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Nuclear Forensics: A Methodology Applicable to Nuclear Security and to Non-Proliferation

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Abstract

Nuclear Security aims at the prevention and detection of and response to, theft, *sabotage*, unauthorized access, illegal transfer or other *malicious acts* involving *nuclear material*". Nuclear Forensics is a key element of nuclear security. Nuclear Forensics is defined as a methodology that aims at re-establishing the history of nuclear material of unknown origin. It is based on indicators that arise from known relationships between material characteristics and process history. Thus, nuclear forensics analysis includes the characterization of the material and correlation with production history.

To this end, we can make use of parameters such as the isotopic composition of the nuclear material and accompanying elements, chemical impurities, macroscopic appearance and microstructure of the material. In the present paper, we discuss the opportunities for attribution of nuclear material offered by nuclear forensics as well as its limitations. Particular attention will be given to the role of nuclear reactions. Such reactions include the radioactive decay of the nuclear material, but also reactions with neutrons. When uranium (of natural composition) is exposed to neutrons, plutonium is formed, as well as ^{236}U. We will illustrate the methodology using the example of a piece of uranium metal that dates back to the German nuclear program in the 1940's. A combination of different analytical techniques and model calculations enables a nuclear forensics interpretation, thus correlating the material characteristics with the production history.

1. Introduction

Nuclear forensics is a methodology that reveals information inherent to nuclear material. Nuclear material has either been subject to technological processing or is entirely of anthropogenic origin. Consequently, nuclear material carries signatures of the process it was subjected to. These signatures may be due to chemical operations (such as dissolution, extraction, ion exchange, precipitation) or they may be associated with physical operations (such as neutron irradiation or radioactive decay). Signatures may be source material inherited (e.g. natural uranium carrying impurities originating from the uranium ore) or process inherited (e.g. Gd is added to nuclear fuel in order to obtain higher burn-

up). In addition to such intentionally added "impurities", also some accidentally added impurities may provide useful information (e.g. corrosion products may point at vessel material).
Uranium and plutonium both contain fissile isotopes, substantiating the broad interest in the history, origin and intended use of these materials. The historically first area of application was related to military intelligence: gaining information on the status of the adversary's nuclear programme. Today, however, a much broader range of applications is conceivable:

- In **non-proliferation** issues, nuclear forensic methodologies are applied. The investigation of particles of highly enriched uranium found in Iran provided hints on Iran's clandestine nuclear programme. The comparison of the uranium isotopic pattern with material obtained from Pakistan showed that the scenario (particles of HEU were imported with equipment procured on the black market from Pakistan) was consistent with the available evidence [[1]].
- The measurement of chemical impurities is increasingly applied in **nuclear safeguards.** Particularly, samples of uranium are analysed in order to establish relations between different samples and check consistency of the impurity pattern with the declared processes.
- Also **environmental samples** can be subject to nuclear forensic investigations. As demonstrated by Ray et al. [[2]] particles found on the seabed and occasionally on the beaches of Dounreay could be attributed to the Material Testing Reactor at Dounreay using electron microscopy in combination with elemental analysis (by X-ray fluorescence).
- The **Nuclear Security** area is certainly the most prominent application of nuclear forensic methods. This comprises combating illicit trafficking but includes also (prevention of) nuclear terrorism.

2. Methodology

Nuclear forensic investigations have to be considered as part of a comprehensive set of measures for detection, interception, categorization and characterization of illicit nuclear material. As mentioned above, nuclear forensic analysis may result in important conclusions on the origin of the material and thus provide the most essential contribution to the prevention of future diversions from the same source. It is therefore crucial to ensure throughout the entire process the integrity and authenticity of the collected evidence. This requires a close collaboration between the various actors on the scene: law enforcement, radioprotection services, forensics experts and nuclear measurement experts. The international technical working group on nuclear smuggling (ITWG) has developed a Model Action Plan for handling cases of seized nuclear material. This action plan lays out the elements that are needed in the instance that illicit nuclear material is uncovered, e.g. incident response, crime scene analysis, collection of evidence, transportation to a nuclear facility, subsequent laboratory analysis, and finally the development of the case.

Nuclear forensics make use of the information inherent to the material, while classical forensics make use of the evidence adherent to the nuclear material (e.g. packing materials, shielding materials, hair, fibre, etc). Like other pieces of evidence, nuclear material intercepted from illicit trafficking carries information that might be useful to illuminate the case. Obviously, classical forensic investigations may be carried out as well as nuclear forensic investigations. The preservation of evidence is of key importance for obtaining a maximum of information on the material, its history and its intended use. Table 1 summarizes the analytical techniques used most commonly in nuclear forensic investigations. Some techniques are applicable to radioactive materials only (e.g. alpha- or gamma spectrometry) but most of the methods are commonly applied in analytical chemistry or in materials science (e.g. Secondary Ion Mass Spectrometry-SIMS, Scanning Electron Microscopy-SEM). In the latter case the techniques need to be adapted to the specific requirements associated with handling radioactive materials (glove-boxes, shielding etc.). Controlling the radiological hazard is paramount to all activities carried out throughout the various stages of the investigation. In the nuclear analytical laboratory, the material is first subjected to visual inspection. This may already reveal useful information on the material itself (e.g. physical form, geometry, primary packing) and provide the starting point for further analysis. This may be complemented by imaging techniques, e.g. optical microscopy for examination of the sample at high magnification.

Table 1 Analytical techniques typically applied in nuclear forensic investigations

Techniques/Methods	First Analysis	Information	Detailed Analysis	Information
Radiological	Estimated total activity Dose rate (α, γ, n) Surface contamination	Radiological hazard Precautions		
Physical characterization	Visual inspection Photography Size measurement	Macroscopic dimensions	SEM (EDX)	Microstructure and elemental composition
	Optical microscopy		XRD	Crystal structure
	Radiography Weighing	Mass	TEM	Microstructure
Traditional forensic analysis	Fingerprints, fibers etc.			
Isotope analysis	γ-spectroscopy	Isotopic composition	Mass spectrometry (SIMS, TIMS, MC-ICP-MS) Radiochemical separations α-spectrometry	Accurate isotopic composition
Elemental/Chemical analysis			ICP-MS XRF	Chemical impurities
			Assay (titration, IDMS) GC/MS	Chemical composition

In the present paper we will focus on parameters and signatures that are related to nuclear physics. We will illustrate the nuclear forensics methodology using an example that dates back to the early days of nuclear fission research.

3. Case study

Soon after the discovery of nuclear fission by Hahn, Meitner and Strassmann [3] it was realized that this process goes along with tremendous release of energy. Also the potential application of such energy releases became apparent: the production of electricity through slow and controlled release or "nuclear explosives" through rapid energy release. At the time, however, the technical solutions for either option still needed to be developed. This was recognized in a number of states and appropriate research programs were launched, though significantly different in size and effort. However, the nuclear arms race had started. A significant program was started in the United States under the scientific guidance of Robert Oppenheimer. Very little information was available at the time on the status of the German nuclear project. The project was carried out under the scientific leadership of Werner Heisenberg (reporting to the Kaiser Wilhelm Institute). A second group, led by Kurt Diebner (reporting to the Army Ordnance Department) also worked on the issue of chain reactions based on neutron induced nuclear fission. The different groups carried out a number of experiments using different moderator materials (paraffin, dry ice, graphite and heavy water) in combination with uranium oxide powder, uranium metal powder and solid uranium metal. At some point in time, uranium metal appeared the most suitable form for further experiments. Heisenberg favoured metal plates (arranged in alternating layers with moderator), while Diebner recognized the superior neutron economy of using fissile material in cubes (completely surrounded by moderator).

In the absence of reliable information and intelligence, the advancement on the way to a Nazi bomb was largely overestimated and the associated fears were dispelled just few weeks before the end of the war. The US military launched the ALSOS mission (teams composed of military personnel and scientists) to search Germany not just for its scientists, but also for their equipment, laboratories and for any strategic material. The second ALSOS mission followed the Allies forces advance from France into Germany in late 1944 and early 1945. At the University of Strasbourg in France they found documents pointing at the small town of Haigerloch located in southern Germany. In the last days of March, American troops entered Heidelberg, and officers of the ALSOS mission occupied the Kaiser-Wilhelm Institute of Physics. There they learned that Otto Hahn was in a small town, south of Stuttgart and that also Heisenberg was in the same area. Moreover, they now knew that the last uranium pile had been evacuated from Berlin to Haigerloch. The ALSOS team arrived at Haigerloch in late April 1945 and discovered the sub-critical installation in a former beer cellar. It was realized that in 1945 the German nuclear scientists were no farther along in the nuclear program than the Americans had been back three years earlier in 1942. With interrogation and enticements of the scientists, a few days later, the agents uncovered a cache of about two metric tons of natural uranium buried in a nearby field. The material was in the form of metal cubes (consisting of natural uranium) showing a mass of some 2,4 kg each. The ALSOS team recovered 659 cubes. The last experiment that the German researchers had carried out, so-called "B-8", consisted of 664 uranium metal cubes, wire suspended into heavy water. Thus, five cubes were missing or to use today's safeguards terminology, they were unaccounted for.

Heisenberg had left Haigerloch a few days before the troops of the Allies occupied the village. After three days and three nights bicycling, he eventually arrived at Urfeld (Bavaria). Some twenty years later, boys playing in the little river "Loisach" spotted a strange looking black stone, cubic in shape, very hard and extremely heavy. The place this cube appeared is only 10 km away from Heisenberg's summer cottage in Urfeld. Thus, it is not unlikely that Heisenberg had taken (at least) one of the cubes with him and disposed of it at the river. After discovery by the children, a senior consultant of the nearby Garmisch hospital found the cube to be slightly radioactive. A co-worker of the Fraunhofer Institute of Atmospheric Physics took possession of the cube and kept it in his cellar. In 1998, the German Federal Office for Radiation Protection (BfS) examined the place and discovered, amongst other items, the above uranium cube.

In 2002 a metallic cube was presented to ITU by a co-worker of the BfS for nuclear forensic investigations. The cube was suspected to originate from the secret German nuclear program conducted during the Second World War under the scientific guidance of Werner Heisenberg. This cube will henceforth be referred to as "Heisenberg cube" (Figure 1).

Two years later, scientists of the Max-Planck Institute for Nuclear Physics in Heidelberg discovered during a clean-up operation a uranium metal plate in an old safe. The material proved to be natural uranium and showed a total mass some 2 kg. The material was attributed to Karl Wirtz, a physicist who had worked with Heisenberg on the nuclear program in the 1940's. According to its mass and geometry, it might have been used in the reactor experiments based on the alternating layer approach. It will henceforth be referred to as "Wirtz plate" (Figure 2).

Figure 1: Uranium metal cube offered to ITU

Figure 2: Uranium metal plate

Some of the results obtained on these two materials will be presented and discussed hereafter, aiming at bringing some experimental evidence in the discussion of the German nuclear program during World War II and, more importantly, to illustrate the methodological approach taken in nuclear forensic investigations.

Experimental Investigation

The generic analytical scheme usually applied to nuclear forensic samples, was slightly modified according to the sample characteristics and to the analytical goal.

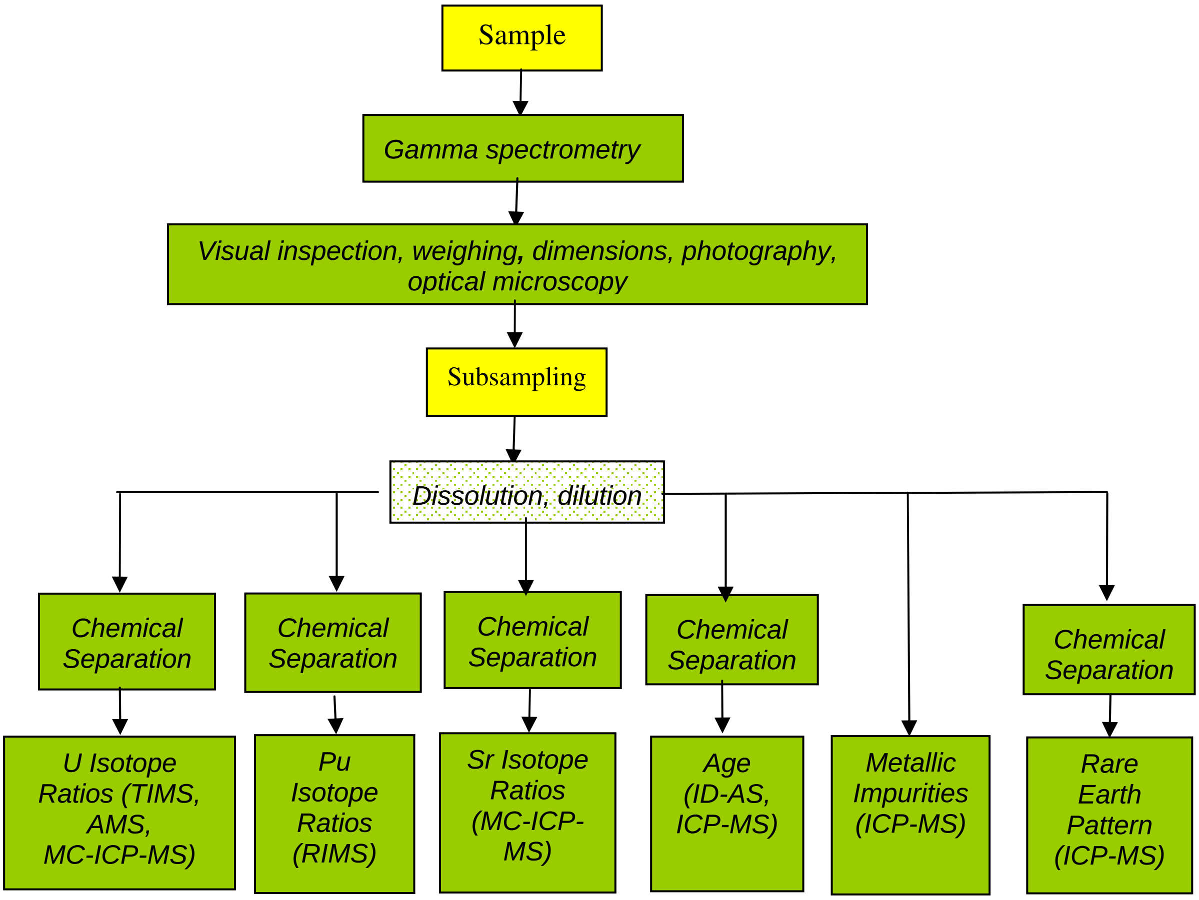

Figure 3 Analytical Scheme applied to the two uranium samples (TIMS = Thermal Ionization Mass Spectrometry, AMS= Accelerator Mass Spectrometry, RIMS= Resonance Ionization Mass Spectrometry, ICP-MS= Inductively Coupled Plasma Mass Spectrometry, MC-ICP-MS= Multi-Collector ICP-MS, ID-AS= Isotope Dilution Alpha Spectrometry)

Hints on the Irradiation History

The two samples described above had been used in experiments aiming at setting up a nuclear reactor. As we know from the written records of these experiments, no self-sustaining chain reaction was obtained. Thus, the "reactors" were rather to be considered as subcritical assemblies. The uranium, however, was used in numerous experiments and irradiated with neutrons. The products of these neutron reactions (or their absence) may provide hints on the irradiation history of the uranium. Apart from neutron induced fission, a number of parasitic neutron reactions may occur as illustrated in figure 4.

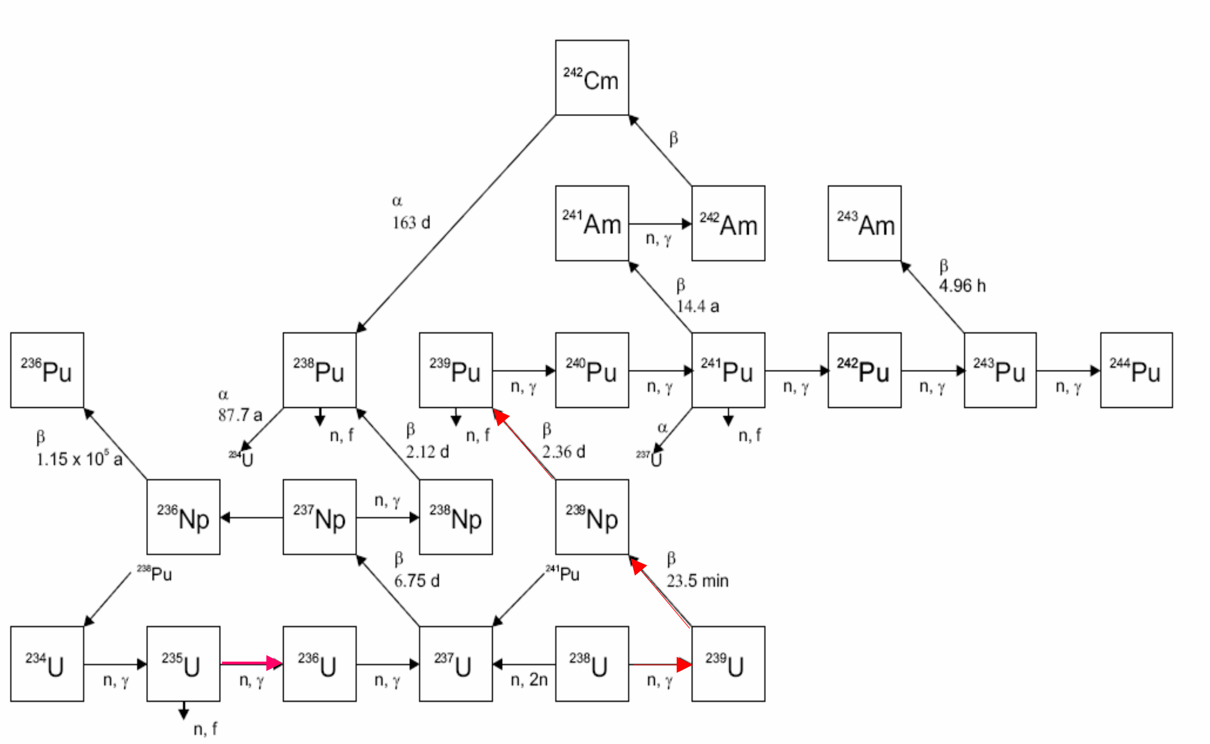

Figure 4 Neutron reactions and subsequent radioactive decay starting from natural uranium

The most prominent products of these reactions are ^{236}U (produced from ^{235}U through neutron capture, mostly in the thermal energy region) and ^{239}Pu (produced from ^{238}U through neutron capture in the epithermal energy region followed by two subsequent β^- decays). As the reactor did not reach criticality, we expect only tiny traces of ^{236}U and ^{239}Pu. In consequence, we need to apply highly sensitive measurement methods for their detection and quantification.

Uranium isotope measurements were carried out by thermal ionisation mass spectrometry (TIMS) using a Triton instrument (Thermo Corporation). A double filament assembly was used and the instrument was run in a modified total evaporation mode [4]. Thus, the ion currents of all isotopes were recorded simultaneously and the signals were integrated over the entire measurement time. This eliminates time dependent isotope fractionation effects. The ^{234}U and ^{236}U ion currents were recorded using micro channeltrons (continuous dynode electron multiplier), while Faraday Cups were used for measuring the signals arising from ^{235}U and ^{238}U. The $n(^{235}\mathrm{U})/\ n(^{238}\mathrm{U})$ isotope abundance ratio in the two samples agrees very well. Similarly, no significant difference in the $n(^{234}\mathrm{U})/\ n(^{238}\mathrm{U})$ ratio was observed.

In none of the two samples a ^{236}U ion current above the detection limit could be recorded by TIMS. The detection limit is mainly determined by the abundance sensitivity of the mass spectrometer used. Further investigations were carried out using the 14UD Pelletron tandem accelerator in the Department of Nuclear Physics at the Australian National University. The methodology is described in more detail in [5]. The results of the measurements do not suggest a significant difference between the three samples. Moreover, the measured $n(^{236}\mathrm{U})/\ n(^{238}\mathrm{U})$ are in the order of magnitude of uranium ores, which is reported to range between 10^{-12} and $3{\cdot}10^{-10}$ [5]. More specifically, for uranium from the Joachimsthal mine (sampled prior to atmospheric nuclear weapons tests), a $n(^{236}\mathrm{U})/\ n(^{238}\mathrm{U})$ ratio of $(7.0 \pm 0.5) \cdot 10^{-11}$ was measured, while earlier work reported a slightly lower value of $(5.8 \pm 0.5) \cdot 10^{-11}$ [5]. Thus, the uranium isotopic composition did not provide solid evidence of an exposure of the uranium to significant neutron fluence.

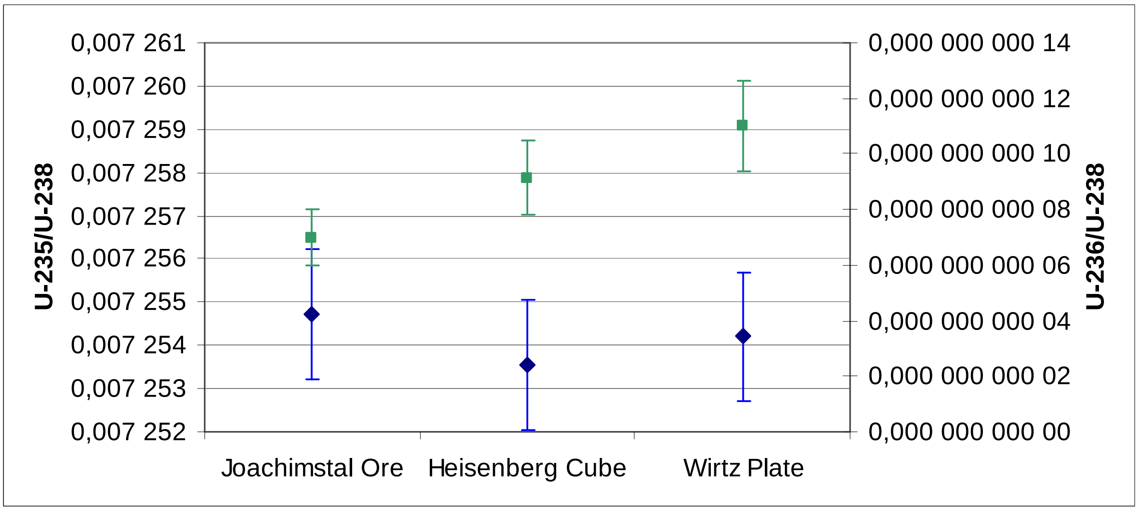

Figure 5 Uranium isotope abundance ratios in the Heisenberg Cube, in the Wirtz Plate and in the respective raw material, i.e. uranium ore from Joachimsthal.
The $n(^{235}U)/ n(^{238}U)$ ratio (◆)was measured by TIMS, and the $n(^{236}U)/ n(^{238}U)$ ratio (■)was determined by AMS. Uncertainties are expresses as combined standard uncertainty according to GUM, with k=1.

As outlined above, also the presence of plutonium could be used as an indicator on the irradiation history of the uranium. The amounts of plutonium to be expected in these samples are fairly small. A rough estimation of the plutonium produced in the experiments carried out in Heisenberg's subcritical assembly suggests a $n(^{239}Pu)/ n(^{238}U)$ ratio inferior to 10^{-14}. It should be noted, however, that the shortage in uranium and in heavy water lead to an exchange of material between the (competing) groups of Heisenberg and Diebner. Also uranium cubes were reportedly shuttled back and forth and irradiated in different experiments. This introduces an additional element of uncertainty when considering the irradiation history of the material. We should furthermore note that also uranium ores contain ultra-trace amounts of plutonium. Small amounts are produced naturally in uranium ores via the same neutron capture reactions as in nuclear weapons and reactors. The spontaneous fission of ^{238}U (though the branching ratio being only $5\cdot10^{-7}$) provides fast neutrons. These neutrons can then be captured (as outlined above) by ^{238}U and form ^{239}Pu. Naturally occurring ^{239}Pu was first discovered by Seaborg et al. in 1948 in pitchblende from the Great Bear Lakes region of Canada [6]. Investigations by AMS on uranium ores of different origins, indicate $n(^{239}Pu)/ n(^{238}U)$ ratios (in pitchblende samples) of few parts in 10^{-13} [5].

The present materials were investigated by means of Resonance Ionization Mass Spectrometry (RIMS). The details of the method are described in [7]. Trace amounts of plutonium could be identified in all three samples as can be seen from figure 6. Repeat measurements of each sample were performed, as can be seen from the graph.

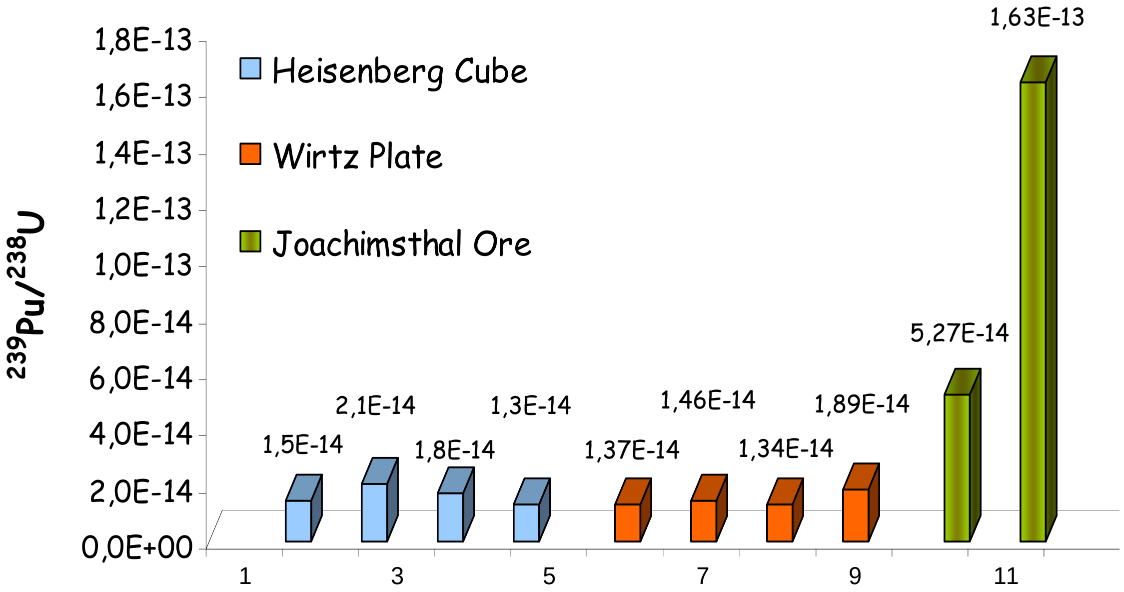

Figure 6 Results of RIMS measurements, showing that the plutonium content in the uranium metal samples is significantly smaller than the plutonium content in the ore.

The lower Pu content in the uranium metal samples compared to the ore from which the uranium used for metal production was mined appears surprising at first glance, in particular because we expect Pu to be generated in the "reactor". We have to note, however, that the material is subjected to significant processing, including purification steps. These chemical purification steps reduce the concentration of accompanying elements. In consequence, also the plutonium concentration is decreased. At this point, we can conclude that the plutonium produced from neutron capture was insufficient to compensate for the losses in plutonium during processing of the uranium material. This sets an upper limit to the fluence of thermal neutrons to which the cube under investigation had been exposed. A more detailed study, including Monte-Carlo modelling calculation of the "reactor" is under way [8].

Age Dating

An important parameter providing information on the authenticity of the two samples and on their production dates is the date of the last chemical purification of the uranium. The latter is referred to as the age of the material, as it describes the time elapsed since the last separation of uranium from its daughter nuclides. The method for age determination of uranium has been described in detail in Refs. [9] and [10]. Basically, aliquots of the respective uranium solution were spiked with a ^{229}Th spike. Uranium and thorium were then separated using a TEVA column (Eichrom Technologies Inc., Darien, Illinois, USA) using a specially developed procedure. The thorium fractions were measured by alpha spectrometry and by MC-ICP-MS. The ^{234}U was quantified by isotope dilution mass spectrometry using ^{233}U as spike isotope; the measurements were performed by thermal ionisation mass spectrometry (MAT 261, Thermo Finnigan, Bremen, Germany).

The age was calculated using the equation of radioactive decay and its derivatives:

$$N = N_0 * \exp(-\lambda t) \qquad \text{(Eq. 1)}$$

$$(N_{U\text{-}234}/N_{Th\text{-}230}) = (N_{0,U\text{-}234} * \exp(-\lambda_{U\text{-}234}*t))/(N_{0,U\text{-}234} - N_{0,U\text{-}234} * \exp(-\lambda_{Th\text{-}230}*t)) \qquad \text{(Eq. 2)}$$

$$t = -\ln(1-R/K)/B \qquad \text{(Eq. 3)}$$

where
R is the measured ^{230}Th/^{234}U atom ratio
K is the activity ratio $(\lambda_{U\text{-}234})/(\lambda_{Th\text{-}230}-\lambda_{U\text{-}234})$
B is a factor combining the ^{234}U and ^{230}Th decay constants $(\lambda_{Th\text{-}230}-\lambda_{U\text{-}234})$

We found for the Heisenberg Cube a production date of September 1943 (± 0.5 years) while the Wirtz plate turned out to originate from an earlier production, i.e. August 1940 (± 0.2 years). It should be noted, however, that the age determined by this method does not reflect the time of machining the uranium metal to the given geometry, nor does it describe the time of metal production (refined uranium oxide was reduced at 1100 °C by means of calcium metal, with a calcium chloride flux, in an atmosphere of the inert gas argon, as described by Irving [11]). The date of the metal cube production is consistent with literature information on the change of reaction design, moving from an alternating layer approach to uranium cubes suspended in heavy water. Also the superior age of the plate (as compared to the cube) is consistent with historical information. In conclusion, the age dating confirmed the authenticity of the two materials and provided experimental evidence of the respective production dates.

4. Conclusion

In conclusion we can say that nuclear forensics methods enabled us to prove the authenticity of the two uranium samples in question. We could also re-establish a fair part of the history of the material and could clearly state that neither of the samples was exposed to a significant number of neutrons. Wherever historical information was available, it showed excellent agreement with our findings. This underlines the power of the methodology of nuclear forensics and its value in a variety of applications

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