

Fingerprinting of Nuclear Material for Nuclear Forensics

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Abstract

Unknown nuclear material may originate from several sources. Nuclear forensics allows by using fingerprinting and comparison with reference data to determine the origin, the intended use, the last legal owner and the smuggling route. These information are essential in the cause of theft or diversion as measures of safeguards can be implemented to prevent future thefts.

Certain measurable parameters can point to a specific material and provide therefore a 'fingerprint' of the unknown material. Comparing the measured parameters with reference material give clues to the origin and the last legal owner.

Characteristic parameters and possible information they contain are presented.

Keywords: nuclear forensics; uranium; plutonium.

1. Introduction: What is nuclear forensics?

As the former Soviet Union disintegrated in the early 1990s a new phenomenon was discovered – 'nuclear smuggling'. The first cases were reported in 1991 in Switzerland and in Italy. New questions had to be answered: intended use of the unknown nuclear material, its origin, the last legal owner and the smuggling route. Techniques to answer these questions were known from nuclear safeguards and material science. Combining these analytic methods was the starting point of nuclear forensics.

Information that is obtained by nuclear forensic analysis can be divided into two groups: endogenic and exogenic information.

Endogenic information is meant as self-explaining information as age, intended use and mode of production, for which only model-calculation might be required for data interpretation.

Exogenic information is meant as information by comparison. To interpretate exogenic information which include geolocation and production data comparison with reference data and reference in-

formation is necessary. Great efforts are made to set up databases containing such reference data.

Case development in nuclear forensics follows a deductive way (Fig. 1). Taking the available results into account a hypothesis or a set of hypotheses are built. Databases and other experts serve for the knowledge to build the hypothesis. Further analysis has to be made to prove the presence of signatures according to the hypothesis. If the signatures are absent in the sample a new hypothesis has to be developed.

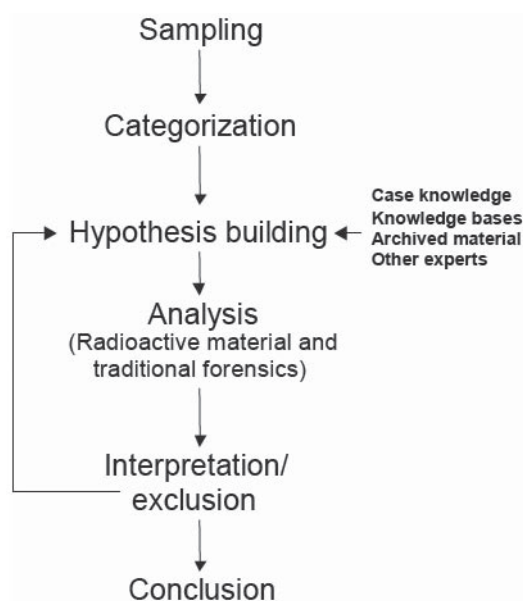


Figure 1: The deductive way in the nuclear forensic process [1].

2. The “nuclear fingerprint” method

To characterize an unknown nuclear material a set of items are measured to establish the so called nuclear fingerprint. Information that form the nuclear fingerprint are:

- Macroscopic parameters (e.g. pellet diameter, height)
- Isotopic composition

- Elemental composition (such as elements and impurities)

In cases of a mixture of components, a powder or if it may be possible that substances of different chemicals or isotopic composition have been added, it is necessary to investigate the microstructural fingerprint which consists of following items:

- Particle morphology
- Particle size and size distribution
- Grain size and size distribution
- Porosity size distribution and density
- Dislocation density and character
- Precipitation of other phases.

2.1. Isotopic patterns of U and Pu

The following information can be obtained by investigating the isotopic patterns:

- The presence of small amounts of U-236 will indicate a contamination with recycled uranium and hence point at reprocessing activities.
- The isotopic composition of plutonium is a useful indicator of the reactor type in which the material was produced.
- Uranium oxide can be found in different forms, e.g. UO_2 or U_3O_8 , which give information on various points of origin in the uranium fuel cycle.

Plutonium is generated as by-product in nuclear reactors when ^{238}U absorbs a neutron creating ^{239}U , which β -decays into ^{239}Np and finally to ^{239}Pu . Also heavier isotopes of Plutonium are produced by further neutron captures. Therefore the isotopic composition may give answers which reactor type was used to produce the unknown nuclear material.

The isotopic composition of Plutonium provides information to indicate the type of the reactor:

- The higher the initial ^{235}U enrichment of the fuel is, the higher is the ^{238}Pu abundance due to multiple neutron capture on ^{237}Np .
- The neutron energy spectrum influences the Pu isotopic composition (the softer the spectrum, the higher is the $^{242}\text{Pu}/^{240}\text{Pu}$ ratio).

The measured isotopic patterns can be compared with model calculations using computer codes (e.g. ORIGEN or SCALE for the RBMK and the VVER). It was demonstrated that the main reactor types can be separated clearly from each other (Fig. 2).

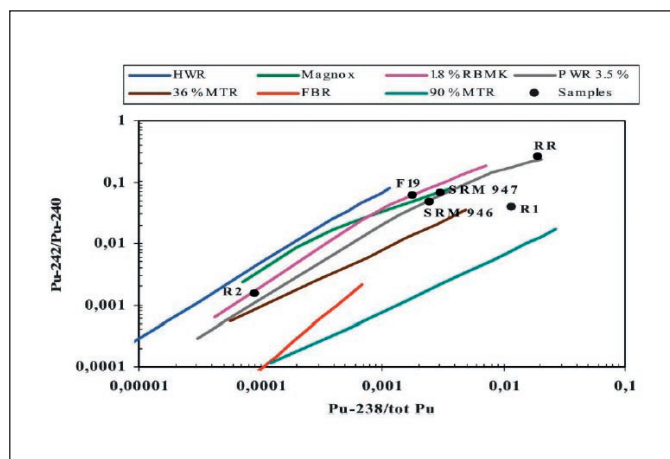


Figure 2: Calculated isotopic composition of Plutonium for various reactor types (continuous line) and measured isotopic composition (points) [2].

2.2. Age determination

The age is defined as the time elapsed since the last chemical processing took place (e.g. production, reprocessing or purification). The age of the material may serve as exclusion parameter in the search for the production or reprocessing plant.

Since radioactive isotopes decay at a rate determined by the initial amount and the half-life of the isotope, the relative amounts of decay products (daughters) in comparison to the parent isotope can be used as chronometer.

The age of the material is short in comparison to the half-life of the observed nuclides. Using the table of nuclides many parent/daughter pairs can be found. The optimal nuclide ratios for Uranium are:

- $^{234}\text{U}/^{230}\text{Th}$
- $^{235}\text{U}/^{231}\text{Pa}$

and for Plutonium:

- $^{238}\text{Pu}/^{234}\text{U}$
- $^{239}\text{Pu}/^{235}\text{U}$
- $^{240}\text{Pu}/^{236}\text{U}$
- $^{241}\text{Pu}/^{241}\text{Am}$.

The radioactive decay of each of these nuclides is unique, therefore measuring the parent/daughter ratio allows to calculate the time elapsed since the last chemical separation. If the material has not been fully separated, the chronometer hasn't been set properly to zero and so misleading information about the age is gained. To avoid this systematic error it is recommended to measure various parent/daughter ratios.

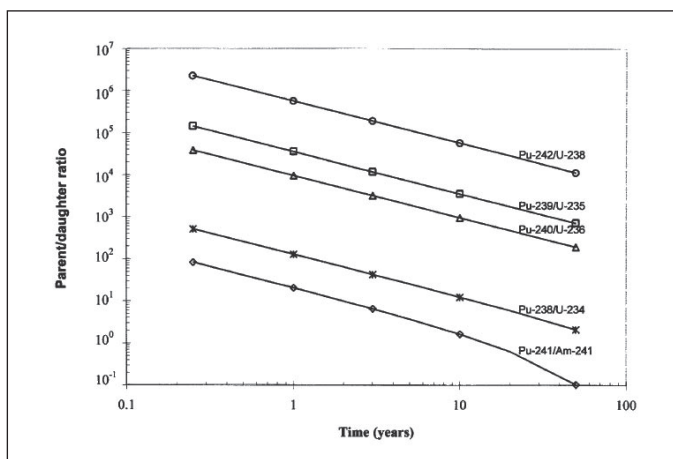


Figure 3: The parent/daughter mass ratios of aged plutonium material [3].

2.3. Metallic impurities

Nuclear material contains metallic impurities at varying concentrations. In the starting materials metallic impurities are accompanying elements, during processing to the intermediate and final product the impurities are drastically reduced. A reduction factor of 10^3 in the impurity level is possible after processing. Impurity patterns within the processing remain for the most mines the same.

Otherwise metallic impurities may enter in the nuclear material at the different processing stages. The systematic behind this is not well understood up to now, but a full theory must contain that the concentration of the impurities are a function of exposure time to the container material or storage tank as they are leached from the surface of the walls.

Nowadays in sample analysis the ratio of elements of similar chemical behaviour are examined because the ratio will vary only within narrow limits.

2.4. Stable Isotopes

Measuring the stable isotopes is a established technique in geolocation. Two substances which are chemically identical have different stable isotope compositions if either their origin and/or their history are not the same. In nuclear forensics the oxygen and the lead isotope ratio measurements are applied.

2.4.1. Oxygen

Natural oxygen exists in three stable isotopes: ^{16}O (99.762%), ^{17}O (0.038%) and ^{18}O (0.200%). Temperature, latitude and distance to the sea cause variations up to 5% in the $^{18}\text{O}/^{16}\text{O}$ ratio.

Water is used as a common solvent in uranium processing. During the processing isotopic ex-

change takes place and the final U-oxide product carries the signature of the $^{18}\text{O}/^{16}\text{O}$ ratio of the used water. Measuring the oxygen isotope ratio provides information about the geographical region where the material was processed. Figure 4 shows the correlation between the geographic location of the production site of uranium oxide examples and the variation in the $(^{18}\text{O})/(^{16}\text{O})$ ratio.

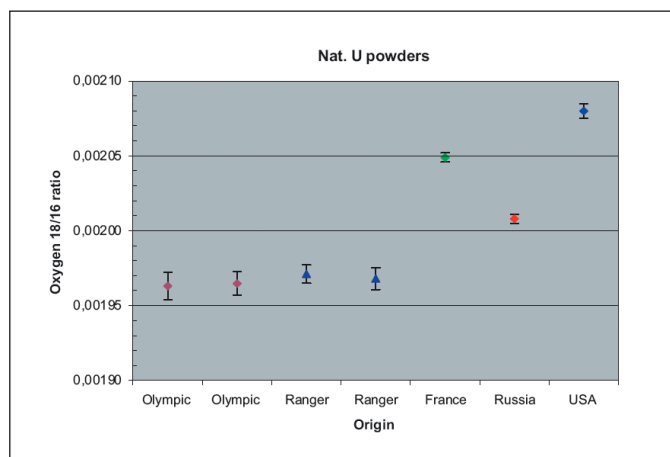


Figure 4: Comparison of the $^{18}\text{O}/^{16}\text{O}$ ratio of U_3O_8 for different uranium mines. Olympic and Ranger are Australian mines [4].

2.4.2. Lead

From the four stable lead isotopes one is primordial (natural) ^{204}Pb and the other three are endproducts of radioactive decay series: $^{238}\text{U} \rightarrow ^{206}\text{Pb}$, $^{235}\text{U} \rightarrow ^{207}\text{Pb}$, $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$. Therefore the stable lead isotope composition gives information on the initial U/Th ratio in the mine and on the age of the ore. Due to the fact that the variations in the composition for different mines are significant, investigating the stable lead isotopes can locate the origin mine.

2.5. Anionic impurities

Uranium crude ore undergoes different chemical processes before it becomes uranium ore concentrate (yellow cake). Since uranium is mined from ores with different mineralogical natures (acidic, alkaline and phosphatic ores) different chemical leaching processes are used. In the subsequent processing also different chemical processes are used for the precipitating and dissolving the uranium.

Different acids are used for the different processes and may leave anionic impurities (Cl^- , F^- , Br^- , NO_2^- , NO_3^- , SO_4^{2-} and PO_4^{3-}). These anions may be an indicator for the process used.

In practice anion ratios are used because the leaching rate in the mines can change and absolute anion concentrations differ more than the ratios.

It has been shown that anionic impurities can distinguish between different mines (Fig. 5), but there are also differences between different sampling campaigns in the same mine (Ranger-old vs. Ranger-fresh and Beverly-old vs. Beverly-fresh in Fig. 5).

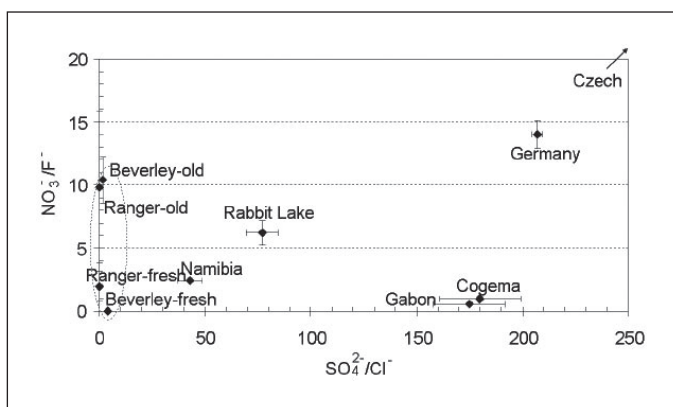


Figure 5: Anion ratios in different uranium ore concentrate samples [5].

2.6. Limitations of these techniques

2.6.1. Cross contamination

There are two problems which may cause cross contamination by investigating the stable lead isotopes. First, natural lead (^{204}Pb) is omnipresent – so special care has to be taken performing the chemical separation – second, lead is often used as shielding material.

Presently the methods of the analysis are continuously improved. If the methods are sensitive enough to detect even metallic impurities from the spatula used to collect the evidence, new problems for the analysts are created.

2.6.2. Reprocessing and enrichment

Presence of ^{236}U can point to reprocessing activities. It has also been shown that in natural uranium variations in ^{236}U and in ^{234}U abundances occur. Better measurement methods have to be developed for ^{236}U abundance levels close to natural abundance.

If nuclear material was reprocessed for non-peaceful purposes the identification of this material is very challenging. Additional information is necessary to calculate predictive signatures for enriched uranium produced from reprocessed uranium [8]:

- The ^{232}U content does not only depend on the operation mode of the production reactor but also on non-reactor-related history (i.e. length of storage periods before and after irradiation).
- HEU may be enriched in a single cascade, but it is also possible to use several interconnected smaller cascades.
- The identification of the enrichment process (gaseous diffusion vs. gas centrifuge) due to small differences in the concentrations of the trace uranium isotopes (^{232}U , ^{234}U and ^{236}U) is very challenging.

2.6.3. Blending

A special challenge to determine origin of nuclear material arises if it is blended. In former times Russia blended the spent VVER fuel with spent fuel of propulsion reactors, after reprocessing this nuclear material is suitable for RBMK reactors [9].

Therefore the nuclear material measured value of the $^{238}\text{Pu}/\text{tot.Pu}$ vs. $^{242}\text{Pu}/^{240}\text{Pu}$ value will not fit the simulated values (Specimen R1 in Fig.2).

Sometimes however cross-contamination has occurred before collection to disguise the origin. Transmission electron microscopy (TEM) is used to determine the grain-size distribution and can therefore indicate that a powder consists of different particle types.

2.6.4. Computer codes

Estimating the uncertainty of all quantities used in the calculations (i.e. cross sections) and determining how these uncertainties propagate through the entire simulation is called uncertainty analysis.

Uncertainty analysis is not implemented in the ORIGEN2 and SCALE code.

An interesting overview how to determine the uncertainty in such computer codes is given in [10].

3. Overview of analytical techniques used in nuclear forensics

Due to the tremendous fingerprint diversity and the requirement of high accuracies of measurement many different analytic techniques have to be applied in nuclear forensics. Figure 6 gives a short overview of information gained from Uranium and Plutonium samples and which analytic techniques are required to obtain this information. A short overview of most widely used techniques is given in [2].

3.1. Including traditional forensic methods

“Wherever he steps, whatever he touches, whatever he leaves, even unconsciously, will serve as a silent witness against him. Not only his fingerprints or his footprints, but his hair, the fibers from his clothes, the glass he breaks, the tool mark he leaves, the paint he scratches, the blood or semen he deposits or collects. All of these and more, bear mute witness against him. This is evidence that does not forget. It is not confused by the excitement of the moment. It is not absent because human witnesses are. It is factual evidence. Physical evidence cannot be wrong, it cannot perjure itself, it cannot be wholly absent. Only human failure to find it, study and understand it, can diminish its value.”

Dr. Edmond Locard

This is the famous Locards Exchange Principle that states that every contact leaves a trace. Traditional forensic methods establish relations between locations, events and individuals - entirely other information than the nuclear forensic methods. In summary forensic methods provide information adherent to the material while nuclear forensic methods provide information inherent to special nuclear material [7].

A detailed description of collecting both nuclear and traditional forensic evidence is given in the Nuclear Forensics Support [1]. During the collection of evidence and analysing the evidence in a laboratory special attention has to be taken on sufficient protection against the radiation.

To fulfil good radiological safety practice the Institute for Transuranium Elements developed jointly with the German Federal Criminal Police a so called glove-box, where contaminated evidence can be visually inspected, photographed and fingerprints and DNA samples can be taken (Fig. 7).



Figure 7: Glove-box for handling of special nuclear material [7].

4. Data interpretation

Measured exogenic information (such as $^{18}\text{O}/^{16}\text{O}$ ratio, Pb isotopic composition, impurities and microstructure) needs comparison with reference data from known samples.

4.1. Supporting information

It is important to have access to reference data and to keep information, that may vary with time (e.g. as seen in 2.5. level of impurities), up to date. The reference information can be gained from Nuclear Materials Database, Open Literature, ITDB, IAEA Research Reactor Database, other databases and comparison samples.

The Nuclear Materials Database was established in collaboration between the ITU in Karlsruhe with the A. A. Bochvar Institute in Moscow. The database contains information on fuels for commercial reactors as collected from open literature and from bilateral agreements with fuel suppliers.

Parameter	Information	Analytical technique
Appearance	Material type (e.g. powder, pellet)	Optical microscopy
Dimensions (pellet)	Reactor type	Database
U, Pu content	Chemical composition	Titration, HKED, IDMS
Isotopic composition	Enrichment \Rightarrow intended use; reactor type	HRGS, TIMS, ICP-MS, SIMS
Impurities	Production process; geolocation	ICP-MS, GDMS
Age	Production date	AS, TIMS, ICP-MS
$^{18}\text{O}/^{16}\text{O}$ ratio	Geolocation	TIMS, SIMS
Surface roughness	Production plant	Profilometry
Microstructure	Production process	SEM, TEM

HKED, hydrid K-edge densitometry; IDMS, isotope dilution mass spectrometry; HRGS, high-resolution gamma spectrometry; TIMS, thermal ionisation mass spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; SIMS, secondary ion mass spectrometry; GDMS, glow discharge mass spectrometry; AS, alpha spectrometry; SEM, scanning electron microscopy; TEM, transmission electron microscopy.

Figure 6: Information that can be obtained from nuclear (U, Pu) material and used analytic techniques [6].

Certain data have limited accessibility (commercially sensitive data such as chemical impurities) or are not shared (detailed information on weapons grade material).

4.2. Exclusion Principle

In order to avoid a full characterization each time when unknown nuclear material is found, the exclusion principle is applied. The exclusion principle works as follows:

1. The first measured information (e.g. pellet dimensions and isotopic composition) are compared with the database entries.
2. The non-matching records are rejected as they could not be manufacturer of the unknown nuclear material.
Exit condition: A single record is left. This is the best case.
3. The remaining records, which match the measurements, are compared to each other in order to identify parameters which could distinguish between these records.
Exit condition: No further parameters can be investigated.
4. These parameters are measured next.
5. The measured data are compared with the reduced database entries.
Go back to 2).

5. Conclusion

Combining various analytic techniques can give information about the origin, the intended use, the last legal owner and the smuggling-route of unknown nuclear material. But this is only possible if enough reference data are available and accessible.

Therefore it is necessary to strengthen the international cooperation and the cooperation with the fuel manufacturers.

Since the beginning of nuclear forensics in the early 1990s more and more parameters proved to be useful and could be applied for the nuclear fingerprint. Hence it is necessary to do furthermore research and development and to keep close cooperation with other sciences whether new characteristic parameters can be investigated.

6. Acknowledgement

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