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LONG-TERM USE OF MIXED URANIUM-PLUTONIUM REFERENCE MATERIALS: CONSIDERATIONS TO ENHANCE THE VALIDITY OF URANIUM ISOTOPIC COMPOSITION REFERENCE VALUES

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ABSTRACT

This work presents some considerations for the preparation and long-term use of uranium-plutonium mixed reference materials. The contribution of uranium nuclides coming from plutonium decay in uranium-plutonium mixed samples can be significant for accurate determinations of uranium isotopic composition. This applies in particular to mixed samples with depleted, natural or low enriched uranium and low uranium/plutonium ratio. The Joint Research Centre of the European Commission in Karlsruhe runs an ISO/IEC 17025 accredited laboratory to give support to the European and other international safeguards authorities by providing high quality analytical measurements. Therefore, the laboratory analyses the uranium and plutonium isotopic composition by Thermal Ionisation Mass Spectrometry (TIMS) and the content by Isotope Dilution TIMS. The methods used to provide such high precision measurements assure measurement accuracy and precision using a stringent quality control concept. To guarantee and to establish traceability of the results to the International System of Units, Certified Reference Materials complemented with the use of laboratory reference materials are used as quality control samples. In nuclear laboratories like in the JRC Karlsruhe, precious laboratory reference materials are used as long as available. However, due to the lack of information about the uranium content in the plutonium occasionally time-consuming re-characterisations are needed. Therefore, the purpose of this study is to evaluate the main parameters affecting the uranium reference values in uranium-plutonium mixed materials. Moreover, the paper presents a simplified set of equations to correct the uranium isotope ratios for the plutonium decay in these samples. An expression to estimate the validity of uranium reference values or time in which the uranium ingrowth is negligible is also proposed.

INTRODUCTION

The European Commission is responsible for the control of all civil fissile nuclear material in the European Union (EURATOM Treaty Chapter VII). One of the main activities of the Joint Research Centre (JRC) is to give support to EURATOM safeguards by providing high quality analytical measurements. The JRC in Karlsruhe runs the Analytical Service (AS) for this purpose.

The laboratory is an ISO/IEC 17025 [1] accredited laboratory and deals with a large variety of samples. Most analyses refer to the determination of the uranium and plutonium isotopic composition by Thermal Ionisation Mass Spectrometry (TIMS) and the content by Isotope Dilution TIMS (ID-TIMS). The International Target Values (ITVs-2010) [2] provide the commonly accepted measurement uncertainty for safeguards analyses under routine conditions and therefore are used as guidelines.

In order to provide high precision analyses for Nuclear Safeguards a stringent quality control (QC) system is set up and needs reference materials as QC samples, as well as, uranium and plutonium reference materials (so-called spikes) as the basis for ID-TIMS to determine the uranium and plutonium content [3, 4].

Certified Reference Materials (CRMs) or Laboratory Reference Materials (LRMs), prepared from CRMs, or other materials calibrated against CRMs are used to cover the quality assurance needs [3, 4].

The majority of the uranium-plutonium mixed samples characterised in the AS contain natural or depleted uranium with a uranium/plutonium ratio below 15. The AS prepares LRMs matching as much as possible these samples. A compromise must be found between the number of QC samples, and the variation in uranium and plutonium amounts and isotopic abundances.

In the Laboratory Information Management System (LIMS) [5] of the AS, plutonium decay corrections are implemented and measurements are automatically calculated to the reference date. However, the correction of uranium amount and isotopic composition arising from the plutonium decay is not so straightforward and it is not yet automatically applied.

The AS prepares batches of LRMs available sometimes for several years and thus, the uranium QC charts need to be updated periodically in order to consider the uranium ingrowth, see Fig. 1. However, a sufficient number of analyses is not always available to re-calculate QC limits for limited periods.

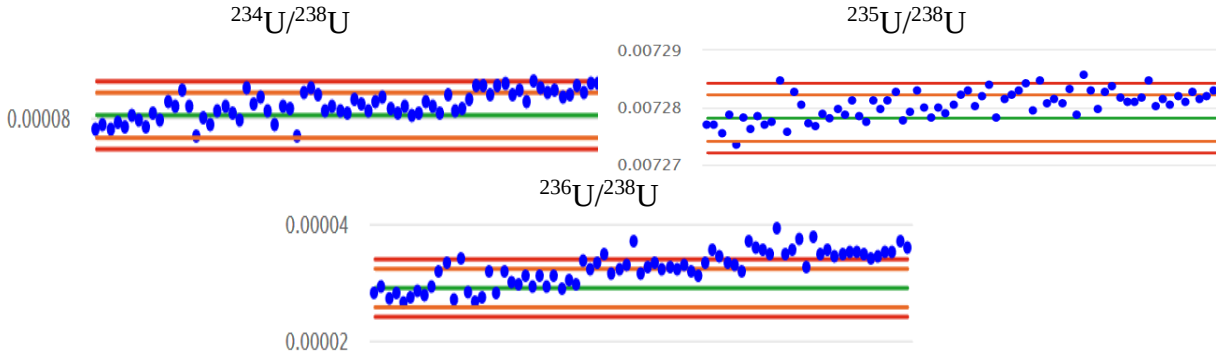

Figure 1. Uranium isotopic ratio measurements from 2015 for a U/Pu TIMS QC sample

This work presents some considerations for the preparation and long-term use of uranium-plutonium mixed LRMs. First, uranium data can be corrected for plutonium decay. Although these calculations can be tedious as they involve data from the two elements. For this

purpose, a simpler correction of uranium isotope ratios to a reference date is proposed. In this study, an expression to estimate the validity of uranium reference values or time in which the uranium ingrowth is negligible is also proposed. Besides this, the expression can be used for the design of LRMs in such a way that the impact of the uranium ingrowth is minimised or even negligible.

URANIUM ISOTOPIC ABUNDANCE IN URANIUM-PLUTONIUM MIXED SAMPLES

The AS prepares uranium-plutonium LRMs with different U/Pu ratios and for some time the amount and isotopic composition of the uranium are considered constant. This time, the validity of uranium reference values, is defined in this work as the time from the reference date in which the uranium ingrowth coming from plutonium decay can be considered as negligible.

The validity of uranium reference values in these LRMs depends on the $^{239}Pu/^{235}U$, $^{240}Pu/^{236}U$, $^{238}Pu/^{234}U$ and $^{242}Pu/^{238}U$ ratios and the assigned uncertainties to the uranium isotope ratios. These ratios are typical uranium/plutonium chronometers for plutonium age determination [6, 7].

The uranium amount in uranium-plutonium mixtures can be calculated from reference values of the uranium and plutonium starting materials. The date of plutonium purification or the amount and isotopic composition of the uranium present in plutonium needs to be known. Otherwise, the uranium needs to be characterized for instance by ID-TIMS.

Then, from the reference date or date of characterisation, the amount of uranium can be estimated considering the plutonium decay. For this study, it can be assumed that the uranium decay is negligible. Then, the amount of the different isotopes of uranium in uranium-plutonium mixed materials is calculated according to the following equations:

$$C_t^{234U} = C_{t0}^{U} * X_{t0}^{234U} + C_{t0}^{Pu} * X_{t0}^{238Pu} * (1 - e^{-(\lambda^{238Pu} * \Delta T)}) \quad \text{Equation 1}$$

$$C_t^{235U} = C_{t0}^{U} * X_{t0}^{235U} + C_{t0}^{Pu} * X_{t0}^{239Pu} * (1 - e^{-(\lambda^{239Pu} * \Delta T)}) \quad \text{Equation 2}$$

$$C_t^{236U} = C_{t0}^{U} * X_{t0}^{236U} + C_{t0}^{Pu} * X_{t0}^{240Pu} * (1 - e^{-(\lambda^{240Pu} * \Delta T)}) \quad \text{Equation 3}$$

$$C_t^{238U} = C_{t0}^{U} * X_{t0}^{238U} + C_{t0}^{Pu} * X_{t0}^{242Pu} * (1 - e^{-(\lambda^{242Pu} * \Delta T)}) \quad \text{Equation 4}$$

C_t^i (mol/g) is the amount of the uranium or plutonium isotope *i* at the date t

$C_t^{U\ or\ Pu}$ (mol/g) is the total amount of uranium or plutonium at the date t

to is the uranium reference date

X_t^i (mol/mol) is the amount fraction of the uranium or plutonium isotope *i* at the date t

Δ_t (days) time difference between the reference date and the determination date

λ^i (days^{-1}) decay constant isotope *i*

Uranium amount ratios $(U^{i}/U^{238})_t$ are calculated from eq. (1-4) according to the following equation:

$$(U^{i}/U^{238})_t = \frac{C_t^{iU}}{C_t^{238U}} \qquad \text{Equation 5}$$

The growth of ^{238}U, second term in the right-hand side of eq. (4), can be considered negligible in this work since the half-life of isotope ^{242}Pu is 3.7x10^5 years [8]. Thus, substituting the terms in eq. (1-4) into eq. (5) the uranium isotope ratios can be corrected to reference date applying the following equations:

$$(U^{234}/U^{238})_{t0} = (U^{234}/U^{238})_t - \frac{1}{R^{U/Pu}} * \frac{X_{to}^{238Pu}}{X_{to}^{238U}} (1 - e^{-(\lambda^{238Pu} * \Delta T)}) \qquad \text{Equation 6}$$

$$(U^{235}/U^{238})_{t0} = (U^{235}/U^{238})_t - \frac{1}{R^{U/Pu}} * \frac{X_{to}^{239Pu}}{X_{to}^{238U}} (1 - e^{-(\lambda^{239Pu} * \Delta T)}) \qquad \text{Equation 7}$$

$$(U^{236}/U^{238})_{t0} = (U^{236}/U^{238})_t - \frac{1}{R^{U/Pu}} * \frac{X_{to}^{240Pu}}{X_{to}^{238U}} (1 - e^{-(\lambda^{240Pu} * \Delta T)}) \qquad \text{Equation 8}$$

$R^{U/Pu}$ is the U/Pu ratio in mol/g at reference date

The only variables in the equations are the isotope ratios to be corrected and the elapsed time from reference date (ΔT). Thus, measured uranium isotope ratios can be corrected for plutonium decay using reference values from certificates or characterisations.

Uranium isotope ratios of a QC sample corrected to reference date

In this section, the equations for the correction of the uranium isotope ratio to the reference date are applied to a LRM used as QC sample for uranium-plutonium isotope ratio measurements by TIMS. The starting materials of the QC sample are the AS LRM plutonium SM3 (^{239}Pu 71%, ^{240}Pu 25%, ^{241}Pu 1.8%, ^{242}Pu 1.7%, ^{238}Pu 0.3%, 2015) and the CRM IRMM EC NRM 101; the U/Pu ratio of the blend is about 15.

49 measurements (in duplicates) are the basis for this study, in total 98 measurements by TIMS. The measurements are performed between March 2015 and July 2019. The reference values are determined from measurements.

The raw data are corrected according to eq. (6-8) to the reference date, March 2, 2015. Furthermore, in order to validate these equations where the ^{238}U is considered constant, the theoretical uranium isotope ratios have been calculated according to eq. (1-5) and corrected applying eq. (6-8). Figures 2-4 show the different measurements and theoretical data at measurement date and at reference date for the uranium isotope ratios. The control limits are displayed three standard deviations above and below the reference value.

The theoretical values corrected to reference date fit well with the reference value, see Fig. 2-4. This confirms that the ^{238}U ingrowth is negligible. Therefore, eq. (6-8) can be applied to correct uranium isotope ratios for verification and QC purposes.

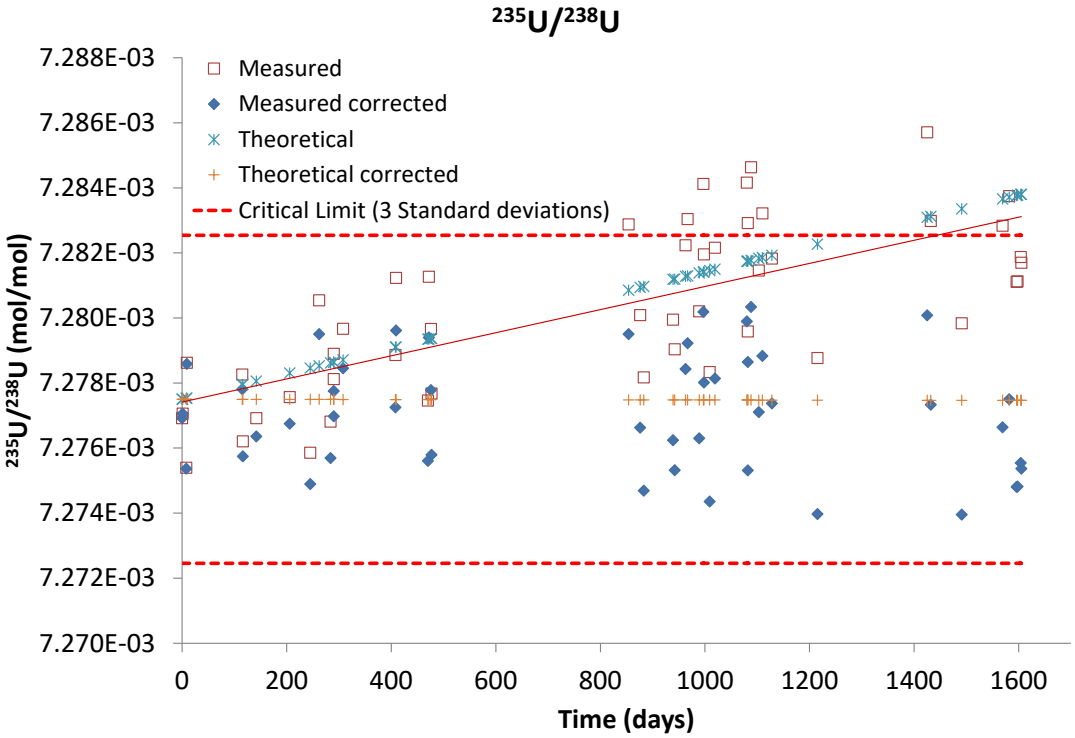

Figure 2. $^{235}U/^{238}U$ isotope ratio at measurement date and corrected to reference date.

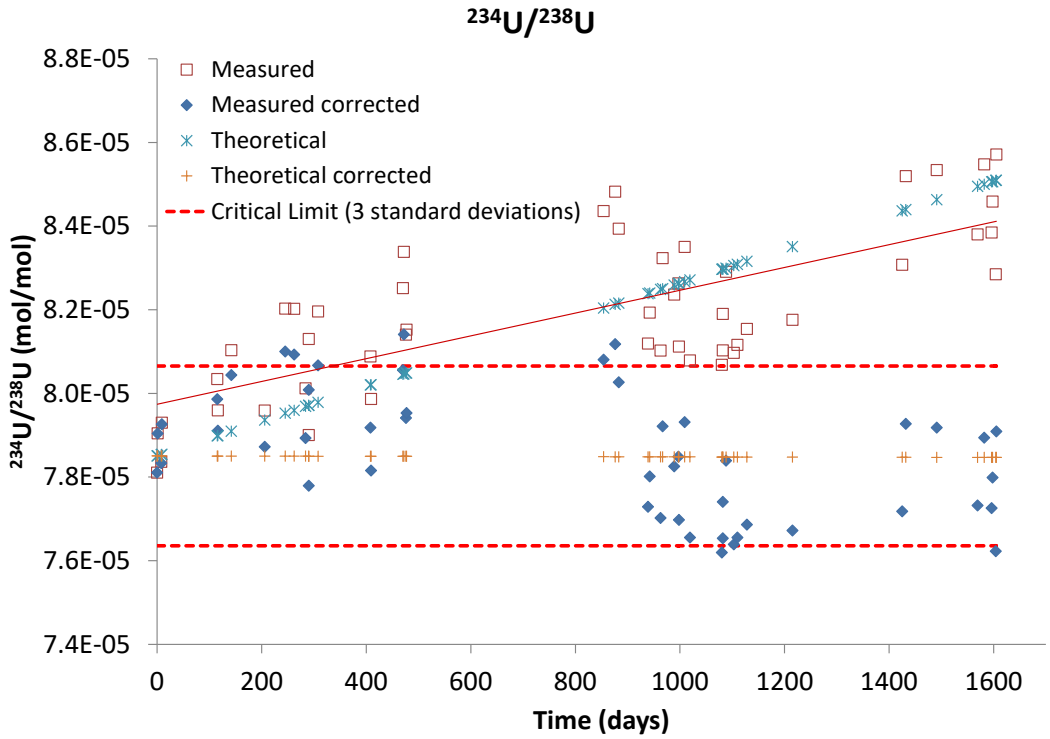

Figure 3. $^{234}U/^{238}U$ isotope ratio at measurement date and corrected to reference date.

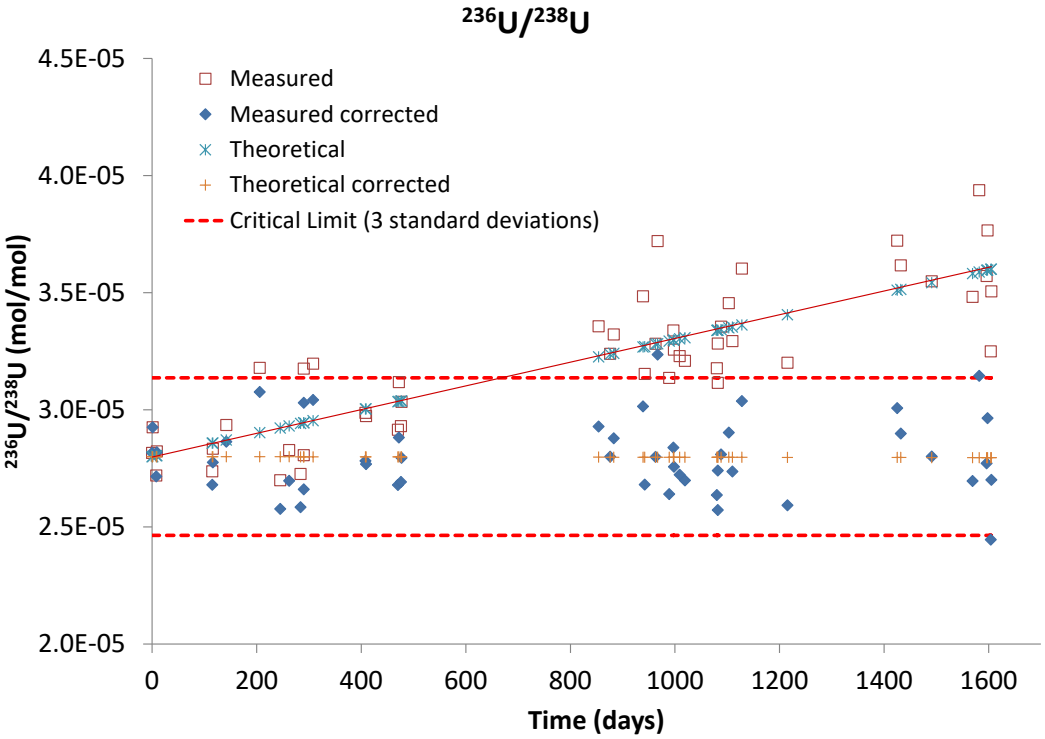

Figure 4. $^{236}U/^{238}U$ isotope ratio at measurement date and corrected to reference date.

Table 1 presents the mean, relative standard deviation (RSD) and bias of the measured and corrected datasets.

Table 1. Mean, relative standard deviation and bias of the measured data at measurement and reference date.

	Measurements			**Measurements at ref. date**		
	$^{234}U/^{238}U$	**$^{235}U/^{238}U$**	**$^{236}U/^{238}U$**	**$^{234}U/^{238}U$**	**$^{235}U/^{238}U$**	**$^{236}U/^{238}U$**
Average	0.0000819	0.0072803	0.0000320	0.0000786	0.0072771	0.0000280
RSD (%)	2.3	0.035	10	1.9	0.025	6
Bias (%)	4.4	0.04	14.4	0.12	-0.01	0.08

The uranium ingrowth in this LRM is significant as we can see in the fig 2-4 and Table 1, representing measurements during a period of four years. Then, either QC charts should be updated periodically or measurements have to be corrected to reference date. As shown in fig. 2-4, the second option allows to have a better overview of the performance of the method and instrument as data produced at a larger period of time can be used for evaluation. Besides, the uncertainty estimated from these analyses is lower since the contribution of the uranium ingrowth is removed.

VALIDITY OF URANIUM REFERENCE VALUES IN URANIUM-PLUTONIUM MIXED SAMPLES

In this section the time interval, hereinafter called validity of uranium reference values, in which the uranium ingrowth coming from plutonium decay can be considered negligible is estimated.

The definition of significant amount of uranium ingrowth is presented. In this study, the ingrowth is considered significant when the bias induced to the reference value equals 1/3 of the uncertainty (k = 2). Thus, the limit and the difference between isotope ratios at determination date and reference date are defined in eq. (9) and (10):

$$Limit_{U^{23i}} = {}^{1}/_{3} * \mathrm{Unc}(U^{23i}, k=2) = \left(\frac{(U^{23i}/U^{238})_t - (U^{23i}/U^{238})_{t0}}{(U^{23i}/U^{238})_{t0}}\right) \quad \text{Equation 9}$$

$$(U^{23i}/U^{238})_t - (U^{23i}/U^{238})_{t0} = {}^{1}/_{3} * \mathrm{Unc}\left(U^{23i}, k=2\right) * (U^{23i}/U^{238})_{t0} \quad \text{Equation 10}$$

Assuming that the ^{238}U ingrowth is negligible and substituting the difference between ratios in eq. (10) into eq. (6-8), the validity of the isotope ratio U^{23i}/U^{238} can be estimated as follows:

$$Validity_{U23i/U238} = \frac{1}{-\lambda^{2xxPu}} * \ln\left(1 - \frac{Limit_{U23i} * R^{U/Pu} * (U^{23i}/U^{238})_{t0} * X_{to}^{238U}}{X_{to}^{2xxPu}}\right) \quad \text{Equation 11}$$

The validity can be calculated in this way while the base of the logarithm is positive. Otherwise, it is higher than 500 years.

This validity has several applications for the evaluation of mixed uranium-plutonium samples. For instance, the validity can be used already for the design of LRMs. It can also be used to estimate the period in which the uranium QC charts must be updated and consequently new reference values established.

Tables 2 presents the validity of uranium isotope ratios for different uranium-plutonium mixed materials. Several mixtures have been simulated using different CRMs and the LRM plutonium SM3 using different uranium/plutonium ratios. Typical uncertainties achieved in the laboratory have been used for the limit calculated as 1/3 of the uncertainty. For this exercise, it was assumed that no uranium was initially present in the plutonium:

Table 2. Validity (years) of uranium isotope ratio reference values

Time(yr)	MP2 - ^{239}Pu 98%, ^{240}Pu 2%						SM3 - ^{239}Pu 72%, ^{240}Pu 25%					
Limit$_U$ 1/3	U/Pu	1	5	10	25	100	1	5	10	25	100	EC101 ^{235}U 0.7 %
234/238=0.53 %		*1.4*	*6.9*	*14*	*39*	*>500*	*0.01*	*0.07*	*0.14*	*0.34*	*1.4*	
235/238=0.016 %		*0.04*	*0.21*	*0.41*	*1.0*	*4.1*	*0.06*	*0.28*	*0.56*	*1.4*	*5.6*	
236/238=5.3 %		*0.14*	*0.69*	*1.4*	*3.4*	*14*	*0.01*	*0.06*	*0.12*	*0.30*	*1.2*	
Limit$_U$ 1/3	U/Pu	1	5	10	25	100	1	5	10	25	100	NBL125 ^{235}U 4 %
234/238=0.53 %		*9.3*	*55*	*155*	*>500*	*>500*	*0.09*	*0.45*	*0.91*	*2.3*	*9.4*	
235/238=0.016 %		*0.23*	*1.2*	*2.3*	*5.8*	*23.1*	*0.31*	*1.6*	*3.1*	*7.8*	*31*	
236/238=5.3 %		*0.07*	*0.35*	*0.69*	*1.7*	*6.9*	*0.01*	*0.03*	*0.06*	*0.15*	*0.61*	

Limit$_U$ 1/3	U/Pu	1	5	10	25	100	1	5	10	25	100	NBL116 ^{235}U 93 %
234/238=0.53 %		*>500*	*>500*	*>500*	*>500*	*>500*	*2.6*	*14*	*29*	*92*	*>500*	
235/238=0.016 %		*5.3*	*27*	*53*	*133*	*>500*	*7.2*	*36*	*72*	*180*	*>500*	
236/238=5.3 %		*206*	*>500*	*>500*	*>500*	*>500*	*18*	*90*	*180*	*458*	*>500*	

^{234}U and ^{236}U are normally minor isotopes and thus, the validity can be very short for them when a significant amount of ^{238}Pu and ^{240}Pu is present in the sample.

However, using a plutonium CRM such as MP2 with mainly ^{239}Pu improves the validity of the minor uranium isotopes. Although enriched ^{235}U and/or higher U/Pu ratio are required to increase the ^{235}U isotope ratio validity.

Validity periods are considerably reduced using typical CRMs uncertainties. For instance, the same exercise can be done for a uranium-plutonium CRM used for ID-TIMS, the IRMM 1027u [9]. Using the validity eq. (11) it can be estimated after which period of time the isotope ratio measurements need to be corrected for plutonium decay for verification. Table 3 presents the validity calculated using typical laboratories uncertainties and the uncertainties of the certificate:

Table 3. Validity (years) of IRMM 1027u

Time (years)	IRMM 1027u – U/Pu 30		
Lab. Unc.		CRM unc.	
234/238=0.53 %	>500	234/238=0.03 %	>500
235/238=0.016 %	33	235/238=0.004 %	8.9
236/238=5.3 %	>500	236/238=0.03 %	6.3

CONCLUSIONS

The work presented demonstrates some possibilities to be more efficient in the laboratory and increasing at the same time the quality of uranium and plutonium measurements. It is shown that for some time uranium reference values in mixed uranium-plutonium samples can be considered constant and no correction for plutonium decay is necessary. This period depends on the combined uncertainties demanded for analyses, uncertainties assigned to reference values and on the characteristics of the sample in terms of uranium and plutonium amount and isotopic composition.

The most accurate approach to deal with the uranium ingrowth is to apply the correction for the plutonium decay. However, these calculations can be tedious and for some periods the decay correction can even be considered as negligible. If the considerations described in this study can be taken into account when working with uranium-plutonium mixed samples several improvements are possible, such as:

- Time and material consuming revalidation of materials can be avoided or postponed

- LRMs can already be designed selecting the starting materials and amounts in such a way that the influence of uranium ingrowth is minimised.

Furthermore, the period in which the uranium ingrowth is negligible can be determined and can be used as criteria to assess when decay corrections are needed, for instance for the recalculation of QC limits.

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