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Feasibility study for the development of plutonium reference materials for age dating in nuclear forensics

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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.

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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).

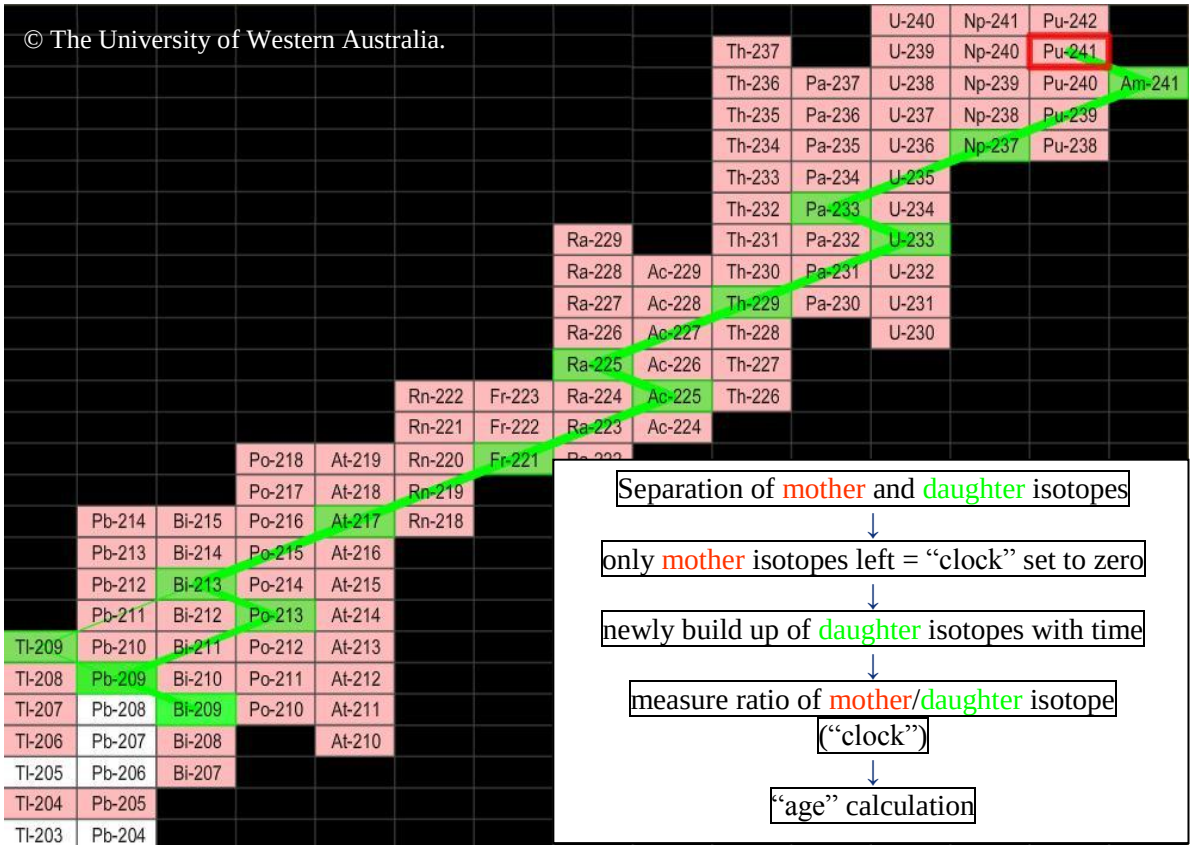

Figure 1. Decay scheme of ^{241}Pu [17]

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 radio-nuclide 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.

$$^{241}Pu_t = {}^{241}Pu_0 * e^{-\lambda * t} \quad [1]$$

$$\lambda = t_{1/2}^{-1} * \ln 2 \quad [2]$$

$$^{241}Am_t = {}^{241}Pu_0 - {}^{241}Pu_t = {}^{241}Pu_0 * (1 - e^{-\lambda * t}) \quad [3]$$

$$R_{241Pu/241Am} = {}^{241}Pu_t / {}^{241}Am_t = e^{-\lambda * t} * (1 - e^{-\lambda * t})^{-1} \quad [4]$$

$$t = \lambda^{-1} * \ln [(R_{241Pu/241Am} + 1) * R_{241Pu/241Am}^{-1}] \quad [5]$$

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.

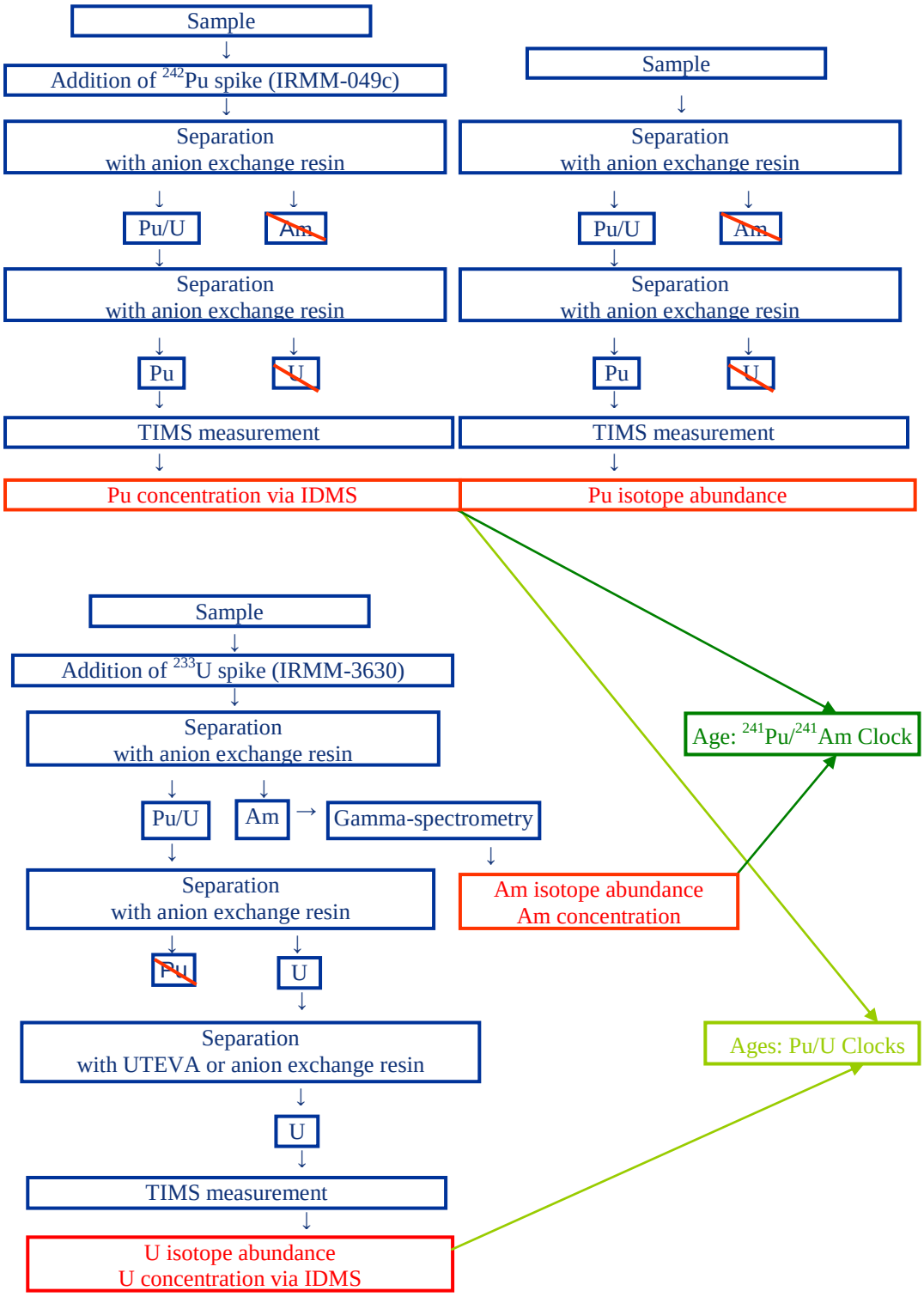

Figure 2. Scheme of analysis for nuclear age dating of Pu materials

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.

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