is useful for States in possession of nuclear material such as uranium fuel used in nuclear power reactors or research reactors. Because it is illegal in most States to possess enriched uranium or plutonium out of regulatory control, the investigative authority may request data on the isotopic composition of uranium or plutonium if uranium- or plutonium-rich materials are encountered

out of regulatory control. Uranium and plutonium isotopic composition data are usually reported as isotope ratios, with the most abundant (major) isotope in the denominator. In many cases, the investigative authority is interested in $^{235}U/^{238}U$ and $^{240}Pu/^{239}Pu$ isotope ratios for uranium and plutonium, respectively.

The isotopic composition of uranium is highly variable in nuclear or other radioactive material. Natural uranium consists of ~0.725 atom % ^{235}U (in ratio form, $^{235}U/^{238}U = 7.25 \times 10^{-3}$ [73]). The abundance of ^{235}U relative to ^{238}U is effectively constant in natural materials containing uranium [74]. Anthropogenic enrichment of uranium and production of depleted uranium as a waste product of enrichment alter the uranium isotopic composition of nuclear fuel cycle material. Nuclear power plants normally utilize uranium fuels in the range of 0.725% (natural) to 6.5% ^{235}U. Research reactors may utilize a much wider range of enrichment, from less than 20% to more than 90% ^{235}U, although the use of high enriched uranium for civilian purposes has greatly declined in recent decades. All uranium-rich material contains ^{234}U (natural $^{234}U/^{238}U \approx 5 \times 10^{-5}$, with small variations in the naturally occurring ratio due to natural processes [75]). Although ^{236}U and ^{233}U do not occur naturally, they may be present in material that has been irradiated in a nuclear reactor, contaminated with irradiated material or exposed to neutrons in some other setting [76].

Plutonium is a non-naturally occurring element produced primarily through the irradiation of uranium in nuclear reactors. Nuclear or other radioactive material samples containing plutonium may contain the isotopes ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu, and the relative abundance of these isotopes may vary significantly. Nuclear material can contain both uranium and plutonium, and some fresh nuclear power plant fuels consist of a mixture of both elements (mixed oxide fuels). Because plutonium is highly toxic and acutely radioactive, it is good practice for laboratory personnel to take extraordinary care when handling and analysing material containing plutonium during a nuclear forensic examination.

Although gamma spectrometry can be used to measure uranium and plutonium isotopic composition, this method is not as precise as many destructive analysis techniques, and ^{236}U cannot be measured by gamma spectrometry. Mass spectrometry is a useful technique for precise analysis of the concentration and isotopic composition of uranium and plutonium. Several plasma mass spectrometry instruments are commonly used for these measurements, including, with increasing measurement precision: (i) quadrupole ICP-MS [77, 78]; (ii) single collector sector field ICP-MS [16, 79–81]; and (iii) multi-collector sector field ICP-MS [82, 83]. In addition, thermal ionization mass spectrometry (TIMS), which utilizes a heated filament instead of a plasma to atomize and ionize the sample for analysis, can produce uranium and plutonium isotopic composition data equal or superior to that of the most precise plasma source mass spectrometry instruments [24, 84–89]. Advanced mass spectrometry techniques necessitate significant technical expertise in isotope ratio analysis and have high operational costs, including the need for clean laboratory space and a continuous stable source of electricity to maintain vacuum systems. Furthermore, these methods involve the acquisition of expensive standard reference materials for calibration and quality control, which can incur additional costs.

Alpha spectrometry is a destructive analysis technique used to determine the specific activity and isotopic composition of alpha emitting radionuclides, such as those of uranium and plutonium [16, 90]. In a nuclear forensic examination, alpha spectrometry can be used to determine enrichment of uranium ($^{235}U/^{238}U$), grade of plutonium ($^{240}Pu/^{239}Pu$) and abundance of other alpha emitting radionuclides, such as ^{237}Np, ^{241}Am, ^{226}Ra [91]. In addition, alpha

spectrometry is an ideal instrumental technique for ^{238}Pu analysis [92]. Alpha spectrometry is a cost effective alternative to advanced mass spectrometry techniques for many States. However, the use of alpha spectrometry involves chemical separation and purification of uranium and plutonium prior to analysis. Therefore, in addition to the alpha spectrometry system itself, a chemical separation capability is usually paired with alpha spectrometry for use in nuclear forensics. Chemical separation involves considerable technical ability and experience on the part of the analyst. Some environmental radioactivity laboratories are equipped with this capability for routine analysis, and States can adapt this capability for use in nuclear forensics. However, nuclear forensic samples may be considerably more radioactive than environmental samples routinely analysed by environmental laboratories, and it is possible to oversaturate an alpha spectrometry system in such a manner as to render it useless for low activity analyses. Dilution of the sample after chemical separation and prior to loading for alpha spectrometry analysis can help avoid alpha detector saturation and damage.

Gamma spectrometry, mass spectrometry and alpha spectrometry techniques are all capable of accurate and precise uranium and plutonium isotopic composition measurements. For example, all three sets of techniques can often determine the isotopic composition of low enriched and high enriched uranium with sufficiently high precision to determine if an interdicted nuclear material is enriched above the natural isotopic composition of 0.725% ^{235}U. In this example, more precise analysis of uranium isotopic composition may be useful only if the material is close to natural isotopic composition or if the investigative authority requests more precise data for some other purpose. In these cases, it may be useful to utilize the more precise mass spectrometry techniques, or to seek assistance from other States if this capability does not exist within the State itself.

Interpretation of uranium and plutonium isotopic composition can be complex but may have considerable value in many investigations of nuclear material out of regulatory control. For example, ^{234}U is inherently enriched alongside ^{235}U in uranium enrichment processes, and therefore tends to be positively correlated with ^{235}U in enriched uranium samples [93]. The ^{235}U/^{238}U and ^{234}U/^{238}U ratios of enriched uranium samples may be indicative of the type of enrichment technique used to produce the material [94]. In reprocessed uranium samples, the presence of ^{236}U may indicate that the material was exposed to neutrons (irradiated) at some point in its history [95]. The isotopic composition of plutonium, especially the minor isotopes ^{238}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu, may provide information about the type of reactor in which the plutonium was produced [96–100]. Different reactor types, such as light water moderated reactors, heavy water moderated reactors and graphite moderated reactors, have different neutron energy spectra and fluxes, as well as different initial ^{235}U enrichments of the fuel, resulting in plutonium isotopic compositions that can be diagnostic of the nuclear reactor in which the material was irradiated [101–103].

6.3. RADIOCHRONOMETRY MEASUREMENTS

The accumulation of daughter nuclides in nuclear or other radioactive material occurs as parent isotopes decay over time. The constant rate of radionuclide decay can allow for calculation of the age of the material (termed 'radiochronometry', or sometimes 'age dating') if the daughter-to-parent nuclide ratio can be determined [104]. For example, the age of a uranium-rich material can be calculated using a precise measurement of the ratio of the parent isotope ^{234}U to its daughter isotope ^{230}Th [105]. The measured age of nuclear or other radioactive material may reflect the time when the separation of the daughter nuclide from its parent nuclide last took place. In this case, the age may also be referred to as the production date of the material

[90]. A crucial assumption for interpretation of the measured age as a production age is complete separation between parent and daughter nuclides at the date of production. Furthermore, for an age result to be accurate, it is assumed that the material behaves as a 'closed system'; that is, neither parent nor daughter nuclide has been removed or added during the time since production other than through decay of the parent nuclide and ingrowth of the daughter nuclide [106].

For daughter-to-parent isotope ratio measurements, precise mass spectrometry techniques are typically preferred over gamma spectrometry due to their superior precision. However, for plutonium-rich material, the age can be obtained using the ^{241}Am/^{241}Pu ratio by gamma spectrometry [24]. Alpha spectrometry can also be used for age determination of uranium and plutonium in some cases [90]. For improved confidence in the results obtained by age dating, at least two independent parent-to-daughter ratios can be used, as some production processes do not result in quantitative removal of all daughter isotopes from the nuclear or other radioactive material. Some examples of daughter-to-parent ratios used for age determination in nuclear forensics are ^{230}Th–^{234}U [107–110], ^{231}Pa–^{235}U [111–117], ^{241}Am–^{241}Pu [24, 118], ^{235}U–^{239}Pu [119–121], and ^{227}Ac–^{235}U [122, 123].

In a nuclear forensic examination, determination of material production age can aid the investigation in several ways. Material age data can assist the investigative authority in determining, or ruling out, the facility from which the material was produced. States with a nuclear fuel cycle have records of when their facilities were producing nuclear or other radioactive material, enabling comparison between the material radiochronometry age and the known timescales of production. Material ages that fall outside of a State's history of nuclear or other radioactive material production may be indicative of material origin outside the State. Confidence in interpretation of material age is increased by analysing more than one parent–daughter pair, such as ^{234}U–^{230}Th and ^{235}U–^{231}Pa in uranium-rich material [124]. Age agreement between two or more parent–daughter pairs is strongly suggestive that the measured ages reflect the true age of material production [125]. Disagreement between measured ages suggests that one or both ages is inaccurate, possibly due to incomplete removal of the daughter nuclide during material production.

6.4. OTHER DESTRUCTIVE ANALYSIS TECHNIQUES

Some States may possess analytical techniques capable of measuring other nuclear forensic signatures not mentioned above. For example, it is possible to use TIMS or multi-collector ICP-MS to measure the strontium, neodymium, lead, molybdenum, samarium and thorium isotopic composition of uranium ore and uranium ore concentrate materials, which can enable linkage of these materials to specific geologic and geographic origins [126–132]. The presence and abundance of fission and activation products, such as ^{90}Sr, can also be measured with high precision in spent fuel and other material exposed to neutrons using these and other advanced techniques [133–138]. Novel isotopic systems, such as those employing molybdenum, can be used to determine (or rule out) the use of specific enrichment and other nuclear fuel cycle processes in the production of the material [139]. Using other types of mass spectrometer, such as dual inlet gas source instruments designed for light stable isotope measurements, it is possible to determine the isotopic composition of oxygen, hydrogen, carbon and other stable isotopes that are present in a material [140–144].

Advanced mass spectrometry techniques can be used to obtain high precision elemental and isotopic data from nuclear or other radioactive material on a spatial scale from tens to hundreds

of microns. Secondary ion mass spectrometry (SIMS) is a spatially resolved analytical technique capable of determining the uranium isotopic composition of nuclear forensic samples on the microscale [145, 146]. This technique has been used to measure microscale uranium isotopic heterogeneities in uranium fuel pellets and to measure the isotopic composition of individual nuclear material particles. Approaches taken by the nuclear safeguards community using SIMS can be applied to particulate nuclear forensic samples [147]. The use of multi-collector sector field ICP-MS instruments in tandem with laser ablation sample introduction systems has demonstrated that this approach can reveal isotopic heterogeneity on the scale of 1×10^{-6} m in bulk and particulate nuclear material [9, 12, 79, 148, 149]. One additional advantage of laser ablation sample introduction systems is the minimal consumption of sample mass during analysis.

7. QUALITY ASSURANCE IN NUCLEAR FORENSIC ANALYSIS

For the results of a nuclear forensic examination to be useful to the investigative authority, the nuclear forensic laboratory often demonstrates and communicates the quality and reliability of measurements in a variety of ways. The nuclear forensic laboratory can take several measures to ensure the quality of nuclear forensic analyses. Many nuclear forensic laboratories have in place a quality assurance and quality control programme. Since most designated nuclear forensic laboratories perform analytical work other than nuclear forensics, they may already be operating under some form of quality assurance and quality control programme for routine work. Many laboratories are certified to meet the International Organization for Standardization (ISO) international standard, which demands the demonstration of reliable results in routine audits. Although a nuclear forensic laboratory is not required by any international body to operate under an international standard such as ISO 17025 (although they may be required to operate under this standard by national law), accreditation increases confidence in the analytical results produced by the laboratory [150].

Most nuclear forensic laboratories follow standard operating procedures for the analyses they are asked to perform in a nuclear forensic examination. Very often, these standard operating procedures are adapted from those used for routine laboratory analysis, such as the analysis of solid radioactive material by gamma spectrometry. Whenever possible, the nuclear forensic laboratory can develop standard operating procedures for the analytical instruments and types of nuclear or other radioactive material they might expect to analyse in the context of nuclear forensics. However, it is helpful for laboratory personnel to remain flexible, since it is possible to receive unexpected types of material for which the laboratory does not have a standard operating procedure prepared in advance. Deviations from a standard operating procedure can be documented in order to ensure that measurement quality is maintained and demonstrated to the investigative authority.

Analyses of standard reference materials alongside nuclear forensic samples are essential for ensuring measurement accuracy [151]. Standard reference materials are typically certified for one or more analytes of interest, in a relevant matrix. For example, a uranium ore concentrate standard reference material may be certified for iron concentration, among other elements, as well as for uranium isotopic composition. In a nuclear forensic examination, most laboratories measure one or more standard reference materials alongside the nuclear forensic sample [152], ensuring that each measured analyte is associated with a corresponding standard reference material measurement. Before reporting data, laboratory personnel typically conduct assessments of standard reference material measurement results in order to ensure that results are within certified values including uncertainties. In addition, it is good practice to use

standard reference materials that match the matrix of the nuclear forensic sample as closely as possible [153]. For example, a uranium fuel pellet standard reference material can be analysed alongside the examination of a uranium fuel pellet material out of regulatory control [154–157]. Standard reference materials for elemental and isotopic composition may be purchased from several suppliers, and new reference materials are continually in development [158–160], including for new analytes [161] and for spatially resolved analysis [162].

Because the need for nuclear forensic examinations may occur infrequently in a State, laboratory personnel may take the opportunity to exercise and improve their skills in nuclear forensic analysis whenever possible. The international community of nuclear forensics practitioners routinely participates in bilateral and multilateral opportunities to exercise the process of a nuclear forensic examination. The 'Collaborative Material Exercise' series of exercises, organized by the Nuclear Forensics International Technical Working Group, is an example of the type of nuclear forensics exercise that many States have participated in [163, 164].

Quantitative data obtained during a nuclear forensic examination are typically associated with statistical measures of uncertainty [165]. Uncertainty, sometimes incorrectly referred to as 'error', is used to quantitatively describe the precision of measurements. Analytical techniques with higher precision produce data with smaller uncertainty, whereas lower precision techniques produce data with larger uncertainty. While the topic of statistical uncertainty in measurement is vast [166], and although nuclear forensic analysts seek to produce data with the minimal possible uncertainty [167], in many cases it is only necessary for the laboratory to produce data that meet the needs and requirements of the investigative authority. For example, if the possession of enriched uranium outside of regulatory control is in violation of a State's laws, and a low enriched uranium fuel pellet is the subject of nuclear forensic examination, it may only be necessary for the laboratory to produce data that demonstrate that the sample is enriched, taking into consideration the uncertainty of the measurement. If the sample is determined to have an enrichment of 3% ^{235}U, with a relatively large uncertainty of ±1.5% ^{235}U, this measurement will have sufficiently demonstrated that the material exceeds the isotopic composition of natural uranium (0.725% ^{235}U) if measurement accuracy can also be established through the use of standard reference materials. In this case, a more precise measurement might not be necessary to meet the needs and requirements of the investigative authority. Therefore, even relatively low-precision measurements may be sufficiently precise to address the needs and requirements of the investigative authority, and measurement accuracy can be demonstrated using standard reference materials, standard operating procedures and through other means.

When reporting measurement uncertainty, the nuclear forensic laboratory may provide sufficient information to ensure that uncertainty calculations can be reproduced if necessary. By reporting the mathematical approach used to quantify uncertainty, the investigative authority can be assured as to the degree of confidence in each datum. Reference [168] describes an approach taken by some nuclear forensic laboratories for uncertainty quantification in nuclear forensics.

8. REPORTING THE RESULTS OF A NUCLEAR FORENSIC EXAMINATION

A nuclear forensic examination typically results in the production of a series of reports containing key data on the physical, chemical, elemental and/or isotopic properties of the nuclear or radioactive material and/or associated non-nuclear material, as well as other findings

and conclusions resulting from the examination. These reported findings can then be used by the investigative authority to aid the investigation and may even be used in criminal or other legal proceedings. Reports can be written in such a way as to ensure that findings are understood by a non-technical audience, such as the investigative authority as well as others (e.g. policymakers, government officials and those involved in legal proceedings) who may consult the reports. Most laboratories prepare reports of findings from nuclear forensic examinations that are consistent with the requirements of the State's legal statutes for use during a criminal investigation.

In addition to relevant nuclear forensic data (including the respective uncertainties), as well as key conclusions, reports may contain descriptions of methods and techniques specific to the production of the data. Methods applied to a nuclear forensic examination often follow standard operating procedures as far as possible. If deviation from a standard operating procedure is necessary (e.g. the analysis of a sample of an unusual matrix), the report may state the nature of the deviations and why they were made. Standard reference material data are typically reported alongside sample data to demonstrate measurement accuracy.

In cases where more than one technique is used to analyse a particular nuclear forensic signature (e.g. uranium isotopic composition, which can be measured by gamma spectrometry, alpha spectrometry or mass spectrometry), the report may stipulate which set of instrumental data is the most reliable. The report may evaluate the consistency of observations derived from the application of multiple, independent methods. In cases where two techniques produce data for a particular nuclear forensic signature that do not agree (i.e. do not overlap within the limits of uncertainty), it is good practice for the laboratory to explain why this might have occurred and to assess the reliability of these data. Very often, it is because the first analytical technique selected was not well suited to the nuclear forensic sample matrix, and another technique was later chosen that was more appropriate.

For techniques used to measure physical nuclear forensic signatures, such as SEM, qualitative observations (e.g. descriptions of the physical appearance of a sample, or of various features observed, including scratches and other signs of damage) are commonly treated as data. It is often difficult to ascribe uncertainty to these observations, and physical descriptions may be subjective, depending on the perspective and expertise of the analyst. Maintaining objectivity is good practice for ensuring that descriptions are understood by the investigative authority and by others not involved in the nuclear forensic examination. Some States have developed a standard vocabulary for the description of nuclear or other radioactive material so that specific descriptions have well defined meanings [36]. Physical descriptions are typically paired with photographs and/or photomicrographs in order to enable the investigative authority to interpret these features in the broader context of the investigation.

In some cases, the investigative authority may request additional laboratory assistance in the interpretation of nuclear forensic data. Nuclear forensic interpretation typically involves the comparison and association of nuclear forensic signatures with information pertaining to types of material and origin and method of production of nuclear or other radioactive material, or with previous cases involving similar material. This information can be obtained from sources including: (i) existing information within the State (e.g. a national nuclear forensic library [169–171], a sealed source registry and/or a nuclear material accountancy and control system); (ii) by performing comparative analysis with similar samples available in the laboratory; (iii) through subject matter expertise.

If no additional analyses are requested by the investigative authority, samples and data generated as a result of the examination may be preserved and stored, consistent with the requirements of national laws and regulations, until the investigation has concluded.

9. INTERNATIONAL COOPERATION AND ASSISTANCE

Not all States have developed sufficient national capacity in nuclear forensics to analyse the types of nuclear or other radioactive material that might be encountered out of regulatory control. Therefore, international cooperation is a useful approach for the development of nuclear forensics in any State. States with experience in the development and implementation of a nuclear forensic capability may be willing to share their knowledge with other States, with the goal of strengthening nuclear security worldwide.

States can assist other States through the sharing of best practices in nuclear forensic analysis, through the implementation of training in nuclear forensics and through participation in bilateral or multilateral exercises involving the analysis of nuclear or other radioactive material, as well as by many other means. In addition, States with developed nuclear forensic capabilities may extend offers of assistance to other States in the examination of nuclear or other radioactive material encountered out of regulatory control, and States may accept offers of assistance. This approach is useful if the analytical needs of a nuclear forensic examination exceed the ability of a State to perform the necessary analyses or for other reasons.

The IAEA has developed a capacity building programme in nuclear forensics, designed to assist States in developing nuclear forensic capabilities. States interested in developing nuclear forensics may request expert missions. Upon such requests, the IAEA assists in the coordination of relevant national stakeholders and in the identification of national resources to be used in nuclear forensics. States may also choose to participate in the IAEA training programme, which utilizes the subject matter expertise of nuclear forensic experts. The IAEA also holds technical meetings on a periodic basis, focused on developments in nuclear forensics [172, 173]. These meetings function as forums for Member States to present developments in their nuclear forensic capabilities as well as advancements in nuclear forensic science. Member States interested in making contributions to the development of nuclear forensic science may apply for participation in IAEA coordinated research activities, which support Member States in research and development activities in nuclear forensics. The IAEA has developed several coordinated research projects in the area of nuclear forensics that have resulted in the publication of technical documents reporting the results of these projects [174, 175].

The Nuclear Forensics International Technical Working Group is another organization that administers several activities designed to assist States in developing and exercising a nuclear forensic capability. The 'Collaborative Material Exercise' series of exercises involves the analysis of nuclear or other radioactive material, enabling States to apply their nuclear forensic capability through actual examination of nuclear or other radioactive material [163]. The 'Galaxy Serpent' series of exercises consists of virtual, web-based exercises designed to illustrate the utility of national nuclear forensic libraries in addressing the needs and requirements of investigative authorities as part of investigations involving nuclear or other radioactive material out of regulatory control [176].

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ANNEX I: SAMPLES AND GENERAL CONSIDERATIONS FOR NUCLEAR FORENSIC EXAMINATIONS

I-1. INTRODUCTION

A wide variety of nuclear and radioactive material and non-radioactive material may be the subject of a nuclear forensic examination. These materials may occur in various amounts, sizes and forms, with widely varying radioactive properties. Traditional forensic evidence contaminated with radionuclides may also be examined. Some considerations for the nuclear forensic examination of various types of nuclear or radioactive material sample are presented below.

I-2. SOLID SAMPLES

Solid samples that may be analysed as samples in a nuclear forensic examination may include nuclear material such as uranium ore, uranium fuel pellets and uranium or plutonium metals of varying isotopic composition. Radioactive samples, such as research reactor targets (irradiated or non-irradiated), radioactive scrap metal, sealed radioactive sources used for industrial or medical purposes and other associated materials, may also be analysed in a nuclear forensic examination. In principle, solid samples present a lower radioactive hazard to the analyst than powder and liquid samples because they do not present an inherent dispersible radioactive material hazard. However, laboratory personnel often consider the potential of inadvertently generating dispersible radioactive material from solid samples, especially during unpacking, handling and sub-sampling (aliquoting). Therefore, manipulation of solid samples may take place in a laboratory environment where dispersible radioactive material can be controlled, such as in a glove bag within a fume hood, or within a glove box. Aliquoting may present a particularly acute challenge, as cutting and grinding processes can easily produce radioactive particles. Physical measurements (such as measurement of sample dimensions) are a form of non-destructive analysis (NDA) technique and are typically taken before any other measurement, and the initial physical state of the solid sample can be documented through photography and optical microscopy.

For some NDA techniques, such as gamma spectrometry, sample preparation is often not performed for analyses of solid samples, provided the sample is small enough to fit in the instrument. In this case, many laboratories work to ensure that the sample is handled in such a manner as to not inadvertently produce dispersible radioactive material. Furthermore, measures can be taken to avoid contamination of the NDA instrument. Solid sample aliquoting is necessary for the use of most destructive analytical techniques, and the potential for sample heterogeneity is often considered when aliquoting a solid sample for analysis. Heterogeneity may occur at a variety of spatial scales and can be physical, chemical, elemental and/or isotopic in nature. Laboratory personnel can make use of data generated from NDA techniques to assess sample heterogeneity. Techniques such as optical microscopy and scanning electron microscopy (SEM) are especially useful for assessing the extent and degree of physical and elemental heterogeneity that may occur in a solid sample. It is more difficult to assess isotopic heterogeneity using these methods; therefore, it is often useful to prepare several aliquots for destructive analysis measurements of isotopic composition, such as mass spectrometry. Replicate destructive analysis measurements of different small aliquots can be used to assess isotopic homogeneity or heterogeneity in a solid sample; if the isotopic composition of several small aliquots of the sample, taken from different portions of the sample, overlap within measurement uncertainty, the analytical team may reach the conclusion that the sample is

isotopically homogeneous on the scale of the aliquots taken. Alternatively, spatially resolved analytical techniques capable of measuring isotopic composition, such as secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (ICP-MS), may be used to characterize sample isotopic heterogeneity on the microscale.

Sealed radioactive sources present an acute radiation hazard that, if mishandled, might cause severe injury or death to laboratory personnel. Most laboratories do not take the risk of breaching of the protective seal that contains the radioactive source, as the vast majority of useful nuclear forensic signatures can be measured using NDA techniques (such as gamma spectrometry), physical characterization using photography, measurement of physical dimensions and features, and perhaps microscopy. Breaching of the protective seal of a sealed radioactive source is typically performed only if absolutely necessary during the investigation, by trained personnel, within a facility capable of protecting laboratory personnel from gamma radiation and dispersible radioactive material that is likely to be generated.

Plutonium-bearing material also presents an acute radiation hazard, and many laboratories seek to detect the possible presence of plutonium, especially prior to aliquoting, which can generate dispersible radioactive material. As an alpha emitter, plutonium is extremely hazardous to laboratory personnel through inhalation and ingestion. Furthermore, contamination of the nuclear forensic laboratory with plutonium may render the laboratory unusable for a period of months or longer. Plutonium can be difficult to detect using gamma spectrometry instrumentation, especially if present with other, more highly active gamma emitters. Uranium-rich irradiated nuclear material may contain trace amounts of plutonium (as well as other activation products, in addition to fission products). Handling of plutonium and plutonium-bearing material is typically performed by trained laboratory personnel who are aware of the hazards and trained in the handling of dispersible radioactive material, using personal protective equipment to ensure containment of plutonium throughout the analyses.

I-3. POWDER SAMPLES

Powder materials that may be analysed as samples in a nuclear forensic examination include solid material encountered in powder form. Other radioactive material that may be encountered in powder form includes uranium ore concentrate, fine-grained material used in the nuclear fuel cycle (e.g. uranium tetrafluoride), contaminated ion exchange resins used in uranium purification processes and radionuclide contamination present on surfaces of non-nuclear material encountered at a radioactive crime scene. In many ways, powder samples are handled and analysed similarly to solid samples. However, powder samples present an inherent dispersible radioactive material hazard that many laboratories work to mitigate in order to protect laboratory personnel and the integrity of the laboratory itself. Many types of nuclear forensic sample may contain a particulate component, present as contamination on otherwise weakly radioactive or non-radioactive materials. Many laboratories take care to ensure that particulate radioactive contamination on solid materials does not contaminate the workspace or laboratory personnel.

Laboratory personnel may consider the possibility of heterogeneity at the individual grain scale, as powder samples may consist of grains or grain populations with widely varying physical, chemical, elemental and isotopic properties. For example, uranium-rich powders may contain grains with a range of isotopic compositions, from enriched to depleted. Uranium ore concentrate samples may contain grains of widely varying elemental and chemical composition and may include residual refractory grains suggestive of geological origin. Spatially resolved

imaging and measurement techniques, such as SEM, are invaluable for characterizing powder samples in the context of a nuclear forensic examination.

When aliquoting powders for use in destructive analysis, consideration is typically given to the amount of material taken for each aliquot. If the objective is to obtain a representative sample of the bulk composition of the powder, larger aliquots may be taken. Alternatively, laboratory personnel may seek to characterize the nuclear forensic signatures of different populations of grains present in the powder. In this latter case, it may be possible to separate out grains from representative populations, either manually or by exploiting some physical property of the particles themselves. Individual grains or grain populations can then be dissolved and analysed. Spatially resolved techniques, such as mass spectrometry with laser ablation sample introduction system, are particularly useful when examining a powder sample with complex populations of particles. With these techniques, it is possible to measure the elemental and isotopic composition of hundreds of individual grains, revealing heterogeneities that would otherwise be undetectable.

I-4. LIQUID AND SLURRY SAMPLES

On occasion, liquid radioactive samples may be encountered in the context of a nuclear forensic examination. In some ways, the handling of liquid samples is a simpler proposition than solids or powders, because liquids can be contained within sealed beakers, bottles or other similar vessels. However, the nature of the liquid matrix may vary, as various acids and solvents are used in the nuclear material production process. If transferring the liquid to a new vessel for storage and analysis (e.g. transfer to a beaker with standardized geometry for gamma spectrometry analysis), many laboratories aim to select a vessel composition that is compatible with the liquid matrix. For example, hydrofluoric acid-containing liquids are incompatible with glass; the use of polytetrafluoroethylene or perfluoroalkoxy alkane vessels may be preferred in this case.

A slurry is a mixture of undissolved solids suspended in and/or settled out of a liquid matrix. Radioactive slurries are common in nuclear facilities, particularly as waste products, and they present unique challenges in handling, aliquoting and analysis. There are several methods that may be used to separate the solid from the liquid components of a slurry, but it is usually necessary to consider the composition of the liquid component, as the separation method chosen might or might not be compatible with the liquid solvent or acid matrix. Centrifugation is a commonly used method to separate solid and liquid phases. Many laboratories take care to ensure that, once separated from the liquid matrix, the solid residue does not produce dispersible radioactive material.

I-5. SAMPLE DISSOLUTION METHODS

Solid and powder samples may involve dissolution (sometimes referred to as 'digestion', with the two terms being used interchangeably) prior to analysis, particularly using destructive analysis techniques. Dissolution of a solid sample involves the physical and chemical breakdown of the molecular structure and conversion to a solution (a homogeneous liquid mixture), typically performed using mineral acids (e.g. HCl, HF, HNO_3) or sometimes organic solvents. Upon dissolution, solid and powder samples can be analysed in solution form. Many destructive analysis techniques, such as mass spectrometry, can measure the elemental and isotopic properties of solutions with high precision. The dissolution of solid samples also enables more accurate and precise measurements using NDA techniques, such as gamma

spectrometry, because solution samples can be measured within containers of constant volume, eliminating the need for geometric correction. Accurate and precise masses for each solid sample aliquot are typically determined prior to dissolution in order to calculate elemental concentrations from measurements performed after digestion.

In nuclear forensics, inorganic materials such as metals, ores, oxides, ceramics and glass are frequently encountered. These materials can be dissolved using mineral acids, although the specific acid or acids most useful for this purpose are highly dependent on sample chemistry. For example, many uranium-rich materials are readily digestible using HCl and/or HNO_3. However, silicate-rich samples such as uranium ores are often best dissolved using HF to break silicon-oxygen bonds, ensuring that the sample is completely in solution. In some cases, H_2SO_4 can be used to ensure the sample aliquot remains in solution. In other cases, using a microwave digestion system can assist in ensuring complete dissolution of the sample. Many sample dissolution methods are described in the scientific literature, and a good first step when deciding on an approach to sample dissolution is to utilize a method that has been successful for the type of sample that is the subject of the nuclear forensic examination. Sample dissolution is sometimes a 'trial and error' process, and a sample is not always completely dissolved on the first attempt. Through subsequent cycles of chemical attack and evaporation, using different acids, solvents, and in some cases oxidizing or reducing agents, it is usually possible to completely dissolve the material.

Regardless of the dissolution method used, many laboratories work to ensure that the sample is not contaminated by dissolution reagents or the liquid vessels themselves. Laboratory personnel may acquire or prepare clean laboratory reagents, including mineral acids and water with minimal concentrations of trace metals. Beakers and other labware, such as disposable pipette tips and centrifuge tubs, may be cleaned of trace impurities using mineral acids and water prior to use, if not purchased at the trace-metal grade purity standard. Many laboratories take special care when samples are brought to evaporation between dissolution steps, because the potential for cross contamination might be high due to the ability of the residue to solidify and form particles that can exit their containers due to static electricity and/or air currents within the laboratory. Total procedural blank measurements can be performed alongside sample measurements to detect the presence of contamination that might impact data quality upon analysis.

I-6. CHEMICAL SEPARATION METHODS AND ISOTOPIC TRACERS

Some elemental and isotopic measurement techniques, such as alpha spectrometry and many forms of mass spectrometry, are optimally performed only when the element of interest has been chemically separated and purified prior to analysis. Chemical purification is typically performed only after complete digestion of the sample and can be performed using a wide variety of techniques, including solvent extraction, co-precipitation and ion exchange chromatography. Successful chemical separation and purification ensures that elements that have the potential to interfere with measurements are quantitatively removed. In mass spectrometry, the removal of interfering elements ensures that direct isobaric and polyatomic interferences do not cause erroneous measurements of the elements of interest. In alpha spectrometry, the production of well defined, narrow peaks is possible after chemical separation of the alpha emitting element of interest.

It is common to utilize isotopic tracers (often called 'spikes', with both terms being used interchangeably) in alpha spectrometry and mass spectrometry for accurate and precise

measurements of isotopic composition and elemental concentration, respectively, in a measurement approach known as isotope dilution. Isotopic tracers are commercially available solutions of high isotopic purity or of monoisotopic composition. In many applications, it is common to use spikes containing isotopes not expected to be present in the sample (e.g. ^{233}U in a uranium-rich material). Mass spectrometry and alpha spectrometry techniques can determine isotope ratios with very high precision, and the use of tracers takes advantage of this benefit. It is possible to calculate the concentration of one or more isotopes of an element with high accuracy and precision by measuring the ratio of the spike isotope to the isotopes of interest. Many laboratories choose to measure an unspiked aliquot of the sample solution to perform the calculation as well. Many isotopic tracers used in nuclear forensics, such as for uranium and plutonium, are commercially available from producers of standard reference materials. In other cases, isotopic tracers can be manufactured and calibrated at the laboratory. For example, the short lived ^{233}Pa isotopic tracer, which enables the precise and accurate measurement of ^{231}Pa for ^{235}U–^{231}Pa age dating, can be continually produced and calibrated in the laboratory due to its half-life of approximately one month.

Although nuclear forensic analyses typically do not demand ultra-high precision for concentration measurements, radiochronometry measurements are greatly improved using this approach. Using mass spectrometry and well calibrated isotopic tracers, it is possible in some cases to obtain material ('production') age data with uncertainty as small as ±1 year or less.

I-7. STANDARD REFERENCE MATERIALS

Standard reference materials are typically analysed alongside nuclear forensic samples to ensure that nuclear forensic data are accurate. Through the analysis of the properties of standard reference materials for which they have been certified (e.g. iron concentration, uranium isotopic composition), the laboratory analytical team can have higher confidence that the data generated for nuclear forensic samples are accurate. Many standard reference materials (such as solutions certified for concentration of specific elements) can be purchased from laboratory suppliers, and the nuclear industry produces standard reference materials relevant to nuclear measurements, such as those certified for ^{235}U/^{238}U and ^{240}Pu/^{239}Pu. Whenever possible, standard reference materials are analysed in the same batch of measurements as nuclear forensic samples. During sample preparation, standard reference materials are usually handled, digested and measured using the same procedures as nuclear forensic samples. For example, in the analysis of a uranium fuel pellet in a nuclear forensic examination, the laboratory team may acquire and analyse a uranium fuel pellet standard reference material which has been certified for uranium isotopic composition and radiochronometry age.

ANNEX II: DESCRIPTIONS OF ANALYTICAL METHODS USED IN NUCLEAR FORENSIC EXAMINATIONS

II-1.   VISUAL INSPECTION AND PHOTOGRAPHY

II-1.1. Introduction and instrumentation considerations

Photographic documentation of samples helps ensure that their physical properties are recorded upon receipt by the laboratory prior to aliquoting and analysis. Photographic documentation can also be used throughout the handling, aliquoting and analysis process. Photography for nuclear forensic examination is typically performed using digital cameras, which can range in sophistication from mobile phone cameras to single lens reflex cameras with zoom lenses. The choice of camera is usually dependent primarily on the desired image resolution. For nuclear forensics, virtually any digital camera will suffice, provided photographs are taken in a systematic and well documented fashion. It is helpful to use a tripod or other stabilizer to ensure that images are not blurry or lacking focus. Lighting may be arranged so that the sample is well lit, and certified colour charts (e.g. the Macbeth ColorChecker) can be used to ensure that the colours captured by the photographs are accurate and can be traced to a standard reference.

II-1.2. Use in nuclear forensic examinations

In nuclear forensics, photography is typically performed upon initial receipt of the sample by the laboratory, especially during the unpacking and initial examination process. Use of a scale (e.g. ruler) enables quantitative measurement of specific features, dimensions and other physical properties of the sample. Photographs can record physical nuclear forensic signatures such as colour, texture, physical dimensions and evidence of handling (e.g. scratches, chips and other imperfections), as well as the homogeneous or heterogeneous physical nature of samples. Photography can be used throughout the nuclear forensic examination to record key details of the sample, as well as the methods used to perform analyses. During aliquoting, each subsample may be photographed prior to dissolution or alteration for destructive analysis.

II-2.   OPTICAL LIGHT MICROSCOPY

II-2.1. Introduction and instrumentation considerations

Optical light microscopy is a non-destructive analysis (NDA) technique used to examine and record macro- and microscale physical features of nuclear forensic samples. Optical light microscopy, especially when paired with a digital imager, can be used to collect physical images of the surfaces of nuclear forensic samples. Many types of optical microscope are commercially available and may be purchased with varying magnification capabilities. Optical light microscopes are relatively simple to use and typically do not necessitate advanced training for their operation. Most optical microscopes with digital imagers can be purchased with image capture software, allowing for control over image properties such as contrast and white balance.

II-2.2. Use in nuclear forensic examinations

Optical light microscopy is particularly useful for identifying regions of interest in a nuclear forensic sample that can be characterized physically and later analysed in further detail using spatially resolved techniques, such as scanning electron microscopy (SEM), or subsampled during aliquoting. Physical heterogeneities and distinguishing features can often be readily identified using optical light microscopy. Optical light microscopy can be used during the process of aliquoting, particularly when removing small amounts of sample material for further analysis. Optical light microscopy can also be used to identify traditional forensic evidence that may be associated with nuclear or other radioactive material.

II-3. LABORATORY ANALYTICAL BALANCE

II-3.1. Introduction and instrumentation considerations

An analytical balance (sometimes referred to as a 'scale') is an instrument used to measure the mass of an object. Most laboratory analytical balances can measure the masses of objects in the gram to milligram range, although balances capable of measuring larger and smaller masses are also commercially available. Many analytical balances make use of a sample chamber that can be enclosed when a mass measurement is taken to ensure that air circulation in the room does not affect the quality of the measurement. Analytical chemistry laboratories are often equipped with one or more analytical balances, which are used in virtually all laboratory applications.

II-3.2. Use in nuclear forensic examinations

The mass of a sample is among the most fundamental measurements in a nuclear forensic examination and is typically the very first quantitative measurement performed (other than dose rate measurements for assessing the radiological hazard and accompanying photography). Analytical balances may be calibrated frequently to ensure measurement accuracy. Balance calibration can be performed using commercially available calibration weights. To establish measurement precision, many laboratories take several mass measurements of a sample if possible. Due to accumulation of static electricity, mass measurements can fluctuate, resulting in small but variable inaccuracies in mass measurement, especially for massing of plastics. Anti-static devices, either installed as a function of the balance itself or the use of an external device, can decrease fluctuations in mass measurement, resulting in increased mass accuracy and precision.

II-4. PROFILOMETRY AND THREE-DIMENSIONAL SCANNING

II-4.1. Introduction and instrumentation considerations

A variety of profilometry and three-dimensional (3D) scanning techniques can be used to analyse the surface and form of objects. Profilometry consists of a set of methods using optical light to qualitatively or quantitatively characterize the topography and relief of a sample surface. Photogrammetry and 3D scanning are methods for qualitative or quantitative characterization of volumes. These techniques are generally non-destructive, although some preparation techniques (e.g. application of reference marks) may alter the sample. Digital cameras can be used with photogrammetry software to manually generate 3D meshes with surface images, but the process is labour intensive if it is not automated. Modern profilometers use laser interferometry to generate two-dimensional (2D) or 3D reconstructions of material surfaces without touching the surface of the sample. Optical scanning usually involves little or no sample preparation. Samples with a matte surface and heterogeneous appearance with contrasting features are ideally suited to optical scanning. Reflective surfaces pose a challenge; lasers deflect from shiny surfaces, whereas photogrammetric techniques are impeded by reflections, which are difficult to distinguish from actual surface features.

II-4.2. Use in nuclear forensic examinations

In nuclear forensics, profilometry is used to characterize the surface of samples, which can provide insight into how materials were manufactured or otherwise produced. In cases where chipped or broken surfaces are identified, profilometry may aid in the determination of the tool or method used to alter the material. 3D scans may be used to determine sample volume, which may then be used to calculate material density and may reveal microscale physical features and structures not readily apparent in photographs.

II-5. PYCNOMETRY

II-5.1. Introduction and instrumentation considerations

Pycnometry is an NDA technique that typically makes use of a gas (or, less commonly, a liquid) to determine the displacement caused by a sample within a fixed volume, allowing for measurement of sample volume. This technique is ideal for determining the volume of irregularly shaped objects. If the sample mass is known (through measurement using an analytical balance), it is possible to calculate the sample density using volume data obtained through pycnometry.

II-5.2. Use in nuclear forensic examinations

Gas pycnometers can be used in nuclear forensics for determining the volume and density of a wide variety of solid materials, including uranium ore, uranium ore concentrate, fuel pellets, radioactive powders, glasses and many other materials. Many metallic materials common in the nuclear fuel cycle have characteristic densities (e.g. uranium metal has a characteristic density of 19.1 g/cm^3), and the calculation of density can help determine the metallurgy of pure metals and alloys. However, samples with closed pore spaces within the volume of the sample can produce erroneous results. Many laboratories use a pycnometry gas that does not react with the sample, typically helium or another inert gas. Many laboratories take particular care while measuring the volume of powder samples by gas pycnometry, because it is possible to inadvertently disperse a radioactive powder when the sample chamber is flooded with gas.

II-6. SCANNING ELECTRON MICROSCOPY

II-6.1. Introduction and instrumentation considerations

SEM is a versatile form of microscopy that uses an electron beam to generate secondary electrons, backscattered electrons and X rays, which are detected and converted to images that can be used to characterize sample topography and elemental composition. SEM provides morphological images using secondary electron imaging as well as imaging of relative electron density (associated with the atomic number) from backscatter electrons. SEM is well suited to the observation of features on a nanometre to micrometre scale as it offers higher spatial resolution and depth of field in comparison to optical microscopy. Many SEM instruments are equipped with energy dispersive spectrometers for semi-quantitative characterization of elemental composition. Wavelength dispersive spectrometers are also increasingly common on modern SEM instruments, as well as electron microprobes. These spectrometers facilitate higher precision measurements of elemental concentrations and, in many conditions, can generate quantitative results. Most modern SEM instruments use secondary electron detectors capable of image resolution of a few nanometres and backscattered electron detectors for spatial distributions of material composition. SEM instruments optimized for elemental characterization are equipped with energy dispersive spectroscopy for rapid detection of X rays from elements excited by the electron beam or wavelength dispersive spectroscopy for detection and counting of individual characteristic X rays from a specific element. Image processing software allows for semi-quantitative assessment of the modal abundance of multiphase materials and automated calculations of grain size distribution, void space distribution and defect abundance. Several SEM software packages allow for quantitative determination of some morphological characteristics.

II-6.2. Use in nuclear forensic examinations

During a nuclear forensic examination, SEM can be used to characterize the morphology of materials. SEM can reveal grain size, shape and microstructures from the micro- to the nanoscale. For example, analysis of UO_2 fuel pellets can reveal the grain size distribution, grain shape, void size and shape, defects, homogeneity of the material, oxidation, cracking, traces of machining, porosity and other relevant properties. Morphological characteristics can be interpreted in the context of the processing history of the material, such as during the nuclear fuel fabrication process. The images of grain sizes of nuclear material can be used to perform comparative analyses between samples. In the case of uranium fuel pellets, the grain size may be related to the initial morphology, time and temperature that was applied to the material during sintering. The energy or wavelength dispersive spectroscopy capability of many SEM instruments provides elemental composition data, which can be quantitative when performed alongside measurements of standard reference materials. Compositional mapping can be a useful tool for measuring spatial distributions of major and trace elements in a bulk material. During a nuclear forensic examination, this technique is commonly applied to inorganic materials such as metals, oxides, minerals, glasses, semiconductors and ceramics.

II-6.3. Additional considerations

SEM imagery is often used for qualitative comparisons between nuclear forensic samples and materials of known production history. Current research in nuclear forensics is focused on developing quantitative methods of physical characterization from data obtained using SEM. Furthermore, research is being performed towards better understanding how particular processes in the nuclear fuel cycle impart specific physical nuclear forensic signatures to nuclear or other radioactive material, and how these nuclear forensic signatures can be interpreted in the context of nuclear forensic examinations.

Preparation for SEM can be challenging for some types of sample. Samples either need to be inherently conducting or, if they are not, covered with a thin conductive coating (e.g. carbon or gold). Variable pressure or environmental SEM instruments are available for analysis of some types of sample and can be used to avoid the need for conductive coatings. Quantitative compositional analysis involves instrumental calibration using standard reference materials. Many laboratories exercise caution when analysing nuclear forensic samples that have the potential to cause the release of dispersible radioactive material.

Capturing a representative set of images for a complex matrix can be difficult, depending on the degree of sample heterogeneity. Laboratory personnel with significant SEM expertise can provide guidance, assisted by subject matter experts in specific types of nuclear or other radioactive material. Quantitative image analysis is a complicated task and benefits from careful integration of sample preparation, imaging and image processing methods, particularly for powdered or particulate samples.

II-7. RAMAN SPECTROSCOPY

II-7.1. Introduction and instrumentation considerations

Raman spectroscopy is a spatially resolved NDA technique that can be used to determine the chemical composition of a sample. This technique induces low frequency vibrational transitions in molecules, resulting in the scattering of incident monochromatic light that reveals characteristic spectral patterns indicative of the crystalline phase or phases present in a sample. A typical Raman spectrometer consists of a monochromatic light source, a notch filter and a detection system, along with system-dependent optics including lenses and mirrors. Most systems make use of a range of laser wavelengths, including visible and infrared wavelengths to assist in the elimination of interferences caused by sample fluorescence. Use of the notch filter is useful for minimizing the Rayleigh scattering peak, which can overwhelm the desired Raman scattering peaks. Interpretation of spectra generated using this technique is generally performed through comparison against a database of the spectra of known molecular forms.

II-7.2. Use in nuclear forensic examinations

Raman spectroscopy is often used in nuclear forensics for identifying and determining the abundance of crystalline solids. In particular, this technique is useful for the determination of crystalline phases for uranium and plutonium oxide materials, such as UO_2, UO_3, U_3O_8, PuO_2 and others. This technique is generally not suitable for the analysis of metallic samples and metal alloys. Most Raman spectrometers benefit from the use of spectral databases for data interpretation. Although these databases contain a wide variety of spectra of known crystalline materials, because nuclear forensic samples may be of unusual composition, it is possible that the crystalline forms of some samples might not be present in commercially available databases.

II-8. X RAY DIFFRACTION SPECTROSCOPY

II-8.1. Introduction and instrumentation considerations

X ray diffraction spectroscopy (XRD) is an NDA technique used to determine the mineralogical or molecular composition of crystalline and semi-crystalline materials. XRD instruments make use of a monochromatic X ray beam and X ray detector to produce a diffraction pattern over a range of diffraction angles. The diffraction pattern produced for each sample is a function of the characteristic d-spacings of the crystal lattices of the crystalline phases present. XRD can provide information on the composition, concentration, and purity of single- or multi-component crystalline materials. Typically, samples are analysed as fine-grained, loose powders mounted to produce a flat surface, although other preparations are possible, depending on the specific application of the technique.

II-8.2. Use in nuclear forensic examinations

XRD is widely used in nuclear forensics to determine the molecular composition of nuclear or other radioactive material, in particular uranium- and plutonium-rich materials such as UO_2, U_3O_8, metallic U, PuO_2 and other materials. XRD is particularly useful for determination of a range of crystalline compositions that may occur in uranium ore and uranium ore concentrate materials. Most XRD instruments include access to spectral databases when an instrument is procured; these databases contain various spectra of known crystalline materials. However, because nuclear forensic samples may be of unusual composition, it is possible that the crystalline forms of some samples might not be present in commercially available databases.

II-9. X RAY FLUORESCENCE SPECTROSCOPY

II-9.1. Introduction and instrumentation considerations

X ray fluorescence spectroscopy (XRF) is an analytical technique used to measure the elemental composition of solid and liquid materials. XRF instruments make use of a primary, monochromatic X ray beam to induce fluorescence in samples. The phenomenon of fluorescence results in the production of secondary X rays, which are characteristic of the elemental composition of the sample. Secondary X rays are measured by one or several detectors, depending on the instrument type. In energy dispersive spectrometry, a single detector is used to both discriminate and quantify the incident secondary X rays. In wavelength-dispersive spectrometry, a series of crystals are used to diffract the X rays of specific wavelengths, based on the known wavelengths of X rays produced by specific elements and the known d-spacings of analyser crystals built into the instrument. In either case, incident X ray intensities can be converted to elemental concentrations through semi-quantitative or quantitative conversion, using the fundamental parameters of X ray generation or through calibration with standard reference materials, respectively. XRF instruments can measure the concentration of most elements with analytical times of tens of minutes. Analyses can be performed non-destructively, provided the sample can fit into the sample chamber of the instrument, with a flat side available for analysis. While in principle XRF is an NDA technique, some applications of this technique benefit from sample preparation. Samples can be altered to optimize analysis as pressed pellets, glass beads or glass discs. Powder samples can also be measured by XRF if contained within a sample cup and supported by a membrane permeable to X rays.

II-9.2. Use in nuclear forensic examinations

XRF is a valuable technique for performing elemental composition analyses non-destructively and is often among the first elemental measurement techniques used in a typical nuclear forensic examination. XRF is particularly useful for a wide range of nuclear material and non-nuclear materials, such as metals, oxides, geological materials and other types of sample. Due to the non-destructive nature of XRF, samples can be initially measured using a semi-quantitative analytical programme, identifying the major and minor elements present in the sample. If needed, additional quantitative measurements can be performed using XRF after additional sample preparation or using other analytical techniques, such as mass spectrometry.

II-9.3. Additional considerations

XRF instruments are less expensive, more user-friendly and more versatile than other elemental concentration analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS). Modern X ray tubes have a lifespan of five or more years if maintained properly. Most XRF instruments can be operated by a technician with basic laboratory experience and training, although analyses of non-standard matrices may necessitate a higher level of expertise. XRF detection limits are in the order of 1−100 parts per million for most elements, limiting the utility of this technique for the analysis of trace constituents present in abundances below the detection limit. Elements lighter than sodium are difficult to analyse with most XRF instruments. Calibration standards do not exist for many sample matrices of interest. Interferences can be difficult or impossible to resolve in some cases (e.g. uranium spectral interference on molybdenum and zirconium). XRF data are usually less precise and sometimes less accurate than ICP-MS results. However, XRF is useful for measuring analytes that are difficult to analyse by ICP-MS, including chlorine, bromine, sulphur and phosphorous. Many samples can be analysed by XRF with little to no sample preparation. For more precise and accurate data, the analysis of a flat and polished face (solid samples) or fine powder is optimal. In cases where sample mass is limited, sample thickness may be a concern. In most cases, quantification of sample composition is performed under the assumption that X rays are generated from a sample that is 'infinitely' thick. In cases where only a thin layer of sample can be used (0.1−0.01 µm), quantitative calculations will systematically underestimate heavy element concentrations. For analysis of thin samples, calibration curves can be determined through measurement of standard reference materials of similar matrices.

II-10. FOURIER TRANSFORM INFRARED SPECTROSCOPY

II-10.1. Introduction and instrumentation considerations

Fourier transform infrared spectroscopy (FTIR) is a spatially resolved technique for the determination of chemical composition. The technique involves the use of infrared light absorbance or emission to produce spectra which result from transitions in vibrational states in molecules present in the sample. Vibrational states are unique to specific functional groups or bonds within molecules, and can serve as a means of identifying unknown compounds and distinguishing between compounds having similar compositions. FTIR allows for rapid analysis of solids, liquids and gases at high spectral resolution (2 cm^{-1}).

In most FTIR instruments, a broadband infrared light source interacts with a sample (e.g. transmission or reflection), and light from the sample is directed to a Michelson interferometer. The Michelson interferometer consists primarily of a beam splitter, two mirrors and a photodetector. Incident light is partially reflected by the beam splitter towards one mirror and partially transmitted through the beam splitter to another mirror. The mirrors reflect the light back at the beam splitter, which recombines the light and partially directs it towards the photodetector. While one of the mirrors is fixed, the other mirror is designed to move over a set distance in such a way that, when the light recombines, it constructively and destructively interferes, resulting in varying intensity at the photodetector as a function of mirror position. This intensity pattern is processed by a fast Fourier transform, which converts it into an intensity spectrum as a function of wavelength. The vibrational modes of a molecule may interact with the incident broadband infrared light source if it experiences a change in dipole moment as it vibrates. Because of this, molecular oxygen and molecular nitrogen do not interact with the incident infrared radiation. Infrared frequencies that match the resonant vibrational frequency of molecular bonds may be absorbed and are thus absent (or suppressed) from the light that is directed into the Michelson interferometer. In infrared absorption spectroscopy, the absorbed frequencies appear at lower intensity in the wavelength spectrum. This resultant spectrum can be used to identify specific bonds and functional groups based on these observed vibrational modes.

II-10.2. Use in nuclear forensic examinations

FTIR is complementary to Raman spectroscopy in the types of vibrational mode that are observable by each technique. Specifically, for a molecule to be 'infrared-active', there needs to be a change in dipole moment, rather than a change in polarizability as necessitated by Raman spectroscopy. A multitude of infrared spectral libraries exist for common compounds, although a database specifically for nuclear forensics has not been developed. FTIR has been used as a means for identification and classification of uranium ore concentrates. Desktop and portable FTIR instruments are commercially available, depending on the application.

II-11. GROSS RADIATION COUNTING TECHNIQUES

II-11.1. Introduction and instrumentation considerations

Initial radiation surveys and radionuclide characterization in the laboratory can be performed using dose meters and contamination meters to determine the magnitude and location of the radiation field and/or the extent of the radioactive contamination. Ionizing radiation can be detected using Geiger-Müller instruments, ion chambers and gas proportional counters which, by interacting with electromagnetic radiation or charged particles, produce electrical signals that are converted to dose rate. Alternate methods for detection of alpha, beta and gamma radiation can also be performed through a variety of solid media, such as with silicon- and germanium-based detectors, cadmium telluride detectors or through scintillation in a solid-state detector such as sodium iodide and cadmium telluride. Liquid scintillation techniques can also be used for the measurement of some specific types of radionuclide, such as ^{3}He or ^{14}C. Neutron detection is typically performed using neutron absorbing materials, as neutrons do not directly produce ionizing radiation when interacting with matter. Neutron detectors typically make use of detector materials with high probabilities for low energy neutron absorption. Common commercially available portable units include gas proportional detectors filled with ^{3}He and boron-based media in solid or gas form.

II-11.2. Use in nuclear forensic examinations

Measurements of dose rate and contamination levels are often performed in the field. Data from in-field measurements can be useful in the development of a nuclear forensic analytical plan. Once materials are received at the laboratory, measurements are often repeated for verification of the initial readings and integrity of package during transport. Radiation detectors are a critical part of safety procedures in a nuclear forensic laboratory, as they are used for monitoring the workspace and samples for contamination. These types of instrument provide an important service for understanding the presence of and potential risk posed by radiation. In addition, some types of handheld radiation equipment can perform preliminary identification of key radionuclides.

II-11.3. Additional considerations

Radiation detection equipment is typically calibrated using radioactive sources of known radiological properties to confirm measurement accuracy under normal operating conditions. In most cases, radiation detection measurements start with a measurement of background radiation levels. Most radiation detection instruments are sensitive to the ambient radiation background, local temperature, moisture and other environmental properties. When working in contaminated areas or locations with other radiation sources or background, laboratory personnel typically aim to shield their detectors and avoid instrument contamination. Some detectors are optimized for low level and/or low energy radiation and can become saturated in areas of high radiation. Nuclear forensic samples containing multiple radionuclides can create signals too complex to be correctly identified by portable detectors. Preliminary identification in the field is useful as a guide but can be confirmed through more robust means in a controlled laboratory environment.

II-12. GAMMA SPECTROMETRY

II-12.1. Introduction and instrumentation considerations

Gamma spectrometry is an NDA technique used to identify and quantify radionuclides which emit gamma radiation. This technique can be applied to a wide range of nuclear or other radioactive material or to evidence contaminated with gamma emitting radionuclides. Nuclear forensic samples can usually be analysed as received, without sample preparation. For more quantitative measurements, comparison to a standard reference material similar to the investigated item is necessary.

For nuclear forensic characterization measurements, high resolution gamma spectrometry systems are often used. This type of system consists of a high purity germanium detector, cooled either by liquid nitrogen or by an electrical cooling system with electronic units, and a computer for displaying, saving and analysing gamma spectra. Low-background shielding made from lead, or another dense metallic material, is often used in order to isolate the detector from natural background radiation and interferences from other radioactive material. Coaxial high purity germanium detectors of a relative efficiency around 30% with beryllium or carbon windows are considered to be broadly applicable to most nuclear forensic applications. In order to maximize the amount of information obtained by gamma spectrometry, nuclear data libraries and software packages that can aid in activity and isotopic ratio determination might be needed. Additionally, a coaxial high purity germanium system can be complemented with a planar high purity germanium system, which can enable the measurements of radionuclides emitting low energy gamma rays (e.g. ^{125}I) with higher accuracy and precision. When measurements from coaxial and planar detectors are used together, the resolution and efficiency advantages may provide additional information about a sample.

II-12.2. Use in nuclear forensic examinations

Gamma spectrometry can be applied during both the categorization and characterization phases of the examination. During the categorization phase of nuclear forensic examination, gamma spectrometry can be used to achieve an initial identification of the radionuclides present in the sample. Gamma spectrometry measurements can then be performed in the laboratory using higher resolution instruments for longer count times. Further characterization measurements using gamma spectrometry can provide data on: (i) the isotopic composition of uranium or plutonium; (ii) the time elapsed since last chemical separation (the model age) of uranium or plutonium, which can help to narrow the possible origins of potential manufacturing facilities; (iii) nuclear forensic signatures of uranium reprocessing, which might link the sample to facilities handling reprocessed uranium; (iv) presence of cross contamination with other radionuclides, which can provide additional information on the production facility; and (v) quantitative determination of the total amount of uranium or plutonium.

II-12.3. Additional considerations

Gamma spectrometry measurements can be performed with little or no sample preparation prior to analysis. Gamma spectrometry is more cost effective than many destructive analysis techniques, and data can be generated in a matter of minutes to hours, although samples with low levels of activity can necessitate longer timescales of analysis. Measurement accuracy and precision can often be improved by using standard reference materials for efficiency and energy calibrations. However, the precision of gamma spectrometry is often lower than that of destructive analysis techniques. Relative uncertainties of at least a few percent are typical for absolute activity measurements and may be as low as 0.1−1% for isotope ratio measurements. Detection limits may vary by many orders of magnitude, depending on radionuclide, and may also depend on sample composition. Some radionuclides decay with very low gamma emission probabilities, resulting in large uncertainties. Some radionuclides do not emit gamma radiation, and therefore cannot be analysed using this technique. ^{236}U, ^{242}Pu or ^{90}Sr and ^{90}Y are examples of isotopes that may be encountered in nuclear forensic examinations of nuclear or other radioactive material that cannot be quantified by gamma spectrometry.

II-13. ALPHA SPECTROMETRY

II-13.1. Introduction and instrumentation considerations

Alpha spectrometry is a destructive analysis technique that can be used to measure the activity of radionuclides that decay via alpha emission. Alpha spectrometry involves dissolution and chemical separation prior to analysis. Purified alpha emitting radionuclides in solution can be deposited as thin films on filters prior to analysis. Alternatively, purified solutions can be electroplated prior to analysis. Samples are analysed by counting the number of alpha particles detected in a sample chamber, resulting in the production of alpha spectra that display peaks corresponding to the characteristic energies of the measured alpha particles. Measured alpha peaks can be integrated, and their activity ratios can be calculated, which can then be converted to atomic ratios.

The type of detector used to quantify alpha emitting nuclides is usually a surface-barrier silicon detector in which alpha particles are deposited in the active volume of the detector. As alpha particles readily interact with matter, including air, the sample chamber is typically held under vacuum conditions. A slight positive pressure (~100 mtorr) is usually maintained to reduce detector contamination from recoiling daughter nuclides. Other detector types include Frisch grid detection systems (a type of gas-proportional counter) and liquid scintillation counters optimized for alpha measurements. These systems may be used as screening tools but typically do not provide the low detection limit and energy resolution needed for nuclear forensics.

II-13.2. Use in nuclear forensic examinations

Alpha spectrometry is the preferred technique for quantifying the abundance of alpha emitting radionuclides with half-lives less than a few hundred years (e.g. ^{210}Po, ^{232}U, ^{238}Pu and some isotopes of Am and Cm). Alpha spectrometry can also be used to determine the activity of longer lived actinides (e.g. ^{235}U) as a more cost effective and sustainable technique relative to mass spectrometry, and these data can be used to calculate isotope ratios. Parent and daughter nuclides (e.g. ^{234}U-^{230}Th) may be quantified to determine radiochronometry age.

II-13.3. Additional considerations

Chemical separation and purification techniques are necessary for alpha spectrometry sample preparation. The methods used to isolate the element of interest are similar to those used to prepare samples for thermal ionization mass spectrometry (TIMS) or ICP-MS. Traditional alpha spectrometry is not able to resolve alpha energy peaks with less than ~50 keV difference such as ^{239}Pu and ^{240}Pu. In some cases, a combination of alpha spectrometry and mass spectrometry can be used to obtain the isotopic composition of Pu and U samples. Increased measurement precision may be obtained using detectors free from contamination and using longer counting times.

II-14. MODIFIED DAVIES-GRAY TITRATION TECHNIQUE FOR URANIUM CONCENTRATION

II-14.1. Introduction and instrumentation considerations

The modified Davies-Gray technique is an electrochemical titration technique for determining the concentration of uranium in solution. Particularly useful for samples with high uranium content, this technique is often used to determine the uranium concentration of dissolved solid uranium metals, alloys, oxides and other materials. Although individual modified Davies-Gray analyses can be performed manually, this technique is greatly aided by using commercially available auto-titration systems, which can be configured for the specific reagents needed. As a destructive analysis technique, the modified Davies-Gray technique is best performed after the complete dissolution of a sample aliquot sufficient to deliver 25–75 mg uranium to the solution (unless the sample is already a liquid). The analyst typically prepares a set of chemical reagents at the requisite concentrations, including the titrant $K_2Cr_2O_7$. The iron and vanadium-bearing reagents are usually prepared on the day of analysis due to their sensitivity to redox reactions.

II-14.2. Use in nuclear forensic examinations

In nuclear forensics, the modified Davies-Gray technique is often used to determine the concentration of uranium in uranium-rich materials, particularly uranium ore and uranium ore concentrate materials. The modified Davies-Gray technique can also be used for uranium fuel pellets and other materials in the fuel cycle containing tens of mg of uranium or more. Relative to other elemental concentration measurement techniques, the modified Davies-Gray technique is a cost effective option, and relative uncertainty of uranium concentration data using this technique can be less than 1%. Ideally, samples are analysed in triplicate to determine measurement uncertainty and to account for the possibility of a failed titration, which can occur for a number of reasons (e.g. stuck stirring bar, overshooting of the potentiometric end point). As the titrant $K_2Cr_2O_7$, contains hexavalent chromium, it is toxic and should be handled using the proper personal protective equipment.

II-15. INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

II-15.1. Introduction and instrumentation considerations

ICP-MS is a highly sensitive and versatile technique used to measure the elemental and isotopic composition of materials dissolved in solution. Samples are typically introduced to the instrument in solutions produced from the dissolution of solid samples. Key attributes of ICP-MS include: (i) the ability to analyse most metallic and semi-metallic elements; (ii) detection limits as good as 1–10 parts per trillion for some elements; (iii) the ability to measure tens of samples within a multi-hour analytical routine; (iv) a wide dynamic concentration range for different analytes when measuring multiple analytes in a single routine (approximately 9 orders of magnitude).

In ICP-MS, samples are ionized in an argon plasma, isotopes of elements are separated based on mass-to-charge ratio using a mass analyser (either a quadrupole or magnetic sector), and relative abundances of isotopes are quantified using Faraday detectors or other types of detector. Fully quantitative element concentrations can be obtained by determining detector response for each analyte in a sample relative to the response generated using reference solutions with certified elemental concentrations. Instrumental background and blank measurement intensities should also be accounted for. The final accuracy and precision of the technique can be calculated based on the analysis of standard reference materials analysed in the same routine as samples. The relative uncertainty of elemental concentration measurements by quadrupole ICP-MS can often be better than 5% relative uncertainty for each element. Isotope ratios can be measured with relative uncertainty better than 1% in many cases, depending on the type of ICP-MS used.

II-15.2. Use in nuclear forensic examinations

Quadrupole ICP-MS is useful for determining the concentration of virtually all metallic elements in a sample. ICP-MS instruments can also be used to measure isotopic composition of some key elements in nuclear forensic samples, such as uranium and plutonium. The triple-quadrupole ICP-MS can be used to provide useful isotope ratios with precision better than 0.1%, while sector field ICP-MS (equipped with single or multi collector) can provide precision lower than 0.01%. By measuring parent-daughter nuclide ratios, determination of sample age can be accomplished via ICP-MS measurements using radiochronometry.

II-15.3. Additional considerations

Quadrupole ICP-MS instrument manufacturers offer benchtop platforms and are less expensive than other types of mass spectrometer. Many models offer useful features such as collision or reaction cells, and some offer multiple quadrupole systems in order to reduce interferences during the measurement. There are several commercial vendors that produce sector field ICP-MS, with similar basic designs and performance. The detector configurations for these types of instrument are customizable at the time of purchase depending on the specific application the instrument will be used for. For example, the addition of multiple ion counters and abundance sensitivity filters can increase the precision of actinide isotopic analyses. Changes to the sample introduction system can result in significant performance enhancements. In particular, the use of high sensitivity sample and skimmer cones together with a desolvating nebulizer can result in an order of magnitude increased sensitivity. In many laboratories, for precise isotopic analysis, the use of desolvating nebulizers is now the most common operating configuration.

ICP-MS (quadrupole or sector field) offers a large flexibility in analysing a wide range of samples, with low detection limits (parts per billion or better) and high precision. The ease of use and versatility of the quadrupole ICP-MS is in part why it has gained popularity in the nuclear forensic analytical community. However, while quadrupole ICP-MS is a relatively inexpensive instrument applied to elemental and isotopic analysis, the more expensive sector field ICP-MS (equipped with single or multi-collector) or TIMS can generate higher precision isotope ratio data. Sector field instruments, especially multi-collector ICP-MS instruments, necessitate higher operational skills, higher maintenance, and higher operational and service costs.

Interferences from high concentrations of polyatomic compounds that may be present in the sample matrix, especially heavy elements, can reduce overall sensitivity and can result in inaccurate measurements. Interferences can be challenging to deal with, even for experienced operators. In addition, contamination of the sample introduction system can cause memory effects, increasing instrumental background. Advances in instrument design, including the introduction of collision and reaction cells in quadrupole ICP-MS, high resolution of sector instruments to manage interferences and aerosol dilution to handle heavy matrices, have enabled analysts to overcome some of these challenges.

Samples are primarily introduced to ICP-MS as solutions, although solid samples can also be analysed in-situ by coupling a laser ablation system to a mass spectrometer. Due to the sensitivity of the technique, sample consumption is small, and a typical sample analysis may consume less than a milligram of mass. To obtain higher quality isotopic data, sample solutions are usually purified before analysis to remove other elements (i.e. all elements other than the element of interest), including potential interfering species. This is usually achieved by ion exchange chromatography, using separation procedures tailored to the element of interest. Dissolved samples are usually introduced to the plasma in clean and dilute mineral acid solutions, such as 2% HNO_3.

II-16. INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

II-16.1. Introduction and instrumentation considerations

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a destructive analysis technique used to determine elemental concentration using characteristic visible light electromagnetic radiation generated during sample ionization in a plasma source. As sample atoms cool following excitation from a plasma, thermally excited electrons emit photons with wavelengths characteristic of elemental composition, which are then detected. Although ICP-AES can measure the concentration of many elements, spectral interferences do occur and can impact the accuracy and precision of measurements of certain elements. However, ICP-AES instruments are robust in dealing with samples dissolved in atypical matrices and containing higher levels of dissolved solids. Therefore, ICP-AES is useful for analysing many kinds of dissolved materials.

II-16.2. Use in nuclear forensic examinations

In nuclear forensics, ICP-AES is a relatively cost effective method for measuring the elemental concentration of many elements without the need for chemical separation. As a destructive analysis technique, ICP-AES requires solid samples to be dissolved prior to analysis, necessitating accurate and precise measurement of aliquot mass prior to analysis. ICP-AES detection limits are in the parts per million range for many elements, and therefore may be unsuitable for some trace elements in nuclear forensic samples. As with any technique involving sample digestion, ICP-AES produces liquid radioactive waste that has to be handled safely and securely. Furthermore, the analysis of radioactive material has the potential to contaminate the instrument itself. Many laboratories make use of a sample introduction system used only for nuclear forensic samples when performing a nuclear forensic examination. Although some laboratories may prefer to use the more versatile ICP-MS technique, ICP-AES remains suitable for many nuclear forensic applications.

II-17. THERMAL IONIZATION MASS SPECTROMETRY

II-17.1. Introduction and instrumentation considerations

TIMS is a destructive analysis technique used to measure the isotopic composition of materials with high precision. For some applications, TIMS is considered the 'gold standard' for isotope ratio measurement, capable of producing $^{235}U/^{238}U$ measurements of better than 0.05%. Samples for TIMS are typically first dissolved, then purified using chemical separation techniques. After purification, samples are then carefully loaded onto filaments composed of rhenium, tantalum or tungsten. Filaments are loaded into an evacuated sample chamber and subjected to a current, which heats, evaporates and ionizes the sample. The ion beam is than accelerated using ion lenses into a magnetic sector, where the beam is separated based on mass-to-charge ratio. Most modern TIMS instruments are multi-collector instruments, enabling simultaneous detection of each isotope for high precision measurements.

II-17.2. Use in nuclear forensic examinations

While most nuclear forensic applications do not need the level of measurement precision offered by TIMS, this technique can be used to determine the isotopic composition of uranium and plutonium in nuclear forensic samples. In addition, TIMS is capable of precise measurements of other isotopic systems, including lead, neodymium, strontium and others. These measurements are most ideally suited to linking uranium ore or uranium ore concentrate materials to a geological origin, or to the precise determination of specific fission and activation products in irradiated nuclear fuel cycle materials.

II-18. SECONDARY ION MASS SPECTROMETRY

II-18.1. Introduction and instrumentation considerations

Secondary ion mass spectrometry (SIMS) is a spatially resolved analytical technique used for determining the isotopic composition of materials with high precision. Using SIMS, it is possible in some cases to determine the isotopic composition of some elements on a spatial scale of 1×10^{-6} m. Although nominally non-destructive, most samples need some degree of sample preparation prior to analysis, and the analysis itself results in the removal of nano- to micrometre-scale layers from the sample. Most SIMS instruments make use of a primary beam composed of either oxygen or caesium, which is focused on the flat surface of a sample. Atoms of the sample are then sputtered from the surface, ionized, accelerated through a sector field mass analyser and detected using an array of detectors. The SIMS technique is expensive and often makes use of technical personnel with extensive experience in the technique for operation.

II-18.2. Use in nuclear forensic examinations

Although widely used in nuclear safeguards applications, SIMS also has applications in nuclear forensics. SIMS has been used to determine spatial variations in uranium isotopic composition in uranium fuel pellets and other nuclear fuel cycle materials and is particularly useful for revealing microscale heterogeneity in samples. Furthermore, SIMS can be used to analyse the isotopic composition of uranium particles on the scale of 1×10^{-6} m, which are typically too small to analyse individually using bulk analytical techniques, such as inductively coupled plasma mass spectrometry.

II-19. STABLE ISOTOPE RATIO MASS SPECTROMETRY USING GAS SOURCE INSTRUMENTS

II-19.1. Introduction and instrumentation considerations

Stable isotope ratio mass spectrometry is a destructive analysis technique used to measure the isotopic composition of light stable isotopic systems, such as hydrogen, nitrogen, oxygen, carbon and sulphur. The stable isotope ratio mass spectrometer typically consists of a sample introduction system (with the sample often introduced as a gas after purification), a mass analyser and a detector or set of detectors. Many stable isotope ratio mass spectrometer systems use a dual inlet configuration. The dual inlet stable isotope ratio mass spectrometer employs two variable volume bellows. One bellows holds a reference gas, and the other bellows holds the sample gas. The bellows are adjusted so that the pressure is equal, and a switching valve is used to alternate between the reference and sample gases to obtain multiple measurements of the isotopic ratios. The dual inlet system allows for high precision measurements but involves off-line preparation of a pure gas from the original sample of interest. Typically, this preparation involves vacuum line chemistry and purification processes.

Continuous flow stable isotope ratio mass spectrometry has lower sample size demands and increases sample throughput using automated sample preparation peripherals. Continuous flow stable isotope ratio mass spectrometer uses a continuous gas stream, usually helium, to carry the sample gas into the stable isotope ratio mass spectrometer inlet. Compared with dual inlet stable isotope ratio mass spectrometer systems, continuous flow systems are typically less precise. However, continuous flow stable isotope ratio mass spectrometer provides a significant advantage by allowing for sample gas preparation to be performed online through interfacing with additional peripheral instruments. Gases in a mixture may be separated and purified by gas chromatography columns prior to introduction at the stable isotope ratio mass spectrometer inlet. Solids and liquids can be combusted or pyrolyzed to make a gas using an automated peripheral instrument, which significantly reduces sample preparation time. This has led to approaches combining stable isotope ratio mass spectrometer with peripherals such as elemental analysers, gas chromatography followed by combustion and liquid chromatography.

II-19.2. Use in nuclear forensic examinations

In nuclear forensics, stable isotope ratio mass spectrometer can be used to analyse the isotopic composition of light stable isotopes in samples. Nuclear material can have light element components, including crystalline materials like UO_2, U_3O_8, $(NH_4)_2U_2O_7$, $U(SiO_4)_{1-x}(OH)_{4x}$ and UTi_2O_6, as well as glasses and other non-crystalline materials. Some laboratories are conducting ongoing research into the measurement and interpretation of light stable isotope nuclear forensic signatures, and interpretation of these nuclear forensic signatures may be complex.

ABBREVIATIONS

FTIR	Fourier transform infrared spectroscopy
IAEA	International Atomic Energy Agency
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ISO/IEC	International Organization for Standardization / International Electrotechnical Commission
NDA	Non-destructive analysis
NSS	Nuclear Security Series
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
TIMS	Thermal ionization mass spectrometry
XRD	X ray diffraction
XRF	X ray fluorescence

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