

## Nuclear forensic investigations with a focus on plutonium

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### Abstract

Since the beginning of the 1990s when the first seizures of nuclear material were reported, the IAEA has recorded over 200 cases of illicit trafficking of nuclear materials. Despite the decreasing frequency of nuclear material seizures, particularly the ones involving weapons-grade material, the issue continues to attract public attention and is a reason for concern due to the hazard associated with such materials. Once illicitly trafficked nuclear material has been intercepted, the questions of its intended use and origin are to be addressed. Especially the origin is of prime importance in order to close the gaps and improve the physical protection at the sites where the theft or diversion occurred. To answer these questions, a dedicated nuclear forensics methodology has been developed. In this paper an overview is given on the methodologies used, on the past and on-going developments and on the experience gathered. Some selected examples shall illustrate the challenges and the complexity associated with this work.

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### 1. Introduction

Illicit trafficking of nuclear material started in the aftermath of the break-up of the Former Soviet Union (FSU). At the beginning of the 1990s, the New Independent States of FSU did not have sufficient control over their large nuclear material supplies and material got relatively easily “lost”. The record year according to the IAEA illicit trafficking database was the year 1994 when 45 confirmed cases of illicit trafficking of nuclear material were recorded. The number has decreased since then and stabilized to around 10 cases per year [1]. Also most of the more recent seizures consist of natural or depleted uranium and only in very rare cases is the material nuclear weapons-grade. Despite the apparent improvement of the situation, the poorly guarded nuclear material still presents a radiological hazard arising from inappropriate handling, transport or storage. Even more serious concerns arise if the material is considered in a terrorist context.

Nuclear material could either be used in a radiological dispersal device, so-called “dirty bomb” or – if available in sufficient quantity and quality – in nuclear explosive devices.

Nuclear forensic investigations have to be considered as part of a comprehensive set of measures for detection, interception, categorization and characterization of illicitly trafficked nuclear material. The aim of the analysis is to give the answers to the following questions: What was its intended use? Where is its origin and who was its last legal owner? For each seized sample a specific analytical strategy needs to be developed, taking into account the particular conditions of the seizure, the very nature of the material and of its packaging and other evidence. The analytical strategy follows a step-by-step approach, where the next step is defined and performed based on actual findings.

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. The methodology developed in nuclear forensics may also be applied for source attribution of nuclear material in environmental samples, e.g. illegal dumping of nuclear waste, contaminated scrap metal or accidental release. The Institute

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for Transuranium Elements (ITU) has been involved in nuclear forensics research since the beginning. During the last 10 years, methods for the age determination of U and Pu, the geolocation of natural U, and the determination of the reactor type from the Pu isotopic composition have been developed [2–9]. In addition approximately 30 samples originating from real seizures of nuclear material have been analyzed [10].

## 2. Methodology

Analytical methods adapted from nuclear safeguards serve as a basis in nuclear forensic analysis. However, they were not sufficient to provide answers to all the questions. Therefore, a dedicated nuclear forensic methodology has been developed. Nuclear forensic investigations draw upon the information inherent to the material. Nuclear material is generally of anthropogenic origin, i.e., the result of a production process. The nature of this process is reflected in the elemental and isotopic composition of the material as well as in its microscopic and macroscopic characteristics. All these parameters can be measured using the appropriate analytical technique (Table 1). This approach combines methods used in the nuclear fuel cycle, materials research and environmental studies, including radiometric and mass spectrometric techniques as well as electron microscopy. The conclusions from such investigations need to be supported by reference data whenever possible.

### 2.1. Reactor type determination

Plutonium is formed as a by-product in nuclear reactors through neutron capture of uranium and subsequent  $\beta$ -decays. A key parameter of seized Pu material is the reactor type where it was produced, which may allow one to trace back its origin. To this end, an isotope correlation has been established, which depends upon the reactor type [6]. The correlation is based on the computer code calculated ratios of isotopes  $^{238,240,242}\text{Pu}$  (Fig. 1). The initial  $^{235}\text{U}$  enrichment of the fuel determines the  $^{238}\text{Pu}$  abundance, whereas the hardness of the neutron spectrum influences the production of the heavier Pu isotopes. With a softer spectrum, relatively more heavy Pu isotopes are produced. In Fig. 1 the isotopic correlations are shown for the most common reactor types, i.e., heavy-water reactors (HWR), gas-cooled reactors (Magnox), graphite-moderated

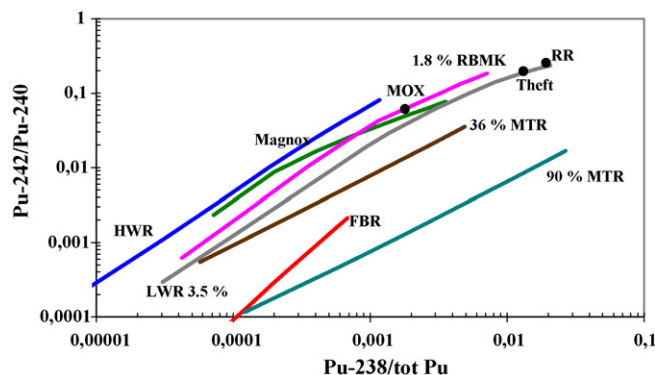


Fig. 1. Use of plutonium isotope correlations for reactor type determination.

reactors (RBMK), light-water reactors (LWR), fast-breeder reactors (FBR) and material-testing reactors (MTR). In addition, three of the four case studies described later in the text are plotted in the figure (called RR, Theft, MOX). Two of the respective samples originate from light-water reactors with initial  $^{235}\text{U}$  enrichments close to 3.5%, whereas one of the samples may originate from a RBMK reactor. However, one should notice that when the isotopic correlations are based on computer code calculations, they give the average plutonium composition in the reactor core. Therefore, in extreme cases, depending on the location where a fuel assembly was exposed to neutrons, the calculated Pu compositions and the actual sample compositions may show notable differences. In addition, if the Pu sample is a mixture of different spent fuels, this correlation (as well as any other correlation) will give misleading results.

### 2.2. Age determination

The age of nuclear material refers to the time span since the last chemical separation. The age is a very important parameter for the origin determination because it may serve to exclude certain production or reprocessing plants, which were not operating at the given time or were not processing the type of material in question. Plutonium has four parent/daughter relations that can be used for the age determination, namely  $^{238}\text{Pu}/^{234}\text{U}$ ,  $^{239}\text{Pu}/^{235}\text{U}$ ,  $^{240}\text{Pu}/^{236}\text{U}$  and  $^{241}\text{Pu}/^{241}\text{Am}$  (Fig. 2). The advantage of using several parent/daughter ratios is that systematic errors can be minimized and that residual U or Am from reprocessing can be detected through inconsistent results.

Table 1  
Techniques used in nuclear forensic analysis

Technique/method	First analysis	Information	Detailed analysis	Information
Radiological	Total activity; dose rate	Radiological hazard; precautions		
Physical characterization	Visual inspection; photography; size/mass measurement; optical microscopy	Macroscopic dimensions; mass	SEM-EDX, TEM, XRD	Microstructural and elemental composition; crystal structure
Isotopic analysis	$\gamma$ -Spectroscopy	Isotopic composition	Mass spectrometry (TIMS, SIMS, ICP-MS), $\alpha$ -spectrometry	Isotopic composition
Elemental/chemical analysis			ICP-MS, XRF, titration, IDMS	Chemical impurities; chemical composition

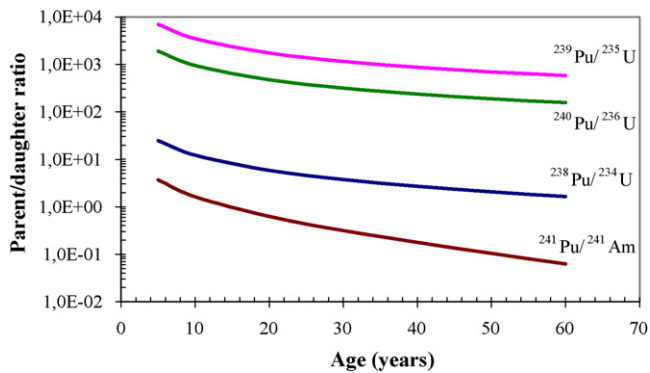


Fig. 2. Parent/daughter relations for plutonium age determination.

The age of nuclear material can be determined precisely by several techniques. A fast method which does not require chemical separation is gamma-spectrometry of the  $^{241}\text{Pu}/^{241}\text{Am}$  ratio. However, in this case the result is based only on one parent/daughter ratio, and in the case of residual Am the results will be positively biased. Other methods for the analysis of bulk material are inductively coupled plasma mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS), where the latter requires chemical separation [2]. For particles analysis, secondary ion mass spectrometry (SIMS) is the method of choice. However, the  $^{241}\text{Pu}/^{241}\text{Am}$  ratio suffers from isobaric interferences due to a limited mass-resolving power and because no chemical separation can be performed prior to the analysis by SIMS. Therefore, this ratio cannot be used. Another drawback of the method is the different ionization efficiencies of U and Pu. This difference must be quantified using standards of known age, and subsequent measurement results must be corrected using a relative sensitivity factor [3].

### 3. Case studies

Since 1992 when the first seized nuclear material arrived at ITU for analysis, about 30 additional samples have been analyzed. The seizures include the whole spectrum of nuclear material, from depleted uranium to highly enriched uranium and from small particles to kilogram quantities. Also a few seizures of plutonium containing material have been analyzed. The investigations of some of the Pu cases are discussed below.

#### 3.1. Pu with “red mercury”

In May 1994 the police were searching the house of a known criminal in Tengen, Germany, expecting to confiscate counterfeit money, but instead 56 g of radioactive material was found (Fig. 3). The analysis showed that the radioactive powder contained 10 wt.% of plutonium with a  $^{239}\text{Pu}$  enrichment of 99.75%. Other main elements in the powder were mercury (61 wt.%), antimony (11 wt.%), oxygen (6 wt.%), iodine (1.6 wt.%) and gallium (0.15 wt.%, which corresponds 4.6 at.%).

The Pu was mixed with a powder of chemical composition  $\text{Sb}_2\text{O}_8\text{Hg}_6$ . Taking into account that also some of the mercury was found as metallic spheres, the sample composition resembles the so-called “red mercury”,  $\text{Hg}_2\text{Sb}_2\text{O}_7$ . “Red mercury” is allegedly used for “producing high-precision conventional and nuclear bomb explosives, ‘stealth’ surfaces and self-guided warheads” [11]. However, a material with these features has never been found and it is believed that the name is simply used to hide other materials during export.

Another interesting component of the material was gallium, which is usually added to Pu in a few atom percent quantities to stabilize the  $\delta$ -phase of Pu. This is required in order to obtain geometrically stable Pu-alloy for atomic weapons. On the other hand, the  $^{239}\text{Pu}$  enrichment was much higher than required for a nuclear weapon, thus the application for this particular material is unknown. The Pu had also partly reacted with the powder; therefore, it would have been possible to use it only after a chemical separation from the rest of the material.

#### 3.2. MOX powder

In August 1994, three men were stopped at Munich airport in Germany carrying a suitcase containing 560 g Pu- and U-oxide powder and 210 g Li-metal (Fig. 4). The powder consisted of 64.9 wt.% of Pu and 21.7 wt.% of U. The  $^{239}\text{Pu}$  enrichment was about of weapons-grade quality, whereas U had a low  $^{235}\text{U}$  enrichment only (Table 2). The piece of Li-metal was enriched to 89.4% in  $^6\text{Li}$ . The MOX powder consisted of three different particle types:  $\text{PuO}_2$ -platelets, rod-shaped  $\text{PuO}_2$  and hexagonal  $\text{U}_3\text{O}_8$  (Fig. 4b).

Light-water reactors (PWR, BWR and VVER) could be excluded as the origin of the Pu. The isotopic composition of Pu after a typical irradiation period of 3 years in these reactors would

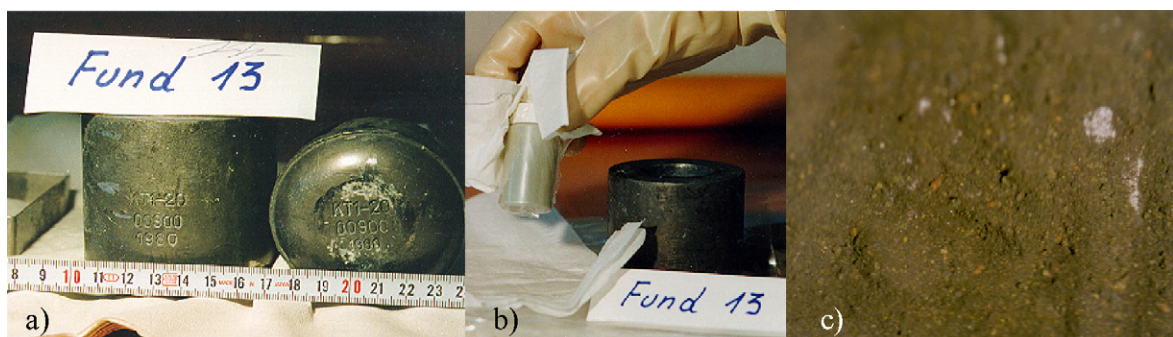


Fig. 3. Seizure of nuclear material at Tengen, Germany, 1994: (a) lead container, (b) plastic vial containing the powder and (c) Pu containing powder.



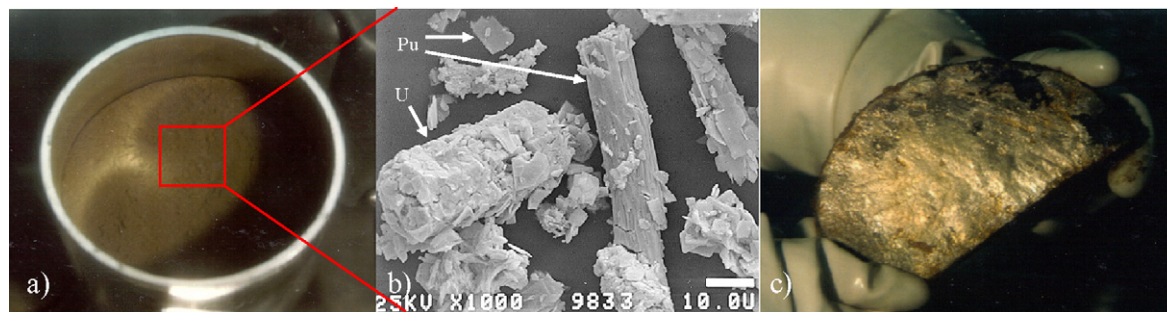


Fig. 4. Seizure of nuclear material at Munich airport, Germany, 1994: (a) MOX-powder, (b) SEM micrograph of the powder and (c) Li-metal.

have been significantly different. Also materials testing reactors using 36–90% enriched  $^{235}\text{U}$  can be excluded, because a higher  $^{238}\text{Pu}$  abundance would have been expected in this case. Most likely, a reactor type with a softer neutron spectrum (e.g. heavy-water or graphite-moderated reactors) was used for production. In this case, the nuclear reactor would have been operated with an initial fuel enrichment of 1.8% of  $^{235}\text{U}$  to yield the U composition of Table 2, assuming of course that the U and Pu are from the same reactor. This scenario was also proposed by the isotopic correlation in Fig. 1. However, the  $^{238}\text{Pu}$  and  $^{242}\text{Pu}$  abundances of the Pu are too high to originate from a low burn-up spent fuel of a RBMK-1000 reactor. Thus, most probably, the Pu is a mixture of different spent fuels (e.g. a low burn-up, i.e., weapons Pu, and a high burn-up fuel) and it has no direct connection with the uranium present. As the powder consists of two different Pu particle types, individual microparticles were analyzed by SIMS in order to determine if their isotopic compositions were identical or if the earlier determined isotopic composition for the bulk material was a result of mixing two different compositions. The  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in platelets and rod-shape particles were slightly different being  $0.1159 \pm 0.0012$  and  $0.1245 \pm 0.0026$ , respectively. However, the difference was much too small that one could conclude that one Pu particle type originates from weapons-grade Pu ( $^{240}\text{Pu}/^{239}\text{Pu} < 0.05$ ) and the other type from high burn-up fuel ( $^{240}\text{Pu}/^{239}\text{Pu} \sim 0.4\text{--}0.7$ ). Thus, the mixing must have taken place before the particles were produced.

The age of the Pu material was determined by gamma-spectrometry (bulk sample) and by SIMS (both particles types). The adjacent U-particles interfered in the SIMS measurements leading to biased results for the  $^{238}\text{Pu}/^{234}\text{U}$  and the  $^{239}\text{Pu}/^{235}\text{U}$  ratios (isobaric interferences for  $^{238}\text{U}$  and  $^{238}\text{Pu}$ , and for  $^{235}\text{U}$  from U-particles and  $^{235}\text{U}$  from  $^{239}\text{Pu}$  decay). As  $^{236}\text{U}$  is a minor isotope in the U material, its interference with the grown-in  $^{236}\text{U}$

from  $^{240}\text{Pu}$  decay was negligible. The ages determined for different particle types from the  $^{240}\text{Pu}/^{236}\text{U}$  ratio were similar (within the uncertainties) and they were consistent with the age obtained from the bulk measurement of the  $^{241}\text{Pu}/^{241}\text{Am}$  ratio by gamma-spectrometry. Both methods gave a production time around the end of  $1979 \pm 0.5$  years.

Even though the  $^{239}\text{Pu}$  enrichment is somewhat too low for military purposes, it is not impossible to produce a nuclear device with Pu of this quality. With regard to the Li-metal, its high enrichment in  $^6\text{Li}$  of 89.4% is noteworthy. One of the possible uses of  $^6\text{Li}$  is its ability to generate energetic tritons via the  $^6\text{Li}(n,\alpha)^3\text{T}$  reaction. Such energetic tritons would then be able to initiate DT nuclear fusion in a thermonuclear weapon. Therefore, it may not be a coincidence that Pu and  $^6\text{Li}$  were found together.

### 3.3. Theft of radioactive waste

In July 2001, Pu was found in a routine urine control of an employee who had been working in a decommissioned reprocessing plant in Karlsruhe, Germany. It was noticed that also his car and his apartment were contaminated. In addition, his girlfriend had incorporated Am and Cs. The employee was arrested and confessed that he had stolen two items, namely a plastic vial containing a liquid and a swipe cloth. He had managed to get both items out of the reprocessing plant about half a year earlier (Fig. 5). The analytical task was two-fold: first of all to confirm that the reprocessing plant in question was really the source of the material, and second, to verify whether the two stolen items were the only sources of the contamination and the incorporation. Besides the two stolen items, analyzed samples included vacuum cleaner bags from three apartments showing signs of contamination, house-hold gloves used to handle the stolen items and pieces of clothing.

All samples were measured first by gamma-spectrometry. The plastic vial contained  $^{238,239,241}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{134,137}\text{Cs}$  and  $^{125}\text{Sb}$ . In addition to these elements, also  $^{154}\text{Eu}$  was found in the swipe cloth. The other items contained the same nuclides in slightly lower activities. In order to quantify the U and Pu isotopes, part of the samples was dissolved in nitric acid and measured by TIMS and ICP-MS.

The isotopic compositions of Pu and U were similar in all samples and resembled the spent fuel last reprocessed in the plant before shut-down. The large amount of Cs ingested by

Table 2

Isotopic composition of Pu and U in MOX powder seized at Munich airport, Germany in 1994

Pu	wt.% $\pm 1$ s	U	wt.% $\pm 1$ s
238	$0.170 \pm 0.003$	234	$0.021 \pm 0.001$
239	$87.58 \pm 0.16$	235	$1.606 \pm 0.001$
240	$10.78 \pm 0.04$	236	$0.049 \pm 0.001$
241	$0.809 \pm 0.005$	238	$98.32 \pm 0.01$
242	$0.658 \pm 0.004$		

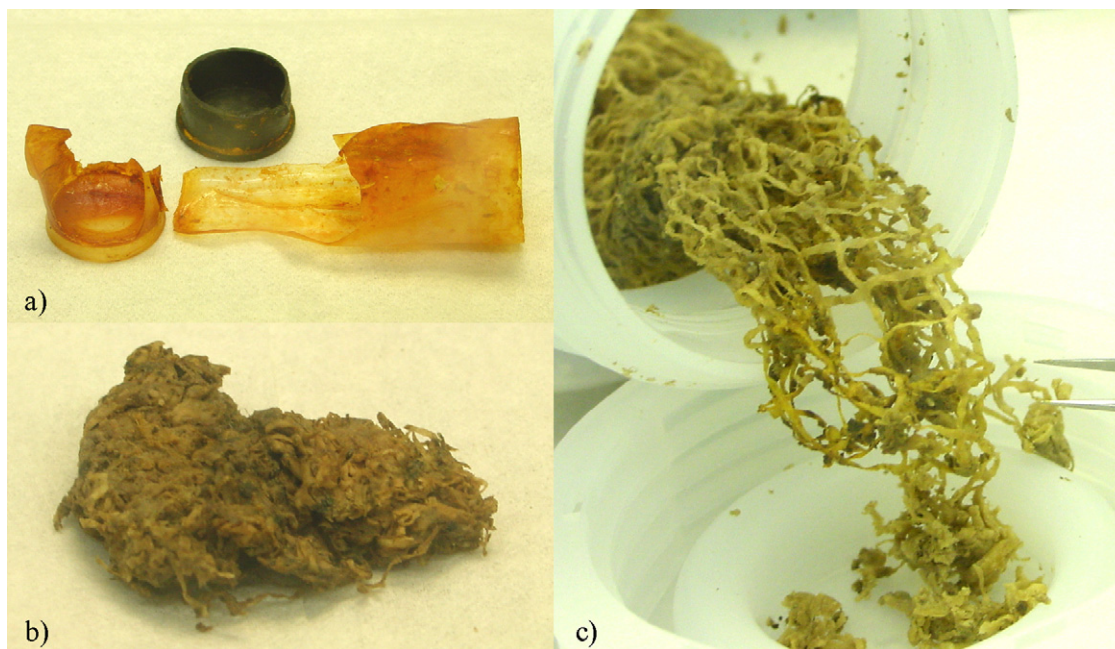


Fig. 5. Theft of nuclear material from WAK, Karlsruhe, Germany, 2001: (a) plastic vial, (b) cellulose fibers of a swipe cloth and (c) nylon part of a swipe cloth.

the thief's girlfriend was difficult to explain from the activity found in the two stolen items. However, the items were most probably washed before having been transferred for the investigations. Since Cs is fairly soluble in water, most of the Cs might have been lost at this stage. The thief was sentenced to prison for breaking the security regulations of the reprocessing plant and for unauthorized possession of radioactive material.

#### 3.4. Pu Round Robin

In 1998, six laboratories participated in a Plutonium Round Robin exercise launched by the International Technical Working Group on nuclear smuggling (ITWG) [12]. The results from ITU presented below were reported within three periods (24 h, 1 week and 2 months after receipt of material), which is the recommended practice of ITWG.

**24 h.** The material is PuO<sub>2</sub> powder with an isotopic composition typical of spent fuel from the commercial fuel cycle (57 wt.% <sup>239</sup>Pu, 26 wt.% <sup>240</sup>Pu by HRGS). The age is 4.7 ± 0.2 years determined from the <sup>241</sup>Pu/<sup>241</sup>Am ratio. However, as the Am was noticed to be inhomogeneously distributed, the age needed to be confirmed with other techniques.

**1 week.** The isotopic composition of Pu was confirmed by TIMS. The Pu content of 83.5 wt.% indicates the presence of major impurities. The <sup>241</sup>Am content was determined to be 2.1 wt.%. The material was likely to be used for MOX fuel production, however, due to the high Am content it is difficult to handle.

**2 months.** The ICP-MS analysis gave as main impurities Gd of natural composition and <sup>237</sup>Np. Electron microscopy investigations showed that the powder consists of PuO<sub>2</sub> platelets of 3.6 μm average size. This is typical for material produced by calcination of oxalates. The investigation also revealed that the

gadolinium was not detectable in the Pu-platelets, but it appeared separately.

**Final conclusion.** The Pu originates from spent fuel reprocessing of light-water reactor fuel. The reactor physics calculations indicate a burn-up of about 40 GWd/t in a PWR. The Np content is not typical for large commercial reprocessing plants in the European Union, but rather points to the shut-down pilot reprocessing plant WAK in Karlsruhe, Germany. The age determined from the <sup>238</sup>Pu/<sup>234</sup>U, <sup>239</sup>Pu/<sup>235</sup>U and <sup>240</sup>Pu/<sup>236</sup>U ratios was significantly lower than the one from the <sup>241</sup>Pu/<sup>241</sup>Am ratio, indicating that the Am was partly co-precipitated when the material was produced. The time of the production was determined to be the second half of 1997 ± 0.1 year. With additional information from a nuclear materials database [13], the Pu source was identified as the nuclear power plant at Stade (KKS), Germany.

#### 4. Conclusions

In the last 15 years we have seen the emergence of a new and potentially hazardous form of smuggling, namely smuggling of nuclear and radioactive materials. This has triggered the development of a new scientific discipline—nuclear forensics, where the main aim of the investigations is to find out the origin of the diverted nuclear material. Existing analytical techniques as used in material science, nuclear safeguards and environmental analysis, were adapted to the specific needs of nuclear forensic investigations. Additionally, new methodologies were developed, aiming at identifying other useful “nuclear fingerprints” in order to reduce the ambiguities often remaining in the interpretation of the analytical results. The hazard involved with nuclear smuggling and the potential relation with nuclear terrorism are the driving forces for deploying and further improving this methodology.

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