Universität für Bodenkultur Wien
University of Natural Resources
and Life Sciences, Vienna

DISSERTATION

Reference materials for age dating in nuclear forensics

Ausgeführt zum Zwecke der Erlangung des akademischen Grades

Doctor rerum naturalium technicarum

unter der Leitung von

Ao. Univ. Prof. Dipl.-Ing. Dr. techn. Thomas Prohaska

Department für Chemie, Abteilung für Analytische Chemie

Universität für Bodenkultur Wien

eingereicht

an der Universität für Bodenkultur Wien

von

Dipl.- Ing. Monika Sturm

Matr.Nr.: 0040239

Wien im Mai 2017

Acknowledgments

Many people were involved in accomplishing this scientific work; many more have been there along the way. I would like to thank all of you for being part of this journey. The list of those who helped to shape the visible output of work is long, but the list of all the wonderful people I met along the way who accompanied and shaped me is even longer. It would be an impossible task to name all of you, thus I will only name a few. I would like to thank…

…Yetunde Aregbe and Thomas Prohaska for making this project possible, for believing in me and in my abilities and in this project; and for their flexibility and their persistence.

….Stephan Richter for the privilege to work with him and for his support throughout the years.

….Roger Wellum for his excellent scientific support and his critical views and interesting discussions that ever so often sparked new ideas and shaped this work intrinsically.

…all my wonderful colleagues from IRMM for their moral and technical support and their friendship. I would like to thank Frances Kehoe, Roger Eykens, Sebastien Mialle, Rozle Jakopic, Carmel Hennessy, Mr Emons, Timotheus Altzitzoglou, Viktor Jobbagy and Heinz Kuehn for their support. Especially Heinz and Frances played a vital role as my ‘office family’ and as the best teachers for TIMS and glove box operation one can wish for.

…Klaus Mayer, Zsolt Varga, Adrian Nicholl from EC-JRC-ITU for their support and advice and their warm welcome at ITU.

...all my present and past colleagues from the VIRIS group especially Johannes Draxler, Monika Horsky, Ondrej Hanousek and Steffi Konegger-Kappel.

…my current colleague and friend Kevin Henderson from IAEA for all the help proofreading and for telling me to get a grip whenever needed.

…last but not least my family and my friends for supporting me and believing in me and my abilities.

Thank you all, I really appreciate it :-)

Abstract

Nuclear forensic investigations play a vital role in nuclear security. Nuclear forensic analyses' results need to be accurate and precise and it needs to be ensured that they can withstand scrutiny in a court of law and from the international community. Therefore Certified Reference Materials (CRMs) for nuclear forensic applications are indispensable, which has also been recently acknowledged in the 2016 Nuclear Security Summit's 'Certified Reference Material Fact Sheet'. At present there are no plutonium CRMs certified for their last separation date available. The determination of the age or the production date has been a pillar of nuclear forensic investigations for about three decades. Knowledge of the age of seized nuclear material can help considerably to limit the number of facilities where seized plutonium samples could have been produced or processed. The relationship of the results of the more regularly applied Pu/U chronometers ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U among each other and with the often neglected or dismissed radio-chronometer ^{242}Pu/^{238}U was scrutinized and re-evaluated. It has been shown that the relationship of these Pu/U chronometers relative to each other can not only boost the confidence in the obtained production date for a particular plutonium sample, but can also - in case of mismatched age dating results for different chronometers - help to reveal the history of the plutonium sample under investigation. The pattern formed by the Pu/U chronometers' age determination results may help to identify incomplete separation during the production or help to reveal the likely nature of a contamination with non-radiogenic uranium. A 'roadmap' for dating of plutonium materials via the respective Pu/U chronometers has been established. Furthermore, an optimized method for U/Pu separation has been developed and a novel approach for the measurement of uranium isotopes by Total Evaporation Thermal Ionisation Mass Spectrometry with a double filament arrangement combined with filament carburization has been investigated. This measurement approach allows the measurement of the isotopic composition of uranium samples that contain traces of plutonium. Separation of residual plutonium in the uranium fraction was achieved directly on the filament. The findings could also prove to be useful for other applications such as the measurement of ^{238}U and ^{238}Pu in mixed oxide fuel type samples without (complete) chemical separation. The scientific work was performed at the European Commission Joint Research Centre - Directorate G - Nuclear Safety & Security - Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (EC-JRC-G.2) Geel, Belgium, formerly Institute for Reference Materials and Measurements (EC-JRC-IRMM), in cooperation with the VIRIS laboratory of the University of Natural Resources and Life Sciences, Vienna, Austria.

Keywords:
Plutonium, Nuclear forensics, Age dating, Certified Reference Material, Mass Spectrometry

Kurzzusammenfassung

Nuklearforensische Untersuchungen spielen in der Nuklearsicherheit eine wichtige Rolle. Die Resultate nuklearforensischer Untersuchungen müssen exakt und richtig sein und es muss sichergestellt werden, dass diese sowohl einer genauen Überprüfung vor Gericht als auch von unabhängigen Wissenschaftlern standhalten. Die Unabdingbarkeit zertifizierter Referenzmaterialien wurde auch auf dem letzten Gipfel für Nukleare Sicherheit in einem ‘Certified Reference Material Fact Sheet’ dezidiert zum Ausdruck gebracht. Zum gegenwärtigen Zeitpunkt sind keine Plutoniumreferenzmaterialien verfügbar, die für den Zeitpunkt der letzten chemischen Trennung der Mutter- von den Tochternukliden zertifiziert sind. Die Bestimmung des Alters oder Produktionszeitpunkts nuklearen Materials wird seit etwa drei Jahrzehnten in der Nuklearforensik angewandt. Kenntnis über das Alter konfiszierten Nuklearmaterials kann erheblich dabei helfen, die Anzahl der möglichen Anlagen einzugrenzen in denen eine Plutoniumprobe hergestellt worden sein könnte. Die Beziehung der Ergebnisse der häufig angewandten Pu/U Chronometer ^{238}Pu/^{234}U, ^{239}Pu/^{235}U und ^{240}Pu/^{236}U zueinander und insbesondere mit dem oft vernachlässigtem Chronometer ^{242}Pu/^{238}U wurde untersucht und re-evaluiert. Es wurde gezeigt, dass die Beziehung der Pu/U Chronometer untereinander nicht nur die Exaktheit der "Altersbestimmung" erhöht, sondern auch – im Fall von nicht übereinstimmenden Resultaten – dabei helfen kann, die Herkunft der untersuchten Proben zu enthüllen. Das Profil, das die Ergebnisse der Pu/U-Chronometer bilden, kann dabei helfen eine unvollständige chemische Trennung zum Produktionszeitpunkt oder eine Urankontamination zu entlarven. Weiters wurde eine chemische U/Pu-Trennungsmethode entwickelt und optimiert sowie ein neuer Ansatz zur massenspektrometrischen Messung (Thermale Ionisationsmassenspektrometrie) von Uranisotopen mit Hilfe der Filamentkarbonisierung unter Anwendung der Doppelfilamenttechnik untersucht. Dieser Messansatz erlaubt die Messung des Uranisotopenverhältnisses in Uranproben, die Spuren von Plutonium enthalten. Eine verbesserte Abtrennung der in der aufgereinigten Uranfraktion verbliebenen Plutoniumspuren wurde während der Messung erreicht. Dieser Ansatz könnte sich auch für andere Anwendungen als nützlich erweisen, z. B. die Messung von ^{238}U und ^{238}Pu in Mischoxidproben. Die wissenschaftliche Arbeit wurde am Direktorat G in der Abteilung für Standards für nukleare Überwachung, Sicherheit und Brennstoffkreislauf der Gemeinsamen Forschungsstellen der Europäischen Kommission (EC-JRC-G.2), dem vormaligen Institut für Referenzmaterialien und Messungen (IRMM), in Geel, Belgien in Kooperation mit dem VIRIS Labor der Universität für Bodenkultur Wien durchgeführt.

Stichwörter:
Plutonium, Nuklearforensik, Altersbestimmung, Zertifizierte Referenzmaterialien, TIMS

Table of content

1 Introduction

1.1 The Nuclear fuel cycle

The nuclear fuel cycle serves the generation of electricity (so-called ‘nuclear power’). It consists of several complex stages and processes from manufacturing nuclear fuel, its irradiation in nuclear power reactors and treatment of the irradiated (spent) fuel. Spent fuel needs to be stored, reprocessed, recycled or disposed of (permanent storage) depending on the type of nuclear fuel cycle. A range of different nuclear reactors and several types of nuclear fuel cycles exist. The type of nuclear fuel cycle applied in any specific country depends on the state’s national policy (IAEA 2009). As the processes involved are very complex only a basic description can be given here. For more detailed information the reader is advised to refer to documents such as the International Atomic Energy Agency (IAEA) publication IAEA-TECDOC-1613 ‘Nuclear Fuel Cycle Information System’ (IAEA 2009) for further reading. Figure 1-1 represents an overview of the processes involved in the nuclear fuel cycle. Not all processes shown in Figure 1-1 and described below may be applicable to every specific nuclear fuel cycle.

A nuclear fuel cycle may be divided into three parts:

- The front-end processes of the fuel cycle occur before the nuclear fuel is irradiated in the nuclear reactor i.e. the production of uranium fuel from uranium that has not been irradiated before. These front-end processes start by locating suitable uranium ore deposits and the development of uranium ore mines and the mining of uranium ore. The uranium ore is subsequently converted into ammonium diuranate. This material is also known as uranium ore concentrate or ‘yellow cake’. It contains 80 to 90% U_3O_8. The production of uranium ore concentrate may involve milling and refining or in-situ leaching. The uranium ore concentrate is converted into other chemical forms in order to obtain UF_6. The UF_6’s ^{235}U content is subsequently increased to a level that is suitable for irradiation in the nuclear reactor. This process is referred to as ‘enrichment’. In this process natural uranium (NU) is split into the by-product depleted uranium (DU) and usually low-enriched uranium (LEU) (or in some cases high-enriched uranium (HEU)). Fuel rods that can be inserted into the reactor as nuclear fuel are produced from the enriched uranium (IAEA 2009).

- For nuclear power reactor operation the nuclear fuel is irradiated with moderated (slowed down) neutrons in the nuclear reactor in order to produce nuclear energy. Irradiation is a process that induces nuclear fission of the fissile nuclides such as ^{235}U in the nuclear fuel which in turn releases energy (heat). This heat is used for the production of steam, which is used for the production of electricity via turbines. The fission process results in the creation of daughter nuclides (fission products) and the release of additional neutrons. These neutrons further a self-sustaining controlled chain reaction. Fuel irradiation can last from one to several years depending on the reactor type (IAEA 2009).

- The term back-end processes describes processes that take place after the irradiated nuclear fuel is discharged from the nuclear reactor. It involves in situ fuel storage in fuel ponds (wet storage) which is followed by away-from-reactor storage in wet or dry conditions. Both in situ and away-from-reactor storage are considered interim storage solutions for spent fuel. The spent fuel may on the one hand be reprocessed by removing non-reusable components in order to recycle the reusable components for nuclear fuel production. On the other hand, the spent nuclear fuel may be conditioned for final disposal. The same is true for non-reusable components stemming from nuclear fuel reprocessing. This nuclear waste is supposed to be stored in facilities for final disposal without the intention of retrieving the material (IAEA 2009).

A nuclear fuel cycle can in some cases be run without recovery and reuse of nuclear materials from the spent fuel. This type of fuel cycle is referred to as a ‘once-through’ or ‘open’ nuclear fuel cycle. Once it is discharged from the reactor, it is ‘cooled’ in cooling ponds at the reactor. Subsequently, the spent fuel is retrieved from the in situ cooling pond and transported into storage locations. The fuel is eventually conditioned and placed in a final repository for long-term storage (IAEA 2009).

Alternatively, there is the so called ‘closed’ fuel cycle where nuclear material is recovered from the spent fuel and reused after appropriate cooling of the irradiated fuel. The plutonium and the remaining uranium are extracted from fission products, activation products, and other actinides present in the spent fuel to be reused in fuel for nuclear reactors. In this way it is possible to recover fissile nuclides such as ^{235}U that has not been burned up and new fissile nuclides such as ^{239}Pu that are produced during the irradiation in the nuclear reactor. The recovered uranium and plutonium may be reprocessed into mixed uranium plutonium oxide

(MOX) fuel for light water reactors and fast reactors. Recovered uranium can also be blended with HEU into new reactor fuel.

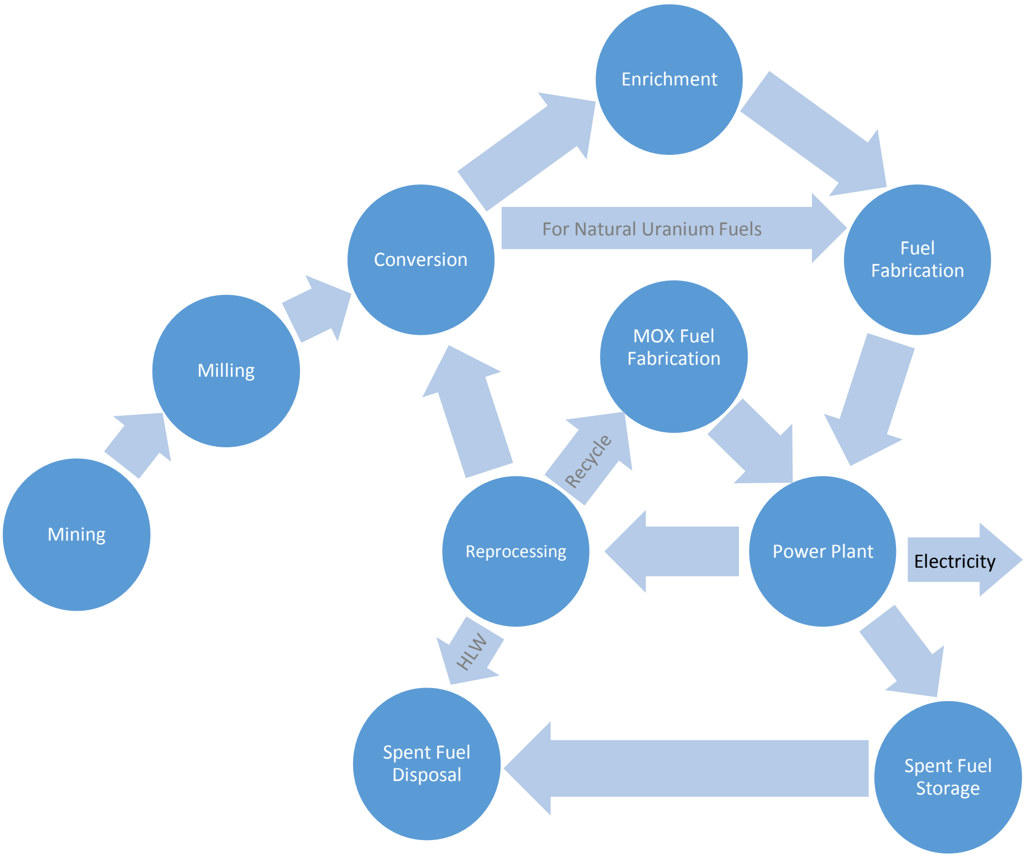


Figure 1-1: Schematic illustration of the nuclear fuel cycle (adapted from (IAEA 2009)). MOX stands for mixed oxide fuel; HLW stands for High Level Waste.

The fabrication of re-enriched uranium (ERU) fuels is also a common nuclear reactor fuel option for reprocessed fuel. Reprocessed uranium from different sources may be blended with fresh uranium in order to design nuclear reactor fuel with the desired properties for specific reactor types. Physical and chemical processes separate the above mentioned valuable components from irradiated nuclear fuel. These processes result in the desired reusable material and high level waste (HLW). The advantages of reprocessing are the more efficient use of fissile material as an energy resource and the reduction of the volume and radiotoxicity of the nuclear waste that eventually requires storage in deep geological repositories (IAEA 2009). The Purex process is the most commonly used technical process for the separation of fission products, uranium and plutonium, from spent nuclear fuel (Baumgärtner and Ertel 1980).

1.1.1 Uranium

The discovery of uranium was first presented to the Berlin Academy of Sciences in 1789 on September 24 by Martin Klaproth. Martin Klaproth named the element he discovered after the most recent planet to have been discovered. This planet had been named Uranus after the muse of astronomy and geometry Urania. Uranium was first extracted in the form of uranium oxide from the mineral pitchblende (Goldschmidt 1989). Natural uranium (NU) is considered a weakly radioactive element. It contains the uranium isotopes ^{234}U, ^{235}U, and ^{238}U (Bleise, Danesi et al. 2003). Their relative masses, half-lives and specific activities are shown in Table 1-1. The ^{238}U/^{235}U isotope ratio was found to vary slightly in nature (Weyer, Anbar et al. 2008). It should be noted that other uranium isotopes such as ^{232}U, ^{233}U, and ^{237}U are not present in NU (IAEA 2007). Minute amounts of ^{236}U (^{236}U/^{238}U $\leq 10^{-10}$) generated by neutron capture in ^{235}U may be present in natural U ores (Hotchkis, Child et al. 2000). Uranium occurs in nature in secondary minerals such as complex oxides, silicates, phosphates and vanadates, and in the form of uranite or pitchblende (uraninite) (Bleise, Danesi et al. 2003). The preparation of uranium metal was first accomplished in 1841 by the French chemist Eugène Peligot. Until the 1930s, the main application for uranium was the production of yellow glass with green fluorescence and glazes for ceramics and porcelain in orange, yellow, red, green and black. Uranyl nitrate has also been used in early photography. Only in the 1930s was the isotopic composition of NU revealed (Goldschmidt 1989). Uranium fission had been first suggested by Ida Noddack in 1934 (Noddack 1934). A 'bursting' of uranium was discovered in 1938 by Otto Hahn and Fritz Strassman (Hahn and Strassmann 1939) and theoretically explained in 1939 by Liese Meitner and Otto Frisch, who introduced the term ‘nuclear fission’ (Meitner and Frisch 1939). This discovery gave rise to the field of nuclear energy, making use of the naturally-occurring fissionable isotope ^{235}U, the fertile naturally occurring isotope ^{238}U and the artificially produced fissionable isotope ^{233}U (Morss, Edelstein et al. 2006).

Table 1-1: The relative masses of ^{234}U, ^{235}U and ^{238}U in natural uranium and their specific activities adapted from (Bleise, Danesi et al. 2003) and their respective half-lives (IAEA 1986)

Isotope	Relative mass (%)	Half-life (a)	Specific activity (Bq/g)
^{234}U	0.006	$2.457(3) \times 10^5$	231×10^6
^{235}U	0.72	$7.037(7) \times 10^8$	80011
^{238}U	99.3	$4.468(5) \times 10^9$	12455

^{238}U is the most abundant U isotope (Table 1-1). Possible parent nuclides of ^{238}U are ^{238}Pa and ^{242}Pu and its initial decay product is ^{234}Th (IAEA 2007). ^{238}U has the lowest specific activity of the naturally occurring uranium isotopes as shown in (Table 1-1) since the radioactivity of radio-nuclides depends on their half-lives (Bleise, Danesi et al. 2003).

^{235}U is a uranium fissile isotope contained in NU (Table 1-1). The initial decay product of ^{235}U is ^{231}Th (IAEA 2007). The high probability of ^{235}U undergoing fission after capturing a thermal neutron makes ^{235}U the most valuable uranium isotope in NU as it can be used for the generation of nuclear energy in a nuclear reactor (IAEA 2009). Its high probability of undergoing fission also makes ^{235}U the nuclide of interest for the generation of nuclear weapons (Smith, Kristo et al. 2008). Uranium materials are therefore categorized by their content of ^{235}U as shown in Table 1-2. LEU is usually used as power reactor fuel. DU is a by-product of enrichment processes as it is depleted in ^{235}U and ^{234}U compared to NU, its radioactivity is typically reduced to about 60 % of the radioactivity of NU (Bleise et al., 2003).

Table 1-2: Categories of uranium (Bleise, Danesi et al. 2003; Smith, Kristo et al. 2008)

Uranium type	^{235}U
Weapons-grade uranium (WGU), pure uranium metal	> 93 %
High-enriched uranium (HEU)	> 20 %
Low-enriched uranium (LEU)	< 20 % (typically 3 – 5 %)
Natural uranium (NU)	0.7 %
Depleted uranium (DU)	< 0.7 % (typically 0.2 - 0.3 %)

^{234}U is the third isotope that is contained in significant amounts in NU (Table 1-1). Its initial decay product is ^{230}Th (IAEA 2007). ^{234}U contributes to the same extent to the radioactivity of NU as ^{238}U. The reason for this is its relatively short half-life (Table 1-1) (Bleise, Danesi et al. 2003). ^{234}U is enriched along with ^{235}U in both centrifuge and diffusion enrichment processes. Hence, the amount content of ^{234}U has to be monitored during enrichment in order to keep its amount content within the internationally accepted product specification of a mass percentage < 1% relative to the mass of ^{235}U in the enriched uranium product. Nuclear fuel with an enrichment of 4% ^{235}U therefore typically contains slightly less than 0.04 % of ^{234}U. The reason for this specification is the fact that ^{234}U can absorb neutrons during reactor operation creating ^{235}U, which can in turn fission and release neutrons. This also leads to the need for higher ^{235}U enrichment in nuclear reactor fuel made from reprocessed uranium

(RepU) affecting the economy of RepU as it imposes the burden of additional enrichment (IAEA 2007).

In addition to the naturally-occurring uranium isotopes, spent uranium fuel and RepU contain synthetic uranium isotopes. ^{232}U, ^{233}U, ^{236}U, and ^{237}U are created during irradiation of uranium fuel in nuclear reactors. These uranium isotopes are called ‘minor uranium isotopes’ along with ^{234}U whereas ^{235}U and ^{238}U are termed ‘major uranium isotopes’.

During nuclear reactor operation, ^{236}U and ^{237}U are generated by successive neutron captures from ^{235}U. Likely parent nuclides of ^{236}U are ^{236}Pa, ^{236}Np, and ^{240}Pu. The amount content of ^{236}U present in irradiated uranium material is directly proportional to the burnup level of the nuclear fuel (IAEA 2007). ^{236}U acts like ^{234}U as a neutron absorbing isotope, also contributing to the need for higher ^{235}U enrichment in nuclear reactor fuel made from reprocessed uranium (RepU). As mentioned above, minute amounts of ^{236}U generated by neutron absorption in ^{235}U may be present in natural U ores (Hotchkis, Child et al. 2000).

1.1.2 Plutonium

Plutonium is often regarded as a man-made element. This widely-accepted perception may be connected to the sequence of events in the discovery of plutonium. In 1940, Dr Glenn T. Seaborg, Joseph W. Kennedy, Edwin M. McMillan, and Arthur C. Wahl first produced ^{238}Pu artificially through deuteron bombardment of ^{238}U. The newly-found element was named plutonium after the planet Pluto, following the trend set by the names of the then-recently discovered elements uranium and neptunium. The latter were named after planets in our solar system in the order of their distance from the sun, starting with Uranus. In 1941 it was discovered that ^{239}Pu can be formed via several intermittent stages by bombarding ^{238}U with neutrons. Since then other plutonium isotopes (^{228}Pu - ^{237}Pu) have been generated. The first clue for plutonium’s existence in nature was only obtained in 1948, when Dr Glenn T. Seaborg succeeded in isolating trace amounts of ^{239}Pu from pitchblende. Plutonium turned out to be a primeval element. Gigaton amounts of ^{239}Pu and ^{244}Pu were formed in supernova explosions during the formation of the universe and of earth (Wallner, Faestermann et al. 2015). These plutonium isotopes can thus be regarded as natural radionuclides humankind and nature have been exposed to since their beginnings. This so-called cosmogenic plutonium, however, decayed over time, as all plutonium isotopes are radioactive. Only minute traces of ^{244}Pu of primordial stellar origin exist on our planet’s crust. ^{239}Pu’s non-anthropogenic presence on earth can also be attributed to spontaneous neutron capture in ^{238}U in natural uranium ore deposits (Taylor 2001; Wilcken, Barrows et al. 2007). Plutonium needs to be regarded as highly radiotoxic due to its high alpha particles emission rate (Wallenius 2001).

Starting from 1945, the ‘nuclear age’ has led to the release of several tons of ^{239}Pu into the atmosphere. The major extent of such releases dates back to atmospheric nuclear weapon tests in the 1950s and 1960s. The five plutonium isotopes ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu are nowadays present on the surface of the Earth. All of these plutonium isotopes decay by the emission of α particles into uranium daughter nuclides except for ^{241}Pu, which decays by β decay forming ^{241}Am. ^{239}Pu and ^{240}Pu are most abundant (Taylor 2001). The isotopic composition of anthropogenic plutonium depends on the source material (type of uranium fuel; see Table 1-2) and its irradiation history. The isotopic composition of the resulting plutonium varies depending on the type of nuclear reactor, its neutron spectrum (thermal or fast neutrons), the neutron flux and the duration of the irradiation (burn-up) in the nuclear reactor. Different types of reactors differ in their neutron energy distributions and thus the yield of plutonium isotopes generated by neutron capture varies depending on the reactor type (Mayer, Wallenius et al. 2012). For example, irradiated nuclear fuel from reactors with a fast neutron spectrum contains primarily ^{239}Pu, while spent fuel from thermal reactors is richer in heavier plutonium isotopes (Wallenius 2001). The longer the nuclear fuel is exposed to neutron irradiation, the more plutonium is generated. In addition, more of the heavier plutonium isotopes are generated with longer duration of the irradiation of the nuclear fuel. The probability of neutron reactions such as neutron capture and fission is a function of the neutron energy (Mayer, Wallenius et al. 2012).

About a third of the energy generated in a nuclear power reactor using ^{235}U based fuel is generated by the fission of ^{239}Pu that has been generated from ^{238}U in the reactor (Taylor 2001). Although ^{239}Pu is the fissile plutonium isotope, plutonium materials are categorised by their ^{240}Pu content. This is due to the fact that ^{240}Pu is considered an undesired impurity for the manufacturing of nuclear weapons as it decays by spontaneous fission. Table 1-3 shows the categories of plutonium materials based on their ^{240}Pu content (Smith, Kristo et al. 2008).

Table 1-3: Categories of plutonium (Smith, Kristo et al. 2008)

Plutonium type	Description	^{240}Pu
Super-grade plutonium (SGPu)	pure plutonium metal	< 3 %
Weapons-grade plutonium (WGPu)	pure plutonium metal	< 7 %
Reactor-grade plutonium (RGPu)	produced in nuclear power reactors	> 19 %
Fuel-grade plutonium (FGPu)	produced in nuclear reactors	7 – 19 %
MOX-grade plutonium (MGPu)	recycled from MOX fuel	> 30 %

1.2 Nuclear Safeguards and Nuclear Security

1.2.1 Nuclear Safeguards

The term ‘nuclear safeguards’ traditionally refers to a set of technical measures by which the correctness and the completeness of the declarations made by states about their nuclear material and activities are verified. IAEA safeguards are applied to states that signed safeguards agreements with the IAEA (Goldschmidt 1999). Euratom safeguards are applied to all EU member states (EURATOM 2012).

As a consequence of the nuclear bomb detonations in Hiroshima and Nagasaki in Japan in 1945, the uncontrolled application of nuclear weapons technology was restricted. Hence, the necessity of nuclear safeguards was first recognized (Goldschmidt 1999).

IAEA Nuclear Safeguards

Discussing the possibility of uncontrolled spread of nuclear weapons technology, Dwight D. Eisenhower, the president of the USA at that time, spoke before the United Nations General Assembly in 1953. The proposals Eisenhower made concerned nuclear disarmament and the promotion of the peaceful use of nuclear energy. His proposals to tackle these issues are known as the ‘Atoms for Peace’ proposals. They were to become the basis for the IAEA Statute of 1957 (Goldschmidt 1999). The article III of the Statute of the International Atomic Energy Agency (IAEA 1989) states with regard to nuclear safeguards:

> *‘The Agency is authorized […] to establish and administer safeguards designed to ensure that special fissionable and other materials, services, equipment, facilities, and information made available by the Agency or at its request or under its supervision or control are not used in such a way as to further any military purpose; and to apply safeguards, at the request of the parties, to any bilateral or multilateral arrangement, or at the request of a State, to any of that State's activities in the field of atomic energy.’*

In 1957 the IAEA Treaty on the Non-Proliferation of Nuclear weapons (NPT) came into force. The NPT deals with the prevention of the proliferation of nuclear weapons, the pursuance of nuclear disarmament and the promotion of the peaceful uses of nuclear energy. The NPT recognises 5 nuclear weapon States (United States of America, Russian Federation, the United Kingdom, France, China) that have Voluntary Offer Agreements with the IAEA covering some or all of their peaceful nuclear activities (IAEA 1972).

In order to secure the legal basis for applying additional measures to strengthen IAEA nuclear safeguards the Model Additional Protocol (INFCIRC/540), was drawn up and approved by the IAEA Board in 1997. These additional measures allow the IAEA to obtain more information about a state’s nuclear programmes. It also allows IAEA inspectors access to additional locations in the State that are relevant to confirming the exclusively peaceful nature of the State’s nuclear programme (Goldschmidt 1999).

Material Balance Evaluation is a group of activities that have the objective of gaining additional assurance on the correctness and completeness of the nuclear material declarations. The safeguards mandate to independently evaluate the material balance (including Material Unaccounted For (MUF), Shipper-Receiver Differences (SRD), and the D statistic (D, quantification of observed discrepancies between inspection data and reported data)) fundamentally depends on the estimates of the measurement errors associated with all nuclear material quantities that enter the material balance. Uncertainty quantification in nuclear safeguards evaluation is primarily concerned with monitoring uncertainty of measurement systems at facilities under comprehensive safeguards agreements so that a material balance evaluation can be conducted and the MUF can be assessed for significance against that quantified uncertainty. To accomplish each of these Analysis Of Variance (ANOVA) methods are applied to paired operator-inspector verification measurements in order to estimate variance components (Walsh, Burr et al. 2017).

Euratom Nuclear Safeguards

The European Union (EU) has a unique regional nuclear safeguard system. The Treaty establishing the European Atomic Energy Community was signed in 1957 (EURATOM 2012) and is known as the Euratom treaty. All 28 member states of the European Union are parties to this treaty. The Euratom treaty states in articles 2 and 81, respectively (EURATOM 2012):

> *‘The Community shall […] make certain, by appropriate supervision, that nuclear materials are not diverted to purposes other than those for which they are intended’*

> *‘The Commission may send inspectors into the territories of Member States. […] [The Euratom] inspectors shall at all times have access to all places and data and to all persons who, by reason of their occupation, deal with materials, equipment or installations subject to the safeguards provided […] to the extent necessary in order to apply such safeguards to ores, source materials and special fissile materials’*

Euratom nuclear safeguards is European law and thus also applicable in the two European Nuclear Weapon States (United Kingdom and France). Euratom safeguards are based on the nuclear operators’ accounting for and declaration of the amounts of nuclear materials in their possession, as well as on the European Commission (EC) verifying the correctness and completeness of such declarations by means of conformity assessment practices. The Euratom safeguards system is based on decades of experience (EC 2014). It is a fully established system that foresees the continuous or intermittent presence of Euratom inspectors at nuclear facilities in the EU. Euratom safeguards conclusions are based on first layer assessment, which includes operators measurement system evaluation, physical verification of nuclear materials and material balance evaluation (Alique, Vaccaro et al. 2015). Measurement data are obtained through destructive and non-destructive assay for nuclear material balance evaluation. Containment and surveillance systems are set up and maintained. Auditing activities and the collection of historical measurement data are also among Euratom’s tasks (Thorstensen and Chitumbo 1995).

Euratom and IAEA co-operation in Nuclear Safeguards

Euratom and the IAEA co-operatively apply nuclear safeguards in order to improve cost-effectivity and efficiency (Thorstensen and Chitumbo 1995). These joined inspection efforts are based on the Euratom/IAEA verification agreement (INFCIRC/193) of 1973 (IAEA 1973). This agreement on the application of nuclear safeguards applies to EU member states that are non-nuclear weapon states and that are party to the NPT. In 1992 the ‘New Partnership Approach’ (NPA) was agreed upon by Euratom and the IAEA in order to further and improve the application of nuclear safeguards within the EU by avoiding the duplication of inspections and other efforts supporting nuclear safeguards.

Common safeguards activities of Euratom and the IAEA are comprised of arrangements termed the ‘observation regime’ and ‘joint team inspections’, which involve staff from both organizations. In ‘Joint team inspections’ inspection activities are performed by Euratom inspectors and IAEA inspectors or by Euratom inspectors under the observation of IAEA inspectors (Thorstensen and Chitumbo 1995). Whereas the IAEA distinguishes between nuclear weapon states and non-nuclear weapon states, the EC inspects all the civilian nuclear installations of the nuclear fuel cycle in the EU - also in France and the United Kingdom, who are the only EU Member States which possess nuclear weapons (EC 2014).

International Target Values

Nuclear safeguards require analytical measurements for the accountancy and control of nuclear material. The 1972 IAEA document INFCIRC/153 'The Structure and Content of Agreements Between the Agency and States Required in Connection with the Treaty on the Non-Proliferation of Nuclear Weapons' states (IAEA 1972):

> *'[…] the system of measurements on which the records used for the preparation of reports are based, shall either conform to the latest international standards or be equivalent in quality to such standards.'*

In nuclear safeguards related measurements this translates as meeting the International Target Values (ITVs) for Measurement Uncertainties in Safeguarding Nuclear Materials (IAEA 2010). ITVs are defined as

> *'[…] uncertainties to be considered in judging the reliability of analytical techniques applied to industrial nuclear and fissile material that are subject to safeguards' verification'* (IAEA 2010).

Operators of nuclear facilities and nuclear safeguards organizations are urged to use ITVs as a reference for the quality of measurements that can be achieved in nuclear material accountancy (Jakopic, Bauwens et al. 2011). The concept of ITVs was developed by the European Safeguards Research and Development Association (ESARDA) Working Group on Standards and Techniques for Destructive Analysis (WGDA). The IAEA adopted this concept in the early 1990s (Deron, Kuhn et al. 1994). The IAEA, ESARDA, the Institute for Nuclear Materials Management (INMM) and other expert groups reassessed the ITVs resulting in the publication of revised ITV values in 2010 (IAEA 2010).

Advancements in analytical techniques constantly lead to more stringent requirements for the performance of laboratories involved in nuclear material accountancy. State-of-the-art certified nuclear reference materials (CRMs) are of vital importance to keep up with these requirements. The European Commission Joint Research Centre – Directorate G – Nuclear Safety & Security - Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (EC-JRC-G.2) Geel, Belgium, formerly Institute for Reference Materials and Measurements (EC-JRC-IRMM) therefore develops and certifies CRMs tailor-made for reliable measurements in fissile material accountancy. Thereby EC-JRC-G.2 aids in fulfilling the EC's obligation under the Euratom Treaty (Jakopic, Bauwens et al. 2011).

1.2.2 Nuclear security

Nuclear security is aimed at preventing and detecting intentional unauthorized activities and crimes such as theft, sabotage, unauthorized access and illegal transfer that are linked to or directed towards nuclear and other radioactive materials or associated facilities and activities. Nuclear safeguards are based on international agreements such as INFCIRC 193 and INFCIRC 540 and have the rank of European law in the EU (IAEA 1973; IAEA 1997; EC 2014). Nuclear security is the responsibility of regulatory bodies at the national level (IAEA 2013). The president of the EC at that time José Manuel Barroso confirmed in his statement at the 2012 Seoul Nuclear Security Summit that the European Union is committed to countering proliferation and to ensure that the best safety, security and non-proliferation standards are followed in countries using nuclear energy (Barroso 2012). The importance of the international initiative on a holistic Safety, Security and Safeguards ('3S') concept for nuclear energy was confirmed at this summit (Seong-whun 2011). At the 2014 Nuclear Security Summit in The Hague, the Netherlands, 24 states signed a joint statement on Forensics in Nuclear Security. This statement encourages the states to work with one another, as well as with the IAEA, in the development and enhancement of nuclear forensics capabilities and standardisation (NSS 2014). The 2016 Nuclear Security Summit ‘Certified Reference Material Fact Sheet’ states that nuclear forensic analyses must yield accurate and precise results that can withstand scrutiny in a court of law and from the international community in order to be effective. Furthermore it describes the need for CRMs as 'indispensable' (NSS 2016). The EC-JRC strives to provide such CRMs and metrological conformity assessment tools for nuclear forensics and nuclear safeguards applications. Nuclear forensics serves nuclear security in helping to solve crimes involving nuclear material. Metrological traceability and quality assurance play a vital role in nuclear forensics.

The results of nuclear forensic investigations need thus not only be scientifically defensible but may also have to withstand being contested in a court of law or during a security response process (Varga, Venchiarutti et al. 2015).

1.3 Nuclear Forensics

Traditional forensic investigations are largely based on the ‘Locard principle’. This framework on criminal investigation has been largely based on the works of the French pioneer Edmont Locard (1877-1966) as well as the works of his predecessors and contemporaries. The Locard principle states that (criminal) events can be linked to the locations (crime scenes) and individuals involved in the event (victims and perpetrators) in the absence of human witnesses. Traces such as fibres of fabric, hair, blood stains, semen, tool marks, fingerprints and foot prints bare silent but factual witness to criminal events. Decades later DNA also became an ally of vital importance to crime scene investigation (Chisum and Turvey 2000).

The advent of the discovery of the first cases of smuggling and illicit trafficking of nuclear material in the early 1990s gave rise to a new discipline within the field of forensic investigation: nuclear forensics. Initially, existing techniques were borrowed from other disciplines such as nuclear safeguards application as specific methods catering specifically to the needs of nuclear forensic investigations were still to be developed. Contrary to identifying the suspect malefactor of the crime as described above, nuclear forensics’ main objective is to gather evidence on the history and origin of seized nuclear material, e.g. uranium or plutonium (Mayer, Wallenius et al. 2005). To address these tasks on an international level, the Nuclear Forensics International Technical Working Group (ITWG) was formed in 1995/1996. This group represents an international association of official responders to nuclear security events. The nuclear forensics experts of ITWG include scientists, law-enforcement, and regulatory officials. The ITWG works towards the best practices in forensic investigations involving nuclear or radioactive material as the object of the investigation as well as when traditional forensic investigations are conducted on items that are contaminated with such materials. Both types of investigations assist in the event of the discovery of nuclear or radioactive material out of regulatory control (Garrett, Mayer et al. 2014).

The goal of nuclear forensics is to use the information on the origin of nuclear material out of regulatory control for the prevention of future diversion and theft of nuclear material from the facility where the material originated from by means of enhancing physical protection measures (Mayer, Wallenius et al. 2005).

Hence, nuclear forensics is a technique whereby future events of a similar nature are prevented as opposed to the classical forensic investigative approach where the focus is largely based on bringing the suspected perpetrator of the crime to justice.

To this end, nuclear forensics utilizes the exclusion principle rather than directly identifying a person/event/location as is possible in an ideal case of traditional forensic investigation, for instance by the means of matching the DNA profile of a wrongdoer left behind at a crime scene with the DNA of a suspect.

In nuclear forensics a set of various parameters of seized nuclear material is investigated (Mayer, Wallenius et al. 2012):

- Isotopic composition and amount contents of major elements (plutonium, uranium)
- Presence and amount contents of impurities e.g. anionic impurities such as fluoride, chloride, nitrate, sulphate, and rare earth elements (REE)
- Isotopic composition of impurities e.g. strontium, lead and oxygen
- Physical appearance (dimensions of larger objects)
- Morphology of particle form and size of powders
- ‘Age’ or ‘production date’ of the material, i.e. the time since the last (complete) removal of the daughter nuclides from the parent material

All of the parameters listed above except the final one help in deciphering the production process of the material and the conditions the material has been subjected to such as burn up in a nuclear reactor and/or the reactor type the material was intended for. Strontium, lead and oxygen isotopes and REE patterns can help narrow down the sites where the uranium ore for producing uranium ore concentrates has been mined (Mayer, Wallenius et al. 2012).

The last parameter listed above in which forensic investigators are interested in is the ‘age’ of the material. On the one hand, the age of the material can be employed to derive the initial composition of the material at the time of its ‘production’ which in turn aids reconstructing the intended use and the production processes the material was subjected to (Wallenius, Peerani et al. 2000). On the other hand, knowledge of the age of the material helps significantly in reducing the number of facilities where the material could potentially have originated from. Facilities that went into operation after the determined ‘production date’ of the seized material can be excluded from the list of possible facilities of origin (Redermeier 2009). A detailed discussion on age determination for nuclear forensic purposes is given in the following chapters.

None of the characteristics listed above, however, is able to directly point to the origin of the seized material and to tell its history. Even careful consideration of all of the parameters for one particular material cannot directly give this information, although isotope correlation using computational programmes such as ORIGEN2/SCALE may be used, for instance, to predict a specific reactor type from the irradiation of seized material (Wallenius, Peerani et al. 2000). Careful interpretation and comparison with materials of similar characteristics with known origin and/or history is needed. Databases for the comparison of findings are therefore of vital importance.

The above-mentioned ITWG fosters a special task group called ‘national nuclear forensic libraries’. This task group works toward the establishment of national libraries that contain information about the nuclear and other radioactive material that is stored in a particular country or was manufactured there, including information about the history and the production process of the materials. Such a library could either be an electronic database or a sample archive. These libraries shall in the future allow the state to readily provide relevant information in case of nuclear security events (Garrett, Mayer et al. 2014).

The IAEA Illicit Trafficking Database (ITDB) was established in 1995 in order to help participating states to tackle nuclear security challenges such as illicit trafficking of nuclear material by enhancing the exchange of authoritative information regarding incidents among states. Furthermore, the ITDB supports the IAEA’s nuclear security programme for instance by analysing trends, threats and the performance of material security system (IAEA 2006).

Although only 4 out of 275 reported cases of illicit activities in a 13-year period from 1993 to 2006 involved plutonium according to the ITDB (IAEA 2006), illegal activities involving plutonium are of major concern from a national and nuclear security perspective (Byerly, Stanley et al. 2016).

1.4 Radio-chronometry

Radio-chronometry is based on the continuously changing elemental composition of various materials due to radioactive decay. The radioactive decay of an unstable parent nuclide leads to the formation of a radioactive disequilibrium with its decay products or so-called ‘daughter nuclides’. This radioactive disequilibrium arises from the radioactive decay of parent and also as ingrowth and subsequent decay of (grand) daughter nuclides (Faure 1977). This principle is routinely employed in the fields of geology and archaeology using different nuclide systems. Corals, bone fossils and marine carbonates can be dated via the $^{234}U/^{230}Th$ and the $^{235}U/^{231}Pa$ chronometers. $^{40}K/^{40}Ar$ and $^{87}Rb/^{87}Sr$ dating as well as the ^{14}C method are regularly used for the chronometry of a variety of rock, mineral and organic samples relevant to geology and archaeology (Gallup, Edwards et al. 1994; Edwards, Cheng et al. 1997). The above-mentioned nuclide systems are used to determine the time that has passed since the geological or organic structure in question was formed.

Unstable nuclides decay forming daughter nuclides following distinct schemes of nuclear decay. In the event that the daughter nuclide is also unstable it decays further into yet another daughter nuclide. The latter is sometimes referred to as granddaughter nuclide to the parent nuclide. In this fashion a so-called decay chain is formed. This process comes to an end once a stable nuclide is formed that does not decay any further (Watchman and Twidale 2002).

The prerequisites of radio-chronometry are (Watchman and Twidale 2002; Stanley 2012):

- There are no (or only negligible) amounts of the daughter nuclide present at the time of formation or production of the material. Any radio-chronometric age determination aims at determining the timespan between this ‘time zero’ and the time of the age determination experiment.

- The sample in question has remained a closed system from ‘time zero’ onwards. No addition or removal of either parent or daughter nuclides has taken place.

- Only ratios forming parent-daughter nuclide pairs that are changing over time are eligible for radio-chronometry until secular equilibrium is reached. At that point in time the number of atoms stemming from the decay of the parent radionuclide is equal to the number of atoms of the daughter radionuclide that are decaying. This means that any chronometer is only applicable for a certain time from ‘time zero’ onwards. This depends on the relationship of the half-lives of parent and daughter nuclide. Once a secular equilibrium is reached, the chronometer is rendered useless. In cases where the daughter nuclide’s half-life is very short a secular equilibrium between this daughter nuclide and its parent nuclide is reached very quickly. In such cases a ‘granddaughter’ nuclide with a more favourable half-life can replace the daughter nuclide in the chronometer. This principle is applied when dating uranium via the ^{235}U/^{231}Pa chronometer (Stanley 2012).

For the period from time zero to the point in time when a secular equilibrium is reached the age of a material can be determined given all of the above mentioned prerequisites are fulfilled. The maximum age that can be determined with a specific chronometer is an inherent property of that chronometer.

Equations 1.4.1 to 1.4.3 describe the process of age determination based on the radioactive decay of the parent and daughter nuclides (Stolz 2005).

The measured amount of the parent nuclides P at the time of the dating experiment (present time) is represented by P_t; t is the time span from the time of the production of the material to the time of the experiment and hence represents the age of the sample. The amount of the parent nuclide P at time zero when the material was formed or produced (t = 0) is P_0. D_t is the measured amount of the daughter nuclide D present in the sample at the time of the experiment. D_0 represents the amount of daughter nuclide D directly after the formation or production of the sample (t = 0). D_0 is assumed to be zero as otherwise the prerequisite for radio-chronometry is not fulfilled and dating of the material in question via this chronometer is rendered impossible. The decay constants λ_P and λ_D of the parent and the daughter nuclide are calculated from their respective half-lives $t_{1/2}$ according to Equation 1.4.3.

$$P_\mathrm{t} = P_0 \times \mathrm{e}^{-\lambda\_\mathrm{P} \times t} \qquad \text{Equation 1.4.1}$$

$$D_\mathrm{t} = D_0 \times \mathrm{e}^{-\lambda\_\mathrm{D} \times t} + \frac{\lambda_\mathrm{P} \times P_0 \times (\mathrm{e}^{-\lambda\_\mathrm{P} \times t} - \mathrm{e}^{-\lambda\_\mathrm{D} \times t})}{(\lambda_\mathrm{D} - \lambda_\mathrm{P})} \qquad \text{Equation 1.4.2}$$

$$\lambda = \frac{\ln 2}{t_{1/2}} \qquad \text{Equation 1.4.3}$$

Hence by assuming that the initial ratio of $D_0/P_0 = 0$ and determining the present ratio of $D_\mathrm{t}/P_\mathrm{t}$ the time span t (age) of the sample can be calculated. A detailed description of the calculation of the age is shown in Equations 1.6.2.5 to 1.6.2.8 for plutonium dating via the chronometer $^{239}Pu/^{235}U$ in chapter 1.6.2.

1.4.1 Age determination in Nuclear Forensics

Although radio-chronometry always applies the same principles, there are differences between age determination in disciplines such as geology and archaeology to age determination for nuclear forensic purposes:

- Nuclear forensic samples are man-made processed artefacts such as plutonium and uranium materials made from refined uranium ore as opposed to samples that have been formed by geological or biological processes such as rocks and corals.

- Nuclear forensic samples have a so-called ‘production date’ which represents the latest manipulation during which the daughter nuclides have been removed from the material leaving their respective parent nuclides behind. Therefore, as opposed to geological or biological samples, nuclear materials can be made ‘young’ again by repeated manipulation. Such manipulations (chemical separation, reprocessing) wipe out the aging history for that particular chronometer until the latest removal of daughter nuclides.

- The time spans looked at in nuclear forensics samples are distinctively different from the time spans of concern in the fields of geology and archaeology. Archaeology deals with millennia; geology is concerned with time spans in the 10^6 to 10^9 year range. In contrast to that nuclear forensics deals with samples that are only decades old at most (Wallenius and Mayer 2000).

As mentioned in chapter 1.3, none of the nuclear materials’ characteristics (isotopic composition and amount contents of major elements, impurities, physical appearance, and age) used in nuclear forensics investigations and nuclear safeguards point directly at the origin and history of seized material. The age of the material is, however, as opposed to the other characteristics listed above, a self-explaining parameter. This means that the determined age does not need to be compared to other samples. This unique feature makes the production date one of the most telling signatures in nuclear forensics (Varga, Venchiarutti et al. 2015).

Chapter 1.4.2 is dedicated to the age determination of plutonium, while a comprehensive overview of uranium radio-chronometry is beyond the scope of this work. Detailed discussions on uranium age determination can be found elsewhere (Mayer, Wallenius et al. 2012; Stanley 2012). A short overview is given here.

- The ^{234}U/^{230}Th chronometer is not only the most prevalent chronometer for the age determination of uranium in nuclear forensics investigations and in nuclear safeguards but has also been used extensively for dating geological samples (Stanley 2012).

- The ^{235}U/^{231}Pa chronometer uses the 'granddaughter' nuclide ^{231}Pa of ^{235}U instead of its daughter ^{231}Th. ^{231}Th has a very short half-life of only about 25.52 hours and hence quickly reaches a secular equilibrium with ^{235}U. This chronometer has been used for dating uranium materials for nuclear forensics studies as well as for dating geological and environmental samples (Stanley 2012).
- The ^{234}U/^{214}Bi chronometer also does not use the direct progeny ^{230}Th of ^{234}U, but a rather distant relation ($^{234}\text{U} \rightarrow {}^{230}\text{Th} \rightarrow {}^{226}\text{Ra} \rightarrow {}^{222}\text{Rn} \rightarrow {}^{218}\text{Po} \rightarrow {}^{214}\text{Pb} \rightarrow {}^{214}\text{Bi}$). This chronometer is only applicable to HEU where ^{234}U is abundant or to old uranium materials allowing enough time for a quantifiable ^{214}Bi ingrowth (Stanley 2012).
- The ^{233}U/^{229}Th chronometer is not very often employed in the age determination of uranium as ^{233}U is rare in most uranium samples (Stanley 2012).

1.4.2 Age determination of Plutonium

Table 1-4 lists the chronometers (^{241}Pu/^{241}Am, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{242}Pu/^{238}U) used for plutonium age determination and the respective half-lives of the parent (^{241}Pu, ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{242}Pu) and daughter nuclides (^{241}Am, ^{234}U, ^{235}U, ^{236}U and ^{238}U). For the age determination of plutonium only direct parent and daughter relationships are used unlike the age determination of uranium materials briefly described in chapter 1.4.1. A reset of the plutonium chronometers occurs for example during reprocessing of irradiated uranium fuel rods when the plutonium is separated from fission products by chemical processes. The daughter nuclides are also removed from the plutonium matrix during this process (Stepanov and Chekmarev 2008).

Table 1-5 gives a summary of literature concerning plutonium age determination during the last 30 years. Despite carful literature research no claims regarding the completeness of the list can be made.

Eleven out of the 23 articles listed employ only one out of the five available chronometers for plutonium age determination (Kirby and Sheehan 1984; Keegan and Gehrke 2003; Nguyen 2006; Varga, Surányi et al. 2007; Zhang, Zhu et al. 2008; Shinonaga, Donohue et al. 2009; Ramebäck, Nygren et al. 2012; Shinonaga, Donohue et al. 2012; Miyamoto, Esaka et al. 2013; Miyamoto, Suzuki et al. 2015; Alamelu and Aggarwal 2016). These studies solely employ the ^{241}Pu/^{241}Am chronometer. Given analytical strategy and instrumentation often used for determining the age of a plutonium sample via the ^{241}Pu/^{241}Am chronometer (determination of ^{241}Am mostly via alpha or gamma spectrometry) as opposed to the Pu/U chronometers (determination of U daughters mostly via TIMS or ICP-MS), this is not surprising. However, it is advantageous to use more than one chronometer whenever possible. On the one hand, if all results agree the confidence in the determined production date of the material is enhanced. On the other hand, if the production dates obtained by several chronometers do not match within their calculated uncertainties, erroneous conclusions can be avoided and additional information on the history of the material may be gained. Inconsistent production dates determined for one sample by different chronometers may be attributed to different events in the history of the sample:

- The sample may actually be a mix of two or more different materials of different production dates. This is a distinct possibility for powder materials (Wallenius, Lützenkirchen et al. 2007).

- The daughter nuclides may not have been completely removed during the ‘production’ of the material. This situation has to be always kept in mind as industrial processes and other manipulations often do not intend to remove the decay products quantitatively because a small fraction of decay products may not be critical for the intended use of the material.

- The integrity of the sample as a closed system is not certain. There may be the possibility of a cross-contamination of the sample material with natural or non-natural uranium. The presence of non-radiogenic uranium in plutonium samples must also be kept in mind as they may have been handled in facilities where uranium is present.

A mixture of different materials can only be resolved by subsampling single particles and analysing them separately, if applicable, whereas non-quantitative removal of decay products and contamination of plutonium samples can be resolved by analysing the relations between the results of the different chronometers. This process has been discussed in detail for the Pu/U chronometers in (Sturm, Richter et al. 2014).

All of the listed publications in Table 1-5 including the publications that are part of this thesis exclusively concern non-particle sample sizes (here termed bulk samples) except for six publications (Wallenius, Tamborini et al. 2001; Wallenius, Lützenkirchen et al. 2007; Shinonaga, Donohue et al. 2009; Shinonaga, Donohue et al. 2012; Miyamoto, Esaka et al. 2013; Miyamoto, Suzuki et al. 2015), which (also) deal with the age determination of plutonium particles.

Chapters 1.4.2.1 to 1.4.2.3 discuss plutonium age determination via the chronometers ^{241}Pu/^{241}Am, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{242}Pu/^{238}U. The work dedicated to the age determination of plutonium published in the scope of this thesis (Sturm, Richter et al. 2014; Sturm, Richter et al. 2016) concentrates on the age determination of plutonium via the Pu/U chronometers ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{242}Pu/^{238}U.

Table 1-4: The chronometers for plutonium age determination and the respective half-lives of the parent and daughter nuclides. The uncertainties are given as originally published: Standard uncertainties are displayed for reference (IAEA 1986); the expanded uncertainty (k = 2) is displayed for reference (Wellum, Verbruggen et al. 2009)

Chronometer	Half-life parent (a)	Reference	Half-life daughter (a)	Reference
^{238}Pu/^{234}U	87.7(3)	(IAEA 1986)	2.457(3) × 10^5	(IAEA 1986)
^{239}Pu/^{235}U	2.411(3) × 10^4	(IAEA 1986)	7.037(7) × 10^8	(IAEA 1986)
^{240}Pu/^{236}U	6563(7)	(IAEA 1986)	2.342(3) × 10^7	(IAEA 1986)
^{241}Pu/^{241}Am	14.325(24)	(Wellum, Verbruggen et al. 2009)	432.7(5)	(IAEA 1986)
^{242}Pu/^{238}U	3.735(11) × 10^5	(IAEA 1986)	4.468(5) × 10^9	(IAEA 1986)

1.4.2.1 The ^{241}Pu/^{241}Am chronometer for plutonium age determination

Out of the 23 publications listed in Table 1-5 eighteen employ the ^{241}Pu/^{241}Am chronometer (Kirby and Sheehan 1984; Moody 1995; Wallenius and Mayer 2000; Keegan and Gehrke 2003; Nguyen 2006; Nygren, Ramebäck et al. 2007; Varga, Surányi et al. 2007; Wallenius, Lützenkirchen et al. 2007; Zhang, Zhu et al. 2008; Chen, Chang et al. 2009; Shinonaga, Donohue et al. 2009; Spencer, Tandon et al. 2009; Ramebäck, Nygren et al. 2012;

Shinonaga, Donohue et al. 2012; Miyamoto, Esaka et al. 2013; Miyamoto, Suzuki et al. 2015; Alamelu and Aggarwal 2016; Byerly, Stanley et al. 2016). Eleven of these articles exclusively describe employing the ^{241}Pu/^{241}Am chronometer (Kirby and Sheehan 1984; Keegan and Gehrke 2003; Nguyen 2006; Varga, Surányi et al. 2007; Zhang, Zhu et al. 2008; Shinonaga, Donohue et al. 2009; Ramebäck, Nygren et al. 2012; Shinonaga, Donohue et al. 2012; Miyamoto, Esaka et al. 2013; Miyamoto, Suzuki et al. 2015; Alamelu and Aggarwal 2016).

Consequently, it is obvious from this literature review that the most prevalent measurement strategies for age dating via the ^{241}Pu/^{241}Am chronometer are gamma spectrometry (Wallenius and Mayer 2000; Keegan and Gehrke 2003; Nguyen 2006; Wallenius, Lützenkirchen et al. 2007; Ramebäck, Nygren et al. 2012) and alpha spectrometry in combination with either TIMS or with ICP-MS (Kirby and Sheehan 1984; Moody 1995; Varga, Surányi et al. 2007; Zhang, Zhu et al. 2008; Chen, Chang et al. 2009; Ramebäck, Nygren et al. 2012; Shinonaga, Donohue et al. 2012; Byerly, Stanley et al. 2016). The disadvantage of these methods is that they provide only results for the ^{241}Pu/^{241}Am chronometer and hence additional experiments (which are often outside of the scope of the project) are required to obtain age dating results for other chronometers with which to compare and validate the result of the ^{241}Pu/^{241}Am chronometer.

It is also possible to determine ^{241}Am by mass spectrometry despite the similarity of its mass to ^{241}Pu. This interfering isotope can be removed by chemical separation; the absence of plutonium in the purified americium fraction can be checked easily by monitoring masses of other plutonium nuclides during the americium measurement with a multi-collector mass spectrometer. The feasibility of the application of mass spectrometry for dating plutonium via the ^{241}Pu/^{241}Am chronometer has already been demonstrated (Wallenius and Mayer 2000; Nygren, Ramebäck et al. 2007; Chen, Chang et al. 2009; Spencer, Tandon et al. 2009; Miyamoto, Esaka et al. 2013; Miyamoto, Suzuki et al. 2015).

The reason for the rare application of TIMS or ICP-MS for the measurement of ^{241}Am is the lack of a suitable commercially available ^{243}Am IDMS (Isotope Dilution Mass Spectroscopy) CRM spike. This problem not only occurs during the age determination of plutonium via the ^{241}Pu/^{241}Am chronometer, but also during the accurate determination of ^{241}Am for nuclear safety and security proposed as well as nuclear safeguards. The IAEA 2014 Technical Meeting on Nuclear Reference Materials for Destructive Analysis recognized the need for such a ^{243}Am IDMS CRM spike. Recommendations towards the solution of this shortage were made. CEA/CETAMA (CEA/DEN Marcoule, France) and EC-JRC initiated a joint project for the preparation and certification of a ^{243}Am CRM spike (Fankhauser, Jakopič et al. 2016). Experiments concerning the age determination of plutonium via the ^{241}Pu/^{241}Am chronometer by TIMS conducted in the course of this thesis served as the 'pioneering' feasibility study for the above-mentioned certification project for a ^{243}Am IDMS CRM spike conducted at EC-JRC. The certification of this ^{243}Am CRM spike is, however, outside the scope of this doctorate thesis.

1.4.2.2 The ^{240}Pu/^{236}U, ^{239}Pu/^{235}U and ^{238}Pu/^{234}U chronometers for plutonium age determination

As far as plutonium chronometry via the Pu/U chronometers is concerned, usually at least three chronometers ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U are examined in parallel. These three chronometers are discussed in this chapter while the ^{242}Pu/^{238}U will be discussed separately in chapter 1.4.2.3.

Out of the twelve articles listed in Table 1-5 that employ at least one of the Pu/U chronometers, nine employ all three of the Pu/U chronometers discussed in this chapter (^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U) (Moody 1995; Wallenius, Peerani et al. 2000; Wallenius, Tamborini et al. 2001; Wallenius, Lützenkirchen et al. 2007; Spencer, Tandon et al. 2009; Sturm, Richter et al. 2014; Byerly, Stanley et al. 2016; Sturm, Richter et al. 2016; Varga, Nicholl et al. 2016). This is hardly surprising as the IDMS experiment that yields the amount content of the plutonium parent nuclides readily yields the amount contents of all available plutonium nuclides without the need for separate experiments. The same is true for the IDMS experiment yielding the amount contents of the uranium daughter nuclides.

Mass spectrometry is the method of choice for the age determination of bulk plutonium samples via the Pu/U chronometers: mostly exclusively TIMS (Moody 1995; Wallenius and Mayer 2000; Wallenius, Peerani et al. 2000; Wallenius, Lützenkirchen et al. 2007; Spencer, Tandon et al. 2009; Sturm, Richter et al. 2014; Sturm, Richter et al. 2016) and ICP-MS (Nygren, Ramebäck et al. 2007; Chen, Chang et al. 2009; Varga, Nicholl et al. 2016) are used in order to determine both parent and daughter nuclides.

For the age determination of plutonium particles via Pu/U chronometers, secondary ion mass spectrometry (SIMS) has been used (Wallenius, Tamborini et al. 2001; Wallenius, Lützenkirchen et al. 2007).

The ^{240}Pu/^{236}U chronometer for plutonium age determination

Concerning the Pu/U chronometers, the ^{240}Pu/^{236}U can be considered the most robust among these as far as contamination with non-radiogenic uranium is concerned. Its result will not be altered by the presence of NU as ^{236}U is not present in natural uranium (De Laeter, Boelke et al. 2003). The risk of an alteration of the age dating result of the ^{240}Pu/^{236}U chronometer by non-radiogenic uranium rich in ^{236}U has been assessed and discussed in detail by Sturm et al. (Sturm, Richter et al. 2014) and was deemed unlikely. Hence, the ^{240}Pu/^{236}U chronometer can be used for assessing the nature of non-radiogenic contamination of a plutonium sample in the event that the other U/Pu chronometers do not match the ^{240}Pu/^{236}U chronometer and each other (Sturm, Richter et al. 2014).

Therefore it is not surprising that all articles featured in Table 1-5 which use Pu/U chronometers also use the ^{240}Pu/^{236}U chronometer: The ^{240}Pu/^{236}U chronometer is often used in combination with the ^{238}Pu/^{234}U and ^{239}Pu/^{235}U chronometers (Moody 1995; Wallenius, Peerani et al. 2000; Wallenius, Tamborini et al. 2001; Wallenius, Lützenkirchen et al. 2007; Spencer, Tandon et al. 2009; Sturm, Richter et al. 2014; Byerly, Stanley et al. 2016; Sturm, Richter et al. 2016; Varga, Nicholl et al. 2016). Two of the articles rely solely on the ^{240}Pu/^{236}U chronometer among the Pu/U chronometers (Nygren, Ramebäck et al. 2007; Chen, Chang et al. 2009) and one uses the ^{240}Pu/^{236}U chronometer in combination with the ^{239}Pu/^{235}U chronometer only (Wallenius, Peerani et al. 2000).

The ^{239}Pu/^{235}U chronometer for plutonium age determination

The ^{239}Pu/^{235}U chronometer's age dating result is usually measured along with other Pu/U chronometers. Its major advantage is its sensitivity to contamination of the plutonium sample with HEU. In such a case this chronometer may yield an older age compared to the age dating results of the ^{238}Pu/^{234}U and the ^{240}Pu/^{236}U chronometers (Sturm, Richter et al. 2014). Ten out of the twelve articles that use Pu/U chronometers shown and featured in Table 1-5 use ^{239}Pu/^{235}U in combination with other Pu/U chronometers (Moody 1995; Wallenius and Mayer 2000; Wallenius, Peerani et al. 2000; Wallenius, Tamborini et al. 2001; Wallenius, Lützenkirchen et al. 2007; Spencer, Tandon et al. 2009; Sturm, Richter et al. 2014; Byerly, Stanley et al. 2016; Sturm, Richter et al. 2016; Varga, Nicholl et al. 2016).

The ^{238}Pu/^{234}U chronometer for plutonium age determination

The ^{238}Pu/^{234}U chronometer's result is less straightforward to obtain than those for the ^{239}Pu/^{235}U and ^{240}Pu/^{236}U chronometers. A peak-tailing correction needs to be performed for the considerably smaller ^{238}Pu signal for influences from the significantly bigger ^{239}Pu in order to avoid artefacts. However it is worthwhile employing the ^{238}Pu/^{234}U chronometer, as it is as powerful indicator for incomplete removal of the radiogenic uranium daughters at the 'production date' in case the ^{238}Pu/^{234}U chronometer gives a younger age compared the

^{239}Pu/^{235}U and ^{240}Pu/^{236}U (and ^{242}Pu/^{238}U) chronometers. Furthermore, the ^{238}Pu/^{234}U chronometer's age result can in such a case help to establish a maximum age of the sample (Sturm, Richter et al. 2014).

Considering the publications listed in Table 1-5, the ^{238}Pu/^{234}U chronometer has exclusively been used in combination with both the ^{239}Pu/^{235}U chronometer and the ^{240}Pu/^{236}U chronometer (Moody 1995; Wallenius, Peerani et al. 2000; Wallenius, Tamborini et al. 2001; Wallenius, Lützenkirchen et al. 2007; Spencer, Tandon et al. 2009; Sturm, Richter et al. 2014; Byerly, Stanley et al. 2016; Sturm, Richter et al. 2016; Varga, Nicholl et al. 2016).

1.4.2.3 The ^{242}Pu/^{238}U chronometer for plutonium age determination

The nuclide pair ^{242}Pu/^{238}U can be used as a chronometer for the age determination of plutonium but it is usually dismissed as of little value.

On the one hand, it is rather cumbersome to obtain a meaningful result from this chronometer: the amount content of radiogenic uranium in aged plutonium samples is low due to the long half-life of the mother nuclide ^{242}Pu. In addition to that, the amount content of ^{238}Pu present in plutonium samples is usually substantial. This poses an analytical challenge as the masses of ^{238}Pu and ^{238}U cannot be distinguished from each other even in stat-of-the-art mass spectrometers. Hence, despite chemical separation of the uranium fraction from the plutonium matrix special provisions have to be applied in order to obtain a meaningful result for the ^{238}U amount content. Either additional methods such as alpha spectrometry for the determination of the remainder of ^{238}Pu in the uranium fraction need to be employed or special measurement conditions such as a combination of carburized TIMS filaments and a correction via the remainder of ^{239}Pu as proposed in (Sturm, Richter et al. 2016) need to be applied. These special provisions lead to higher uncertainties for the age dating results of this chronometer, rendering it less attractive as a chronometer considering the number of relatively care-free chronometers (^{241}Pu/^{241}Am, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and, ^{240}Pu/^{236}U) available for the age determination of plutonium.

On the other hand, the low amount content of radiogenic ^{238}U in aged plutonium samples renders the ^{242}Pu/^{238}U chronometer extremely sensitive to the presence of non-radiogenic uranium. Especially as ^{238}U is not only the major nuclide in NU but is also not scarce in many other uranium materials from LEU to HEU.

However in these apparent 'weaknesses' of the ^{242}Pu/^{238}U nuclide pair as chronometer for the age determination of plutonium, lies its strength as a very powerful indicator for the presence of non-radiogenic uranium (Sturm, Richter et al. 2014).

Although the sensitivity of the ^{242}Pu/^{238}U nuclide pair to contamination with uranium at trace levels is recognised (Moody 1995; Mayer, Wallenius et al. 2012; Varga, Nicholl et al. 2016), its results have not been investigated further for additional information on non-radiogenic uranium contained in the sample. For instance unexpected amounts of ^{238}U were dismissed as traces of NU from chemicals used in the preparation of the samples for measurement although ‘not comfortably so’ as more ^{238}U than expected from chemicals had been found (Moody 1995).

Some interest in the ^{242}Pu/^{238}U chronometer has arisen recently (Byerly, Stanley et al. 2016) which seems to be associated with research that has been published as part of this thesis (Sturm, Richter et al. 2014). Within this work, the use of the ^{242}Pu/^{238}U nuclide pair as a powerful indicator for the presence of non-radiogenic uranium in aged plutonium samples and also as a tool to determine the nature of such a contamination has been clearly demonstrated (Sturm, Richter et al. 2014).

Table 1-5: An overview of literature concerning age determination of plutonium. CPC stands for Controlled potential coulometry, Alpha for alpha spectrometry, Gamma for gamma spectrometry, and WDX for Wavelength-Dispersive X-ray spectrometry; b indicates analysis of bulk material while p indicates the analysis of particles

^{238}Pu/^{234}U	^{239}Pu/^{235}U	^{240}Pu/^{236}U	^{242}Pu/^{238}U	^{241}Pu/^{241}Am	Method	Bulk/ Particle	Reference
				x	Alpha/MS	b	(Kirby and Sheehan 1984)
x	x	x	x		TIMS	b	(Moody 1995)
				x	Gamma		
				x	Alpha /TIMS		
x	x	x		x	TIMS	b	(Wallenius and Mayer 2000)
				x	Gamma		
	x	x			TIMS	b	(Wallenius, Peerani et al. 2000)
x	x	x			SIMS	p	(Wallenius, Tamborini et al. 2001)
				x	Gamma	b	(Keegan and Gehrke 2003)
				x	Gamma	b	(Nguyen 2006)
		x		x	ICP-MS	b	(Nygren, Ramebäck et al. 2007)
				x	Gamma	b	(Wallenius, Lützenkirchen et al. 2007)
		x			SIMS	p	
x	x	x			TIMS	b	
				x	Alpha/ ICP-SFMS	b	(Varga, Surányi et al. 2007)
				x	Alpha/ TIMS	b	(Zhang, Zhu et al. 2008)
				x	WDX/TIMS	p	(Shinonaga, Donohue et al. 2009)
x	x	x		x	TIMS	b	(Spencer, Tandon et al. 2009)
		x		x	ICP-MS	b	(Chen, Chang et al. 2009)
				x	Alpha/ICP-MS		
				x	Alpha/LSC		
				x	Gamma	b	(Ramebäck, Nygren et al. 2012)
				x	ICP-MS/ Alpha		
				x	Alpha /TIMS/ICP-MS	p	(Shinonaga, Donohue et al. 2012)
				x	ICP-MS	p	(Miyamoto, Esaka et al. 2013)
x	x	x	x		TIMS	b	(Sturm, Richter et al. 2014)
				x	ICP-MS	p	(Miyamoto, Suzuki et al. 2015)
x	x	x	x		TIMS	b	(Sturm, Richter et al. 2016)
x	x	x	x		ICP-MS	b	(Varga, Nicholl et al. 2016)
				x	Alpha/ TIMS	b	(Alamelu and Aggarwal 2016)
x	x	x	x		TIMS/CPC	b	(Byerly, Stanley et al. 2016)
				x	TIMS/ Alpha/ Gamma		

1.5 Certified Reference Materials

In general the aim of any measurement is to compare the result with those of others. Internationally accepted quality assurance tools aid in establishing confidence in the comparability and reliability of measurement results. Quality control and quality assurance systems aim at ensuring a high level of confidence in these results. This is achieved by implementing reference measurements, the use of certified reference materials (CRMs), and tools to assess the conformity of measurements such as inter-laboratory comparisons (Jakopic, Bauwens et al. 2011). In addition, confidence in the integrity and quality of measurement results and services is of great importance. An increasing number of laboratories therefore strive to be accredited for ISO/IEC 17025 in order to provide evidence that they fulfil the general requirements for the competence of testing and calibration laboratories and in order to enhance the confidence in the integrity and quality of their measurement results and services (ISO 2005) (Sturm, Richter et al. 2010).

As '*the value of chemical measurements depends upon the level of confidence that can be placed in the results*' (CITAC and Eurachem 2002), results obtained by different laboratories and methods need to be inter-comparable. This is established by linking the result of the measurement to a primary unit of measurement defined in the International System of Units (SI). Traceability to primary unit of measurement can be achieved by comparison of known reference values through the use of CRMs. CRMs are needed to demonstrate that the measurement performance meets the requirements of the analysis. The validation of measurement procedures and calibration of instruments also require CRMs (Sturm, Richter et al. 2010).

CRMs are materials that are sufficiently homogeneous and stable with respect to one or more specified properties as stated in ISO Guide 30. The accompanying CRM certificate contains the value of the specified property, its associated uncertainty and a statement of metrological traceability. For the certification of a material as a CRM, the material needs to be characterized to be fit for the intended use (ISO 2008). As analytical instrumentation and measurement techniques evolve towards increased precision the values and uncertainties of a CRM need to meet state-of-the-art of analytical techniques. Hence, a constant effort to re-certify existing CRMs in order to issue up-dated certificates and to create new CRMs needs to be undertaken (Jakopič, Sturm et al. 2013).

One of the providers of CRMs to the international community is the EC-JRC in Geel, Belgium. The EC-JRC-G.2 not only operates European Union Reference Laboratories in but also deals with the reliability and accuracy of health diagnostics, food and feed safety and quality, advanced materials, aviation security, and nuclear safety and security (EC-JRC 2016).

1.5.1 Certified Reference Materials for nuclear applications

As far as nuclear safety and security is concerned, EC-JRC provides an extensive range of uranium and plutonium CRMs certified for concentrations and isotope ratios. Other major providers of nuclear CRMs are the US Department of Energy New Brunswick Laboratory Programme Office (NBL), Argonne, Illinois, USA (Mathew, Essex et al. 2014; NBL 2017), CETAMA (CEA Committee for the establishment of analysis methods), France (Hanssens, Viallesoubranne et al. 2008) and V.G. Khlopin Radium Institute (KRI), St Petersburg, Russian Federation (Stepanov 1990).

Plutonium and uranium CRMs play a vital role in nuclear safeguards for fissile material control, nuclear forensic investigations and in environmental and geological research. In order to comply with the quality control requirements analytical instrumentation needs to be calibrated, methods need to be validated and the reproducibility of measurement results needs to be assured.

Organisations such as the ESARDA, the INMM and the IAEA provide international platforms linking reference material producers, safeguards authorities and laboratories such as the IAEA and the Japan Atomic Energy Agency (JAEA) laboratories. Their aim is to foster the development of nuclear CRMs by organising technical meetings and workshops (Jakopič, Sturm et al. 2013).

As mentioned previously the availability of CRMs that reflect state-of-the-art analytical performance is of vital importance. This is especially true for nuclear CRMs that are used on a routine basis in nuclear laboratories involved in safeguards verification measurements and nuclear material accountancy. Some of these CRMs have, however, been produced and certified decades ago (IAEA 2010; Jakopic, Bauwens et al. 2011).

A powerful tool to meet this need are inter-calibration campaigns comparing CRMs on a metrological basis by applying state-of-the-art measurement procedures (Jakopič, Verbruggen et al. 2010).

Traditional nuclear CRMs for bulk analysis of nuclear material in routine safeguards applications exist in different forms in order to meet the specific requirements for a variety of applications. They can be grouped as follows:

- Elemental composition: nuclear CRMs may contain either uranium, plutonium or thorium or a defined mix of uranium and plutonium (IRMM 2015). Mixed plutonium/uranium CRMs for instance are used as IDMS ‘spikes’ for samples from reprocessing plants and nuclear fuel solutions that contain both uranium and plutonium (Jakopič, Sturm et al. 2013; Jakopič, Aregbe et al. 2016).
- Application: depending on the intended use of the CRM two categories can be distinguished:
    - So called ‘spike CRMs’ are used for IDMS (De Bièvre and Debus 1965; De Bièvre and Peiser 1997). These CRMs are very well characterized for their isotopic composition as well as amount content. Low uncertainties are of vital importance for both properties as they are used for the determination of the amount content of the analyte in the sample. Large uncertainties of a spike CRM easily become the by far major component in the uncertainty of the measurement result. Fit-for-purpose uncertainties for IDMS spikes are especially important for material accountancy in nuclear safeguards verification measurements in view of the concept of ‘material unaccounted for’ (MUF) where the statistical significance of inspector-operator differences is assessed (IAEA 2010). These CRMs must be kept under weight control if they are in the liquid form and intended for repeated use after the initial opening of the vessel containing the CRM. They are often highly enriched in a nuclide that is not commonly found in the sample at all or only at trace levels such as ^{233}U (Jakopič, Bauwens et al. 2013). The advantage of these CRMs is that a simplified form of the IDMS calculation can be used and the measurement of the un-spiked fraction of the sample can be omitted. This is the case for instance in un-irradiated uranium samples which can be spiked with ^{233}U. However, natural uranium is also routinely used as an IDMS spike in safeguards laboratories, when the samples in question are known to differ in their isotopic composition from natural uranium. Double spikes contain two

spiking isotopes that are not present in typical samples such as ^{233}U and ^{236}U in a 1:1 ratio with very low abundances of the other uranium nuclides. By applying these double spikes internal mass fractionation corrections can be applied for high precision isotope ratio measurements in the sample (Verbruggen, Alonso et al. 2008).

  - ‘Isotopic CRMs’ or ‘Isotopic Reference Materials’ (IRMs) (Jakopič, Bauwens et al. 2013) are primarily certified for the isotopic composition of either uranium, plutonium or thorium (IRMM 2015). In terms of safeguards verification measurements the major isotope ratios of $^{235}U/^{238}U$ and $^{240}Pu/^{239}Pu$ are especially of interest for verification measurements checking the completeness and correctness of states’ declarations. However, nuclear material analysis in safeguards is increasingly making use of the information inherent to the material, such as the minor isotope ratio signatures (ASTM 2016). Contrary to Euratom safeguards measurements, uncertainties are not calculated for routine measurements of isotope ratios in IAEA safeguards samples by TIMS although isotopic CRMs are used as Quality Control (QC) standards and the results of these are checked against the uncertainties stated on the CRM certificates as well as International Target values (ITVs) (IAEA 2010). In addition to the use of isotopic CRMs as QC standards for TIMS and ICP-MS, they also serve as mass fractionation standards for Total Evaporation (TE) TIMS measurements (Jakopic, Richter et al. 2009; Sturm, Richter et al. 2014) and Modified Total Evaporation (MTE) TIMS measurements. For the latter there is an increasing demand for isotopic CRMs with low uncertainties on the minor isotope ratios of uranium i.e. $^{234}U/^{238}U$ and $^{236}U/^{238}U$ (Richter and Goldberg 2003; Richter, Kühn et al. 2011). In ICP-MS measurements isotopic CRMs also serve as standards for mass bias correction (Kappel 2012).

- Physical form and packaging: nuclear CRMs can be distinguished by their physical appearance (liquid, solid, gaseous):

  - Gaseous/solid UF_6 CRMs are distributed in Monel (copper-nickel alloy) ampoules (IRMM 2015) or occasionally P-10 Teflon tubes which are frequently used for subsampling UF_6 (Neuhoff 2008). These CRMs are intended to be used for calibration for isotope mass spectrometry measurements.

- Isotopic CRMs are often supplied as a solid such as U_3O_8 for uranium (Neuhoff 2008), and dried plutonium nitrate (De Bièvre 1996) or plutonium sulphate tetrahydrate for plutonium (Uriano 1982).
- Liquid isotopic plutonium and uranium CRMs in nitric acid solutions are also common (IRMM 2015). IDMS spikes are supplied either in the liquid form or as a solid as described below. In order to avoid changes in the amount content of the analyte caused by evaporation of the solvent (such as 1 M nitric acid), they are distributed in sealed quartz ampoules for uranium (Verbruggen, Alonso et al. 2008) and in glass vials for plutonium (Emons 2011).
- So called Large Dried Spikes (LSDs) are distributed in the form of evaporated solutions in penicillin vials. In order to ensure its integrity, the entire spike must be fixed to the bottom of the vial and can be embedded in a layer of an organic polymer such as Cellulose Acetate Butyrate (CAB) as stabiliser (Buják, Delva et al. 2017). This is of importance because such plutonium/uranium spikes are used in reprocessing plants and at the Euratom safeguards on-site laboratories for nuclear accountancy and verification measurements of the uranium and plutonium amount contents in solutions of spent nuclear fuel. An aliquot of sample is directly weighed into the vial containing the dried spike and it must be ensured that all of the spiking material readily dissolves in the sample. The spiking material must be prevented from relocating to places inside the penicillin vial where it is inaccessible for dissolution such as the cap (Jakopic, Bauwens et al. 2011).

Ideally, the types of nuclear CRMs described above are produced gravimetrically from very well characterized high-purity metal and compounds such as purified oxides (Verbruggen, Alonso et al. 2008; IRMM 2015). The certification process is often linked to round-robin exercises and inter-calibration with existing CRMs (Jakopič, Verbruggen et al. 2010).

1.5.2 Certified Reference materials for nuclear age determination

For nuclear forensic and nuclear safeguards investigations of samples of special interest another specific type of reference material is needed: CRMs for the age determination of nuclear material of plutonium and uranium are needed for instrument calibration, quality control, method validation and quality assurance. This is of particular importance during nuclear forensic investigations as the results need to be scientifically and above all juridically sound as they may be contested during the security response or the prosecution process. (Varga, Venchiarutti et al. 2015).

Recently the CRMs IRMM-1000a and IRMM-1000b for age determination of uranium via the $^{234}U/^{230}Th$ chronometer were released by the EC-JRC (Varga, Nicholl et al. 2012; Varga, Venchiarutti et al. 2015; Venchiarutti, Varga et al. 2016). CRM-125A uranium dioxide-pellets (Bakhtiar 2013a) and CRM U630 triuranium octoxide (Bakhtiar 2013) are also radio-chronometry standards for uranium age determination based on the $^{234}U/^{230}Th$ chronometer. CRM-125A and CRM U630 are certified for 'model purification dates', while IRMM-1000a and IRMM-1000b are certified for the production date of the material.

However, no CRM currently exists for the age determination of plutonium samples, although a need for such a CRM has also been expressed by the nuclear safeguards and nuclear forensics communities. To remedy this, the EC-JRC has set-up in the scope of this thesis a feasibility study concerning CRMs for plutonium age determination (Sturm, Richter et al. 2010). Although CRMs for age determination of plutonium and uranium could nominally be described as ‘Isotopic CRMs’ with mixed elemental composition of either plutonium and uranium for plutonium age determination or of uranium and thorium for uranium age determination, they differ significantly from the CRMs for bulk analysis of nuclear material in routine safeguards applications described above:

- Firstly, the ratios of the two elements – in this case parent and daughter isotope – differ significantly from the ratios found in other ‘Isotopic CRMs’ with mixed elemental composition. CRM IRMM-1027o for instance has a Pu/U ratio of about 0.03 g/g as a typical example for an ‘Isotopic CRM’ with mixed elemental composition (Jakopič, Bauwens et al. 2013). By contrast, a CRM for plutonium age determination would typically need to have a Pu/U ratio of about 450 g/g representing an approximately 41-year-old aged plutonium sample with an isotopic composition similar to that of CRM NBS 946 (Uriano 1982). This is due to the fact that only a fraction of the plutonium nuclides decays to uranium even in a relatively long period such as 41 years (Sturm, Richter et al. 2014).
- Secondly, regular CRMs are certified for the isotope ratios and if applicable for the amount contents of the element(s) they contain. For instance CRM IRMM-1027o is certified for the isotopic composition of uranium and plutonium and the respective masses of uranium and plutonium per unit (Jakopič, Bauwens et al. 2013). By contrast, CRMs for nuclear age determination need to be certified for the ‘separation date’ such as IRMM-1000a and IRMM-1000b (Varga, Nicholl et al. 2012; Varga,

Venchiarutti et al. 2015) or ‘model production dates’ such as CRM-125A (Bakhtiar 2013a) and CRM U630 (Bakhtiar 2013). The ‘age’ or the (model) ‘separation date’ are not directly measurable quantities as they need to be calculated from the ratio of the mother nuclide and the related daughter nuclide. The nuclide ratio continuously changes due to the decay of the parent nuclide (^{234}U in case of IRMM-1000a and IRMM-1000b) and the subsequent increase (and also radiogenic decay) of the daughter nuclide (^{230}Th). The more time that elapses between the certification and the use of the CRM, the higher the measured ratio of parent to daughter nuclide becomes (Varga, Venchiarutti et al. 2015). Although radiogenic decay also occurs in typical nuclear CRMs, the changes in relation to the elements and nuclides of interest are more noticeable in CRMs for age determination due to the extreme ratio of nuclides (and thus elements of interest).

As mentioned above, there are no currently available CRMs for the age determination of plutonium (Sturm, Richter et al. 2014). Uranium age dating CRMs CRM-125A (Bakhtiar 2013a) and CRM U630 (Bakhtiar 2013) as well as IRMM-1000a and IRMM-1000b have only relatively recently been made available (Varga, Venchiarutti et al. 2015). This has meant that researchers have been forced to rely on other materials to serve as proxies for QC CRMs certified for their separation date and for the development of age determination methodology. The Guide to Quality in Analytical Chemistry recommends the use of a material with suitable properties and stability as a laboratory measurement standard in the absence of a suitable CRM (CITAC and Eurachem 2002). For plutonium age determination some materials and the information concerning their ‘age’ used for this purpose by the respective authors for their research are listed below (Sturm, Richter et al. 2010):

- Isotopic CRMs and information given on their respective certificates: the use and interpretation of information provided on the certificate of isotopic CRMs differs from author to author. The issuing date of the certificate when a CRM was first certified for instance has been used (Shinonaga, Donohue et al. 2009) as the separation date of a CRM for plutonium age determination while other authors simply refer to a ‘date on certificate’ (Nguyen 2006). Others make assumptions such as that the purification of the material used for the CRM production was carried out three months prior to the assay date given on the certificate (Keegan and Gehrke 2003).

- Historic in-house records: this kind of information on the history of a material used as a reference for age determination is referred to as ‘old records recovered together with the material' (Wallenius and Mayer 2000), 'archive purification dates' (Varga, Nicholl et al. 2016) or 'package notes' (Wallenius 2001). Although the information might be accurate, it is virtually impossible for the reader or reviewer to verify.

- Literature: literature references such as 'the World Nuclear Industry Handbook, Nuclear Engineering International, 1998' are also given by some authors (Wallenius, Peerani et al. 2000) as well as comparisons to other studies (Varga, Nicholl et al. 2016).

- Unpublished results of round robin exercise: the results of a round robin test that had not yet been published at the time of the publication of the concerned article were used as the reference age by Wallenius et al. (Wallenius, Peerani et al. 2000).

- Personal communication: some authors also rely on 'personal communication' which, similar to 'historic in-house records', are very hard for the reader and reviewer to verify (Wallenius, Peerani et al. 2000; Nygren, Ramebäck et al. 2007).

- Historic information: an example for the use of such an information source is the use of the time of the detonation in a nuclear weapon test in the area where the material referred to originated from as the reference age (Nygren, Ramebäck et al. 2007).

Those reference dates became the most suitable solution available to researchers at the time that their research was conducted in the absence of a CRM certified for the separation date (Sturm, Richter et al. 2010). This lack of specific age dating CRMs can lead to the situation where several reference separation dates are used by different research groups for the very same material. Different reference ages can be found for the isotopic plutonium CRM SRM 947 for instance (Wallenius, Peerani et al. 2000; Shinonaga, Donohue et al. 2009). Consequently it is very often impossible for the critical reviewer or reader to confirm the validity of the claims made about the 'age' and the quality of the material used:

- Are the assumed separation dates (time zero) correct or at least reasonably justifiable?
- Has the material been tampered with after separation? Is there any possibility that it has been contaminated with any other material such as natural or other uranium that would compromise the chronometers in question? How was the material handled in the facility from where it originated?

- Has the separation of the material been complete at the assumed ‘time zero’?

The latter is not necessarily so as the complete removal of all traces of daughter nuclides was in many cases not the prime focus when the material was separated as it may not have been intended for use as a reference for age determination.

Some of these difficulties can be overcome by thoroughly testing the material using several of the available chronometers in the case of plutonium age determination via the Pu/U chronometers (^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{242}Pu/^{238}U), especially when the rarely employed chronometer ^{242}Pu/^{238}U is considered as an indicator for the presence of non-radiogenic uranium (Sturm, Richter et al. 2014). However, this requires considerable resources in terms of instrument and operator time. In addition, it is not ideal to have no well characterized material to be used as a test sample for method development when a laboratory is just about to enhance its capabilities to include nuclear age determination. Furthermore it is not always possible to test the material used as age reference for the validity of the claims made about its assumed age. In cases when there is only one chronometer available there is no way to intrinsically confirm the age dating result even when it matches the assumed age. This situation for instance arises when only one chronometer is available for instrumentation reasons as is the case when plutonium is dated using the ^{241}Pu/^{241}Am chronometer via gamma spectrometry (Keegan and Gehrke 2003; Nguyen 2006). In the case of uranium age determination, the chronometer ^{234}U/^{230}Th is mostly used as other possible chronometers are often not readily available due to the nature of the sample or are not practicable due to technical constraints. There is for instance no suitable protactinium tracer available for the application of the ^{235}U/^{231}Pa chronometer and the ^{234}U/^{214}Bi chronometer can be used exclusively for the age determination of HEU (Varga and Surányi 2007).

Three quite different approaches can be envisioned in order to obtain a CRM certified for the separation date for age determination of nuclear material using one or more predefined chronometers (Bürger, Croatto et al. 2008):

- the certification of an aged material that has been separated for another purpose: a prerequisite for this approach is that the separation date and the quality of the separation (separation factor) of the concerned mother nuclide(s) from their respective daughter nuclides must be well-documented. This strategy is maybe applicable to the re-certification of an existing isotopic CRM. An advantage of this method is that the CRM would be certified for an ‘old age’ which might be advantageous as in many cases it may mimic the condition of a unknown seized sample in a nuclear forensic investigation. This strategy was chosen for uranium chronometry CRMs CRM-125A (Bakhtiar 2013a) and CRM U630 (Bakhtiar 2013) which are certified for a 'model purification date' of the $^{234}U/^{230}Th$ chronometer.

- synthetic mixing of purified enriched fractions of parent nuclides and their respective daughter nuclides in a ratio that would represent a specific ‘age’: the advantage of this approach would be that CRMs could be tailor-made for any age range and in this case it would be possible to simultaneously produce several CRMs with a variety of fictive separation dates. However, it would be very challenging if not impossible to produce a CRM that represents more than one chronometer and the characterization of the starting materials would also be a major undertaking.

- quantitative removal of daughter nuclides from the mother nuclide of bulk material leading to a material with a documented separation date and completeness of separation: this strategy has been chosen for the preparation and certification of CRMs IRMM-1000a and IRMM-1000b for age determination of uranium materials via the $^{234}U/^{230}Th$ chronometer (Varga, Nicholl et al. 2012; Varga, Venchiarutti et al. 2015). This method has the clear advantage that the process of the certification can be thoroughly controlled, closely monitored, and rigorously documented. The material also possesses all of the properties that could be expected from an unknown sample of similar chemical composition and age. In this case residual daughter nuclides present after the purification of the parent nuclides can be taken into account in the uncertainty of the separation date stated on the CRM certificate if applicable (Venchiarutti, Varga et al. 2016).

As far as CRMs for plutonium age determination are concerned, the EC-JRC envisages in the future to produce plutonium CRMs certified for the separation date. This project will utilise the latter option of quantitative removal of daughter nuclides from the mother nuclide leading to a material with a documented separation date and completeness of separation (Sturm, Richter et al. 2010). This plutonium age determination CRM would also be tested in an inter-laboratory comparison, as was done according to ISO 17043:2010 with IRMM-1000a and IRMM-1000b in the inter-laboratory comparison REIMEP-22 (Regular European Inter-

Laboratory Measurement Evaluation Programme) on ‘*U Age-dating – determination of the production date of a uranium certified test sample*’ (Varga, Nicholl et al. 2012; Varga, Venchiarutti et al. 2015; Venchiarutti, Varga et al. 2015). REIMEP-22 established the state-of-the-practice of the participating laboratories in determining the age of seized uranium material, a key parameter in nuclear forensics, and its related uncertainty (Venchiarutti, Varga et al. 2015).

1.6 Methodology

1.6.1 Thermal Ionization Mass Spectrometry

Thermal Ionization Mass Spectrometry (TIMS) provides a means to measure isotope ratios based on the formation of ions in a vacuum on heated metal ribbons called filaments. The ions are separated according to their mass-to-charge-ratio in a magnetic sector field (Bürger, Vogl et al. 2015). Figure 1-2 shows one of the Triton (Thermo-Fisher Scientific, Bremen, Germany) TIMS multi-collector instruments on which the present work was conducted. Figure 1-3 shows the configuration of this instrument.

Figure 1-2: Triton TIMS installed at EC-JRC-G.2 (Photo reproduced by the courtesy of EC-JRC-G.2).

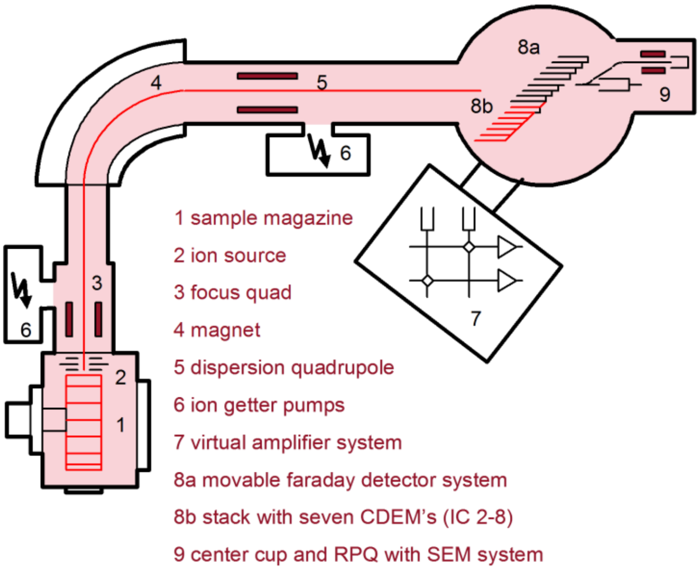


Figure 1-3: Configuration of the Triton TIMS at EC-JRC-G.2 (Jakopic, Richter et al. 2009). (Reproduced by courtesy of ESARDA, the European Safeguards Research and Development Association).

Only Faraday cup detectors and the double filament technique have been used for the measurements performed in the current work. Additionally, the Total Evaporation measurement technique (TE) has been applied as described in the next chapter. Degassed zone-refined rhenium filaments (Thermo-Fisher Scientific, Bremen, Germany) were used as both evaporation and ionisation filaments. In double filament TIMS measurements, a small volume (typically 1 µL) of the purified solution of the analyte is pipetted onto the evaporation filament and dried. The ionisation filament is placed parallel to the evaporation filament. During the measurement the analyte atoms are evaporated from the evaporation filament surface. When the atoms strike the ionisation filament they are ionized and can be separated according their mass-to-charge-ratio in the magnetic sector (Bürger, Vogl et al. 2015).

1.6.1.1 Total Evaporation TIMS measurement

Mass fractionation of the nuclides of the analysed element is a major source of systematic bias in TIMS as illustrated in Figure 1-4. It can be clearly seen that the lighter nuclides (^{235}U in Figure 1-4) are evaporated predominately in the beginning of the measurement while the heavier nuclides (^{235}U in Figure 1-4) are evaporated predominately towards the end of the measurement when the sample is close to exhaustion (Fiedler 1995). Although mass bias cannot be completely eliminated by the method of Total Evaporation (TE), it is greatly minimized by the fact that unique isotope ratios are calculated from the integrated sums of the measurement signals for each isotope collected during the measurement until such time as the sample is exhausted. The robustness of the TE TIMS measurement technique is highlighted by the fact that mass fractionation effects are for example only in the range of 0.01% for the $^{235}U/^{238}U$ ratio. Hence, TE measurements of uranium and plutonium major isotope ratios are deemed suitable for IAEA safeguards measurements without applying mass fractionation corrections (Bürger, Balsley et al. 2012). Nevertheless, mass bias corrections may be applied to isotope ratios obtained by TE TIMS in order to ensure that the results are traceable to SI units by linking them to a CRM. This has been done in the present work (Sturm, Richter et al. 2014).

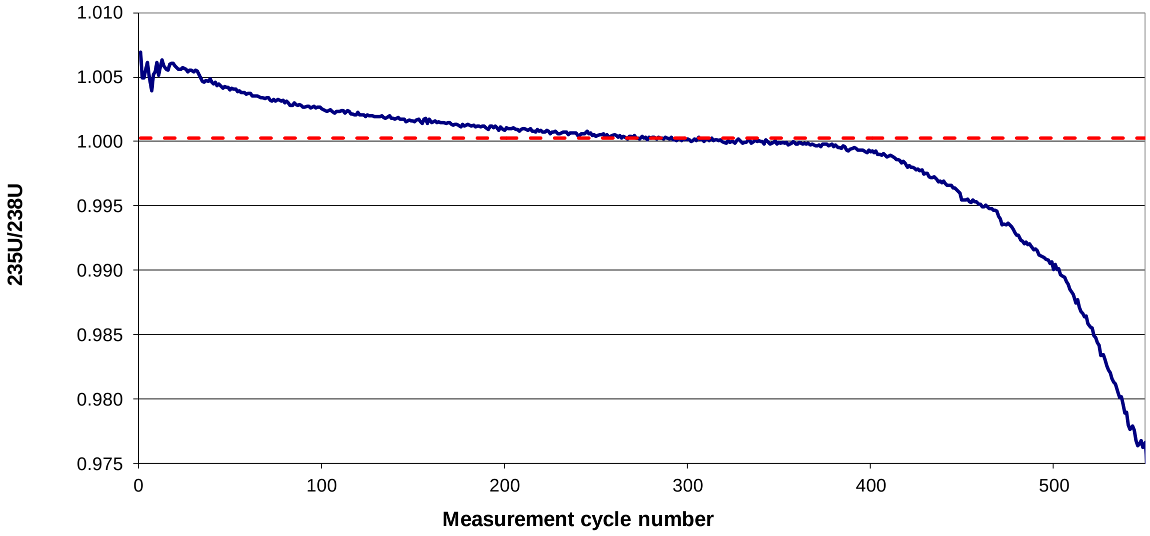


Figure 1-4: Mass fractionation of the $^{235}U/^{238}U$ isotope ratio during total evaporation data acquisition of CRM IRMM-074/10, the certified value is shown as a red line (Taylor and Wellum 2006).

The concept of total evaporation was initially known as ‘flash evaporation’ upon its first mention in 1987 by Romkowski (Romkowski, Franzini et al. 1987; Kühn 1991; Fiedler 1995): The Faraday cups of a multi-collector TIMS instrument are set up in such a way that all isotopes of interest can be detected simultaneously. Isotopes of interest for uranium measurements are ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U, and for plutonium ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu. The signals of the isotopes of interest of the analysed element are measured on the multi-collector Faraday cup array until the entire sample is exhausted (‘totally evaporated’). The summed intensities of all detected isotopes are maintained at a set target value by regulating the current that is applied to the evaporation filament. This is illustrated in Figure 1-5.

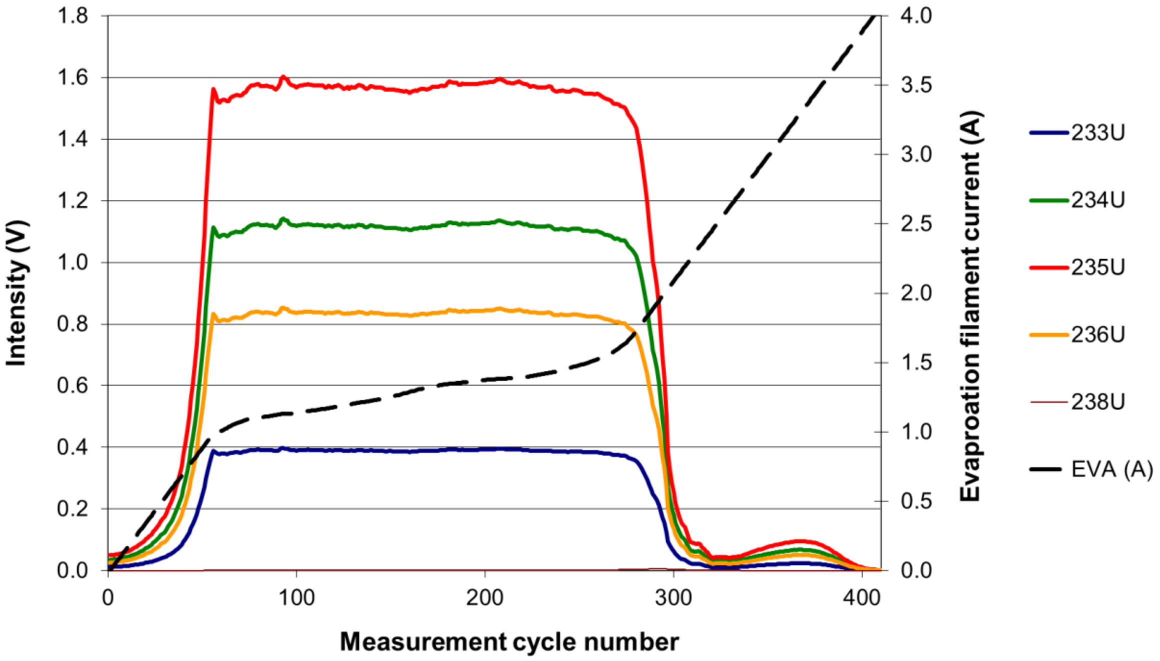


Figure 1-5: Total Evaporation data acquisition of a uranium fraction separated from the isotopic plutonium CRM NBS 946 (Uriano 1982) spiked with ^{233}U spike IRMM-3630.0.4 (Richter, Alonso et al. 2009) showing uranium signals (^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U) in V and the evaporation filament current (EVA) in A.

Mass fractionation effects caused by variations in the evaporation and ionisation of the sample are thus minimized. However, these effects cannot be completely prevented as a small amount of analyte is lost during the signal optimization of the TE measurement routine as described below. Additionally, only a small fraction of the sample is ionized, not all of which reaches the detectors. The ratio of ions detected to atoms loaded onto the filament (overall efficiency) is significantly less than 1% for both uranium and plutonium (Bürger, Balsley et al. 2012). The efficiency may also not be constant during the measurement. This change in efficiency in combination with the (mass fractionation-related) drift of the ratio is the reason for possible small biases in TE measurements (Richter, Kühn et al. 2011). TE also reduces the differences in mass fractionation effects stemming from varying sample amounts loaded on the filament. Hence, the TE TIMS measurement results are less dependent on the sample size (Fiedler 1995).

The TE measurement procedure for the measurement of isotope ratios of uranium routinely applied at EC-JRC-G.2 is described here as an example for the steps involved in this type of measurement (Sturm, Richter et al. 2016).

The TE measurement can be divided into two parts:

- **Optimization of the analyte ionization and ion detection:**

^{187}Re signal ion source tuning. A current of 4300 mA is initially applied to the ionization filament. This leads to the formation of rhenium ions from which the filament ribbon is made. The current on the ionization filament is increased until the ^{187}Re signal measured on the central Faraday cup exceeds 20 mV. This signal is subsequently used for checking and adjusting of the mass calibration by so-called ‘peak centering’. Additionally, the ^{187}Re signal is used for an automatic routine that optimizes the ion source lenses’ settings. After completion of these steps the ionization filament current is then raised until the ^{187}Re signal exceeds 120 mV. The ionization filament current is maintained at this value for remainder of the TE measurement routine for this particular filament including data collection.

^{238}U signal ion source tuning. In this step, a switch is made from monitoring ^{187}Re at the centre Faraday cup to the detector array set up for uranium and a current is applied to the evaporation filament holding the uranium sample. The uranium isotope that is expected to be the most abundant in the sample is pre-defined to be monitored in this step of the uranium TE measurement procedure. In many typical uranium samples such as DU, NU and LEU this is ^{238}U. This does not apply in some cases such as with samples of HEU. However, even then the analyst can usually expect a sufficiently abundant ^{238}U ion signal.

The evaporation filament current is increased subsequently until the ^{238}U signal exceeds 30 mV. Ion source focusing and peak centering steps are then performed on this signal as described above for ^{187}Re. The objective of ‘peak centering’ is aimed to check and adjust the mass calibration while ion source focusing optimizes the ion transmission to the detector array by adjusting the settings of the ion source lenses.

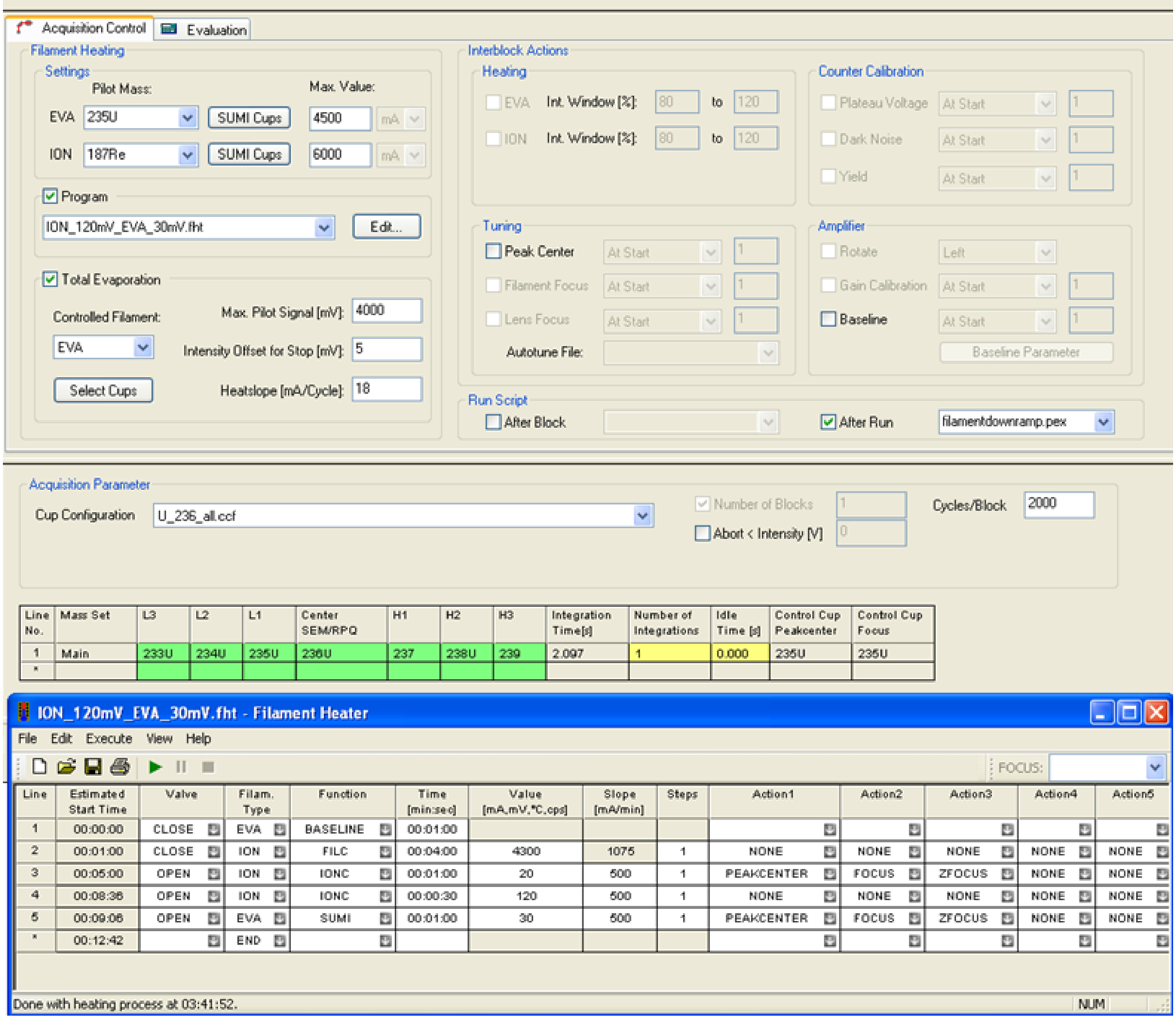
In this step it is important to keep the uranium signals relatively low compared to the total summed uranium signals collected during data acquisition, otherwise the isotope ratios measured during data collection can be unduly biased due to the loss of sample that occurs before the collection of the data starts. As shown in Figure 1-4, mass fractionation takes place during the data acquisition and the phenomenon of preferred evaporation of lighter ions compared to heavier ions starts as soon as the evaporation of the sample from the filament begins. This means that during peak centering and ion source focussing a greater proportion of lighter isotopes compared to the heavier isotopes is lost before the data collection actually commences. It should be borne in mind that this loss of information before data is collected cannot be completely avoided.

- **Data acquisition**

  For TE data acquisition the current that is applied to the evaporation filament is increased automatically until the targeted sum of the detected signals of the isotopes of interest is reached. The current is automatically adjusted in order to maintain the targeted sum of signals (Figure 1-5). The isotopes of interest for uranium measurements are typically ^{233}U, ^{234}U, ^{235}U, ^{236}U and ^{238}U. A typical targeted sum of signals is 4500 mV for a sample size of approximately 100 ng uranium. When the sample is close to exhaustion, the increase of the evaporation filament current cannot then compensate for the drop of the uranium signals and the signals continue to drop despite increased heating. Once the sum of pre-defined uranium signals fall below a predetermined endpoint such as 30 mV the data acquisition is stopped. The currents applied to the evaporation and ionization filament are then switched off.

These steps are essentially the same for plutonium TE. However, in this case the currents applied to the ionization and evaporation filament may vary in order to accommodate the evaporation and ionization properties of plutonium. The different requirements for TE of different elements stem from differences in the first ionization potentials. The first ionization potential is the energy required to remove a valence electron of an isolated gaseous atom to form a cation. The first ionization potential for uranium is ~ 6.2 eV and ~ 6.1 eV for plutonium (Bürger, Vogl et al. 2015). The yield of singly charged plutonium ions is reported to be 5-10 times greater than that of singly charged uranium ions (Aggarwal, Saxena et al. 1994). In the case of plutonium TE measurements, ^{239}Pu is usually used as the pilot mass to optimize the formation and transition of plutonium ions to the detector array. The signals of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, and ^{244}Pu are used to control the current applied to the evaporation filament during data collection.

Figure 1-6 shows a screenshot of the Triton software and illustrates the measurement method and filament heating procedure for uranium TE measurements used at EC-JRC-G.2, adjusted for the measurement of uranium fractions purified from plutonium samples as applied in (Sturm, Richter et al. 2014) and (Sturm, Richter et al. 2016). In contrast to monitoring the ^{238}U signal during filament heating, as described above, ^{235}U was used. This was decided upon due to the fact that only minute amounts of radiogenic ^{238}U are present in aged plutonium samples. Additionally, the 238 mass (both ^{238}U and ^{238}Pu) was excluded from sum of the signals (^{233}U, ^{234}U, ^{235}U, and ^{236}U) that control the current applied to the evaporation filament during data collection. This change was made in order to take only the evaporation and ionization properties of the uranium analyte into account. Traces of ^{238}Pu are present in the purified uranium fraction of aged plutonium samples, but ^{238}Pu cannot be distinguished from ^{238}U in the mass spectrometer. Plutonium also has different evaporation and ionization properties to uranium. A detailed discussion can be found in (Sturm, Richter et al. 2016).



Filament Heating

Settings

Pilot Mass: / Max. Value:

EVA 235U 4500 mA

ION 187Re 6000 mA

☑ Program

ION_120mV_EVA_30mV.fht

☑ Total Evaporation

Controlled Filament: EVA

Max. Pilot Signal [mV]: 4000

Intensity Offset for Stop [mV]: 5

Heatslope [mA/Cycle]: 18

Interblock Actions

Heating

☐ EVA Int. Window [%]: 80 to 120

☐ ION Int. Window [%]: 80 to 120

Counter Calibration

☐ Plateau Voltage At Start 1

☐ Dark Noise At Start 1

☐ Yield At Start 1

Tuning

☐ Peak Center At Start 1

☐ Filament Focus At Start 1

☐ Lens Focus At Start 1

Autotune File:

Amplifier

☐ Rotate Left

☐ Gain Calibration At Start 1

☐ Baseline At Start 1

Run Script

☐ After Block

☑ After Run filamentdownramp.pex

Acquisition Parameter

Cup Configuration U_236_all.ccf

☑ Number of Blocks 1

☐ Abort < Intensity [V] 0

Cycles/Block 2000

Line No.	Mass Set	L3	L2	L1	Center SEM/RPQ	H1	H2	H3	Integration Time[s]	Number of Integrations	Idle Time [s]	Control Cup Peakcenter	Control Cup Focus
1	Main	233U	234U	235U	236U	237	238U	239	2.097	1	0.000	235U	235U
*													

ION_120mV_EVA_30mV.fht - Filament Heater

Line	Estimated Start Time	Valve	Filam. Type	Function	Time [min:sec]	Value [mA,mV,°C,cps]	Slope [mA/min]	Steps	Action1	Action2	Action3	Action4	Action5
1	00:00:00	CLOSE	EVA	BASELINE	00:01:00								
2	00:01:00	CLOSE	ION	FILC	00:04:00	4300	1075	1	NONE	NONE	NONE	NONE	NONE
3	00:05:00	OPEN	ION	IONC	00:01:00	20	500	1	PEAKCENTER	FOCUS	ZFOCUS	NONE	NONE
4	00:08:36	OPEN	ION	IONC	00:00:30	120	500	1	NONE	NONE	NONE	NONE	NONE
5	00:09:06	OPEN	EVA	SUMI	00:01:00	30	500	1	PEAKCENTER	FOCUS	ZFOCUS	NONE	NONE
*	00:12:42		END										

Done with heating process at 03:41:52.

Figure 1-6: Measurement method and filament heating procedure of a Triton mass spectrometer for the uranium TE measurement routine used at EC-JRC-G.2 adjusted for the measurement of uranium fractions purified from plutonium samples as applied in (Sturm, Richter et al. 2014) and (Sturm, Richter et al. 2016).

The calculation of the isotope ratios for TE measurements is shown in Equation 1.6.1.1 for a measurement of ^{235}U/^{238}U (Richter, Kühn et al. 2011):

$$\frac{n(^{235}\mathrm{U})}{n(^{238}\mathrm{U})} = \frac{\sum I(^{235}\mathrm{U})}{\sum I(^{238}\mathrm{U})} = \frac{\sum\left[I(^{238}\mathrm{U})\times\frac{I(^{235}\mathrm{U})}{I(^{238}\mathrm{U})}\right]}{\sum I(^{238}\mathrm{U})} \qquad \text{Equation 1.6.1.1}$$

$n(^{235}U)/n(^{238}U)$ is the result of the determination of the $^{235}U/^{238}U$ isotope ratio in the sample. $I(^{235}U)$ and $I(^{238}U)$ are the signal intensities in V for ^{235}U and ^{238}U respectively, which are recorded during data acquisition. $I(^{235}U)$ can also be expressed as the sum of the recorded ratios of the signal intensities of $^{235}U/^{238}U$ ($I(^{235}U) * I(^{238}U)^{-1}$) weighted by the ^{238}U ion signal intensities ($I(^{238}U)$) (Richter, Kühn et al. 2011).

1.6.1.2 Filament carburization

Filament carburization is a process used to alter the work function of rhenium filaments by carbon addition. The work function W represents the thermodynamic work which is needed in a vacuum for the removal of one electron from the filament surface to a state at rest close to the filament surface. This is shown in Equation 1.6.1.2. The charge of the electron is represented by $-e$, the electrostatic potential in the vacuum close to the surface by Φ, and E_F represents the electrochemical potential of electrons inside the material, also called the 'Fermi level' (Kittel 2004).

$$W = -e\Phi - E_F \qquad \text{Equation 1.6.1.2}$$

Carbon is believed to change the work function of the filament. When applying heat, a solid-solid solution of carbon in rhenium is formed as carbon dissolves into the rhenium (Kelley and Robertson 1985; Kraiem, Richter et al. 2011). There are different possibilities for sources of carbon such as graphite powder (Shinonaga, Esaka et al. 2008; Shinonaga, Donohue et al. 2009) and the vapour of organic substances. An advantage of organic gases is that they are free from NU which might cause contamination of the samples.

In the recent years benzene vapour has often been used for this purpose (Jakopic, Richter et al. 2009; Jakopic, Richter et al. 2010; Kraiem, Richter et al. 2011; Kraiem, Richter et al. 2011). A mixture of propane and butane gas can also serve as a vaporous carbon source representing a less toxic alternative to benzene which is a carcinogenic chemical; in fact no level of benzene exposure can be determined below which there is no health risk (EC 1991).

The process of carburization of rhenium filaments with the vapour of organic substances involves the following steps (Jakopic, Richter et al. 2009):

The rhenium filaments are installed in a special filament carburization device as shown in Figure 1-7. The apparatus is subsequently evacuated and once a vacuum pressure $< 1 \times 10^{-6}$ mbar is reached a current is applied to the filaments following a heating routine.

The purpose of this routine is the degassing and cleaning of the filaments. A valve is then opened to release the carbon containing gas such as propane and butane gas into the chamber containing the filaments. Subsequently, a current of 4 A is applied to the filaments resulting in a temperature of about 1600-1700 °C during the carburization process. The pressure in the carburization chamber is adjusted to 5×10^{-3} mbar and maintained for 1 hour. The filaments are allowed to cool for several hours before they can be used.

The use of carburized filaments changes the measurement behaviour of uranium (Kraiem, Mayer et al. 2010) and plutonium by TIMS by altering chemical processes on the filament (Kelley and Robertson 1985). The carbon from the solid-solid solution in rhenium forms carbides with the plutonium or uranium analyte on the filament surface which leads to an increase in the ionization efficiency (Kelley and Robertson 1985; Kraiem, Richter et al. 2011). In contrast to the formation of plutonium oxide ions (Kelley and Robertson 1985) and uranium oxide ions (Kraiem, Richter et al. 2011) during the TIMS measurement when un-carburized filaments are used, carbides are formed when carburized filaments are used. Carbides dissociate at higher temperatures to singly-charged ions, while oxides evaporate at lower temperatures and hence do not get a chance to form uranium or plutonium ions, respectively. This leads to an increase of the ionization efficiency of the analyte when carburized filaments are used. Due to this phenomenon filament carburisation has been used for the measurement of samples with limited sample size such as the measurement of single uranium particles (Shinonaga, Esaka et al. 2008; Kraiem, Richter et al. 2011) and single plutonium particles (Shinonaga, Esaka et al. 2008; Shinonaga, Donohue et al. 2009) and also environmental plutonium samples (pg amounts) (Jakopic, Richter et al. 2009; Jakopic, Richter et al. 2010).

It has also been reported that singly charged ions of plutonium are formed at higher temperatures when filament carburization is used compared to un-carburised filaments (Kelley and Robertson 1985).

The changes of the filament chemistry introduced by the application of carburized rhenium filaments can also be used to improve the signal behaviour during the measurement of uranium and plutonium. For example it is possible to reduce the effect of residual plutonium in a uranium fraction purified from a plutonium sample by the application of filament carburization (Sturm, Richter et al. 2016).

Figure 1-7: Carburization device (left) with filament holder (magazine) (right bottom) and the opened vacuum chamber holding the magazine (right top). (Reproduced by permission of ESARDA, the European Safeguards Research and Development Association) (Jakopic, Richter et al. 2009).

1.6.2 Metrology - uncertainty contributions in plutonium age determination

Metrology is the science of measurements and its application involves expressing any measurement result as measured quantity value with its associated measurement uncertainty. Metrological traceability links measurement results to metrological references. This is accomplished through a documented unbroken chain of comparisons. All steps in this chain of comparisons must be associated with stated measurement uncertainties. Metrological traceability therefore gives measurement results credibility and transparency. The Guide to the expression of Uncertainty in Measurement (GUM) and the EURACHEM guides have found widespread use in the measurement community (JCGM100 2008; Ellison and Williams 2012).

Chapters 1.6.2.1 to 1.6.2.4 take a detailed look at the uncertainties obtained from dating CRM NBS 946 by ID TIMS using the Pu/U chronometers ^{240}Pu/^{236}U, ^{239}Pu/^{235}U, ^{238}Pu/^{234}U and ^{242}Pu/^{238}U. The results have been published by Sturm et al (Sturm, Richter et al. 2014) but the scope of the latter publication had not allowed such a detailed examination of the uncertainties. All results discussed refer to the reference date of October 18, 2011 and uncertainties are expanded uncertainties (k = 2).

Chapters 1.6.2.1 to 1.6.2.3 demonstrate that for the chronometers ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{238}Pu/^{234}U the major factors contributing to the total combined uncertainties of the age determination results were the half-lives (IAEA 1986) and the amount contents of the parent nuclides. The predominant contributor to the uncertainty budgets of the amount contents of ^{239}Pu, ^{240}Pu and ^{242}Pu was the uncertainty of the amount content of ^{242}Pu in the spike used for Pu IDMS IRMM-049c (De Bièvre 1997).

As far as the ^{238}Pu/^{234}U chronometer is concerned, the uncertainty of the amount content of ^{242}Pu in the plutonium IDMS spike is still the major contributor to the uncertainty of the amount content of ^{238}Pu despite the need for a peak tailing correction for the influence of ^{239}Pu on the ^{238}Pu signal. This clearly demonstrated the importance of IDMS spike CRMs with state-of-the-art uncertainties as well as accurately determined half-lives. The latter has also been strongly emphasised by Pommé et al (Pommé, Jerome et al. 2014; Pommé 2015). A detailed discussion on half-lives with respect to age determination of plutonium has been published by Sturm et al (Sturm, Richter et al. 2014). In the latter publication age dating results were calculated with the half-lives given in Table 1-4 (IAEA 1986; Wellum, Verbruggen et al. 2009) as well as another source of half-lives (Be, Chiste et al. 2006). The half-lives given in Table 1-4 were used as they represent a set of half-lives that is regularly used by organisations such as the EC in CRM certificates e.g. for CRM IRMM-049d (Emons 2011). As several sources of half-lives are available it is of vital importance to state the source for the half-lives that were used to calculate age dating results (IAEA 1986; Be, Chiste et al. 2006; Wellum, Verbruggen et al. 2009; Varga, Nicholl et al. 2016; LNHB 2017).

The age determination result's uncertainty for the ^{242}Pu/^{238}U chronometer is largely dominated by the by the uncertainty of the amount content of ^{238}U as discussed in chapter 1.6.2.4 and (Sturm, Richter et al. 2014).

Isotope Dilution Mass Spectrometry (IDMS) was used for the determination of the amount contents of the parent and daughter nuclides. To this end TE TIMS measurements were conducted on the purified uranium and plutonium fraction of each sample. The measured isotope ratios of uranium and plutonium were corrected for mass fractionation effects occurring during the respective TE measurements. The resulting amount contents of the parent and daughter nuclide were subsequently used to calculate the age of the sample using the above mentioned chronometers. The calculations used to obtain these results and the propagation of the associated respective uncertainties in order to obtain metrologically sound results that are traceable to SI units are discussed below.

Mass fractionation correction

Mass fractionation cannot be completely eliminated by the TE method, so an external correction for these effects was applied in the present work using the certified and measured isotope ratios of the gravimetrically prepared isotopic CRM IRMM-074/10 (Taylor and Wellum 2006; Richter, Alonso et al. 2009) for uranium and isotopic CRM IRMM-290A/3 (De Bièvre 1996) for plutonium (Sturm, Richter et al. 2014). For this purpose the respective CRM was measured on each sample magazine to ensure that the CRM for mass fractionation correction was measured under the same sample loading and instrument conditions as the samples. In the case of the uranium TE measurements five filaments of IRMM-074/10 were measured on one magazine while each uranium sample was measured as 4 replicates. For the plutonium TE measurements six filaments of IRMM-290A/3 were measured per magazine along with 5 replicates of each plutonium sample. These mass fractionation standards were placed on the first and the last filament of the measurement sequence and between the samples. The mass fractionation correction and calculation of the associated uncertainty was performed on an Excel spread sheet. Although the mass fractionation correction was not significantly contributing to the total combined uncertainty (mass fractionation factor *K* obtained for the ^{235}U/^{238}U ratio with CRM IRMM-074/10 for example ~ 1.00019), the mass fractionation correction was applied to isotope ratios obtained by TE TIMS in order ensure that the results are traceable to SI units by linking them to a CRM. The data was then imported into the GUM workbench software (MetrodataGmbH, Weil am Rhein, Germany) for the calculation of the amount contents of the nuclides using the IDMS calculation as described below.

The 'exponential law' is considered as the most suitable method for accounting for the mass fractionation in TIMS. Other possibilities include the power law, the linear law, or the Rayleigh law, although the difference between these approaches for accounting for mass fractionation is insignificant for elements in the higher mass range such as uranium (Andreasen and Sharma 2009; Richter, Kühn et al. 2011). The mass fractionation factor *K* for is calculated according to Equation 1.6.2.1 from the certified major isotope ratio in the standard $R_{235\text{-U/238-U\_Std\_certified}}$ and the measured isotope ratio in the standard $R_{235\text{-U/238-U\_Std\_measured}}$ shown here for uranium (Richter, Kühn et al. 2011).

$$K = \frac{R_{235\text{-U/238-U\_Std\_certified}}}{R_{235\text{-U/238-U\_Std\_measured}}} \qquad \text{Equation 1.6.2.1}$$

The mass fractionation factor *K* is subsequently used to correct the measured ^{235}U/^{238}U isotope ratio in the sample as shown in Equation 1.6.2.2. The corrected ^{235}U/^{238}U ratio is named $R_{235\text{-U/238-U\_sample\_corrected}}$, while $R_{235\text{-U/238-U\_sample\_measured}}$ stands for the measured ^{235}U/^{238}U isotope ratio.

$$R_{235\text{-U/238-U\_sample\_corrected}} = R_{235\text{-U/238-U\_sample\_measured}} \times K^{3/3} \qquad \text{Equation 1.6.2.2}$$

Depending on the mass difference of the isotopes forming the ratio that is used for the calculation the mass fractionation factor *K* and the mass difference of the isotopes forming the concerned isotope ratio of the sample, the calculation of the corrected isotope ratio in the sample differs following the exponential law. Equation 1.6.2.3 illustrates the calculation of the corrected ^{234}U/^{238}U ratio, $R_{234\text{-U/238-U\_sample\_corrected}}$, from the measured ^{234}U/^{238}U ratio, $R_{234\text{-U/238-U\_sample\_measured}}$.

$$R_{234\text{-U/238-U\_sample\_corrected}} = R_{234\text{-U/238-U\_sample\_measured}} \times K^{4/3} \qquad \text{Equation 1.6.2.3}$$

Isotope Dilution Mass Spectrometry (IDMS)

Isotope Dilution Mass Spectrometry (IDMS) was used for the determination of the amount contents of the parent and daughter nuclides. IDMS is based on the isotope ratios in the sample, in the so-called ‘spike’ and in the mixture of defined masses of sample and spike material that are metrologically weighed. The isotope ratios and amount content of the analyte in the spike are known from the CRM certificate. The isotope ratios in the un-spiked sample and in the sample spike blend are determined by measurement (De Bièvre and Debus 1965; De Bièvre and Peiser 1997). Equation 1.6.2.4 gives an example for the calculation of the amount content of ^{239}Pu by IDMS.

$$c_{239\text{-Pu\_sample}} = \frac{c_{242\text{-Pu\_spike}} \times R_{239\text{-Pu/242-Pu\_sample}} \times m_{\text{spike}} \times (R_{239\text{-Pu/242-Pu\_spike}} - R_{239\text{-Pu/242-Pu\_blend}})}{m_{\text{sample}} \times (R_{239\text{-Pu/242-Pu\_blend}} - R_{239\text{-Pu/242-Pu\_sample}})}$$

Equation 1.6.2.4

$c_{239\text{-Pu\_sample}}$ represents the amount content of ^{239}Pu in the sample while $c_{242\text{-Pu\_spike}}$ is the known (certified) amount content of ^{242}Pu in the IDMS spike. $R_{239\text{-Pu/242-Pu\_spike}}$ is the known (certified) ^{239}Pu/^{242}Pu ratio in the spike, while $R_{239\text{-Pu/242-Pu\_sample}}$ and $R_{239\text{-Pu/242-Pu\_blend}}$ are the ^{239}Pu/^{242}Pu measured in the un-spiked sample and the spike sample blend, respectively. The metrologically weighed masses of the spike solution and the sample solution are termed m_{spike} and m_{sample}. For sample NBS 946, CRM IRMM-049c (De Bièvre 1997) and IRMM-3630 (Richter, Alonso et al. 2009) were used as spikes for plutonium IDMS and uranium IDMS, respectively (Sturm, Richter et al. 2014).

Uncertainty propagation

The software tool used for the calculation of the total combined uncertainties of the age dating results was the GUM workbench software (Metrodata GmbH, Weil am Rhein, Germany) (Sturm, Richter et al. 2014; Sturm, Richter et al. 2016). For the age determination of each sample three GUM workbench files were created:

- U IDMS: This file calculates the amount contents of the uranium nuclides in the sample using the IDMS equation; mass fractionation corrected uranium isotope ratios are directly imported into the GUM workbench file from the respective Excel spread sheet.

- Pu IDMS: This file calculates the amount contents of the plutonium nuclides in the sample via IDMS equation; mass fractionation corrected plutonium isotope ratios are directly imported into the GUM workbench file from the respective Excel spread sheet.

- Age determination: This file directly imports the results of the uranium and plutonium IDMS GUM workbench files and calculates the age of the sample at a set reference date.

The final GUM workbench file contains the equations required for calculating the age of a nuclear sample as discussed in chapter 1.4 in Equations 1.4.1 to 1.4.3 (Stolz 2005). However these equations were entered in the manner suggested by (Wallenius, Mayer et al. 2006) shown in Equations 1.6.2.5 to 1.6.2.8 for the chronometer ^{239}Pu/^{235}U, while for Equations 1.4.1 to 1.4.3 the general connotations *P* and *D* were used for the parent nuclide and daughter nuclide, respectively.

$$t = -\frac{\ln\frac{1-R}{K}}{B} \qquad \text{Equation 1.6.2.5}$$

$$R = \frac{^{235}U_t}{^{239}Pu_t} \qquad \text{Equation 1.6.2.6}$$

$$K = \frac{\lambda_{239\text{Pu}}}{\lambda_{235\text{U}} - \lambda_{239\text{Pu}}} \qquad \text{Equation 1.6.2.7}$$

$$B = \lambda_{235\text{U}} - \lambda_{239\text{Pu}} \qquad \text{Equation 1.6.2.8}$$

t in Equation 1.6.2.5 is the result of the age determination of the sample; *t* represents the time span between the last removal of the daughter nuclide ^{235}U from the parent nuclide ^{239}Pu and the calculation date of the age of the sample. In Equation 1.6.2.6, $^{239}Pu_t$ and $^{235}U_t$ represent the amount contents of ^{239}Pu and ^{235}U at the present time, and hence *R* stands for the ratio of ^{235}U/^{239}Pu at the present time. The decay constants $\lambda_{239\text{Pu}}$ and $\lambda_{235\text{U}}$ used in Equation 1.6.2.7 and Equation 1.6.2.8 can be calculated from the half-lives of ^{239}Pu and ^{235}U, respectively, according to Equation 1.4.3. This approach for the calculation of the age of a nuclear sample takes the decay of the daughter nuclide ^{235}U into account.

1.6.2.1 Uncertainty contributions to the age dating result of the ^{240}Pu/^{236}U chronometer

The ^{240}Pu/^{236}U chronometer yielded an age of 41.16 +/- 0.11 a for the above-mentioned reference date of October 18, 2011 for CRM NBS 946 (Sturm, Richter et al. 2014). The upper part of Figure 1-8 illustrates the major factors that contribute to the uncertainty of the age dating result. The uncertainty of the age of the sample is largely dominated by the half-life of ^{240}Pu of 6563(7) a (IAEA 1986) followed by the amount content of the parent nuclide ^{240}Pu and the amount content of the daughter nuclide ^{236}U. The half-life of ^{236}U's contribution to the uncertainty budget is not displayed as its contribution to the total combined uncertainty was less than 0.01 %. The ^{236}U half-life used for the calculation was $2.342(3) \times 10^7$ a (IAEA 1986).

The lower left part of Figure 1-8 shows the major factors contributing to the uncertainty of the amount content of ^{236}U. The amount content of ^{233}U in IRMM-3630 (Richter, Alonso et al. 2009) used as spike for U IDMS comes second to the metrologically weighed mass of the spike in the IDMS blend. It can be seen that mass of the sample in the IDMS blend as well as the measured ratios of ^{233}U/^{235}U and of ^{236}U/^{235}U in the IDMS blend also contribute significantly to the total combined uncertainty of the amount content of ^{236}U. Other possible sources of uncertainty such as the ratio of ^{235}U/^{233}U in IRMM-3630 and the ^{236}U half-life (IAEA 1986) taken into account contributed to less than 0.01 % of the total combined uncertainty. The ^{236}U half-life was used in this instance for harmonizing the measurement dates of the amount contents of daughter and parent nuclides.

The lower right part of Figure 1-8 shows the major factors contributing to the uncertainty of the amount content of ^{240}Pu. The amount content of ^{242}Pu in the spike used for Pu IDMS IRMM-049c (De Bièvre 1997) clearly dominates the uncertainty budget of the amount content of ^{240}Pu. The mass of the spike IRMM-049c in the IDMS blend, the measured ^{239}Pu/^{242}Pu ratio in IDMS blend, the mass of the sample in the IDMS blend and the measured ^{240}Pu/^{239}Pu ratio in the un-spiked sample also contribute to some extend to the total combined uncertainty of the amount content of ^{240}Pu. Other possible sources of uncertainty such as the half-lives of the concerned Pu nuclides (IAEA 1986) and the certified ^{239}Pu/^{242}Pu in IRMM-049c (De Bièvre 1997) taken into account contributed to less than 0.01 % of the total combined uncertainty.

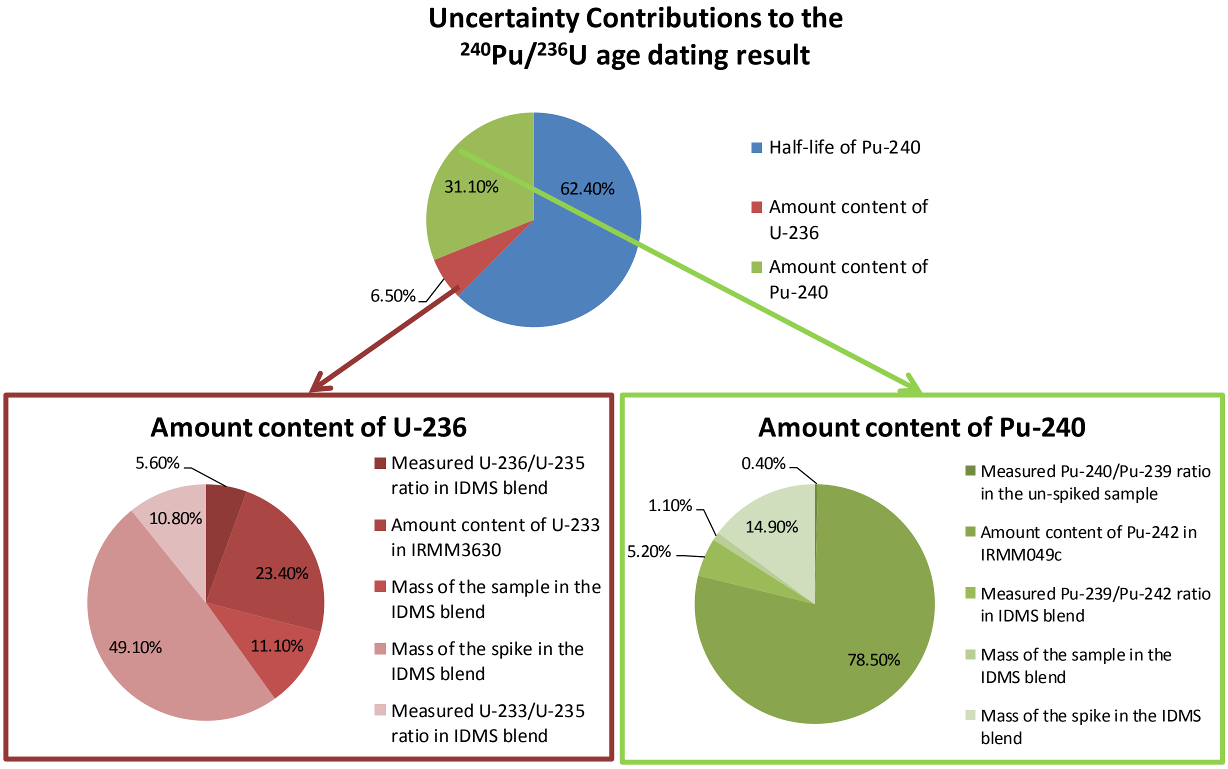


Figure 1-8: Uncertainty contributions to the age dating result of NBS 946 via the ^{240}Pu/^{236}U chronometer.

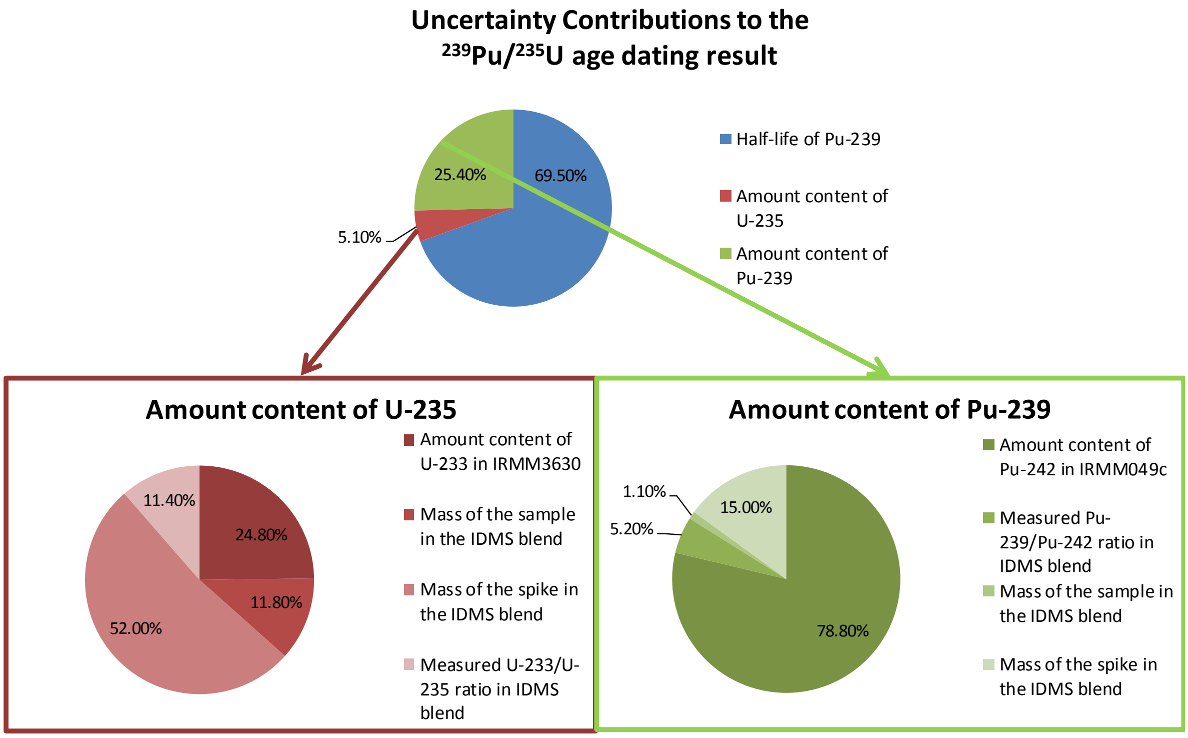


Figure 1-9: Uncertainty contributions to the age dating result of NBS 946 via the ^{239}Pu/^{235}U chronometer.

1.6.2.2 Uncertainty contributions to the age dating result of the ^{239}Pu/^{235}U chronometer

For the age dating result of the ^{239}Pu/^{235}U chronometer the major factors contributing to the total uncertainty are similar to those for the ^{240}Pu/^{236}U chronometer. The ^{239}Pu/^{235}U chronometer yielded an age of 41.12 +/- 0.12 a for the above mentioned reference date of October 18, 2011 for CRM NBS 946 (Sturm, Richter et al. 2014). The upper part of Figure 1-9 shows that the uncertainty of the age of the sample is again dominated by the half-life of ^{239}Pu of 2.411(3) × 10^4 a (IAEA 1986), the amount content of the parent nuclide ^{239}Pu and the amount content of the daughter nuclide ^{235}U. The half-life of the daughter nuclide's contribution to the uncertainty is again not shown as its contribution to the total combined uncertainty was less than 0.01 %. The ^{236}U half-life used for the calculation was 7.037(7) × 10^8 a (IAEA 1986).

The uncertainty budget of the amount content of ^{235}U is dominated by the weight of the spike IRMM-3630 (Richter, Alonso et al. 2009) in the IDMS blend as shown in the lower left part of Figure 1-9. The amount content of ^{233}U in IRMM-3630, the mass of the sample in the IDMS blend and the measured ration of ^{233}U/^{235}U in the IDMS blend also contribute significantly to the uncertainty of the amount content of ^{235}U.

The lower right part of Figure 1-9 shows the major factors contributing to the uncertainty of the amount content of ^{239}Pu. The situation is very similar to the uncertainty of the amount content of ^{240}Pu described above. The amount content of ^{242}Pu in the spike used for Pu IDMS IRMM-049c (De Bièvre 1997) clearly dominates the uncertainty budget followed by the mass of the spike IRMM-049c in the IDMS blend, the measured ^{239}Pu/^{242}Pu ratio in IDMS blend, and the mass of the sample in the IDMS blend.

1.6.2.3 Uncertainty contributions to the age dating result of the ^{238}Pu/^{234}U chronometer

For the age dating result of the ^{238}Pu/^{234}U chronometer the major factors contributing to the total uncertainty are similar to those for the ^{240}Pu/^{236}U and ^{239}Pu/^{235}U chronometer. The ^{239}Pu/^{235}U chronometer yielded an age of 40.09 +/- 0.29 a for the above mentioned reference date of October 18, 2011 for CRM NBS 946 (Sturm, Richter et al. 2014). It can be seen in the upper part of Figure 1-10 that the half-life of the parent nuclide's contribution to the total combined uncertainty is even more pronounced than the chronometers discussed above. The halt-life of ^{238}Pu of 2.411(3) × 10^4 a (IAEA 1986) accounts for more than 90% of the total combined uncertainty of the age dating result of the ^{238}Pu/^{234}U chronometer. The amount content of the parent nuclide ^{238}Pu and the amount content of the daughter nuclide ^{234}U also contribute significantly to the uncertainty budget. The contribution of the amount content of the daughter nuclide ^{234}U is in this case, however, less than 1 %.

The uncertainty budget of the amount content of ^{234}U is dominated by the weight of the spike IRMM-3630 (Richter, Alonso et al. 2009) in the IDMS blend as shown in the lower left part of Figure 1-10. The amount content of ^{233}U in IRMM-3630, the mass of the sample in the IDMS blend and the ^{233}U/^{235}U and ^{234}U/^{235}U ratio measured in the IDMS blend also contribute significantly to the uncertainty of the amount content of ^{235}U.

The lower right part of Figure 1-10 shows the major factors contributing to the uncertainty of the amount content of ^{238}Pu. The amount content of ^{242}Pu in the spike used for Pu IDMS IRMM-049c (De Bièvre 1997) once again plays a dominant role in the uncertainty budget.

In the case of ^{238}Pu a correction for the peak tailing from mass 239 to mass 238 was applied to the measurement of the purified plutonium fraction. This correction is reflected in the uncertainty budget. The measured ^{238}Pu/^{239}Pu ratio in the un-spiked sample also contributes significantly to the uncertainty. Details about the peak-tailing correction can be found in (Sturm, Richter et al. 2014). This is also the reason for the larger uncertainty of the ^{238}Pu/^{234}U chronometer’s age dating result (40.09 +/- 0.29 a) compared to those of the ^{240}Pu/^{236}U (41.16 +/- 0.11 a) and the ^{239}Pu/^{235}U chronometers (41.12 +/- 0.12 a). The mass of the sample and the spike IRMM-049c in the IDMS blend, the measured ^{239}Pu/^{242}Pu ratio in the IDMS blend also contributed significantly to the uncertainty of the amount content of ^{238}Pu.

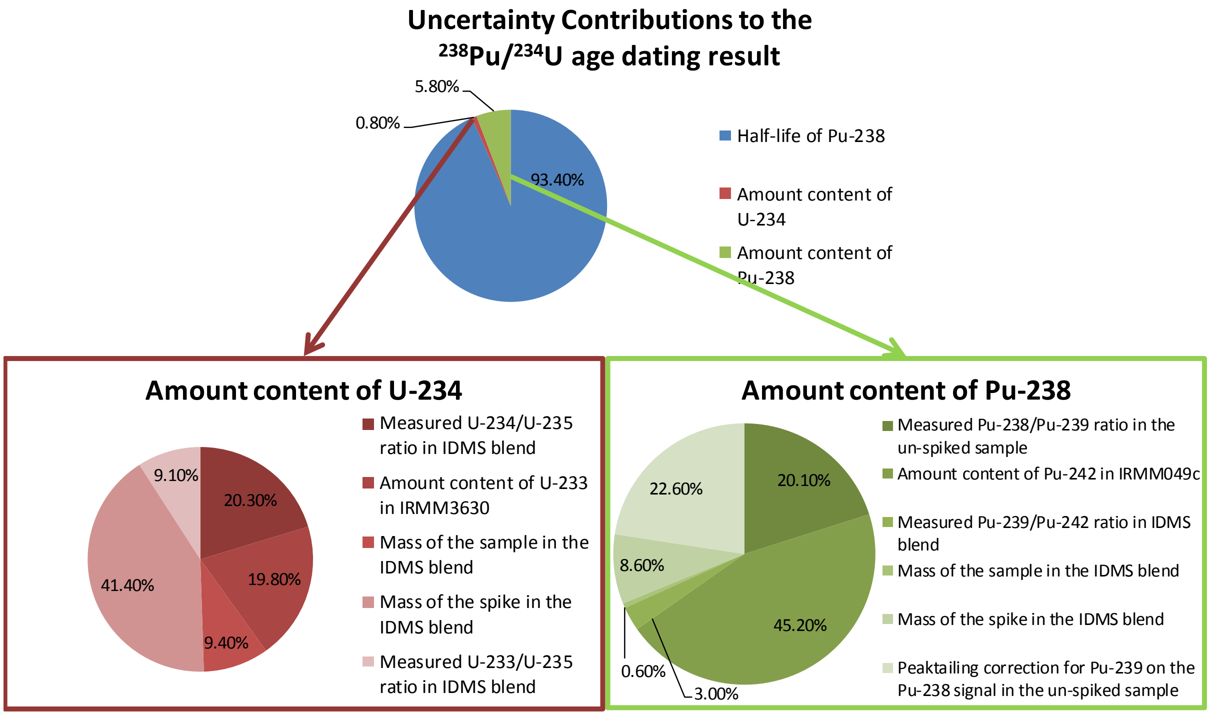


Figure 1-10: Uncertainty contributions to the age dating result of NBS 946 via the ^{238}Pu/^{234}U chronometer.

1.6.2.4 Uncertainty contributions to the age dating result of the ^{242}Pu/^{238}U chronometer

The ^{242}Pu/^{238}U nuclide ratio can also be used as a chronometer for the age determination of plutonium. However, it is more useful as an indicator for the presence of non-radiogenic uranium in the sample. A detailed overview can be found in (Sturm, Richter et al. 2014). For NBS 946 the ^{242}Pu/^{238}U chronometer yielded an age of 43.4 +/- 4.5 a for the above-mentioned reference date of October 18, 2011 for CRM NBS 946 (Sturm, Richter et al. 2014).

The upper part of Figure 1-11 illustrates the major factors that contribute to the uncertainty of the age dating result. The uncertainty is clearly dominated by the amount content of ^{238}U. The only other factor that contributes more than 0.01 % to the total combined uncertainty is the half-life of ^{242}Pu of 3.735(11) × 10^5 a (IAEA 1986). The uncertainty contribution of the amount content of ^{242}Pu to the age dating result in this case is insignificant. The factors contributing to the uncertainty of the amount content of ^{242}Pu are nonetheless shown in the lower right corner of Figure 1-11 for the sake of completeness.

The uncertainty budget of the amount content of ^{238}U is shown in the lower left part of Figure 1-11. The uncertainty is solely dominated by the isotope ratios measured in the sample-spike blend for U IDMS, namely the ratios of mass 238 (^{238}U + ^{238}Pu) to ^{235}U and to mass 239 (^{239}Pu) in IDMS blend. Details of the measurement and correction of the amount content of ^{238}U in aged plutonium samples for the age determination of plutonium can be found in (Sturm, Richter et al. 2014) and (Sturm, Richter et al. 2016).

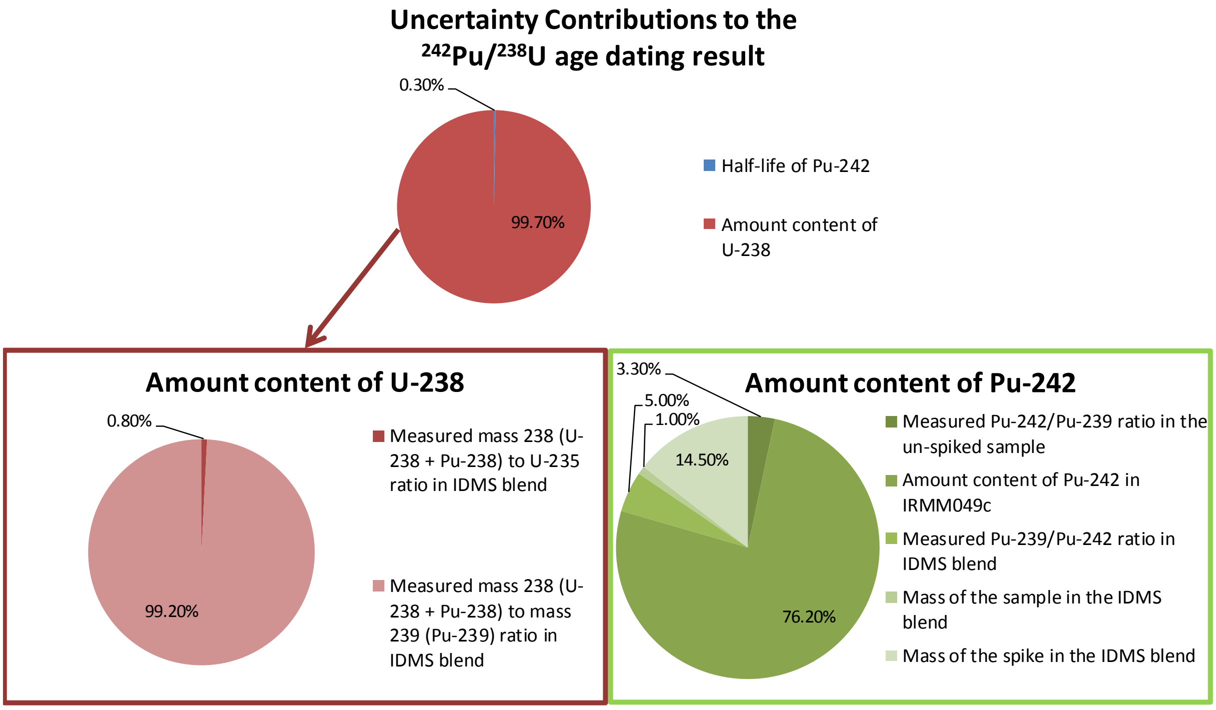


Figure 1-11: Uncertainty contributions to the age dating result of NBS 946 via the ^{242}Pu/^{238}U chronometer.

1.7 References

Aggarwal, S. K., M. K. Saxena, et al. (1994). "Studies on the evaporation and ionisation behaviour of uranium and plutonium in thermal ionisation mass spectrometry." Int. J. Mass Spectrom. Ion Processes **139**(0): 111-126.

Alamelu, D. and S. K. Aggarwal (2016). "Determining the age and history of plutonium using isotope correlations and experimentally determined data on isotopic abundances of plutonium and 241Am." Journal of Radioanalytical and Nuclear Chemistry **307**(1): 277-284.

Alique, O., S. Vaccaro, et al. (2015). The use of measurement uncertainty in nuclear materials accountancy and verification. 37th ESARDA Symposium on Safeguards and Nuclear Non-Proliferation, Manchester (UK), ESARDA and the Joint Research Centre of the European Commission.

Andreasen, R. and M. Sharma (2009). "Fractionation and mixing in a thermal ionization mass spectrometer source: Implications and limitations for high-precision Nd isotope analyses." International Journal of Mass Spectrometry **285**(1–2): 49-57.

ASTM (2016). ASTM C1832 - 16 Standard Test Method for Determination of Uranium Isotopic Composition by the Modified Total Evaporation (MTE) Method Using a Thermal Ionization Mass Spectrometer. Book of Standards ASTM International. **12.01**.

Bakhtiar, S. (2013). Certificate of Analysis CRM U630 Uranium (U3O8) Isotopic and Radiochronometric Standard. Argonne, Illinois, USA, New Burnswick Laboratory, U.S. Department of Energy.

Bakhtiar, S. (2013a). Certificate of Analysis CRM 125-A Uranium (UO2) Pellet Assay, Isotopic, and Radiochronometric Standard. Argonne, Illinois, USA, New Burnswick Laboratory, U.S. Department of Energy.

Barroso, J. (2012). Speech 'EU Action on Nuclear Safety Nuclear Security'. Nuclear Security Summit. Seoul, South Korea.

Baumgärtner, F. and D. Ertel (1980). "The modern purex process and its analytical requirements." Journal of Radioanalytical Chemistry **58**(1-2): 11-28.

Be, M., V. Chiste, et al. (2006). "Halve-lives, Table of recommended values." Laboratoire Natonal Henri Becquerel Note Technique(DETECS/LNHB/2006-58).

Bleise, A., P. R. Danesi, et al. (2003). "Properties, use and health effects of depleted uranium (DU): a general overview." J. Environ. Radioact. **64**(2–3): 93-112.

Buják, R., L. Delva, et al. (2017). "Long-term stability of cellulose acetate butyrate thin films for nuclear certified reference materials." Journal of Radioanalytical and Nuclear Chemistry **311**(1): 877-886.

Bürger, S., S. D. Balsley, et al. (2012). "Uranium and plutonium analysis of nuclear material samples by multi-collector thermal ionisation mass spectrometry: Quality control, measurement uncertainty, and metrological traceability." International Journal of Mass Spectrometry **311**(0): 40-50.

Bürger, S., P. Croatto, et al. (2008). Radiochronometry of nuclear materials. 49th INMM Annual Meeting, Nashville, Tennessee USA, Institute of Nuclear Materials Management.

Bürger, S., J. Vogl, et al. (2015). CHAPTER 14 Thermal Ionisation Mass Spectrometry. Sector Field Mass Spectrometry for Elemental and Isotopic Analysis, The Royal Society of Chemistry**:** 381-438.

Byerly, B. L., F. Stanley, et al. (2016). "Forensic investigation of plutonium metal: a case study of CRM 126." Journal of Radioanalytical and Nuclear Chemistry: 1-10.

Chen, Y., Z.-y. Chang, et al. (2009). "Studies on the age determination of trace plutonium." J. Radioanal. Nucl. Chem. **281**(3): 675-678.

Chisum, W. J. and B. Turvey (2000). "Evidence Dynamics: Locard's Exchange Principle & Crime Reconstruction." Journal of Behavioral Profiling **1**(1).

CITAC and Eurachem (2002). Guide to Quality in Analytical Chemistry - An Aid to Accreditation.

De Bièvre, P. (1996). Certificate Isotopic Reference Material IRMM-290b Geel, Belgium, Institute for Reference Materials and Measurements.

De Bièvre, P. (1997). Certificate Spike Isotopic Reference Material IRMM-049c Geel, Belgium, Institute for Reference Materials and Measurements.

De Bièvre, P. and H. S. Peiser (1997). "Basic equations and uncertainties in isotope-dilution mass spectrometry for traceability to SI of values obtained by this primary method." Fresenius J. Anal. Chem. **359**(7): 523-525.

De Bièvre, P. J. and G. H. Debus (1965). "Precision mass spectrometric isotope dilution analysis." Nuclear Instruments and Methods **32**(2): 224-228.

De Laeter, J. R., J. K. Boelke, et al. (2003). "Atomic weights of the elements: Review 2000 (IUPAC Technical Report)." Pure Appl. Chem. **75**(6): 683-800.

Deron, S., E. Kuhn, et al. (1994). "1993 international target values for uncertainty components in fissile isotope and element accountancy for the effective safeguarding of nuclear materials." JNMM (Journal of the Institute of Nuclear Materials Management);(United States) **22**(2).

EC-JRC. (2016). "Analytical laboratories." Retrieved 08.01.2017, 2017, from https://ec.europa.eu/jrc/en/research-facility/analytical-laboratories.

EC (1991). Recommendation from the Scientific Committee on Occupational Exposure Limits for benzene. Social Europe, European Commission- Employment, Social Affairs and Inclusion.

EC. (2014). "20141007 Nuclear Safeguards Brochure." Retrieved 08.01.2017, 2017, from https://ec.europa.eu/energy/en/content/safeguards-brochure.

Edwards, R. L., H. Cheng, et al. (1997). "Protactinium-231 Dating of Carbonates by Thermal Ionization Mass Spectrometry: Implications for Quaternary Climate Change." Science **276**(5313): 782-786.

Ellison, S. L. R. and A. Williams (2012). Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition.

Emons, H. (2011). Certificate Spike Isotopic Reference Material IRMM-049d Geel, Belgium, Institute for Reference Materials and Measurements.

EURATOM (2012). "CONSOLIDATED VERSION OF THE TREATY ESTABLISHING THE EUROPEAN ATOMIC ENERGY COMMUNITY (2012/C 327/01)." Official Journal of the European Union.

Fankhauser, A., R. Jakopič, et al. (2016). A NOVEL CERTIFIED REFERENCE MATERIAL – 243Am. 1st International Conference on Radioanalytical and Nuclear Chemistry (RANC-2016), Budapest, Hungary.

Faure, G. (1977). Principles of isotope geology.

Fiedler, R. (1995). "Total evaporation measurements: experience with multi-collector instruments and a thermal ionization quadrupole mass spectrometer." International Journal of Mass Spectrometry and Ion Processes **146–147**(0): 91-97.

Gallup, C. D., R. L. Edwards, et al. (1994). "The Timing of High Sea Levels Over the Past 200,000 Years." Science **263**(5148): 796-800.

Garrett, B. C., K. Mayer, et al. (2014). The Nuclear Forensics International Technical Working Group (ITWG) - An overview. International Conference on Advances in

Nuclear Forensics: Countering the Evolving Threat of Nuclear and Other Radioactive Material out of Regulatory Control. Vienna, Austria, IAEA.

Goldschmidt, B. (1989). URANIUM'S SCIENTIFIC HISTORY 1789 - 1939. Fourteenth International Symposium, London, UK, Uranium Institute, London, UK.

Goldschmidt, P. (1999). "The IAEA Safeguards System moves into the 21st century." Supplement to the IAEA Bulletin **41**(4): 1-22.

Hahn, O. and F. Strassmann (1939). "Über den Nachweis und das Verhalten der bei der Bestrahlung des Urans mittels Neutronen entstehenden Erdalkalimetalle." Naturwissenschaften **27**(1): 11-15.

Hanssens, A., C. Viallesoubranne, et al. (2008). Reference materials and interlaboratory comparison for actinide analysis. Atalante 2008: Nuclear fuel cycle for a sustainable future. Montpellier, France, CEA.

Hotchkis, M. A. C., D. Child, et al. (2000). "Measurement of 236U in environmental media." Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **172**(1–4): 659-665.

IAEA (1972). INFCIRC/153 The Structure and Content of Agreements Between the Agency and States Required in Connection with the Treaty on the Non-Proliferation of Nuclear Weapons, IAEA.

IAEA (1973). INFCIRC/193, IAEA.

IAEA (1986). "Decay data of the Transactinium Nuclides." Technical Reports Series **No. 261**.

IAEA (1989). STATUTE AS AMENDED UP TO 23 FEBRUARY 1989.

IAEA (1997). INFCIRC 540 Model Protocol Additional to the Agreement(s) Between State(s) and the International Atomic Energy Agency for the Application of Safeguards, IAEA.

IAEA (2006). IAEA Illicit Trafficking Database (ITDB). Fact Sheet, International Atomic Energy Agency.

IAEA (2007). "Management of Reprocessed Uranium - Current Status and Future Prospects." IAEA Technical Documents(IAEA-TECDOC-1529).

IAEA (2009). Nuclear Fuel Cycle Information System, IAEA. **IAEA-TECDOC-1613**.

IAEA (2010). "International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials." IAEA-STR-368.

IAEA (2013). "Nuclear Security Fundamentals - Objective and Essential Elements of a State’s Nuclear Security Regime." IAEA Nuclear Security Series **20**.

IRMM (2015). NUCLEAR CERTIFIED REFERENCEMATERIALS. IRMM.

ISO (2005). ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories. Geneva, International Organization for Standardization.

ISO (2008). ISO Guide 30:1992/Amd 1:2008 – Terms and definitions used in connection with reference materials. Geneva, International Organization for Standardization.

Jakopič, R., Y. Aregbe, et al. (2016). "Verification measurements of the IRMM-1027 and the IAEA large-sized dried (LSD) spikes." Journal of Radioanalytical and Nuclear Chemistry: 1-11.

Jakopič, R., J. Bauwens, et al. (2013). Preparation and Certification of Large-Sized Dried (LSD) Spike IRMM-1027o. JRC Reference Materials. Luxembourg, European Commission.

Jakopic, R., J. Bauwens, et al. (2011). "Preparation and development of new Pu spike isotopic reference materials at IRMM." ESARDA BULLETIN(46): 65 - 71.

Jakopic, R., S. Richter, et al. (2010). "Determination of 240Pu/239Pu, 241Pu/239Pu and 242Pu/239Pu isotope ratios in environmental reference materials and samples from Chernobyl by thermal ionization mass spectrometry (TIMS) and filament carburization." Journal of Analytical Atomic Spectrometry **25**(6): 815-821.

Jakopic, R., S. Richter, et al. (2009). "Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with "multiple ion counting" and filament carburization." International Journal of Mass Spectrometry **279**(2-3): 87-92.

Jakopic, R., S. Richter, et al. (2009). Isotope Ratios Measurements in Environmental Samples Using Thermal Ionization Mass Spectrometry (TIMS) and Filament Carburization. 31st ESARDA Annual Meeting Symposium on Safeguards and Nuclear Material Management, Ispra (Italy), ESARDA and the Joint Research Centre of the European Commission.

Jakopič, R., M. Sturm, et al. (2013). "Certified reference materials and reference methods for nuclear safeguards and security." Journal of Environmental Radioactivity **125**(0): 17-22.

Jakopič, R., A. Verbruggen, et al. (2010). "An inter-calibration campaign using various selected Pu spike isotopic reference materials." J. Radioanal. Nucl. Chem. **286**(2): 449-454.

JCGM100 (2008). Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM 100:2008 (GUM 1995 with minor corrections) Paris, France, BIPM Joint Committee for Guides in Metrology.

Kappel, S. (2012). Uranium and Plutonium Isotopic Fingerprinting of Single Particles by Laser Ablation - Multi Collector - Inductively Coupled Plasma Mass Spectrometry, University of Natural Resources and Life Sciences, Vienna.

Keegan, R. P. and R. J. Gehrke (2003). "A method to determine the time since last purification of weapons grade plutonium." Appl. Radiat. Isot. **59**(2-3): 137-143.

Kelley, J. M. and D. M. Robertson (1985). "Plutonium ion emission from carburized rhenium mass spectrometer filaments." Analytical Chemistry **57**(1): 124-130.

Kirby, H. W. and W. E. Sheehan (1984). "Determination of 238Pu and 241Am in 239Pu by alpha-spectrometry." Nucl. Instrum. Methods **223**(2-3): 356-359.

Kittel, C. (2004). Introduction to Solid State Physics, Wiley.

Kraiem, M., K. Mayer, et al. (2010). "Experimental investigation of the ionization mechanisms of uranium in thermal ionization mass spectrometry in the presence of carbon." International Journal of Mass Spectrometry **289**(2â€“3): 108-118.

Kraiem, M., S. Richter, et al. (2011). "Investigation of uranium isotopic signatures in real-life particles from a nuclear facility by thermal ionization mass spectrometry." Anal. Chem. **83**(8): 3011-3016.

Kraiem, M., S. Richter, et al. (2011). "Development of an improved method to perform single particle analysis by TIMS for nuclear safeguards." Analytica Chimica Acta **688**(1): 1-7.

Kühn, H. (1991). Total Flash Evaporation for U and Pu. 12th International Mass Spectrometry Conference, Amsterdam.

LNHB. (2017, 04.10.2016). "Laboratoire National Henri Becquerel Recommended Data." Retrieved 15.01.2017, 2017, from http://www.nucleide.org/DDEP_WG/DDEPdata.htm.

Mathew, K. J., R. M. Essex, et al. (2014). "Uncertainties achievable for uranium isotope-amount ratios: estimates based on the precision and accuracy of recent characterization measurements." Journal of Radioanalytical and Nuclear Chemistry **305**(1): 277-282.

Mayer, K., M. Wallenius, et al. (2005). "Nuclear forensics - A methodology providing clues on the origin of illicitly trafficked nuclear materials." Analyst **130**(4): 433-441.

Mayer, K., M. Wallenius, et al. (2012). "Nuclear Forensic Science: Correlating Measurable Material Parameters to the History of Nuclear Material." Chem. Rev. **113**(2): 884-900.

Meitner, L. and O. R. Frisch (1939). "Disintegration of Uranium by Neutrons: a New Type of Nuclear Reaction." Nature **143**: 239-240.

Miyamoto, Y., F. Esaka, et al. (2013). Precise age determination of a single plutonium particle using inductively coupled plasma mass spectrometer. Radiochimica Acta. **101:** 745.

Miyamoto, Y., D. Suzuki, et al. (2015). "Accurate purification age determination of individual uranium–plutonium mixed particles." Analytical and Bioanalytical Chemistry **407**(23): 7165-7173.

Moody, K. J. (1995). Determination of plutonium metal origins, Lawrence Livermore National Laboratory. **UCRL-ID-120253**.

Morss, L. R., N. M. Edelstein, et al. (2006). Uranium. The Chemistry of the Actinide and Transactinide Elements, Springer Netherlands**:** 253-698.

NBL. (2017). "Certified Reference Materials (CRMs)." Retrieved 15.01.2017, 2017, from https://science.energy.gov/nbl/certified-reference-materials/.

Neuhoff, J. (2008). Certificate of Analysis CRM 113-B Uranium Hexafluoride Assay and Isotopic Standard. Aragonne, Illinois, USA, New Brunswick Laboratory, U.S. Department of Energy.

Neuhoff, J. (2008). Certificate of Analysis CRM U500 Uranium Isotopic Standard, U.S. Department of Energy.

Nguyen, C. T. (2006). "Verification of the 239Pu content, isotopic composition and age of plutonium in Pu-Be neutron sources by gamma-spectrometry." Nucl. Instrum. Methods Phys. Res., Sect. B **251**(1): 227-236.

Noddack, I. (1934). "Über das Element 93." Angewandte Chemie **47**(37): 653-655.

NSS (2014). JOINT STATEMENT in the context of the Nuclear Security Summit 2014: Forensics in Nuclear Security The Hague, the Netherlands, Nuclear Security Summit.

NSS (2016). Nuclear Security Summit: Certified Reference Material Fact Sheet. Washington, D.C., USA, Nuclear Security Summit.

Nygren, U., H. Ramebäck, et al. (2007). "Age determination of plutonium using inductively coupled plasma mass spectrometry." J. Radioanal. Nucl. Chem. **272**(1): 45-51.

Pommé, S. (2015). "The uncertainty of the half-life." Metrologia **52**(3): S51.

Pommé, S., S. M. Jerome, et al. (2014). "Uncertainty propagation in nuclear forensics." Applied Radiation and Isotopes **89**(0): 58-64.

Ramebäck, H., U. Nygren, et al. (2012). "Uncertainty assessment in gamma spectrometric measurements of plutonium isotope ratios and age." Nucl. Instrum. Methods Phys. Res., Sect. B **287**(0): 56-59.

Redermeier, A. (2009). "Fingerprinting of Nuclear Material for Nuclear Forensics." ESARDA BULLETIN(43): 71-76.

Richter, S., A. Alonso, et al. (2009). "A new series of uranium isotope reference materials for investigating the linearity of secondary electron multipliers in isotope mass spectrometry." International Journal of Mass Spectrometry **281**(3): 115-125.

Richter, S. and S. A. Goldberg (2003). "Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry." International Journal of Mass Spectrometry **229**(3): 181-197.

Richter, S., H. Kühn, et al. (2011). "Improvements in routine uranium isotope ratio measurements using the modified total evaporation method for multi-collector thermal ionization mass spectrometry." Journal of Analytical Atomic Spectrometry **26**(3): 550-564.

Romkowski, M., S. Franzini, et al. (1987). Mass spectrometric analysis of sub-nanocurie samples of uranium and plutonium. 9th International Symposium on Safeguards and Nuclear Material Management, London, ESARDA.

Seong-whun, C. (2011). Setting the Agenda for the Success of the Nuclear Security Summit in Seoul. National Strategy, 17. Seongnam, South Korea, Sejong Institute. **17**.

Shinonaga, T., D. Donohue, et al. (2012). "Production and Characterization of Plutonium Dioxide Particles as a Quality Control Material for Safeguards Purposes." Analytical Chemistry **84**(6): 2638-2646.

Shinonaga, T., D. Donohue, et al. (2009). "Age determination of single plutonium particles after chemical separation." Spectrochimica Acta Part B: Atomic Spectroscopy **64**(1): 95-98.

Shinonaga, T., F. Esaka, et al. (2008). "Isotopic analysis of single uranium and plutonium particles by chemical treatment and mass spectrometry." Spectrochimica Acta Part B: Atomic Spectroscopy **63**(11): 1324-1328.

Smith, D. K., M. J. Kristo, et al. (2008). "Documentation of a model action plan to deter illicit nuclear trafficking." J. Radioanal. Nucl. Chem. **276**(2): 415-419.

Spencer, K. J., L. Tandon, et al. (2009). "Refinement of Pu parent–daughter isotopic and concentration analysis for forensic (dating) purposes." Journal of Radioanalytical and Nuclear Chemistry **282**(2): 549-554.

Stanley, F. E. (2012). "A beginner's guide to uranium chronometry in nuclear forensics and safeguards." Journal of Analytical Atomic Spectrometry **27**(11): 1821-1830.

Stepanov, A. V. (1990). Activity of VG Khlopin Radium Institute in the area of analytical quality control. IAEA-AL--039, International Atomic Energy Agency (IAEA).

Stepanov, S. I. and A. M. Chekmarev (2008). "Concept of spent nuclear fuel reprocessing." Dokl. Chem. **423**(1): 276-278.

Stolz, W. (2005). Radioaktivität: Grundlagen - Messung - Anwendungen Vieweg+Teubner Verlag.

Sturm, M., S. Richter, et al. (2010). Feasibility study for the development of plutonium reference materials for age dating in nuclear forensics. International Symposium on Safeguards: Preparing for Future Verification Challenges. Vienna, Austria, IAEA.

Sturm, M., S. Richter, et al. (2014). "Evaluation of chronometers in plutonium age determination for nuclear forensics: What if the ‘Pu/U clocks’ do not match?" Journal of Radioanalytical and Nuclear Chemistry **302**(1): 399-411.

Sturm, M., S. Richter, et al. (2016). "Optimized Chemical Separation and Measurement by TE TIMS Using Carburized Filaments for Uranium Isotope Ratio Measurements Applied to Plutonium Chronometry." Analytical Chemistry **88**(12): 6223-6230.

Taylor, D. M. (2001). Environmental plutonium - creation of the universe to twenty-first century mankind. Plutonium in the Environment. A. Kudo, Elsevier. **Volume 1:** 1-14.

Taylor, P. and R. Wellum (2006). Certificate isotopic reference material IRMM-074 Geel, Belgium, Institute for Reference Materials and Measurements.

Thorstensen, S. and K. Chitumbo (1995). "Safeguards in the European Union: The New Partnership Approach." IAEA BULLETIN **1**: 25-28.

Uriano, G. A. (1982). National Bureau of Standards Certificate of Analysis Standard Reference Material 946 Plutonium Isotopic Standard, U.S. Department of Energy.

Varga, Z., A. Nicholl, et al. (2012). "Development and validation of a methodology for uranium radiochronometry reference material preparation." Anal. Chim. Acta **718**: 25-31.

Varga, Z., A. Nicholl, et al. (2016). "Plutonium age dating (production date measurement) by inductively coupled plasma mass spectrometry." Journal of Radioanalytical and Nuclear Chemistry **307**(3): 1919-1926.

Varga, Z., A. Nicholl, et al. (2016). "Remeasurement of 234U Half-Life." Analytical Chemistry **88**(5): 2763-2769.

Varga, Z. and G. Surányi (2007). "Production date determination of uranium-oxide materials by inductively coupled plasma mass spectrometry." Analytica Chimica Acta **599**(1): 16-23.

Varga, Z., G. Surányi, et al. (2007). "Determination of plutonium and americium in environmental samples by inductively coupled plasma sector field mass spectrometry and alpha spectrometry." Microchem. J. **85**(1): 39-45.

Varga, Z., C. Venchiarutti, et al. (2015). "IRMM-1000a and IRMM-1000b uranium reference materials certified for the production date. Part I: methodology, preparation and target characteristics." Journal of Radioanalytical and Nuclear Chemistry: 1-9.

Varga, Z., C. Venchiarutti, et al. (2015). "IRMM-1000a and IRMM-1000b uranium reference materials certified for the production date. Part I: methodology, preparation and target characteristics." Journal of Radioanalytical and Nuclear Chemistry **307**(2): 1077-1085.

Venchiarutti, C., Z. Varga, et al. (2015). REIMEP-22 inter-laboratory comparison: “U Age Dating – determination of the production date of a uranium certified test sample”. Radiochimica Acta. **103:** 825.

Venchiarutti, C., Z. Varga, et al. (2016). "IRMM-1000a and IRMM-1000b: uranium reference materials certified for the production date based on the 230Th/234U radiochronometer. Part II: certification." Journal of Radioanalytical and Nuclear Chemistry **308**(1): 105-111.

Verbruggen, A., A. Alonso, et al. (2008). Preparation and Certification of IRMM-3636, IRMM-3636a and IRMM-3636b. JRC Scientific and Technical Reports. Luxembourg, European Commission.

Wallenius, M. (2001). Origin determination of reactor produed plutonium by mass spectrometrc techniques: application to nuclear forensic science and safeguards. PhD PhD, University of Helsinki.

Wallenius, M., K. Lützenkirchen, et al. (2007). "Nuclear forensic investigations with a focus on plutonium." J. Alloys Compd. **444-445**: 57-62.

Wallenius, M. and K. Mayer (2000). "Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry." Fresenius J. Anal. Chem. **366**(3): 234-238.

Wallenius, M., K. Mayer, et al. (2006). "Nuclear forensic investigations: Two case studies." Forensic Sci. Int.(156): 55-62.

Wallenius, M., P. Peerani, et al. (2000). "Origin Determination of Plutonium Material in Nuclear Forensics." Journal of Radioanalytical and Nuclear Chemistry **246**(2): 317-321.

Wallenius, M., G. Tamborini, et al. (2001). "The "age" of plutonium particles." Radiochim. Acta **89**(1_2001): 55.

Wallner, A., T. Faestermann, et al. (2015). "Abundance of live 244Pu in deep-sea reservoirs on Earth points to rarity of actinide nucleosynthesis." Nature Communications **6**: 5956.

Walsh, S. J., T. Burr, et al. (2017). "Discussion of the IAEA Error Approach to Producing Variance Estimates for Use in Material Balance Evaluation and the International Target Values, and Comparison to Metrological Definitions of Precision." JNMM, Journal of the Institute of Nuclear Materials Management(XLV(2)): 4-14.

Watchman, A. L. and C. R. Twidale (2002). "Relative and 'absolute' dating of land surfaces." Earth-Science Reviews **58**(1-2): 1-49.

Wellum, R., A. Verbruggen, et al. (2009). "A new evaluation of the half-life of 241Pu." J. Anal. At. Spectrom. **24**(6): 801-807.

Weyer, S., A. D. Anbar, et al. (2008). "Natural fractionation of 238U/235U." Geochimica et Cosmochimica Acta **72**(2): 345-359.

Wilcken, K. M., T. T. Barrows, et al. (2007). "AMS of natural 236U and 239Pu produced in uranium ores." Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **259**(1): 727-732.

Zhang, H.-T., F. R. Zhu, et al. (2008). "Age determination of plutonium material by alpha spectrometry and thermal ionization mass spectrometry." Radiochim. Acta **96**(6): 327-331.

2 Publications

This chapter contains the scientific publications required for fulfilling the aim of this thesis. First author publications published in peer-reviewed scientific journals are indicated by an asterisk. Permission for reproduction of the articles was granted by the respective publishers.

Publication I:

Optimized Chemical Separation and Measurement by TE TIMS Using Carburized Filaments for Uranium Isotope Ratio Measurements Applied to Plutonium Chronometry

Sturm M, Richter S, Aregbe Y, Wellum R, Prohaska T

Analytical Chemistry 88 (12), 2016: p. 6223-6230.

(Reproduced by permission of the American Chemical Society)

Publication II

Evaluation of chronometers in plutonium age determination for nuclear forensics: What if the 'Pu/U clocks' do not match?

Sturm M, Richter S, Aregbe Y, Wellum R, Mialle S, Mayer K, Prohaska T

Journal of Radioanalytical and Nuclear Chemistry 2014. p. 1-13.

(Reproduced by permission of Akadémiai Kiadó Zrt.)

Publication III

Certified reference materials and reference methods for nuclear safeguards and security

Jakopic R, Sturm M, Kraiem M, Richter S, Aregbe Y

Journal of Environmental Radioactivity, 2013. 125:p. 17-22.

(Reproduced by permission of Elsevier Limited)

Publication IV

Preparation and Development of New Pu Spike Isotopic Reference Materials at IRMM

Jakopic R, Bauwens J, Richter S, Sturm M, Verbruggen A, Wellum R, Eykens R, Kehoe F, Kuehn H, Aregbe Y.

ESARDA Bulletin December 2011 (46); 2011. p. 65-71. JRC65089

(Reproduced by permission of ESARDA, the European Safeguards Research and Development Association)

Publication V

Destructive Analysis: Effective Analytical Support to Nuclear Safeguards and Non-Proliferation

Sturm M

ESARDA BULLETIN, 2010(45). p. 56-65.

(Reproduced by permission of ESARDA, the European Safeguards Research and Development Association)

Publication VI

Age determination of plutonium for nuclear forensics

Sturm M, Richter S, Aregbe Y, Wellum R, Altzitzoglou T, Jobbagy V, Mialle S, Mayer K, Prohaska T

In Conference Proceedings: 35th ESARDA Symposium proceedings, Bruges, 27-30 May, ISBN: 978-92-79-32730-8, Institute for Transuranium Elements; 2013. p. 572-577. JRC83924

(Reproduced by permission of ESARDA, the European Safeguards Research and Development Association)

Publication VII

Feasibility Study for the Development of Plutonium Reference Materials for Age Dating in Nuclear Forensics.

Sturm M, Richter S, Aregbe Y, Wellum R, Altzitzoglou T, Verbruggen A, Mayer K, Prohaska T

In Conference Proceedings: Proceedings of Symposium on International Safeguards: Preparing for Future Verification Challenges. Vienna (Austria): IAEA; 2010. p. 1-8. JRC60800

(Reproduced by permission of IAEA confirmed by Stephen Pullinger, Communication Adviser, Office of Deputy Director General, Department of Safeguards, International Atomic Energy Agency)

Publication VIII:

Isotope Ratios Measurements in Environmental Samples Using Thermal Ionization Mass Spectrometry (TIMS) and Filament Carburization

Jakopic R, Richter S, Sturm M, Kuehn H, Aregbe Y

In Conference Proceedings: Proceedings of the 31st ESARDA Annual Meeting Symposium on Safeguards and Nuclear Material Management, ISBN: 978-92-79-13054-0, LB-NA24038-EN-Z. Ispra (Italy): ESARDA and the Joint Research Centre of the European Commission; 2009. p. Session 6 - 019 (1-5). JRC52196

(Reproduced by permission of ESARDA, the European Safeguards Research and Development Association)

2.1 Publication I

Reprinted with permission from Optimized Chemical Separation and Measurement by TE TIMS Using Carburized Filaments for Uranium Isotope Ratio Measurements Applied to Plutonium Chronometry. Sturm M, Richter S, Aregbe Y, Wellum R, Prohaska T. Analytical Chemistry, 2016, Article ASAP, DOI: 10.1021/acs.analchem.5b03852. Copyright (2016) American Chemical Society.

analytical chemistry
Article
pubs.acs.org/ac

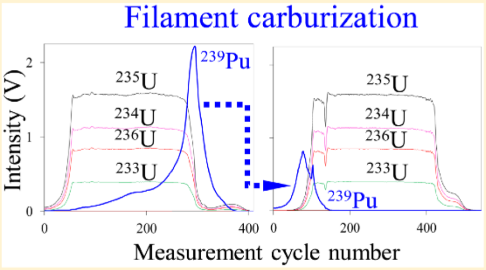
Optimized Chemical Separation and Measurement by TE TIMS Using Carburized Filaments for Uranium Isotope Ratio Measurements Applied to Plutonium Chronometry

Monika Sturm,[*,†] Stephan Richter,[‡] Yetunde Aregbe,[‡] Roger Wellum,[‡] and Thomas Prohaska[†]

[†]Department of Chemistry, VIRIS Laboratory, University of Natural Resources and Life Sciences (BOKU), Vienna, Konrad-Lorenz-Strasse 24, A-3430 Tulln, Austria

[‡]European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Retieseweg 111, B-2440 Geel, Belgium

ABSTRACT: An optimized method is described for U/Pu separation and subsequent measurement of the amount contents of uranium isotopes by total evaporation (TE) TIMS with a double filament setup combined with filament carburization for age determination of plutonium samples. The use of carburized filaments improved the signal behavior for total evaporation TIMS measurements of uranium. Elevated uranium ion formation by passive heating during rhenium signal optimization at the start of the total evaporation measurement procedure was found to be a result from byproducts of the separation procedure deposited on the filament. This was avoided using carburized filaments. Hence, loss of sample before the actual TE data acquisition was prevented, and automated measurement sequences could be accomplished. Furthermore, separation of residual plutonium in the separated uranium fraction was achieved directly on the filament by use of the carburized filaments. Although the analytical approach was originally tailored to achieve reliable results only for the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, and ^{240}Pu/^{236}U chronometers, the optimization of the procedure additionally allowed the use of the ^{242}Pu/^{238}U isotope amount ratio as a highly sensitive indicator for residual uranium present in the sample, which is not of radiogenic origin. The sample preparation method described in this article has been successfully applied for the age determination of CRM NBS 947 and other sulfate and oxide plutonium samples.



Nuclear forensic age determination aims to discover the history of seized nuclear material. The emphasis of such an investigation is to identify the latest legal owner and the production place of the material. Information about the production process and the intended use of the seized material is gained from the analysis of the chemical composition and the physical appearance of the sample. The "age" of the material helps to limit the number of potential facilities of origin of the material to those that were operational at the time of the production or processing of the material.[1] The "age" of a nuclear material is defined as the time span elapsed since the last chemical separation of mother nuclides from their respective daughter nuclides during enrichment or reprocessing. Several chronometers (i.e., parent/daughter nuclide pairs) are used for the determination of the age of plutonium: ^{241}Am/^{241}Pu, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, and ^{240}Pu/^{236}U.[2] The age can be calculated via the appropriate decay equations by using the measured nuclide ratios. The resulting "model age", however, only coincides with the true age in case the initial removal of the daughter nuclides was complete and the sample has been a closed system.[3] This is not always the case for seized nuclear material. In addition to the above-mentioned nuclide pairs, the ^{242}Pu/^{238}U ratio can be employed as a useful tool for monitoring the presence of nonradiogenic uranium in the plutonium sample.[4] Bulk samples of plutonium are mostly dated via the ^{241}Pu/^{241}Am chronometer using gamma spectrometry[2,5−8] or alpha spectrometry combined with either thermal ionization mass spectrometry (TIMS) or with inductively coupled plasma mass spectrometry (ICP-MS).[8−12] TIMS[2,5] and ICP-MS[12,13] have become the methods of choice for dating plutonium via the plutonium/uranium chronometers. Alpha spectrometry has been used as a complementary method to TIMS, as well.[9,14]

This article is part of work that has been carried out by the EC-JRC-IRMM (Institute of Reference Materials and Measurements, Geel, Belgium) and EC-JRC-ITU (Institute for Transuranium Elements, Karlsruhe, Germany) for the preparation of plutonium and uranium reference materials certified for separation dates.[15,16] The focus of the presented study was the sample preparation of the uranium fraction for plutonium age determination by total evaporation (TE) TIMS.[17] The measurement of uranium isotope amount contents from the

Received: October 12, 2015
Accepted: May 31, 2016
Published: May 31, 2016

DOI: 10.1021/acs.analchem.5b03852
Anal. Chem. 2016, 88, 6223−6230

decay of plutonium is hampered by the low concentration of the uranium isotopes. Since $^{242}Pu/^{238}U$ is used as powerful indicator for nonradiogenic uranium in a plutonium sample, a special aim of this work was to optimize the procedure in a way that the ^{238}U amount content could be determined by isotope dilution mass spectrometry (IDMS)[18] along with the amount contents of the other uranium nuclides with reasonable accuracy. As a consequence, finding an answer to dealing with the isobaric interference of ^{238}Pu when measuring ^{238}U isotope is of vital importance. Several studies on the characterization of mixed uranium−plutonium oxides (MOX) and of unseparated safeguards samples containing plutonium and uranium emphasize the topicality of the measurement of ^{238}Pu in the presence of ^{238}U and vice versa by mass spectrometry.[14,19−24] These articles deal with materials that contain 3 to 300 times more uranium than plutonium,[14,20,22] materials that have a 1:1 ratio of plutonium and uranium,[21,23] and with materials that contain up to 5 to 10 times[19,22] more plutonium than uranium. U/Pu ratios between 1:10 and 100:1 for direct safeguards measurements of $^{235}U/^{238}U$ and $^{240}Pu/^{239}Pu$ in unseparated samples have also been investigated.[24] As far as the age determination of plutonium is concerned, NBS 946 contains, for example, about 450 times more plutonium than uranium ($g \cdot g^{-1}$) since only a small fraction of plutonium has decayed to uranium in the 41 years elapsed since the last purification of the plutonium from its uranium daughter nuclides.[4] The plutonium content of such a sample can be reduced to a ratio of about 0.02 Pu/U ($g \cdot g^{-1}$) in the purified uranium fraction by chemical purification of the uranium fraction applying the optimized separation procedure described in the Materials and Methods section of this article. Double rhenium filament assemblies were used in most of the studies using TIMS for isotope amount ratio measurements of uranium and plutonium, respectively, including ^{238}Pu in the presence of ^{238}U and vice versa.[14,19−22] In order to separate the interfering uranium and plutonium signals, interfering element correction (IEC),[14,19,20] peak fitting,[21] and the continuous heating method[22,23] were applied.

Filament carburization has been used for enhancing the ionization efficiency for single uranium[25,26] and plutonium particles[25,27] as well as for environmental plutonium samples (pg amounts)[28,29] as it influences the measurement behavior of uranium[30] and plutonium by changing chemical processes on the filament.[31] Furthermore, a shift of the formation of single charged ions to higher temperatures was also reported for plutonium.[31] Graphite powder[25,27] and benzene vapor[26,28,29,32] were used as a carbon source in these studies. The increase in the ionization efficiency is attributed to the fact that carbon, uranium, and plutonium form carbides, which dissociate at higher temperatures to single charged ions as opposed to the formation of oxide ions of plutonium[31] and uranium[32] without carburization. Carbon is believed to change the work function of the filament by forming a solid−solid solution in rhenium. Carbon dissolves on the filament surface upon heating and forms carbides with the analyte.[31,32] Contrary to previous publications by others,[25−29] the enhancement of the ionization effciency was not the major purpose for the use of filament carburization in this study. The purpose of applying carburized zone-refined rhenium filaments was to improve the signal behavior during the uranium TE measurement of the uranium fraction pruified from a plutonium sample. This arrangement aided also the removal of residual plutonium during filament heating prior to data acquisition. To our knowledge, this work describes for the first time the application of routine TE measurements in combination with filament carburization to remove the residual plutonium and to delay the ionization of uranium. The method presented in this study was successfully applied for age determination of other plutonium sulfate and oxide samples published elsewhere.[4]

■ MATERIAL AND METHODS

Analytical Strategy. The results for the nuclide amount ratios $^{238}Pu/^{234}U$, $^{239}Pu/^{235}U$, $^{240}Pu/^{236}U$, and $^{242}Pu/^{238}U$ for plutonium age determination are obtained in two independent isotope dilution experiments measured by TE TIMS: one determining the amount contents of the plutonium nuclides and the other determining the amount contents of the uranium nuclides.[4] Prior to these measurements the plutonium and uranium fractions are purified by chemical separation steps from the plutonium sample, whereby the inevitable remainder of plutonium including ^{238}Pu in the separated uranium fraction is of major concern. The purification and measurements determining the plutonium nuclides' amount contents via IDMS is described elsewhere in detail[4] as this publication focuses on the determination of the uranium nuclides' amount contents of aged plutonium samples.

Samples, Chemicals, and Reference Materials. The plutonium sulfate isotopic certified reference materials (CRM) NBS 946 (NBL CRM 136; National Bureau of Standards, Washington, DC, U.S.A.)[33] and NBS 947 (NBL CRM 137; National Bureau of Standards)[34] were used for method development. The materials were dissolved in concentrated HNO_3 (69% (g/(100)g), p.a.; Merck, Darmstadt, Germany) and sample solutions with a plutonium content of about 0.002 $g \cdot g^{-1}$ in 5 $mol \cdot L^{-1}$ HNO_3 were prepared. Dilutions of concentrated HNO_3 in purified reagent grade I water (Milli-Q Water Purification System (18MΩ); Millipore, Billerica, MA, U.S.A.) were used for all diluted HNO_3 solutions.

The amount contents of both plutonium and uranium nuclides were determined by IDMS. The sample aliquots for plutonium IDMS were purified using anion-exchange columns (Bio-Rad AG1-X4, 100−200 mesh; Bio-Rad Laboratories Ltd., Hercules, CA, U.S.A.), and the ^{242}Pu certified reference material IRMM-049d (Institute for Reference Materials and Measurements, Geel, Belgium)[35] was used as IDMS spike.[4,36] The following chemicals and resins were used for the preparation of the sample aliquots for uranium IDMS: Anion-exchange columns (Bio-Rad AG1-X4, 100−200 mesh; Bio-Rad Laboratories Ltd., Hercules, CA, U.S.A.) and extraction chromatographic UTEVA columns (UTEVA; Eichrom Technologies, Lisle, IL, U.S.A.) were used for the chemical purification of the uranium fraction. $FeCl_2$ (p.a.; Merck, Darmstadt, Germany), $NH_2OH.HCl$ (p.a.; Merck, Darmstadt, Germany), and $NaNO_2$ (p.a.; Merck, Darmstadt, Germany) were used for valence adjustment of plutonium, and H_2O_2 (30% p.a.; Merck, Darmstadt, Germany) was used to remove traces of organic compounds. The CRM IRMM-074/10[37] was used for the calibration of the mass spectrometer for mass fractionation during uranium measurements. IRMM 3630 served as the ^{233}U spike for uranium IDMS.[38]

Instrumentation. All measurements were accomplished applying the TE method for TIMS using the double filament technique on a Triton (Thermo Fisher Scientific, Bremen, Germany) TIMS multicollector instrument.[17] Degassed zone-refined rhenium filaments (Thermo Fisher Scientific, Bremen, Germany) were used as ionization as well as evaporation filaments. All ion currents were measured on Faraday cups. About 100 ng of uranium were loaded per evaporation filament. The carburization of the filaments was accomplished as described elsewhere.[28] A propane/butane gas mixture served as carbon source instead of benzene.[39]

Chemical Purification of the Uranium Fraction. The procedure developed for the purification of the uranium fraction from aged plutonium materials is based on the separation procedure to separate uranium from plutonium routinely applied at JRC-IRMM.[40] This is depicted as separation procedure A in Figure 1. Procedure A consists of a plutonium valence adjustment to Pu(IV) called "Redox I" and a separation on anion-exchange columns. These steps are repeated twice. Further optimizations (procedures B–E) were based on separation procedure A. All chemical separations were carried out in glove boxes. The use of hydrochloric acid was avoided because of its corrosive properties. UTEVA columns (Eichrom Technologies LLC, Lisle, IL, U.S.A.) were used in separation procedures B–E (Figure 1B–E). The term "Redox II" in Figure 1 (procedures C–E) refers to the reduction of Pu(VI) to Pu(III), which was expected to give better U–Pu separation results on UTEVA columns compared to Redox I. An additional step for the destruction of organic compounds in the final uranium fraction was introduced in separation procedure D and E. The individual steps such as valence adjustment and column separations used in separation procedure A–E are described in the following paragraphs.

Pu Valence Adjustment "Redox I". The valence adjustment of plutonium to Pu (IV) is referred to as Redox I hereafter: The sample solution is evaporated to dryness after dissolution of plutonium sulfate and dissolved in 200 μL of nitric acid (c = 2 mol·L^{-1}). Subsequently, 50 μL of iron(II) chloride solution (c = 1.25 mol·L^{-1}) is added to the dried sample solution in order to reduce the plutonium to Pu(III). Subsequently, 100 μL of hydroxyl ammonium chloride solution (c = 1 mol·L^{-1}) is added. The addition of 100 μL sodium nitrite solution (c = 1 mol·L^{-1}) aids the oxidation of Pu(III) to Pu(IV). Finally, 430 μL of concentrated nitric acid is added to obtain Pu(IV) in a solution made up of nitric acid (c = 8 mol L^{-1}).

Separation on Anion-Exchange Column. The sample solution is loaded on anion-exchange columns (Bio-Rad AG1-X4) conditioned with nitric acid (c = 8 mol L^{-1}), and the uranium fraction is eluted with nitric acid (c = 8 mol L^{-1}). The resulting purified uranium fraction is subsequently evaporated to dryness. The above-described steps are repeated at least once more for separation procedure A (Figure 1A).

Pu Valence Adjustment "Redox II". The sample solution is evaporated to dryness prior to the reduction of Pu(VI) to Pu(III) and subsequently taken up in 200 μL of nitric acid (c = 2 mol L^{-1}). Next, 50 μL of iron(II) chloride solution (c = 1.25 mol L^{-1}) is added in order to reduce Pu(VI) to Pu(III). Then 190 μL of concentrated nitric acid is added after mixing and a waiting period of 5 min to achieve 8 molar nitric acid (c = 8 mol L^{-1}) in the sample solution for separation procedures B–D. The final sample solution was adjusted to 5 molar nitric acid (c = 5 mol L^{-1}) for separation procedure E. Pu(III) is expected to behave like Am(III), which does not bind to UTEVA during the separation while Pu(IV) is bound to the UTEVA resin and could thus be eluted along with U(VI).[41]

Separation on UTEVA Columns. UTEVA was specifically developed for the separation of uranium, plutonium, and americium. The extractant in the UTEVA Resin, diamyl, amylphosphonate, forms nitrato complexes with actinide elements.[13] Plutonium and americium are washed from the column with 10 mL of nitric acid (c = 8 mol L^{-1}) for separation procedures B–D, and the uranium fraction is eluted from the column with 16 mL of nitric acid (c = 0.02 mol L^{-1}). The resulting purified uranium fraction is subsequently evaporated to dryness. Ten milliliters of nitric acid (c = 5 mol L^{-1}) and 4 mL of nitric acid (c = 1 mol L^{-1}) containing 0.1 M $NH_2OH.HCl$ are used for the elution of plutonium and americium of separation procedure E to ensure that plutonium remains in its reduced form (Pu(III)) and could thus be eluted more efficiently from the UTEVA column.

Destruction of Organic Compounds. The uranium fraction collected from the second separation column is evaporated to dryness on a hot plate. Subsequently, 1 mL of concentrated nitric acid and 0.5 mL of H_2O_2 are added in separation procedures D and E. The solution is evaporated once again to dryness after a reaction time of >15 min. This is repeated three times. This procedure destroys possible organic compounds bleeding from the column, minimizing the visibly raised deposits of the dried sample solution on the filaments.

Preparation of the Filament Loading Solution. Finally, the dried purified uranium residue is taken up by nitric acid (c = 1 mol L^{-1}). The target uranium amount content for the filament loading solution was 50 ng/μL. Two microliters (2 × 1 μL) was directly pipetted on each evaporation filament without further dilution steps in order to reduce the starting amount of the sample. The absence of further dilution steps increases undesired compounds such as iron and organic compounds in the filament loading solution compared to the uranium routine analysis at EC-JRC-IRMM.

Optimized Separation Procedure. As a result, procedure E was considered the optimum uranium separation procedure for the aged plutonium samples (Figure 1E). It consists of two separation steps: First, one separation step on an anion-exchange columns (Bio-Rad AG1-X4) combined with "Redox I" is carried out. This step is followed by valence adjustment "Redox II" to adjust the valence of plutonium to Pu(III) and subsequent purification of the uranium fraction on an UTEVA column. In order to avoid possible oxidation of Pu(III) during the UTEVA separation by the high concentration of nitric acid (c = 8 mol L^{-1}), as used in separation procedures B–D, the 8 molar nitric acid (c = 8 mol L^{-1}) was replaced by 5 molar nitric acid (c = 5 mol L^{-1}). Furthermore, an additional elution step wih nitric acid (c = 1 mol L^{-1}) plus 0.1 M $NH_2OH·HCl$ was introduced to ensure that plutonium remains in its reduced form (Pu(III)). Organic compounds in the purified uranium solution are destroyed as much as possible with H_2O_2 as described above.

Data Reduction. The separation factor for removal of plutonium in the purified uranium fraction was calculated as follows according to eq 1.[15,42]

$$S_{\mathrm{U/Pu}} = R_{\mathrm{U/Pu}}/R_{\mathrm{U/Pu\_0}} \tag{1}$$

$R_{\mathrm{U/Pu\_0}}$ is the U/Pu ratio in the initial sample solution before purification, and $R_{\mathrm{U/Pu}}$ is the U/Pu ratio after the separation in the purified fraction. In order to quantify the amount content of plutonium in the uranium fraction after purification of NBS 946 for the calculation of $R_{\mathrm{U/Pu}}$, a metrologically weighed amount of unspiked sample solution was purified according to procedure E. The purified uranium fraction was directly eluted from the UTEVA column into a vial containing a weighed amount of the ^{242}Pu IDMS spike. The resulting blend was subsequently measured using the Pu TE method. The amount content of

^{239}Pu was determined by IDMS. The isotope ratios measured in an unspiked purified plutonium fraction were used for calculating the amount contents of all other plutonium nuclides in the purified uranium fraction. The amount content of uranium in the uranium fraction after the separation procedure E for calculating $R_{U/Pu}$ was measured by purifying once again an unspiked metrological weighed aliquot of the sample solution by separation procedure E. This purified uranium fraction was blended with a weighed amount of the ^{233}U IDMS spike as described above for plutonium and subsequently measured with the U TE method. This amount content of uranium in the uranium fraction after purification was used for the calculation of the uranium recovery of the separation procedure as well as for calculating the separation factor for the removal of plutonium. $R_{U/Pu}$ in eq 1 was calculated from the amount contents of plutonium and uranium in the purified uranium fraction described above. R_{U/Pu_0} was calculated from results of the regular IDMS experiments for plutonium and uranium that were used for calculating the age dating results.

Uncertainty Calculation. The calculation of combined standard uncertainties of all results was performed using the software GUM workbench 2,4 (Metrodata GmbH, Weil am Rhein, Germany).

■ RESULTS AND DISCUSSION

Optimization of the Chemical Separation. The recovery of the uranium purification procedure routinely applied at EC-JRC-IRMM (procedure A) turned out to be insufficient to provide uranium signals suitable for TE measurements of the spiked uranium fraction obtained from aged plutonium samples. Procedure A had been designed for starting amounts of 10 to 60 mg uranium. Several dilution steps are foreseen after the separation to achieve the required uranium mass concentration of 100 ng/μL of which 1 μL is loaded onto the evaporation filament. The investigated plutonium sample NBS 946 contains, for example, about 450 times more plutonium than uranium, since only a small fraction of the plutonium decays to uranium. Attempts were made to reduce the amount of the initial plutonium sample needed for plutonium age determination, because the available amounts of plutonium samples for nuclear forensic age determination are usually limited. Consequently, it was necessary to optimize the chemical uranium separation procedure for the purpose of plutonium age determination. Hence, a sample solution of NBS 946 containing not more than about 5 mg Pu (∼10 mg plutonium sulfate tetrahydrate) should suffice to be separated to obtain 0.2 mL of the purified uranium fraction with an uranium mass concentration of 50 ng/μL taking into account a spiking ratio of 1:10 for ^{233}U/^{235}U and an overall recovery of the separation procedure of >90%. The dried purified uranium fraction had thus to be taken up in a rather small volume of nitric acid ($c = 1$ mol L^{-1}; 0.2 mL) without any further dilution steps serving directly as filament loading solution. Several purification procedures based on separation procedure A using UTEVA columns in addition to anion-exchange columns were tested (Figure 1). The result for both procedures B and C was that enough uranium was recovered from the sample to obtain reasonable uranium signals in uranium TE TIMS measurements. The measures taken to reduce the starting amount of the sample lead, however, also to undesired consequences; visible deposits on the loaded evaporation filaments were observed. Possible sources for these deposits are organic compounds bleeding from the columns and elements such as iron used for plutonium valence adjustment.

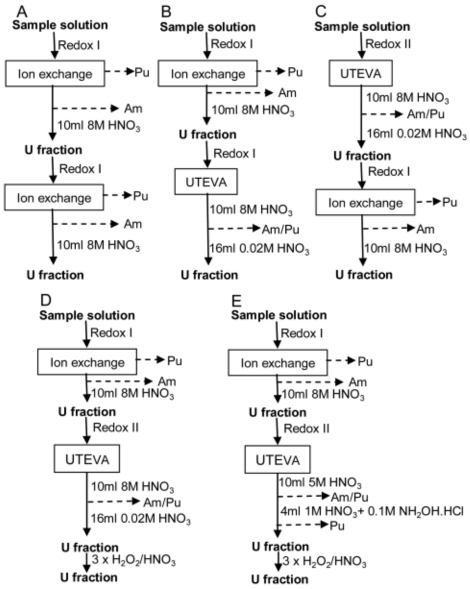


Figure 1. Schematics for separation procedures A to E tested for purification of the uranium fraction from aged plutonium samples for plutonium age determination.

As the U TE measurement of the uranium fraction obtained by procedure B appeared to contain less plutonium as compared to procedure C, this was further optimized in procedures D and E. An additional step of H_2O_2 treatment was introduced in separation procedure D and E in order to destroy possible organic compounds bleeding from the column, minimizing the visible raised deposits of the dried sample solution to a rust-colored spot on the filament. The rust color of the remaining visible spot can be attributed to iron introduced during the valence adjustment of plutonium (Redox I and Redox II). This was an important advancement because these raised deposits on the evaporation filament, which appeared after loading and drying the purified uranium solution, reduced the distance between the evaporation filament and the ionization filament in an inconsistent manner and also posed the risk of losing part of the sample during filament handling such as mounting the filaments on the turret. The consequences of this observation for the U TE measurement are described in the next paragraph. Measurements showed further reduced plutonium signals during the uranium TE data acquisition for separation procedure E compared to procedure D (Figure 3). Procedure E was therefore considered the best choice for separating uranium from aged plutonium samples for dating, see (Figure 1E).

Optimization of the U TE Measurement. The visible deposits on the loaded evaporation filaments observed for separation procedure B and C lead to a problem at the start of the TE measurement routine. This was caused by an elevated uranium ion formation by passive heating during rhenium signal optimization. Although these visible deposits on the loaded filaments were considerably reduced using separation procedure D and E, this could not be resolved completely by the optimization of the chemical separation.

The normal TE measurement routine foresees the optimization of the uranium ion signals prior to the TE data acquisition. The first step of this routine involves heating the ionization filament with a current of about 4300 mA in order to achieve an ^{187}Re signal (>20 mV) that can be used for peak centering and focusing to ensure optimal ionization filament conditions. Subsequently, the ^{187}Re signal is raised above 120 mV. As soon as this signal threshold for the ^{187}Re signal is exceeded, the evaporation filament is heated and a defined uranium ion signal (usually the most abundant uranium isotope) is monitored. As soon as 30 mV for this uranium signal or pilot mass are exceeded, focusing and peak centering steps are initiated for the uranium signal. Once these steps are completed, the TE data acquisition is started. During the data acquisition, the evaporation filament heating current is continuously increased striving to achieve a set target value (such as 4500 mV) for the sum of a number of predefined uranium signals (usually ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U) which leads to the typical flat plateaus of the TE signals. The evaporation filament current continues to increase until the sample is exhausted (totally evaporated) and the signals drop despite the increased heating current on the evaporation filament. The uranium signals are kept reasonably low (just above 30 mV for the most abundant uranium isotope) during the uranium signal optimization prior to the TE data acquisition in order to minimize possible biases of the TE results due the mass fractionation (i.e., a loss of lighter uranium ions prior to the data acquisition). The ^{238}U signal is routinely monitored as the pilot mass in this filament heating procedure as it is (in general) the most abundant isotope. ^{235}U was chosen for the measurement of the uranium fraction of aged plutonium samples because the concentration of radiogenic ^{238}U is very low in aged plutonium samples that are not mixed with nonradiogenic uranium.[4]

During the uranium signal optimization, it was observed that before the active heating of the evaporation filament had started, the ^{235}U signal exceeded the 30 mV threshold already due to passive heating by the ionization filament during the optimization steps involving the ^{187}Re signal. Hence, the further actions of focusing and peak center of the uranium signal were not triggered by the instrument software. The ^{235}U signal therefore had to be reduced manually below 30 mV by stepwise lowering of the current on the ionization filament (see Figure 2 showing a measurement of a ^{233}U spiked fraction of NBS 947). Apart from making automated measurement sequences of several filaments pairs impossible, this leads to an unpredictable additional loss of sample ionization and thus additionally biased TE results due to mass fractionation before the start of the TE data acquisition. Introducing major changes in the filament heating protocol to circumvent this issue was not considered practicable in order to prevent the loss of an unknown amount of uranium prior to starting the TE measurement. The reason for this premature uranium ionization has not been investigated in detail, but organic and inorganic components that remained in the sample solution or that were introduced during sample preparation are most probably mainly responsible for this complex unusual behavior of uranium signals during TIMS TE measurements. Oxygen contained in these undesired components might have caused the formation of UO_2, which would be responsible for the loss of uranium at lower filament temperatures. The fact that filament carburization turned out to be a remedy for this issue as described in the next section supports this theory. Figure 2 shows in addition to the uranium ion signals the presence of a ^{239}Pu peak at the end of the uranium TE measurement. The signal at mass 239 was recorded but excluded from the sum of uranium signals that determines the start, the heating profile, and end of the TE data acquisition. The ^{239}Pu signal measured at mass 239 was used for the correction of the signal of ^{238}U for ^{238}Pu remaining in the uranium fraction after purification. Although all plutonium nuclides are present in the residual plutonium remaining in the purified uranium fraction, only ^{239}Pu is reported in Figures2−5, despite that both ^{239}Pu and ^{238}U+^{238}Pu signals were recorded. This is due to the scaling of the figure, because ^{239}Pu represents more than 85% ($g \cdot g^{-1}$) and 75% ($g \cdot g^{-1}$) of the plutonium nuclides in NBS 946 and NBS 947, respectively, while the ^{238}U +^{238}Pu signal is much lower compared to the ^{239}Pu signal and the other uranium nuclides' signals (see also uranium nuclide amount contents in Table 2).

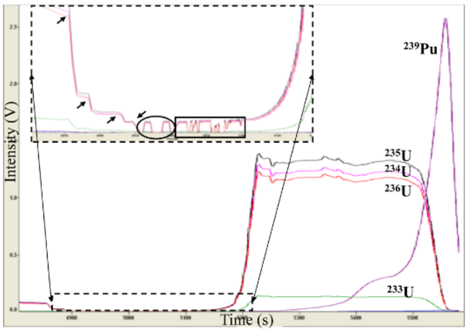


Figure 2. Measurement signals during the filament heating procedure and TE data acquisition for measurement of the uranium fraction of NBS 947 spiked with IRMM-3630.0.4 purified by separation procedure B using noncarburized ionization and evaporation filaments. Magnified view: heating procedure prior to the start of the TE data acquisition; peak-centering and focusing of the U signals are indicated by oval and square shapes, respectively; each manual decrease of the current heating the ionization filament by100 mA is indicated by arrows.

Experimental Optimization of Filament Carburization. Filament carburization was found to be not only a suitable solution to avoid additional loss of uranium prior to the TE data acquisition and to enable automated uranium TE measurements. It also shifted the plutonium peak that can be observed in Figure 2 at the end of the uranium TE acquisition to the start of the TE measurement (Figure 3). (Filament carburization was applied for all experiments depicted from Figure 3 onward unless indicated otherwise.) The effects of carburization of the ionization filament, the evaporation filament, or of both filaments were tested with a fraction of the loading solution originating from uranium separation procedure B of the sample NBS 946 spiked with ^{233}U. Separation procedure B was used for this purpose as procedure A did not yield enough uranium for the TE measurement and separation procedures C to E were developed in parallel. The result of this experiment can be viewed in Figure 5 as far as the signal behavior during uranium TE data acquisition is concerned. Figure 6 depicts the ^{233}U/^{235}U ratios in the

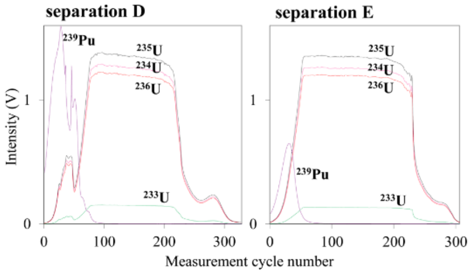


Figure 3. TE measurement signals of the uranium fraction of sample NBS 947 spiked with IRMM-3630.0.4 using carburized ionization filaments purified by separation procedure D and E.

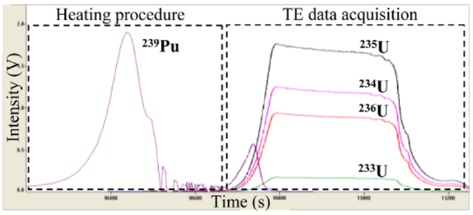
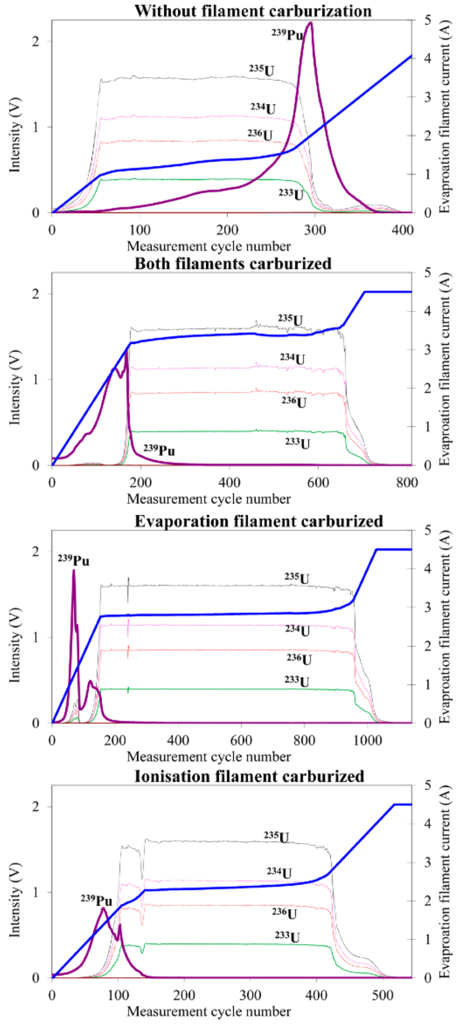


Figure 4. Filament heating procedure and TE data acquisition of the uranium fraction of sample NBS 946 spiked with IRMM-3630.0.4 purified by separation procedure B using a carburized ionization filament.

above-mentioned sample solution showing the influence of filament carburization on the loss of lighter isotopes relative to heavier isotopes. We did not observe any significant differences in the signal behavior whether the ionization filament, the evaporation filament, or both filaments are carburized. Finally, only the ionization filament was carburized. The reason was that this setup has the advantage that the sample solution does not need to be loaded on brittle carburized filaments minimizing the loss of filaments due to operator errors. Filament carburization also leads to a shift of the Pu signal from the end of the uranium TE data acquisition to the start of the evaporation during the optimization signal procedure prior to the TE data acquisition. Hence, only a part of a second smaller ^{238}Pu peak overlaps with the uranium TE data collection and thus disturbs the measurement of ^{238}U when filament carburization is used (Figure 4). Table 1 shows the ^{238}U/^{235}U ratios measured in a purified uranium fraction of NBS 946 spiked with ^{233}U before and after correction for ^{238}Pu using different combinations of carburized and uncarburized filaments. A corrected value for the ^{238}U/^{235}U ratio using no carburization is not shown because the formation of the remaining plutonium ions seems more variable between filaments. This is evident from the much larger uncertainty of the ^{238}U/^{235}U ratio compared to using carburized filaments.

Result of the Optimized Sample Preparation and Measurement Strategy. The uranium recovery of separation procedure E was 99.64 ± 0.09%. A separation factor $S_{U/Pu}$ of 20981 ± 43 (k = 2) for the removal of plutonium in the purified uranium fraction was achieved for NBS 946 applying separation procedure E (see eq 1). This means after the purification of the uranium fraction the Pu/U ratio was reduced from about 445 ± 66 to 0.020 ± 0.0031 (g·g^{-1}, k = 2). The ^{238}Pu/^{238}U ratio (g·g^{-1}, k = 2) was reduced from 4000 ± 420 to 0.19 ± 0.02. Hence, although the total plutonium amount content was reduced to about 2% of the total uranium amount content in the purified uranium fraction, the amount content of remaining ^{238}Pu still equaled about 20% of the amount content of ^{238}U in the same uranium fraction. The portion of this remaining ^{238}Pu acquired during the uranium TE data acquisition depends on when the major plutonium peak appears relative to the uranium signals in the uranium TE data acquisition stage (compare Figure 2 and Figure 3). Hence,


Without filament carburization

Both filaments carburized

Evaporation filament carburized

Ionisation filament carburized

Figure 5. Measurement signals and evaporation filament current of the uranium fraction of NBS 946 spiked with IRMM-3630.0.4 purified by separation procedure B using different combinations of carburized and noncarburized filaments.

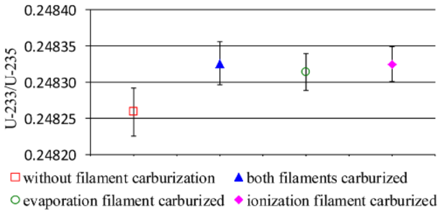


Figure 6. $^{233}U/^{235}U$ ratios ($k = 1$) of the uranium fraction of NBS 946 spiked with IRMM-3630.0.4 purified by separation procedure B using different combinations of carburized and noncarburized filaments.

the portion of measured ^{238}Pu ions during the uranium TE data acquisition is reduced when filament carburization is applied. Consequently, one would expect a reduction of the apparent ^{238}U amount content after correction for ^{238}Pu by less than 20% when filament carburization is applied, because a considerable fraction of ^{238}Pu is evaporated before the start of the uranium TE data acquisition. However, an observed difference of about 20% between the corrected and the uncorrected ^{238}U amount content (Table 1) remains although filament carburization was applied. This can be explained by the differences in the ionization yields of uranium and plutonium: during a simultaneous measurement of uranium and plutonium, the yield of Pu$^+$ ions is 5−10 times greater than that of U$^+$ ions.[20] Therefore, more Pu$^+$ ions are formed compared to U$^+$ ions, although other authors observed a certain quenching effect on the Pu$^+$ ion formation when uranium and plutonium are measured simultaneously.[24]

Table 1. $^{238}U/^{235}U$ Ratios in a Purified Uranium Fraction of NBS 946 Spiked with IRMM-3630.0.4 Using Different Combinations of Carburized and Non-Carburized Filaments[a]

	$^{238}U/^{235}U$	
carburized filament(s)	measured	corrected for ^{238}Pu
none	$1.03 \times 10^{-3} \pm 3.00 \times 10^{-4}$	-
both	$8.55 \times 10^{-4} \pm 2.40 \times 10^{-5}$	$6.00 \times 10^{-4} \pm 2.90 \times 10^{-5}$
ionization	$8.22 \times 10^{-4} \pm 6.80 \times 10^{-5}$	$6.05 \times 10^{-4} \pm 6.80 \times 10^{-5}$
evaporation	$7.28 \times 10^{-4} \pm 2.10 \times 10^{-5}$	$6.03 \times 10^{-4} \pm 2.40 \times 10^{-5}$

[a] Ratios as measured as well as ratios corrected for ^{238}Pu are shown. The uncertainties are expanded uncertainties (k = 2).

Correction of ^{238}U Amount Content for ^{238}Pu. The contribution of residual ^{238}Pu to the signal at mass 238 (^{238}U and ^{238}Pu) in the uranium IDMS experiment was calculated by applying the ratio $R_{238/239\_Pu}$ obtained from the plutonium IDMS experiment to the signal measured at mass 239 (^{239}Pu) in the uranium TE measurement according to eq 2. $R_{238/239\_U}$ is the ratio of the measured signal at mass 238 (^{238}U + ^{238}Pu) to ^{239}Pu and c_{238U_U} is the uncorrected amount content of ^{238}U. Both $R_{238/239\_U}$ and c_{238U_U} are obtained from the IDMS experiment with the purified uranium fraction.

The ^{238}U amount content c_{238U} is calculated.

$$c_{238U} = c_{238U\_U}{}^{*}(R_{238/239\_U} - R_{238/239\_Pu})^{*}R_{238/239\_U}{}^{-1} \tag{2}$$

The $^{242}Pu/^{238}U$ "chronometer" gives a significantly older age dating result compared to the age dating result of the $^{240}Pu/^{236}U$ chronometer when this correction is omitted leading to the false conclusion that the sample contains uranium of nonradiogenic origin. As laid out in detail in a previous publication, the $^{242}Pu/^{238}U$ nuclide pair is a sensitive indicator for nonradiogenic uranium in aged plutonium samples.[4] The amount contents of ^{234}U and ^{235}U as well as the age dating results using $^{238}Pu/^{234}U$ and $^{239}Pu/^{235}U$ chronometers are shown in Table 2.

Table 2. Age Dating Results of the Pu/U Chronometers and Amount Content of ^{238}U with and without Correction for ^{238}Pu on the Amount Content of ^{238}U for sample NBS 947[a]

age dating results	
$^{238}Pu/^{234}U$	40.85 ± 0.3 a
$^{239}Pu/^{235}U$	40.91 ± 0.12 a
$^{240}Pu/^{236}U$	40.91 ± 0.12 a
$^{242}Pu/^{238}U$[b]	44.8 ± 4.8 a
$^{242}Pu/^{238}U$[c]	54.1 ± 4.3 a
amount content	
c_{234U}	$7.0724 \times 10^{-9} \pm 4.8 \times 10^{-12}$ mol/g
c_{235U}	$7.6023 \times 10^{-9} \pm 4.5 \times 10^{-12}$ mol/g
c_{236U}	$6.7407 \times 10^{-9} \pm 4.1 \times 10^{-12}$ mol/g
c_{238U}[b]	$8.36 \times 10^{-12} \pm 900 \times 10^{-15}$ mol/g
c_{238U}[c]	$10.11 \times 10^{-12} \pm 800 \times 10^{-15}$ mol/g

[a] The uncertainties are expanded uncertainties (k = 2); reference date: 18.10.2011. [b] with correction of the ^{238}U amount content for ^{238}Pu. [c] without correction of the ^{238}U amount content for ^{238}Pu.

Age Dating Results and Uncertainties. The major contributor to the uncertainties of amount contents of ^{236}U, ^{235}U, and ^{234}U were introduced by the measured isotope ratios and the amount content of ^{233}U in the uranium IDMS spike. The measured isotope ratios in the uranium IDMS blend and the correction for residual ^{238}Pu were the major contributors to the uncertainty of the amount content of ^{238}U. The amount content of ^{238}U was also the major contributor (>99%) to the total combined uncertainty of the result for the $^{242}Pu/^{238}U$ "chronometer", whereas the half-lives[43] and the amount contents of the plutonium nuclides were the major contributors to the results of the $^{238}Pu/^{234}U$, $^{239}Pu/^{235}U$, and $^{240}Pu/^{236}U$ chronometers. The major uncertainty contributions to the amount content of ^{238}Pu came from the ^{242}Pu spike for plutonium IDMS and the correction for peak tailing from ^{239}Pu.

The half-lives[43] and uncertainty of the ^{242}Pu spike for plutonium IDMS were the major contributors to the amount contents of ^{239}Pu, ^{240}Pu, and ^{242}Pu. The uncertainties of the plutonium nuclides' amount contents for plutonium age determination have been discussed elsewhere[4] in detail.

■ CONCLUSIONS

The combination of an optimized chemical separation procedure and the use of carburized filaments enabled the determination of ^{238}U by TE TIMS in aged plutonium samples. Reliable measurement results within fit-for-purposes uncertainties were proven using NBS 947, representing a 41-year-old plutonium sample. Although the analytical approach was originally tailored for the three "common" chronometers ($^{238}Pu/^{234}U$, $^{239}Pu/^{235}U$, and $^{240}Pu/^{236}U$) for plutonium dating, the optimization of the procedure additionally allowed the use of the $^{242}Pu/^{238}U$ nuclide amount ratio as a sensitive indicator of residual nonradiogenic uranium, which can easily be found in

DOI: 10.1021/acs.analchem.5b03852
Anal. Chem. 2016, 88, 6223−6230

seized plutonium materials. The accuracy of the determination of ^{238}U is fit for this purpose since the ^{242}Pu/^{238}U isotope amount ratio is not used as "chronometer" in the commonly used sense.[4] The goal of automated routine TE TIMS measurements was achieved. The use of filament carburization for separating plutonium and uranium signals on one filament should be investigated further for future other applications such as ^{238}U and ^{238}Pu measurement in MOX samples with incomplete chemical separation.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: monika.sturm@boku.ac.at.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank Rüdiger Kessel for providing for the program GUM work bench 2.4 (Metrodata, Germany) for the uncertainty evaluation and Frances Kehoe, Roger Eykens and Heinz Kuehn for their support in the IRMM nuclear chemistry and mass spectrometry laboratories as well as Kevin Henderson for proofreading.

■ REFERENCES

(1) Mayer, K.; Wallenius, M.; Fanghänel, T. *J. Alloys Compd.* **2007**, *444−445*, 50−56.

(2) Wallenius, M.; Mayer, K. *Fresenius' J. Anal. Chem.* **2000**, *366*, 234−238.

(3) Mayer, K.; Wallenius, M.; Hedberg, M.; Lützenkirchen, K. *Radiochim. Acta* **2009**, *97*, 261−264.

(4) Sturm, M.; Richter, S.; Aregbe, Y.; Wellum, R.; Mialle, S.; Mayer, K.; Prohaska, T. *J. Radioanal. Nucl. Chem.* **2014**, *302*, 399−411.

(5) Wallenius, M.; Lützenkirchen, K.; Mayer, K.; Ray, I.; de las Heras, L. A.; Betti, M.; Cromboom, O.; Hild, M.; Lynch, B.; Nicholl, A.; Ottmar, H.; Rasmussen, G.; Schubert, A.; Tamborini, G.; Thiele, H.; Wagner, W.; Walker, C.; Zuleger, E. *J. Alloys Compd.* **2007**, *444−445*, 57−62.

(6) Keegan, R. P.; Gehrke, R. J. *Appl. Radiat. Isot.* **2003**, *59*, 137−143.

(7) Nguyen, C. T. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *251*, 227−236.

(8) Ramebäck, H.; Nygren, U.; Tovedal, A.; Ekberg, C.; Skarnemark, G. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2012**, *287*, 56−59.

(9) Kirby, H. W.; Sheehan, W. E. *Nucl. Instrum. Methods Phys. Res.* **1984**, *223*, 356−359.

(10) Zhang, H.-T.; Zhu, F. R.; Xu, J.; Dai, Y. H.; Li, D. M.; Yi, X. W.; Zhang, L. X.; Zhao, Y. G. *Radiochim. Acta* **2008**, *96*, 327−331.

(11) Varga, Z.; Surányi, G.; Vajda, N.; Stefánka, Z. *Microchem. J.* **2007**, *85*, 39−45.

(12) Chen, Y.; Chang, Z.-y.; Zhao, Y.-g.; Zhang, J.-l.; Li, J.-h.; Shu, F.-j. *J. Radioanal. Nucl. Chem.* **2009**, *281*, 675−678.

(13) Nygren, U.; Ramebäck, H.; Nilsson, C. *J. Radioanal. Nucl. Chem.* **2007**, *272*, 45−51.

(14) Aggarwal, S. K.; Kumar, S.; Saxena, M. K.; Shah, P. M.; Jain, H. C. *Int. J. Mass Spectrom. Ion Processes* **1995**, *151*, 127−135.

(15) Varga, Z.; Nicholl, A.; Wallenius, M.; Mayer, K. *Anal. Chim. Acta* **2012**, *718*, 25−31.

(16) Varga, Z.; Venchiarutti, C.; Nicholl, A.; Krajkó, J.; Jakopič, R.; Mayer, K.; Richter, S.; Aregbe, Y. *J. Radioanal. Nucl. Chem.* **2016**, *307*, 1077−1085.

(17) Callis, E. L.; Abernathey, R. M. *Int. J. Mass Spectrom. Ion Processes* **1991**, *103*, 93−105.

(18) De Bièvre, P.; Peiser, H. S. *Fresenius' J. Anal. Chem.* **1997**, *359*, 523−525.

(19) Aggarwal, S. K.; Alamelu, D. *Int. J. Mass Spectrom.* **2005**, *241*, 83−88.

(20) Aggarwal, S. K.; Saxena, M. K.; Shah, P. M.; Kumar, S.; Jairaman, U.; Jain, H. C. *Int. J. Mass Spectrom. Ion Processes* **1994**, *139*, 111−126.

(21) Lee, C.-G.; Suzuki, D.; Saito-Kokubu, Y.; Esaka, F.; Magara, M.; Kimura, T. *Int. J. Mass Spectrom.* **2012**, *314*, 57−62.

(22) Saito-Kokubu, Y.; Suzuki, D.; Lee, C.-G.; Inagawa, J.; Magara, M.; Kimura, T. *Int. J. Mass Spectrom.* **2012**, *310*, 52−56.

(23) Suzuki, D.; Saito-Kokubu, Y.; Lee, C.-G.; Esaka, F.; Magara, M.; Kimura, T. *Chem. Lett.* **2012**, *41*, 90−91.

(24) Raptis, K.; Duhamel, G.; Ludwig, R.; Balsley, S.; Bürger, S.; Mayorov, V.; Koepf, A.; Hara, S.; Itoh, Y.; Yamaguchi, K.; Yamaguchi, T.; Ninagawa, J. *J. Radioanal. Nucl. Chem.* **2013**, *296*, 585−592.

(25) Shinonaga, T.; Esaka, F.; Magara, M.; Klose, D.; Donohue, D. *Spectrochim. Acta, Part B* **2008**, *63*, 1324−1328.

(26) Kraiem, M.; Richter, S.; Kühn, H.; Stefaniak, E. A.; Kerckhove, G.; Truyens, J.; Aregbe, Y. *Anal. Chem.* **2011**, *83*, 3011−3016.

(27) Shinonaga, T.; Donohue, D.; Ciurapinski, A.; Klose, D. *Spectrochim. Acta, Part B* **2009**, *64*, 95−98.

(28) Jakopic, R.; Richter, S.; Kühn, H.; Benedik, L.; Pihlar, B.; Aregbe, Y. *Int. J. Mass Spectrom.* **2009**, *279*, 87−92.

(29) Jakopic, R.; Richter, S.; Kuhn, H.; Aregbe, Y. *J. Anal. At. Spectrom.* **2010**, *25*, 815−821.

(30) Kraiem, M.; Mayer, K.; Gouder, T.; Seibert, A.; Wiss, T.; Thiele, H.; Hiernaut, J. P. *Int. J. Mass Spectrom.* **2010**, *289*, 108−118.

(31) Kelley, J. M.; Robertson, D. M. *Anal. Chem.* **1985**, *57*, 124−130.

(32) Kraiem, M.; Richter, S.; Kühn, H.; Aregbe, Y. *Anal. Chim. Acta* **2011**, *688*, 1−7.

(33) Uriano, G. A. *National Bureau of Standards Certificate of Analysis Standard Reference Material 946 Plutonium Isotopic Standard*; National Bureau of Standards: Gaithersburg, MD, 1982.

(34) Uriano, G. A. *National Bureau of Standards Certificate of Analysis Standard Reference Material 947 Plutonium Isotopic Standard*; National Bureau of Standards: Gaithersburg, MD, 1982.

(35) Emons, H. *Certificate Spike Isotopic Reference Material IRMM-049d*; Institute for Reference Materials and Measurements: Geel, Belgium, 2011.

(36) Jakopič, R.; Verbruggen, A.; Eykens, R.; Kehoe, F.; Kühn, H.; Kushigeta, Y.; Jacobsson, U.; Bauwens, J.; Richter, S.; Wellum, R.; Aregbe, Y. *J. Radioanal. Nucl. Chem.* **2010**, *286*, 449−454.

(37) Taylor, P.; Wellum, R. *Certificate isotopic reference material IRMM-074*; Institute for Reference Materials and Measurements: Geel, Belgium, 2006.

(38) Richter, S.; Alonso, A.; Aregbe, Y.; Eykens, R.; Kehoe, F.; Kühn, H.; Kivel, N.; Verbruggen, A.; Wellum, R.; Taylor, P. D. P. *Int. J. Mass Spectrom.* **2009**, *281*, 115−125.

(39) The Scientific Committee on Occupational Exposure Limits. *Recommendation from the Scientific Committee on Occupational Exposure Limits for benzene*; European Commission − Employment, Social Affairs and Inclusion: Brussels, Belgium, 1991.

(40) Jakopič, R.; Bauwens, J.; Buják, R.; Eykens, R.; Hennessy, C.; Kehoe, F.; Kühn, H.; Richter, S.; Aregbe, Y. *Preparation and Certification of Large-Sized Dried (LSD) Spike IRMM-1027o*; JRC Reference Materials; European Commission: Brussels, Belgium, 2013.

(41) UTEVA Resin and associated protocols. Eichrom Technologies, LLC: Lisle, IL, 2011.

(42) Sandell, E. B. *Anal. Chem.* **1968**, *40*, 834−835.

(43) International Atomic Energy Agency (IAEA). *Decay Data of the Transactinium Nuclides*; Technical Reports Series, No. 261; IAEA: Vienna, Austria, 1986.

2.2 Publication II

J Radioanal Nucl Chem
DOI 10.1007/s10967-014-3294-8

Evaluation of chronometers in plutonium age determination for nuclear forensics: What if the 'Pu/U clocks' do not match?

M. Sturm · S. Richter · Y. Aregbe ·
R. Wellum · S. Mialle · K. Mayer · T. Prohaska

Received: 28 February 2014

Abstract This article discusses the age dating results of plutonium/uranium chronometers with a focus on the consequences for age plutonium determination when the basic assumptions of the methodology are not fully met: Incomplete removal of the daughter nuclides at the production date and uranium contamination of plutonium samples. In addition to the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U, the ^{242}Pu/^{238}U chronometer is discussed. The ^{242}Pu/^{238}U radiochronometer has only scarcely been used, due to its high sensitivity to residual uranium. However, it can be a very useful indicator for uranium contamination of aged plutonium samples.

Keywords Plutonium · Nuclear forensics · Age dating · Isotope dilution mass spectrometry · Certified reference material · TIMS

Introduction

Since the early 1990s more than one hundred cases of illicit trafficking involving uranium or plutonium materials have been reported to the IAEA's Incident and Trafficking Database (ITDB) [1]. These incidents gave rise to the development of the discipline of nuclear forensic science [2]. In such cases nuclear forensic investigations are applied in addition to traditional forensics. Traditional forensics focuses on evidence such as traces (fingerprints, fibres and other residues) left behind by the culprit in order to identify linkages between (suspect) individuals and events (crimes). In contrast to that, nuclear forensics aims at re-establishing the history of the seized material and provides hints on the possible origin of the material. To this end, the isotopic and elemental composition (major elements and impurities) of the material in combination with macroscopic (such as dimensions) and microscopic (such as particle size and shape) morphological aspects are investigated [2–8]. These findings help in determining the production process and/or the purpose the material was intended for by comparing it against open source information or information accessible in specific databases [9]. Another key parameter helping to discover the latest legal owner and production place of seized nuclear material is the 'age' of that material [9]. In this context, the 'age' of nuclear material is defined as the time elapsed between the production of the material and the measurement date.

The date of the last chemical separation of the 'daughter' nuclides (decay products) from the 'mother' nuclides is considered the production date of a nuclear material such as plutonium. This means that plutonium decay products including ^{241}Am, ^{234}U, ^{235}U, ^{236}U and ^{238}U are removed from their respective 'mother nuclides' ^{241}Pu, ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{242}Pu.

Such manipulations that separate the daughter nuclides from their respective mother nuclides—and thus set the 'clock' to zero—occur for instance during reprocessing [10]. The following isotopic systems are commonly used as radiochronometers or—'clocks'—for the age determination of

M. Sturm (✉) · T. Prohaska
University of Natural Resources and Life Sciences, Vienna, Austria
e-mail: sturm.monika@gmail.com; monika.sturm@boku.ac.at

S. Richter · Y. Aregbe · R. Wellum · S. Mialle
European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel, Belgium

K. Mayer
European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany

plutonium: ^{241}Pu/^{241}Am, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U [11].

Radiochronometry, however, relies on a few basic assumptions: (i) the daughter nuclides should be completely removed from their respective parent nuclides at time zero ($t = 0$), (ii) the material shall be considered as closed system (i.e. no parent or daughter nuclide shall be added or removed during the time interval under consideration), and (iii) parent and daughter nuclides shall be in radioactive disequilibrium [12].

The determination of the age is based on the equations describing the radioactive decay, as shown in Eqs. (1) to (3) for the chronometer ^{239}Pu/^{235}U [13]. The amount of the mother nuclide ^{239}Pu at the time of the measurement (present time) is represented by $^{239}\mathrm{Pu}_t$. The amount of ^{239}Pu at the time of the separation ($t = 0$) is $^{239}\mathrm{Pu}_0$. $^{235}\mathrm{U}_t$ is the amount of ^{235}U at the present time. $^{235}\mathrm{U}_0$ represents the amount of ^{235}U directly after the separation at $t = 0$. According to the basic assumption of complete removal of the daughter nuclides, $^{235}\mathrm{U}_0$ is assumed to be zero for the purpose of age determination. The decay constants λ_{Pu} and λ_{U} of mother and daughter nuclides can be calculated from their half-lives $t_{1/2}$ according to Eq. (3).

$$^{239}\mathrm{Pu}_t = {}^{239}\mathrm{Pu}_0 \times \mathrm{e}^{-\lambda\_\mathrm{Pu} \times t} \tag{1}$$

$$\begin{aligned} ^{235}\mathrm{U}_t = {}^{235}\mathrm{U}_0 \times \mathrm{e}^{-\lambda\_\mathrm{U} \times t} + \lambda_{\mathrm{Pu}} \times (\lambda_{\mathrm{U}} - \lambda_{Pu})^{-1} \times {}^{239}\mathrm{Pu}_0 \\ \times \left(\mathrm{e}^{-\lambda\_\mathrm{Pu} \times t} - \mathrm{e}^{-\lambda\_\mathrm{U} \times t}\right) \end{aligned} \tag{2}$$

$$\lambda = t_{1/2}^{-1} \times \ln 2 \tag{3}$$

The ^{241}Pu/^{241}Am clock is the most commonly used chronometer for plutonium age determination. The preferred methods for dating with this clock in bulk samples are gamma spectrometry [5, 11, 14–16] and combinations of alpha spectrometry either with thermal ionisation mass spectrometry (TIMS) or with inductively coupled plasma mass spectrometry (ICP-MS) [16–20]. Since this article focuses on the plutonium/uranium clocks for plutonium age determination, the age dating results of the ^{241}Pu/^{241}Am clock for the investigated samples will be published elsewhere.

In case of dating plutonium via the plutonium/uranium clocks, the chronometers ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U are usually considered. This work also takes the ^{242}Pu/^{238}U clock into account. The age dating results of this clock have only scarcely been used. The ^{242}Pu/^{238}U clock is usually not considered because of the long half-life of the mother nuclide ^{242}Pu, the resulting low amount of the daughter nuclide ^{238}U and its sensitivity to uranium contamination at trace level [9]. The present article investigates how the age dating results of the ^{242}Pu/^{238}U clock can systematically not only be used to detect contamination of plutonium samples with uranium but also how to identify the nature of the contamination (such as natural or enriched uranium).

Concerning the plutonium/uranium clocks, the ^{240}Pu/^{236}U is considered to be the most reliable clock for the age determination of plutonium. The reasons for this choice will be explained in detail in the following chapters of this publication. The measurement techniques used for dating bulk plutonium samples via the plutonium/uranium clocks are TIMS [5, 11] and ICP-MS [20, 21]. Occasionally the ^{238}Pu/^{234}U clock and the ^{239}Pu/^{235}U clock are looked at in addition to the ^{240}Pu/^{236}U clock [5, 11]. For most age determination measurements of plutonium particles secondary ion mass spectrometry (SIMS) is applied, preferably on the ^{240}Pu/^{236}U clock [5, 22].

Considering more than one clock for the age determination of plutonium is recommended because this underpins the reliability of the result and enables additional information about the material to be gained, while using only one clock might lead to erroneous conclusions. Inconsistent age dating results of the different clocks may indicate that the sample consists of a mixture of two or more different materials of different ages [5]. In case of incomplete removal of the decay products from the parent nuclides at time zero a similar effect can occur. Any addition of daughter isotopes during the time between the initial separation and the age dating measurement may also lead to inconsistent results from the different clocks. The possibility of a contamination of a plutonium sample—for instance in the facility where it was manipulated—with natural or non-natural uranium should be kept in mind too. The latter two scenarios—incomplete separation at time zero as well as a contamination with uranium—will result in characteristic relative patterns of the plutonium/uranium clocks and can thus not only help to interpret inconsistent age dating results in a more concise way but may also give additional information on the history of the sample. Unless indicated otherwise the half-life values given in Table 1 were used for all calculations in this work.

Experimental

Table 2 lists the isotopic composition of the plutonium samples that are discussed in this article. One of them is the widely distributed reference material NBS 946 (NBL CRM 136; National Bureau of Standards, Washington, DC, USA) [23]. This material has been certified for its isotopic composition and is well described in literature including publications dealing with age determination [11].

All the samples discussed in this article are $\mathrm{PuO_2}$ samples except for the plutonium sulphate sample NBS 946. The oxide samples were dissolved in a 1:1,000 mixture of HF (40 % (wt%); ultrapure; J.T. Baker, Center Valley, PA,

Table 1 The half-lives of plutonium mother nuclides and their respective daughter nuclides used for age dating of plutonium

Clock	Half-life mother (a)	Reference	Half-life daughter (a)	Reference
^{238}Pu/^{234}U	87.7(3)	[24]	2.457(3) × 10^5	[24]
^{239}Pu/^{235}U	2.411(3) × 10^4	[24]	7.037(7) × 10^8	[24]
^{240}Pu/^{236}U	6563(7)	[24]	2.342(3) × 10^7	[24]
^{241}Pu/^{241}Am	14.325(24)	[25]	432.7(5)	[24]
^{242}Pu/^{238}U	3.735(11) × 10^5	[24]	4.468(5) × 10^9	[24]

The uncertainties are kept as originally published: standard uncertainties are displayed for Ref. [24]; the expanded uncertainty ($k = 2$) is used for Ref. [25]

Table 2 Isotopic composition of the plutonium samples as determined by TIMS; the grades of plutonium are according to Ref. [10]; the uncertainties are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Sample ID	% (w/w)					Grade
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	
NBS 946	0.1876(2)	86.1055(10)	12.5112(10)	0.6036(1)	0.5921(2)	Fuel
ACH-104-1	0.7217(4)	76.4222(27)	19.0213(26)	1.6720(6)	2.1628(11)	Reactor
ACH-104-2	0.0571(3)	84.9913(23)	14.2870(23)	0.3042(2)	0.3604(3)	Fuel
ACH-104-3	1.0312(3)	65.8144(36)	26.6770(36)	2.0656(8)	4.4117(23)	Reactor

Table 3 Concentrations of the uranium nuclides in a sample solution with about 0.002 g plutonium per gram solution of sample NBS 946 determined by ID TIMS; the uncertainties are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Nuclide	Concentration (mol/g)	Uncertainty (mol/g)	Relative uncertainty (%)
^{234}U	5.9575 × 10^{-9}	4.5 × 10^{-12}	0.075
^{235}U	8.3969 × 10^{-9}	5.6 × 10^{-12}	0.067
^{236}U	4.4745 × 10^{-9}	3.1 × 10^{-12}	0.069
^{238}U	3.89 × 10^{-12}	400 × 10^{-15}	10

USA) in concentrated HNO_3 (69 % (wt%). p.a.; Merck, Darmstadt, Germany). The plutonium sulphate sample was dissolved in concentrated HNO_3 (69 % (wt%); p.a.; Merck, Darmstadt, Germany).

In order to achieve desired molarities of HNO_3 mentioned hereafter concentrated HNO_3 (69 % (wt%). p.a.; Merck, Darmstadt, Germany) was diluted with deionized water (Milli-Q Water Purification System (18 MΩ); Millipore, Billerica, MA, USA). Sample solutions were prepared with a final plutonium content between 0.002 and 0.01 g/g in HNO_3 ($c = 5$ mol/L).

The concentrations of mother (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) and daughter nuclides (^{234}U, ^{235}U, ^{236}U, ^{238}U) were determined in two separate isotope dilution mass spectrometry (IDMS) measurements using TIMS [26]. All aliquots of the sample solutions and the spiking solutions were weighed metrologically.

The ^{242}Pu spike certified reference material (CRM) used to prepare the blends for plutonium IDMS was IRMM-049d (Institute for Reference Materials and Measurements, Geel, Belgium) [27]. Only for sample NBS 946 the ^{242}Pu spike CRM IRMM-049c (Institute for Reference Materials and Measurements, Geel, Belgium) [28] was used. In addition to the spike-sample blends, an aliquot of the un-spiked sample solution had to be analysed for the isotopic composition of the plutonium, since the spiking isotope ^{242}Pu is present in the sample. IRMM 3630 was used as ^{233}U spike for the measurement of the concentrations of the uranium nuclides by IDMS, since it only contains only very low amounts of ^{234}U, ^{235}U, ^{236}U and ^{238}U; details about this material can be found in the second column of Table 1 in Ref. [29]. No additional measurements of the un-spiked samples were required for the IDMS experiment concerning the uranium nuclides' concentrations because the spiking isotope ^{233}U was not expected to be present in the samples. The blend mixtures were evaporated to near dryness and the residues were dissolved in 2 molar HNO_3. The sample aliquots for the determination of plutonium were purified using anion-exchange columns (Bio-Rad AG1-X4, 100–200 mesh; Hercules, CA, USA) according to [30]. The chemical separation of the uranium fraction prior to the measurement of the uranium nuclides was accomplished using a combination of anion-exchange columns (Bio-Rad AG1-X4, 100–200 mesh; Hercules, CA, USA) and extraction chromatographic columns (UTEVA; Eichrom Technologies, Lisle, IL, USA). All measurements were done applying the total evaporation (TE) method [31] a Triton (Thermo Fisher Scientific, Bremen, Germany) TIMS multi-collector instrument. For the measurement of the uranium nuclides carburized filaments were used [32]; the corresponding sample preparation procedure will be published elsewhere in detail. The mass spectrometer was calibrated for mass fractionation by measuring the certified reference materials IRMM-074/10 (Institute for Reference Materials and Measurements, Geel, Belgium) [33] for uranium and IRMM-290A/3 (Institute for Reference Materials and Measurements, Geel, Belgium) [34] for plutonium.

The concentrations of the mother and daughter nuclides were subsequently used to form the ratios necessary for age determination as described in Eqs. (1)–(3).

The total combined uncertainties of all results were calculated using the software GUM workbench (Metrodata GmbH, Weil am Rhein, Germany). A correction for ^{238}Pu in the purified uranium fraction was necessary for the proper calculation of the ^{238}U concentration. This correction leads to a higher uncertainty of the concentration of ^{238}U compared to the other uranium nuclides. Due to the low content of uranium in aged plutonium samples, it was not possible to remove all the plutonium completely from the purified uranium fraction that was prepared for the uranium IDMS measurements. ^{238}Pu interferes with ^{238}U due to the similarity of the masses. The mass resolution of 1.9×10^5 required to resolve these nuclides cannot be achieved by current mass spectrometers [35]. In order to correct for the contribution of ^{238}Pu to the signal at mass 238, the signal at mass 239 was also measured during the TE TIMS measurement of uranium and the ^{238}Pu/^{239}Pu ratio from the plutonium TIMS measurement was used for the correction of the concentration of ^{238}U.

Regarding the plutonium determination, a correction for peak tailing from mass 239 to mass 238 was applied to the measurement of the purified plutonium fraction.

This correction was necessary since the investigated samples contain a lot more ^{239}Pu than ^{238}Pu (see Table 2). The ratio of mass 237–mass 238 from uranium measurements was used for the correction for peak tailing of the plutonium measurements. For this purpose the mean of the ratios of mass 237–mass 238 of nine filaments loaded with the certified reference materials IRMM-074/10 (Institute for Reference Materials and Measurements, Geel, Belgium) measured on two different days was calculated; its standard error was calculated the mean was and subsequently used for the correction ($R_{\text{peaktailing}}$ in Eq. (4)). This calculation resulted in a value of $7.05 \times 10^{-6} \pm 1.03 \times 10^{-6}$ ($k = 1$) for $R_{\text{peaktailing}}$. The uncertainty of this correction was propagated; it accounts for about 22 % of the uncertainty of the concentration of ^{238}Pu. The measured ratio of the signal at mass 238 to the signal at mass 239 is represented by $R_{238/239\text{measured}}$ in Eq. (4). $R_{238\text{Pu}/239\text{Pu}}$ is the corrected ^{238}Pu/^{239}Pu ratio that was subsequently used for the calculation of the concentration of ^{238}Pu.

$$R_{238\text{Pu}/239\text{Pu}} = R_{238/239\text{measured}} - R_{\text{peaktailing}}. \quad (4)$$

Results

The widely distributed isotope ratio reference material NBS 946 served as model sample for the examination of age dating using different plutonium/uranium clocks in this work. The resulting ages are reported in Table 4 ('Determined age') and agree well with the reported dates for the production of NBS 946 in 1970 [36]. This sample therefore represents an example for an ideal age dating result since all three commonly used plutonium/uranium clocks (^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U) match within their uncertainties. The major contributions to the total combined uncertainties of the age dating results of these clocks were the half-lives [24] and the concentrations of the plutonium nuclides. The major contributor to the concentrations of the plutonium nuclides ^{239}Pu and ^{240}Pu was the uncertainty of reference materials that were used as spikes for plutonium ID TIMS. Second to the uncertainty of the ^{242}Pu spike for plutonium ID TIMS, the correction for peak tailing from ^{239}Pu was found to be a major contributor to the concentration of ^{238}Pu. Hence, a higher total combined uncertainty can be observed for the age dating result of the ^{238}Pu/^{234}U clock compared to the ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks.

The age dating result of the ^{242}Pu/^{238}U clock is also not significantly different from the other plutonium/uranium clocks for this sample. Nonetheless, it is evident that the total combined uncertainty of this clock is significantly higher. The ^{242}Pu/^{238}U clock is normally not considered due to the low concentrations of mother and daughter nuclides, the ubiquity of ^{238}U and the respective measurement challenges. The concentration of ingrown ^{238}U in an aged plutonium sample is usually significantly lower than the concentrations of the other uranium nuclides and has a higher uncertainty (see Table 3). The reason for the high uncertainty of the concentration of ^{238}U is the correction for residual ^{238}Pu in the uranium fraction during uranium IDMS. The concentration of ^{238}U is thus the main contributor (about 99 %) to the total combined uncertainty of the age dating result of the ^{242}Pu/^{238}U clock.

The age dating results for sample NBS 946 have been chosen as a basis for demonstrating the main factors that can lead to erroneous results of the plutonium/uranium clocks: Hypothetical scenarios for a contamination with natural uranium and for an incomplete separation at time zero were developed to demonstrate how the age dating results of the plutonium/uranium clocks shift in absolute terms and relative to one another (see Table 4).

In the following paragraphs, the influence of uranium contamination and incomplete separation at time zero are discussed for hypothetical scenarios calculated for NBS

Table 4 Results of the age determination of sample NBS 946 determined by ID TIMS ('Determined age'); assuming a contamination of the plutonium sulphate with 0.06 % (w/w) natural uranium ('Natural uranium contamination'); and assuming that only 90 % of the uranium was removed during the last separation ('Incomplete separation'); the uncertainties are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Clock	Determined age (a)		Calculated 'age' (a)			
	–		Natural uranium contamination		Incomplete separation	
	Value	Uncertainty	Value	Uncertainty	Value	Uncertainty
^{238}Pu/^{234}U	41.09	0.29	41.09	0.29	42.39	0.29
^{239}Pu/^{235}U	41.12	0.12	41.51	0.12	42.82	0.12
^{240}Pu/^{236}U	41.16	0.11	41.16	0.11	42.85	0.11
^{242}Pu/^{238}U	43.4	4.5	111×10^3	690	45.1	4.5

946 and for the results obtained for the samples ACH 104-1, ACH 104-2 and ACH 104-3.

Contamination of an aged plutonium sample with uranium

In case of a contamination of a plutonium sample with natural uranium it can be expected that the result for the ^{239}Pu/^{235}U clock is shifted to an older age relative to the ^{238}Pu/^{234}U and ^{240}Pu/^{236}U age dating results. Therefore, in the following calculations, a hypothetical contamination of the original solid plutonium sulphate material by 0.06 % (w/w × 100) natural uranium was assumed for NBS 946. The extent of this assumed contamination has deliberately been chosen as such to induce a significant difference between the results of the ^{239}Pu/^{235}U clock and the ^{240}Pu/^{236}U clock; it is hence the minimum amount of a contamination with natural uranium that would introduce a significant shift of the age dating result of ^{239}Pu/^{235}U clock relative to the age dating result of the ^{240}Pu/^{236}U clock for this sample. The age dating result of the ^{240}Pu/^{236}U chronometer is not influenced by a contamination with natural uranium since ^{236}U is not present in natural uranium [37]. A contamination with natural uranium can, however, result in a significantly higher age for the ^{239}Pu/^{235}U compared to the result for the ^{240}Pu/^{236}U clock. It is evident that the ^{242}Pu/^{238}U clock gives a much higher result for the calculated age. It can be seen from Table 4 and Fig. 1 that the ^{242}Pu/^{238}U age dating result increases to an extremely high value in case of this assumed contamination scenario. Therefore—even though measuring the ^{242}Pu/^{238}U ratio might not be useful for plutonium age dating—it can give valuable additional information on uranium contaminations that contain ^{238}U. Due to the long half-life of the mother nuclide ^{242}Pu in combination with its usually rather low concentration compared to the other plutonium nuclides (see Tables 1, 2) the expected concentration of ^{238}U is very low assuming the sample has not been contaminated with ^{238}U after time zero (such as sample NBS 946; see Table 3 'Determined age'). The nuclide ^{238}U is moreover the most abundant uranium nuclide in many uranium materials that could possibly contaminate a plutonium sample. A very high age resulting for the ^{242}Pu/^{238}U clock suggests that a contamination has taken place and the amount of contamination can be estimated:

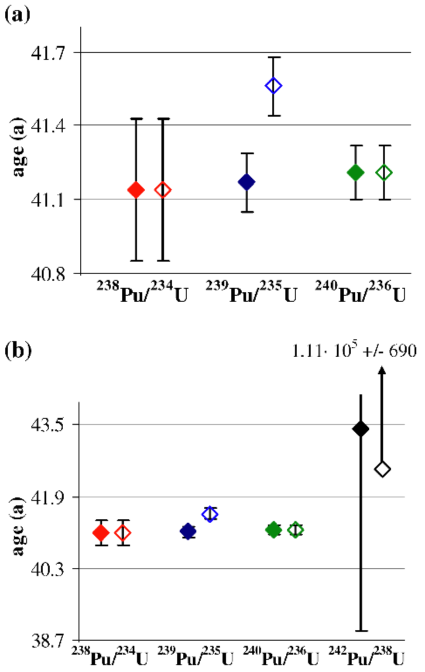


Fig. 1 Influence of contamination with natural uranium on the age dating results of sample NBS 946; **a**, **b** represent different age scales; All uncertainties shown are expanded uncertainties ($k = 2$); reference date: 18.10.2011; *full symbols* age calculated from results determined by ID TIMS; *empty symbols* age calculated from the results determined by ID TIMS assuming a contamination of the plutonium sulphate sample with 0.06 % (w/w) of natural uranium

If the sample is contaminated by natural uranium ($x(^{238}U) = 0.992742(10)$; $x(^{235}U) = 0.007204(6)$; $x(^{234}U) = 0.000054(5)$ [37]) we can assume that the age dating result of the $^{240}Pu/^{236}U$ clock is not influenced by the contamination. Thus, the expected concentrations of ^{234}U, ^{235}U and ^{238}U in the uncontaminated sample can be calculated with the age dating result of the $^{240}Pu/^{236}U$ clock, which is assumed to be the true age of the uncontaminated sample. First the concentrations of the mother nuclides ^{238}Pu, ^{239}Pu and ^{242}Pu at time zero are calculated from the measured concentrations (present time) using the respective decay equation (Eq. (1)). Based on these values, the theoretical concentrations of their daughter nuclides ^{234}U, ^{235}U and ^{238}U in the uncontaminated sample at the time of the age determination (present time) can be calculated using Eq. (2). These concentrations are subtracted from the actually measured values for the concentrations of ^{234}U, ^{235}U and ^{238}U. The calculated 'excess' of these uranium nuclides represents the uranium contamination. Based on the ratio of $^{235}U/^{238}U$ in the determined 'excess', it is possible to see whether the contamination actually resembles as assumed natural uranium or has another isotopic composition. In case the nature of the contamination differs from natural uranium, it is of vital importance to be aware of the fact that the assumption for this calculation was that the $^{240}Pu/^{236}U$ clock is not influenced by the contamination and thus represents the true age of the sample. This means the calculation is only valid for uranium contaminations that do not contain amounts of ^{236}U that significantly alter the age dating result of the $^{240}Pu/^{236}U$ clock of the sample under investigation. The risk for an alteration of the age dating result of the $^{240}Pu/^{236}U$ clock by a contamination containing ^{236}U has been assessed. It has been calculated that in sample NBS 946 about 1.4 µg ^{236}U per gram plutonium sulphate would be needed to significantly change the age dating result of the $^{240}Pu/^{236}U$ clock (expanded uncertainty; $k = 2$).

In comparison to that only 50 ng ^{238}U per gram plutonium sulphate sample introduce a significant change in the result of the $^{242}Pu/^{238}U$ clock (expanded uncertainty; $k = 2$) despite of the larger uncertainty of this clock (see Table 4).

This means a contamination with a $^{236}U/^{238}U$ ratio of about or more than 30 (w/w) would be required to significantly change the result of the $^{240}Pu/^{236}U$ clock without introducing significant changes in the age dating result of the $^{242}Pu/^{238}U$ clock of this sample; this scenario is rather unusual. It is rather unlikely that ^{236}U contained in a non-natural uranium contamination will have a significant influence on the age dating result of the $^{240}Pu/^{236}U$ clock: ^{236}U is contained in reprocessed uranium and irradiated uranium fuel [38]: Irradiated uranium fuel contains about 160–190 times more ^{238}U than ^{236}U depending on the initial enrichment of the uranium and the burn-up of the fuel. Although spent fuel based on enriched reprocessed uranium contains about 330 % more ^{236}U than spent fuel based on enriched natural uranium, it contains still almost five times more ^{238}U than ^{236}U. Also the cooling time has no significant influence on the relative contents of ^{238}U and ^{236}U in spent uranium fuel [38].

Depending on the extent of any contamination it is also possible that a contamination with natural uranium—despite of an elevated age dating result of the $^{242}Pu/^{238}U$ clock—does not cause a significant change in the age dating result for the $^{239}Pu/^{235}U$ clock compared to the results for the $^{240}Pu/^{236}U$ clock. In this case the deviation arising from the contamination would be smaller than the uncertainties of the results of both the $^{240}Pu/^{236}U$ and the $^{239}Pu/^{235}U$ clocks. Depleted uranium contains only 0.2–0.3 % of ^{235}U compared to about 0.7 % ^{235}U in natural uranium [39]. Hence the influence on the $^{239}Pu/^{235}U$ clock will be even less in case of a contamination with depleted uranium.

Although natural uranium also contains ^{234}U, it can be seen in Table 4 that the age dating result of the $^{238}Pu/^{234}U$ clock for sample NBS 946 does not change when subjected to the contamination scenario described above (a hypothetical contamination of the original solid plutonium sulphate material by 0.06 % (w/w × 100) natural uranium). The reasons for the insensitivity of the $^{238}Pu/^{234}U$ clock to contamination with natural uranium are the low content of ^{234}U in natural uranium ($x(^{234}U) = 0.000054(5)$ [37]) and the short half-life of ^{238}Pu of 87.7(3) a [13]. The latter leads to a ^{234}U concentration that is comparable to the concentrations of ^{235}U and ^{236}U in an uncontaminated aged plutonium sample (see Table 3), despite of the low content in ^{238}Pu compared to the other plutonium nuclides (see Table 2).

At least 5.6 µg ^{234}U per gram plutonium sulphate would be needed to significantly change the age dating result of the $^{238}Pu/^{234}U$ clock (expanded uncertainty; $k = 2$) in sample NBS 946. In comparison to that 50 ng ^{238}U or 4.6 µg ^{235}U per gram plutonium sulphate sample introduce a significant change in the result of the respective clocks (expanded uncertainty; $k = 2$) in this sample.

Hence, a contamination with a $^{234}U/^{238}U$ ratio of about 118 (w/w) or more would be required to significantly change the result of the $^{238}Pu/^{234}U$ clock without introducing significant changes in the age dating result of the $^{242}Pu/^{238}U$ clock of this sample. A uranium contamination would be required to have a $^{234}U/^{235}U$ ratio of at least 1.25 (w/w) in order to be able to change the age dating result of the $^{238}Pu/^{234}U$ clock significantly without changing the age dating result of the $^{239}Pu/^{235}U$ clock.

Due to the $^{234}U/^{235}U$ ratio of $7.5 \times 10^{-3} \pm 1.4 \times 10^{-3}$ (w/w; $k = 2$) in natural uranium [37], it is very unlikely that the age dating result of the $^{238}Pu/^{234}U$ clock will be influenced by a contamination with natural uranium. The same goes for other uranium contaminations: the ^{234}U/^{235}U ratio in enriched uranium for uranium fuel production is kept below the internationally accepted product specification of 10 mg ^{234}U/g ^{235}U. The ^{234}U/^{235}U ratio in spent uranium fuel based on enriched natural uranium lies around 0.02–0.04 (w/w) depending on the initial enrichment in ^{235}U and the burn-up of the fuel; spent uranium fuel based on reprocessed uranium can have a ^{234}U/^{235}U ratio around 0.9 [38]. Depleted uranium has a molar ratio of ^{234}U/^{235}U around 0.04–0.05 [40].

No significant shift of the age dating results of ^{238}Pu/^{234}U clock to older age has been found in any of the analysed samples that were found to have been contaminated with uranium as described below. In the following paragraphs, the samples ACH 104-1 to 3 are evaluated with respect to the robustness of the evaluated clocks and a possible uranium contamination.

Sample ACH-104-2 is a good example for an aged plutonium sample most likely contaminated with natural uranium (Table 5; Fig. 2). It is evident that the three clocks ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U are in good agreement within their stated uncertainties, but the ^{242}Pu/^{238}U clock yields a significantly older age dating result. In this case it is not possible to directly draw conclusions about the nature of the uranium contamination, since the age dating result of the ^{239}Pu/^{235}U clock is not significantly different from the age dating results of the ^{238}Pu/^{234}U clock and the ^{240}Pu/^{236}U clock. Only the age dating result of the ^{242}Pu/^{238}U clock is shifted towards an older age. Consequently, it is not possible to calculate the 'excess' of ^{235}U as described above, since this fraction of the measured ^{235}U that belongs to the contamination is masked by the uncertainty of the age dating result of the ^{239}Pu/^{235}U clock itself as well as by the uncertainties of the age dating results of ^{238}Pu/^{234}U clock and of the ^{240}Pu/^{236}U clock. It is only possible to calculate the minimal concentration of ^{235}U that would have to be added in order to shift the age dating result of the ^{239}Pu/^{235}U clock to a significantly older age than the age dating result of the ^{240}Pu/^{236}U clock.

Table 5 Results of the age determination of sample ACH-104-2 determined by ID TIMS; the uncertainties are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Clock	Determined 'age' (a)	
	Value	Uncertainty
^{238}Pu/^{234}U	29.22	0.26
^{239}Pu/^{235}U	29.256	0.083
^{240}Pu/^{236}U	29.135	0.074
^{242}Pu/^{238}U	3889	24

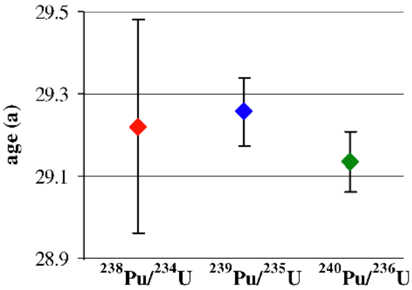


Fig. 2 Results of the age determination of sample ACH-104-2 determined by ID TIMS for the clocks ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U; all uncertainties shown are expanded uncertainties ($k = 2$); reference date: 18.10.2011

From this calculated concentration of ^{235}U and the 'excess' in ^{238}U (that can be calculated as described for NBS 946 in the beginning of this chapter) a ^{235}U/^{238}U ratio of $0.034336 \pm 26 \times 10^{-6}$ (w/w; $k = 2$) is derived for sample ACH-104-2. It can be concluded that the actual uranium contamination of sample ACH-104-2 must have a ^{235}U/^{238}U ratio <0.034 (w/w). Hence a contamination with a small amount of low enriched uranium (LEU) or natural uranium is likely. A contamination with depleted uranium is also possible.

ACH-104-1 and ACH-104-3 represent two examples for aged plutonium samples obviously showing a contamination with enriched uranium.

The age dating results of the plutonium/uranium clocks of sample ACH-104-1 are shown in Table 6 and Fig. 3. It can be seen that the age dating results of the ^{239}Pu/^{235}U and ^{242}Pu/^{238}U clocks are significantly different from the age dating results of the ^{240}Pu/^{236}U and the ^{238}Pu/^{234}U clocks. Proceeding as described above—assuming that the result of the ^{240}Pu/^{236}U clock has not been altered by the contamination—the 'excesses' of ^{235}U and ^{238}U were calculated. The estimated ^{235}U/^{238}U ratio in the 'excess' is 0.043 ± 0.034 (w/w; $k = 2$). This corresponds to 4.1 ± 3.1 % ($k = 2$; mol/mol) of ^{235}U in the sum of ^{238}U and ^{235}U. This calculation is just a coarse estimation of the composition of the contamination since it neglects all other uranium nuclides. This result corresponds, nonetheless, to a LEU contamination. LEU is defined as uranium that has been enriched to less than 20 % ^{235}U. LEU with an enrichment of typically 3–5 % is used in light water power reactors [41]. Uranium fuel for a light water reactor could consequently be a possible source for the contamination. Assuming that the contamination mainly consists from ^{235}U and ^{238}U and thus not taking any other uranium nuclides into account, the uranium contamination would represent 0.032 ± 0.021 % (w/w × 100) of the original solid plutonium oxide material of sample ACH-104-1.

Table 6 Results of the age determination of sample ACH-104-1 determined by ID TIMS; the uncertainties are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Clock	Determined 'age' (a)	
	Value	Uncertainty
^{238}Pu/^{234}U	29.06	0.21
^{239}Pu/^{235}U	29.744	0.084
^{240}Pu/^{236}U	29.057	0.073
^{242}Pu/^{238}U	8700	5900

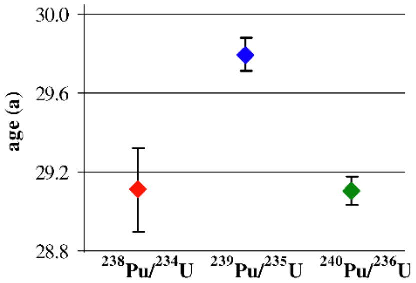


Fig. 3 Results of the age determination of sample ACH-104-1 determined by ID TIMS for the clocks ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U; all uncertainties shown are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Table 7 Results of the age determination of sample ACH-104-3 determined by ID TIMS; the uncertainties are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Clock	Determined 'age' (a)	
	Value	Uncertainty
^{238}Pu/^{234}U	29.22	0.21
^{239}Pu/^{235}U	81	0.23
^{240}Pu/^{236}U	29.266	0.074
^{242}Pu/^{238}U	10300	330

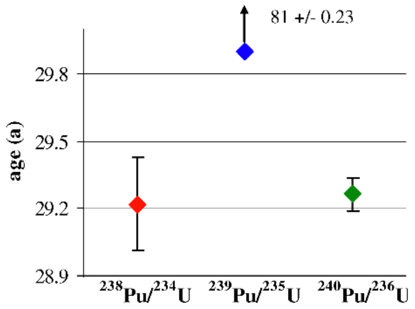


Fig. 4 Results of the age determination of sample ACH-104-3 determined by ID TIMS for the clocks ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U; all uncertainties shown are expanded uncertainties ($k = 2$); reference date: 18.10.2011

The age dating results of the plutonium/uranium clocks of sample ACH-104-3 are shown in Table 7 and Fig. 4. Similarly to sample ACH-104-1, the age dating results of the ^{239}Pu/^{235}U and the ^{242}Pu/^{238}U clocks are significantly different from the age dating results of the ^{240}Pu/^{236}U and the ^{238}Pu/^{234}U clocks. In this case the 'excess' of both ^{235}U and ^{238}U were calculated, as well. Once again it was assumed that the result of the ^{240}Pu/^{236}U clock has not been altered by the contamination.

The calculated ^{235}U/^{238}U ratio in the contamination is 1.154 ± 0.036 (w/w; $k = 2$), which corresponds to 53.53 ± 0.79 % (w/w; $k = 2$) of ^{235}U in the sum of ^{238}U and ^{235}U. In this case, the isotopic composition of the contamination points to a contamination with high-enriched uranium (HEU). A likely source for this uranium contamination would be an uranium reference material with a ^{235}U/^{238}U ratio close to unity such as IRMM-072 [29] or CRM U500 [42]. Furthermore, the contamination could consist of uranium fuel for a research reactor [43]. Another less likely source for this HEU contamination is uranium fuel for naval reactors: Uranium fuel with an enrichment in the range of 3–93 % ^{235}U is used in naval reactors. According to literature [44] several nuclear-powered Russian submarines and ships were built in the 1970s and 1980s that can be fuelled with uranium fuel with an enrichment of ^{235}U close to 50 % (from 45 to 55 % ^{235}U for the concerned naval reactors). Assuming that once again the contamination mainly consists of ^{235}U and ^{238}U and thus not taking any other uranium nuclides into

Table 8 Half-lives of plutonium mother nuclides and their respective daughter nuclides used for age dating of plutonium from Ref. [46]; uncertainties are standard uncertainties

Clock	Half-life mother (a)	Reference	Half-life daughter (a)	Reference
^{238}Pu/^{234}U	87.74(3)	[46]	$2.455(6) \times 10^{5}$	[46]
^{239}Pu/^{235}U	$2.410(3) \times 10^{4}$	[46]	$7.04(1) \times 10^{8}$	[46]
^{240}Pu/^{236}U	6561(7)	[46]	$2.342(4) \times 10^{7}$	[46]

account, the contamination makes up $0.1587 \pm 2.3 \times 10^{-3}$ % (w/w; $k = 2$) of the original solid plutonium oxide material of sample ACH-104-3.

Incomplete separation at time zero

Another scenario that shifts the plutonium/uranium clocks relative to each other in a distinctive way is an incomplete removal of the daughter nuclides during the last manipulation of the material (i.e. incomplete purification of the plutonium at time zero). The scenario discussed does not refer to plutonium that is freshly separated from irradiated uranium fuel, but plutonium material that has been purified more than once. Plutonium which is separated from irradiated uranium fuel by an industrial process may still contain significant amounts of the uranium matrix [45]. It is thus not suited for plutonium age determination via the plutonium/uranium clocks, since the prerequisite (i) of nuclear age determination that all the 'daughter' nuclides should be completely removed from their respective parent nuclides at time zero ($t = 0$) is not met and plutonium age determination can be expected to be significantly biased.

The effect of an incomplete removal of the uranium nuclides during the last chemical separation from the plutonium matrix is discussed. The uranium isotopes present in a sample under investigation will consist of residual uranium and radiogenic uranium. This results in two main issues for nuclear forensic interpretation: the results of the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{242}Pu/^{238}U clocks are shifted to an older age due to the 'excess' of uranium and secondly the uranium isotopes may provide hints on the initially used uranium fuel for plutonium production. In order to exploit the latter, the age provided by the parent/daughter pair which is least affected by residual uranium (usually ^{240}Pu/^{236}U) can be used to calculate the amount of radiogenic uranium isotopes. Correcting the measured uranium isotopic composition for the radiogenic contribution will result in the isotopic composition of the uranium fuel (used for plutonium production) at the end of irradiation. A more quantitative discussion hereof is, however, beyond the scope of the present paper.

Only the three commonly used plutonium/uranium chronometers for plutonium age determination (^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U) are discussed in this chapter, since no significant shift of the result of the ^{242}Pu/^{238}U clock from the age dating results of the other plutonium/uranium clocks was observed for the example described below (see Table 4 'Incomplete separation' and 'Determined age').

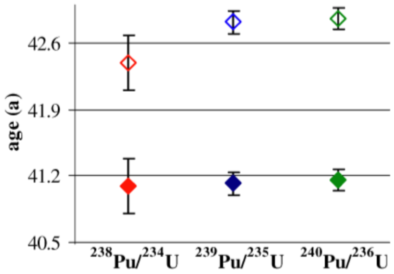


Fig. 5 Influence of assumed incomplete separation on age dating results of sample NBS 946; all uncertainties shown are expanded uncertainties ($k = 2$); reference date: 18.10.2011; *full symbols* age calculated from results determined by ID TIMS; *empty symbols* values calculated from the results determined by ID TIMS assuming only 90 % of the uranium was removed during the last separation. It is also assumed that the first removal of the daughter nuclides took place 17 years prior to the last separation

The result for the ^{238}Pu/^{234}U clock is shifted to a younger age relative to the ^{239}Pu/^{235}U and ^{240}Pu/^{236}U age dating results. This can be explained by the half-lives of the mother and daughter isotopes pairs shown in Table 1: The half-life of ^{238}Pu of only 87.7(3) a is considerably shorter than the half-lives of ^{239}Pu and ^{240}Pu, 2.411(3)·10^4 a and 6563(7) a, respectively [24]. This scenario is illustrated in Table 4 (Incomplete separation) and Fig. 5 for NBS 946. The values shown for this scenario have been calculated assuming the following hypothetical history of the sample, chosen in a way that a significant difference between the results of the ^{238}Pu/^{234}U clock and the ^{240}Pu/^{236}U clock is induced: 17 years before the last separation (second separation) the material had been 'produced' by separating the mother nuclides from its daughter nuclides (first separation) around 1953. This first separation was achieved with a high decontamination factor, leaving practically no uranium nuclides in the plutonium material. Furthermore, it was assumed that the 'true time span' since the last separation (second separation) was the actually determined age dating result for the ^{240}Pu/^{236}U clock (41.16 ± 0.11 ($k = 2$) calculated for 18.10.2011; see Table 4 'Determined age').

The second separation that took place 17 years after the initial isolation of the plutonium from its daughter nuclides was assumed to be incomplete leaving 10 % of the daughter nuclides that have built up during these 17 years in the plutonium material.

Care must be taken not to accomplish such interpretations without careful consideration of other effects on the age dating results of the different plutonium/uranium clocks that are artefacts of the sample preparation, measurement or data treatment. An example for such an artefact that has to be considered in some samples is explained in the following paragraph simulating incomplete separation:

During the TE TIMS measurement of the plutonium isotopes a peak tailing effect can be observed from mass 239 to mass 238. The plutonium samples for age

Table 9 Results of the age determination of the samples NBS 946 (a) and ACH-104-2 (b) determined by ID TIMS including the result for the ^{238}Pu/^{234}U clock without correction of the ^{238}Pu measurement signal for peak tailing from the ^{239}Pu measurement signal using two different sets of half-lives (from [22] and [44]); the uncertainties are expanded uncertainties ($k = 2$); reference date: 18.10.2011

	'Age' (a)		'Age' ^{238}Pu uncorrected (a)		'Age' (a)		'Age' ^{238}Pu uncorrected (a)	
Half-life	[24]		[24]		[46]		[46]	
Clock	Value	Uncertainty	Value	Uncertainty	Value	Uncertainty	Value	Uncertainty
(a) NBS 946								
^{238}Pu/^{234}U	41.09	0.29	40.97	0.29	41.105	0.080	40.992	0.072
^{239}Pu/^{235}U	41.12	0.12	–	–	41.10	0.12	–	–
^{240}Pu/^{236}U	41.16	0.11	–	–	41.15	0.11	–	–
(b) ACH-104-2								
^{238}Pu/^{234}U	29.22	0.26	28.94	0.21	29.23	0.11	28.955	0.072
^{239}Pu/^{235}U	29.256	0.083	–	–	29.243	0.081	–	–
^{240}Pu/^{236}U	29.135	0.074	–	–	29.126	0.071	–	–

determination usually contain a lot more ^{239}Pu than ^{238}Pu (see Table 2). The apparent higher number of ^{238}Pu nuclides shifts the nuclide ratio ^{238}Pu/^{234}U to a value that represents a 'younger' age relative to the ^{239}Pu/^{235}U and the ^{240}Pu/^{236}U clocks. This creates a pattern of the plutonium/uranium clock's age dating results that looks similar to the scenario of incomplete separation described above.

The first two columns of Table 9 show the results of the age determination of the samples NBS 946 (a) and ACH-104-2 (b) for the ^{238}Pu/^{234}U clock with and without correction of the ^{238}Pu measurement signal for peak tailing from the ^{239}Pu measurement signal. In both cases, the ^{238}Pu/^{234}U clocks show a shift towards lower absolute age values, even though the shift is not significant. Nonetheless, the resulting pattern of the three different plutonium/uranium clocks can potentially be interpreted as incomplete removal of the uranium daughter nuclides at time zero (compare to Fig. 6a). The reason for the different effects on the two different samples can be explained by the difference of relative amounts of ^{238}Pu and ^{239}Pu (see Table 2). The analytical artefact is more pronounced when a higher ^{239}Pu/^{238}Pu ratio is measured. The ratios of ^{239}Pu/^{238}Pu in NBS 946 and ACH-104-2 are 459.04 ± 0.60 and 1487.5 ± 8.5 ($k = 2$), respectively.

Uncertainties of plutonium half-lives

The main contribution to the expanded combined uncertainties of the age dating results of the ^{238}Pu/^{234}U clock is the half-life of ^{238}Pu followed by the concentration of ^{238}Pu. The main contribution to the uncertainty of the concentration of ^{238}Pu is the uncertainty of the IDMS spike followed by peak tailing correction, and the measured ratio of ^{238}Pu/^{239}Pu, which is significantly lower than the ratios of the other plutonium nuclides to ^{239}Pu (see Table 2).

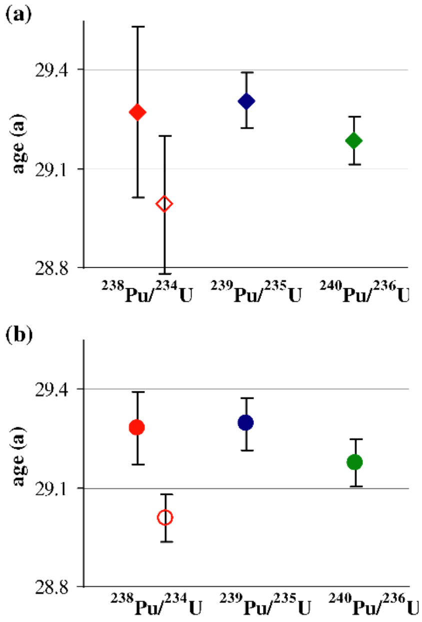


Fig. 6 Influence of omitting the correction of the ^{238}Pu measurement signal for peak tailing from the ^{239}Pu measurement signal on age dating results of sample ACH-104-2; age dating results for ^{238}Pu/^{234}U; ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks are shown: *full symbols* age calculated from results determined by ID TIMS; *empty symbols* results determined by ID TIMS for the ^{238}Pu/^{234}U clock without correction of the ^{238}Pu measurement signal for peak tailing from the ^{239}Pu measurement signal. **a** Half-life values from Ref. [24] used for the data evaluation. **b** Half-life values from Ref. [46] used for the data evaluation. All uncertainties shown are expanded uncertainties ($k = 2$); reference date: 18.10.2011

Since the half-life is nevertheless—as for the ^{239}Pu/^{235}U and the ^{240}Pu/^{236}U clock's age dating results—the main contributor to the uncertainty of the ^{238}Pu/^{234}U age dating result, the source of half-lives used for age dating can determine whether a 'pattern' of different clocks is visible or not. The half-lives of the uranium and plutonium nuclides from Ref. [24] listed in Table 1 were used for the calculation of all data shown in this article hitherto. This set of half-lives was chosen since it is representative for a set of half-lives that is actually being used in nuclear laboratories: The EC-JRC-IRMM gives a reference to this set of half-lives on each IRMM plutonium reference material certificate such as for the certified reference material IRMM-049d (Institute for Reference Materials and Measurements, Geel, Belgium) [27] which was issued in 2011.

Using a different set of half-lives such as Ref. [46], however, changes the situation: The last two columns of Table 9 show the age dating results for samples NBS 946 and ACH-104-2 using the half-lives given in Table 8. The age dating result for the ^{238}Pu/^{234}U clock for sample ACH-104-2 without correction of the ^{238}Pu signal for peak tailing from the ^{239}Pu signal is significantly different from the results of the ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks. This can also be seen in Fig. 6b. The corresponding values for sample NBS 946, however, are still overlapping within their uncertainties.

The weight of the contribution of the peak tailing correction to the total combined uncertainty of the age dating result of the clock ^{238}Pu/^{234}U depends highly on the choice of the ^{238}Pu half-life: In sample NBS 946 the uncertainty contribution of the peak tailing correction changes from 5.8 to 76.6 % when the half-life of ^{238}Pu is changed from the half-lives published by the IAEA [24] to those published by Be et al. [46], since the uncertainties of these published half-lives have quite different uncertainty values.

Discussion

When the age dating results for the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{242}Pu/^{238}U clocks are considered for plutonium age dating the following conclusions can be drawn depending on the observed measurement results:

- All the results are in agreement with each other: no further assessment is required and the last separation date can be determined with a high level of confidence.
- The age dating results of the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks agree with each other, but the ^{242}Pu/^{238}U clock indicates an older age: the contamination can consist of a small amount of enriched, natural or depleted uranium; only the upper limit for the ^{235}U/^{238}U ratio in the contamination can be estimated. The results of the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks represent the production date.
- The age dating results of the ^{238}Pu/^{234}U and the ^{240}Pu/^{236}U clock agree with each other, but the ^{239}Pu/^{235}U clock and the ^{242}Pu/^{238}U clock give an older age: The ^{235}U/^{238}U ratio in the contamination can be estimated. HEU is a probable source for the uranium contamination. Especially in this case it must be kept in mind that the contamination could (theoretically) also contain a significant amount of ^{236}U since the nature of the contamination is not known, but the ^{240}Pu/^{236}U clock's result has been used as the reference for the 'true age without contamination' for the calculation of the nature of the uranium contamination. The age dating results of the ^{238}Pu/^{234}U and the ^{240}Pu/^{236}U clock can with precautions be interpreted as the production date of the sample.
- The age dating results of the ^{239}Pu/^{235}U and ^{240}Pu/^{236}U (and ^{242}Pu/^{238}U) clocks match, but the ^{238}Pu/^{234}U clock results in a younger age: When an artefact due to an omitted peak tailing correction for peak tailing from ^{239}Pu to mass 238 can be excluded, the last removal of the daughter nuclides at time zero has been incomplete. This means that all the results show an older age than the actual age. It can be concluded that the sample must be younger than the age dating result of the ^{238}Pu/^{234}U clock.
- The results of the different clocks do not fit with each other and none of the above mentioned explanations is eligible: The sample is probably a mixture of different materials of different ages; or the sample has been contaminated with uranium and the separation at time zero has been incomplete. None of the determined age dating results can be trusted in this case.

Conclusion

Age determination is undoubtedly a powerful tool to limit the number of facilities where seized plutonium samples could have been produced or processed for nuclear forensic investigations. For plutonium age dating it is, however, advisable to use more than one parent/daughter pair in order to ensure the reliability of the radiochronometric results. Ideally all of the clocks will yield consistent results providing a reliable 'age' of a nuclear material. Inconsistent results of the various Pu/U clocks may be attributed to uranium present in the sample which is not of radiogenic origin. Uranium contamination in plutonium samples may arise from incomplete separation of the two elements at the initial stage or it may be due to uranium which was (accidentally) added to the plutonium after the last chemical separation.

With this study the authors achieved to establish a ‘roadmap’ for dating of plutonium materials via the respective plutonium/uranium clocks. According to our findings, the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks are most likely to lead to consistent age values (even showing robustness against small contaminations with uranium). If the age dating result of ^{242}Pu/^{238}U clock is high in comparison to the other plutonium/uranium clocks, contamination with a small amount of enriched uranium or with natural or depleted uranium can be suspected. In case of a positive bias of the ^{239}Pu/^{235}U clock compared with the results for ^{238}Pu/^{234}U and ^{240}Pu/^{236}U clocks along with the elevated result of ^{242}Pu/^{238}U clock, a contamination with enriched uranium might have occurred. If the ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks agree within respective uncertainties but the ^{238}Pu/^{234}U clock gives a lower result then incomplete separation at time zero is likely assuming an analytical artefact arising from omitted peak tailing correction can be excluded. Hence, a careful evaluation of different radiochronometers may reveal additional information on the uranium contaminant.

Unfortunately, there is at present no plutonium CRM available certified for its separation date. In order to improve this situation the EC-JRC-IRMM and the EC-JRC-ITU (European Commission, Joint Research Centre, Institute for Transuranium Elements) are closely cooperating in projects for the production of plutonium (and uranium [47]) CRMs certified for separation dates. These CRMs are aimed at meeting a repeatedly expressed need of laboratories involved in nuclear forensics, nuclear safeguards and nuclear security, since they will provide a solid metrological basis for age dating measurements of nuclear materials and establish proper confidence in the conclusions based on these measurements.

Acknowledgments The authors would like to thank Rüdiger Kessel for providing for the program GUM work bench 2.4 (Metrodata, Germany) for the uncertainty evaluation and Frances Kehoe, Roger Eykens and Heinz Kuehn for their support in the IRMM nuclear chemistry and mass spectrometry laboratories.

References

1. Webb G (2013) Tracking traffickers—the IAEA Incident and Trafficking Database. IAEA Bull 54(2):22
2. Mayer K, Wallenius M, Fanghänel T (2007) Nuclear forensic science—from cradle to maturity. J Alloys Compd 444–445:50–56
3. Mayer K, Wellum R (2004) Reference materials for destructive analysis in nuclear safeguards. ESARDA Bull 32:75–82
4. Wallenius M, Mayer K, Ray I (2006) Nuclear forensic investigations: two case studies. Forensic Sci Int 156:55–62
5. Wallenius M, Lützenkirchen K, Mayer K, Ray I, de las Heras LA, Betti M, Cromboom O, Hild M, Lynch B, Nicholl A, Ottmar H, Rasmussen G, Schubert A, Tamborini G, Thiele H, Wagner W, Walker C, Zuleger E (2007) Nuclear forensic investigations with a focus on plutonium. J Alloys Compd 444–445:57–62
6. Pajo L, Schubert A, Aldave L, Koch L, Bibilashvili YK, Dolgov YN, Chorokhov NA (2001) Identification of unknown nuclear fuel by impurities and physical parameters. J Radioanal Nucl Chem 250(1):79–84
7. Pajo L, Mayer K, Koch L (2001) Investigation of the oxygen isotopic composition in oxidic uranium compounds as a new property in nuclear forensic science. Fresenius J Anal Chem 371(3):348–352
8. Kraiem M, Richter S, Kühn H, Stefaniak EA, Kerckhove G, Aregbe Y (2011) Investigation of uranium isotopic signatures in real-life particles from a nuclear facility by thermal ionization mass spectrometry. Anal Chem 83(8):3011–3016
9. Mayer K, Wallenius M, Varga Z (2012) Nuclear forensic science: correlating measurable material parameters to the history of nuclear material. Chem Rev 113(2):884–900
10. Stepanov SI, Chekmarev AM (2008) Concept of spent nuclear fuel reprocessing. Dokl Chem 423(1):276–278
11. Wallenius M, Mayer K (2000) Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry. Fresenius J Anal Chem 366(3):234–238
12. Mayer K, Wallenius M, Hedberg M, Lützenkirchen K (2009) Unveiling the history of seized plutonium through nuclear forensic investigations. Radiochim Acta 97(4–5):261–264
13. Stolz W (2005) Radioaktivität: Grundlagen—Messung—Anwendungen Vieweg + Teubner Verlag
14. Keegan RP, Gehrke RJ (2003) A method to determine the time since last purification of weapons grade plutonium. Appl Radiat Isot 59(2–3):137–143
15. Nguyen CT (2006) Verification of the 239Pu content, isotopic composition and age of plutonium in Pu–Be neutron sources by gamma-spectrometry. Nucl Instrum Methods Phys Res Sect B 251(1):227–236
16. Ramebäck H, Nygren U, Tovedal A, Ekberg C, Skarnemark G (2012) Uncertainty assessment in gamma spectrometric measurements of plutonium isotope ratios and age. Nucl Instrum Methods Phys Res Sect B 287:56–59
17. Kirby HW, Sheehan WE (1984) Determination of 238Pu and 241Am in 239Pu by alpha-spectrometry. Nucl Instrum Methods 223(2–3):356–359
18. Zhang H-T, Zhu FR, Xu J, Dai YH, Li DM, Yi XW, Zhang LX, Zhao YG (2008) Age determination of plutonium material by alpha spectrometry and thermal ionization mass spectrometry. Radiochim Acta 96(6):327–331
19. Varga Z, Surányi G, Vajda N, Stefánka Z (2007) Determination of plutonium and americium in environmental samples by inductively coupled plasma sector field mass spectrometry and alpha spectrometry. Microchem J 85(1):39–45
20. Chen Y, Chang Z-y, Zhao Y-g, Zhang J-l, Li J-h, Shu F-j (2009) Studies on the age determination of trace plutonium. J Radioanal Nucl Chem 281(3):675–678
21. Nygren U, Ramebäck H, Nilsson C (2007) Age determination of plutonium using inductively coupled plasma mass spectrometry. J Radioanal Nucl Chem 272(1):45–51
22. Wallenius M, Tamborini G, Koch L (2001) The “age” of plutonium particles. Radiochim Acta 89 (1_2001):55
23. Uriano GA (1982) National Bureau of Standards Certificate of Analysis Standard Reference Material 946 Plutonium Isotopic Standard. U.S. Department of Energy, Washington, DC
24. IAEA (1986) Decay data of the Transactinium Nuclides. Technical Reports Series No. 261

25. Wellum R, Verbruggen A, Kessel R (2009) A new evaluation of the half-life of 241Pu. J Anal At Spectrom 24(6):801–807
26. De Bièvre P, Peiser HS (1997) Basic equations and uncertainties in isotope-dilution mass spectrometry for traceability to SI of values obtained by this primary method. Fresenius J Anal Chem 359(7):523–525
27. Emons H (2011) Certificate Spike Isotopic Reference Material IRMM-049d Institute for Reference Materials and Measurements. Geel, Belgium
28. De Bièvre P (1997) Certificate Spike Isotopic Reference Material IRMM-049c Institute for Reference Materials and Measurements. Geel, Belgium
29. Richter S, Alonso A, Aregbe Y, Eykens R, Kehoe F, Kühn H, Kivel N, Verbruggen A, Wellum R, Taylor PDP (2009) A new series of uranium isotope reference materials for investigating the linearity of secondary electron multipliers in isotope mass spectrometry. Int J Mass Spectrom 281(3):115–125
30. Jakopič R, Verbruggen A, Eykens R, Kehoe F, Kühn H, Kushigeta Y, Jacobsson U, Bauwens J, Richter S, Wellum R, Aregbe Y (2010) An inter-calibration campaign using various selected Pu spike isotopic reference materials. J Radioanal Nucl Chem 286(2):449–454
31. Callis EL, Abernathey RM (1991) High-precision isotopic analyses of uranium and plutonium by total sample volatilization and signal integration. Int J Mass Spectrom Ion Processes 103(2–3):93–105
32. Jakopic R, Richter S, Kühn H, Benedik L, Pihlar B, Aregbe Y (2009) Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with "multiple ion counting" and filament carburization. Int J Mass Spectrom 279(2–3):87–92
33. Taylor P, Wellum R (2006) Certificate isotopic reference material IRMM-074 Institute for Reference Materials and Measurements. Geel, Belgium
34. De Bièvre P (1996) Certificate Isotopic Reference Material IRMM-290b Institute for Reference Materials and Measurements. Geel, Belgium
35. Gourgiotis A, Granet M, Isnard H, Nonell A, Gautier C, Stadelmann G, Aubert M, Durand D, Legand S, Chartier F (2010) Simultaneous uranium/plutonium separation and direct isotope ratio measurements by using CO2 as the gas in a collision/reaction cell based MC-ICPMS. J Anal At Spectrom 25(12):1939–1945
36. Mason P (2010) A documentary history of the United States' first plutonium isotopic reference materials. Paper presented at the 51st Annual INMM Meeting Baltimore
37. De Laeter JR, Boelke JK, De Bievre P, Hidaka H, Peiser HS, Rosman KJR, Taylor PDP (2003) Atomic weights of the elements: review 2000 (IUPAC Technical Report). Pure Appl Chem 75(6):683–800
38. IAEA (2007) Management of reprocessed uranium—current status and future prospects. IAEA Technical Documents (IAEA-TECDOC-1529)
39. Bleise A, Danesi PR, Burkart W (2003) Properties, use and health effects of depleted uranium (DU): a general overview. J Environ Radioact 64(2–3):93–112
40. Boulyga SF, Testa C, Desideri D, Becker JS (2001) Optimisation and application of ICP-MS and alpha-spectrometry for determination of isotopic ratios of depleted uranium and plutonium in samples collected in Kosovo. J Anal At Spectrom 16(11):1283–1289
41. Smith DK, Kristo MJ, Niemeyer S, Dudder GB (2008) Documentation of a model action plan to deter illicit nuclear trafficking. J Radioanal Nucl Chem 276(2):415–419
42. Neuhoff J (2008) Certificate of analysis CRM U500 uranium isotopic standard. U.S. Department of Energy, Washington, DC
43. Glaser A (2002) The conversion of research reactors to low-enriched fuel and the case of the FRM-II. Sci Glob Secur 10(1):61–79
44. Ma C, von Hippel F (2001) Ending the production of highly enriched uranium for naval reactors. Nonprolif Rev (Spring 2001) 8:8
45. Aggarwal SK, Saxena MK, Shah PM, Kumar S, Jairaman U, Jain HC (1994) Studies on the evaporation and ionisation behaviour of uranium and plutonium in thermal ionisation mass spectrometry. Int J Mass Spectrom Ion Process 139:111–126
46. Be M, Chiste V, Dulieu C (2006) Halve-lives, Table of recommended values. Laboratoire National Henri Becquerel Note Technique (DETECS/LNHB/2006-58)
47. Varga Z, Nicholl A, Wallenius M, Mayer K (2012) Development and validation of a methodology for uranium radiochronometry reference material preparation. Anal Chim Acta 718:25–31

2.3 Publication III

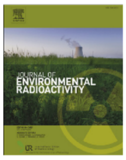
Reprinted from Journal of Environmental Radioactivity, Vol. 125, Jakopic R, Sturm M, Kraiem M, Richter S, Aregbe Y, Certified reference materials and reference methods for nuclear safeguards and security, Pages No. 17-22, Copyright (2013), with permission from Elsevier.

Journal of Environmental Radioactivity 125 (2013) 17–22

Contents lists available at SciVerse ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad



Certified reference materials and reference methods for nuclear safeguards and security

R. Jakopič [a],*, M. Sturm [a,b], M. Kraiem [c], S. Richter [a], Y. Aregbe [a]

[a] *European Commission – Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Retieseweg 111, 2440 Geel, Belgium*
[b] *University of Natural Resources and Life Sciences (BOKU), Vienna, Austria*
[c] *New Brunswick Laboratory (NBL), Argonne, USA*

ARTICLE INFO

Article history:
Received 6 February 2013
Accepted 17 February 2013
Available online 15 March 2013

Keywords:
Certified reference materials
Nuclear safeguards and security
IDMS
Traceability
Age dating
Quality control

ABSTRACT

Confidence in comparability and reliability of measurement results in nuclear material and environmental sample analysis are established via certified reference materials (CRMs), reference measurements, and inter-laboratory comparisons (ILCs). Increased needs for quality control tools in proliferation resistance, environmental sample analysis, development of measurement capabilities over the years and progress in modern analytical techniques are the main reasons for the development of new reference materials and reference methods for nuclear safeguards and security.

The Institute for Reference Materials and Measurements (IRMM) prepares and certifies large quantities of the so-called "large-sized dried" (LSD) spikes for accurate measurement of the uranium and plutonium content in dissolved nuclear fuel solutions by isotope dilution mass spectrometry (IDMS) and also develops particle reference materials applied for the detection of nuclear signatures in environmental samples. IRMM is currently replacing some of its exhausted stocks of CRMs with new ones whose specifications are up-to-date and tailored for the demands of modern analytical techniques. Some of the existing materials will be re-measured to improve the uncertainties associated with their certified values, and to enable laboratories to reduce their combined measurement uncertainty.

Safeguards involve the quantitative verification by independent measurements so that no nuclear material is diverted from its intended peaceful use. Safeguards authorities pay particular attention to plutonium and the uranium isotope ^{235}U, indicating the so-called 'enrichment', in nuclear material and in environmental samples. In addition to the verification of the major ratios, $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{240}\mathrm{Pu})/n(^{239}\mathrm{Pu})$, the minor ratios of the less abundant uranium and plutonium isotopes contain valuable information about the origin and the 'history' of material used for commercial or possibly clandestine purposes, and have therefore reached high level of attention for safeguards authorities. Furthermore, IRMM initiated and coordinated the development of a Modified Total Evaporation (MTE) technique for accurate abundance ratio measurements of the "minor" isotope-amount ratios of uranium and plutonium in nuclear material and, in combination with a multi-dynamic measurement technique and filament carburization, in environmental samples.

Currently IRMM is engaged in a study on the development of plutonium reference materials for "age dating", i.e. determination of the time elapsed since the last separation of plutonium from its daughter nuclides. The decay of a radioactive parent isotope and the build-up of a corresponding amount of daughter nuclide serve as chronometer to calculate the age of a nuclear material. There are no such certified reference materials available yet.

1. Introduction

The prime objective of the Institute for Reference Materials and Measurements (IRMM) is to build confidence in comparability of measurements by the production and dissemination of internationally accepted quality assurance tools. This is established via

---

* Corresponding author. Tel.: +32 14571617.
E-mail address: rozle.jakopic@ec.europa.eu (R. Jakopič).

0265-931X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jenvrad.2013.02.013

certified reference materials (CRMs), reference measurements and conformity assessment tools (i.e. inter-laboratory comparisons). The fundamental role of CRMs in measurements is to establish traceability of a measured value to a primary unit of measurement, such as defined in the International System of Units (SI). IRMM is a recognized provider of nuclear reference materials and supplies the international community with different types of them, in particular uranium and plutonium isotopic reference materials (IRM), covering a wide range of concentrations and isotope ratios. These nuclear reference materials are particularly needed for instrument calibration, validation of analytical methods, and for assessing the reproducibility of measurement results in compliance with the quality control requirements for various fields of application such as fissile material control (nuclear safeguards), nuclear forensics, geological and environmental sciences.

Some of the existing reference materials have been on the market for decades. IRMM interacts regularly on the development of new nuclear reference materials with several other international reference material suppliers (e.g. New Brunswick Laboratory (NBL) of the U.S. Department of Energy, CETAMA) as well as with safeguards authorities and laboratories (e.g. IAEA, JAEA) via the international platforms of ESARDA (European Safeguards Research and Development Association), INMM (Institute for Nuclear Materials Management) and IAEA (International Atomic Energy Agency) technical meetings and workshops. Due to progress in modern analytical techniques and instrumentation, the analytical measurement community is in need of new plutonium and uranium CRMs with considerably smaller uncertainties of their certified values. This is of importance for helping laboratories in reducing their measurement uncertainty and fulfilling the measurement requirements for laboratory performance in safeguards verification and nuclear material accountancy (International Atomic Energy Agency, 2010; Jakopic et al., 2011). To meet this request, IRMM launched in 2009 an inter-calibration campaign, inter-linking several plutonium spike CRMs available at the institute on a metrological basis, and applying state-of-the-art measurement procedures. The following nuclear isotopic CRMs were part of this campaign: IRMM-049b (^{242}Pu), IRMM-049c (^{242}Pu), IRMM-046b (^{242}Pu and ^{233}U), IRMM-083 (^{240}Pu) and IRMM-081a (^{239}Pu). A good agreement was achieved for all spikes, except for a mixed U/Pu spike, IRMM-046b, for which the new experimental values and expanded uncertainties are provided in a new certificate issued by IRMM in 2010 (Jakopic et al., 2010a).

Recently, two ^{239}Pu spike CRMs, IRMM-082 and IRMM-086, and the IRMM-042a were included in the inter-calibration scheme. IRMM-042a is a ^{244}Pu spike CRM certified in 1986 with a relative expanded uncertainty of about 0.2% ($k = 2$). Due to a small bias observed in the certified values from recent measurements (Jakopic et al., 2011) and a relatively large combined uncertainty, it was decided to issue a new certificate for IRMM-042a in compliance with ISO Guide 34:2009 and ISO/IEC 17025:2005. Some of the results for IRMM-042a and IRMM-086 will be discussed in this paper.

Another fundamental and new challenge is to develop CRMs required for "age" dating in nuclear forensics. The "age" is defined as the time elapsed since the last chemical separation of the mother and daughter isotopes. Assuming that the separation is complete and that all daughter isotopes have been removed from the original material, the "age" of the material can be determined by measuring the ratio of the daughter to mother radio-nuclides (Wallenius and Mayer, 2000; Wallenius et al., 2006). In particular for the determination of the unknown age of a plutonium material, different clocks (pairs of mother and daughter isotopes) can be used, i.e. ^{241}Am/^{241}Pu, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U, and possibly ^{242}Pu/^{238}U. Thermal Ionization Mass Spectrometry (TIMS) is applied for the measurement of the plutonium and uranium isotope ratios after chemical separation, while ^{241}Am is usually measured by γ-spectrometry.

There are three possibilities to produce a reference material for nuclear age dating, which are 1) the characterization of an existing (old) material with well-known separation date, 2) the quantitative separation of bulk material leading to a material with well documented separation date and completeness of separation ("clock" set to zero), and 3) the preparation of a synthetic mixture of purified fractions of mother and daughter isotopes that mimics a certain age for the material. IRMM is currently developing reference materials for "age dating" in co-operation with the JRC, Institute for Transuranium Elements (ITU, Karlsruhe, Germany) by applying the first two approaches. For a feasibility study, the reference plutonium materials NBS 946, NBS 947 and NBS 948, where the date of the last separation is only approximately known, have been selected for investigation (Jakopic et al., 2011). The results obtained for NBS 946 are presented in this paper.

In addition to the development of new isotopic reference materials, IRMM is also supporting the safeguards and measurement community in providing state-of-the-art reference methods to detect undeclared nuclear materials and/or activities in compliance with the Treaty on the non-proliferation of nuclear weapons (NPT) and the Additional Protocol (INFCIRC 540) (International Atomic Energy Agency, 1997) in conjunction with the comprehensive safeguards agreement (INFCIRC 153, corrected). Accurate isotopic measurement of environmental samples (bulk and particle analysis) is the most powerful tool to detect undeclared nuclear activities (Sturm, 2010). In particular, the uranium and/or plutonium isotope ratios can be used as "fingerprints" for discriminating between different origins/sources of contamination. In the case of plutonium isotopes, the $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ isotope ratio is a good indicator to distinguish between different types of contamination, e.g. nuclear power plant accidents, discharges from reprocessing facilities, nuclear weapon testing, etc. In addition, the $n(^{241}\text{Pu})/n(^{239}\text{Pu})$ and $n(^{242}\text{Pu})/n(^{239}\text{Pu})$ isotope ratios can provide information on the production processes of a nuclear material (Jakopic et al., 2010b). For uranium the so-called major uranium isotope ratio $n(^{235}\text{U})/n(^{238}\text{U})$ gives information about the enrichment level of nuclear materials, while the isotopic abundance of the so-called minor uranium isotopes (i.e. ^{234}U and ^{236}U) might be useful to provide a detailed picture of the activities conducted within nuclear installations (e.g. enrichment or reprocessing). Due to the low amounts of plutonium and uranium in environmental samples and in sub-micrometre uranium-containing particles, highly sensitive analytical techniques are needed to measure isotope ratios accurately, especially the minor abundant isotope ratios (Truyens et al., 2011). At IRMM, the TIMS technique with Multiple Ion Counting (MIC) has been applied for the analysis of plutonium in soil and sediment samples as well as for uranium single particle analysis. MIC enables the simultaneous measurement of all the isotopes of interest, and is advantageous whenever the sample size is restricted. In addition, the carburization technique was applied to the rhenium mass spectrometry filaments to enhance the ionization efficiency of U and Pu in the TIMS ion source, resulting in more stable ion beams with higher counting rates for the minor isotopes (Jakopic et al., 2010b; Kraiem et al., 2011a,b; Jakopic et al., 2009).

As a result of the continuous exchange between reference laboratories, safeguards laboratories and experts in the field, a new version of the "modified total evaporation" (MTE) method for isotopic analysis by multi-collector TIMS, with high analytical performance and designed in a more user-friendly and routinely applicable way, was developed at IRMM, in collaboration with several "key nuclear mass spectrometry laboratories" worldwide (NBL, ITU, SGAS-IAEA). MTE is a new tool which is found to be useful for the accurate measurement of the uranium minor abundant isotope ratios in nuclear material, and in combination with a multi-dynamic measurement procedure, for plutonium in environmental samples. Since the principle of the "total evaporation" (TE) process is applied to the samples, the measurement of the major uranium isotope-amount ratio $n(^{235}U)/n(^{238}U)$ is routinely performed with a precision of 0.01–0.02%. Moreover, with the use of an appropriate CRM comparator for the external mass bias correction of the major ratio, an accuracy of about 0.02% can be achieved. But the most significant improvement using MTE is in the analytical performance achieved for the minor isotope-amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$, which is superior to the present IAEA requirements. These improvements are particularly useful for enabling more detailed conclusions from the analytical results for the source attribution of nuclear material in environmental samples. This method is now routinely used at all collaborating laboratories, and it is requested to be implemented by other expert nuclear laboratories in the field of nuclear safeguards and geochemistry (Richter et al., 2011).

2. Experimental

2.1. Preparation of the blends and chemical treatment of Pu

As part of an inter-calibration campaign, blend mixtures for IDMS analyses were prepared by substitution weighing. IRMM-082 and IRMM-086 (^{239}Pu) were inter-linked with IRMM-049b (^{242}Pu) and IRMM-083 (^{240}Pu) spikes, while IRMM-042a (^{244}Pu) with IRMM-049d (^{242}Pu), IRMM-083 (^{240}Pu) and an external quality control solution Eqrain-11 as shown in Fig. 1. The blend mixtures were evaporated to near dryness and the residue was dissolved in 2 M HNO_3. A redox cycle was done in which plutonium was first reduced to Pu(III) by addition of 1.25 M $FeCl_2$ and 1 M $NH_2OH\cdot HCl$ and then oxidised to Pu(IV) by addition of 1 M $NaNO_2$. Finally, concentrated nitric acid was added to obtain Pu(IV) in 8 M HNO_3. The separation of Pu was accomplished by passing the sample through a preconditioned anion-exchange column (Bio-Rad AG1-X4, 100–200 mesh). The column was washed with 8 M HNO_3 and finally, Pu eluted with 0.35 M HNO_3 and evaporated to near dryness (Jakopic et al., 2010a). The residue was re-dissolved in 1 M HNO_3 and was loaded onto a pre-degassed zone-refined rhenium double filaments for isotopic measurement on Triton (Thermo Fisher Scientific, Bremen, Germany) TIMS multi-collector instrument. The isotopic measurements were performed in the total evaporation (TE) mode (Richter and Goldberg, 2003). The isotopic reference material IRMM-290/A3 was selected as a comparator to correct the measured isotopic ratios for mass fractionation effects.

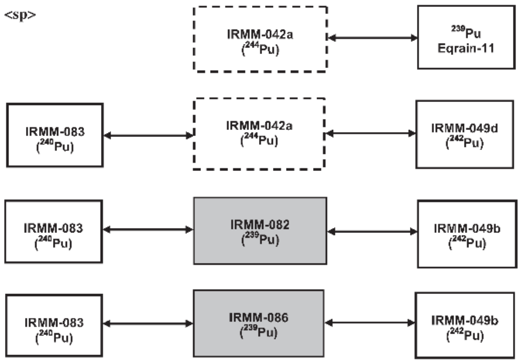


Fig. 1. Inter-calibration scheme of IRMM Pu spike CRMs and Eqrain-11.

2.2. Chemical treatment of NBS 946 for "age" determination measurements

NBS-946 ($PuSO_4{\cdot}4H_2O$) is a fuel grade material with an isotopic composition of 0.19% ^{238}Pu, 86.08% ^{239}Pu, 12.51% ^{240}Pu, 0.64% ^{241}Pu and 0.58% ^{242}Pu (2010). The sample solution was prepared by dissolving the plutonium sulphate in concentrated nitric acid while careful heating on a hot plate inside a glove box. The final sample solution was prepared in 5 M HNO_3.

Aliquots of this sample solution were spiked with ^{233}U spike (IRMM-3630) and ^{242}Pu spike (IRMM-049c), respectively, for the amount content determination of uranium and plutonium by isotope dilution mass spectrometry (IDMS). In addition, an aliquot of the un-spiked sample solution was also analysed by TIMS for the determination of the Pu isotopic composition. No additional measurements for the U isotopic abundance were required because ^{233}U is originating only from the IRMM-3630 spike and is not present in the sample.

The above-mentioned sample aliquots were chemically purified on anion exchange and extraction chromatographic columns (UTEVA) prior to isotope ratio measurements on the Triton TIMS (Richter and Goldberg, 2003). The procedure for the uranium separation is shown in Fig. 2. For the separation and purification of plutonium, anion exchange columns of the same type as mentioned above (Section 2.1) were used.

3. Results and discussion

3.1. Pu inter-calibration

The Pu amount content in IRMM-086 was determined by IDMS using two different spikes, IRMM-049b (^{242}Pu spike) and IRMM-083 (^{240}Pu spike). The certified values of both spike CRMs were previously verified by IDMS using the large-sized dried (LSD)

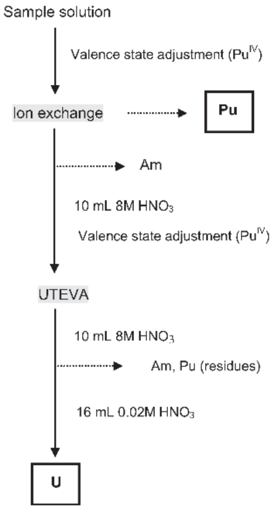


Fig. 2. The chemical separation of U and Pu for NBS-946 material.

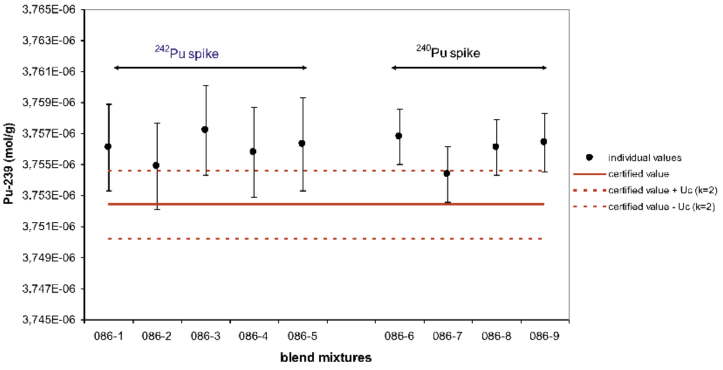


Fig. 3. Amount concentration of ^{239}Pu in IRMM-086 compared with the measured values by IDMS (with expanded uncertainties, $k = 2$).

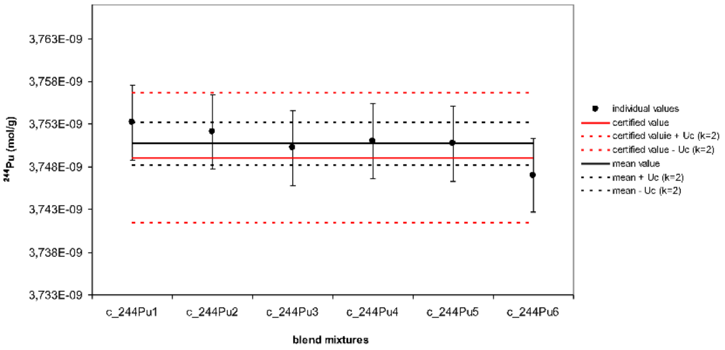


Fig. 4. Amount concentration of ^{244}Pu in IRMM-042a compared with the measured values by IDMS (with expanded uncertainties, $k = 2$).

spikes, IRMM-1027m and ^{239}Pu IRMM-081a (Jakopic et al., 2010a). The IRMM 1027 LSD spikes are a fundamental part of the fissile material control of irradiated nuclear fuel. They are prepared and certified by metrological weighing of uranium and plutonium metals, and have certified values that are traceable to the SI in the shortest possible way (Verbruggen et al., 2009). The results for the verification measurements of IRMM-086 are presented in Fig. 3. The solid red line represents the certified value of IRMM-086, the dotted red line is the expanded uncertainty of the certified value, and the circles show the measurement results with respective expanded uncertainties for blends prepared with IRMM-049b and IRMM-083. The Pu amount content and its uncertainties were calculated according to ISO GUM (International Organization for Standardization, 2008). It can be seen from Fig. 3 that the results agree with the certified value within uncertainties. Nevertheless, a small positive 'bias' of about 0.1% from the certified value was observed.

The Pu amount content in IRMM-042a was determined by IDMS using IRMM-049d. The solid red line represents the certified value of IRMM-042a, the dotted red line the expanded uncertainty of the certified value and the circles show the measurement results with respective expanded uncertainties for blends prepared with IRMM-049d. The mean value is shown with solid black line together with expanded uncertainty with dotted black line. From Fig. 4 it can be seen that the certified value from 1986 for IRMM-042a was confirmed in this inter-calibration exercise within a considerable smaller uncertainty.

3.2. *Pu age determination of NBS 946*

The results for the "age" determination of NBS 946 for three different clocks, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U are shown in Table 1 (Jakopic et al., 2011). A good agreement between different "clocks" has been achieved for the NBS 946 material. The estimated separation time for NBS 946 of May 1970 seems to be a good fit taking into consideration that the first certificate for this reference material has been issued on March 12, 1971. Taking into account the time for the characterization and certification until the issuing of the certificate, a separation around May 1970 appears to be realistic.

This result proves that it is feasible to develop and characterize a Pu CRM for 'age dating' based on metrological concepts. IRMM is currently characterizing a set of Pu materials with a relative abundance of ^{240}Pu ranging for "age" from reactor- to fuel- to weapon-grade. In parallel, IRMM is currently producing in co-

Table 1
The age of NBS SRM 946 calculated for October 17, 2010 for the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U clocks with expanded uncertainties ($k = 2$).

"Clock"	Age [a]	Expanded uncertainty ($k = 2$) [a]	Calculated separation date
^{238}Pu/^{234}U	40.35	0.13	May 1970
^{239}Pu/^{235}U	40.43	0.12	
^{240}Pu/^{236}U	40.48	0.11	

<sp>

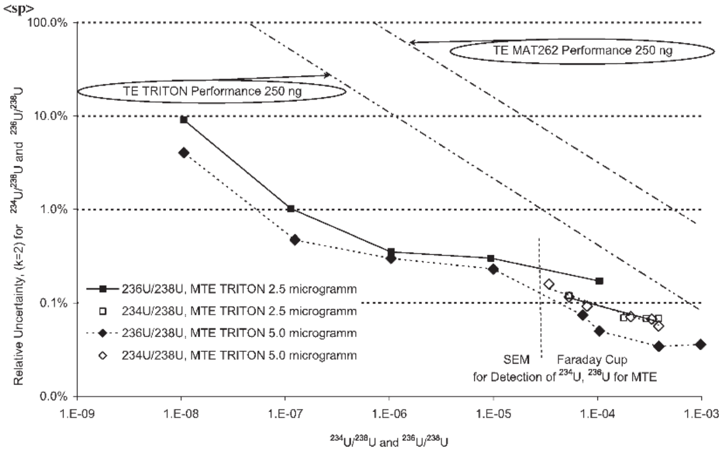


Fig. 5. Relative uncertainties, expressed with a coverage factor $k = 2$, for MTE measurements of minor ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ for two different sample loadings (2.5 mg and 5 mg), using a SEM or a Faraday detector for ^{236}U using Triton TIMS (Richter et al., 2011).

Table 2
Plutonium isotope ratios measured by TIMS in IAEA 135 and IAEA 368.

Sample	Method	Isotope amount ratio (March 2009)		
		$n(^{240}Pu)/n(^{239}Pu)$	$n(^{241}Pu)/n(^{239}Pu)$	$n(^{242}Pu)/n(^{239}Pu)$
IAEA 135	TIMS (SM)	0.2128 ± 0.0010	0.00793 ± 0.00099	0.0081 ± 0.0010
	TIMS (MD)	0.2129 ± 0.0005	0.00751 ± 0.00004	0.00713 ± 0.00004
IAEA 368	TIMS (SM)	0.0347 ± 0.0003	0.00058 ± 0.00053	0.00086 ± 0.00056
	TIMS (MD)	0.0342 ± 0.0001	0.00021 ± 0.00003	0.00033 ± 0.00009

operation with ITU one plutonium and one uranium material certified for separation date and confirmed completeness of separation (“clock” set to zero).

3.3. *Reference measurements using TIMS in combination with MIC and filament carburization for environmental and nuclear samples*

The performance of the modified total evaporation (MTE) technique for the minor uranium isotope ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ is shown in Fig. 5. All ratios below about 3×10^{-5} are measured using the Secondary Electron Multiplier (SEM) detector; all ratios above this limit were measured using Faraday cups only. Fig. 5 shows the expanded uncertainties with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95%. Starting from the lowest value of the $n(^{236}U)/n(^{238}U)$ ratio, the relative uncertainties decrease with increasing ratio as expected from counting statistics considerations. For $n(^{236}U)/n(^{238}U)$ ratios ranging between 10^{-6} and 10^{-5}, the uncertainties are found to be relatively constant at a level of about 0.3%, which is ascribable to the constant uncertainty contributions stemming from the SEM related corrections like non-linearity correction. Above a ratio of 10^{-5}, the relative uncertainties decrease again until the ratio of 10^{-3} is reached where the major uncertainty component becomes the uncertainty associated with the mass fractionation correction using the major isotope ratio $n(^{235}U)/n(^{238}U)$. Fig. 5 also shows calculated regression lines for the observed uncertainties in “classical” total evaporation (TE) measurements performed on a Triton (250 ng sample loading) and a MAT 262 TIMS instruments (the predecessor instrument, 250 ng sample loading) at IAEA-SGAS. These TE measurements were performed without ion counting or including peak tailing corrections, therefore the uncertainties are considerably larger compared to those obtained using the MTE Triton method even if considering the difference in sample size (Richter et al., 2011).

For Pu isotope ratio measurements in environmental samples using the MIC system, the MTE method was successfully combined with a multi-dynamic (MD) measurement procedure, in this case for the purpose of eliminating significant drift of the ion counter efficiencies. Within the same measurement runs, the uncertainties for the major ratio $n(^{240}Pu)/n(^{239}Pu)$ were significantly improved compared to literature values by using the TE principle. The results for two reference materials IAEA 135 and IAEA 368 for the $n(^{240}Pu)/n(^{239}Pu)$, $n(^{241}Pu)/n(^{239}Pu)$ and $n(^{242}Pu)/n(^{239}Pu)$ for multi-dynamic (MD) and static mode (SM) are shown in Table 2 (Jakopic et al., 2010b).

4. Conclusions

The European Commission is committed to accelerate, simplify, and modernise standardization procedures in line with the European Council Conclusions of the 4th of February 2011. IRMM quality control tools are contributing to this standardisation process and to the technical convergence of nuclear safeguards, nuclear forensics and nuclear security. Material standards, reference measurements, performance criteria and conformity assessment are indispensible tools towards reliable and comparable measurements results in fissile material and environmental sample analysis. In particular, efforts are made by IRMM in the further development of reference materials and methods for safeguards verification, detection of undeclared activities and nuclear forensics. The recent IRMM Pu

CRMs inter-calibration-campaigns, the development of new CRMs and the launch of inter-laboratory comparisons (e.g. REIMEP-17, NUSIMEP-8) for measurements of uranium and plutonium amount content and isotopic abundances in fissile material and environmental samples, are meeting the needs of EURATOM and international safeguards authorities, industry and the measurement community. All these achievements in identifying the needs and priorities for quality control tools in proliferation resistance, nuclear material and environmental sample analysis are very much based on the continuous exchange between safeguards authorities, reference material producers, industry, expert laboratories and data evaluators via the respective platforms of ESARDA, INMM and IAEA.

References

International Atomic Energy Agency, 2010. International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials. IAEA-STR-368.

International Atomic Energy Agency, 1997. Model Protocol Additional to the Agreement(s) between State(s) and the International Atomic Energy Agency for the Application of the Safeguards. INFCIRC 540 (corrected).

International Organization for Standardization, 2008. ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement.

Jakopic, R., Bauwens, J., Richter, S., Sturm, M., Verbruggen, A., Wellum, R., Eykens, R., Kehoe, F., Kühn, H., Aregbe, Y., 2011. Preparation and development of new Pu spike isotopic reference materials at IRMM. ESARDA Bull. 46, 65–71.

Jakopic, R., Verbruggen, A., Eykens, R., Kehoe, F., Kühn, H., Kushigeta, Y., Jacobsson, U., Bauwens, J., Richter, S., Wellum, R., Aregbe, Y., 2010a. An inter-calibration campaign using various selected Pu spike isotopic reference materials. J. Radioanal. Nucl. Chem. 286, 449–454.

Jakopic, R., Richter, S., Kühn, H., Aregbe, Y., 2010b. Determination of ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotope ratios in environmental reference materials and samples from Chernobyl by thermal ionisation mass spectrometry (TIMS) and filament carburization. J. Anal. At. Spectrom. 25, 815–821.

Jakopic, R., Richter, S., Kühn, H., Benedik, L., Pihlar, B., Aregbe, Y., 2009. Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with "multiple ion counting" and filament carburization. Int. J. Mass. Spectrom. 279, 87–92.

Kraiem, M., Richter, S., Kühn, H., Aregbe, Y., 2011a. Development of an improved method to perform single particle analysis by TIMS for nuclear safeguards. Anal. Chim. Acta 688, 1–7.

Kraiem, M., Richter, S., Kühn, H., Stefaniak, E.A., Kerkhove, G., Truyens, J., Aregbe, Y., 2011b. Investigation of uranium isotopic signatures in real-life particles from nuclear facility by thermal ionisation mass spectrometry. Anal. Chem. 83, 3011–3016.

Richter, S., Kühn, H., Aregbe, Y., Hedberg, M., Horta-Domenech, J., Mayer, K., Zuleger, E., Bürger, S., Boulyga, S., Köpf, A., Poths, J., Mathew, K., 2011. Improvements in routine uranium ratio measurements using the modified total evaporation method for multi-collector thermal ionisation mass spectrometry. J. Anal. At. Spectrom. 26, 550–564.

Richter, S., Goldberg, S.A., 2003. Improved techniques for high accuracy isotope ratio measurements of nuclear material using thermal ionisation mass spectrometry. Int. J. Mass. Spectrom. 229, 181–197.

Sturm, M., 2010. Destructive analysis: Effective analytical Support to nuclear safeguards and non-proliferation. ESARDA Bull. 45, 56–65.

Truyens, J., Stefaniak, E.A., Mialle, S., Aregbe, Y., 2011. NUSIMEP-7: Uranium Isotope Ratios in Uranium Particles. EUR 25179 EN.

Verbruggen, A., Bauwens, J., Eykens, R., Jacobsson, U., Jakopic, R., Kehoe, F., Kühn, H., Kushigeta, Y., Richter, S., Aregbe, Y., 2009. Preparation and Certification of IRMM-1027m; Large-sized Dried (LSD) Spike. EUR 24119 EN.

Wallenius, M., Mayer, K., 2000. Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry. Fresen. J. Anal. Chem. 366, 234–238.

Wallenius, M., Mayer, K., Ray, I., 2006. Nuclear forensic investigations: two case studies. Forensic. Sci. Int. 156, 55–62.

2.4 Publication IV

ESARDA BULLETIN, No. 46, December 2011

Preparation and development of new Pu spike isotopic reference materials at IRMM

Rožle Jakopič, Jeroen Bauwens, Stephan Richter, Monika Sturm, Andre Verbruggen, Roger Wellum, Roger Eykens, Frances Kehoe, Heinz Kühn and Yetunde Aregbe
Institute for Reference Materials and Measurements (IRMM)
Joint Research Centre, European Commission
Retieseweg 111, B-2440 Geel, Belgium
E-mail: rozle.jakopic@ec.europa.eu

Abstract

Reliable isotope measurements of nuclear material and the availability of reference materials with small uncertainties in the certified values are of great importance for safeguarding of nuclear materials. They provide the basis for a credible measurement system in the verification of states declarations of their nuclear activities. Worldwide needs for continued and improved Isotopic Reference Materials (IRM) are the main reason for developments of new nuclear reference materials at IRMM. Measurement capabilities of laboratories have evolved considerably over the years, along with progress in modern analytical techniques. Some plutonium reference materials, however, have been on the market for decades and they need to be re-certified to smaller uncertainties. Moreover, new reference materials with appropriately small uncertainties in the certified values need to be made available enabling measurement laboratories to reduce their combined measurement uncertainties. Such high quality plutonium isotopic reference materials are essential for laboratories striving to meet the International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials (ITVs).

The preparation and the certification of such materials are demanding and challenging tasks that require state-of-the-art measurement procedures and equipment. The Institute for Reference Materials and Measurements (IRMM) has repeatedly demonstrated its capabilities in plutonium analysis and represents one of the few institutes that supplies plutonium IRMs worldwide. An inter-calibration campaign has been set up at IRMM inter-linking selected plutonium spike IRMs. In the scope of this compatibility study, new reference materials have been prepared for Isotope Dilution Mass Spectrometry (IDMS) in nuclear fuel cycle measurements.

A new series of large-sized dried (LSD) spikes, IRMM-1027n, has been prepared and certified for plutonium and uranium amount content and isotopic composition. These mixed spikes are applied to measure the uranium and plutonium content of dissolved fuel solutions using IDMS. They are prepared by IRMM to fulfil the existing requirements for reliable spike IRMs in fissile material control from European Safeguards authorities and customers from industry.

IRMM-046b, a mixed uranium-plutonium spike IRM of highly enriched ^{233}U and ^{242}Pu that dates from 1995, was re-certified for isotope amount content and isotopic composition, each with considerably smaller combined uncertainties. IRMM-046c, a new mixed uranium-plutonium spike, and IRMM-049d, a highly enriched ^{242}Pu spike, have been prepared. IRMM-049d was prepared from the same stock solution as its predecessor IRMM-049c, dating from 1996, but the new ^{242}Pu spike has certified values with smaller combined uncertainties. The traceability of the certified values to the SI is established through an unbroken chain of comparisons, all having stated uncertainties.

IRMM is also co-operating with the Institute for Transuranium Elements (EC-JRC-ITU) in a feasibility study on the development of Pu reference materials for "age dating" in nuclear forensics. In the course of this work, the reference materials NBS SRM 946, 947 and 948 (NBL CRM 136, 137 and 138) will be investigated among others.

Keywords: plutonium; spike isotopic reference materials; IDMS, traceability.

1. Introduction

Confidence in comparability and reliability of measurement results in nuclear material analysis is established via reference materials, reference measurements and inter-laboratory comparisons. They provide the basis for a strong verification system to safeguard nuclear activities in line with the Treaty on the Non-Proliferation of Nuclear Weapons (NPT) and the Euratom Treaty, including the respective implementing regulations, such as the Comprehensive Safeguards Agreements (INFCIRC 153, corrected) [1], the Additional Protocol (INFCIRC 540) [2] or the European Commission's Regulation on the application of Euratom Safeguards (No 302/2005).

The Institute for Reference Materials and Measurements (IRMM) is one of the leading institutes worldwide that develops and certifies nuclear reference materials to fulfil the existing requirements for reliable certified reference materials (CRMs) in fissile material accountancy. Worldwide needs and advancements in analytical techniques over the last decade have led to more stringent requirements for laboratory performance in nuclear material accountancy.

The International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials (ITVs) are "uncertainties to be considered in judging the reliability of analytical techniques applied to industrial nuclear and fissile material that are subject to safeguards' verification" [3]. The IAEA took over the concept of ITVs in the early 1990's from the ESARDA Working Group on Standards and Techniques for Destructive Analysis (WGDA). During 2010, the ITVs were revisited by the IAEA, ESARDA, INMM and other expert groups and published as ITV2010 in November 2010. They are intended to be used by plant operators and safeguards organizations, as a reference of the quality of state-of-practice measurements achievable in nuclear material accountancy.

Some nuclear CRMs were approaching exhaustion; therefore a programme has been set up at IRMM to replace these materials. Two new nuclear materials, IRMM-046c and IRMM-049d, used in nuclear material analysis by IDMS, have been prepared. The certification of these new CRMs was part of an IRMM compatibility study inter-linking various plutonium spike CRMs on a metrological basis, applying state-of-the art measurement procedures [4]. Furthermore, IRMM prepares and certifies on a regular basis IRMM-1027 large-sized dried (LSD) spikes which are applied for the analysis of spent fuel solution at reprocessing plants.

IRMM is also engaged in a feasibility study for the development of plutonium reference materials for age dating, to be used for method validation purposes in nuclear forensics applications. The "age" of a nuclear material is defined as the time that has passed since the last chemical separation of the mother and daughter isotopes. Different "clocks" (pairs of mother and daughter radionuclides) can be used for the determination of the unknown age of a material. In the case of plutonium, the isotope pairs ^{241}Pu/^{241}Am, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U, and, possibly, 242Pu/238U can be used as "clocks". Some preliminary results for NBS SRM 946 will be presented here.

2. Need for new nuclear CRMs

The accurate verification of the plutonium and uranium amount contents in nuclear materials requires the continuous supply of well certified spike IRMs. The worldwide demands for certified spike materials have evolved considerably over the years, leading to the development of new plutonium and uranium reference materials with smaller uncertainties in the certified values.

A new certificate for IRMM-046b, a mixed uranium-plutonium spike of highly enriched ^{233}U and ^{242}Pu, was issued in 2010 for isotope amount content and isotopic composition, each with considerably smaller combined uncertainties than in the previous certificate from 1995. In addition, to guarantee future provision of these valuable spike materials to the nuclear measurement community, IRMM-049d, a highly enriched ^{242}Pu spike, has been prepared and certified by IDMS and another mixed uranium-plutonium spike, IRMM-046c, is currently in preparation. For the measurement of plutonium, the isotope ^{242}Pu is valuable as a spike because this isotope is usually found only as a minor component of plutonium in the nuclear fuel cycle.

The isotopic reference material IRMM-1027 series have been used for the measurement of Pu and U amount content in dissolved fuel solution for some 20 years. They are designed for fissile material accountancy by Euratom Safeguards authorities at on-site laboratories at La Hague and Sellafield. A new set of IRMM-1027 LSD spikes, containing about 50 mg of uranium and about 1.8 mg of plutonium, was prepared and certified for plutonium and uranium amount content and isotopic abundance. The amount content of the spikes is such that no dilution of a typical sample of dissolved fuel from a reprocessing facility is needed before the measurement by IDMS. The preparation and the certification of the new batch, IRMM-1027n, are discussed in more detail in the certification report [5].

3. Experimental

3.1. Preparation of IRMM-1027n

High purity metals were chosen as starting materials for the IRMM-1027 LSD series. Plutonium MP2 metal (98 % ^{239}Pu) from Cetama, natural uranium (EC NRM 101) and highly enriched ^{235}U metal (NBL CRM-116) were dissolved in concentrated nitric acid in a 3 L long-necked borosilicate flask.

Approximately 1200 units were dispensed into penicillin vials using a validated automated system. The solution in each vial was dried down and then covered with a light layer of an organic polymer, cellulose acetate butyrate (CAB), as stabiliser during storage and transport [5, 6].

3.2. Preparation of IRMM-049d and IRMM-046c

For the preparation of the IRMM-049d spike reference material, a stock solution was made by dissolving $_{242}$Pu metal in 5 mol·L^{-1} nitric acid. This stock solution was purified from the daughter products and other impurities by anion exchange. The eluted Pu fraction was evaporated to dryness and dissolved in 5 mol·L^{-1} nitric acid to obtain a 10 mg Pu per g solution. From that purified Pu solution, a fraction was taken and diluted with 5 mol·L^{-1} nitric acid to obtain the final concentration of ^{242}Pu of 0.1 mg Pu per g solution.

For preparation of the mixed plutonium-uranium IRMM-046c spike, ^{233}U metal was dissolved in 8 mol·L^{-1} nitric acid and purified by anion exchange. The uranium fraction was eluted with 8 mol·L^{-1} nitric acid and evaporated to dryness. A fraction of a 10 mg Pu per g solution, already used for the preparation of IRMM-049d, was added to uranium and diluted with 8 mol·L^{-1} nitric acid. The final concentration of ^{242}Pu was 0.1 mg Pu per g solution and of ^{233}U 1 mg per g solution.

Different steps of the preparation of IRMM-049d and IRMM-046c isotopic reference materials are shown in Figure 1.

3.3. Isotope measurements by Thermal Ionisation Mass Spectrometry (TIMS)

Isotope Dilution Mass Spectrometry (IDMS) was applied for the measurements of the plutonium and uranium amount contents. This is a reliable analytical technique and widely used in nuclear safeguards, especially when high quality results with small measurement uncertainties are needed.

Prior to mass spectrometry, a chemical procedure using anion exchange was applied [4]. The purified fractions of uranium and plutonium were prepared in 1 mol·L^{-1} nitric acid and loaded on a Re filament. The isotopic ratios of uranium and plutonium were measured on a Triton TIMS (Thermo Fischer Scientific) using the total evaporation technique [7, 8]. With the total evaporation technique, the measurement is continued until the sample is exhausted. This is done in order to minimize mass fractionation effects. The mass spectrometers were calibrated for mass fractionation by measuring IRMM-074/10 uranium and IRMM-290A/3 plutonium isotopic reference materials.

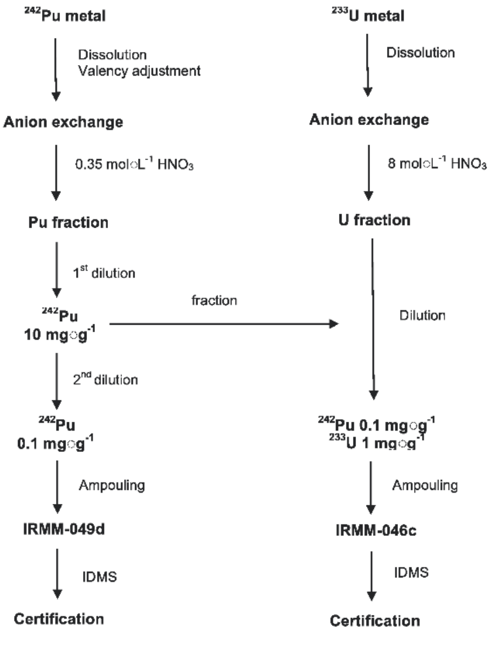


Figure 1: The flowchart for the preparation of IRMM-049d and IRMM-046c.

4. Results and Discussion

4.1. IRMM-1027n

The certification of the 1027 LSD series is done by gravimetry. This allows the isotopic contents of the LSD spike to be certified based on the certificates of the metals (chemical purity and isotopic abundance), the masses of the metals and the solution. As a result the certified values of the uranium and plutonium isotopic contents have small uncertainties. In addition, the certified values of amount contents and isotopic composition are verified by IDMS. With this approach, IRMM provides high-quality isotopic reference materials to the nuclear measurement community applying two independent "primary" methods for certification and verification, underpinning the confidence in the certified values.

The U amount content of 1027n was therefore certified based on the values from mass metrology of the validated automated system. From the eleven measurements used to assess the homogeneity of the whole series (1200 units), four were selected at random to verify the U amount content by IDMS [5]. The results of the verification measurements are shown in Figure 2. The IDMS measurement results agreed well with the values for uranium amount content calculated from the amounts of dissolved metals and solution.

The situation was different in the case of plutonium. After applying the same procedure during preparation of the stock solution as in previous batches of the IRMM-1027 series it was found that the Pu metal did not dissolve completely. A fine white deposit was observed, even after several weeks of a continuous dissolution process. Taking into account the limited supply of plutonium metal and that IRMM has a long record of demonstrated measurement capabilities in plutonium analysis; it was decided not to discard the batch solution. The uranium metals were added to the solution and after homogenisation, filtered through a separation column [4]. Due to this incomplete dissolution of the MP2 Pu metal a deviation of about -1.2 % from the gravimetric value for the Pu amount content was observed. It was decided to certify the plutonium amount content by IDMS applying Thermal Ionisation Mass Spectrometry. IDMS can be regarded in this case as a "primary" measurement method, which has proven to provide accurate results for previous batches of the IRMM-1027 series. The recently certified uranium-plutonium IRMM-046b CRM was used as a spike for the IDMS, linking the certification for Pu amount content of IRMM-1027n to the IRMM compatibility study on selected Pu spikes [4]. The certified value for the ^{239}Pu amount content was calculated as the mean value of the certification measurements and is 2.791 3 (12) 10^{-6} mol·g^{-1} [5]. The results for the plutonium amount content are also traceable to the SI via MP2 but with two additional steps in the traceability chain

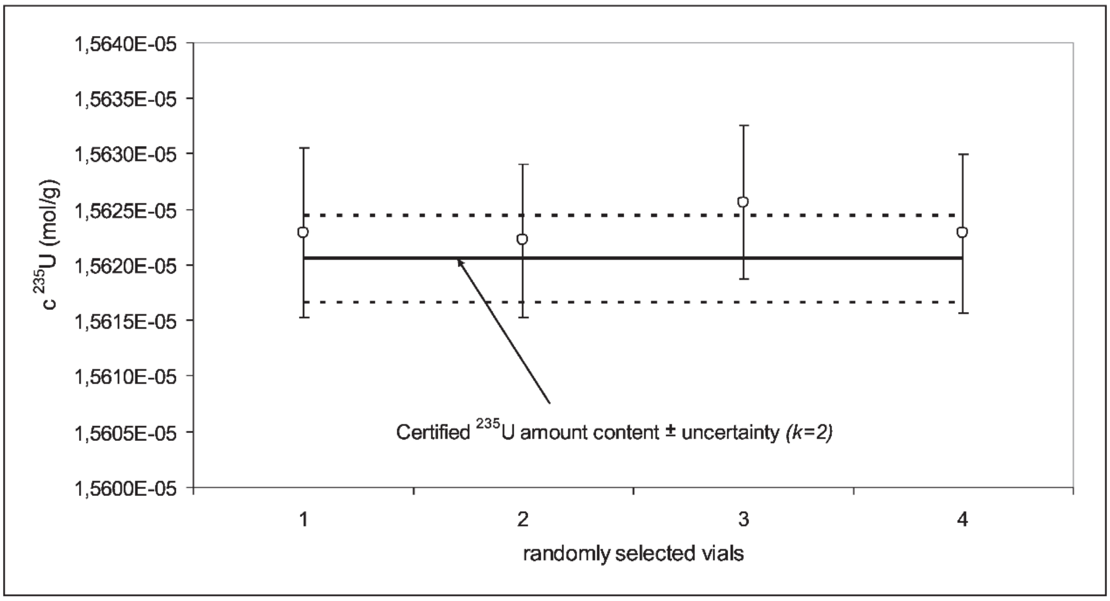


Figure 2: Amount content of ^{235}U in IRMM-1027n (from the masses of metals and solution) compared with the measured values by IDMS (with expanded uncertainties, *k=2*).

IRMM-1027n – via IRMM-046b – via IRMM-1027m (and verified by Eqrain-11) – via MP2 to SI [4]. The Pu amount content in IRMM-1027m was certified by gravimetry via MP2. IRMM-1027m was then used for the re-certification of the IRMM-046b spike reference material by IDMS. Finally, IRMM-1027n was certified by IDMS via the newly certified IRMM-046b. In addition, IRMM-046b was also successfully used as spike reference material for the determination of the plutonium amount content of the external quality control Eqrain-11 certified test sample. In the framework of the ongoing support task EC A 1806, *Verification of mixed U-Pu Spikes,* between IRMM, IAEA and ITU additional verification measurements of IRMM-1027n will be available in the near future.

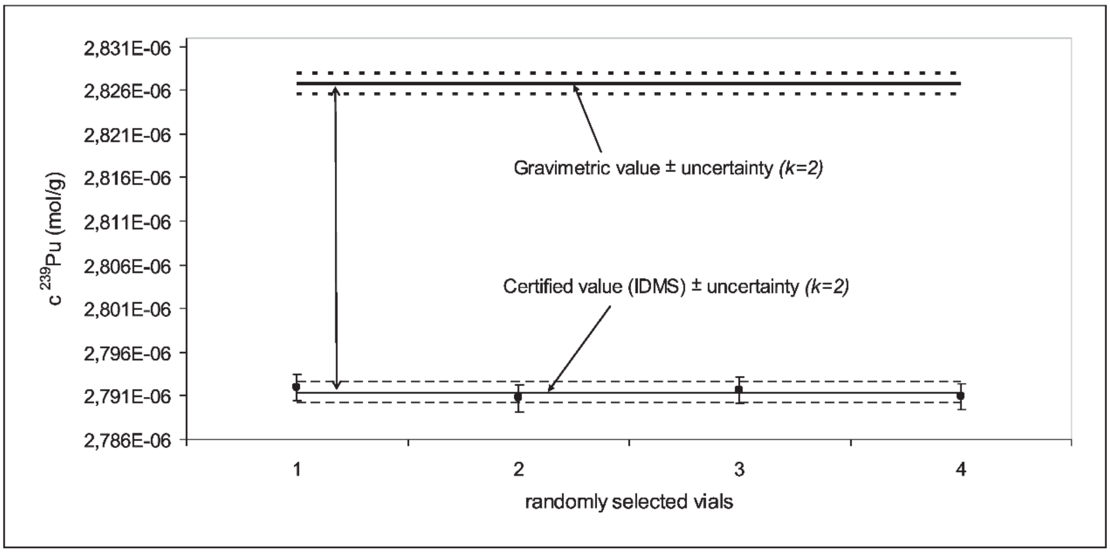


Figure 3: Amount content of ^{239}Pu in IRMM-1027n (from the masses of metals and solution) compared with the measured values by IDMS (with expanded uncertainties, *k=2*).

The individual IDMS results together with the certified value are shown in Figure 3.

4.2. IRMM-049d, IRMM-046b and IRMM-046c

IRMM produces and maintains solutions of enriched uranium and plutonium isotopes designed for mass-spectrometric isotope dilution measurements of nuclear materials. They are part of a systematic IRMM programme to supply various nuclear reference materials at different concentrations.

To replace exhausted stocks of CRMs used for isotope dilution mass spectrometry, IRMM prepared and certified IRMM-046c, a new mixed uranium-plutonium spike, and IRMM-049d, a highly enriched ^{242}Pu spike. Both of these new Pu CRMs have a similar certified value as its predecessor, but with considerably smaller combined uncertainties. Advancements and development of state-of-the-art mass spectrometric techniques and instrumentation over the years resulted in a reduction in measurement uncertainty by a factor of 3 or more. Table 1 illustrates this achievement, comparing the relative expanded uncertainties of various IRMM CRMs.

		Rel Uc *(k=2)* in %	
	Year of certification	**^{242}Pu**	**^{233}U**
old IRMM-046b	1995	0.15	0.15
recertified IRMM-046b	2010	0.039	0.021
IRMM-046c (indicative values)	2011 ongoing		
IRMM-049 (exhausted)	1989	0.15	
IRMM-049c	1996	0.13	
IRMM-049b	1998	0.067	
IRMM-049d	2011	0.049	

Table 1: Relative expanded uncertainties of selected spike isotopic reference materials.

4.3 External plutonium inter-laboratory comparison programme Eqrain-11

Eqrain is the inter-laboratory comparison programme organised at regular intervals for the analysis of uranium and plutonium by CETAMA (Commission d'ETAblissement des Méthodes d'Analyse du CEA). The certified test samples of Eqrain-11 consisted of three plutonium nitrate solutions (M29, M57 and M107) with undisclosed values for Pu amount content.

IRMM linked the participation in Eqrain-11 to an inter-calibration campaign by determining the plutonium isotope content, applying IDMS using various selected spikes, and to the certification of IRMM-046b, IRMM-046c and IRMM-049d. The aim of the campaign was to check the quality of various selected spikes and to demonstrate IRMM`s measurement capabilities for plutonium measurement via external quality tools. The results reported by IRMM were in excellent agreement with the reference value provided by CETAMA [4]. Eqrain-11 is still ongoing; therefore the plutonium amount content and the reference values are not disclosed in this paper. As an example, the IDMS measurement results for sample M107, normalised to the Eqrain-11 reference value, are shown in Figure 4.

4.4. Preliminary results of NBS SRN-946 for "age" dating

To resolve the current lack of nuclear reference materials certified for their separation date needed in nuclear forensics, several plutonium materials with different isotopic compositions and production dates are being characterized at IRMM in the course of a feasibility study for reference materials for nuclear age dating. The results for three of the plutonium-uranium "clocks" for NBS SRM 946 – a plutonium reference material certified for isotopic composition – are shown in Figure 5. These measurements were performed by TIMS applying IDMS. The ages derived from these three different mother-daughter isotope systems (^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U) do not differ significantly from each other.

5. Conclusions

The prime objective of the IRMM is to build confidence in the comparability of measurements by the production and dissemination of internationally accepted quality assurance tools, including high-quality certified reference materials. A new series of LSD spikes for IDMS determinations of uranium and plutonium content in solutions of spent nuclear fuel from reprocessing plants has been prepared. The uranium content was certified based on gravimetry and successfully verified by IDMS on individual vials. Plutonium was certified by IDMS via a recently recertified IRMM-046b spike reference material.

New isotopic reference materials IRMM-046b and IRMM-046c, mixed uranium-plutonium, and IRMM049d, highly enriched in ^{242}Pu, were prepared and certified for amount content by IDMS. These materials were prepared in the framework of IRMM`s programme to supply various spike isotopic reference materials at different concentrations to the nuclear safeguards and nuclear material measurement community.

Furthermore, IRMM has successfully demonstrated Pu measurement capabilities via external quality tools by par-

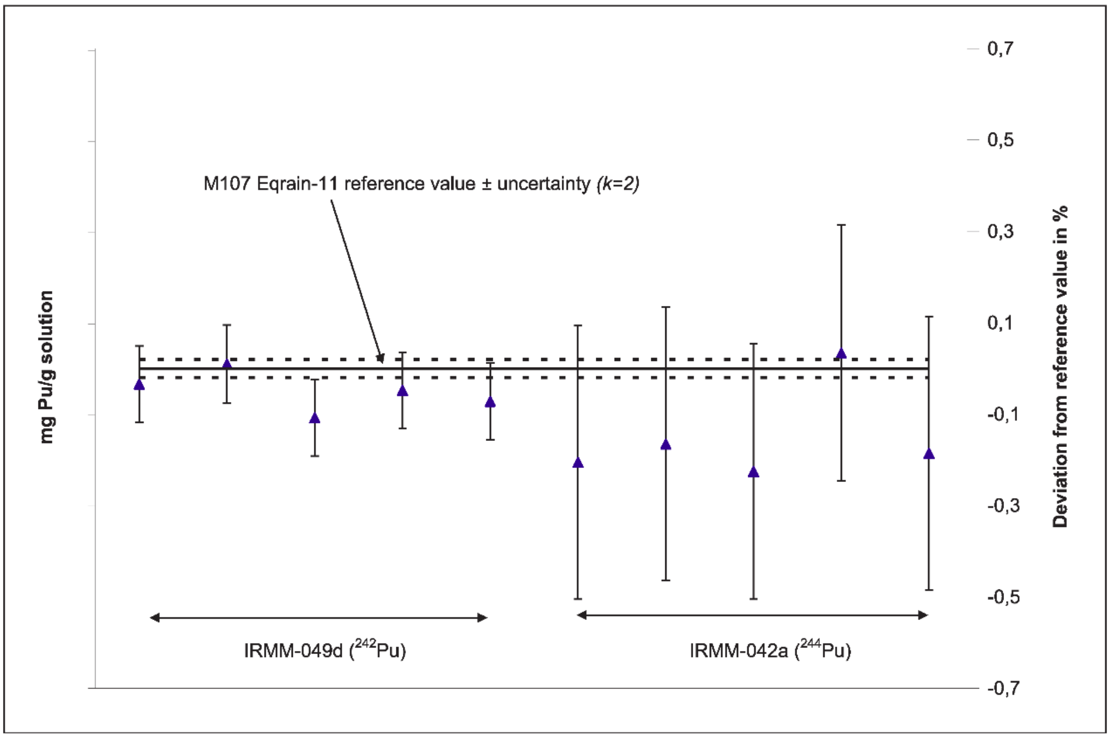


Figure 4: Normalised amount content of ^{239}Pu in Eqrain-11 M107 sample compared with the measured values by IDMS (with expanded uncertainties, *k=2*).

ticipation in Eqrain-11, applying IDMS and using various selected Pu spike reference materials. With the development of new plutonium spike isotopic reference materials, IRMM significantly contributes to the availability of these materials in the future. IRMM is regularly exchanging views with the customers and users of Pu reference materials on further needs and developments, using fora such as ESARDA Working Group on Standards and Techniques for Destructive Analysis (WGDA).

References

[1] The structure and content of agreements between the agency and states required in connection with the Treaty on non-proliferation of nuclear weapons, INFCIRC 153 (corrected), Vienna, June 1972.

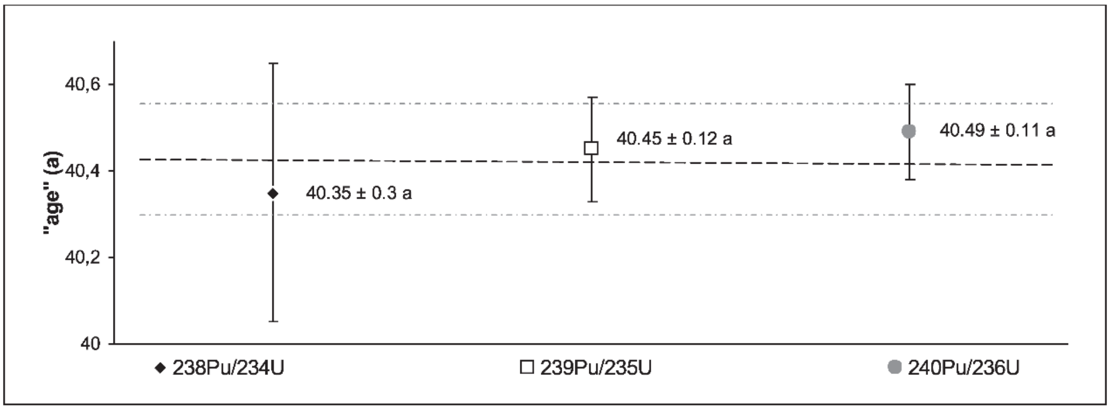


Figure 5: Age in years of NBS SRM 946 (calculated for 17 October 2010) for the "clocks" ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U with expanded uncertainties *(k=2)*.

[2] Model protocol additional to the agreement(s) between state(s) and the International Atomic Energy Agency for the application of Safeguards, INFCIRC 540 (corrected), Vienna, September 1997.

[3] International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials, IAEA-STR-368, Vienna, November 2010.

[4] Jakopič, R., Verbruggen, A., Eykens, R., Kehoe, F.; Kühn, H., Kushigeta ,Y., Jacobsson, U., Bauwens, J., Richter, S., Wellum, R., Aregbe, Y., An inter-calibration campaign using various selected Pu spike isotopic reference materials*; J. Radioanal. Nucl. Chem.; 286;* 2010; p 449-454.

[5] Jakopicˇ, R., Bauwens, J., Drooghmans, T., Eykens, R., Jacobsson, U., Kehoe, F., Kühn, H., Kushigeta, Y., Richter, S., Verbruggen, A., Wellum, R., Aregbe, Y.; Preparation and Certification of IRMM-1027n, Large-Sized Dried (LSD) Spike; EUR EN.

[6] Verbruggen, A., Bauwens, J., Van de Steene, N., Jacobsson, U., Eykens, R., Wellum, R., Aregbe, Y.; An automated system for the preparation of Large Sized Dried (LSD) Spikes, ATALANTE Conference 2008, Montpellier (France), May 19-22, 2008.

[7] Richter, S., Goldberg, SA; Improved techniques for high accuracy isotope ratio measuremeof nuclear material using thermal ionisation mass spectrometry *; Int. J. Mass Spectrom.; 229;* 2003; p 181-197.

[8] Richter, S., Kühn, H., Aregbe, Y., Hedberg, M., Horta-Domenech, J., Mayer, K., Zuleger, E., Bürger, S.,Boulyga, S., Köpf, A., Poths, J., Mathew, K., Improvements in routine uranium ratio measurements using the modified total evaporation method for multi-collector thermal ionization mass spectrometry, *J. Anal. At. Spectrom.; 26;* 2011; p 550-564.

2.5 Publication V

ESARDA BULLETIN, No. 45, December 2010

Best student essay from the 6th ESARDA course on Nuclear Safeguards and Non Proliferation

Destructive Analysis: Effective Analytical Support to Nuclear Safeguards and Non-Proliferation

M. Sturm
European Commission, Joint Research Centre, IRMM, B-2440 Geel, Belgium
E-mail: monika.sturm@ec.europa.eu

Abstract

Nuclear safeguards are measures to verify that states comply with their international obligations (Non-Proliferation Treaty and Euratom Treaty) to refrain from using nuclear materials for the development of nuclear weapons, but using it solely in the peaceful civil nuclear fuel cycle...

Destructive Analyses (DA) of nuclear material and of environmental samples collected inside and in the vicinity of nuclear facilities are a key strategy among other complementary measures applied in nuclear material accountancy, control and verification. A great variety of analytical methods is used in order obtain the desired information from a given sample. The chosen method must be applicable to meet the requirements pre-defined by nuclear safeguards. Analytical methods for DA of bulk samples of nuclear material as well as for the assay of single particles found on swipe samples are presented in this paper. Furthermore the drawbacks and benefits of DA for nuclear safeguard purposes are discussed along with considerations concerning the choice of the appropriate analytical method, including the use of quality control tools.

Keywords: destructive analysis; nuclear material; safeguards; bulk sample; environmental sample.

1. Introduction

The main task of nuclear safeguards is the timely detection of a diversion of nuclear material from declared nuclear facilities, the timely detection of misuse of a declared nuclear plant for non-peaceful purposes, and the detection of undeclared nuclear materials and activities. Nuclear activities are proliferation sensitive if they can lead to weapon-usable material, namely plutonium and highly enriched uranium. Nuclear safeguards under comprehensive safeguards agreements (CSA) of the Non-Proliferation Treaty (NPT) cover, therefore, conversion, enrichment and fuel fabrication facilities as well as reactors, critical assemblies, spent fuel storage facilities and reprocessing plants. The Additional Protocol (AP) of the Non-Proliferation Treaty extends the safeguards coverage also to uranium ore mines, uranium ore concentration facilities and heavy water production. Nuclear facilities within the EU are safeguarded by the nuclear safeguard inspectors of both IAEA and Euratom. The IAEA inspectors operate according to the comprehensive safeguards agreements of the NPT while Euratom inspectors operate according to the Euratom Treaty. Euratom and IAEA inspectors cooperate, for instance, in the use of equipment, research and development and have joint team inspections. Nuclear plant designers must consider safeguards at an early design stage and make provisions that the facility can be effectively safeguarded. In addition to providing design and process flow information, the operator must keep complete and coherent accounting records and report any changes on the inventory i.e., for shipments, receipts, processing and storage. Inspectors verify operator's declarations via independent measurements applying destructive (DA) and non destructive (NDA) methods as well as by placing safeguards monitoring, surveillance and seals systems. A proper implemented inspection scheme needs to meet the three safeguards goals of “significant quantity”, “timeliness of detection” and “detection probability”. They determine the number of items to be verified. The common basis for safeguards system design under the NPT and the Euratom Treaty is to choose the number of items to be verified in such a way that the targeted probabilities for risk of ‘false alarm’ and ‘non detection’ of a diversion of a defined quantity of nuclear material within characteristic time are met: for example ensuring the detection of removal of 8 kg plutonium within one month with a detection probability of 95%. The three safeguards goals are defined in similar ways by both Euratom Treaty and NPT. Key materials such as spent fuel solutions, plutonium nitrate, plutonium oxide, uranylnitrate, uranium oxide, mixed (plutonium and uranium) oxide (MOX) and uranylhexafluoride are routinely sampled for destructive bulk analysis according to the nuclear inspection scheme.

Up to the early 90s only the declarations made by the operator of the nuclear facility could be verified for their correctness in compliance with the NPT. Assurance of the absence of undeclared nuclear material (completeness) was not part of the safeguards authorities’ mandate. Triggered by the discovery of the clandestine nuclear weapons programme of Iraq in 1991 and first appearances of the new phenomenon of illicit trafficking of nuclear material in the 1990s, the Additional Protocol of the NPT was approved by the IAEA’s Board of Governors in May 1997. It enabled among other improvements complementary access for IAEA inspectors to all installations of the nuclear fuel cycle including mines and concentration plants, as well as to related research and development facilities, even on short notice. Methods for remote sampling of gases to detect uranium enrichment and plutonium separation facilities are still under development while destructive analysis of environmental swipe samples is already part of the routine safeguards protocol. Particularly, data obtained by single particle analysis from swipe samples are a powerful safeguards tool providing information on history and origin of the nuclear material [1].

Destructive analysis (DA) is a key tool for safeguards in addition to surveillance, seals and non-destructive analysis (NDA). DA is defined as measurements introducing a significant change to the batch of material: The sample aliquot taken from the batch for measurement is subsequently not returned to the batch. DA is applied when accurate measurement results with small measurement uncertainties are required. The performance of the analytical methods applied has to provide analytical measurement results that meet the International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials [2]. Safeguards laboratories can be located and operated on-site or samples can be sent for analysis to qualified off-site laboratories. In the field of nuclear material and environmental destructive sample analysis safeguards authorities work with a network of analytical laboratories to check correctness and completeness of declarations. Physical verification measurements of fissile material are carried out at the on-site laboratories at the European reprocessing plants in La Hague (F) and Sellafield (UK). Furthermore DA is the strategy of choice for special samples in terms of isotope composition, sample matrix or concentration and for non-routine analysis such as nuclear forensic investigations.

2. Routine bulk samples

In order to check the correctness and completeness of the declarations made by the operator concerning the facility's material balance, representative aliquots of plutonium and/or uranium containing material are taken by the safeguards inspectors. These samples are called bulk samples. The quantitative content of plutonium and/or uranium as well as their isotopic composition (enrichment) is of safeguard's interest [3]. Some techniques such as K-edge densitometry (KED) and X-ray fluorescence (XRF) can be applied for destructive as well as in non-destructive analysis depending on whether the sample is returned to the batch after analysis or not [4].

2.1. Frequently applied DA techniques for elemental assay in bulk samples

2.1.1. Isotope Dilution Mass Spectrometry

Isotope dilution mass spectrometry (IDMS) is based on the addition of a known amount of a "spike" to a known amount of the dissolved sample. This "spike" is an enriched isotope solution; its addition to the sample solution leads to a change in the isotope ratio [5]. The isotope ratios in the spiked sample solution and the un-spiked sample solution are measured by mass spectrometry while the isotopic composition of the spike can be obtained form the reference material certificate [6]. In case of absence of the isotope used for spiking in the un-spiked sample a separate measurement of the un-spiked sample is not necessary [7]. The elemental concentration in the sample can be calculated using the known (weighed) amounts of sample and spike as well as the isotopic compositions mentioned above. ^{242}Pu, ^{244}Pu, ^{239}Pu, ^{240}Pu are often used as spikes for plutonium assays [5] while for IDMS measurements of Uranium mainly ^{233}U and to a smaller extend ^{235}U and ^{236}U are used as spikes [7]. The mass spectrometric method routinely used for the measurement of the isotope ratios is thermal ionization mass spectrometry (TIMS) as applied in the laboratory shown in Figure 1. Recently laboratories applying multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) have demonstrated via participation in interlaboratory comparisons that their measurement performance is comparable to TIMS [8]. Depending on the mass spectrometric measurement technique, e.g. total evaporation, and on the certified spike isotopic reference material used, relative expanded uncertainties for IDMS in the range of 0.025% to 0.1% can be achieved [9-11].

2.1.2. X-Ray Fluorescence

X-ray fluorescence (XRF) is used to measure the elemental concentrations of plutonium and uranium of solutions [4]. In order to generate fluorescent X-rays in the sample matrix, the sample is irradiated with X-rays emitted from an X-ray tube or radioactive source. The X-rays subsequently emitted by the sample are detected [13]. Either ratios of uranium and plutonium such as Pu/Pu+U [14] or absolute concentrations of plutonium and uranium are measured. The latter requires instrument calibration with suitable standards. Relative expanded measurement uncertainties

Figure 1: Nuclear mass spectrometry laboratory at IRMM (picture courtesy of IRMM) [12].

of about 0.5% have been demonstrated [7]. XRF is also applied (in combination with hybrid K-edge densitometry) for the measurement of solutions in the reprocessing facility in La Hague [4]. Additionally, XRF has also shown potential for the determination of metal impurities in nuclear materials such as U_3O_8 [15].

2.1.3. Titration

The concentrations of plutonium and uranium can also be determined by titration.

The Davies and Gray potentiometric titration method is the most widely used titration method for uranium [16]. U(IV) is titrated with potassium dichromate after reduction of U(VI) to U(IV). The reduction step is necessary because uranium is mostly present as U(VI) in nitric acid sample solutions. This method is widely used by plant operators as well as in safeguards analytical laboratories. Both Davies and Gray titration and isotope dilution mass spectrometry methods have comparable levels of accuracy for the determination of pure uranium materials. Higher uncertainties must be expected for mixed oxides containing uranium and plutonium [17].

Plutonium can also be determined by potentiometric titration. First the plutonium is oxidised to Pu(VI) with argentic oxide in nitric acid solution; the excess of the argentic oxide is removed with sulphamic acid. Then a weighed amount of Fe(II) is added. Fe (II) subsequently reacts with Pu(VI). The excess of Fe (II) then is titrated potentiometrically with a standard potassium dichromate solution. This method can also be applied to nitrate solutions containing a large amount of uranium. The coefficient of variation is usually better than 0.2% [18].

2.1.4. K-Edge Densitometry

K-edge densitometry (KED) is suitable for the determination of uranium and plutonium concentrations in solutions. When both elements are present in the same sample solution, however, the K-edge densitometry measurement should be combined with K-edge X-ray fluorescence densitometry (K-XRF) in order to take interferences caused by K-absorption edges in the same energy region into account.

For a KED measurement the sample solution is transferred in a vessel with defined path length and passed through by a highly collimated X-ray beam. The x-ray transmission is measured as a function of energy in critical energy regions (K-edges). Volume concentrations from 25 g/L to approximately 400 g/L of uranium or plutonium can be obtained using calibration curves. In order to transform the measured volume concentrations (g/L) to mass concentrations (g/g) the density of the sample solution must be known [7]. An example for K-edge densitometry in fuel material can be viewed in [19].

2.1.5. Gravimetric assay

Gravimetric assays of plutonium or uranium are primary measurement methods with high precision and accuracy. The weighing form of uranium for the assay is U_3O_8, produced by ignition of uranyl nitrate at about 1000°C. The applied ignition temperature and elemental impurities such as calcium and phosphorus can lead to deviations of the stoichiometry of U_3O_8 due to formation of complexes such as uranates. These effects must be considered. Impurities can for instance be measured by GD-MS, SS-MS or ICP-MS [7]. A gravimetric determination of uranium in uranyl nitrate is described in [20]. There are also gravimetric methods for the determination of plutonium such as ISO method ISO 8425:1987 for the determination of plutonium in pure plutonium nitrate solutions.

2.2. Less frequently applied DA techniques for elemental assay in bulk samples

2.2.1. Spectrophotometry

Plutonium and uranium concentrations can also be determined by spectrophotometric methods. Although these methods are rarely used for nuclear safeguards applications, they are simple and fast measurement methods in process control such as the spectrophotometric determination of uranium in process streams [21]. The spectrophotometer measures the absorbance of light that passes through the sample: A monochromator ensures that the light has the desired wavelength or a very narrow range of wavelengths. The light that leaves the monochromator passes through the sample solution which is placed in a cuvette with defined length. The absorbance of the light is a function of the concentration in the sample solution [22]. Such a spectrophotometric technique can also be used for the assay of plutonium concentrations after solvent extraction [23].

2.2.2. Coulometry

Coulometry is not frequently applied for routine verification measurements in nuclear safeguards despite its potential to provide precise and accurate measurement results [7]. A current is applied to the sample solution triggering oxidation or reduction of the analyte (uranium or plutonium) to another valence state. When all of the analyte is transformed a shift in the potential of the working electrode can be observed marking the endpoint of the titration. The magnitude of the current and the titration time are used to determine the amount of the analyte in the sample solution. Given that the volume of the sample solution is known the concentration can be determined [24]. A method for a coulometric plutonium assay is described in [25]: Pu(VI) is reduced to Pu(IV) with help of a ferrous mediator. This method has a precision better than 0.1% for 5 mg and 1.2% for 0.1 mg plutonium. [26] describes the determination of uranium by constant current coulometry based on a modified version of the titration method by Davis and Gray [16]. Measurement results with relative standard uncertainties of 0.1% can be obtained by coulometry.

2.3. Isotope assay in bulk samples

2.3.1. Thermal Ionization Mass Spectrometry

Thermal Ionization Mass Spectrometry (TIMS) is the most commonly used tool for nuclear safeguards to obtain precise, isotope ratio measurement results of uranium and plutonium. It is also applied, in combination with the correct use of certified reference materials, in isotope dilution assays for the accurate determination of plutonium and uranium concentrations. A mass spectrum of natural uranium is show in Figure 2.

Micro-gram to nano-gram quantities of the analyte are loaded as oxides or in aqueous chloride or nitrate solutions on a filament (small metal ribbon). In case of liquid samples an electric current is applied to the filament in order to accelerate the drying process of the sample solution on the filament [27]. Prior to transferring the sample to the filament, the filaments are degassed in order to evaporate contaminants from the surface of the filaments [28]. Additionally, filaments can be carburized prior to sample loading. As a consequence of the formation of plutonium or uranium carbides a larger portion of +1 charged ions and less oxide species of the analyte are formed, leading to more intense and stable ion beams [29]. The carburisation technique is used for environmental samples where the analyte is only present in the pico-gram range [28].

During the measurement the sample is heated to >1600°C in vacuum and thereby vaporized and partially ionized. The resulting ion beam is focused by ion optics and split into beams with specific mass to charge ratios in a magnetic sector. The ion beams are measured one after another in case of a single detector instrument in so called peak-jumping mode. In case of a multi-collector instrument several ion beams are measured simultaneously [27]. In order to decrease the total measurement uncertainty the "total evaporation method" can be applied. It combines the complete evaporation of the sample with multiple ion collection: the entire sample is evaporated and ionised in order to eliminate measurement bias caused by an increased amount of lighter ions produced in the beginning of the measurement as well as an increased amount of heavy ions in the end of the measurement. Traditional TIMS methods provide for example isotope amount ratios with relative expanded uncertainties of 0.11–0.14% for samples with 0.50–20.0 mass % of ^{235}U, while the total evaporation method lowers uncertainties to 0.039–0.077% for the same type of samples [30]. The development of the "modified total evaporation" has recently significantly improved the measurement performance particularly for the minor abundant isotopes [31, 32].

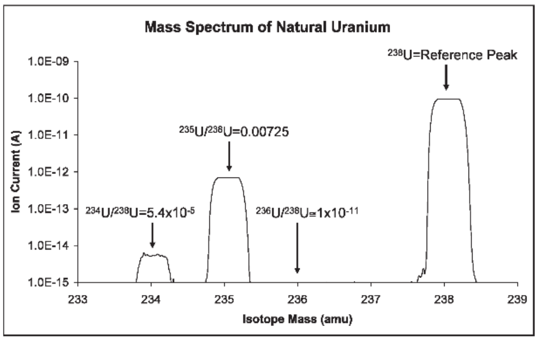


Figure 2: Mass Spectrum of Natural Uranium [33].

2.3.2. Gas Source Mass Spectrometry

Gas source mass spectrometry is mostly applied in enrichment plants. This technique is only occasionally used for nuclear safeguards due to the fact that this type of mass spectrometer can exclusively measure uranium hexafluoride (UF6) samples. The enrichment of uranium hexafluoride is measured directly after ionisation by electron impact. The resulting ions pass a magnetic sector field before they are detected with a similar detection system as described for TIMS. Prior to the measurement, volatile compounds such as HF (hydrofluoric acid) must be removed. Milligrams amounts of UF6 are required and the sample throughput is low since the measurement procedure usually requires the use of two certified isotopic reference materials per sample in order to minimize effects such as drifts, non-linearity and memory effects. Isotope ratios with relative standard deviations as low as 0.012% can be obtained [34].

2.3.3. Alpha-Spectrometry

Alpha spectrometry is a useful technique for the determination of alpha-particle emitting radionuclides in environmental and nuclear fuel samples. A major drawback of this technique is the extensive sample preparation such as electro disposition after anion exchange purification in order to produce thin sample layers and remove interfering elements [35]. Since the resolution of commercially available silicium detectors is not sufficient for quantitative analysis of actinides (such as ^{240}Pu, ^{239}Pu, ^{238}Pu, ^{241}Am, ^{233}U, ^{234}U and ^{232}U), complex and highly sophisticated computer algorithms need to be used to obtain isotope ratios such as $^{240}Pu/^{239}Pu$. Alternatively, high resolution alpha spectrometers can be used. The uncertainties for the determination of $^{240}Pu/^{239}Pu$ with high resolution alpha-particle spectrometers are in the range of 0.4-1.6% [36].

2.4. Combined methods

There are also methods combining different measurement techniques and principles in order to obtain more information about the sample. Two combined methods are discussed below.

2.4.1. COMPUCEA

COMPUCEA stands for Combined Procedure for Uranium Concentration and Enrichment Assay. This compact and transportable system allows high-accuracy uranium elemental assay and enrichment determination for uranium oxide powders and pellets from enrichment plants. Consequently transport of radioactive material can be avoided since COMPUCEA be used on-site. The sample is dissolved in nitric acid and the sample solution is subsequently measured using L-edge densitometry and passive gamma counting to obtain the uranium concentration and the ^{235}U enrichment. COMPUCEA is routinely used for inventory verification at European LEU (low-enriched uranium) fuel fabrication plants [37].

2.4.2. Hybrid K-Edge/K-XRF Densitometry

Hybrid K-edge/K-XRF densitometry (HKED) is a combination of K-edge densitometry (KED) and X-ray fluorescence (XRF) measurements (Figure 3). It constitutes an accurate and reliable method for the determination of the concentrations of uranium and plutonium in sample solutions. HKED is thus often used for nuclear material accountancy verification in reprocessing plants.

An X-ray generator produces an energy spectrum of bremsstrahlung photons which are directed through a vial containing the sample. This X-ray beam passes through the sample vial of well-defined path-length to a detector that measures a transmission spectrum using the absorption edges for the concentration determination. An X-ray fluorescence detector is placed at a backward angle of typically 150° relative to the X-ray beam. Concentrations lower than 50 g/L are covered by the XRF measurement while KED covers higher concentrations. Combining these two techniques allows with proper instrument calibration concentration measurements of uranium and plutonium with a combined relative uncertainty of <1% at concentration levels above 0.5 g/L [4].

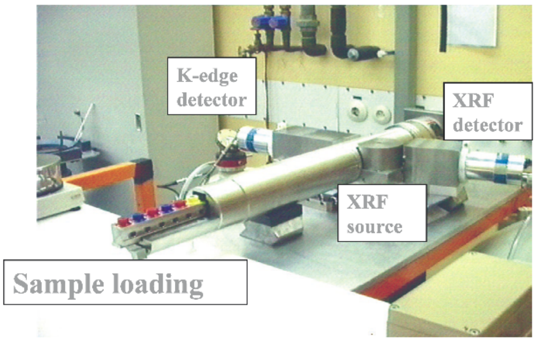


Figure 3: Hybrid K-Edge/K-XRF Densitometer (picture courtesy of ITU) [38].

3. Environmental and swipe samples

Environmental sampling has become a vital tool of treaty verification since the legal basis for environmental sampling in nuclear safeguards was enhanced by the Additional Protocol (1997) complementing the Non-Proliferation Treaty (1968). Provisions for both location specific and wide-area environmental sampling are included in the Additional Protocol [39].

Most environmental samples subject to destructive analysis are so called “swipe samples” taken at nuclear facilities such as enrichment plants as well as at locations suspected of undeclared nuclear activities. Dust is taken up with a cotton cloth by swiping surfaces. Particles and aerosols are often released when nuclear material is manipulated. Theses particles can thus be found in many locations in and possibly around a nuclear facility. They “carry” an isotopic fingerprint related to the processes in the installation and the source of the material Swipe samples taken at a facility that has been operated over a long period can potentially provide additional information about equipment, plant design, operational parameters and the history of the facility, because it is difficult to clean up and remove released particles [40]. The analysis of environmental samples for nuclear safeguard purposes can be divided in bulk and particle analysis. The result of a bulk analysis applying similar methods as previously described for bulk analysis of nuclear material samples is the average isotopic composition of all particles sampled with the cotton cloth. Single particle analysis involves the measurement of singular individual particles containing for instance sub-pg to pg amounts of uranium [41, 40].

3.1. Single particle analysis

3.1.1. Secondary Ion Mass Spectrometry (SIMS)

Single particle analysis can help to verify the completeness of records and to unveil undeclared nuclear activities. One of the most important methods for the measurement of isotopic ratios of single uranium containing particles (Figure 4) is Secondary Ion Mass Spectrometry (SIMS) [40]. Prior to the measurement the particles are deposited on carbon disks by liquid phase extraction or vacuum impaction. In order to produce secondary ions originating from the sample surface a primary ion beam is focused on the sample. The secondary ions are separated according to their mass to charge ratio in a sector field mass spectrometer using a combination of an electrostatic analyzer and a magnetic analyzer [42].

A major drawback of SIMS using Small Geometry SIMS instruments (SG SIMS) are isobaric interferences reducing the accuracy of the measurement especially when ratios of minor uranium isotope are measured, i.e. $^{236}U/^{235}U$ and $^{234}U/^{235}U$. Large Geometry SIMS instruments (LG SIMS) provide higher mass resolution and ion transmission. Both LG SIMS and SG SIMS instruments are based on double focusing mass spectrometers, but LG SIMS uses a magnetic sector with a larger radius. SIMS measurements can be automated using ion imaging for fast screening in order to locate single particles and for measuring the enrichment of these particles. Thus particles of interest can be located among large numbers of other particles (Figure 5). The main limitations of LG-SIMS compared to TIMS are the necessary hydrogen correction for ^{236}U [40] and difficulties in measuring plutonium isotopes due to isobaric interferences from ^{238}UH on ^{239}Pu and from ^{241}Am on ^{241}Pu [41].

3.1.2. Fission Track Thermal Ionization Mass Spectrometry

Fission track thermal ionization mass spectrometry (FT TIMS) is routinely used in nuclear safeguards for the analysis of single uranium containing particles: The particles from a swipe sample are deposited onto one or between two polycarbonate films serving as fission track detector [44, 45]. The particle baring film is irradiated by thermal neutrons in a nuclear reactor. With increased neutron flow, the detection limit can be lowered. Single particles containing fissile isotopes such as ^{235}U or ^{239}Pu are located by their fission track clusters on the polycarbonate film under an optical microscope. Each located single particle is then transferred to a filament for isotopic TIMS analysis using a micro manipulator [44]. A major disadvantage of FT TIMS compared to SIMS is the time consumed till measurement results are obtained and the need for a reactor for neutron activation; thus FT TIMS requires more laboratory resources. On the other hand TIMS does not require hydrogen correction for ^{236}U [40].

3.1.3. SEM-EDX/TIMS

SEM-EDX/TIMS stands for a technique for analysis of single uranium and plutonium particles combining scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) and thermal ionization mass spectrometer (TIMS). Uranium containing reference particles are shown in Figure 4.

The sample particles are first transferred to a graphite planchet using a vacuum impactor prior to applying the SEM-EDX/TIMS technique. The particles can be fixed on the graphite by organic coating that is subsequently removed by evaporation as described in [41]: The particles deposited on the carbon planchet are analysed with an EDX spectrometer attached to an SEM in order to find uranium or plutonium containing particles of interest . These particles are one by one picked-up using a micro-manipulator in the sample chamber of the SEM. Each particle can then be directly transferred to a filament for TIMS analysis similarly to the FT TIMS method. The clear advantage of SEM-EDX/TIMS over FT TIMS is that it is less time consuming and does not require a reactor facility [41].

Another option which is not commonly used yet in nuclear safeguards is to perform chemical separations on single

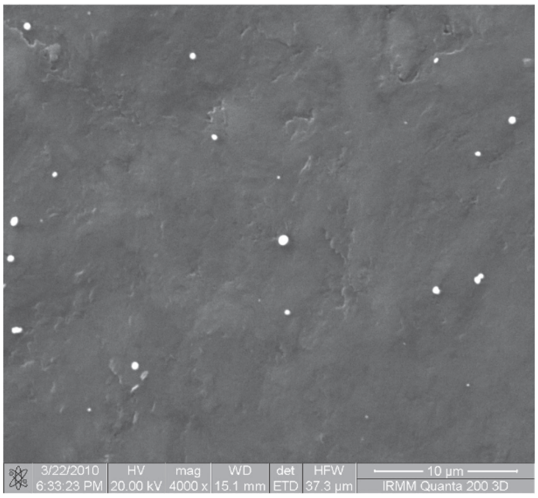


Figure 4: IRMM uranium reference particles (picture courtesy of IRMM) [47].

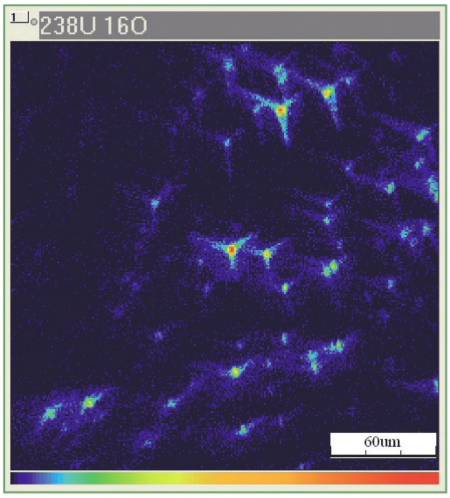


Figure 5: Ion image of uranium reference particles by SIMS (picture courtesy of ITU) [43].

particles in order to remove isobaric interferences for isotope dilution mass spectrometry or isotope ratio assay: single particles are identified and relocated by SEM-EDX and chemically separated/spiked prior to the TIMS measurement [41]. This technique has for instance been used by the authors of [46] for age determination of single plutonium particles.

3.1.4. Laser Ablation Inductively Coupled Mass Spectrometry

Laser ablation inductively coupled mass spectrometry (LA-ICP-MS) has not been implemented as a routine method for the analysis of single particles in nuclear safeguards yet. It seems, however, to be a promising technique offering rapid and accurate determination of the isotopic composition of individual uranium particles [47]. Similarly to techniques using TIMS, particles of interest have to be identified before the mass spectrometric measurement but moving single particles to filaments is not necessary: The surface holding the particles is placed in the laser ablation chamber of the laser ablation system and a laser beam is focused on the surface of a single particle. An aerosol is formed when a laser beam strikes the surface of the sample. These aerosol particles are transported into the inductively coupled argon plasma by an argon gas flow where they are atomized and ionized. The ions are separated according to their mass to charge ratio in the mass spectrometer either in a quadrupol or in a combination of electrostatic analyser and magnetic sector field. Instruments deploying the latter principle exist as single and multi detector instruments (simultaneously detecting several signals) while quadrupol instruments only have a single detector. Sector field instruments can be operated in higher mass resolution ($m/\Delta m$) than quadrupol instruments. The authors of [48] developed for instance a method for the measurement of ^{234}U, ^{235}U, ^{236}U and ^{238}U isotopes in single particles with diameters down to 10 µm. Especially multi-collector sector field instruments show potential for the analysis of safeguards related particle samples offering short analysis time and minimal sample preparation [49]. The accuracy of measurement of the uranium isotope ratios is limited due to the short transient signals from laser ablation with prompt signal variations and to potential fragmentation rather than vaporization of particles. LA-ICP-MS measurement performance for a single particle with a size of about 1 µm or smaller is not yet adequate for routine safeguards analysis. LA-MC-ICP-MS for particle analysis is a technique under development that should be further investigated and improved. Particularly the combination of multi-collector sector field ICP-MS with femto second lasers might be promising for particle analysis. Advantage of LA-MC-ICP-MS is that less complex sample preparation in combination with shorter time for analysis leads to a higher potential sample through-put compared to SIMS or TIMS analysis [47].

4. Benefits and drawbacks of Destructive Analysis

The major benefit of DA in nuclear safeguards clearly lies in the high quality of the obtained measurement results that are provided to safeguards authorities. DA is the basis for a system of accurate measurement results for uranium and plutonium isotopic compositions and element concentrations with small combined uncertainties conform to the latest standards in nuclear safeguards. State of the art analytical procedures and measurement techniques in combination with the correct use of reference materials and quality control tools establish traceability, reliability and comparability of measurement results in fissile material accountancy and environmental sample analysis. Therefore the availability and development of suitable nuclear reference materials for method validation and instrument calibration is a prerequisite [50]. DA methods are the methods of choice when accurate and reliable measurement results with uncertainties estimated according to international guidelines are required, increasing the confidence in the conclusions drawn by safeguards authorities [51].

DA is also the strategy of choice for special samples (in terms of isotope composition, sample matrix or concentration), environmental samples and non-routine samples such as sized material in nuclear forensic investigations: Whenever nuclear material is discovered in places out of the regulatory control of nuclear safeguards, nuclear forensic investigations are applied in addition to traditional forensics. Nuclear forensics focuses on reconstructing the origin and the history of the sample. Isotopic and elemental compositions as well as physical appearance are analysed. In this way information on the production process, intended use and age of the material can be obtained [52]. The questions to be answered are similar in case of “forensics” samples and single particles from swipe samples routinely taken in nuclear facilities. The origin and history (production process, intended use, age) are also of interest for these samples. Single particle analysis, however, has to deal with the added difficulty of very small sample sizes (pg-range). Highly sensitive and accurate measurement methods as offered by DA are beneficial to cope with such small amounts of analytes.

The major drawbacks of DA are that DA is time consuming and expensive compared to NDA: High investments need to be made in order to obtain and maintain high precision analytical instruments. DA techniques may also be more demanding in terms of operator skills. Both timely delays until the measurement data are available as well as higher costs compared to NDA originate partially in the need of transporting the samples to the safeguards laboratory where they are analysed: The transport of nuclear samples is logistically challenging because special licenses are required and transport regulations are stringent. The disadvantages of timely delay as well as costly and logistically challenging sample transports can partially be overcome by measurement campaigns in on-site laboratories. On-site laboratories are directly located at the inspected facilities. Euratom operates such on-site laboratories for instance in nuclear reprocessing plants in Cap de La Hague in France and in Sellafield in the UK [53]. Furthermore combined methods such as COMPUCEA also allow in field-measurements at nuclear installations.

Another drawback is that for DA analyses aliquots from a (large) bulk of nuclear material is taken. Conclusions on the whole bulk of nuclear material are drawn by safeguards authorities based on accurate measurement results of these sub-samples under the assumption that these samples taken by inspectors are representative for the whole badge. Thus DA also requires a well considered sampling strategy on the collected samples to be verified by independent measurements, which introduces an additional uncertainty component to the final result.

Furthermore nuclear waste is generated when DA is performed creating additional costs as well as logistic and environmental considerations concerning treatment, transport and storage. The waste needs to be transformed in a physical form that is suitable for storage in order to reduce volume and/or weight: compressing of un-burnable waste, combustion of burnable waste and evaporation of solvent in case of liquid waste. It is then eventually transported for final storage and/or recycling.

4.1. DA or NDA?

DA involves measurement techniques which are carried out in such a way that the sample being measured is not returned to the batch it was taken from, hence introducing a significant change. Contrary to DA, NDA can be performed without changing the physical and/or chemical form of the sample. Thus by means of NDA equipment installed in a nuclear facility the material flow can even be followed and monitored via remote data collection. Radiometric techniques do not even require the opening of sample containers since the radiation emitted by the nuclear material is measured. These radiometric techniques can be subdivided in either be passive and active measurement techniques. The first measures radiation produced by spontaneous decay while the latter measures radiation induced by activation of the sample material with an external source. The purpose of both DA and NDA is to measure the concentration (amount) and isotopic composition (enrichment) of nuclear material. The major points to be considered when choosing the appropriate measurement technique from all the possibilities offered by both NAD and DA are:

- the required accuracy and selectivity of the measurement method which influences the overall measurement uncertainty;
- the acceptable time delay from sampling until the data are available which is directly linked to the safeguard goal of "timeliness of detection";
- the total cost from sampling till data generation and interpretation including transport issues and waste management.

Summarising it can be said that the method of choice has to be suitable for the analyte under investigation and "fit for purpose" taking into account the available resources., Availability of analytical instruments and authorised operators has to be taken in account when deciding not only between NDA and DA but also when choosing the appropriate method within NDA and DA methods, respectively [1]. Both DA and NDA methods have to meet the International Target Values for Measurement Uncertainties in Safeguarding Nuclear Materials. The International Target Values are uncertainties to be considered in judging the reliability of analytical techniques applied to industrial nuclear and fissile material, which are subject to safeguards verification [2]. DA and NDA techniques are complementary in providing answers on specific safeguards questions in fissile material accountancy and environmental analysis. In this light the ESARDA DA and NDA working groups are regularly holding joint meetings being a platform of exchange of information on DA and NDA methods among experts from safeguards authorities, industry and research organisations.

5. Conclusion

Destructive Analysis is one of many complementary measures applied in Nuclear Safeguards, which help to monitor and optimise the successful implementation of the safeguard goals as defined in the NPT and the Euratom treaty. A great variety of analytical methods ensures that the information needed to answer specific questions relevant to nuclear safeguards can obtained. Different analytical methods are needed to cope with samples of different sizes, concentrations and enrichment as well as chemical and physical form. DA and NDA supplement each other in this task. They play, therefore, along with other safeguards strategies a vital role in promoting the peaceful use of nuclear energy and in counteracting the abuse of nuclear material.

6. Acknowledgement

The author would like to thank the Working Group on Training & Knowledge Management of the European Safeguards Research and Development Association for organising the 6th ESARDA course on Nuclear Safeguards and Non Proliferation.

7. List of abbreviations

AP	Additional Protocol of the Non-Proliferation Treaty
COMPUCEA	Combined Procedure for Uranium Concentration and Enrichment Assay
DA	Destructive Analysis
EDX	Energy Dispersive X-ray spectrometry

EU	European Union
Fe	Iron
FT TIMS	Fission Track Thermal Ionization Mass Spectrometry
GD-MS	Glow Discharge Mass Spectrometry
HF	Hydrofluoric acid
HKED	Hybrid K-Edge/K-XRF Densitometry
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
KED	K-Edge Densitometry
LA-ICP-MS	Laser Ablation Inductively Coupled Mass Spectrometry
LEU	Low-Enriched Uranium
LG SIMS	Large Geometry Secondary Ion Mass Spectrometry
MOX	Mixed plutonium and uranium Oxide
NDA	Non-Destructive Analysis
NPT	Non-Proliferation Treaty
Pu	Plutonium
SEM	Scanning Electron Microscope
SEM-EDX/TIMS	combination of Scanning Electron Microscopy, Energy Dispersive X-ray spectrometry and Thermal Ionization Mass Spectrometry
SG SIMS	Small Geometry Secondary Ion Mass Spectrometry
SIMS	Secondary Ion Mass Spectrometry
SIMS	Secondary Ion Mass Spectrometry
SS-MS	Spark Source Mass Spectrometry
TIMS	Thermal Ionization Mass Spectrometry
U	Uranium
UF_6	Uraniumhexafluoride
XRF	X-Ray Fluorescence (XRF)

References

[1] Jansseeens-Maenhout, G., ed. *Nuclear Safeguards and Non-Proliferation Course Syllabus*. 2008, Office for Official Publications of the European Communities: Luxembourg.

[2] Aigner, H., et al., *International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Materials*. ESARDA BULLETIN, 2002(31): p. 39-61.

[3] Mayer, K. and R. Wellum, *Sample Analysis Methods for Accountancy and Verification – A Compendium of Currently Applied Analytical Methods*. ESARDA BULLETIN, 2002(31): p. 6-10.

[4] Berlizov, A.N., et al., *A quantitative Monte Carlo modelling of the uranium and plutonium X-ray fluorescence (XRF) response from a hybrid K-edge/K-XRF densitometer*. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 2010. 615(1): p. 127-135.

[5] Alamelu, D. and S.K. Aggarwal, *Effect of radioactive decay of Pu isotopes on the determination of Pu concentration with high accuracy by isotope dilution mass spectrometry (IDMS) and isotope dilution alpha spectrometry (IDAS)*. Journal of Alloys and Compounds, 2007. 444-445: p. 643-646.

[6] Ingelbrecht, C., et al., *New U/Pu metallic spikes for safeguards accountancy measurements at reprocessing plants*. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 1997. 397(1): p. 30-33.

[7] Aregbe, Y., *Destructive Sample Analysis for Nuclear Safeguards, in Nuclear Safeguards and Non-Proliferation Course Syllabus*, G. Jansseeens-Maenhout, Editor. 2008, Office for Official Publications of the European Communities: Luxembourg.

[8] Richter, S., et al., *REIMEP 18: Inter-Laboatory Comparison for the Measurement of uranium Isotopic ratios in Nitric Acid Solution – Report to Participants*. 2006, European Commission.

[9] Richter, S. and S.A. Goldberg, *Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry*. International Journal of Mass Spectrometry, 2003. 229(3): p. 181-197.

[10] Richter, S., et al., *The isotopic composition of natural uranium samples–Measurements using the new $n(^{233}U)/n(^{236}U)$ double spike IRMM-3636*. International Journal of Mass Spectrometry, 2008. 269(1-2): p. 145-148.

[11] Verbruggen, A., et al., *Preparation and Certification of IRMM-3636, IRMM-3636a and IRMM-3636b*, in *JRC Scientific and Technical Reports*. 2008, European Commission: Luxembourg.

[12] IRMM, *Nuclear mass spectrometry laboratory at IRMM* 2008, EC-JRC-IRMM.

[13] Arai, T., *Introduction, in Handbook of Practical X-Ray Fluorescence Analysis*. 2006. p. 1-31.

[14] Diels, P. and R. Lecocq, *Determination of the Pu/U+Pu ratio in FBR fuel pellets by X-ray fluorescence analysis*. Journal of Nuclear Materials, 1982. 106(1-3): p. 115-120.

[15] Natarajan, V., et al., *Determination of metallic impurities in U_3O_8 using energy dispersive X-ray fluorescence spectrometry*. Spectrochimica Acta Part B: Atomic Spectroscopy, 2008. 63(7): p. 817-819.

[16] Davies, W. and W. Gray, *A rapid and specific titrimetric method for the precise determination of uranium using iron(II) sulphate as reductant*. Talanta, 1964. 11(8): p. 1203-1211.

[17] Bickel, M., *The Davies-Gray titration for the assay of uranium in nuclear materials: a performance study*. Journal of Nuclear Materials, 1997. 246(1): p. 30-36.

[18] Drummond, J.L. and R.A. Grant, *Potentiometric determination of plutonium by argentic oxidation, ferrous reduction and dichromate titration*. Talanta, 1966. 13(3): p. 477-488.

[19] Cromboom, O., L. Koch, and R. Wellum, *The determination of uranium and plutonium in fuel materials by titration and by K-edge absorption*. Journal of Nuclear Materials, 1991. 178(2-3): p. 249-253.

[20] Vita, O.A., C.R. Walker, and E. Litteral, *The gravimetric determination of uranium in uranyl nitrate*. Analytica Chimica Acta, 1973. 64(2): p. 249-257.

[21] Murty, B.N., et al., *Spectrophotometric determination of uranium in process streams of a uranium extraction plant*. Talanta, 1997. 44(2): p. 283-295.

[22] Natelson, S., *Separation and spectrophotometric determination of the elements: By. Wiley, New York, 1986. 678 pp., $159.00*. Microchemical Journal, 1987. 35(3): p. 385-385.

[23] Mendoza, P., D. Jackson, and T. Niemczyk, *Precision of a plutonium analytical method using solvent extraction and spectrophotometry*. Journal of Radioanalytical and Nuclear Chemistry, 1991. 150(2): p. 435-444.

[24] DeFord, D.D., *Electroanalysis and Coulometric Analysis*. Analytical Chemistry, 1960. 32(5): p. 31-37.

[25] Chitnis, R., S. Talnikar, and R. Bhogale, *Determination of plutonium by secondary coulometric titration with internally generated iron(II)*. Journal of Radioanalytical and Nuclear Chemistry, 1979. 49(1): p. 63-70.

[26] Chitnis, R., S. Talnikar, and A. Paranjape, *Constant current coulometric method for the determination of uranium in active process solutions*. Journal of Radioanalytical and Nuclear Chemistry, 1980. 59(1): p. 15-21.

[27] Platzner, I.T., *Modern Isotope Ratio Mass Spectrometry*. 1997, Chichester: Wiley.

[28] Jakopic, R., et al., *Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with "multiple ion counting" and filament carburization*. International Journal of Mass Spectrometry, 2009. 279(2-3): p. 87-92.

[29] Kelley, J.M. and D.M. Robertson, *Plutonium ion emission from carburized rhenium mass spectrometer filaments*. Analytical Chemistry, 1985. 57(1): p. 124-130.

[30] de Oliveira, O.P., et al., *Evaluation of the* $n(^{235}U)/n(^{238}U)$ *isotope ratio measurements in a set of uranium samples by thermal ionization mass spectrometry*. International Journal of Mass Spectrometry, 2005. 246(1-3): p. 35-42.

[31] Richter, S., et al., *Improvements for Routine Uranium Isotope Ratio Measurements using the Modified Total Evaporation Method, in preparation*. 2010.

[32] Aregbe, Y., et al., *Report on the Workshop on Measurements of Minor Isotopes in Uranium*. ESARDA BULLETIN, 2008(40): p. 59-69.

[33] ESARDA. *TECHNICAL SHEET ABOUT (NUCLEAR) MASS SPECTROMETRY*. 2010 [cited 25.10.2010]; Available from: http://esarda2.jrc.it/references/Technical_sheets/ts-mass-spectrometry-071212.pdf.

[34] Pereira de Oliveira Junior, O., et al., *Demonstrating the metrological compatibility of uranium isotope amount ratio measurement results obtained by GSMS, TIMS and MC-ICPMS techniques*. International Journal of Mass Spectrometry. 291(1-2): p. 48-54.

[35] Sheppard, S.C., *Handbook of radioactivity analysis, Second edition: M.F. L'Annunziata (ed) 2003. Academic Press, ISBN: 0-12-436603-1*. Journal of Environmental Radioactivity, 2004. 72(3): p. 365-367.

[36] Aggarwal, S.K. and D. Alamelu, *High resolution alpha-particle spectrometry for the determination of* $^{240}Pu/^{239}Pu$ *atom ratio in Pu samples from PHWR*. Journal of Alloys and Compounds, 2007. 444-445: p. 656-659.

[37] Erdmann, N., et al., *COMPUCEA: A High-Performance Analysis Procedure for Timely On-site Uranium Accountancy Verification in LEU Fuel Fabrication Plants*. ESARDA BULLETIN, 2009. No. 43 (December 2009): p. 30-39.

[38] ITU, *Hybrid K-Edge/K-XRF Densitometer* 2010, EC-JRC-ITU.

[39] Kalinowski, M., et al., *Environmental Sample Analysis, in Verifying Treaty Compliance*. 2006. p. 367-387.

[40] Ranebo, Y., et al., *Improved isotopic SIMS measurements of uranium particles for nuclear safeguard purposes*. Journal of Analytical Atomic Spectrometry, 2009. 24(3): p. 277-287.

[41] Shinonaga, T., et al., *Isotopic analysis of single uranium and plutonium particles by chemical treatment and mass spectrometry*. Spectrochimica Acta Part B: Atomic Spectroscopy, 2008. 63(11): p. 1324-1328.

[42] Detter-Hoskin, L.D. and K.L. Busch, *SIMS: Secondary Ion Mass Sprectrometry, in SURFACE ANALYSIS OF PAPER*, T.E. Conners and S. Banerjee, Editors. 1995, CRC Pres LLC.

[43] ITU, *Ion image of uranium reference particles by SIMS*. 2010, EC-JRC-ITU.

[44] Shen, Y., et al., *Study on analysis of isotopic ratio of uranium-bearing particle in swipe samples by FT-TIMS*. Radiation Measurements, 2008. 43(Supplement 1): p. S299-S302.

[45] Lee, C.-G., et al., *Improved Method of Fission Track Sample Preparation for Detecting Particles Containing Fissile Materials in Safeguards Environmental Samples*. Japanese Journal of Applied Physics, 2006. 45(10).

[46] Shinonaga, T., et al., *Age determination of single plutonium particles after chemical separation*. Spectrochimica Acta Part B: Atomic Spectroscopy, 2009. 64(1): p. 95-98.

[47] Boulyga, S. and T. Prohaska, *Determining the isotopic compositions of uranium and fission products in radioactive environmental microsamples using laser ablation ICP–MS with multiple ion counters*. Analytical and Bioanalytical Chemistry, 2008. 390(2): p. 531-539.

[48] Varga, Z., *Application of laser ablation inductively coupled plasma mass spectrometry for the isotopic analysis of single uranium particles*. Analytica Chimica Acta, 2008. 625(1): p. 1-7.

[49] Lloyd, et al., *Precise and accurate isotopic analysis of microscopic uranium-oxide grains using LA-MC-ICP-MS*. 2009, Royal Society of Chemistry: Cambridge, ROYAUME-UNI. p. 7.

[50] Mayer, K. and R. Wellum, *Reference Materials for Destructive Analysis in Nuclear Safeguards*. ESARDA BULLETIN, 2004. 32: p. 75-82.

[51] Wellum, R. and M. Berglund, *The Application of the Guide to Uncertainty in Measurements in Safeguards*. ESARDA BULLETIN, 2002. 31: p. 11-17.

[52] Mayer, K. and M. Wallenius, *Nuclear Forensic Methods in Safeguards*. ESARDA BULLETIN, 2008(38): p. 44-51.

[53] Mayer, K. and R. Wellum, *Striving for Quality in Nuclear Analytical Laboratories, Summary of a dedicated meeting of the ESARDA DA Working Group, 27 November 2003, Geel*. ESARDA BULLETIN, 2006(33): p. 40-42.

2.6 Publication VI

Age determination of plutonium for nuclear forensics

<u>Monika Sturm</u>1), Stephan Richter2), Yetunde Aregbe2), Roger Wellum2), Timotheos Altzitzoglou2), Viktor Jobbagy2), Sebastién Mialle2), Klaus Mayer3), Thomas Prohaska1)

1) University of Natural Resources and Life Sciences, Vienna, Austria
2) European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel, Belgium
3) European Commission, Joint Research Centre, Institute Transuranium Elements, Karlsruhe, Germany
E-mail: monika.sturm@boku.ac.at, stephan.richter@ec.europa.eu

Abstract:

Nuclear forensics focuses on the origin and the history of seized nuclear material in order to discover its latest legal owner and production place. The chemical composition as well as the physical appearance provide information on the production process and the intended use. The "age" of the material helps to limit the number of possible facilities to those, which were active at the time of the production or processing of the material.
The "age" of a nuclear material is the time elapsed since the last chemical separation of mother and daughter nuclides during enrichment or reprocessing. Different "clocks" (i.e. parent/daughter nuclide pairs) can be used for the determination of the age of plutonium: ^{241}*Am/*^{241}*Pu,* ^{238}*Pu/*^{234}*U,* ^{239}*Pu/*^{235}*U and* ^{240}*Pu/*^{236}*U.*

At present there are no nuclear reference materials available that are certified for the separation date of plutonium providing a solid metrological basis for age dating measurements and thus increasing the confidence in the conclusions based on these measurements. In order to meet the need of laboratories involved in nuclear forensics and age dating of nuclear material, the Institute for Reference Materials and Measurements (EC-JRC-IRMM) is closely cooperating with the Institute for Transuranium Elements (EC-JRC-ITU).

The widely distributed isotope ratio reference material SRM 946 (NBL CRM 136) has been dated among other samples as part of a feasibility study on plutonium reference materials certified for the separation date.

The results of the ^{238}*Pu/*^{234}*U,* ^{239}*Pu/*^{235}*and* ^{240}*Pu/*^{236}*U clocks measured by isotope dilution thermal ionization mass spectrometry will be presented and discussed. The findings of the age determination agree well with the reported dates for the production of NBS 946 in 1970.*

Keywords: plutonium, nuclear forensics, dating, age, reference material

1. Introduction

Since the early 1990s more than one hundred cases of illicit trafficking of uranium and plutonium materials have been reported. These occurrences gave rise to the development of the discipline of nuclear forensic science [1]. In such cases nuclear forensic investigations are applied in addition to traditional forensics. Traditional forensics focuses on evidence such as traces (fingerprints, fibres and other residues) left behind by the culprit in order to identify linkages between (suspect) individuals and events (crimes). In contrast to that, nuclear forensics aims at re-establishing the history of the seized material and provide hints on the possible origin of the material. To this end, the isotopic and elemental composition (major elements and impurities) in combination with dimensions of larger objects, and particle form and particle size of powders, respectively, are investigated. These findings help in determining the production process and/or the purpose the material was intended for by comparison with the entries in databases containing facility specific attributes of nuclear material. Another key parameter helping to discover the latest legal owner and production place of seized nuclear material is the “age” of the material.

1.1. Principles of plutonium age dating

The time span since the last removal of the “daughter” nuclides (decay products) from the “mother” nuclides is defined as the "age" of nuclear material such as plutonium. Such manipulations that separate the mother nuclides from their daughter nuclides - and thus set the “clock” to zero - occur for instance during reprocessing. The following isotopic systems are commonly used as "clocks" for the age dating of plutonium: $^{241}Pu/^{241}Am$, $^{238}Pu/^{234}U$, $^{239}Pu/^{235}U$ and $^{240}Pu/^{236}U$ [2]. Radiochronometry, however, relies on a few basic assumptions: the daughter nuclides should be completely removed from their respective parent nuclides at t=0, the material shall be considered as closed system, i.e. no parent or daughter nuclide shall be added or removed during the time interval under consideration, and parent and daughter nuclide shall be in radioactive disequilibrium.

The determination of the age is based on the equations describing the radioactive decay, as shown in equation 1 to 3 for the chronometer $^{239}Pu/^{235}U$ [3]. The amount of the mother nuclide ^{239}Pu at the time of the measurement (present time) is represented by $^{239}Pu_t$. The amount of ^{239}Pu at the time of the separation (t=0) is $^{239}Pu_0$. $^{235}U_t$ is the amount of ^{235}U at the present time. The decay constants λ of mother and daughter nuclide can be calculated from their half-lives $t_{1/2}$ according to equation 3.

$$^{239}Pu_t = {}^{239}Pu_0 * e^{-\lambda\_239Pu * t} \qquad (1)$$

$$^{235}U_t = \lambda_{239Pu} * (\lambda_{235U} - \lambda_{239Pu})^{-1} * {}^{239}Pu_0 * (e^{-\lambda\_239Pu * t} - e^{-\lambda\_235U * t}) \qquad (2)$$

$$\lambda = t_{1/2}^{-1} * \ln 2 \qquad (3)$$

Consequently, the time span t that elapsed since the last separation can be determined by calculating back to the time when no daughter nuclides were present. Assuming the complete absence of the daughter nuclides at the time of the last separation, one can thus determine when the last chemical separation of the daughter nuclides took place. Table 1 lists the parent/daughter nuclide pairs that can be applied for the determination of the age of plutonium materials.

Clock	Half-life mother (a)	Reference	Half-life daughter (a)	Reference
$^{238}Pu/^{234}U$	87.74(3)	[4]	$2.455(6)\cdot10^5$	[4]
$^{239}Pu/^{235}U$	$2.410(3)\cdot10^4$	[4]	$7.04(1)\cdot10^8$	[4]
$^{240}Pu/^{236}U$	6561(7)	[4]	$2.342(4)\cdot10^7$	[4]
$^{241}Pu/^{241}Am$	14.325(24)	[5]	432.6(6)	[4]
$^{242}Pu/^{238}U$	$3.73(3)\cdot10^5$	[4]	$4.468(5)\cdot10^9$	[4]

Table 1: Isotope pairs formed by plutonium mother nuclides and their respective daughter nuclides

It is advisable to use more than one chronometer nuclide pair for the age dating of plutonium in order to enhance the reliability of the results and to gain additional information about the material. Using only one clock might lead to erroneous conclusions, as systematic errors (e.g. arising from incomplete separation at t=0) remain undetected. Inconsistent age dating results of several parent/daughter pairs may point at incomplete removal of the decay products from the parent nuclides. In case the sample consists of a mixture of two or more different materials a similar effect can occur [6]. Any addition of daughter isotopes during the time between the initial separation and the age dating measurement may also lead to inconsistent results from different clocks. The possibility of a contamination of a plutonium sample in the facility where it was manipulated with natural or non-natural uranium should be kept in mind.

1.2. CRMs for plutonium age dating

Presently, no plutonium materials are available with a metrologically sound certification for their separation date, including a stated quality of the separation from daughter nuclides. The need for Certified Reference Materials (CRM) for age dating has repeatedly been expressed by members of the nuclear safeguards and nuclear forensics communities. Such CRMs would assist in providing a more solid metrological basis for age dating measurements, serve for method validation and increase the credibility of the conclusions based on these measurements.

In order to address this challenge the EC-JRC-IRMM (European Commission, Joint Research Centre, Institute for Reference Materials and Measurements) and the EC-JRC-ITU (Institute for Transuranium Elements) are closely co-operating on the certification of uranium [7] and plutonium materials certified for their separation date.

2. Methods and candidate CRM materials

After the chemical separation of the plutonium, uranium and americium fractions from the sample matrix, isotope dilution mass spectrometric measurements (IDMS) are performed by Thermal Ionisation Mass Spectrometry (TIMS). All TIMS measurements were done applying the total evaporation method [8]. ^{241}Am has also been measured by gamma-ray spectrometry and alpha spectrometry. The protocols for the chemical separation procedures isolating the elements of interest (Pu, U, Am) prior to analysis were optimized successfully. This allowed the metrological determination of nuclide amount ratios formed from the determined amount contents of the respective mother (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) and daughter (^{234}U, ^{235}U, ^{236}U, ^{238}U and ^{241}Am) nuclides.

The first step of this study was to select suitable plutonium materials. Firstly the plutonium isotope reference materials NBS SRM 946, NBS SRM 947 and NBS SRM 948 with reported dates of the individual production stages were selected. These samples also served as samples for method development. Secondly, plutonium materials that are not described in literature were selected. The latter do not only serve as candidate materials for CRMs for nuclear age dating but are as well suitable as samples for future inter-laboratory comparison exercises on age determination of plutonium. In total seven different materials covering an age range of almost 20 years were selected. Furthermore they also have a range of plutonium isotopic compositions that covers fuel grade, reactor grade and weapon grade plutonium (classification according to [9]).
The results of the age determination of plutonium/uranium clocks of the widely distributed isotope ratio reference material NBS SRM 946 (NBL CRM 136) will be discussed hereafter. Furthermore two possible scenarios are discussed illustrating why it may be a good idea to measure - when possible - more than one clock; not only the absolute age determined by each clock helps to unravel the history of the material but also how the clocks stand relative to each other may tell a tale of its own.

3. Results and Discussion

As mentioned above the widely distributed isotope ratio reference material NBS SRM 946 (NBL CRM 136) has been dated among other samples. The findings of the age determination agree well with the reported dates for the production of NBS SRM 946 in 1970 [12]. The results of the age determination can be found in Table 2 and Figure 1. One can easily see in case of this sample all three commonly used plutonium/uranium clocks (^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U) are in good agreement with each other. In addition to that the result for the usually not employed clock ^{242}Pu/^{238}U shown in Table 2 is also not significantly different from the above mentioned clocks. The clock ^{242}Pu/^{238}U is normally not considered due to the low concentrations of mother and daughter nuclides, the ubiquity of ^{238}U and challenges when measuring ^{238}U that lead to higher uncertainties.

Clock	Determined “age” (a)	
	Value	Uncertainty
$^{238}Pu/^{234}U$	41.09	0.29
$^{239}Pu/^{235}U$	41.12	0.12
$^{240}Pu/^{236}U$	41.16	0.11
$^{242}Pu/^{238}U$	43.4	4.5

Table 2: Results of age determination of sample NBS 946 determined by ID TIMS calculated for 18.10.2011; All uncertainties are expanded uncertainties (k=2).

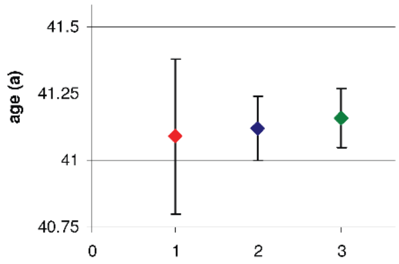


Figure 1: Results of age determination of sample NBS 946 determined by ID TIMS calculated for 18.10.2011 using the following clocks: $^{238}Pu/^{234}U$ (1); $^{239}Pu/^{235}U$ (2); $^{240}Pu/^{236}U$ (3); All uncertainties are expanded uncertainties (k=2).

However, the interpretation of the results of the age determination of a given sample is not always that straight forward. One possible reason for that can be that the sample under investigation is a mixture of two or more materials that were mixed; Apart from that is possible that the separation procedure did not remove the daughter nuclides completely at time zero or that a contamination of the plutonium sample with natural uranium or other uranium occurred. The latter two lead to characteristic patterns of the plutonium/uranium clocks relative to each other and can thus not only help to interpret the results in a more concise way but also may give additional information of the possible history of the sample. Care must be take, however, not to attempt such interpretations without careful consideration of effects on the age dating results of the different clocks that are artefacts of the sample preparation and measurement procedure such as incomplete separations during sample preparation or corrections one should apply in order to obtain interpretable results.

In case of a contamination of the plutonium sample with uranium it is quite likely that one will observe that the result for $^{239}Pu/^{235}U$ clock is shifted to a higher age relative to the $^{238}Pu/^{234}U$ and $^{240}Pu/^{236}U$ dating results. Apart from that the $^{242}Pu/^{238}U$ age dating result will rise to a very high value which is a clear sign for a contamination with natural uranium.

Another scenario that shifts the plutonium/uranium clocks relative to each other is incomplete removal of the daughter nuclides during the last manipulation of the material. In that case the results of all plutonium/uranium clocks will be shifted to an older age due to the excess of uranium. However, the result for the $^{238}Pu/^{234}U$ clock is shifted to a younger age relative to the $^{239}Pu/^{235}U$ and $^{240}Pu/^{236}U$ dating results. This can be explained by the half lives of the respective mother daughter nuclide pairs shown in Table 1.

4. Conclusions and Outlook

The age determination of nuclear material is challenging and not always straight forward due to the nature of the samples; thus for the age estimation of a sample, such as material seized in nuclear forensics investigations, it is advisable to use more than one clock. This helps to ensure the reliability of the results and to exclude the possibility that the sample under investigation is for instance a mixture of two or more materials, has not been separated completely at time zero or has been contaminated with for instance uranium. The latter two lead to characteristic patterns of the plutonium/uranium clocks relative to each other and can thus not only help to interpret the results in a more concise way but also may give additional information of the possible history of the sample.

To meet the needs of the nuclear safeguards and security community, the EC-JRC-IRMM and the EC-JRC-ITU are closely cooperating towards the production of nuclear CRMs certified for the separation date suitable for nuclear age dating.

5. Acknowledgements

The authors would like to thank Rüdiger Kessel for providing for the program GUM work bench 2.4 (Metrodata, Germany) for the uncertainty evaluation.

6. Legal matters

6.1. Privacy regulations and protection of personal data

I agree that ESARDA may print my name/contact data/photograph/article in the ESARDA Bulletin/Symposium proceedings or any other ESARDA publications and when necessary for any other purposes connected with ESARDA activities.

6.2. Copyright

The author agrees that submission of an article automatically authorises ESARDA to publish the work/article in whole or in part in all ESARDA publications – the bulletin, meeting proceedings, and on the website.

The author declares that their work/article is original and not a violation or infringement of any existing copyright.

7. References

1. Mayer, K., M. Wallenius, and T. Fanghänel, *Nuclear forensic science--From cradle to maturity.* Journal of Alloys and Compounds, 2007. **444-445**: p. 50-56.

2. Wallenius, M. and K. Mayer, *Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry.* Fresenius' Journal of Analytical Chemistry, 2000. **366**(3): p. 234-238.

3. Stolz, W., *Radioaktivität: Grundlagen - Messung - Anwendungen*2005: Vieweg+teubner Verlag.

4. Be, M., V. Chiste, and C. Dulieu, *Note Technique DETECS/LNHB/2006-58: Halve-lives, Table of recommended values*2006: Laboratoire Natonal Henri Becquerel.

5. Wellum, R., A. Verbruggen, and R. Kessel, *A new evaluation of the half-life of 241Pu.* Journal of Analytical Atomic Spectrometry, 2009. **24**(6): p. 801-807.

6. Wallenius, M., et al., *Nuclear forensic investigations with a focus on plutonium.* Journal of Alloys and Compounds, 2007. **444-445**: p. 57-62.

7. Varga, Z., et al., *Development and validation of a methodology for uranium radiochronometry reference material preparation.* Analytica Chimica Acta. **718**: p. 25-31.

8. Wallenius, M., P. Peerani, and L. Koch, *Origin Determination of Plutonium Material in Nuclear Forensics.* Journal of Radioanalytical and Nuclear Chemistry, 2000. **246**(2): p. 317-321.

9. Shinonaga, T., et al., *Age determination of single plutonium particles after chemical separation.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2009. **64**(1): p. 95-98.

10. Callis, E.L. and R.M. Abernathey, *High-precision isotopic analyses of uranium and plutonium by total sample volatilization and signal integration.* International Journal of Mass Spectrometry and Ion Processes, 1991. **103**(2–3): p. 93-105.

11. DOE. *Additional Information Concerning Underground Nuclear Weapon Test of Reactor-Grade Plutonium.* 2010 January 21, 2010 17.08.2010]; Available from: https://www.osti.gov/opennet/forms.jsp?formurl=document/press/pc29.html#ZZ3.

12. Mason, P., *A Documentary History of the United States' First Plutonium Isotopic Reference Materials*, in *51st Annual INMM Meeting*2010, Institute of Nuclear Materials and Measurements: Baltimore, MD, USA.

2.7 Publication VII

IAEA-CN-184/16

Feasibility study for the development of plutonium reference materials for age dating in nuclear forensics

M. Sturm[a], S. Richter[a], Y. Aregbe[a], R. Wellum[a1], T. Altzitzoglou[a], A. Verbruggen[a1], K. Mayer[b], T. Prohaska[c]

[a]European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel, Belgium

[b]European Commission, Joint Research Centre, Institute Transuranium Elements, Karlsruhe, Germany

[c]University of Natural Resources and Life Sciences, Vienna, Austria

monika.sturm@ec.europa.eu

Abstract. Isotopic reference materials certified for the age of nuclear material (uranium, plutonium) are needed in the fields of nuclear forensics and environmental measurements. Therefore a feasibility study for the development of plutonium reference materials for age dating has been started recently at the Institute for Reference Materials and Measurements (EC-JRC-IRMM). The "age" of the material is defined as the time that has passed since the last chemical separation of the mother and daughter isotopes (e.g. ^{241}Pu and ^{241}Am). Assuming that the separation has been complete and all the daughter isotopes have been removed from the original material during this last separation, the age of the material can be determined by measuring the ratio of daughter and mother radio-nuclides, e.g. ^{241}Am/^{241}Pu. At a given time after the last separation and depending on the half lives of the radio-nuclides involved, a certain amount of the daughter radionuclide(s) will be present. For the determination of the unknown age of a material different "clocks" can be used; "clocks" are pairs of mother and daughter radio-nuclides, such as ^{241}Am/^{241}Pu, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U, and possibly ^{242}Pu/^{238}U. For the age estimation of a real sample, such as material seized in nuclear forensics investigations or dust samples in environmental measurements, it is advisable to use more than one clock in order to ensure the reliability of the results and to exclude the possibility that the sample under question is a mixture of two or more materials. Consequently, a future reference material certified for separation date should ideally be certified for more than one "clock" or several reference materials for different "clocks" should be developed. The first step of this study is to verify the known separation dates of different plutonium materials of different ages and isotopic compositions by measuring the mother (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) and daughter (^{234}U, ^{235}U, ^{236}U, ^{238}U and ^{241}Am) isotope abundances and to estimate the achievable uncertainties of the calculated ages. Thermal ionisation mass spectrometry (TIMS) is applied for the measurement of the plutonium and uranium isotope ratios after chemical separation of the plutonium and uranium fractions from the sample matrix, while ^{241}Am is measured by gamma-ray spectrometry. In the course of this work the reference materials NBS SRM 946, 947 and 948 (NBL CRM 136, 137 and 138) will be investigated among others.

---

[1] retired

1 Introduction

In these times of a "nuclear renaissance" on the one side and of concerns on nuclear proliferation and nuclear terrorism on the other hand, aspects of non-proliferation and nuclear security need to be given increased attention. This entails addressing also the associated technical challenges and developing sound solutions which enable and support defendable conclusions [1]. These concerns were concisely summarised by the words of the president of the United States of America, Barack Obama, on April 7, 2009 in Prague, addressing the topics of nuclear security and post-cold-war weapons: "In a strange turn of history, the threat of global nuclear war has gone down, but the risk of a nuclear attack has gone up." [2]

Therefore not only the nuclear safeguards system needs to be strengthened and kept up to date for present and future challenges, but nuclear forensics also needs to be ready to provide substantiated answers in a timely manner in case of need. The first cases of illicit trafficking of nuclear material occurred in the early 1990s, and since then more than one hundred cases of illicit trafficking of nuclear material have been reported. [3] Whenever nuclear material (uranium, plutonium) is discovered being out of regulatory control, nuclear forensic investigations may be applied in addition to traditional forensics. While traditional forensics recover and analyse evidence such as fingerprints, genetic markers along with other traces like fibres and residues left behind by the malefactor in order to identify the individual who committed the crime, nuclear forensics focuses on providing hints on the origin and the history of the seized material. Nuclear forensics uses rather the exclusion principle than directly pointing to one conclusion: databases containing facility specific attributes of nuclear material aid in narrowing down possible origins of the material in question. In order to find the latest legal owner of the nuclear material the isotopic and elemental composition (major elements and impurities) in combination with its physical appearance (dimensions of larger objects; particle form and size of powders) are determined. These three parameters assist in determining the production process and/or reactor type the material was intended for. Additionally the "age", i.e. the time since the last separation, of the material can be determined. This information is of crucial importance for the investigators, since it helps in reducing the number of facilities where the material has possibly been separated considerably due to the fact that all facilities built after the separation date can be ruled out.[4] Knowledge of the date of the last separation of the material also enables the exact initial composition of the material to be calculated. [5]

2 Reference materials for nuclear age dating – status quo

As the Guide to Quality in Analytical Chemistry states, "the value of chemical measurements depends upon the level of confidence that can be placed in the results".[6] In order to ensure a high level of confidence in measurement results in general, quality control and quality assurance systems need to be established. Comparability of results obtained by different laboratories and methods is achieved by comparison to known reference values. Consequently, confidence in measurements is ensured by the verification of measurement results and the establishment of traceability through the use of certified reference materials. Certified reference materials are also required for the validation of measurement procedures and calibration of instruments. Analysts need to prove that their measurement procedures are "fit for purpose", i.e. the measurement performance meets the requirements of the analysis. Although the need to establish the above mentioned goals in order to produce and publish sound analytical results is crucial as such, it is not always straight forward. In addition to that, confidence in the integrity and quality of measurement results and services is of great importance, resulting in more and more laboratories striving for accreditation, e.g. ISO/IEC 17025. [7]

Certified reference materials are defined by ISO Guide 30 as sufficiently homogeneous and stable materials with respect to one or more specified properties. These materials are characterized to be fit for the intended use by a metrologically valid procedure and are accompanied by a certificate that provides the value of the specified property, its associated uncertainty and a statement of metrological traceability.[8] Realistically speaking, it is not always possible to use a certified reference material because of the unavailability of materials certified for the properties under investigation, such as the "age" of a nuclear material. In these cases, it is recommended that "a material with suitable properties and stability should be selected [...] and used as a laboratory measurement standard".[6] It should be noted, however, that the "age" of the material is not a directly measurable quantity. Ratios of the numbers of atoms of the mother nuclide and of the related daughter nuclide are measured. The measurements can be carried out by gamma ray spectrometry or preferably by isotope dilution mass spectrometry. Based on these measurements, the age of the material is calculated. In consequence, the actual measurement requires spike reference materials for quantification of the amount of mother and daughter nuclide as well as isotopic reference materials for calibration of the measurement apparatus (e.g. instrumentation). The motivation for developing age dating reference materials is largely based on the need for validating analytical procedures and for applying quality control (to demonstrate that the procedure is well under control). Providing confidence in measurement results by demonstrating that the whole analytical process is well under control is of major importance in nuclear forensics which is a top priority on the political agenda [9]. Presently, no reference materials certified for their "age" are available. In their absence, researchers have been using materials with well known and well documented separation date as replacement. Thus, scientists have to rely on various sources for "reference ages", for method development and quality control. The sources of information for the given "reference age" (of materials used so far for method development) in literature are fairly inhomogeneous. Yet authors indicate on what grounds they assumed a certain "reference age" such as dates on certificates, old documentation and interlaboratory comparisons [5, 10-15]. Most of those assumed reference dates might be well justified but, the lack of nuclear reference materials actually certified for the separation date leads to situations where different reference ages (separation dates) for the same material can be found in different publications such as for the material SRM 947 in [5] and [13]. Another problem caused by the lack of nuclear reference materials certified for the separation date is the absence of proof of complete separation possibly leading to ambiguous results even when applying sophisticated measurement techniques. In consequence, the availability of nuclear reference materials properly certified for their "age" would provide a more solid metrological basis for age dating measurements and would thus increase the value of the conclusions based on these measurements. It is therefore not surprising that the need for nuclear reference materials certified for age has been repeatedly expressed by members of the nuclear safeguards and nuclear forensics community. Because of this feasibility a study for the development of plutonium reference materials for age dating has recently been started at the Institute for Reference Materials and Measurements (EC-JRC-IRMM) in cooperation with the Institute for Transuranium Elements (EC-JRC-ITU) in order to meet the present needs of laboratories involved in nuclear forensics analysis.

3 Age dating of plutonium

Unstable isotopes decay following distinct decay schemes until a stable isotope is formed, such as illustrated in Figure 1 for the decay of ^{241}Pu. The principle of measuring declining amounts of the originating so called mother isotope relative to the amounts of the formed daughter isotopes has been used for the age determination of minerals and rocks by geologists for many years. The chemical composition of rock mass changes with time, thus the age can be derived from measuring the ratio of mother to daughter isotope. Isotope pairs such as ^{226}Ra/^{238}U, ^{230}Th/^{234}U and ^{231}Pa/^{235}U are deployed as chronometers in geology providing "absolute" methods for the determination of the time that has passed since the formation of the rock [16] whereby the assumption has to be made that during the rock formation parent and daughter isotopes were completely separated during the process. Similarily, the "age" of nuclear material is defined as the time that has passed since the last chemical or physical separation of the mother and daughter isotopes, e.g. ^{241}Pu and ^{241}Am (Figure 1).

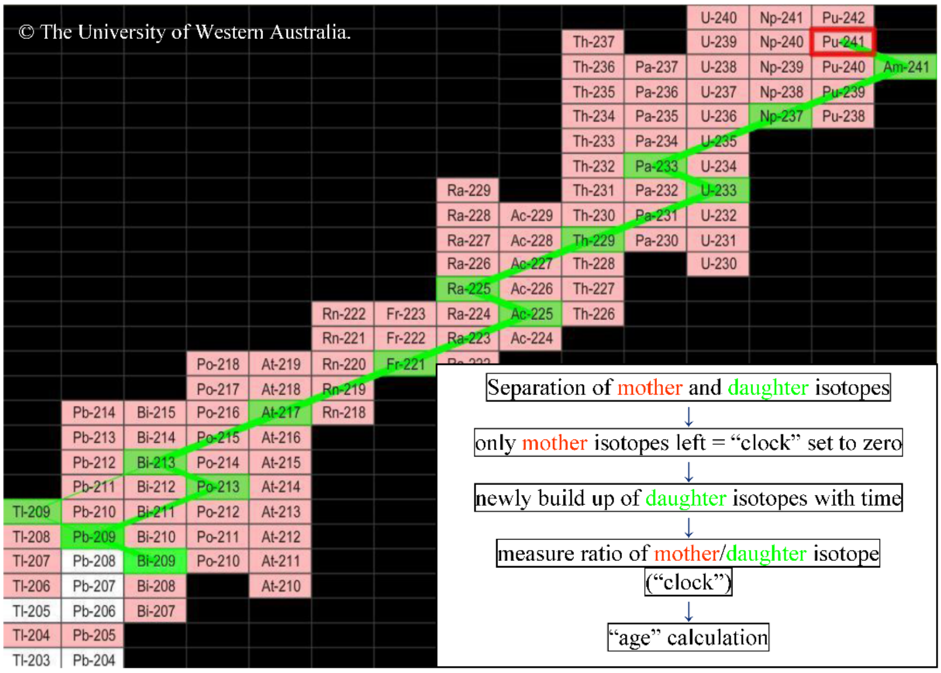


Figure 1. Decay scheme of ^{241}Pu [17]

Assuming that the separation has been complete and all the daughter isotopes have been removed completely from the original material, the age of the material can be determined by measuring the ratio of mother and daughter radionuclides, e.g. ^{241}Pu/^{241}Am. At a given time after the separation and depending on the half-lives of the radionuclides involved, a certain amount of the daughter radionuclide has built up. For the determination of the age of nuclear material, different chronometers or "clocks" can be used. These "clocks" are distinct pairs of mother and daughter radio-nuclides. The isotope pairs formed by plutonium mother isotopes and their respective daughter isotopes plus their half-lives are given in Table 1.

Table 1: Isotope pairs formed by plutonium mother isotopes and their respective daughter isotopes

Clock	Half-life mother	Reference	Half-life daughter	Reference
^{236}Pu/^{232}U	2.87(1) a	[18]	70(1) a	[18]
^{238}Pu/^{234}U	87.74(3) a	[18]	$2.455(6)\cdot10^5$ a	[18]
^{239}Pu/^{235}U	$2.410(3)\cdot10^4$ a	[18]	$7.04(1)\cdot10^8$ a	[18]
^{240}Pu/^{236}U	6561(7) a	[18]	$2.342(4)\cdot10^7$ a	[18]
^{241}Pu/^{241}Am	14.325(24) a	[19]	432.6(6) a	[18]
^{242}Pu/^{238}U	$3.73(3)\cdot10^5$ a	[18]	$4.468(5)\cdot10^9$ a	[18]
^{244}Pu/^{240}Pu	$80.0(9)\cdot10^6$ a	[18]	6561(7) a	[18]

^{241}Pu/^{241}Am, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U are considered useful for age dating of plutonium materials [20]. Equations 1 to 5 illustrate an age calculation using the isotope pair ^{241}Pu/^{241}Am. $^{241}Pu_t$ is the amount of ^{241}Pu at the present time t (i.e. time of the measurement) while $^{241}Pu_0$ is the amount of ^{241}Pu at the time of the separation. The decay constant λ can be calculated from the half-life $t_{1/2}$ according to equation 2. $^{241}Am_t$ is the amount of ^{241}Am at the present time t; $R_{241Pu/241Am}$ is the measured ratio ^{241}Pu/^{241}Am at the present time t.

$$^{241}Pu_t = {}^{241}Pu_0 * e^{-\lambda * t} \qquad [1]$$

$$\lambda = t_{1/2}^{-1} * \ln 2 \qquad [2]$$

$$^{241}Am_t = {}^{241}Pu_0 - {}^{241}Pu_t = {}^{241}Pu_0 *(1 - e^{-\lambda * t}) \qquad [3]$$

$$R_{241Pu/241Am} = {}^{241}Pu_t / {}^{241}Am_t = e^{-\lambda * t} * (1 - e^{-\lambda * t})^{-1} \qquad [4]$$

$$t = \lambda^{-1} * \ln [(R_{241Pu/241Am} + 1) * R_{241Pu/241Am}^{-1}] \qquad [5]$$

For the age estimation of a real sample, such as material seized in nuclear forensics investigations or a dust sample in environmental measurements, it is advisable to use more than one clock in order to ensure the reliability of the results. Otherwise wrong conclusions could be reached: Non matching chronometers can be a result of incomplete separation i.e. not all clocks have been set to "zero" during the separation [10]. Non matching clocks can also result from a sample that is a mixture of two or more different materials. Consequently, a future reference material certified for separation date should ideally be certified for more than one "clock" or several reference materials for different "clocks" need to be developed.

4 Experimental Setup

There are basically three possible strategies to produce isotopic reference materials certified for the age of nuclear material [21]:

- Characterization of an existing (old) material with well-known separation date
- Quantitative separation (set clock to time "zero") of bulk material leading to a material with documented separation date and completeness of separation
- Mixture of purified fractions of mother and daughter isotopes to mimic a certain “age”

This study deals with the first two of those strategies primarily focusing at the characterisation of a known material in the first place. Thus, the first step of this study is to verify the known separation dates of different plutonium materials differing in age and enrichment. Mother (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) and daughter (^{234}U, ^{235}U, ^{236}U, ^{238}U and ^{241}Am) isotope abundances are determined in order to calculate not only the age using different clocks but also to estimate the uncertainties of the calculated ages ideally combining the results of several isotope pairs. The experimental setup for the measurements is shown in Figure 2. Thermal ionisation mass spectrometry (TIMS) is applied for the measurement of the plutonium and uranium isotope ratios. After chemical separation of the plutonium and uranium fractions from the sample matrix, isotope abundance measurements as well as isotope dilution mass spectrometric measurements (IDMS) are performed. ^{241}Am is measured by gamma-ray spectrometry.

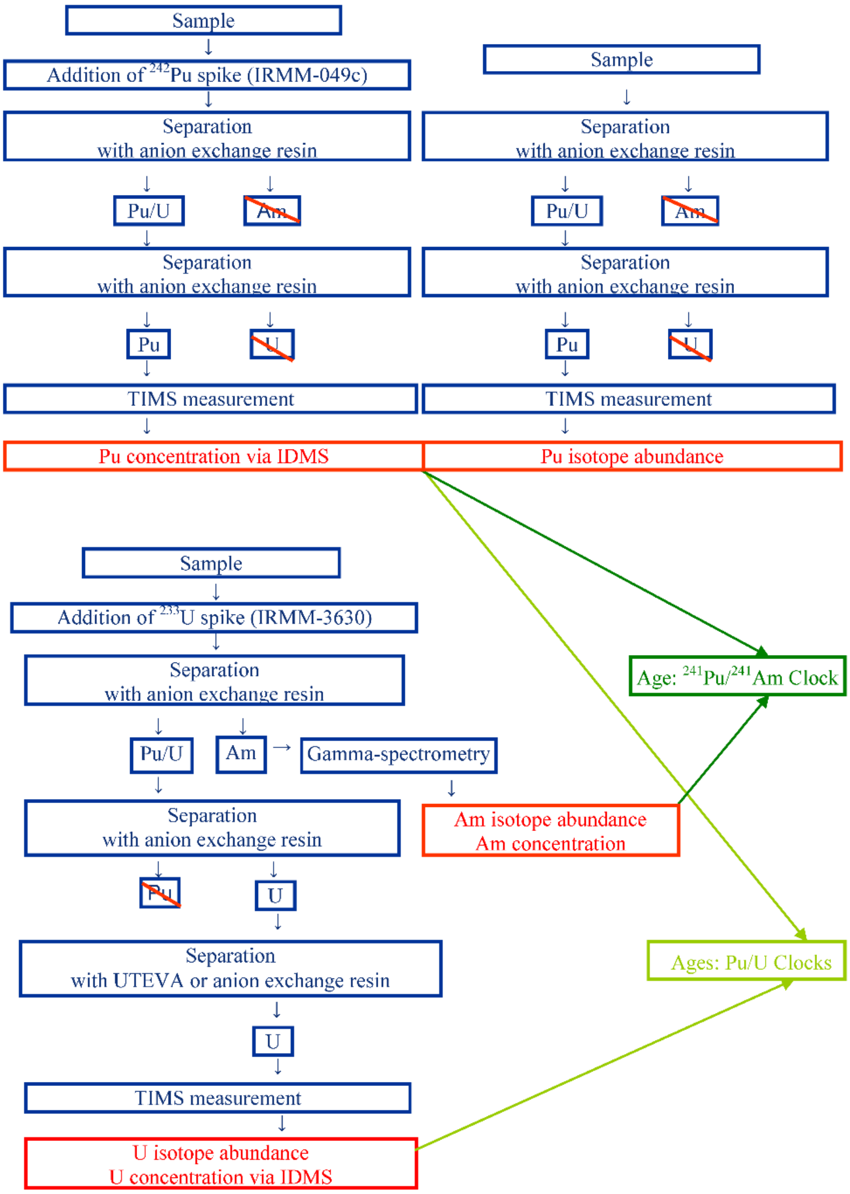


Figure 2. Scheme of analysis for nuclear age dating of Pu materials

5 Selected starting materials

The selected candidate starting materials for reference materials for nuclear age dating are shown in Table 2. The applied classification into grades is explained in Table 3. In the course of this work the well known reference materials certified for isotopic abundance NBS SRM 946, 947 and 948 (NBL CRM 136, 137 and 138) will be investigated among others. Certification for the age of widely distributed materials like the above mentioned provides a powerful tool to scientists to improve the quality of age dating of nuclear material.

Table 2. The candidate starting materials for reference materials for nuclear age dating

		Isotopic composition of plutonium (%)					
Sample	**Material**	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	**grade**
ACH-104-1[2]	PuO_2	0,85	73,32	18,3	5,46	2,08	fuel grade
ACH-104-2[2]	PuO_2	0,07	84,34	14,2	1,03	0,36	fuel grade
ACH-104-3[2]	PuO_2	1,2	62,3	25,4	6,7	4,2	reactor grade
ACH-103[2]	PuO_2	0,01	93,4	6,3	0,2	0,04	weapon grade
NBS 946[3]	$Pu(SO_4)_2.4H_2O$	0,19	86,07	12,51	0,64	0,58	fuel grade
NBS 947[3]	$Pu(SO_4)_2.4H_2O$	0,23	78,76	19,05	0,74	1,22	reactor grade
NBS 948[3]	$Pu(SO_4)_2.4H_2O$	0,01	91,93	7,95	0,08	0,03	fuel grade

Table 3. Classification into grades of plutonium materials by the U.S. Department of Energy [22]

Grades	**Pu-240 Content**
Weapon grade	< 7 %
Fuel grade	7-19 %
Reactor grade	> 19 %

6 Conclusion

Isotopic reference materials certified for the age of nuclear material are clearly needed in the fields of nuclear forensics, since information about the separation date is crucial for nuclear forensic investigators. Knowledge of the age of an unknown sample not only helps to reduce the number of facilities where the material has possibly been separated, but also enables the initial composition of the material to be calculated. Especially in a highly sensitive field like nuclear forensics where measurement results can potentially lead to far reaching consequences the reliability of the obtained age of an unknown sample must be assured by the use of reference materials certified for the property of "age". These certified reference materials should combine the following properties:

- Certification for the time elapsed since the last separation, i.e. removal of the daughter isotopes from the mother isotope.
- The completeness of this separation must be guaranteed for the clock(s) the material is certified for.
- Ideally, one single certified reference material should be certified for several clocks; alternatively, a set of certified reference materials complementing one another should be made available.
- The value for the age of the certified reference material and its uncertainty should ideally combine uncertainties obtained from all the clocks under investigation

A feasibility study for such a certified reference material for the age of plutonium material is currently conducted by the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Geel, Belgium in cooperation with the Institute for Transuranium Elements, Karlsruhe, Germany.

References

1. IAEA. *International Status and Prospects of Nuclear Power.* 2009 [cited; Available from: http://www.iaea.org/Publications/Booklets/NuclearPower/np08.pdf

---

[2] Material originating from BELGONUCLEAIRE, Dessel, Belgium

[3] Material originating from National Bureau of Standards, Washington, D.C., USA

2. Obama, B. *Remarks by President Barack Obama; April 5, 2009; Hradcany Square, Prague, Czech Republic.* Speeches & Remarks 2009 [cited 2010 11.08.2010]; Available from: http://www.whitehouse.gov/the_press_office/Remarks-By-President-Barack-Obama-In-Prague-As-Delivered/.
3. Mayer, K., M. Wallenius, and T. Fanghänel, *Nuclear forensic science--From cradle to maturity.* Journal of Alloys and Compounds, 2007. 444-445: p. 50-56.
4. Redermeier, A., *Fingerprinting of Nuclear Material for Nuclear Forensics.* ESARDA BULLETIN, 2009(43): p. 71-76.
5. Wallenius, M., P. Peerani, and L. Koch, *Origin Determination of Plutonium Material in Nuclear Forensics.* Journal of Radioanalytical and Nuclear Chemistry, 2000. 246(2): p. 317-321.
6. CITAC and Eurachem, *Guide to Quality in Analytical Chemistry - An Aid to Accreditation.* CITAC/Eurachem Guide. 2002.
7. ISO, *ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories.* 2005, Geneva: International Organization for Standardization.
8. ISO, *ISO Guide 30:1992/Amd 1:2008 – Terms and definitions used in connection with reference materials.* 2008, Geneva: International Organization for Standardization.
9. Ulicny, W., *oral presentation: National Technical Nuclear Forensics: Overview, QA, and Expertise Development* W. Ulicny, Editor. 2009, U.S. Department of Homeland Security, Domestic Nuclear Dedection Office
10. Wallenius, M. and K. Mayer, *Age determination of plutonium material in nuclear forensics by thermal ionisation mass spectrometry.* Fresenius' Journal of Analytical Chemistry, 2000. 366(3): p. 234-238.
11. Wallenius, M., *Origin determination of reator produed plutonium by mass spectrometrc techniques: application to nuclear forensic science and safeguards*, in *Faculty of Science, Department of Chemistry, Laboratory of Radiochemistry.* 2001, University of Helsinki: Helsinki. p. 68.
12. Nygren, U., H. Ramebäck, and C. Nilsson, *Age determination of plutonium using inductively coupled plasma mass spectrometry.* Journal of Radioanalytical and Nuclear Chemistry, 2007. 272(1): p. 45-51.
13. Shinonaga, T., et al., *Age determination of single plutonium particles after chemical separation.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2009. 64(1): p. 95-98.
14. Nguyen, C.T., *Verification of the 239Pu content, isotopic composition and age of plutonium in Pu-Be neutron sources by gamma-spectrometry.* Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2006. 251(1): p. 227-236.
15. Keegan, R.P. and R.J. Gehrke, *A method to determine the time since last purification of weapons grade plutonium.* Applied Radiation and Isotopes, 2003. 59(2-3): p. 137-143.
16. Watchman, A.L. and C.R. Twidale, *Relative and [`]absolute' dating of land surfaces.* Earth-Science Reviews, 2002. 58(1-2): p. 1-49.
17. UWA. *decay chain explorer.* 2007 [cited 17.08.2010]; Available from: http://spice.duit.uwa.edu.au/samples/ast0197/.
18. Be, M., V. Chiste, and C. Dulieu, *Note Technique DETECS/LNHB/2006-58: Halve-lives, Table of recommended values.* 2006: Laboratoire Natonal Henri Becquerel.
19. Wellum, R., A. Verbruggen, and R. Kessel, *A new evaluation of the half-life of 241Pu.* Journal of Analytical Atomic Spectrometry, 2009. 24(6): p. 801-807.
20. Mayer, K., M. Wallenius, and I. Ray, *Nuclear forensics - A methodology providing clues on the origin of illicitly trafficked nuclear materials.* Analyst, 2005. 130(4): p. 433-441.
21. Bürger, S., et al. *Radiochronometry of nuclear materials.* in *49th INMM Annual Meeting.* 2008. Nashville, Tennessee USA: Institute of Nuclear Materials Management.
22. DOE. *Additional Information Concerning Underground Nuclear Weapon Test of Reactor-Grade Plutonium.* 2010 January 21, 2010 [cited 17.08.2010]; Available from: https://www.osti.gov/opennet/forms.jsp?formurl=document/press/pc29.html#ZZ3.

2.8 Publication VIII

Isotope Ratios Measurements in Environmental Samples using Thermal Ionization Mass Spectrometry (TIMS) and Filament Carburization

Rožle Jakopič, Stephan Richter, Monika Sturm, Heinz Kühn and Yetunde Aregbe

Institute for Reference Materials and Measurements
Joint Research Centre, European Commission
Retieseweg 111, Geel 2440 Belgium
E-mail: rozle.jakopic@ec.europa.eu

Abstract:

Thermal Ionization Mass Spectrometry (TIMS) is a widely used mass spectrometric technique for the determination of the isotopic composition of plutonium. Moreover, advances in the last decades have led to increasingly high precision and accuracy of the isotope ratio measurements using multiple ion counting detection system. High precision plutonium isotope measurements would allow distinguishing different types of plutonium contamination and could be used as a finger print to track various sources of plutonium in the environment. To measure plutonium isotope ratios with high precision and accuracy, stable ion beams with high intensity are desired. This is sometimes difficult to achieve, especially when measuring plutonium in low amounts.

In this study, carburization of the Re filaments was used to increase the ionization efficiency of plutonium. Carburized filaments were prepared in a special vacuum chamber in which benzene vapour was introduced as a pure source of a carbon. As a result of the carburization of the filaments higher efficiencies were obtained. This carburization technique was combined with a multi-dynamic measurement technique using the multiple ion counting system and applied to two sediment samples IAEA 135 and IAEA 368; respectively. The results in term of plutonium isotope ratios are presented and compared with the literature values.

Keywords: TIMS; Pu isotope ratios; carburization; environmental samples

1. Introduction

Various man-made radioactive elements are present in the environment as a result of human activities. Such element is also plutonium which can be regarded as one of the most important nuclides for safeguards. Plutonium is found in the environment as a result of nuclear weapon tests, nuclear reactor accidents, discharges from reprocessing plants, dumping of nuclear waste and accidents with nuclear devices. On the other hand, plutonium is also produced from uranium in nuclear reactors. For assessing different sources of plutonium contamination, information on the isotopic composition is necessary. It is known that the ^{240}Pu/^{239}Pu isotope ratio is a good indicator to identify different types of plutonium contamination, however also other plutonium isotope ratios, such as ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu, could be useful as additional information on the production processes of nuclear material. For global fallout the average ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu isotope ratios are 0.176 ± 0.014 and 0.0086 ± 0.0017, respectively [1]. Weapons grade plutonium can be characterized by ^{240}Pu/^{239}Pu ratios < 0.07, whereas in plutonium from nuclear reactors, ratios of 0.4 or higher can be expected [2-5].

For determination of plutonium isotope ratios mass spectrometric techniques such as thermal ionization mass spectrometry (TIMS), accelerator mass spectrometry (AMS) and inductively coupled plasma mass spectrometry (ICP-MS) are most widely used. They offer high precision and accurate results which would enable to better distinguish between different types of Pu contamination. To measure smallest amounts of plutonium (< 10^{-10} g), high ionization efficiency and a sophisticated detection system are desirable; especially if isotopes having low abundance need to be measured. Thermal ionization mass spectrometry (TIMS) in combination with a multiple ion counting detection (MIC) system holds the potential to meet this requirement.

Different approaches are described in the literature in order to enhance the overall efficiency of plutonium. In this study, carburization of the filaments using pure benzene gas as a carbon provider was tested and implemented at IRMM. Carbon serves as a reducing agent, promoting the production of actinide ions at the expense of undesirable oxide species. The higher proportion of +1 ions resulted in a substantially more intense ion beam for a given amount of material [3, 6]. The carburization technique in combination with the multi-dynamic measurement technique using the MIC system was already applied to the NBL -137 isotopic standards and NUSIMEP 5 inter-laboratory campaign samples [3, 7]. Here, the results for the complete isotopic composition for two reference sediment samples IAEA 135 and IAEA 368 are presented.

2. Experimental

2.1. Chemical separation of Pu

Samples were leached with hot 8M HNO_3 for 3h. After the separation of the leachant and the residue, the actinides were co-precipitated on CaC_2O_4 to remove iron. The oxalate precipitate was fumed several times with conc. HNO_3 and H_2O_2 and dissolved in 2M HNO_3. After the adjustment of the oxidation state of Pu to Pu(IV), the solution was made 8M HNO_3 using conc. HNO_3 and loaded on an anion exchange column. The column was washed with 8M HNO_3 and 9M HCl to remove matrix elements and thorium. Pu(III) was eluted from the column with 0.1M NH_4I-9MHCl and the solution evaporated to near dryness [8]. Pu fraction was further purified with TEVA columns.

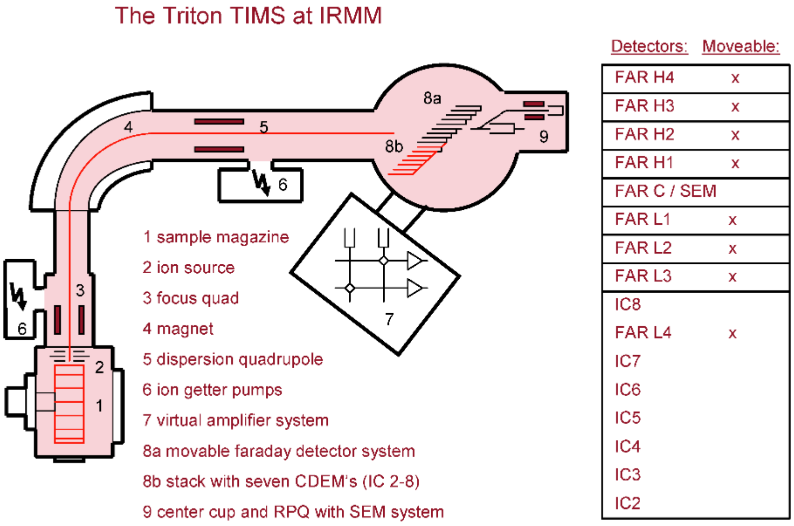
2.2. Carburization of the Re filaments

Rhenium filaments were placed into the filament carburization device and evacuated. After a sufficient vacuum pressure was established (< $1 \cdot 10^{-6}$ mbar), the filaments were subjected to a heating routine for degassing and cleaning. After degassing the benzene was introduced into the chamber through a valve and the filament current was adjusted to a 4A, corresponding to a temperature of ca. 1600-1700 °C. During the carburization, the benzene pressure was kept constant at the pressure of $5 \cdot 10^{-3}$ mbar for 1 hour. After the carburization was complete, the filaments were left to cool overnight before loading Pu solution [3].

Figure 1: Carburization device (left) and a vacuum chamber with a filament magazine (right).

2.3. Triton TIMS

On the IRMM Triton thermal ionization mass spectrometer, nine Faraday cups, one conventional discrete dynode electron multiplier, and seven CDEMs (continuous dynode electron multiplier) were installed. The width of the CDEMs is identical to the standard Faraday cups, and thus the ion counters can be aligned with single unit mass spacing for the measurement of high mass elements such as U and Pu (see Fig. 1). The advantage of multiple ion counting is the simultaneous collection of several isotopes of a given element. It overcomes many of the problems such as transient signal variation in sample emission and ionization, which would significantly reduce the attainable precision of a single collector measurement. For a given sample, a multiple ion counting measurement makes use of a greater number of ions counted for each isotope compared to a peak-jumping measurement using only a single ion counting detector and therefore provides improved counting. Multiple ion counting is thus advantageous for the cases where the sample size is restricted [9, 10].



Detectors:	Moveable:
FAR H4	x
FAR H3	x
FAR H2	x
FAR H1	x
FAR C / SEM	
FAR L1	x
FAR L2	x
FAR L3	x
IC8	
FAR L4	x
IC7	
IC6	
IC5	
IC4	
IC3	
IC2	

Figure 2: The configuration of the Triton TIMS at IRMM.

2.4. Multi-dynamic measurement technique

Multi-dynamic measurement technique provides improvements in accuracy and precision by applying an internal calibration for the CDEM detectors during the measurement. When all isotopes of interest are detected simultaneously in several steps of a multi-dynamic mass cycle, the isotope ratio can be calculated in a way that the calibration factors of all ion counters are eliminated for so called minor ratios, e.g. for the ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu ratios in case of plutonium. In contrast, the so called major ratio ^{240}Pu/^{239}Pu is measured in a peak-jumping mode using IC3 in steps 1/2, using IC4 in steps 2/3 and using IC5 in steps 3/4, see Table 1, and is therefore also independent on the efficiencies of the CDEMs. A correction factor, the so-called K-factor, for the ^{240}Pu/^{239}Pu ratio has to be determined externally using the known ^{240}Pu/^{239}Pu isotope ratio of the NBL-137 isotopic standard in order to correct the major ratio for mass fractionation, to be measured using the same technique on the same sample magazine [9, 10]. Table 1 shows the mass cycle for plutonium isotopes in a multi-dynamic measurement.

Channel:	IC2	IC3	IC4	IC5	IC6	IC7
Step:						
1	239	240	241	242		
2		239	240	241	242	
3			239	240	241	242
4				239	240	241

Table 1: The multi-dynamic mass cycle for plutonium measurement

3. Results and Discussion

Different parameters such as carburization current, benzene pressure and time of exposure were studied in order to find the best conditions for an isotopic measurement. The efficiency of plutonium was improved significantly. Moreover, the carburization technique in combination with multi-dynamic measurement technique using the multiple ion counting system (MIC) was successfully applied to NBL-137 isotopic standard and NUSIMEP-5 samples of the inter-laboratory comparison campaign. The detailed results are published in [3].

In this paper, the results of analysis of two reference materials IAEA 135 and IAEA 368 are presented. IAEA 135 (Irish Sea Sediment) is the sediment influenced by the discharges from the reprocessing plant in Sellafield, and IAEA 368 (Pacific Ocean Sediment) is the sediment collected at the French Polynesia, where nuclear tests were carried out.

	IAEA 135 (Irish Sea Sediment)		IAEA 368 (Pacific Ocean Sediment)	
Isotope ratio	Average	Rel. Uc., k=2 [%]	Average	Rel. Uc., k=2 [%]
$^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$	0.2129	0.23	0.03419	0.34
$^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$	0.00751	0.36	0.000211	8.3
$^{242}\mathrm{Pu}/^{239}\mathrm{Pu}$	0.00713	0.51	0.000334	25.3

Table 2: Plutonium isotope ratios in IAEA 135 and IAEA 368.

In table 2, the obtained $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$, $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ and $^{242}\mathrm{Pu}/^{239}\mathrm{Pu}$ isotope ratios are given for IAEA 135 and IAEA 368. The value for the major isotope ratio in IAEA 135, $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$, is 0.21290 ± 0.00049. This value is higher than 0.176 ± 0.014, the average ratio due to global fallout [1]. The results agree well with the value of 0.207 ± 0.006 obtained by Lee et al. [11] and 0.211 ± 0.004 given by Muramatsa et al. [5] which were determined using ICP-MS or AMS. The uncertainty of the new TIMS value is about a factor of 10 smaller. The values for $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ and $^{242}\mathrm{Pu}/^{239}\mathrm{Pu}$ isotope ratios in IAEA 135 were 0.007510 ± 0.000027 and 0.007130 ± 0.00036, respectively. It can also be seen that despite approximately 100 times lower values for minor isotopes in IAEA 135, the uncertainty was still in the same order of magnitude as it was for the major ratio. The $^{242}\mathrm{Pu}/^{239}\mathrm{Pu}$ agrees within the uncertainty with the value of 0.0068 ± 0.0007 reported by Lee at al. [11], while the $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ isotope ratio was lower than 0.0221 ± 0.0080 observed by Lee.

On the other hand, the $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ value obtained in IAEA 368 was 0.03419 ± 0.00011. This is much lower value than the average for global fallout. In fact the results indicate that the sediment contained weapons grade plutonium ($^{240}\mathrm{Pu}/^{239}\mathrm{Pu} < 0.07$), which was already assumed. The result for $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ agrees within the uncertainty with the value of 0.043 ± 0.008 reported by Muramatsu et al. [5]. The range of obtained results for $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ and $^{242}\mathrm{Pu}/^{239}\mathrm{Pu}$ was 10 times lower than in IAEA 135, so higher uncertainties were expected. The values for $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ and $^{242}\mathrm{Pu}/^{239}\mathrm{Pu}$ isotope ratios in IAEA 368 were 0.000211 ± 0.000018 and 0.000334 ± 0.000085, respectively.

4. Conclusions

It has been shown that the multi-dynamic technique using the multiple on counting system (MIC) and filament carburization could be applied to different environmental samples. As a result of enhanced efficiency of plutonium due to the carburization technique, results with small uncertainties were obtained not only for the $^{240}\mathrm{Pu}/^{239}\mathrm{Pu}$ isotope ratio but also for $^{241}\mathrm{Pu}/^{239}\mathrm{Pu}$ and $^{242}\mathrm{Pu}/^{239}\mathrm{Pu}$. This is very important because the minor ratios provide additional information on the source identification of plutonium in the environment. Unfortunately, little information is available on plutonium isotope ratios in the literature so the results obtained in this study could contribute and complement the "data base" for values for reference materials already existing in the literature.

5. Acknowledgements

The authors wish to express their thanks to S. Balsley and A. Shakhashiro from IAEA, Vienna who kindly supplied the IAEA 368 and IAEA 135 reference samples.

6. References

[1] Krey, P. W., Hardy, E. P., Pachucki, C., Rourke, F., Coluzza, J., Benson, W. K.; *Mass isotopic Composition of Global Fall-out Plutonium in Soil; Transuranium Nuclides in the Environment; IAEA-SM-199/3;* IAEA; Vienna; 1976; p 671.

[2] Yamana, H., Yamamoto, T., Moriyama, H.; *Isotopic ratio of Pu released from fuel cycle facilities – importance of radiochemically pure* ^{236}*Pu as a tracer; Plutonium in the Environmen – Edited proc.* 2nd *Invited International Symposium; A. Kudo (Ed.); Elsiever,* Amsterdam; 2001; p 31.

[3] Jakopic, R., Richter, S., Kühn, H., Benedik, L., Pihlar, B., Aregbe, Y; *Isotope ratio measurements of pg-size plutonium samples using TIMS in combination with "multiple ion counting" and filament carburization; Int. J. Mass Spectrom.; 279;* 2009; p 87-92.

[4] Hrnecek, E., Jakopic, R., Wallner, A., Steier, P.; *A combined method for the determination of the isotopic vector of plutonium isotopes in environmental samples; J. Radioanal. Nucl. Chem.; 276;* 2008; p 789-793.

[5] Muramatsu, Y., Uschida, S., Tagami, K., Yoshida, S., Fujikawa, T.; *Determination of plutonium concentration and its isotopic ratio in environmental materials by ICP-MS after separation using ion-exchange and extraction chromatography; J. Anal. At. Spectrom.; 14;* 1999; p 859-865.

[6] Kelley, J. M., Robertson, D. M.; *Plutonium ion emission from carburized rhenium mass spectrometer filaments; Anal. Chem.; 57;* 1985; p 124-130.

[7] Benedik, L., Altzitzoglou, T., van Ammel, R., Pomme, S., Richter, S., Sibbens, G., Stolarz, A., Verbruggen, A; Wellum, R.; *NUSIMEP 5: uranium, plutonium and caesium abundances in a saline matrix*, EUR 22286 EN.

[8] Jakopic, R., Tavcar, P., Benedik, L.; *Sequential determination of Pu and Am radioisotopes in environmental samples; a comparison of two separation procedures; Appl. Radiat. Isot.; 65;* 2007; p 504-511.

[9] Richter, S., Alonso-Munuz, A., Kühn, H., Stolarz, A., Benedik, L; Wellum, R.; *Implementing the multiple ion counting system for the Triton TIMS at IRMM and Introducing the multi-dynamic measurement technique for low-level actinide isotopic analysis*; EUR 22225 EN.

[10] Richter, S., Ott, U., Bergmann, F., Pihlar, B., Aregbe, Y; *Multiple ion counting in isotopic abundance mass spectrometry; Int. J. Mass Spectrom. Ion Processes; 136;* 1994; p 91-100.

[11] Lee, S. H., Gastaud, J., La Rosa, J. J., Liong Wee Kwong, L, Povinec, P. P., Wyse, E., Fifield, L. K., Hausladen, P. A., Di Tada, L. M., Santos, G. M.; *Analysis of plutonium in marine samples by radiometric, ICP-MS and AMS techniques; J. Anal. Nucl. Chem.; 248;* 2001; p 757-764.

3 Summary and conclusions

Nuclear forensic investigations play a vital part in the field of nuclear security. Nuclear forensic analytical results need to be accurate and precise and it also needs to be ensured that they can withstand scrutiny in a court of law and from the international community. CRMs tailor-made for nuclear forensic applications are therefore indispensable, which has also been emphasised at the last Nuclear Security Summit, Washington, USA 2016. At present there are no available plutonium CRMs certified for their separation date. In this doctorate thesis the need for certified reference materials for the age determination of plutonium for nuclear forensic applications has been discussed and documented in detail and a foundation has been laid towards the development of plutonium CRMs certified for their separation date. The capability for the age determination of plutonium has been established at EC-JRC-G.2, Geel, Belgium where the experiments for this thesis were carried out. As a result of this work plutonium CRMs certified for their production date are envisaged to be produced in the foreseeable future by the JRC. Possible candidate materials for the preparation of such a CRM have been identified.

Furthermore, the need for a suitable commercially available ^{243}Am IDMS spike CRM has been identified for the age determination of plutonium via the ^{241}Pu/^{241}Am chronometer by means of mass spectrometric measurements. This marks the starting point for a joint project of CEA/CETAMA (CEA/DEN Marcoule, France) and EC-JRC for the preparation and certification of such a spike. The author's current position at IAEA SG Laboratories in Seibersdorf, Austria, has allowed the author to actively participate in this project under an EC-IAEA support task in order to enhance the cooperation between CRM users and producers on a technical level.

The determination of the age or production date of uranium and plutonium samples has for decades been a pillar of nuclear forensic investigations. Knowledge of the age of seized nuclear material can help considerably to limit the number of facilities where seized plutonium samples could have been produced or processed. The major part of the research accomplished during this doctorate thesis has therefore been dedicated to plutonium age determination and a thorough examination of the Pu/U chronometers for the age determination of plutonium. The relationship of the results of the more regularly applied Pu/U chronometers ^{238}Pu/^{234}U, ^{239}Pu/^{235}U and ^{240}Pu/^{236}U and the often neglected or dismissed radio-chronometer ^{242}Pu/^{238}U was scrutinized and re-evaluated. It has been shown that the relationship of these Pu/U chronometers relative to each other can not only boost the confidence in the obtained production date for a particular plutonium sample, but can also - in the case of mismatched age dating results for different chronometers - help to reveal the history of the plutonium sample under investigation. The pattern formed by the Pu/U chronometers' age determination results may help to identify incomplete separation during the production of the material and give a maximum age for the sample. In other cases this may point not only towards the presence of non-radiogenic uranium in the sample but may also help reveal the likely nature of this uranium contamination. The presented work has therefore not merely contributed towards making inconclusive results conclusive but also in extracting additional information concerning the history of the sample under investigation 'hidden' within the sample itself. A 'roadmap' for the dating of plutonium materials via the respective Pu/U chronometers has been established and it has been shown that the ^{242}Pu/^{238}U radio-chronometer rightfully deserves a place among the Pu/U chronometers as a sensitive indicator of the presence of non-radiogenic uranium for the age determination of plutonium for nuclear forensic purposes.

The need for up-to-date half-lives has been highlighted as well as the need for state-of-the-art IDMS spike CRMs for both plutonium and uranium.

Furthermore, an optimized method for U/Pu separation has been developed and a novel approach for the measurement of uranium isotopes by total evaporation TIMS with a double filament setup combined with filament carburization has been investigated. This specific measurement approach allows the measurement of the isotopic composition of uranium separated from a plutonium matrix and thus still containing traces of plutonium. This approach not only achieved reliable results for the ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, and ^{240}Pu/^{236}U chronometers in order to determine the age of plutonium samples but also demonstrated the use of the ^{242}Pu/^{238}U isotope amount ratio as a highly sensitive indicator for residual non-radiogenic uranium in the plutonium sample without the need for any additional analytical instrumentation in addition to TIMS.

It was shown that by the application of filament carburization for TE TIMS measurements applying the double filament technique, a separation of residual plutonium in the uranium fraction was achieved directly on the filament. The findings could also prove to be useful for other applications such as the measurement of ^{238}U and ^{238}Pu in MOX type samples without (complete) chemical separation in the field of nuclear safeguards in addition to the investigated use for nuclear forensics purposes.

4 Appendices

4.1 List of Tables

4.2 List of Figures

4.3 List of Abbreviations

ANOVA	Analysis Of Variance
CEA	Commissariat à l'énergie atomique et aux énergies alternatives
CETAMA	CEA Committee for the establishment of analysis methods
CPC	Controlled Potential Coulometry
CRM	Certified Reference Material
D	D statistic (quantification of observed discrepancies between inspection data and reported data)
DEN	Direction de l'Energie Nucléaire of CEA
DU	Depleted Uranium
EC	European Commission
EC-JRC-G.2	European Commission Joint Research Centre – Directorate G – Nuclear Safety & Security - Unit G.2 - Standards for Nuclear Safety, Security and Safeguards, Geel, Belgium, formerly Institute for Reference Materials and Measurements (EC-JRC-IRMM)
ERU	Re-Enriched Uranium
ESARDA	European Safeguards Research and Development Association
EU	European Union
Euratom	European Atomic Energy Community
FGPu	Fuel-grade Plutonium
GUM	Guide to the Expression of Uncertainty in Measurement
HEU	High-Enriched Uranium
HLW	High Level Waste
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IEC	International Electrotechnical Commission
INMM	Institute for Nuclear Materials Management
IRM	Isotopic Reference Material
IRMM	Institute for Reference Materials and Measurements
ISO	International Organization for Standardization
ITDB	IAEA Illicit Trafficking Database
ITU	Institute for Transuranium elements
ITV	International Target Value
ITWG	Nuclear Forensics International Target Working Group

JAEA	Japan Atomic Energy Agency
JRC	Joint Research Centre
KRI	V.G. Khlopin Radium Institute
LEU	Low-Enriched Uranium
LNHB	Laboratoire National Henri Becquerel
MGPu	MOX-grade Plutonium
MOX	Mixed Oxide Fuel
MTE	Modified Total Evaporation
MUF	Material Unaccounted For
NBL	New Brunswick Laboratory
NPT	Treaty on the Non-Proliferation of Nuclear Weapons
NU	Natural Uranium
QC	Quality Control
REE	Rare Earth Elements
REIMEP	Regular European Inter-Laboratory Measurement Evaluation Programme
RepU	Reprocessed Uranium
RGPu	Reactor-grade Plutonium
SCALE	Standardised Computer Analysis for Licensing Evaluation
SGPu	Super-grade Plutonium
SI	International System of Units
SIMS	Secondary Ion Mass Spectrometry
SRD	Shipper-Receiver Differences
TE	Total Evaporation
TIMS	Thermal Ionization Mass Spectrometry
WDX	Wavelength-Dispersive X-ray spectrometry
WGDA	ESARDA Working Group on Standards and Techniques for Destructive Analysis
WGPu	Weapons-grade Plutonium
WGU	Weapons-grade Uranium

4.4 Curriculum Vitae

.

PERSONAL DATA

Name	Monika Sturm
Date and place of birth	1982/07/28 in Leoben, Austria
Nationality	Austrian

CONTACT

E-Mail	m.sturm@iaea.org
Office phone:	(+43-1) 2600-28125
Current office address:	IAEA Laboratories, A-2444 Seibersdorf, Austria

EDUCATION

October 2009 to date	Doctorate thesis at the University of Natural Resources and Life Sciences (BOKU), Vienna, Austria; the scientific work was performed at the European Commission Joint Research Centre – Directorate G – Nuclear Safety & Security - Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (EC-JRC-G.2) Geel, Belgium, formerly Institute for Reference Materials and Measurements (EC-JRC-IRMM) Title: ‘Reference materials for age dating in nuclear forensics’
April 2008	Graduation from the University of Natural Resources and Life Sciences (BOKU), Vienna, Austria, receiving the academic degree of Diplomingenieur (equivalent to Master of Science); Summa cum Laude (‘Mit Auszeichnung bestanden’)
2007 – 2008	Master's thesis at the Institute of Analytical Chemistry at the Department of Chemistry, University of Natural Resources and Life Sciences (BOKU), Vienna, Austria

	Title: ‘Migration studies of fish by measurement of strontium isotope ratios and multi-elemental patterns in otoliths using LA-ICP-MS’
2000 – 2008	Study of Food Science and Biotechnology at the University of Natural Resources and Applied Life Sciences (BOKU), Vienna, Austria
2000	Matura (school leaving certificate, university entry qualification), Summa cum Laude (‘Mit ausgezeichentem Erfolg’)
1992 – 2000	Secondary school (Realgymnasium); BG/BRG Leoben Neu, Leoben, Austria

WORK EXPERIENCE

March 2014 to date	Mass Spectrometry Operator at the International Atomic Energy Agency (IAEA); Department of Safe Guards, Division of Safe Guards Analytical Services, IAEA Laboratories, Seibersdorf, Austria Mass spectrometry analysis of safeguards samples by TIMS and rigorous evaluations of data generated on samples, standards, and quality check materials to ensure that the required level of quality is maintained, followed by data reporting to a LIMS system.
October 2009 – September 2012	Grant holder at the European Commission Joint Research Centre – Directorate G – Nuclear Safety & Security - Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (EC-JRC-G.2) Geel, Belgium, then Institute for Reference Materials and Measurements (EC-JRC-IRMM) (see also above in Education)
May 2008 - January 2009	Traineeship at the Isotope Measurement Unit of the Institute for Reference Materials and Measurements (EC-JRC-IRMM), Geel, Belgium (now European Commission Joint Research Centre – Directorate G – Nuclear Safety & Security - Unit G.2 - Standards for Nuclear Safety, Security and Safeguards (EC-JRC-G.2) Geel, Belgium) Installation of an Elan 6000 quadrupole ICP-MS in the controlled area, development and optimisation of a sample

	preparation method for the complete dissolution of soil samples using microwave digestion, method development and measurements on the Elan 6000 ICP-MS, basic knowledge in TIMS
Summer 2005	Work placement at AGES – Austrian Agency for Health and Food Safety, Section for alcoholic, non-alcoholic drinks and dietary supplements, Vienna, Austria Various jobs in the chemical laboratory including HPLC
Summer 2005	Work placement at Gösser Brewery, Leoben, Austria Routine analysis of beer in the chemical laboratory
Winter 2003	Work placement at Austria Hefe - Mautner Markhof, Vienna, Austria Routine analysis of baker's yeast in the chemical laboratory

OTHER RELEVANT TRAINING

ITRAC-3: 3rd International Training Course on Illicit Trafficking and Radiological Consequences with Nucleonica

Organized by EC-JRC-ITU, May 11-13, 2011, Haus der Wirtschaft, Karlsruhe, Germany

Advanced course 'Safeguards'

Organized by SCK-CEN, April 31 and May 1, 2011, SCK, Mol, Belgium

Use of Reference Materials and the Estimation Of Measurement Uncertainty

Organized by EC-JRC-IRMM, April 27-28, 2011, IRMM, Geel, Belgium

“Introduction to Nucleonica – a 1-day training course"

Organized by EC-JRC-ITU, January 25, 2011, EC-JRC-ITU, Karlsruhe, Germany

6th ESARDA Course on Nuclear Safeguards and Non-Proliferation

Organised by the European Safeguards Research & Development Association (ESARDA) hosted by the Nuclear Safeguards Unit of the Institute for the Protection and Security of the Citizen (EC-JRC-IPSC), March 21-26 2010, Ispra, Italy

Production of Certified Reference Materials
Organized by EC-JRC-IRMM, December 14-15, 2009, IRMM, Geel, Belgium

GRANTS

Merit scholarships (Leistungsstipendium):
University of Natural Resources and Life Sciences, Vienna (2001)
University of Natural Resources and Life Sciences, Vienna (2002)
University of Natural Resources and Life Sciences, Vienna (2003)
University of Natural Resources and Life Sciences, Vienna (2004)

LANGUAGE SKILLS

German	mother tongue
English	fluent in writing and speaking
Dutch	basic knowledge

PBLICATIONS

PEER-REVIEWED ARTICLES

Sturm M., S. Richter, Y. Aregbe, R. Wellum, T. Prohaska, Optimized Chemical Separation and Measurement by TE TIMS Using Carburized Filaments for Uranium Isotope Ratio Measurements Applied to Plutonium Chronometry. Analytical Chemistry 88 (12), 2016: p. 6223-6230.

Sturm, M., S. Richter, Y. Aregbe, R. Wellum, S. Mialle, K. Mayer, T. Prohaska, Evaluation of chronometers in plutonium age determination for nuclear forensics: What if the ‘Pu/U clocks’ do not match?, Journal of Radioanalytical and Nuclear Chemistry, 2014: p. 1-13.

Jakopic R., M. Sturm, M. Kraiem, S. Richter, Y. Aregbe, Certified reference materials and reference methods for nuclear safeguards and security. Journal of Environmental Radioactivity, 2013. 125:p. 17-22.

Jakopic R., J. Bauwens, S. Richter, M. Sturm, A. Verbruggen, R. Wellum, R. Eykens, F. Kehoe, H. Kuehn, Y.Aregbe, Preparation and Development of New Pu Spike Isotopic Reference Materials at IRMM. In: 33rd ESARDA Annual Meeting - Symposium on Safeguards and Nuclear Material Management; 16 May 2011; Budapest (Hungary). ESARDA Bulletin December 2011 (46); 2011. p. 65-71. JRC65089

Zitek, A., M. Sturm, H. Waidbacher and T. Prohaska, Discrimination of wild and hatchery trout by natural chronological patterns of elements and isotopes in otoliths using LA-ICP-MS. Fisheries Management and Ecology, 2010. 17(5): p. 435-445.

OTHER PUBLICATIONS

Sturm, M., Destructive Analysis: Effective Analytical Support to Nuclear Safeguards and Non-Proliferation. ESARDA BULLETIN, 2010(45): p. 56-65.

http://esarda2.jrc.it/bulletin/bulletin_45/B_2010_045_11.pdf

CONFERENCE PROCEEDINGS

Sturm M., S. Richter, Y. Aregbe, R. Wellum, T. Altzitzoglou, V. Jobbagy, S. Mialle, K. Mayer , T. Prohaska. Age determination of plutonium for nuclear forensics. In Conference Proceedings: 35th ESARDA Symposium proceedings, Bruges, 27-30 May, ISBN: 978-92-79-32730-8, Institute for Transuranium Elements; 2013. p. 572-577. JRC83924

Sturm M., S.Richter, Y. Aregbe, R. Wellum, T. Altzitzoglou, A. Verbruggen, K. Mayer, T. Prohaska. Feasibility Study for the Development of Plutonium Reference Materials for Age Dating in Nuclear Forensics. In Conference Proceedings: Proceedings of Symposium on International Safeguards: Preparing for Future Verification Challenges. Vienna (Austria): IAEA; 2010. p. 1-8. JRC60800

Jakopic R., S. Richter, M. Sturm, H. Kuehn, Y. Aregbe. Isotope Ratios Measurements in Environmental Samples Using Thermal Ionization Mass Spectrometry (TIMS) and Filament Carburization. In Conference Proceedings: Proceedings of the 31st ESARDA Annual Meeting Symposium on Safeguards and Nuclear Material Management, ISBN: 978-92-79-13054-0, LB-NA24038-EN-Z. Ispra (Italy): ESARDA and the Joint Research Centre of the European Commission; 2009. p. Session 6 - 019 (1-5). JRC52196

PRESENTATIONS AT SCIENTIFIC CONFERENCES

ORAL PRESENTATIONS

Sturm M., S. Richter, Y. Aregbe, R. Wellum, T. Altzitzoglou, V. Jobbagy, T. Prohaska. Nuclear age dating of plutonium. Oral presentation in: 9. ASAC JunganalytikerInnen Forum 2013, 21 – 23 June 2013, Vienna (Austria), Technische Universität Wien (Organiser)

Sturm M., S.Richter, Y. Aregbe, R. Wellum, K. Mayer, T. Prohaska. Age determination of plutonium. Oral presentation in: DOC DAY 2013, 10 October 2013, Tulln (Austria), Universtpät für Bodenkultur Wien (Organiser)

Sturm M., S. Richter, Y. Aregbe, R. Wellum, T. Altzitzoglou, V. Jobbagy, S. Mialle, K. Mayer, T. Prohaska. Age determination of plutonium for nuclear forensics. Oral presentation in: 35th Annual ESARDA Symposium on International Safeguards, 27-30 May 2013, Bruges (Belgium), Belgian Nuclear Research Centre (SCK-CEN) (Organiser). JRC83924

Jakopič R., M. Sturm, M. Kraiem, S. Richter, Y. Aregbe. Certified reference materials and reference methods for nuclear safeguards and security. Oral presentation in: The 6th International Symposium on IN SITU Nuclear Metrology as a Tool for Radioecology (INSINUME 2012); 11 June 2012; Brussels (Belgium); Institute for Radioelements (IRE) (Organiser). JRC68772

Jakopič R., M. Sturm, J. Bauwens, R. Bujak, C.Hennessy, R. Eykens, F. Kehoe, H. Kühn, S. Richter, Y. Aregbe. Pu CRMs for "age dating". Oral presentation in: International Workshop on Certified Reference Materials for Nuclear Measurements; 14-16 November 2011; Saclay (France); CEA-Saclay (Organizer)

Jakopič R., J. Bauwens, R. Bujak, C. Hennessy, R. Eykens, F. Kehoe, H. Kühn, S. Richter, M. Sturm, Y. Aregbe. IRMM developments on Certified Reference Materials. Oral presentation in: ESARDA WGDA meeting, 10 November 2011; Vienna; IAEA-SGAS (Organizer)

Jakopic R., J. Bauwens, R. Eykens, F. Kehoe, H. Kuehn, S. Richter, M. Sturm, A. Verbruggen, R. Wellum, Y. Aregbe. Development of New Pu CRMs and Research Activities at IRMM. Oral presentation in: CETAMA Seminar: Nuclear Analytical Chemistry - New challenges and future trends; 24 May 2011; Montpellier (France); Cetama, CEA (Organiser). JRC64668

Jakopic R., J. Bauwens, S. Richter, M. Sturm, R. Eykens, F. Kehoe, H. Kuehn, Y. Aregbe, A. Verbruggen, R. Wellum. Preparation and Development of New Pu Spike Isotopic Reference Materials at IRMM. Oral presentation in: 33rd ESARDA Annual Meeting: Symposium on Safeguards and Nuclear Material Management; 16 May 2011; Budapest (Hungary); The European Safeguards Research and Development Association (ESARDA) (Organiser). JRC62380

Zitek A., J. Irrgeher, M. Sturm, M. Brunner, B. Dillinger, T. Prohaska. IsoMark - a comprehensive assessment of the potential of isotopes in hard parts of freshwater fish to determine origin and migratory patterns using LA-(MC)-ICP-MS. Oral presentation in: European Geosciences Union General Assembly, 2-7 May 2010, Vienna (Austria); European Geosciences Union (Organiser)

Zitek A., J. Irrgeher, M. Sturm, M. Brunner, K. Sailer, M. Altmann, B. Dillinger, H. Waidbacher, T. Prohaska. IsoMark - a comprehensive assessment of the potential of isotopes in hard parts of freshwater fish to determine origin and migratory patterns using LA-(MC)-ICP-MS. Oral presentation in: Third INPAR workshop. Isotopes for improved management of nitrate pollution in aqueous resources (INPAR), 6 May 2010, Vienna (Austria); Environment Agency Austria (Organiser)

Jakopic R., S. Richter, M. Sturm, H. Kuehn, Y. Aregbe. Pu Isotope Ratio Measurements in Environmental Samples Using Thermal Ionization Mass Spectrometry (TIMS) and Filament Carburization. Oral presentation in: The 31st ESARDA Annual Meeting; 26 May 2009; Vilnius (Lithuania); European Safeguards Research and Development Association (ESARDA) (Organiser). JRC51233

Sturm, M., A. Zitek, S. Boulyga, P. Galler, T. Prohaska. Migration studies of fish by isotope ratio measurements. PUMPAYA 2007: 3rd BOKU-Corvinus University - Workshop on Spectroscopy, July 5 - 7, 2007, Nagymaros, Hungary.

POSTERS

Sturm M., S. Richter, Y. Aregbe, R. Wellum, K. Mayer, T. Prohaska. Plutonium age dating reloaded. Poster presentation in: European Geosciences Union General Assembly, April 27 - May 02, 2014, Vienna, Austria; European Geosciences Union (Organiser)

Sturm M., S. Richter, Y. Aregbe, R. Wellum, K. Mayer, T. Prohaska. Plutonium age dating for nuclear forensics: A close-up on the Pu/U chronometers. Poster presentation in: 8th International Conference on Isotopes and Expo (8ICI), August 24 - 28, 2014, Chicago, Illinois, USA; American Nuclear Society (ANS) (Organiser)

Sturm M., S. Richter, Y. Aregbe, R. Wellum, K. Mayer, T. Prohaska. Plutonium age dating. Poster presentation in: 10. ASAC JunganalytikerInnen Forum 2014, 13 - 14 June 2014, Tulln (Austria), Universität für Bodenkultur, Wien – Campus Tulln (Organiser)

Sturm M., S. Richter, Y. Aregbe, A. Verbruggen, T. Altzitzoglou, R. Wellum, T. Prohaska, K. Mayer. Feasibility Study for the Development of Plutonium Reference Materials for Age Dating in Nuclear Forensics. Poster presentation in: European Geosciences Union General Assembly, April 05 - 08, 2011, Vienna, Austria; European Geosciences Union (Organiser). JRC64335

Sturm M., S. Richter, Y. Aregbe, A. Verbruggen, T. Altzitzoglou, R. Wellum, T. Prohaska, K. Mayer. Feasibility Study for the Development of Plutonium Reference Materials for Age Dating in Nuclear Forensics. Poster presentation in: Symposium on International Safeguards: Preparing for Future Verification Challenges; 01 November 2010; Vienna (Austria); International Atomic Energy Agency (Organiser). JRC60503

Sturm M., S. Richter, Y. Aregbe, A. Verbruggen, T. Altzitzoglou, R. Wellum, T. Prohaska, K. Mayer. Reference Materials for Age Dating in Nuclear Forensics. Poster presentation in: The Future of Reference Materials - Science and Innovation; 23 November 2010; Geel (Belgium); European Commission - Joint Research Centre - IRMM (Organiser). JRC61825