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Nuclear forensics: strategies and analytical techniques

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ABSTRACT

The development of nuclear forensics as a field of science arose in response to international demand for methods to investigate the illicit trafficking of nuclear materials. After being seized, unknown nuclear material is collected and analyzed by a set of analytical methods. The fingerprints of these materials can be identified and further used during the investigations. Data interpretation is an extensive process aiming to validate the hypotheses made by the experts, and can help confirm the origin of seized nuclear materials at the end of the process or investigation.
This work presents the set of measures and analytical methods that have been inherited by nuclear forensics from several fields of science. The main characteristics of these methods are evaluated and the analytical techniques employed to determine the fingerprint of nuclear materials are described.

KEYWORDS: ***nuclear forensics, fingerprints, uranium, plutonium, analytical techniques, particle analysis***

Introduction

In the early 1990's the first instances of nuclear smuggling and illicit traffic of nuclear material were detected [1; 2] (Figure 1). Such incidents lead to the development of nuclear forensics science and new strategies to characterize and interpret seized nuclear materials in order to identify its source. Characterization includes the determination of the chemical and isotopic composition, physical condition, provenance and history of the material, whereas interpretation uses the characterization to reconstruct the history of the material [2; 3; 4]. Therefore, nuclear forensics is a critical element of the response to illicit nuclear trafficking.

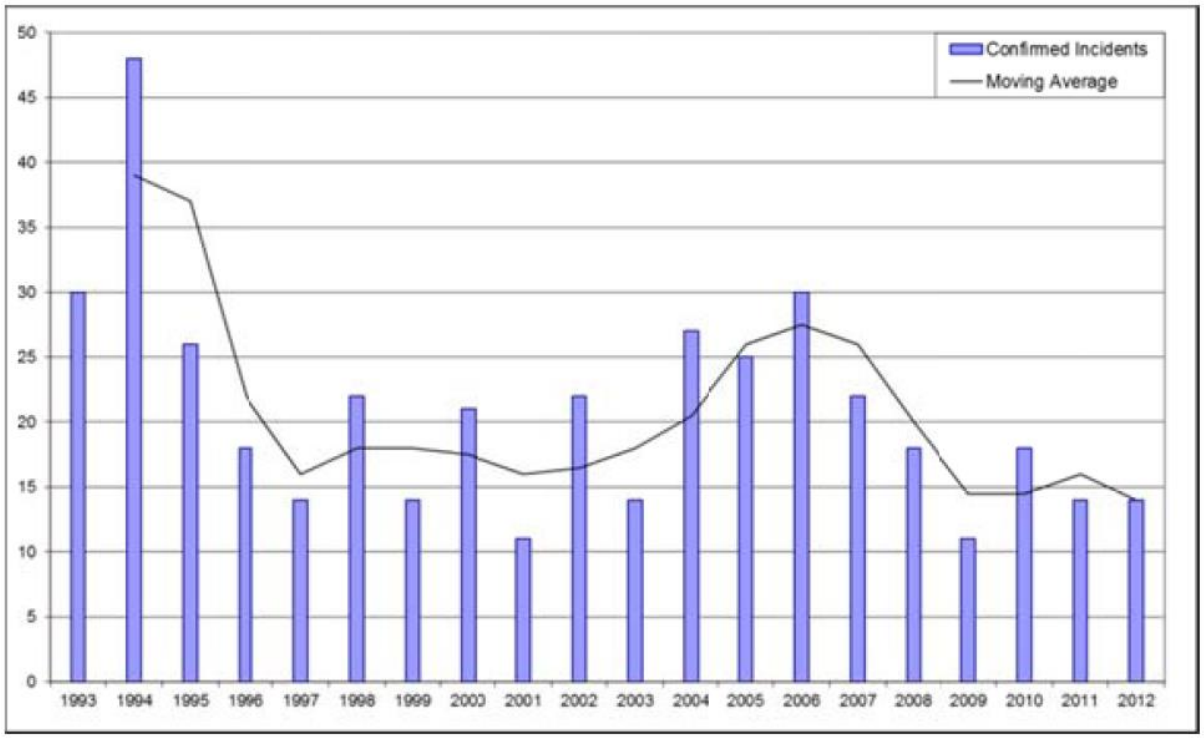


Figure 1 – confirmed incidents involving nuclear material from the Incident Trafficking Database (ITDB) [5].

Nuclear forensics seeks answers to several interrelated questions, such as: What is this material? Where was the control of nuclear material lost? Where was it produced? What laws were broken? [6] One of the main questions to be answered is the origin of the seized material. Basically, all nuclear or radioactive material contain some chemical, physical, radiological and isotopic characteristics which, together, allows to establish its identity (fingerprint) and, as consequence, its origin.

Fingerprinting process is a mean to answer these questions, and to provide the legal authorities with a consistent interpretation of the illicit act. More specifically, fingerprints are determined by certain qualities of the material, such as impurities, age, stable isotopes and microstructures. These qualities are incorporated during the industrial process whereby the material itself contains the indelible trace of its own origins. However, the determination of the fingerprints is only a small part of the overall process. A nuclear forensics investigation must evaluate the measurements and intelligence data together in order to guarantee the “four

C's" (3):

- Consistency of information
- Coherence between samples
- Conformity of findings with declared process
- Comparison of data

Owing to the interdisciplinary characteristics of nuclear forensics, professionals involved in nuclear forensics investigations must come from different specialities. They should be able to provide responses from characterization to full nuclear forensic interpretation. It also involves laboratories capable to handle, in safe, nuclear materials or radioactive material. These laboratories should carefully separate the traditional forensic evidence from the nuclear forensic evidence to be sent to the experts of each speciality following a defined protocol well known. The nuclear forensic laboratories should have analytical techniques capable to analyze nuclear and environmental materials at trace levels. Moreover, the cooperation between nuclear forensics laboratories enhances the interpretation of the acquired data [7].

The investigation of a nuclear forensic case begins with the interdiction of the crime scene by the law enforcement officer or another State force. The ongoing process continues with the collection of traditional forensic evidences, which includes photographic documentation, compass orientation together with GPS orientation, DNA, as well as the presence of biological and environmental evidences. The nuclear forensic process, indeed, begins with many incident scenarios to be analyzed and tested. This process is iterative (Figure 2). After the seized material has been sampled and categorized, the experts can build origin hypotheses and test them based on the results of the analysis [2; 7]. This is mainly done by comparing the main chemical, physical and nuclear characteristics of the samples, allowing experts to exclude or validate their hypotheses until a unique interpretation has been left, which culminates with the conclusion of the investigation.

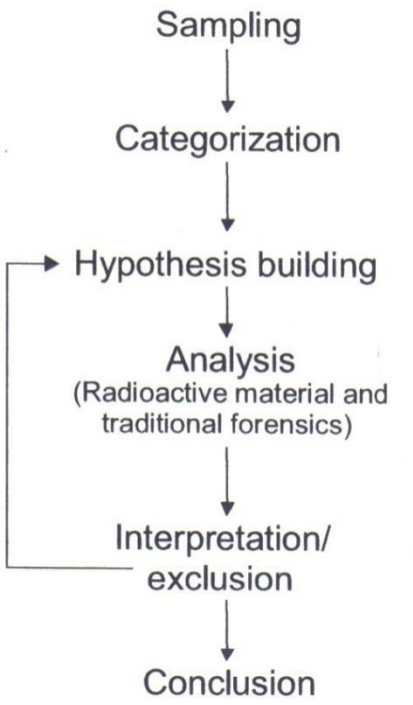


Figure 2 – Nuclear forensics fingerprinting process [7].

Analytical techniques

There is an extensive set of analytical techniques used in nuclear forensics investigations. The main techniques are TIMS, SIMS, inductively coupled plasma mass spectrometry (ICP-MS), multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS), sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), high resolution gamma spectrometry (HRGS), scanning electron microscopy/energy dispersive spectrometry (SEM/EDS), transmission electron microscopy (TEM) and recently laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser ablation multi collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). Table 1 summarizes the characteristics of the main analytical techniques used in nuclear forensics investigations:

Table 1- Analytical techniques used in nuclear forensics investigations [7].

Measurement goal	Technique	Type of Information	Typical detection limit	Spatial resolution
Survey	HRGS	Isotopic	ng–µg	
Elemental and isotopic	Chemical assay	Elemental	Mg	
	Radiochemistry/RA	Isotopic	fg-pg	
Bulk analysis	Counting methods	Elemental		
	TIMS	Isotopic	pg-ng	
	ICP-MS	Isotopic/ Elemental	pg-ng	
	MC-ICP-MS	Isotopic/ Elemental	fg/g - ng/g	
	XRD	Molecular	~5 at%	
	GC-MS	Molecular	µg/g	
	XRF	Elemental	10 µg/g	
	GD-MS	Isotopic/ Elemental	0.1 ng/g -10 µg/g	
	Infrared	Molecular	µg/g	
Microanalysis	TIMS	Isotopic	pg-ng	
	ICP-MS	Isotopic/ Elemental	pg-ng	
	MC-ICP-MS	Isotopic/ Elemental	fg/g - ng/g	
	SIMS	Isotopic/ Elemental	0.1 ng/g -10 µg/g	0.2 – 1 µm
	SEM/EDS or WDS	Elemental	0.1 – 2 at%	1 µm
	LA-ICP-MS	Isotopic/ Elemental	ng-µg	few µm
	LA-MC-ICP-MS	Isotopic/ Elemental	fg/g - ng/g	few µm
Imaging	Visual inspection	Macroscopic	0.1 mm	
	Optical microscopy	Microscopic		1 µm
	SEM	Structure		1.5 nm
	TEM	Crystallography		0.1 nm

HRGS is the most important radiometric screening technique and allows direct sample analysis, but it is limited to non-stable isotopes. As it measures the emitting gamma rays, a considerable time period is necessary for precise determination of minor isotopes [8].

Mass spectrometric techniques as TIMS, ICP-MS and MC-ICP-MS have been successfully employed to perform bulk analysis. TIMS is the technique of choice for the international atomic energy agency (IAEA) laboratories. In this technique, the sample is deposited on a metallic filament which is heated. If the ionization potential of the element is lower than the filament, a fraction of atoms is carried to the mass analyzer. TIMS measures isotopic ratios ranging from tens of fg to ng, and is capable to measure isotope ratios of the order of 10^{-6} [7]. Nevertheless, it requires laborious sample preparation procedures which include chemical separation of the analyte to be analysed. If this separation is imperfect the ionization can be poor, thus compromising the precision.

ICP-MS has the ability to perform faster analysis than TIMS, although it does not deliver the same level of precision. Its detection limits are in the order to pg/g. Nevertheless, the latest generation of MC-ICP-MS improved the capability to detect ultra-trace quantity of uranium and plutonium [9], due to its ability to detect more than one isotope simultaneously.

The combination of ICP-MS and MC-ICP-MS with laser ablation has been successfully employed for both bulk analysis of highly enriched uranium (HEU) [10] and for particle analysis [11; 12; 13]. This combination is robust and reliable for uranium and plutonium measurements. Its main advantage is the ability to analyze sub-micrometer single particles directly from the sample, without any time consuming preparation procedures. However, more development is necessary in order to achieve better precision.

SIMS is the main technique for uranium and plutonium particle analysis owing to its location and direct analysis capability. The secondary ions produced by SIMS are generated by a focused primary ion beam (O_2^+, Cs^+ or Ga^+) which sputters the sample. Another invaluable advantage is the depth profile, which allows the experts to measure the compositional gradient of the nuclear material seized [7]. TIMS has been also used to carry out particle analysis, however it is necessary to first locate the particle by SEM or fission track (FT) — which needs a neutron reactor [14]. After locating the particle the next step is to manipulate the particles and load them on a filament.

Imaging techniques provide invaluable information to determine process fingerprints. Optical microscopy provides the microscopic structure of the sample. SEM has greater magnification than optical microscopy and can magnify the image up to 10,000x with a tungsten filament or up to 500,000x with a field emission gun (FEG). Important information is generated by the backscattered electrons which carry information about the atomic number of the area being imaged and can be used to detect spatial phases. Secondary electrons are a good choice to determine the topology. Information also can be extracted from X rays to determine the spectrum of the sample by means of EDS. Using TEM, magnifications of several millions times higher than SEM [7] can be achieved, allowing the crystal phase in the material to be determined. However, the sample must be ultra-thin and this process is almost prohibitively expensive.

The set of analytical techniques and methods used by nuclear forensics experts were established through extensive discussions and consultations, and from two inter-laboratorial comparison programmes [3; 7], and are a consensus among the members of nuclear forensics community – achieved after long discussions and consultations. If the national nuclear forensics laboratory is not able to perform certain analyses, a sample of the material should be sent to another specialized nuclear forensics laboratory or to the IAEA. Table 2 presents the sequence for laboratory analysis suggested by IAEA in the case of a real incident of a seizure of nuclear or radiological materials:

Table 2- Sequence for laboratory analysis suggested by IAEA [7].

Techniques/methods	24 h	1 week	2 months
Radiological	Total activity		
	Dose rate (α, β, γ, n)		
	Surface contamination		
Physical	Visual inspection	SEM/EDS	TEM (EDS)
	Radiography	XRD	
	Photography		
	Weight		
	Dimensions		
	Optical microscopy		
	Density		
Traditional forensics	Fingerprinting, fibres		
Isotope analysis	γ spectroscopy	SIMS, TIMS, ICP-MS	Radiochemical separation
	α spectroscopy		
Elemental/chemical		ICP-MS	GC-MS
		XRF	
		Titration	
		IDMS	

Characteristics parameters

All data obtained sample analysis are important during a nuclear forensics investigation. However, some of them bring the most important information for the investigation procedure as a whole. The main characteristics parameters are presented below:

Age determination

The age of a nuclear material can be determined for unstable isotopes and is defined as the time that has passed since the last chemical or physical separation of the mother and daughter isotopes. Age is determined through radioactive decay by quantifying the parents and daughters nuclides, which is specific to each element [4]. For example, plutonium age determination is performed by gamma spectrometry (GS) using mainly the $^{241}Pu/^{241}Am$ ratio. In the case of uranium, $^{234}U/^{230}Th$ is the recommended ratio [3]. Figure 3 illustrates a decay chain used to determine the age of nuclear materials used in nuclear forensics investigations.

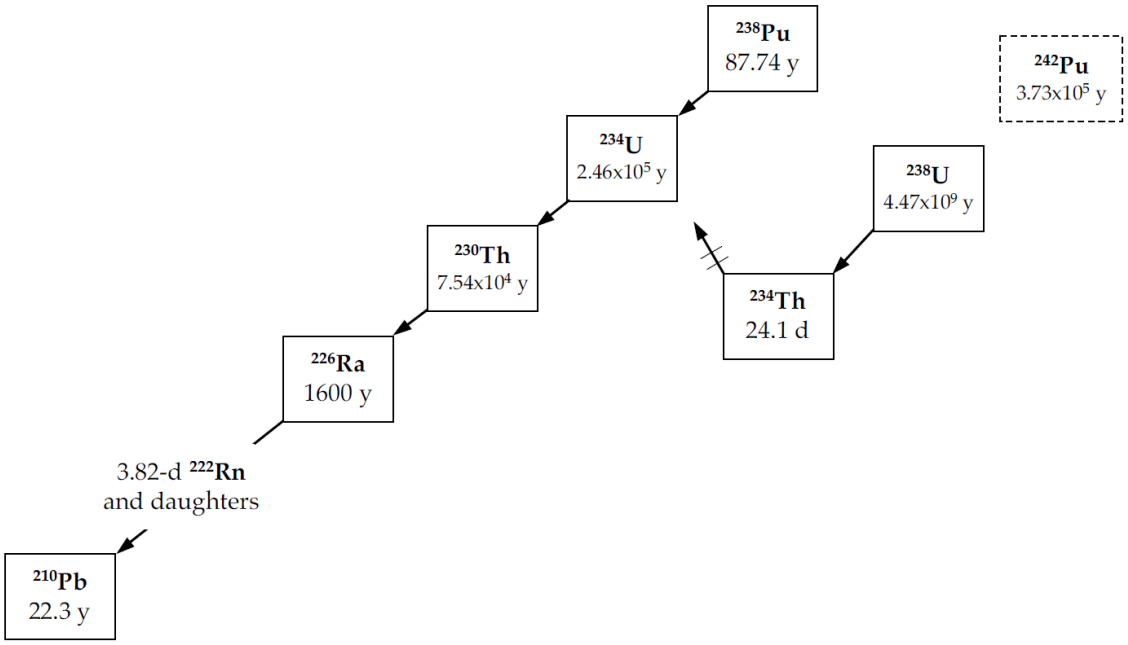


Figure 3- Radio-chronometer used in nuclear forensics investigations [4].

There are others isotope ratios used for such measurement as those shown in Table 3:

Table 3- Mother and daughter ratios for age determination of plutonium and uranium.

Plutonium	$^{236}Pu/^{232}U$
	$^{238}Pu/^{234}U$
	$^{239}Pu/^{235}U$
	$^{240}Pu/^{236}U$
	$^{241}Pu/^{241}Am$
	$^{242}Pu/^{238}U$
	$^{244}Pu/^{240}Pu$
Uranium	$^{234}U/^{230}Th$
	$^{235}U/^{231}Pa$

There are more than one chronometer to determine the age of both uranium and plutonium (Table 2). Figure 4 presents the time evolution of mother and daughter of plutonium decay:

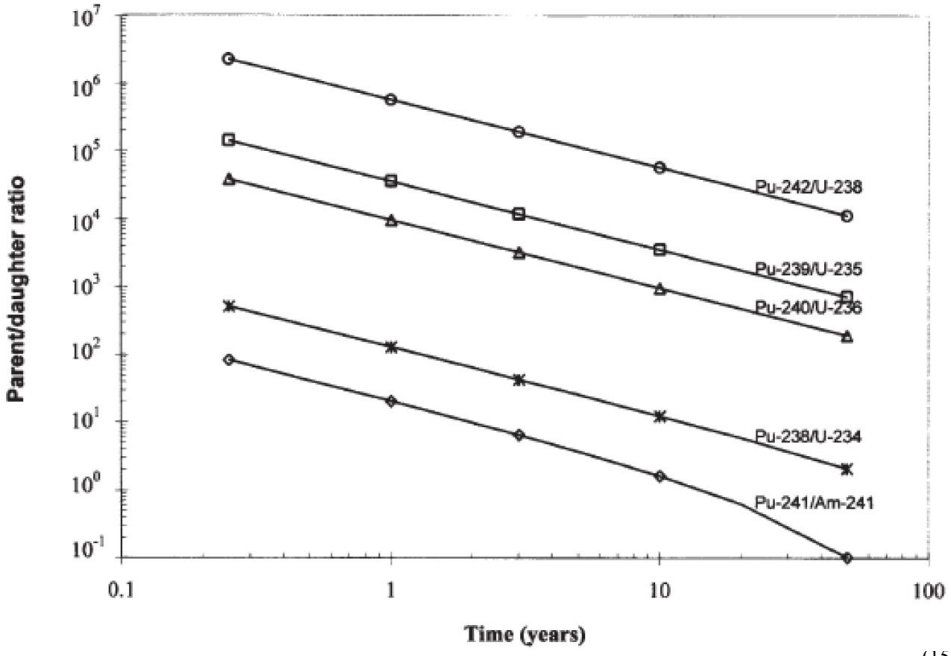


Figure 4- Mother and daughter evolution from plutonium material [15].

Considering a real life, it is recommended to perform at least two isotope ratios measurements in order to avoid incorrect inferences due to non-matching chronometers.

Metallic impurities

Metallic impurities are present from the start of nuclear processing, and they tend to decrease as the process nears completion. These impurities can also be added at different stages of the process. As the concentration of these elements varies randomly, the ratios between the elements can be measured rather than their absolute concentration. Nuclear forensics experts recommend choosing elements of similar chemical behaviour, such as the rare earth elements, because they vary within narrow limits [3]. Figure 5 shows the concentration of rare earth elements in fifteen different samples - note that the samples 1 to 5 are mutually compatible.

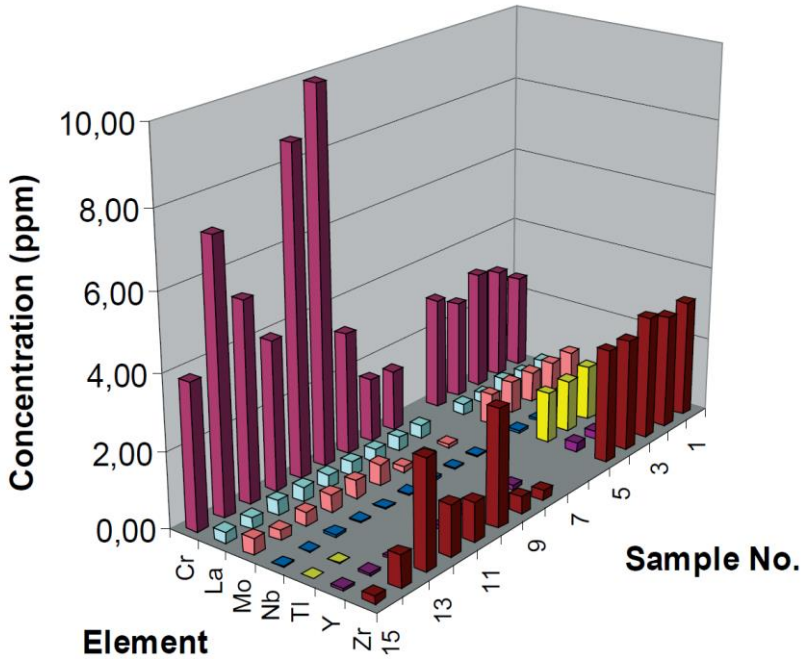


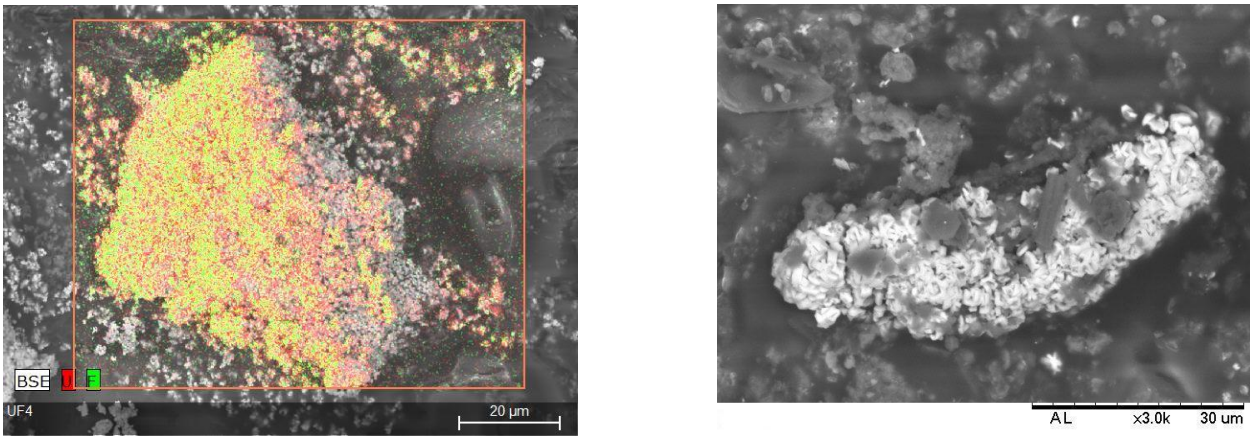
Figure 5- Rare earth elements present in fifteen different samples from an intermediate uranium product [3].

Anionic impurities

Anionic impurities such as Cl^-, F^-, SO_4^- and NO_3^- can be added to nuclear material during the nuclear fuel cycle process, depending on the type of ore and the chemical reagents used to extract the uranium. Different patterns are observed from samples that underwent distinct separation processes or which were separated in different locations. This represents additional information regarding the origin of the material, and some studies have demonstrated that these impurities can even separate uranium extracted from different mines [3].

Microstructure

Microstructure information about nuclear material (mainly uranium) reflects the manufacturing process to which the material has been exposed. However, this information is more qualitative than quantitative. Characteristics that can be revealed when analyzing the microstructure include: shape, surface and particle and grain size distribution. Figure 6(a) and 6(b) show two UF_4 particles. Figure 6(a) represents a micrography from a UF_4 standard, whereas the Figure 6(b) is a micrography of a particle found in a real life swipe sample collected in a uranium conversion facility.



(a) (b)

Figure 6- (a) UF_4 standard; (b) particle from real life swipe sample.

Isotopic composition

Since the establishment of the strengthened safeguards, minor abundant isotopes (^{234}U and ^{236}U) have become the subject of high interest because they indicate samples that have undergone the same enrichment process. $^{234}U/^{238}U$ can indicate origin or the enrichment process when analyzed with other parameters, such as $^{235}U/^{238}U$. The presence of ^{236}U is an indicator of reprocessed uranium: the sample could be contaminated with recycled uranium or may even have passed through a recycling process itself [3; 9; 12].

Another methodology adopted from reactor physics which has been used in safeguards since 1970's is the isotope correlation [3]. Its use is based on the fact that physical laws governing the nuclear fuel irradiation are immutable. The isotopic relationships are common characteristics of all spent fuels from a given type of reactor. Thus, based on a nuclear forensic library containing burnup data, as well as the isotopic inventory of known nuclear irradiated fuels, it is possible to establish several mathematical correlations and use them with the data obtained by the analysis of the seized sample [16; 17]. Moreover, using the isotope correlation allows experts to deduce the amount of a specific isotope indirectly [3].

A strong indicator of reactor type is the build up of plutonium, which is also dependent on the initial level of uranium enrichment. Figure 7 shows an isotope correlation between $^{242}Pu/^{240}Pu$ and ^{238}Pu/total Pu from several reactors. It clearly discriminates the reactors types, enabling experts to assign the samples to their respective reactors.

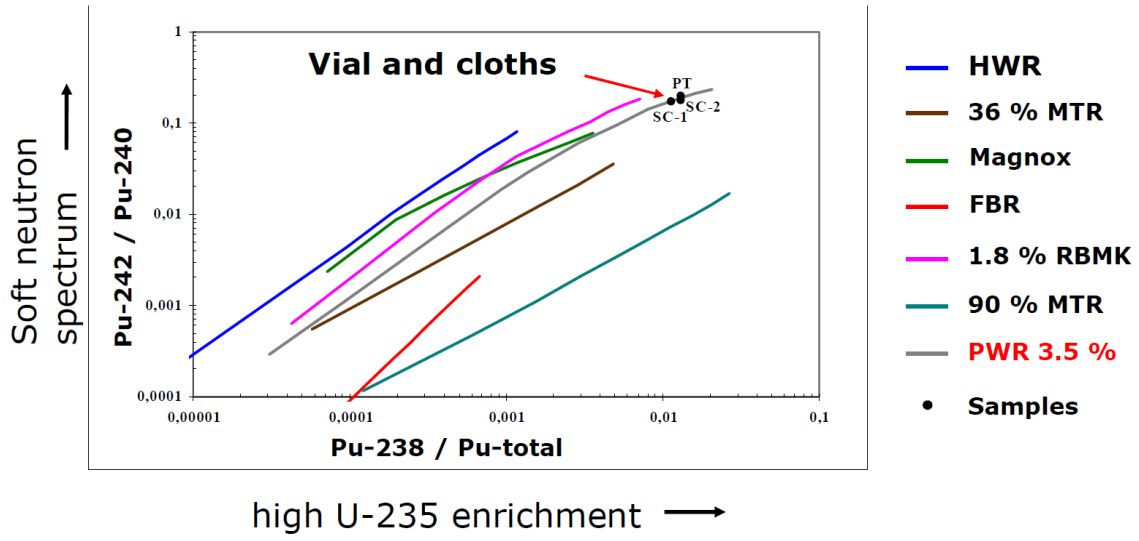


Figure 7- Pu isotope correlation for different types of reactors [18].

Stable isotopes

Another factor which provides information related to the history and origin of a nuclear material is the stable isotope composition, because materials of different origin have different stable isotope composition. For example, the variation in the $n(^{18}O)/n(^{16}O)$ ratio has been demonstrated [19] as an effective great tool for geolocation of facilities which handle uranium oxide [3]. Moreover, this ratio can be applied to individual particles using secondary ion mass spectrometry (SIMS), because it is compatible with bulk analysis performed by thermal ionization mass spectrometry (TIMS).

Nuclear forensics has also incorporated methods from geochemistry and environmental sciences, such as the stable isotope composition of lead. This parameter can indicate if the lead presence in the sample is from nuclear or natural decay. For instance, when analyzing the lead isotope composition of yellow cake one could distinguish between natural uranium materials from different origins [20]. However, this method demands special care in the sample preparation step in order not to introduce any natural lead. Figure 8 presents the lead isotope composition of yellow cake from different mines. It should be noted that the samples from Beverly have compatible lead isotope composition, whereas the samples from other mines are distinct.

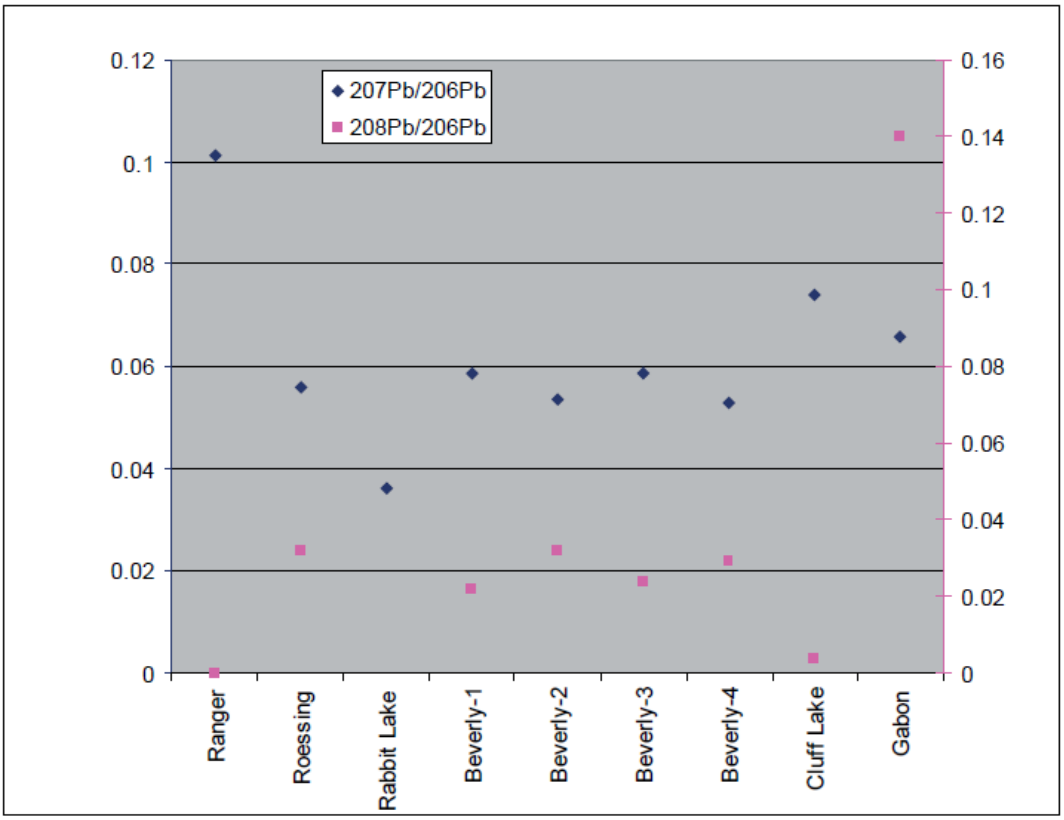


Figure 8- Lead isotope composition of yellow cake from different mines [13].

Conclusion

Nuclear fingerprinting is used in nuclear forensics by combining several analytical methods derived from multiple fields of science. It can help legal authorities to recreate the history and origin of seized nuclear materials and provides the legal basis for the attribution of the source of the nuclear material.

Owing to the iterative process of testing different hypotheses by means of comparisons between certain patterns, it is important to develop and establish an international database of the several characteristics of nuclear materials. This will allow experts to attribute more precisely the origin of the material.

More effort must also be made regarding the development of analytical techniques capable of analyzing single particles, in order to deliver more accuracy and precision without laborious sample preparation. This will contribute to the reliability and agility of the nuclear forensics investigation.

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