

Radiochronometry by Mass Spectrometry: Improving the Precision and Accuracy of Age-Dating for Nuclear Forensics

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Abstract. The model-date of a nuclear material is an important signature in a nuclear forensic investigation. Assuming the material is homogeneous, this parameter is fixed and exact, but it may or may not be the same as the purification date. The decay of a radioactive parent to a radioactive or stable daughter is the basis of the radiochronometers that record this model-date. If upon purification, only the parent isotope is present in the material, then the model-date will be the same as the purification date. Otherwise, if any of the daughter isotope remains upon purification, then the model-date will be further in the past. Regardless, it is a fixed and characteristic signature of the material, and will not vary as long as the system remains closed, *i.e.*, there is no post-purification fractionation of parent and daughter. Measurements of the parent-daughter pairs ^{234}U - ^{230}Th , ^{235}U - ^{231}Pa , ^{241}Pu - ^{241}Am , ^{137}Cs - ^{137}Ba and ^{90}Sr -(^{90}Y)- ^{90}Zr can be used to determine the model-dates of a variety of nuclear materials. All of these pairs are measured more precisely by mass spectrometric methods, because, for a given sample, more atoms can be measured by mass spectrometry than decays measured by radiometric methods. State programs have recognized the importance of precise and accurate model-dates as a signature of a nuclear material, and efforts to improve precision and accuracy are being made internationally by national laboratories and institutions charged with developing standards and reference materials. Efforts within the United States include the production of new certified reference materials (U-Th and Cs-Ba radiochronometer standards) and spikes (^{229}Th , ^{134}Ba , ^{243}Am , ^{236}Np , ^{233}U), and the development of guidance on the interpretation of radiochronometry data. Enhancement of radiochronometric methods and the development of tools needed to improve accuracy and precision are supported collaboratively by the U.S. Department of Homeland Security, U.S. Department of Justice Federal Bureau of Investigation, the U.S. Department of Energy at DOE National Laboratories and U.S. national metrology institutes.

1. Introduction

With their groundbreaking paper, Edwards *et al.* [1] demonstrated that measurements by mass spectrometry can significantly improve the precision of age-dates of geologic materials using the ^{230}Th - ^{234}U radiochronometer, relative to measurements of these isotopes by alpha spectrometry. Edwards' work spurred a renaissance in ^{230}Th - ^{234}U geochronology, and the development of mass spectrometry methods to measure ^{231}Pa [2,3]. This early work was done by thermal ionization mass spectrometry (TIMS). A good history of this field and an assessment of detection limits for different analytical methods are given in Goldstein and Stirling [4], and analytical improvements continue [5].

As defined in the *International vocabulary of metrology* [6], precision is “the closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions.” It is a measure of the repeatability and the reproducibility [6, 7] of a series of measurements. Within the isotope geochemistry community, internal precision is often used for repeatability, and external precision is used for reproducibility. No distinction is made between these here, and precision describes the closeness of agreement of different measurements. In mass spectrometry, precision is a principal contributor to the uncertainty of the measurement.

Although precise analyses of U and Th, which have relatively high first ionization energies can be made by TIMS (*e.g.*, [8]), most laboratories have transitioned such analyses to inductively coupled plasma source mass spectrometers (ICPMS). Figure 1 illustrates why this is so. The precision calculated in Fig. 1 is based purely on counting statistics ($N^{0.5}/N$) and assumes the following: one milligram of natural uranium; both daughters were completely removed at time = 0; ICPMS efficiency (ions measured/atoms available) = 1%; TIMS efficiency = 0.1%; counting time = 1 week; and the precision on the measurement of the denominator (the U isotope) for all methods is 0.1%. This figure shows estimates of the theoretical precision for measurement of the daughter/parent ratio that may be obtained by mass spectrometry vs decay counting. This “best case” does not include uncertainties from spike calibration, instrument backgrounds, analytical blanks, instrumental bias or fractionation corrections, and sample/spike ratio measurement. Only when all of these uncertainties are propagated appropriately, can the accuracy of the measurement be assessed, assuming that a “conventional true value” or a best estimate of this can be assigned [7].

Adoption of mass spectrometry for nuclear forensic radiochronometry was somewhat delayed relative to the rapid advances in geochronology, but it was soon recognized that even recently purified uranium, if present in abundance, has easily measured daughter products [9,10]. For example, 1 mg of natural uranium, aged only 100 days, has as much ingrown ^{230}Th as 1 g of average coral that is 100 years old.

2. Radiochronometry for Nuclear Forensics

Equation (1) describes the decay over time of a radioactive parent isotope (N_1) to a radioactive daughter (N_2), when there is no daughter present at the purification time, $t(0)$. Time, t , is positive, measured from that purification time, and λ_1 and λ_2 , are the decay constants of the parent and daughter, respectively.

$$N_2(t) = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} N_1(t) (1 - e^{(\lambda_1 - \lambda_2)t}) \quad (1)$$

This can be solved for t , the age of the material.

$$t = \frac{1}{(\lambda_1 - \lambda_2)} \ln \left[1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1} \right] \quad (2)$$

In Eq (2), R is the daughter/parent atomic ratio as measured on, or corrected to, the reference date. The reference date is usually the date when the in-grown daughter was separated from the parent for analysis. Subtracting t from the reference date, one obtains the model-date, denoted this because of

the model assumption that there was no daughter present at the purification time. Even if this assumption is not valid and some daughter remained at the purification time, for the relatively long-lived daughters, ^{230}Th and ^{231}Pa , the model-date will be essentially constant.

If the decay constants of the radionuclides are correct, the model-date determined today should be the same as will be determined ten years from now.

Other decay products of radioactive material that might be the subject of nuclear forensic investigation, *e.g.*, ^{137}Cs and ^{90}Sr , are stable isotopes (^{137}Ba and ^{90}Zr , respectively) and must be measured by mass spectrometry (*e.g.*, [11]). Equations (1) and (2) simplify.

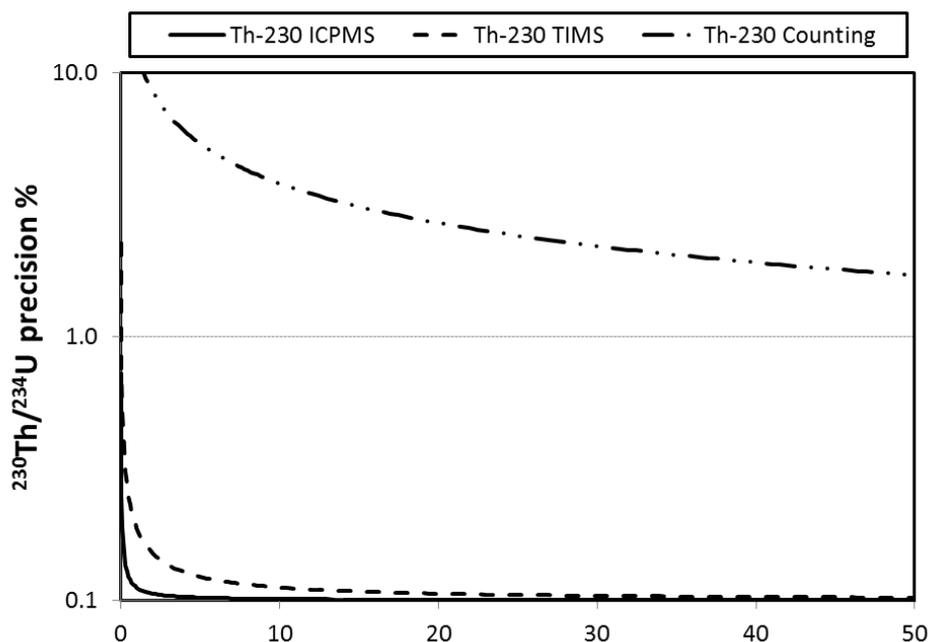
$$N_2(t) = N_1(t)(e^{\lambda_1 t} - 1) \quad (3)$$

$$t = \frac{1}{\lambda_1} \ln[1 + R] \quad (4)$$

However, in this case, the model assumption that the parent was purified from its daughter completely at $t(0)$ usually does not hold, and correction for this must be made in the numerator of R .

$$t = \frac{1}{\lambda_1} \ln \left[1 + \frac{N_2(t) - N_2(0)}{N_1(t)} \right] \quad (5)$$

In Eq (5), the number of daughter atoms present in the sample at the time of purification, $N_2(0)$, must be known. For stable isotopes, this can usually be determined through the measurement of other stable isotopes of the daughter element, with the assumption of a normal isotopic abundance at that time.



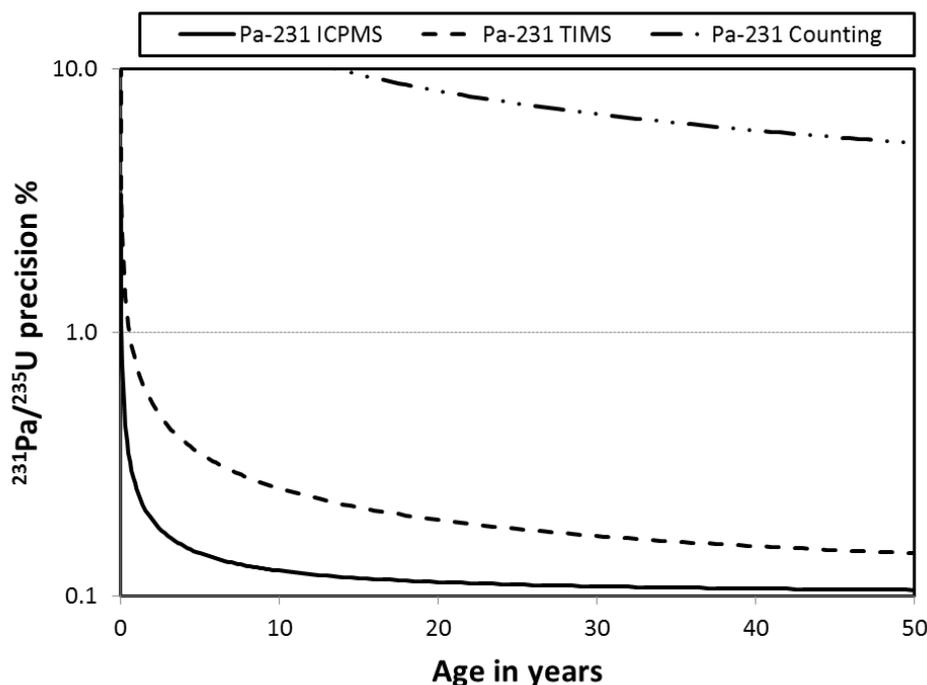


Fig. 1. Age dating 1 mg of natural uranium. Estimated precision, based on counting statistics, on the measurement of the daughter/parent ratios for different analytical methods. See text for assumptions.

3. Improving the Precision of Age-dating

The following is an excerpt from the introduction of NBS Special Publication 260-27, Standard Reference Materials: Uranium Isotopic Standard Reference Materials [12]:

The complete analytical method for any isotopic measurement is divisible into three broad areas; chemistry, instrumentation and mass spectrometric procedure. A prerequisite for an accurate isotopic measurement is an evaluation of the error contributions from these three sources. Since any of these can cause a serious loss of precision and accuracy, equal attention must be given to all phases of the measurement.

While it is possible to measure the daughter/parent ratio in a sample of uranium by ICPMS without chemical purification [9, 13], or even by laser ablation [13, 14], better precision is obtained by the isotope dilution method where the sample is spiked, parent and daughter are separated, and the analyses are made on purified samples [10, 13, 15, 16]. The following discussion assumes this method is used for analysis.

A measure of precision is the relative combined uncertainty of the mass spectrometric analysis. To reduce this uncertainty the following components must be optimized.

3.1. Measurement precision

Age-dating uranium-bearing materials using the isotope dilution method requires separate analyses of both the daughter and parent isotopes. ^{229}Th and ^{233}Pa are used as the spike isotopes for measurement of the daughters. Usually, many measurements of $^{230}\text{Th}/^{229}\text{Th}$ and $^{231}\text{Pa}/^{233}\text{Pa}$ are made and the precision of these measurements is a component of the uncertainty on the calculated value for the daughter. This measurement precision depends on the stability of the ion beam and the stability of the instrument response. For TIMS, the beam stability depends on many factors: how much sample is present, its purity, how it is loaded, on what filament, and how the sample is heated to bring it to run conditions. For ICPMS, it depends on, *inter alia*, the sample introduction system, the gas pressures,

the torch position tuning and the RF power supply. The electronics of modern mass spectrometers are remarkably stable, but providing a stable laboratory environment is also important.

If these isotope ratio measurements are made on a multi-collector instrument, it is possible to improve the precision by taking advantage of the simultaneous collection capability to reduce the effects of temporal fluctuations in beam intensity. If both ^{230}Th and ^{229}Th are measured on the same ion counting electron multiplier by peak-jumping, and the signal from ^{232}Th is measured simultaneously on Faraday cups, then improved precision can be realized by calculation of the ratio according to Eq (6).

$$\frac{^{230}\text{Th}}{^{229}\text{Th}} = \left(\frac{^{230}\text{Th}}{^{232}\text{Th}} \frac{F1}{F2} \right)_I \left(\frac{^{232}\text{Th}}{^{229}\text{Th}} \right)_{II} \quad (6)$$

In this equation, *I* and *II* refer to the two static multi-collection cycles. The ^{232}Th signal cancels, and the relative Faraday cross-calibration factor $F2/F1$ (the relative Faraday gain factor) is a well-known value that is determined independently. For a given sample, there may not be sufficient ^{232}Th for a Faraday measurement. At LLNL, we have observed that by judicious spiking of the sample with ^{232}Th , this analytical method can improve the precision.

Similarly, the parent uranium isotope can be measured more precisely with a multi-collector mass spectrometer. Several options are available depending on the level of ^{234}U in the sample. For depleted U, U-Nat or LEU, the abundance of ^{234}U may be insufficient for measurement on a Faraday cup. In this case, ^{234}U is best measured on an ion-counter. The spike isotope for U analysis, ^{233}U , can either be added in sufficient quantity to allow simultaneous collection of ^{233}U , ^{235}U and ^{238}U on Faraday cups, or added to be sub-equal to ^{234}U and measured on the same ion-counter, employing a peak-jumping strategy as described above for ^{230}Th . More commonly, the isotopic composition of the uranium is measured un-spiked to determine the ^{234}U abundance, and a separate spiked sample is used for the ^{234}U concentration measurement, putting ^{233}U on a Faraday collector [15]. For HEU, simultaneous multi-collection of all U isotopes on Faraday cups is often possible.

It is possible to improve precision with modern instruments by running at high beam intensities and putting ^{234}U on a Faraday cup or through the use a double-spike, ^{233}U - ^{236}U , for these analyses [5]. However, this could compromise detection limits for U-isotopes on an instrument dedicated to low-level analyses for nuclear forensics.

Repeatability is also, in no small way, dependent on the experience of the operator and how they tune the instrument and adjust the ion beam intensities. Following is another quotation from NBS Special Publication 260-27 [12]:

When the operator performs ideally and accomplishes his task, he is merely an appendage of the instrument and does not significantly increase the confidence limits of the measurement. When the operator performs poorly or unsatisfactorily, not only are the confidence limits expanded but the operator is likely to become the limiting factor in the measurement.

When an accomplished art teacher was asked by a student what they must do to learn to draw, the response was: “Well, you must draw—draw—draw.” Likewise, in order to make reproducible mass spectrometry analyses from session to session, you must analyze—analyze—analyze.

3.2. Spike calibration

The ^{233}U , ^{229}Th and ^{233}Pa spikes used for measurement of the daughter and parent by isotope dilution mass spectrometry (IDMS) should be defined on a molar (or atomic) basis, *e.g.*, atoms $^{229}\text{Th}/\text{g-spike}$. Of these, only ^{233}U certified on a molar basis is available currently from the Institute for Reference Materials and Measurements (IRMM). At present, there is no ^{229}Th reference material certified on a molar basis, although such standard is in the process of certification at New Brunswick Laboratory (NBL), and is discussed below. A ^{229}Th radioactivity standard is available from the US National

Institute of Standards and Technology (NIST), but for use directly as a spike, the half-life of ^{229}Th must be used to calculate the spike concentration on a molar basis. Because the uncertainty on the half-life is large, propagation of the uncertainty to the molar concentration is undesirable. Further, there will never be a certified reference material for ^{233}Pa due to its short half-life (27 days). This spike is produced either by milking from ^{237}Np or by neutron irradiation of ^{232}Th . It is purified and calibrated on an as-needed basis, and then, only has a useful lifetime of 3-4 months [3, 8, 16].

Nevertheless, most laboratories working in this field have ^{233}U and ^{229}Th spike materials, and the necessary quantity of ^{237}Np to prepare a ^{233}Pa spike. The in-house calibration of these spikes should be made versus standard reference materials that are certified on a molar basis. Such standards may be obtained for uranium and thorium.

A few notes of caution are in order regarding the calibration of ^{229}Th spikes using ^{232}Th standard solutions. The best standards available have expanded uncertainties ($k=2$) of approximately 0.4%, e.g. NIST SRM 3159. Some vendors of commercial Th solution standards quote expanded uncertainties ($k=2$) of 0.2% and claim traceability to NIST SRM 3159, which is impossible and erroneous. The NIST certificate clearly states: *“When the traceable values of such standards are assigned using this SRM for calibration, the uncertainties assigned to those values must include the uncertainty of the certified value of this SRM, appropriately combined with the uncertainties of all calibration measurements.”*

Further, NIST SRM 3159 is not currently available, and it was prepared from thorium oxide which can be problematic due to the highly hygroscopic nature of this material. Many laboratories prepare in-house ^{232}Th solutions from thorium metal, which can be weighed accurately with smaller uncertainty and results in improved precision when used for spike calibration.

^{233}Pa spike calibration is a special case. A ^{231}Pa standard reference material that can be used for this purpose does not exist at this time. Instead, each laboratory that has developed methods to measure ^{231}Pa by IDMS uses an idiosyncratic approach. However, all approaches have in common the use of ^{231}Pa derived by decay from a known quantity of ^{235}U . Secular equilibrium “standards” are used most commonly [2, 3, 8, 16], but ^{231}Pa derived from a U-standard of known age is also useful [16]. Even more useful to the nuclear forensic community would be a ^{231}Pa standard reference material certified on a molar basis. This would be a difficult task for the standards institutes, but not an impossible one.

The precision of the analyses required for calibration is affected by the same issues of measurement precision discussed above. These analyses should be fully reproduced several times, that is, mixtures with different spike/standard ratios should be prepared and measured.

3.3. Bias corrections

Corrections for instrumental mass bias (ICPMS), or fractionation (TIMS) rely on stable and reproducible measurement conditions and on analyses of standard reference materials. Both the uncertainties on the isotopic composition of these standards, and the uncertainties of those analyses should be propagated appropriately in the bias corrections.

4. Improving Accuracy

To assess the accuracy of a radiochronometry measurement a best estimate of the true value must be established. Until recently, no certified reference materials for ^{230}Th - ^{234}U age-dating were available, and accuracy could not be assessed. For an unknown sample subject to nuclear forensic examination this will probably always be the case, because “conventional true values” (see definition B.2.4 in [7]) are unlikely to be assigned. Even so, if a radiochronometry measurement of an unknown is associated with an accurate measurement of a standard with a reference value, a certain transfer of “accuracy” can be inferred, as well as traceability to a national standards base. More plainly, it’s just good quality control and quality assurance practice to analyze such samples.

For ^{230}Th - ^{234}U age-dating, certified reference materials now exist. In the US, the Domestic Nuclear Detection Office of the Department of Homeland Security National Technical Nuclear Forensics Center (DNDO/DHS/NTNFC) supported the certification of model purification dates for two different uranium materials. The certifications were done by New Brunswick Laboratory and certificates have been issued for NBL CRM U630 and CRM 125-A. CRM U630 is HEU (63% ^{235}U) U_3O_8 powder, and CRM 125-A is LEU (4% ^{235}U) UO_2 pellet. These are good surrogates for the type of materials that are likely to be subject to nuclear forensic examination. As such, analyses of these materials by the same methods that are applied to unknowns are the best test of accuracy that can be made.

New radiochronometry standards have also been prepared by the European Commission's Joint Research Center at the Institute for Transuranium Elements (JRC-ITU) and JRC-IRMM. The strategy for development of these standards was to purify uranium from its daughters, thus establishing a well-known purification date. One of these standards was distributed internationally to laboratories participating in the IRMM's Regular European Interlaboratory Measurement Evaluation Program (REIMEP-22). More information on these standards will be presented at this conference.

To address the difficulties of ^{229}Th spike calibrations that are necessary for the measurement of ^{230}Th , mentioned above, the US Department of Energy's New Brunswick Laboratory, in collaboration with NIST and supported by the DHS and DOE/NNSA, has developed a new ^{229}Th standard that will be certified on a molar basis. This solution standard has been calibrated against a high-purity ^{232}Th metal standard by mass spectrometry. The certification of this standard is in process.

Other radiochronometry standards and certified spikes for nuclear forensics are being developed in the US with the support of DNDO/DHS/NTNFC. Standards with certified model purification dates are in preparation for the ^{137}Cs - ^{137}Ba radiochronometer, as is a ^{134}Ba enriched spike which will enable more precise measurements of ^{137}Ba . In collaboration with United Kingdom's National Physical Laboratory, NIST and NBL are preparing a ^{243}Am standard for ^{241}Am - ^{241}Pu radiochronometry of samples containing plutonium. Recently, high-purity ^{233}U has been recovered from storage at Oak Ridge National Laboratory and efforts are underway to prepare a new standard from this. Efforts are also underway to prepare a ^{236}Np standard for analyses of ^{237}Np .

Finally, a four-partner US interagency program has been established known as the Bulk Special Nuclear Materials Analysis Program (BSAP). The partners are the DHS/NTNFC, DOE/NNSA, DOE-IN, and the FBI. Each of these governmental agencies have an interest in the assurance of precise and accurate analyses of nuclear material, and recognize the unique information that radiochronometry of nuclear materials can provide. In support of this interest, a Radiochronometry Guidance document is in preparation for the BSAP which will define terms, summarize state-of-the-art analytical practices, and provide guidelines for the calculation, reporting and interpretation of radiochronometry results.

5. Conclusions

In a nuclear forensic investigation, it is recognized that the model-date of uranium and other nuclear materials is an important signature. This signature is very likely unique and can allow constraints to be placed on the time the material was last purified chemically. Analyses by mass spectrometry provide improved precision on model-dates, and small date/time differences can be seen between materials that may be identical in other respects.

Improving the measurement precision involves improvements to all aspects of the analyses to obtain greater signal/noise and smaller uncertainties. These include improvements to the purification methods used to prepare samples for analysis (*e.g.*, lower blank, with high recovery and purity to eliminate isobaric interferences), to the instrumental analytical methods (the way that samples are introduced or loaded, and the data collection schemes), and to the instruments themselves. Improved precision on model-dates will result from improved determinations of radionuclide decay constants [17], and through the use of standards and spikes with smaller uncertainties.

The accuracy of a radiochronometry model-date, for both radioactive and stable daughter products can only be evaluated through analyses of standard reference materials. A few standards exist, and others are in development, but different materials for a number of radiochronometers are needed.

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Advances in Nuclear Forensics Analysis at CEA/DIF: Radiochronology Studies

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Abstract. In the frame of the Nuclear Forensics, one important analytical development is age dating of uranium materials. Two procedures have been established to date small quantities of uranium (from 1 µg up to 100 µg) with two radioactive chronometers ($^{234}\text{U}/^{230}\text{Th}$ and $^{235}\text{U}/^{231}\text{Pa}$). As our equipments are dedicated to trace analysis, only micro-quantities of nuclear materials can be handled in the laboratory in order to avoid contamination. So we use small columns of chromatographic resins to separate thorium or protactinium from uranium. Measurements are performed on ICP-MS for Th and Pa and TIMS for U. The detection limit (DL) for ^{230}Th and ^{231}Pa determination is close to 1 fg. The procedures were validated on certified reference material NBS U100. Datation analyses using the U-Th chronometer were also carried out on real-life samples.

1. Introduction

Analytical laboratories at CEA/DIF are part of the NWAL (Network of Analytical Laboratories in support of IAEA's nuclear safeguards) for the analysis of environmental samples since 2001 for both bulk and particle analysis. Part of the expertise inherited from environmental analysis is now used to develop capabilities in nuclear forensics analysis. The production date (or last purification) of a nuclear material is one of the evidence to determine the origin of a material. The date of purification can be obtained by measuring the ratio between one of the isotopes of the element of interest and its radioactive decay product. In the case of uranium, two couples daughter/parent are currently used: $^{234}\text{U}/^{230}\text{Th}$ and $^{235}\text{U}/^{231}\text{Pa}$ [1-4]. The calculated production date is estimated with the following equation (1):

$$t = \frac{1}{(\lambda_p - \lambda_d)} \times \ln \left(1 + \frac{N_d}{N_p} \times \frac{(\lambda_p - \lambda_d)}{\lambda_p} \right) \quad (1)$$

where λ_p and λ_d are the decay constants of parent (^{234}U or ^{235}U) and daughter product (^{230}Th or ^{231}Pa), N_d/N_p is the atom ratio of daughter over parent and t the time elapsed since the last purification of the material.

Fifty years after its last purification, a quantity of 10 µg of natural uranium produces only 100 fg of ^{230}Th and less than 5 fg of ^{231}Pa . The difference in the abundance of ^{231}Pa compared to the abundance of ^{230}Th is due to the longest half life of ^{235}U ($7.0381 \times 10^8 \pm 0.0048 \times 10^8$) compared to ^{234}U ($245\,250 \pm 490$ years). For “young” materials, the Th/U chronometer is more relevant except for large samples (>10 mg), or highly enriched uranium. Moreover, Pa chemistry is complicated to implement, and it is difficult to get ^{233}Pa for Pa quantification. This explains why the U/Th chronometer is more wide-

spread than the U/Pa. The use of two different chronometers is useful for material incompletely purified (*ie* material produced remaining trace amount of Th or Pa).

In this paper we describe the chemical protocols developed in the laboratory and we show and discuss the results obtained for a reference material and for real samples.

2. Validation of the methods with reference material

2.1. Chemical purifications

Uranium, thorium and protactinium were quantified using isotopic dilution, adding known amount of ^{233}U for uranium (IRMM, Geel, Belgium), ^{229}Th for thorium (AEA Technology, Harwell, UK) and ^{233}Pa for protactinium (home made from ^{237}Np solution [5]). U measurements were performed by TIMS (Triton, Thermofisher), whereas Th and Pa measurements were performed by ICP-MS (Element XR, Thermofisher).

All acids used were of ultrapure grade (Merck, Darmstadt, Germany).

The uranium material was dissolved in 8M HNO_3 and separated in two sub-samples A and B. The A sample was used for U/Th purification. ^{229}Th was added to the solution, and an aliquot was taken for ^{233}U tracing, evaporation and direct U measurement by TIMS. The remaining A solution was evaporated, and residue recovered in 9.5M HCl and injected in 100 μL AG1X8 microcolumn [6]. Thorium was eluted with 9.5M HCl, then uranium was eluted with 1.2 mL 2M HNO_3 . This U fraction can be kept for high precision U isotopic measurement but not for U quantification. The Th fraction was analyzed with ICP-MS.

The B sample was evaporated to dryness and taken up in 9.5M HCl. ^{233}Pa was added to the solution, and an aliquot was taken for ^{233}U tracing, evaporation and direct U measurement by TIMS. The remaining B solution was introduced on a AG1X8 3.5 mL column, and Pa was eluted with 9M HCl + 0.05 M HF mixed solution. Pa measurements were performed with ICP-MS.

2.2. Validation of the protocols

The certified reference material NBS 100 was analyzed four times with each method in order to validate the protocols. The quantity of uranium used for $^{234}\text{U}/^{230}\text{Th}$ chronometer was between 4 μg , whereas we used 300 to 600 μg of uranium for the $^{235}\text{U}/^{231}\text{Pa}$ chronometer. The size of the samples has been limited in order to avoid any contamination of the laboratory that is dedicated to trace analyses.

Model ages were calculated according to Eq. (1) for each replicate and a model date was estimated. Results were compared to the date of purification given by [7]. They are shown in Figures 1 and 2. Whatever the chronometer used, results are all consistent with the reference date. Experimental uncertainties were mainly due to the small quantities of ^{230}Th and ^{231}Pa in the samples. To reduce measurement uncertainty, the stability and sensitivity of the ICP-MS used for thorium and protactinium measurement would have to be improved or carried out with an instrument with lower detection limits.

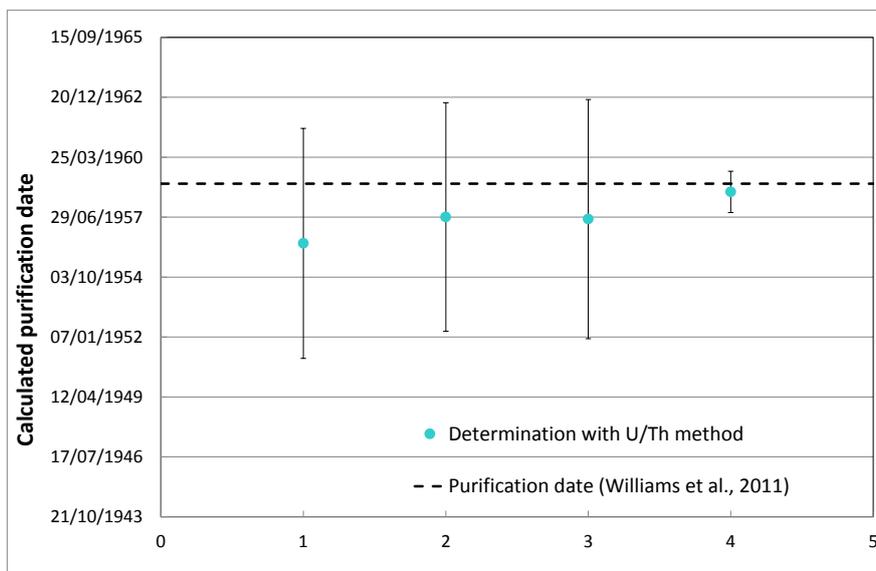


FIG. 1. Calculated purification date for the reference material NBS U100 with the U-Th chronometer

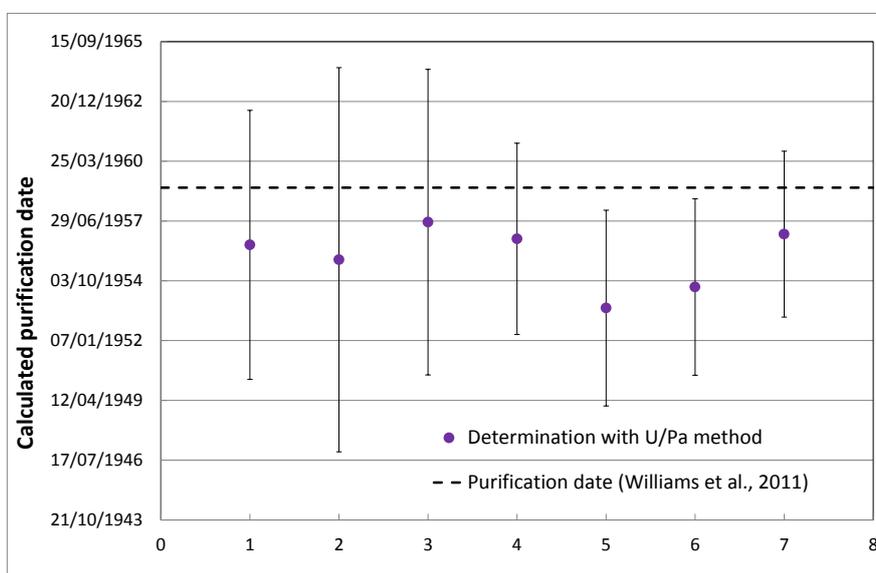


FIG. 2. Calculated purification date for the reference material NBS U100 with the U-Pa chronometer

3. Tests on real samples

As for a real nuclear forensic investigation we applied the datation method based on the $^{234}\text{U}/^{230}\text{Th}$ chronometer to 6 debris of uranium metals collected at the same place, in order to determine if the samples are of the same origin or not. Each fragment was lixiviated with 8 M HNO_3 . This method limits the contamination risks due to a complete dissolution of the sample so that the quantity of U handled was kept as low as possible. The same protocol described in the previous section was applied to each sample. All samples are depleted uranium, but with two distinct $^{235}\text{U}/^{238}\text{U}$ isotopic compositions. This is partly in agreement with the production date of the uranium in the samples (Fig. 3). At least two different origins maybe three according to isotopic measurements can be expected according to age of the samples.

Other analytical methods would be useful in order to make a more complete investigation on such sample.

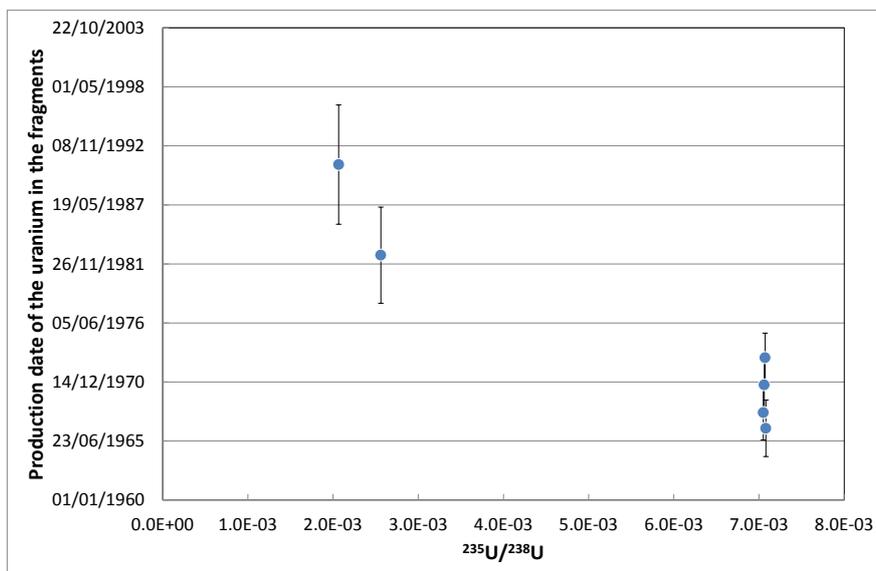


FIG. 3. Results of age dating and $^{235}\text{U}/^{238}\text{U}$ isotopic measurements carried out on U debris

4. Conclusion

We developed and validated two methods based respectively on the $^{234}\text{U}/^{230}\text{Th}$ and $^{235}\text{U}/^{231}\text{Pa}$ chronometers in order to determine the production date of various U materials. These methods have been validated with the Uranium isotopic standard NBS U100. These methods were designed for application to limited amounts of uranium, in the μg range for the $^{234}\text{U}/^{230}\text{Th}$ chronometer and in the 100s of μg for the $^{235}\text{U}/^{231}\text{Pa}$ chronometer. The $^{234}\text{U}/^{230}\text{Th}$ method has been applied to 6 uranium samples. The production date obtained shows clearly at least two different origins. These results combined with uranium isotopic composition help in ascertaining part of the history of the material.

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Protactinium-231 (²³¹Pa) Measurement for Isotope Chronometry in Nuclear Forensics

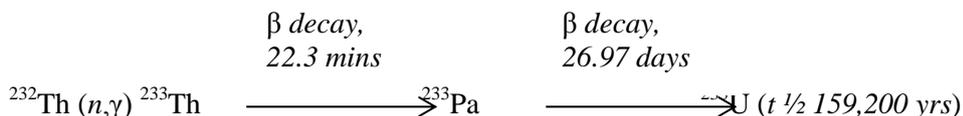
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Abstract. One of the key nuclear forensic signatures of the processing history of an unknown nuclear material is the material's age i.e., the time since the material was last chemically processed. Agreement between the results from two different chronometric pairs increases the confidence in the age dating analysis. The ²³¹Pa/²³⁵U chronometric system has been found to be a useful complementary system to the more commonly applied ²³⁰Th/²³⁴U system. The Australian Nuclear Science and Technology Organisation's (ANSTO) Nuclear Forensic Research Facility (NFRF) is currently developing the capability to measure ²³¹Pa ($t_{1/2} = 32,760$ years) and then apply these measurements to age dating for nuclear forensic investigations. This paper will focus on the procedure developed for ²³³Pa production by neutron irradiation of Th and the radiochemical separation of ²³³Pa from Th. The work completed to date and work planned will be described.

1. Introduction

Uranium series disequilibria measurements have been used for radiometric dating for many decades, mainly for elucidating geological and environmental processes. Recently, such measurements have been applied to the dating of nuclear materials (i.e., determination of the time since the material was last processed) for nuclear forensic applications. While ²³⁰Th/²³⁴U is the most widely employed uranium chronometric system, the ²³⁵U decay scheme also yields a highly valuable chronometric relationship, ²³¹Pa/²³⁵U. Although this latter approach has been shown to represent a viable complementary system to ²³⁰Th/²³⁴U, in particular for highly enriched uranium materials (²³⁵U > 20%), it has largely remained underutilised in most investigations. The reason for this is the challenging chemistry required to separate Pa and the need to produce an artificial spike isotope, ²³³Pa, for accurate mass spectrometry measurements. ANSTO is well placed to develop a ²³¹Pa measurement capability as the ²³³Pa spike required for ²³¹Pa measurement by isotope dilution mass spectrometry can be produced by neutron irradiation of Th in our 20 MW Open Pool Australian Lightwater (OPAL) research reactor. The scheme for ²³³Pa production is as follows:



An advantage of this means for ²³³Pa spike production over milking ²³³Pa from the alpha decay of ²³⁷Np is that once calibrated no further ²³³Pa grows in from residual Np. The procedure developed in this work for separation of Pa from Th avoids the use of highly hazardous perchloric acid [1].

Various methods for Pa measurement have been described such as alpha (for ^{231}Pa) and gamma (for ^{233}Pa) spectrometry [2], thermal ionisation mass spectrometry (TIMS) [3], multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and recently accelerator mass spectrometry (AMS) [4]. As ANSTO do not currently have access to a TIMS or a MC-ICP-MS for radioactive samples, the use of a quadrupole inductively coupled plasma mass spectrometer (ICP-qMS) was investigated for its potential for $^{231}\text{Pa}/^{233}\text{Pa}$ measurement.

2. Work to date

2.1. Target irradiation and measurement

The Th target for ^{233}Pa production was prepared based on the procedure described in Bourdon et al., 1999. [5]. The thermal neutron flux at the LE2 pneumatic irradiation position within the OPAL reactor was approximately $7.5 \times 10^{12} \text{ n.cm}^{-2}.\text{s}^{-1}$. Appropriate software [6] was used to calculate the activity of ^{233}Pa generated corresponding to various initial masses of ^{232}Th , irradiation times and cooling times (time elapsed once the irradiated Th is removed from the reactor). Initial parameters selected were a starting mass of 100 μg of Th, 9 hours irradiation and a 4 day cooling time (to give a ^{233}Pa activity of approximately 120 kBq) but the irradiation time was later increased to 20 hours (to produce an activity of around 200 kBq).

A summary of the target preparation procedure follows: a 100 μL aliquot of 1000 $\mu\text{g/mL}$ Th standard solution (Astral Scientific, $\text{Th}(\text{NO}_3)_4$ solution, 3% (abs) HNO_3) was placed into a Teflon beaker. The aliquot was dried to a small drop on a hot plate. The drop was then deposited onto a cleaned and weighed 2 cm^2 piece of Al foil and dried completely using a heat lamp. On completion of drying, the foil was allowed to cool, re-weighed, then carefully folded and loaded into a clean high density polyethylene (HDPE) 'snap-cap' capsule (Posthumus plastics). The capsule had been thoroughly cleaned to ensure no residual organics or other contaminants were present and was handled using gloves only. The target was then included in a 'can assembly' for loading into the reactor.

Once the irradiated target had cooled for 4 days, the ^{233}Pa content in the target was measured using gamma-ray spectrometry (HPGe detector; Ortec GEM35-70 (P-type, 35% relative efficiency) connected to an Ortec DSPEC-50 digital spectrometer). The detector was calibrated for energy and efficiency by measuring a series of calibrated point sources at a distance of $\sim 23\text{cm}$ from the detector end-cap. The absolute efficiency of the detector (in this geometry) was calculated to produce a calibration curve using 'Hyperlab' software. Hyperlab corrected the activity of each calibration source at the time of its measurement and then used the relative gamma abundances of each peak (it has an extensive nuclear data library built-in) to produce the points on the curve, which was then fitted using a 6th order polynomial.

The irradiated Th target was measured for 1 hour at approximately the same source-detector distance. For this initial measurement, the irradiated HDPE capsule containing the Al foil was placed into another, slightly larger, capsule and placed directly on the detector sample holder. Hyperlab uses all of the significant peaks it finds (see Table 2) and calculates a weighted average to produce the final activity. No correction was performed for the difference in geometry between the reference efficiency curve and the sample, resulting in a slightly lower reported activity. For comparison, the activity of one of the target dissolutions was also measured. An aliquot of the target dissolution was dried and measured on a Canberra Type GC 5019 (HPGE 50% relative efficiency) detector and compared to a point source calibration, similar to the measurement procedure described above. The measured (decay corrected) activity was 3.5 % greater than that obtained on the solid target.

The gamma-ray spectrum of the irradiated target is shown in Figure 1 and a list of the significant gamma-ray peaks for ^{233}Pa is given in Table 1. Five targets have been irradiated to date; the measured activity of ^{233}Pa produced using a 9 hour irradiation ranged from 105 to 125 kBq (corresponding to $\sim 0.15 \text{ ng } ^{233}\text{Pa}$; specific activity of $^{233}\text{Pa} = 7.687 \times 10^{14} \text{ Bq/g}$). Other isotopes detected were $\sim 1 \text{ kBq } ^{72}\text{Ga}$ ($t_{1/2} = 14.1 \text{ h}$, from Al foil), $\sim 0.8 \text{ kBq } ^{51}\text{Cr}$ ($t_{1/2} = 27.70 \text{ d}$, from plastic capsule), traces of ^{214}Pb

and ^{214}Bi from the lead shielding and ^{65}Zn ($t_{1/2} = 244.06$ d). No other impurities able to be measured using gamma spectrometry were present.

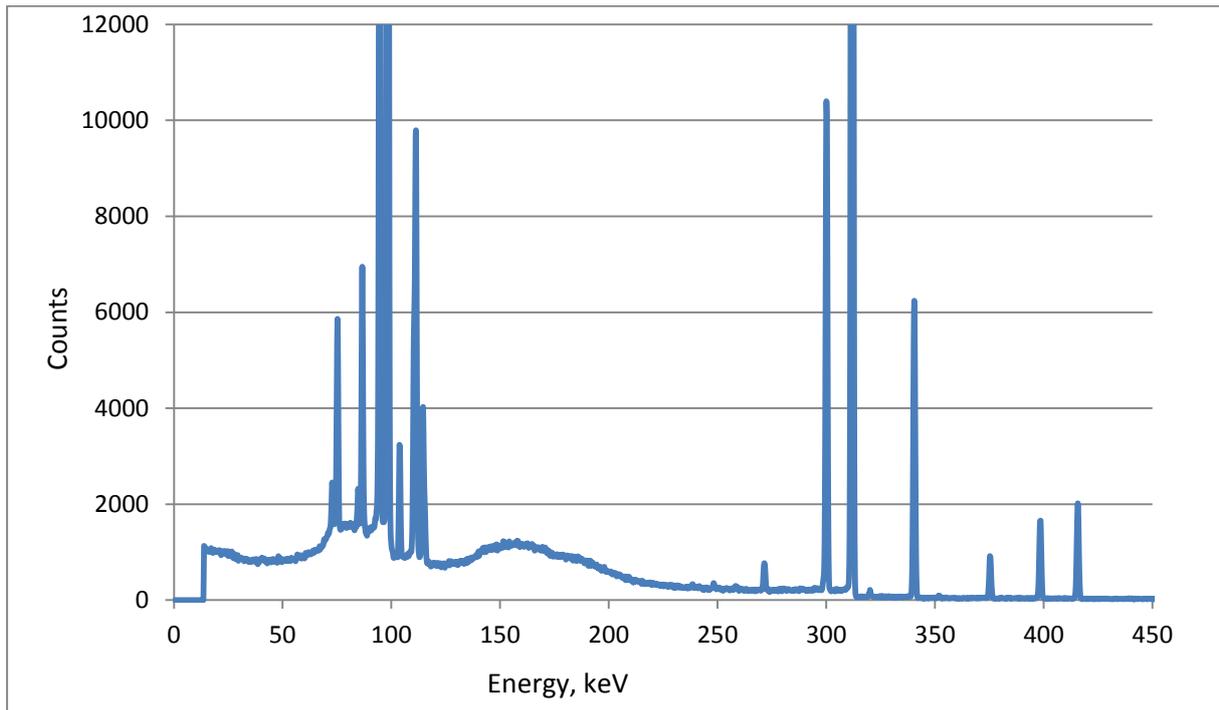


FIG. 1. *Gamma-ray spectrum of ^{233}Pa*

Table I. List of gamma-ray energies of ^{233}Pa [7]. The ‘found peaks’ were used to calculate the total activity of ^{233}Pa in the irradiated target

Energy (keV)	Line Intensity (Relative)	Found Peak (keV)
40.35	0.039	
51.5	0.0008	
57.9	0.0009	
75.3	1.39	75.27
86.7	1.97	86.57
92	0.004	
103.83	0.87	103.83
248.5	0.059	248.31
258.2	0.0039	258.58
271.48	0.328	271.56
298.5	0.035	298.86
300.12	6.62	298.86
311.89	38.6	311.92
340.47	4.47	340.48
375.45	0.679	375.39
398.46	1.39	398.44
415.79	1.745	415.69

2.2. Separation of Pa from Th

The procedure developed here is based on the one described by Bourdon et al., 1999 and Koornneef et al., 2010 [5, 8]. The irradiated Al foil target was dissolved in 10 mL of 9 M HCl. This solution was loaded onto an anion exchange column (2 mL Bio-Rad pre-filled poly-prep AG1-X8 resin, 100-200 mesh) that had been conditioned with 6 mL of 9 M HCl. Once loaded with the dissolved target solution, the column was washed with ~3 column volumes (cv) of 9 M HCl to remove Th and Al. Protactinium remains on the column in 9 M HCl while thorium does not; protactinium (V) (and uranium (VI)) forms anionic chloride complexes (see below) while thorium (IV) does not. Protactinium was eluted from the column with 9 M HCl + 0.1 M HF (~3 cv).

Protactinium yields during chemical separations were monitored using a gamma counter (2480 Wizard2, Wallac/Perkin Elmer with a NaI detector). Aliquots of the various fractions were adjusted to a fixed volume (1 mL) to eliminate geometry factors. The gamma counter was normalised for ^{233}Pa using the 311.9 keV peak (using the irradiated target prior to dissolution). A handheld radiation monitor was used as a quick check of ^{233}Pa content in the wash solutions, Pa fraction and the column during the separations. Once the target was dissolved in 9 M HCl, separation of Pa from Th was carried out soon after as even in strong aqueous HCl solutions Pa shows a strong tendency to hydrolyse. After extended periods of time colloidal dispersions may form, particles of which show a tendency to adhere to the walls of the vial, be it glass or polyethylene [9].

Protactinium binds strongly to the column and it was found that an increased number of washes (~ 6-7 cv) could be used to remove as much Th as possible with no Pa breakthrough. In this way a separation/decontamination factor of Pa from Th of greater than 2×10^4 for this first column could be achieved. The chemical yield of ^{233}Pa was close to 100%. Any residual ^{232}Th in the spike may interfere

with ^{233}Pa or ^{231}Pa measurements using mass spectrometry so further separations were carried out until the Pa/Th ratio was greater than 10. For further separations all traces of HF must be removed from the eluant to render the Pa adsorbable by the ion exchange resin. There are several reported means of removing HF: repeated evaporation of HCl/HF solution to dryness and addition of HCl [10]; addition of boric acid to complex fluoride ions (e.g [5] [3]) where avoiding drying down may prevent Pa loss by hydrolysis; and addition of perchloric acid and evaporation at 180 °C to fume off all the fluoride ions [1]. Alternatively, Regelous et al.[11] chose to increase the concentration of HF as Pa is strongly adsorbed onto anionic exchange resin in strong (>2 M) HF as fluoride complexes (see Fig. 2).

Barnett et al. [12] demonstrated that treating a mixed HCl/HF elutriant with boric acid successfully rendered Pa resorbable by anion exchange resin. Boric acid forms a very stable fluoborate ion, releasing the Pa from the fluoride ion and rendering the Pa resorbable as a chloride complex. Figure 2 shows the distribution coefficients of Pa(V) as functions of the HCl and HF concentration taken from Kim et al.[13]. Barnett et al.[12] suggested optimum treatment of the 9 M HCl/0.1 M HF eluent was to dilute the HF to <0.03 M with 9 M HCl and add 0.1 M boric acid (H_3BO_3). It was found in the current work that it was necessary to add excess H_3BO_3 (>0.1 M), take the solution to near dryness and then make up to ~10-15 mL with 9 M HCl to obtain chemical recoveries of ^{233}Pa of >90%.

The chemistry of Pa during the separations has been described in the literature; anionic complexes of Pa present in > 8 M HCl are PaCl_8^{3-} , PaOHCl_7^{3-} and PaOCl_6^{3-} [14]. According to Kim, et al. (1973), in HF solutions of low acidity, Pa forms oxo and hydroxo fluoride complexes of positive and neutral charge. Above 0.001 M hydrogen and fluoride ion concentration, mainly PaF_7^{2-} ions exist, whereas at high fluoride concentration PaF_8^{3-} ions are present and at high acidity the HPaF_7^- species is possible. In 9 M HCl/0.1M HF the complexes most likely to be present are HPaF_7^- and PaF_7^{2-} [14].

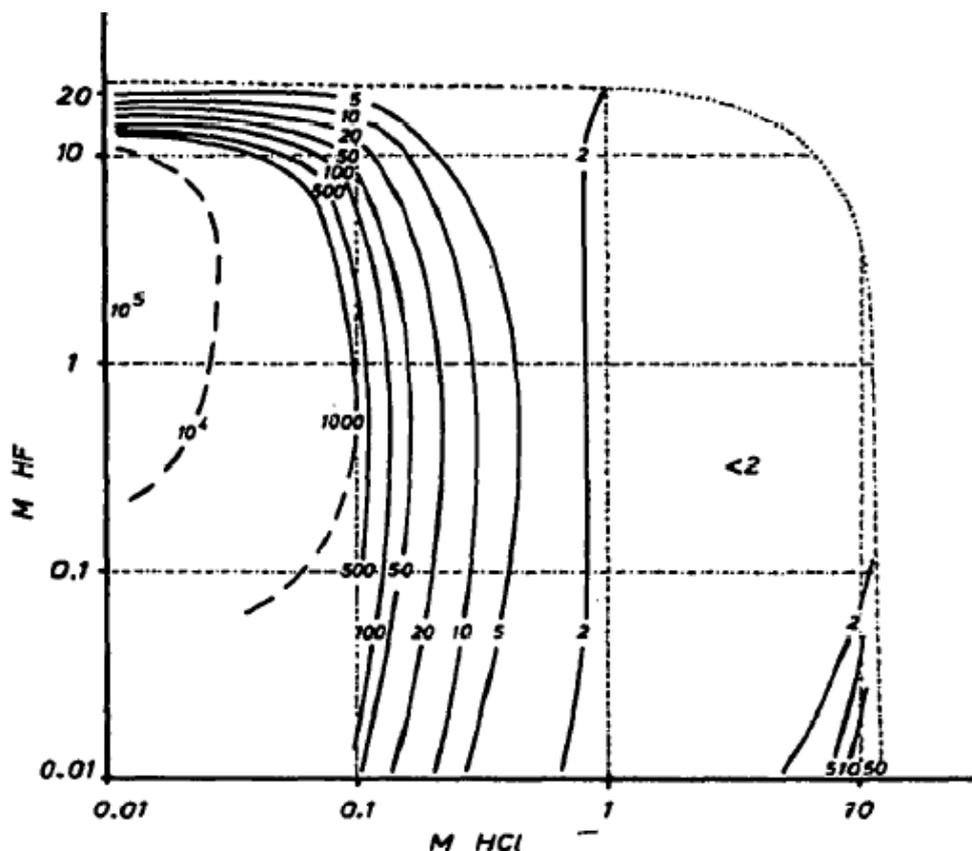


FIG. 2. Distribution coefficients of Pa(V) as functions of the hydrochloric and hydrofluoric acid concentration, from Kim et al. [13]

For ICP-MS analysis, the 9 M HCl/0.1 M HF eluants were evaporated to near dryness and made up in 2% HNO₃/0.4% HF; fluoride ions strongly complex Pa and prevent its hydrolysis. As ²³³Pa decays to ²³³U with a short half-life (26.97 days), measurements were carried out within a few days of separation.

3. Planned Work

3.1. Measurement of Pa using ICP-qMS

Recently, quadrupole ICP-MS has been used for ²³⁰Th/²³⁴U dating of ancient carbonates [15] and its potential for ²³¹Pa/²³⁵U dating for nuclear forensics is currently being investigated here. Mass spectrometric measurements were carried out using a Bruker 820 ICP-MS housed in a laboratory designed to handle radioactive materials and equipped with a low-flow (100 μL min⁻¹) PFA micro-concentric nebulizer (flow rate controlled using peristaltic pump) connected to a Peltier-cooled PFA Scott-type spray chamber. Prior to the analysis of samples the instrument was tuned using a 1 ng g⁻¹ multielement solution (Varian High-Purity Standards). Ion optics were optimised for maximum U sensitivity; sensitivity was approximately 3.0x10⁵ cps for 1 ng g⁻¹ ²³³U.

The limit of detection (based on the three times the standard deviation of the blank method) for ²³³Pa was ~ 0.5 pg/g. Preliminary test work using a previously dated HEU sample from a Nuclear Forensics International Technical Working Group (ITWG) interlaboratory comparison exercise [16] as an unknown, NBS U100 to calibrate the ²³³Pa spike solution [1], and NBS U500 for instrumental mass bias correction, gave good agreement for the ²³¹Pa/²³⁵U age of the material (i.e., result determined here overlapped with previously determined age within the uncertainty of ~7%, k=2).

3.2. Separation and Measurement of Th and Pa

The planned U/Th/Pa separation scheme for uranium samples is given in Figure 3. This procedure allows for the measurement of U isotopics, ²³⁰Th and ²³¹Pa, to enable the application of both the ²³⁰Th/²³⁴U and ²³¹Pa/²³⁵U isotope chronometers in a single sample dissolution.

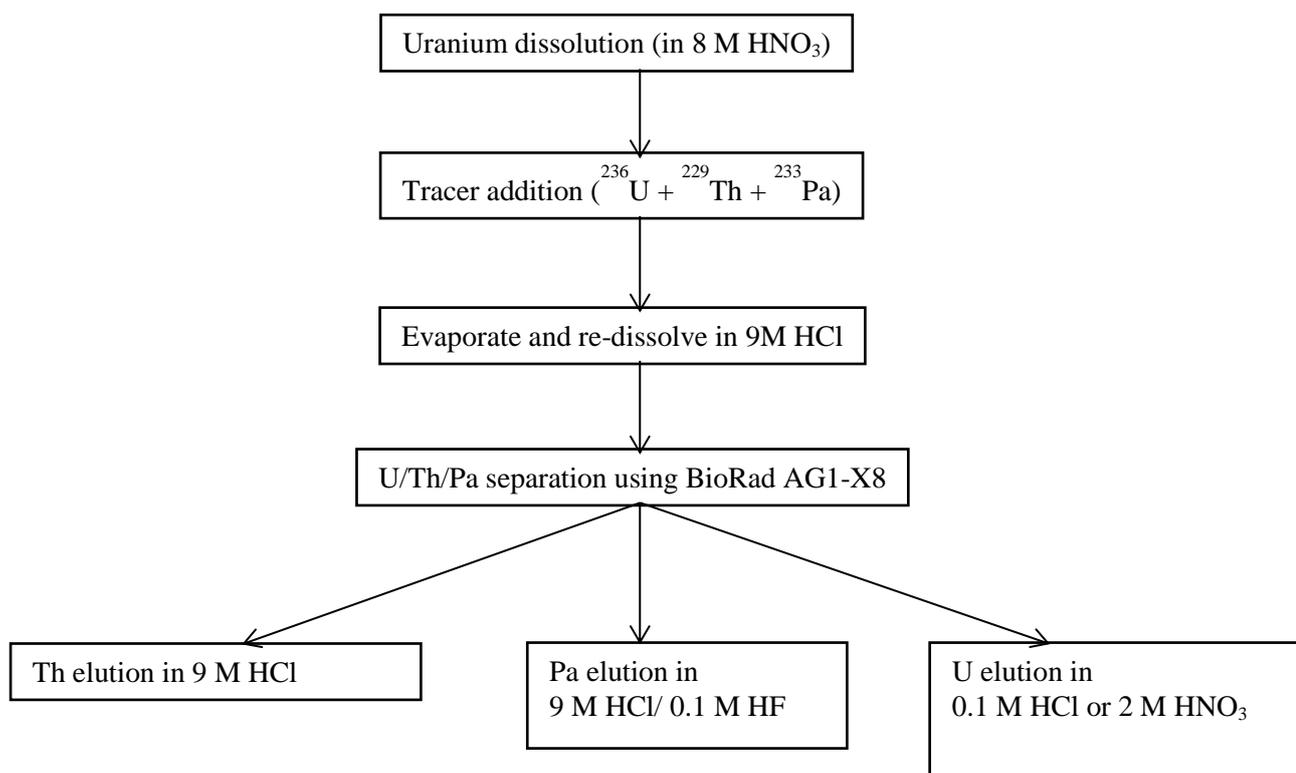


FIG. 3. Summary of radiochemical separation scheme for U, Th and Pa for uranium materials.

Validation of the separation and measurement procedure is planned using previously measured NBS uranium standards [1, 17].

3.3. MC-ICP-MS and AMS

ANSTO is currently in the process of purchasing a MC-ICP-MS instrument in collaboration with the University of Wollongong, Australia. The potential of MC-ICP-MS for Pa measurement has been demonstrated previously and was recently used for the first time for nuclear forensics [1]. We will also develop a procedure using MC-ICP-MS measurement here. In addition, ANSTO's Centre for Accelerator Science (CAS) has recently taken delivery of a 1MV accelerator system custom designed with the capability to perform high efficiency, high precision accelerator mass spectrometry (AMS) across the full mass range. High mass resolution analyzers, at low and high energy, coupled to a novel fast isotope switching system, will enable high quality analysis of actinide radioisotopes. This instrument will be investigated for its potential for measurement of very low (femtogram) Pa concentrations.

4. Conclusions

Procedures for the production and radiochemical separation of ^{233}Pa have been developed at ANSTO to allow ^{231}Pa measurement for $^{231}\text{Pa}/^{235}\text{U}$ isotope chronometry for nuclear forensic investigations. Future work will focus on mass spectrometric measurements of a range of U-bearing samples using quadrupole ICP-MS, MC-ICP-MS and AMS.

ACKNOWLEDGEMENTS

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Uranium Age Dating by Gamma Spectrometry

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Abstract. For determining the origin of nuclear material out of regulatory control, information on the age of the material seems relevant. A new method for uranium age dating was developed by using high resolution gamma-spectrometry (HRGS) based on determining the daughter/parent activity ratio $^{214}\text{Bi}/^{234}\text{U}$ by directly measuring the count rates of the relevant gamma peaks of ^{214}Bi and ^{234}U . The method is non-destructive and does not require the use of reference materials of known ages. It works well first of all for high-enriched and aged material. The least enriched uranium sample dated by HRGS was a 5% enriched oxide material, the age of which was determined as 54 ± 7 y. The youngest sample was a 6.7 ± 0.7 y old metallic U of 90.8% enrichment. In order to extend capabilities and improve sensitivity and accuracy of the method, a higher efficiency (well-type) detector was provided.

1. Introduction

Centre for Energy Research, also as the legal successor of the late Institute of Isotopes (IKI), Budapest, has a comprehensive nuclear forensics analytical capability enabling Hungarian authorities to provide information on the origin and history of nuclear and other radioactive material outside of regulatory control and ensuring effective national and international response. The institute is officially engaged in determining the characteristics of material such as physical form, chemical composition, isotopic composition, nuclear material mass, impurities, date of production, identifying reprocessed uranium, etc. Both NDA and destructive (DA) methods are in use and developed for examining such characteristics. U-bearing materials assayed by NDA and DA methods in Hungary include: Powder (oxide and other U compounds); Certified DU, NU, LEU, HEU reference materials; Seized DU, NU, LEU oxide reactor fuel pellets of CANDU, RBMK, VVER-440, VVER-1000 types; Seized fuel rods (broken), VVR-SM research reactor fuel assemblies, EK-10 fuel rods, Sealed sources; U-ore. Oxide and metallic HEU samples – as unknown materials - provided by the Nuclear Forensics International Technical Working Group (ITWG) for launching Round Robin (RR) exercises are also included.

For identifying the provenance of unknown material, the age of a sample has a unique significance in the nuclear forensic analysis. Although usually provide more sensitive analysis with lower detection limits, destructive (DA) methods (mass spectrometry, α -spectrometry) have certain drawbacks in such activities/applications, namely lack of promptness, sample preparation, need for preservation of evidence. They cannot be used e.g. for items which cannot be dismantled. Among other non-destructive assay (NDA) methods, high resolution gamma-spectrometry (HRGS) has long been routinely used for quantitative assay of U-bearing nuclear materials. No special sample preparation is necessary, whereas assay of some material as a whole is possible, without sampling (e. g. reactor fuel rods). Preservation of evidence can easily be ensured. This is essential for nuclear forensic application, where the materials are evidences in juristic procedure. At the same time destructive methods preserve their traditional role, and combination of different analytical techniques increase the confidence in the results and can help to further narrow down the set of possible origins and intended uses of the

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investigated materials. In the last years NDA methods used in the institute were complemented by destructive methods as high-resolution mass-spectrometry and scanning electron microscopy (SEM/EDS).

For categorization and characterization, including determination of the origin of nuclear material out of regulatory control, information on the age of the material seems relevant. The daughter/parent ratio as a function of decay time is widely used for determining the age of radioactive samples. The age of a sample is the time elapsed from the last chemical separation of the material. In the case of uranium, age dating is somewhat difficult because the relevant isotopes (^{234}U , ^{235}U , ^{238}U) have very long half-lives, so only small amounts of daughter nuclides could grow in. In contrast, the age of nuclear materials is, at most, merely a few decades, which is very short compared to the long half-lives of the parent isotopes. Therefore, one would expect that the daughter nuclides could only be quantified after destructive chemical separation, followed by mass-spectrometry or alpha-spectrometry. However, it has been demonstrated that the daughter/parent activity ratio for $^{214}\text{Bi}/^{234}\text{U}$ can be obtained by directly measuring the count rates of the relevant gamma-ray peaks of ^{214}Bi and ^{234}U by low background HRGS. A new method for uranium age dating was developed by using HRGS based on determining the daughter/parent activity ratio $A_{\text{Bi}214}/A_{\text{U}234}$ [1, 2]. The method is non-destructive and does not require the use of reference materials of known ages.

The daughter/parent ratio is directly related to the peak ratio technique used widely in gamma spectrometry. By relying on peak ratios, there is no need to know absolute detection efficiencies. Allowing the activity ratio to be determined without use of standards or without determination of geometry-dependent calibration constants, the relative efficiency (intrinsic) calibration method is based on the use of a relative efficiency curve as a function of energy [2, 3]. It is determined from the same spectrum as the measured activity ratios. The analyst determines several gamma intensities from individual U-isotopes, and normalizes the data to a common (relative) efficiency curve which, at the same time, accounts for the attenuation of different energy gamma rays in the absorbers and in the sample as well. The peak ratio method using intrinsic calibration e.g. for U isotope abundance measurements as well as a relative method for mass determination of nuclear materials in the form of pellets and powder are used, based on a standard U calibration set (certified reference material), applying attenuation correction. Among practical applications, we assayed materials whose integrity is to be maintained thus destructive methods are to be avoided. Such dismountable U-bearing materials like fuel assemblies used in research reactor or a fission ionization chamber containing ^{235}U above 90% abundance cannot even be analyzed by destructive methods at all. These objects may occur in illicit trafficking, too.

Upon examining illicit nuclear materials, ^{234}Th (24 d half-life) is practically in radioactive equilibrium with its parent ^{238}U in the occurring samples. Thus, determination of the daughter/parent ratio $^{230}\text{Th}/^{234}\text{U}$ is the first candidate for age dating of U samples. Indeed, determination of this ratio is the basis of mass spectrometric U dating [4]. Since ^{230}Th does not, however, emit abundant gamma rays, a different daughter isotope was needed to be found for the use of HRGS. Next member of the ^{234}U decay series is ^{226}Ra , without intense gamma emission again, but its short half-life descendants have useful gamma lines, especially ^{214}Bi , whose the 609.3 keV line was appropriate to measure.

2. The principle of uranium age dating

Build-up of ^{230}Th after purification of the material and its mass spectroscopic analysis is a first order basis for U age dating. Using the law of radioactive decay, the atom ratio $^{230}\text{Th}/^{234}\text{U}$ at time T after production of the sample can be calculated with a good approximation as

$$\frac{N_{\text{Th}230}}{N_{\text{U}234}} = \frac{m_{\text{Th}230}}{m_{\text{U}234}} \frac{M_{\text{U}}}{M_{\text{Th}}} = \lambda_{\text{U}234} T, \quad (1)$$

where λ_{U234} is the decay constant of ^{234}U . The atom ratios N_i are expressed in terms of mass m and molar mass M values. Then the age T can be calculated from mass spectrometric measurements.

Considering gamma spectrometry, whereas ^{234}U has well measurable gamma rays, ^{230}Th decays further to ^{226}Ra , which in turn decays to ^{214}Bi through 3 short-lived isotopes. ^{214}Bi has several measurable gamma lines, which may be used for estimating its activity. The time needed for secular equilibrium between ^{226}Ra and ^{214}Bi is about 2 weeks, so it can be assumed that the activities of ^{226}Ra and ^{214}Bi are equal at the time of the measurement. Hence, the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ at time T after purification/enrichment can be calculated with a good approximation as

$$\frac{A_{Bi214}}{A_{U234}} = \frac{A_{Ra226}}{A_{U234}} = \frac{1}{2} \lambda_{Th230} \lambda_{Ra226} T^2, \quad (2)$$

where the λ_i -s are the respective decay constants. ^{234}U can be detected by its 120.9 keV gamma line. Calculated atom ratio $^{230}\text{Th}/^{234}\text{U}$ and the activity ratio $^{214}\text{Bi}/^{234}\text{U}$ are plotted as a function of the elapsed time T in Fig. 1. The upper curve showing the atom ratio $^{230}\text{Th}/^{234}\text{U}$ as a function of the age is relevant for mass spectrometry, whereas the lower one showing the activity ratio $^{226}\text{Ra}/^{234}\text{U} = ^{214}\text{Bi}/^{234}\text{U}$ refers to gamma spectrometric age dating.

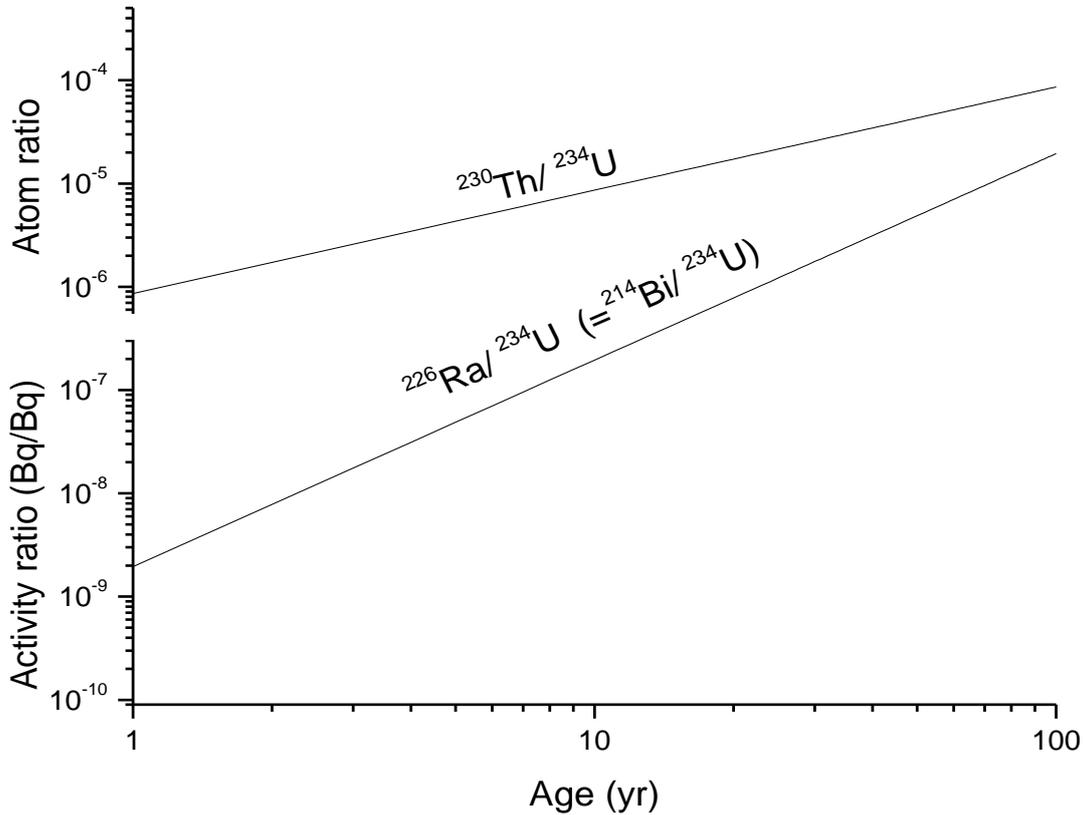


FIG. 1. Atom ratio $^{230}\text{Th}/^{234}\text{U}$ and activity ratio $^{214}\text{Bi}/^{234}\text{U}$ as functions of the U age

For determining ^{214}Bi activity, the 609.3 keV gamma line (along with ^{238}U peaks) was recorded by a 150 cm^3 coaxial HPGe spectrometer in a low-background iron chamber with a wall thickness of 20 cm. The activity of ^{234}U was measured by observing its gamma peak at 120.9 keV (along with ^{235}U peaks) by planar HPGe detectors under normal laboratory conditions. U gamma spectra are routinely

analyzed in the 0/300 keV region by the module MGAU of the advanced Multi-Group-Analysis (MGA) computer code (upgraded, see [5] and references therein), using intrinsic calibration [3], which provides reliable results in the range of 0.05 to 95 % ^{235}U abundances. In addition, we developed “manual” procedures as well.

The activity ratio $A_{\text{Bi}214}/A_{\text{U}234}$ can be determined in several ways from the gamma spectra of a sample. A reliable method uses a reference material of approximately like age, enrichment, and form, as the investigated sample. Another approach does not require reference materials but uses the absolute efficiency of the detector determined by “point-like” standard sources [1]. That is, the activities of ^{214}Bi and ^{234}U in the sample are measured in an efficiency-calibrated geometry. In an alternate approach, a relative efficiency (intrinsic) calibration is used to determine the activity ratio $A_{\text{Bi}214}/A_{\text{U}234}$, without the use of any standard or reference materials [2]. The method is based on the use of a relative efficiency curve as a function of energy. It is determined from the same spectrum as the measured intensities. The activity ratio can be obtained from the measured intensity ratio, the relative efficiencies taken at the corresponding energies, and from the values of the emission probabilities taken from literature. It means that one determines several gamma intensities from individual U-isotopes, and normalizes the data to a common (relative) efficiency curve which, at the same time, accounts for the attenuation of different energy gamma rays in the absorbers and in the sample as well, provided that a sufficient amount of the investigated material is available (depending on detector efficiency). The relative efficiency calibration is applicable to samples of arbitrary shape and chemical form (e.g. fuel rods).

As a matter of fact, ^{234}U undergoes enrichment/depletion in parallel with ^{235}U . Hence, for lower ^{235}U abundances, the amount of ^{234}U (and therefore of ^{214}Bi) is lower as well, so the corresponding activity is more difficult to measure and the uncertainty caused by the variation of the natural background becomes greater. In addition, a Compton background caused by the peaks of ^{238}U daughters is also present in the spectrum, hindering the evaluation of the ^{214}Bi peaks. A lower limit on the ^{235}U abundance of the material exists that allows determining the age by gamma-spectrometry, depending on the amount and the age of the material, detector efficiency and background level. Using our 150 cm³ coaxial Ge detector in a low-background iron chamber. Using this equipment, the age of 5 g of uranium oxide powder of natural isotopic composition could only be measured, if it were about 30 years old, whereas for 90 % enriched HEU the lower bound is around 2 years.

3. Applications and results

The method was discovered and first applied on the occasion of an inter-laboratory comparison organized by ITWG in 2001 (Round Robin Exercise), where a 90 % enriched oxide sample was assayed. Our age result obtained by HRGS was consistent with those of other labs measured by mass spectrometry (Table 1).

Table I. Measured ages of RR 2001 samples

HRGS	MS, other labs
$23 \pm 3\text{y}$	$22.4 \pm 0.2\text{y}$
	$22.4 \pm 1.2\text{y}$
	$23.5 \pm 0.5\text{y}$

The method was tested with 90 % and 36 % ^{235}U -containing samples of ages known as $> 41\text{y}$ from records. The measured age of the sample 90% was $43 \pm 2\text{y}$; that of the sample 36% was found $43 \pm 5\text{y}$ by relative efficiency calibration and $45 \pm 4\text{y}$ by determining absolute detector efficiency.

Applications extended to dating low-, medium-, and high-enriched seized and reference samples, HEU oxide powder and metal lumps, HEU and LEU reactor fuel rods, LEU pellet and powder, in the enrichment range of 4.4 to 90%.

Results of a certified reference material (CRM) of 10% ^{235}U content, measured in ITU, Karlsruhe, and in IKI, Budapest, agree well with each other and are consistent with certificate. The result of a CRM of 5 % enrichment was consistent with the certificate. Result of a LEU pellet of 4.4% ^{235}U content was confirmed by LA-ICP-MS.

Research reactor fuel rods (type VVR-SM), enriched to 36%, of known ages as 39, 38, 21, and 6 y were dated as 45 ± 4 , 40 ± 3 , 29 ± 4 , and < 13 y, respectively. A 10% enriched EK-10 fuel rod of age either 39 or 47 y according to records was dated 47 ± 4 y old.

Because of the low activity of ^{214}B in young as well as LEU material, the fluctuation of the natural background due to atmospheric ^{222}Rn , precursor of ^{214}Bi , has a substantial influence on the result. In order to reduce this effect, the sample to be measured was tightly surrounded by polystyrene foam in the iron chamber. In addition, N_2 vapour was directed around the sample through a pipe from the cryostat of the detector to drive out the air from its surroundings with the assumption that any possible radon activity in liquid nitrogen has already decayed by the time of the measurement. Systematic control of the 609 keV peak in the background spectrum confirmed this expectation when performing measurements in the iron chamber.

In Table II age data measured for two U metal samples enriched to around 90% ^{235}U , distributed by the ITWG for the following Round Robin Exercise (2010) are shown. One can see that results are consistent and the deviation is systematic between the ages of the two samples.

Table II. Age dating results of the HEU metal RR samples

<i>RR 2010</i>	<i>HRGS</i>	<i>Supplier</i>
Sample A	$7.3 \pm 0.7\text{y}$	6.88y
	$7.0 \pm 0.35\text{y}$	
Sample B	$6.7 \pm 0.7\text{y}$	6.25y

The second result of sample A was measured by a 110 cm^3 GCW2023 well-type detector (see the spectrum in Fig. 2 below).

Due to the Compton tail of high energy ^{238}U and ^{208}Tl lines, the sensitivity of detecting the 609 keV ^{214}Bi line decreases toward low enrichment. This is illustrated in Fig. 2, where relevant spectrum details of U-samples enriched to 4.5 % and 92 % taken by the 110 cm^3 volume well-type HPGe detector, are shown. The absolute efficiency for detecting the 609 keV line was 1.25 %. Whereas this peak is visible and well evaluable in the HEU spectrum – see the second result of sample A in Table II above, – it is suppressed by the intense Compton continuum in the LEU spectrum so that age determination was not possible.

The least enriched uranium dated in our lab by HRGS was an oxide material enriched to 5%; the age of which was found to be 54 ± 7 years. The youngest sample was a 6.7 ± 0.7 year old metallic U of 90.8% enrichment.

The sensitivity and the range of applicability of the method may be improved by using a detector of higher efficiency, e.g. a bigger well-type Ge detector. By a 300 cm^3 well-type detector, the sensitivity of the method could be improved so that the lower bound of the method would be around 1 year for 90% enriched uranium and about 15 years for natural uranium, under the present background conditions.

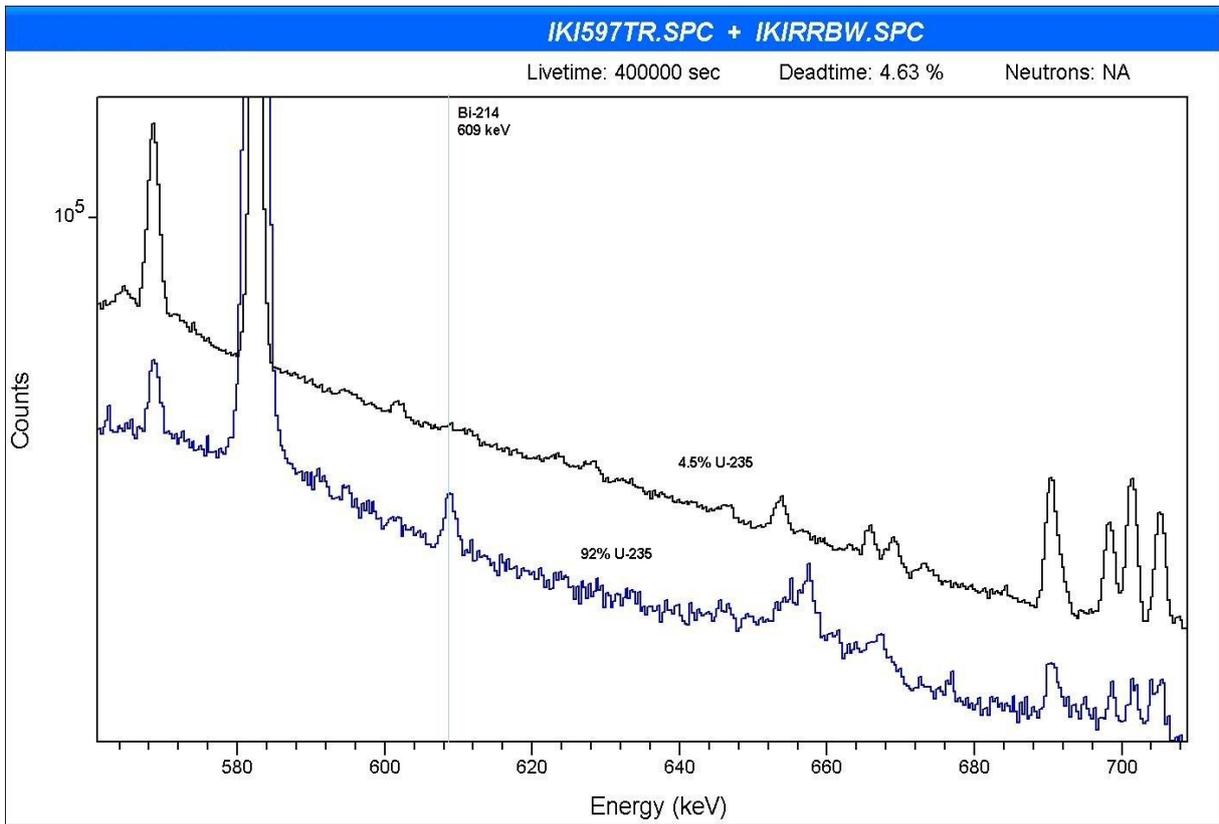


FIG. 2. LEU and HEU spectra, taken by a 110 cm^3 well Ge detector type GCW2023

Summarized age results obtained in the laboratory, plotted against the measured activity ratios $A_{\text{Bi214}}/A_{\text{U234}}$ are shown in Fig. 3. below.

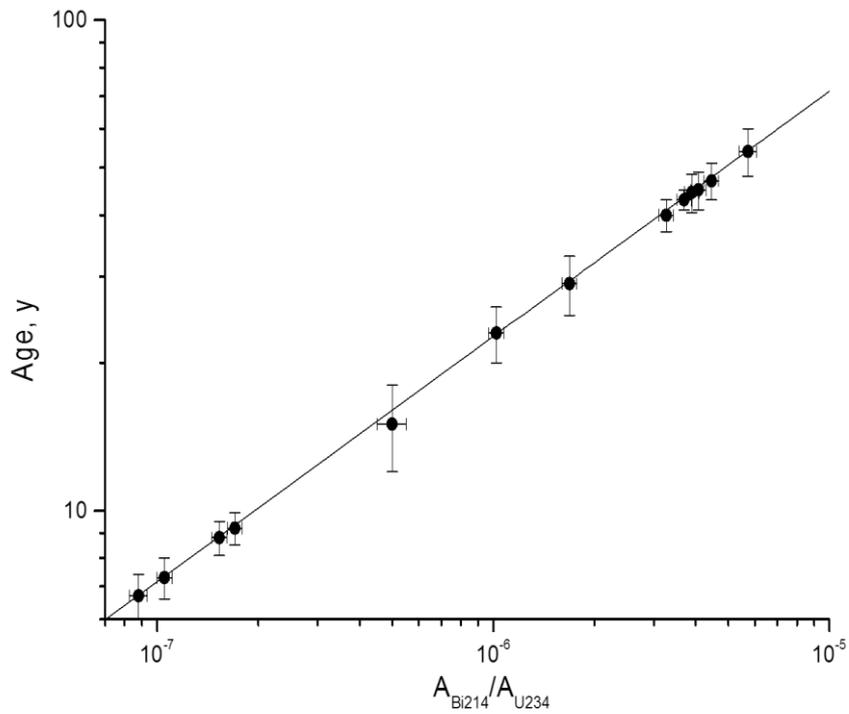


FIG. 3. U age determinations by gamma spectrometry at our laboratory so far

4. Assessed lower limits of age dating

The Compton tail of ^{238}U lines (and some time of ^{208}Tl peaks coming from the decay of ^{232}U being present in reprocessed material) decreases sensitivity of detecting the 609 keV line of ^{214}Bi toward low enrichment, thereby determining lower limits of age dating, depending on the enrichment. A model calculation was carried out for a series of Ge detectors, taking into account detector parameters, including our present big coaxial detector and various well-type crystals, see the list below.

Detector types:

- Coax. Type PIGC 3520, 150 cm^3 (34% rel. eff.), sample on detector cap
- Well type GCV2023, 110 cm^3 (20% rel. eff.)
- Well type GCV4023, 200 cm^3 (40% rel. eff.)
- Well type GCV5023, 260 cm^3 (50% rel. eff.)
- Well type GCV6023, 300 cm^3 (60% rel. eff.)
- Well type GCV6023*, 300 cm^3 (60% rel. eff.), small mass sample (1g), placed on bottom of the well

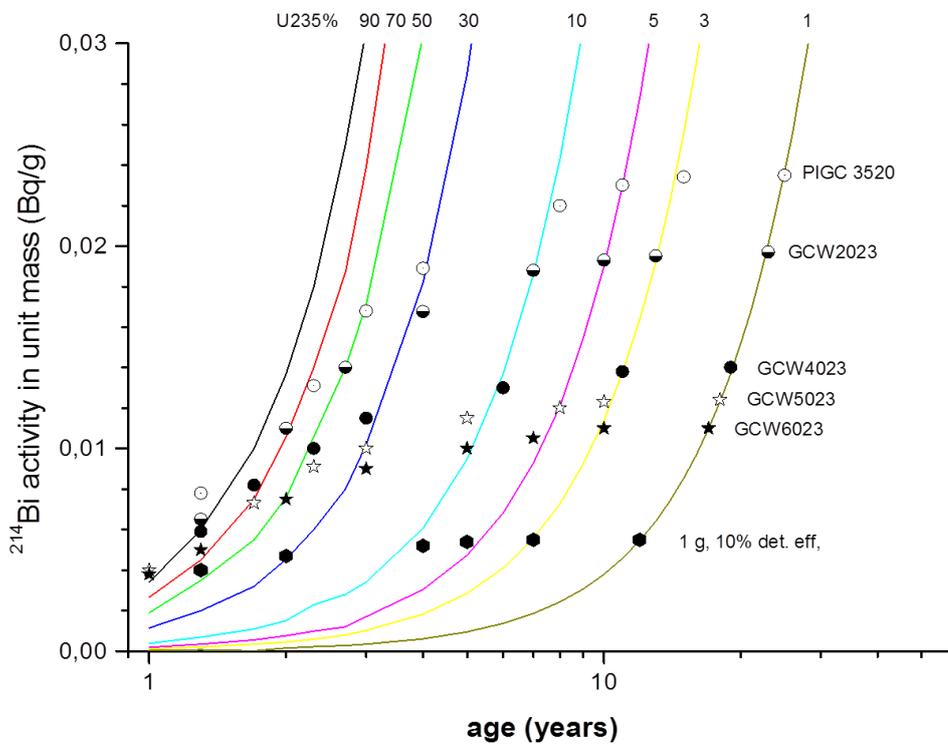


FIG. 4. The specific activity of ^{226}Ra (^{214}Bi) as a function of the age of U samples enriched to 1 – 90 %

Curves represented in the figure by the point series denote sensitivities limited by the Compton tail for individual detectors, for sample amounts of 5 g and 3 d acquisition times (except for the lowest curve relating to sample mass of 1g placed on bottom of the well). The method is only applicable for continuous lines corresponding to various enrichments above the point series in the figure, pertaining to individual detector types.

Detectability of the 609 peak is limited, in addition, by the natural background as well.

Assessed lower detection limits of specific ^{214}Bi activities for the detectors as function of ^{235}U enrichment are shown in Table III and Fig. 5. It is seen that lower age limits decrease with increasing enrichment and detector efficiency.

Table III. Assessment of lower limit of age dating as a function of enrichment for various detectors

²³⁵ U enr., %		1	3	5	10	30	50	70	90
		Minimum age, y							
Ge detector	PIGC3520	24	14	10	7	4	3	2.2	1.9
	CGW2023	22	12	9	6.5	3.5	2.7	2	1.8
	CGW4023	19	11	8.5	5.7	3.2	2.4	1.9	1.6
	CGW5023	18	10	8	5.2	3	2.2	1.8	1.5
	CGW6023	17	9.5	7	5	2.8	2	1.5	1.3
	1g, 10%, CGW6023*	12	7	5.2	3.7	2	1.5	1.2	1

*Small mass (1g) sample is placed on the bottom of the well

Tabulated data are represented also in graphical form in Fig. 5 below.

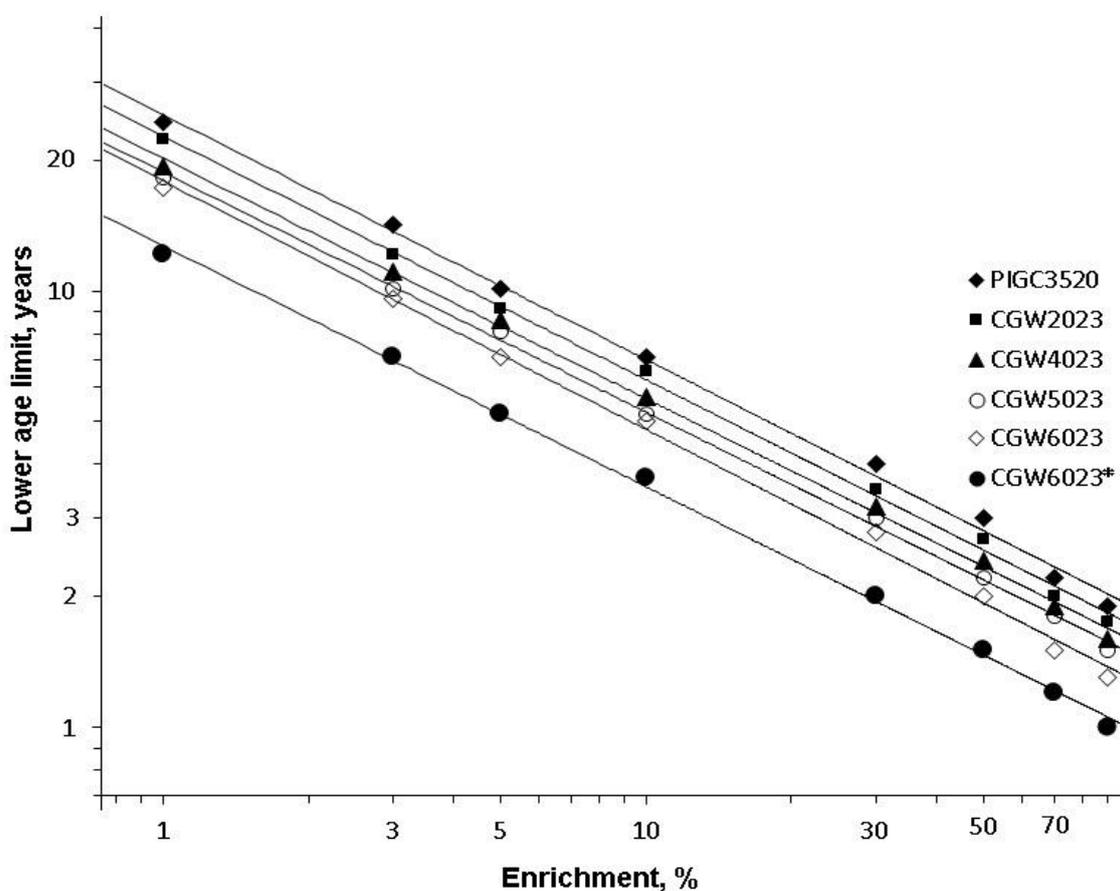


FIG. 5. Lower limit of age dating as a function of enrichment for various detector types

Note that ICP-MS is capable of dating NU of 0.2 years old at least, but dating of even younger LEU and HEU materials is also possible of course (it depends also on the amount of the material). By laser ablation (LA-ICP-MS) it is not as sensitive as the destructive method, but it may be the only applicable method in certain cases.

5. Summary

- Advantages of gamma-spectrometry:
 - non-destructive
 - no sample preparation
 - preservation of evidence
 - relatively simple equipment
 - provides a faster result in general
 - no dismantling (e.g. fuel)
 - suitable for in-field analysis
- HRGS for uranium age dating:
 - 13 samples of various ages and enrichments were dated so far
 - The youngest: age 6.7 ± 0.7 yr, E=91%
 - The less enriched: E=4.4 %, age of 54 ± 7 y
 - With the new well detector, for 5gU, the lowest age limit expected to ~6 y for samples of E=5%, whereas to ~1 y for samples of E=90 %,
 - for NU it is expected to ~15 y.
- “Difficult” samples: low-enriched young samples
- Further development:
 - higher efficiency detector
 - suppression of background fluctuations

The following observations can finally be concluded:

- Results from HRGS analysis are in sound agreement with mass spectrometric measurements.
- Two methods were developed that do not require reference material of known age.
 - Relative efficiency calibration: in arbitrary measurement geometry, chemical form.
- The accuracy of age dating measurements by HRGS is close to that of age dating by of mass-spectrometry in certain cases (aged material, high enrichment). The “difficult” samples are the same as in the case of mass spectrometry: low-enriched and “young” uranium.
- HRGS provides a faster result in general in age dating of HEU, and is non-destructive.
- Although DA methods usually provide more sensitive analysis with lower detection limits, they cannot be used for the characterization of items which cannot be dismantled.
- Combination of different analytical techniques increases the confidence in the results and can help to further narrow down the set of possible origins and intended uses of the investigated materials.
- Better detectors are needed to improve accuracy.
- Age dating by HRGS is suitable for in-field analysis.

It can be summarized that gamma-spectrometric age dating of uranium is, within the described limits, a reliable tool for determining the age of uranium samples encountered in combating illicit trafficking of nuclear materials and in nuclear safeguards.

The Centre for Energy Research (EK, Budapest) possessing a high resolution ICP-SFMS mass spectrometer and a scanning electron microscope is capable of nuclear forensic characterization of most types of nuclear material. It is hoped that the newly acquired large CWG 6023 well-type HPGe would render possible a more comprehensive and successful activity of it.

ACKNOWLEDGEMENTS

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