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Certification of a new plutonium metal reference material: the CETAMA MP4 standard

Sébastien Picart¹ · Marielle Crozet¹ · Giacomo Canciani¹ · Ygor Davrain¹ · Caroline Bertorello¹ · Danièle Cardona² · Guillaume Legay² · Guillaume Bailly² · David Bauduret² · Nelly Caussignac² · Céline Zeleny² · Alexandre Quemet¹ · Sarah Baghdadi¹ · Christophe Maillard¹ · Vincent Dalier¹ · Anne Boyer¹ · Laure Montreuil¹ · Steve Jan¹ · Sébastien Mialle³ · Céline Cruchet³ · Hélène Isnard³ · Wilfried Pacquentin³ · Franck Doreau¹ · Paul Estevenon¹ · Julie Lorino¹ · Loïc Picard¹ · Stephan Richter⁴ · Yetunde Aregbe⁴ · Ana-Maria Sanchez Hernandez⁵ · Hélène Schorle⁵ · Evelyn Zuleger⁵ · Razvan Buda⁵ · Urska Repinc⁶ · Markus Kohl⁶ · Joe Hiess⁶ · Georges Duhamel⁶ · Mika Sumi⁶ · Danièle Roudil¹ · Cédric Rivier¹

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Abstract

This paper describes the production and certification of a new plutonium (Pu) metal reference material called MP4. The material's certification was carried out through an interlaboratory comparison (ILC) involving eight expert laboratories. By performing extensive data analysis on the ILC's results it was possible to establish the certified reference values for several quantities such as the Pu isotopic abundance and the Pu mass fraction. Thanks to its comprehensive set of certified values and its reduced mass compared to MP2, MP4 constitutes a novel and rare standard for Pu fissile material accountancy and nuclear safeguards activities.

Keywords Plutonium · Metal · Reference material · Certification · Isotopic abundance · Mass fraction

Introduction

In the nuclear industry as well as in nuclear research laboratories, measurement accuracy is fundamental for monitoring radioactive materials: (1) to characterize the material flow balance in nuclear facilities (criticality risk management); (2) to meet the needs of nuclear safeguards and nuclear

forensics; (3) to control environmental emissions in line with regulatory constraints.

As most of the analytical methods implemented to monitor radioactive materials are relative in nature, the use of Certified Reference Materials (CRMs) is essential for the instrument calibration and validation of analytical methods. Indeed, the quality of analytical characterization strongly depends on the instrument's calibration and thus, to a large extent, on the metrological quality of the standard employed for calibration. For many of the methods used, those CRMs are consumed little by little and need to be renewed periodically to ensure their availability [1].

For Pu measurements, high-purity Pu standards are the cornerstone of modern Pu material accountancy due to their role in the calibration of the analytical tools used to characterize Pu-containing materials [2–7].

Due to the rarity of facilities with the capability to purify, manufacture, and package high-purity and military grade Pu in metal form, the production of such Pu metal CRMs remains to this day a particularly complex task. Furthermore, the certification of the reference values requires a large analytical workforce to assess its homogeneity and its

✉ Sébastien Picart
sebastien.picart@cea.fr

¹ CEA, DES, ISEC, DMRC, Univ. Montpellier, Marcoule, France

² CEA, DAM, Valduc, Is-sur-Tille, France

³ CEA, DES, ISAS, DRMP, Univ. Paris-Saclay, Gif-sur-Yvette, France

⁴ Joint Research Centre (JRC), European Commission, Geel, Belgium

⁵ Joint Research Centre (JRC), European Commission, Karlsruhe, Germany

⁶ IAEA, SGAS, NML, Seibersdorf, Austria

stability and characterize the material in compliance with the ISO 33405 standard [8]. These elements combine to render the production of a Pu metal CRM a particularly arduous and time-intensive endeavor.

In light of this, more than ten years ago, the Commission for the Establishment of Analytical Methods (CETAMA) and the Valduc research center of the French Alternative Energies and Atomic Energy Commission's (CEA) joined forces to launch the production of a novel Pu metal CRM. This new high-purity CRM, named MP4 was developed to replace the CETAMA's MP2 CRM stocks as well as to meet novel demands for Pu standards with masses below 500 mg for nuclear material transport issues.

The present document describes the production and certification of the MP4 CRM at the CETAMA. Manufacturing and packaging of MP4 took place over the 2017–2019 period and was followed by the material's certification between 2021 and 2023 through the organization of an interlaboratory comparison (ILC) involving expert laboratories in nuclear analytical chemistry of the CETAMA's network.

Historical background to the production of plutonium metal standards in the USA and France

Historically, the elaboration of Pu metal standards began in the USA with the production, of the Standard Reference Material (SRM) 949 and the following SRM 949 series (a to f) by the New Brunswick Laboratory (NBL) in coordination

with the Los Alamos National Laboratory (LANL). The production of these CRMs spread steadily from the 1960s to the 1980s (see Table 1) with the last production being that of SRM 949 g (later renamed CRM 126), a CRM certified for Pu and Pu-239 amount content in 1986 [1, 3, 4, 9]. Almost twenty years later, a new source of Pu material was produced and packaged as the CRM 126A standard. CRM 126A was certified in terms of the quantities of Pu amount content (mass fraction) and all isotope ratios of Pu relative to Pu-239 (from Pu-238 to Pu-242) at the reference date of July 30, 2003. Currently, the production by the NBL and LANL of a new Pu metal standard, CRM 126B, is on-going (production initiated in April 2023) [9] with the CRM's certificate expected in 2025–2026.

The French Pu metal CRMs are reported in Table 2. In France, the desire to produce a Pu metal primary standard emerged in the 1970s. The first French plutonium metal CRM, named "Metal Plutonium" (MP1) was produced in the form of beads which was certified in terms of mass and Pu mass fraction quantities at the reference date of May, 1975. In 1984, MP1 was followed by France's second Pu metal CRM, MP2, which was certified in terms of mass, Pu mass fraction and Pu isotopic quantities at the reference date of January, 1988. The next standard, known as MP3 material, was fabricated in the 2000's but was not certified because the material was found to be not homogeneous with respect to impurities from the manufacturing process. At the beginning of 2011, a new program was launched for producing the MP4 CRM which was certified 12 years later in June 2023.

Table 1 List of USA produced Pu metal CRMs and some of their characteristics

Standard name	Date of certification	Form/number	w_{Pu} (g/100 g) at date of issue ($k=2$)	Mass (g)	M_{Pu} (g/mol)	Certified Pu isotopic abundance	w_{Am} ($\mu\text{g/g}$) at date of issue	Container	References
SRM 949	1962	Piece	99.97 ± 0.03			No	126		[9]
SRM 949a	10/12/1964	Piece	99.91 ± 0.03	$\sim 1 \text{ g} \pm 0.05 \text{ mg}$	239.11	No	600	Sealed glass tube	[1, 10]
SRM 949b	06/04/1967	Piece	99.99 ± 0.08	$\sim 1 \text{ g} \pm 0.05 \text{ mg}$	239.07	No	10	Sealed glass tube	[11]
SRM 949c	18/11/1969	Piece	99.99 ± 0.06	$\sim 1 \text{ g} \pm 0.05 \text{ mg}$	239.08	No	70	Sealed glass tube	[12]
SRM 949d	23/01/1973	Piece	99.99 ± 0.05	$\sim \text{g} \pm 0.05 \text{ mg}$	239.08	No	23	Sealed glass tube	[13]
SRM 949e	28/07/1975	Piece	99.996 ± 0.100	$\sim 1 \text{ g} \pm 0.05 \text{ mg}$	239.08	No	63	Sealed glass tube	[14]
SRM 949f	1982	Piece	99.99 (99.90–100.00)	0.5 g		No	21	Sealed glass tube	[9]
CRM126	01/10/1985	Pieces/229	99.962 ± 0.018	$1 \text{ g} \pm 0.2 \text{ g}$	239.073	No	37	Sealed glass tube	[15–17]
CRM126a	30/07/2003	Pieces/1200	99.960 ± 0.026	$1 \text{ g} \pm 0.2 \text{ g}$	239.115113 ± 0.000015	Yes	183	Sealed glass tube	[1, 18]
CRM126b	In progress	Piece		$\sim 1 \text{ g}$		Yes		Swagelok knuckle	[9, 19]

Table 2 List of French Pu metal CRMs and some of their characteristics

Standard name	Date of certification	Form/number	w_{Pu} (g/100 g) at ref date	Mass (g)	M_{Pu} (g/mol)	Certified Pu isotopic abundance	w_{Am} (µg/g) at ref. date	Container	References
MP1	05/1975	Beads	99.997 ± 0.050	~0.35–0.75 ± 0.042	239.10	No	250	Sealed glass tube	[2, 20, 21]
MP2	01/01/1988	Ingot/> 2000	99.96 ± 0.04	~0.5–0.7 ± 0.012 mg	239.075	Yes	155	Sealed glass tube	[22]
MP3	Abandoned	Piece	–	–	–	–	18	–	[23]
MP4	30/06/2023	Piece/152	99.806 ± 0.038	~0.35 ± 0.020 mg	239.06880 ± 0.00089	Yes	99.3 ± 3.3	Sealed glass tube	[24]

MP4 material production

Production of the MP4 CRM was carried out at the CEA's Valduc research center using plutonium metal from a single batch of plutonium which had been purified in the early 1990s. Figure 1 shows the different steps involved in the production and certification process for the CRM. As can be seen in the flowsheet presented in Fig. 1, the purified-plutonium metal was cast into rods in June 2017 at the CEA-Valduc research Center. Once the bars had been demolded, sampling was carried out within the rods at different heights (upper and lower levels) with destructive analysis performed on the samples in order to assess the homogeneity of the MP4 in terms of impurities. The impurities tested comprised metallic elements such as nickel (Ni), iron (Fe), chromium (Cr), tantalum (Ta), copper (Cu), calcium (Ca), aluminum (Al), boron (B), cadmium (Cd), cobalt (Co), molybdenum (Mo), gallium (Ga), magnesium (Mg), titanium (Ti), tungsten (W), and lead (Pb), as well as some light elements such as carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and Pu progeny (uranium (U) and americium (Am) isotopes). Apart from the actinides, these impurities represent contaminants potentially introduced during the metal's production process i.e. from the reagents (several chloride-based salts), equipment, Ta vessels, graphite mold), or moist air oxidation (O₂, water (H₂O)). Other metallic impurities (Fe, Cr, Ni, etc.) may reflect the use of stainless steel parts during the Pu processing and manufacturing steps. The precise method and statistical analysis used for the impurity studies performed during the homogeneity tests are presented in detail in the following section of the paper.

Once the homogeneity of the metal had been confirmed at an acceptable level with respect to production specifications (homogeneity standard uncertainty below 250 µg/g, see next chapter), the rods were machined into pieces with a mass close to 450 mg (gross mass before stripping). The produced pieces were then electropolished [25], rinsed and dried before being weighed and packaged in two glass-sealed ampoules under argon atmosphere.

Three manufacturing campaigns were carried out between 2017 and 2019. The final campaign in March 2019 suffered from some oxidation problems arising from a premature oxidation of the Pu metal rod during storage [26] leading to the samples produced during this campaign to be discarded. From the retained campaigns, a total of 152 samples of MP4 with a mass close to 350 mg were manufactured (Fig. 2 shows three samples of MP4 stored in their double ampoule containers).

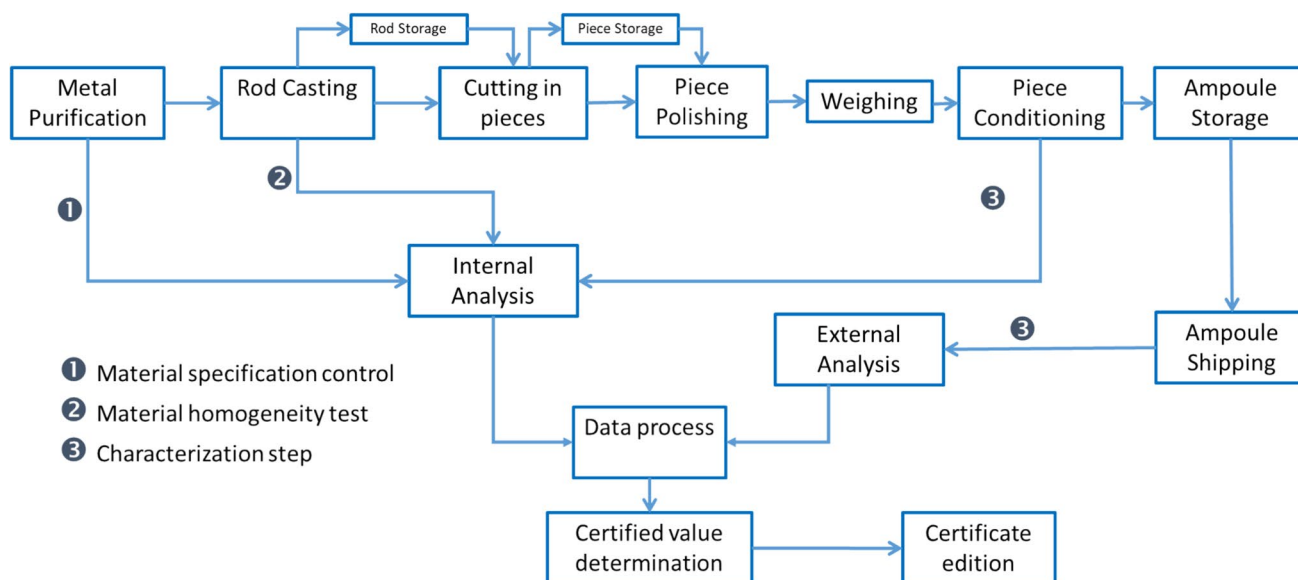


Fig. 1 MP4 production flowsheet

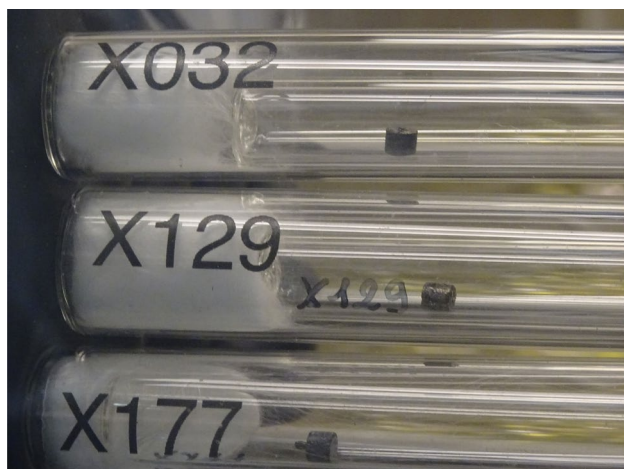


Fig. 2 MP4 Pu metal pieces in their glass-sealed ampoules

Material homogeneity

First evaluation

Homogeneity of the produced MP4 samples was ensured through an extensive analysis procedure. In terms of Pu isotopic abundance, MP4 CRM was prepared from a single batch of Pu metal and as such the Pu isotopic composition can be assumed to be homogeneous [7]. To verify that this material was homogeneous with regards to the Pu mass fraction, measurements of the mass fractions of impurities present in the metal were carried out by the CEA Valduc on eight different samples (lathe turnings) taken from four different evenly spaced bars in the barrel mold used to cast

the Pu metal, with each sample being positioned high or low within the bar. The impurity measurement results on the eight samples were processed by using a two-factor analysis of variance (ANOVA- with the factors used being the bar and the position in the bar) for each element analyzed. Through the ANOVA analysis it was possible to assess the *between-bar* and *between-position* variances. These two variances were judged to be non-significant in comparison to the *within-measurement* variance. The homogeneity variance for the CRM was therefore expressed as the measurement variance of all eight results.

More precisely, the post-fabrication analysis focused on 16 metallic elements and four light elements (C, O, N, H), as well as on the Pu progeny i.e. the Am-241, U-235, U-236, and U-238 isotopes. Only the mass fractions of eight metallic impurities (Al, Cu, Ga, Mo, Ni, Pb, Ta, W) and two light elements (C, O), as well as those of the Am and U isotopes were seen to be present in quantities above the detection limit (10 µg/g). The mean mass fraction values for these species as well as their homogeneity standard uncertainties are reported in Table 3.

Complementary oxygen analyses

Following the Pu metal oxidation issue during storage before conditioning, a new series of oxygen analyses by inert gas fusion technique of the conditioned pieces was undertaken in June 2019 to ensure that their oxygen content had not changed significantly compared with the average content measured after manufacture, and above all to estimate its impact on the homogeneity of the MP4 material. This new

Table 3 Mean mass fractions and homogeneity standard uncertainties for the impurities present in the MP4 CRM above the detection limit

w_i ($\mu\text{g/g}$)	C	O	Al	Cu	Ga	Mo	Ni	Pb	Ta	W	Am	U-235	U-236	U-238*
Mean value	15.1	31	21.5	13	12.0	44.7	10.59	28.7	382	11.3	73.3	620	40.28	16.8
Homogeneity standard uncertainty	4.1	22	6.0	12	2.4	4.9	0.43	6.7	38	2.4	1.5	11	0.71	2.8

* U-238 data to be considered with caution, given the Pu-238 isobaric interference. Analysis of C and O by Interstitial Gas analyzer techniques; analysis of metallic impurities including Am by Inductively Coupled Plasma—Atomic Emission Spectroscopy after separation from plutonium by liquid–liquid extraction; analysis of U isotopes by Inductively Coupled Plasma—Mass Spectrometry after dilution

series of O analyses involved six pieces conditioned in ampoules and sampled according to cutting and packaging factors. According to the measurements, the oxygen amount content did increase but no significant factor effects were observed. Therefore, a new O mass fraction value was calculated by taking the mean of these six new results, and its standard uncertainty was considered equal to the standard deviation of this series of measurements.

$$w_O = (180 \pm 88) \mu\text{g/g} (k = 1)$$

Standard uncertainty of homogeneity

From the uncertainties of all the analyzed impurities, it was then possible to express the standard uncertainty of homogeneity, u_{hom} , equal to the squared sum of the standard uncertainties of all impurities:

$$u_{hom} = u_{\sum w_i} = \sqrt{\sum u_{w_i}^2} = 98 \approx 100 \mu\text{g/g}$$

Heterogeneity (standard uncertainty of homogeneity) was in compliance with the manufacturing specifications (100 vs. 250 $\mu\text{g/g}$) and the material was judged homogeneous with a homogeneity standard uncertainty of 100 $\mu\text{g/g}$ for the Pu mass fraction.

Material characterization

Following production and homogeneity tests, MP4's properties were characterized through a dedicated ILC the purpose of which was to determine the characterization values for the Pu isotopic composition and Pu mass fraction of the CRM, as well as their associated uncertainties. The ILC involved eight different laboratories from the CEA (France), JRC-Geel (Belgium), JRC-Karlsruhe (Germany), and the IAEA (Austria) which are longstanding members of the CETAMA network and have been identified as analytical expert laboratories (see Table 4). Each lab received a certain number of MP4 units according to the analyses performed.

A total of 28 randomly selected samples of MP4 were sent to the laboratories for measurement. Table 5 summarizes the analyses each laboratory performed as well as the technique, instrument and CRMs used to calibrate their instruments.

In the cases wherein one laboratory was brought to analyze several pieces of MP4, the expression of the final results was taken to be the arithmetic mean of the different analysis results (Eq. 1) and its standard uncertainty was the square root of the squared sum of the individual standard uncertainties divided by the number of results (Eq. 2): although the results are not strictly independent, as they are analyzed by the same instrument, they were taken to be independent (at least for the sample preparation aspect) for the purposes of the present work.

Table 4 Participating laboratories and planned analyses for the MP4 certification ILC

Institution	Laboratory	Planned analyses
IAEA Seibersdorf	NML	(U, Pu, Am) amount contents/(U, Pu) isotopic composition
CEA Marcoule	LAAT	(U, Pu, Am, metallic impurities) amount contents/(U, Pu, Am) isotopic composition
CEA Marcoule	LSEM	C amount content
CEA Marcoule	LAMMAN	Pu amount content
CEA Saclay	LANIE	(U, Pu) isotopic composition
CEA Valduc	LCA	(U, Am, metallic impurities, C, O) amount contents/(U, Pu) isotopic composition
JRC Geel		Pu isotopic composition
JRC Karlsruhe		(U, Pu, Am, metallic impurities, C, O) amount contents/(U, Pu) isotopic composition
	Total provisioned samples	28

Table 5 Summary of analyses performed by laboratories for MP4 characterization and CRM used for instrument calibration

Measurand	Laboratory(*)	Analysis method (**)	Measurement instrument	CRM
Pu mass fraction <i>direct determination</i>	CEA-LAAT	ID-TIMS	Thermo Fisher Sc. Triton MC-TIMS	IRMM-49d
	CEA-LAMMAN	CPC	CEA coulometer 2.6	AOIP SN8310, MP2
	JRC-Karlsruhe	ID-TIMS	Thermo Fisher Sc. Triton MC-TIMS	MP2, IRMM 290f
	IAEA-NML	CPC	SRNL coulometer	CRM126A/MP2
		ID-TIMS	Thermo Fisher Sc. Triton MC-TIMS	CRM130, KRI_RM2-662, IRMM-049d, IRMM-049e
Pu mass fraction <i>indirect determination</i>				
Am mass fraction	CEA-LAAT	ID-TIMS gamma spectrometry	Thermo Fisher Sc. Triton MC-TIMS	LNHB 11284 LEA standard
	CEA-LCA	ICP-AES	PerkinElmer Optima 4300 DV	LEA standard
	IAEA-NML	alpha spectrometry gamma spectrometry	Mirion Alpha Analyst Mirion HRGS BEGeP	CRM 137 –UKAEA 90099 ISOCS
	JRC-Karlsruhe	gamma spectrometry	HPGe Ortec Ametek	CBNM-EC-NRM-271
U mass fraction	CEA-LAAT	ID-TIMS	Thermo Fisher Sc. Triton MC-TIMS	IRMM-054
	CEA-LCA	ICP-MS	Thermo Fisher Sc. X-Series	Techlab LMS-2AN
	IAEA-NML	ID-TIMS	Thermo Fisher Sc. Triton MC-TIMS	NBL 111-A
	JRC-Karlsruhe	HR-ICP-MS	Thermo Fisher Sc. Element 2 HR-ICP-MS	EC101, EC110, NBL-125
C mass fraction	CEA-LCA	IGA	LECO-CS-444	LECO 502-455
	CEA-LSEM	IGA	Sylab	ECISS 299-1, OPERA 104
	JRC-Karlsruhe	IGA	ELTRA-CS-800	ECISS-284-2
O mass fraction	CEA LCA	IGA	LECO TCH-600	LECO 502-456/501-643/501-644, Alpha resources AR1653
Metallic impurities mass fraction	CEA-LCA	ICP-AES	Perkin Elmer Optima 4300 DV	O2Si and Techlab standards
	CEA-LAAT	ICP-AES	Perkin Elmer Optima 8300 DV	PerkinElmer standards
		ICP-MS	Perkin Elmer ELAN DRce	PerkinElmer standards
	JRC-Karlsruhe	ICP-MS	Thermo Fisher Sc. Element 2 HR-ICP-MS	PerkinElmer, Inorganic Ventures standards
Pu isotope ratio	CEA-LAAT	TIMS alpha spectrometry	Thermo Fisher Sc. Triton MC-TIMS	MP2 LEA standards
	CEA-LANIE	TIMS	Thermo Fisher Sc. Triton plus MC-TIMS	MP2
	CEA-LCA	TIMS	Finnigan MAT-261 MC-TIMS	NBL CRM138
	JRC-Geel	TIMS	Thermo Fisher Sc. Triton MC-TIMS	IRMM-290-A3
	JRC-Karlsruhe	TIMS alpha spectrometry	Thermo Fisher Sc. Triton MC-TIMS	MP2, IRMM 290F
	IAEA-NML	TIMS alpha spectrometry	Thermo Fisher Sc. Triton MC-TIMS Mirion Alpha Analyst	MP2, NBL CRM 137-136-138 CRM137-UKAEA 90099
U isotope ratio	CEA LAAT	TIMS	Thermo Fisher Sc. Triton MC-TIMS	IRMM-054
	CEA-LCA	ICP-MS	Thermo Fisher Sc. X-Series	Techlab LMS-2AN
	CEA LANIE	TIMS	Thermo Fisher Sc. Triton plus MC-TIMS	IRMM-199
	JRC-Karlsruhe	HR-ICP-MS	Thermo Fisher Sc. Element 2 HR-ICP-MS	IRMM-199, NBS SRM U-930
	IAEA-NML	TIMS	Thermo Fisher Sc. Triton MC-TIMS	CRM 111a
Mass	CEA-LCA	weighing	Mettler XPR2	Zwiebel standards

(*)LAAT: Atalante Analysis Laboratory; LAMMAN: Nuclear Material Metrology Laboratory; JRC: Joint Reserach Center of the European Commission; IAEA-NML: Nuclear Material Laboratory of the International Atomic Energy Agency; LCA: Actinide Chemistry Laboratory; LSEM: Actinide Material Elaboration and Solid Chemistry Laboratory; LANIE: Elemental and Istotopic Nuclear Analytical development Laboratory

(**) CPC: Controlled Potential Coulometry; ID-TIMS: Isotope Dilution Thermal Ionization Mass Spectrometry; ICP-MS: Inductively-Coupled Plasma Mass Spectrometry; HR-ICP-MS: High Resolution Inductively-Coupled Plasma Mass Spectrometry; IGA: Interstitial Gas Analyzer; ICP-AES: Inductively-Coupled Plasma Atomic Emission Spectrometry

$$\bar{x} = \frac{\sum_i x_i}{n} \quad (1)$$

$$u(\bar{x}) = \frac{\sqrt{\sum u^2(x_i)}}{n} \quad (2)$$

Statistical methods applied to the determination of the consensual mean value

The consensual value is calculated either by the classical weighted mean approach or the Der Simonian & Laird (DL) weighted mean approach (Eq. 3) [27]. In the former case, each result is weighted with a factor w_i inversely proportional to the square root of the claimed laboratory uncertainty u_i (Eq. 4):

$$\text{classical or DL weighted mean} = \sum_i w_i x_i \quad (3)$$

$$w_i = \frac{1}{u_i^2} \quad (4)$$

In the latter case, the weight factor takes into account, if necessary, the laboratory effect leading to scattered results. It introduces an excess variance term, known as “Excess variance”, or “unexplained” uncertainty, known as “Dark uncertainty” written τ which changes the weight factor by increasing the laboratory variance u_i^2 , by a term τ^2 common to all laboratories and reflecting the “unexplained” laboratory effect. The weighting factor, w_i , then writes (Eq. 5):

$$w_i = \frac{1}{u_i^2 + \tau^2} \quad (5)$$

In this case, in the graphical display of the results (see Fig. 3) a second coverage interval (shaded in light blue) overlays the laboratory coverage interval (in blue hatching) and enables a visualization taking into account the inter-laboratory variance according to the DL theory. Further information about the DL approach can be found in the following references [28–30].

Plutonium isotopic measurements for material characterization

In order to measure the Pu isotopic composition of the MP4 samples, two different analysis techniques were applied; the Pu isotope ratios (relative to Pu-239, the major isotope) were all measured by multi collector thermal-ionization mass spectrometry (MC-TIMS) except

for the Pu-238 to Pu-239 isotope ratio which was also measured by alpha spectrometry by some laboratories (provided that the Pu-240 to Pu-239 isotope ratio had been determined previously by TIMS). The use of these two techniques resulted in the assignment of five laboratory codes to TIMS measurements and one code to the alpha spectrometry measurements of the Pu-238 to Pu-239 isotopic ratio. Only the Pu-238, Pu-240, Pu-241 and Pu-242 minor isotopes were detected above the detection limit. As such, only these four ratios were measured and expressed in mol/mol as reported in Table 6.

The analysis results with their coverage intervals ($k=2$) in hatched pattern are also displayed in Fig. 3 by order of increasing value and are compared to the consensual mean value (red line) with its coverage interval (red shaded area).

It should be noted that all values are decay corrected to a reference date of June 30th 2023[31] and that different values were considered as outliers and not taken into account because their uncertainty was too high (according to Cochran test) or their values too far from the consensus value (according to Grubbs test).

The resulting consensual values for the Pu isotopic ratios of MP4 are shown in Table 6 along with their expanded uncertainties in both absolute and relative terms ($k=2$).

Americium mass fraction and isotopic measurements

Am is considered as an impurity in the MP4 CRM. Nonetheless, the mass fraction of Am in the material was a key element towards the indirect determination of the mass fraction of Pu in the material ($w_{\text{Pu}} = 1 - \sum w_{\text{impurities}}$). The isotopic abundance of Am in MP4 was measured by the LAAT (Atalante Analysis Laboratory) through TIMS analysis. From the isotopic analyses, it was observed that the Am in MP4 is present exclusively in the form of Am-241, with Am-242 m/Am-241 and Am-243/Am-241 ratios being measured below the detection limit (5.010^{-5}).

The exclusive presence of Am as the Am-241 isotope in MP4 can be explained by the generation pathway for this element from the radioactive decay of the Pu-241 isotope. From these considerations, the molar mass M_{Am} of the Am impurities in MP4 was considered equivalent to that of the Am-241 isotope $M_{\text{Am-241}}$, i.e. [32]:

$$M_{\text{Am}} = M_{\text{Am-241}} = 241.0568273 \text{ g/mol} \quad (6)$$

During the certification ILC, the Am mass fraction was measured by ID-TIMS, ICP-AES, gamma and alpha spectrometry, leading to the assignment of six laboratory codes. The measurement results are reported in Table 7 and have

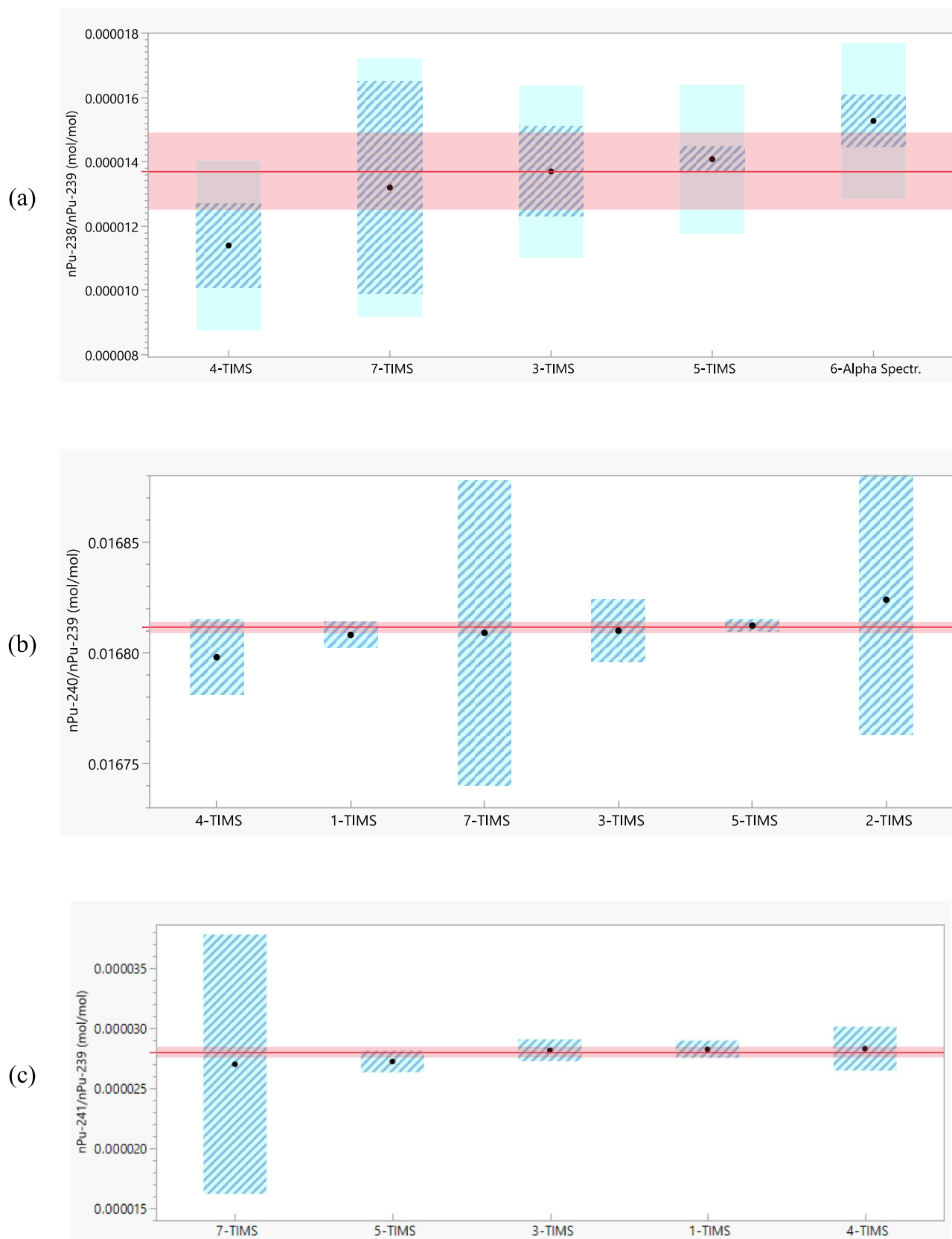


Fig. 3 Plutonium isotope ratio data for individual measurements with their coverage interval (in blue hatched form, $k=2$) overlaid by the DL coverage interval (light blue shaded form, $k=2$). The consensual

mean value is plotted as a red solid line with its coverage interval (red shaded form, $k=2$). **a** Pu-238/Pu-239; **b** Pu-240/Pu-239; **c** Pu-241/Pu-239; **d** Pu-242/Pu-239

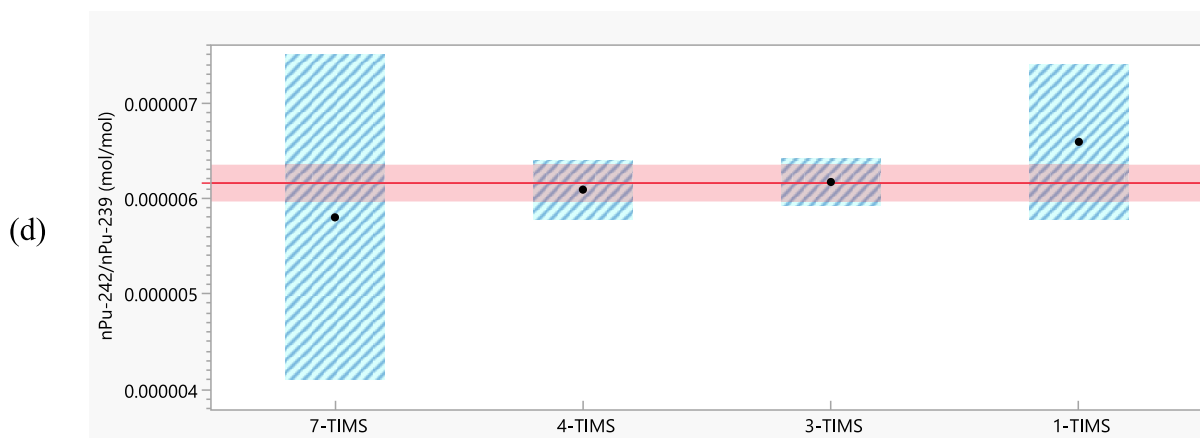


Fig. 3 (continued)

Table 6 Pu isotope ratio measurement results for material characterization expressed in mol/mol

Sample ID	Lab code instrument	$n(^{238}\text{Pu})/n(^{239}\text{Pu})$	$n(^{240}\text{Pu})/n(^{239}\text{Pu})$	$n(^{241}\text{Pu})/n(^{239}\text{Pu})$	$n(^{242}\text{Pu})/n(^{239}\text{Pu})$
X036-X094	1-TIMS	<i>0.00001922(50)</i>	0.0168081(59)	0.00002825(64)	0.00000659(81)
X50-X121-X145	2-TIMS	<i>0.000032(25)</i>	0.016824(35)	<i>0.000031(19)</i>	
X066	3-TIMS	0.0000137 (14)	0.016811(14)	0.00002817(86)	0.00000617(25)
X055	4-TIMS	0.0000114(13)	0.016798(17)	0.0000283(18)	0.00000609(31)
X080-X101-X172	5-TIMS/Alpha spectr	0.00001408(41)	0.0168123(26)	0.00002723(83)	
X066	6-Alpha spectr	0.00001527(81)			
X126-X150	7-TIMS	0.0000132(33)	0.016809(69)	0.000027(11)	0.0000058(17)
Consensual value for characterization					
Value	mol/mol	$1.37 \cdot 10^{-5}$	$1.68114 \cdot 10^{-2}$	$2.796 \cdot 10^{-5}$	$6.16 \cdot 10^{-6}$
Uncertainty	mol/mol ($k=2$)	$0.12 \cdot 10^{-5}$	$0.00023 \cdot 10^{-2}$	$0.046 \cdot 10^{-5}$	$0.19 \cdot 10^{-6}$
Rel. uncertainty	($k=2$)	8.8%	0.014%	1.6%	3.1%

Values in italic were considered as outliers and were not taken into account in a first approach

Experimental values are averages of replicate measurements for one or several pieces for a laboratory and an associated method. The numbers in parentheses are the expanded uncertainties with coverage factor of 2 corresponding to the last two digits of the isotope ratio values. Consensual values for characterization are shown at the end of the table. All reported values are decay corrected to the reference date of June 30th 2023

been plotted in Fig. 4 with the exception of the results of lab code three which were considered outlier values.

From the results of the ILC analyses, a consensual value for the Am mass fraction in MP4 was determined by the classical weighted mean approach as the dark uncertainty term τ was found to be equal to 0. This consensual value is reported in Table 7 with its expanded uncertainty in both absolute and relative terms ($k=2$).

Uranium isotopic measurements

U is another impurity present in the MP4 CRM. This impurity arises exclusively from the alpha radioactive decay of the Pu-238, Pu-239, Pu-240 and Pu-242 isotopes. As such, its isotopic abundance corresponds to a mixture of

the isotopes U-234, U-235, U-236 and U-238, with U-235, daughter isotope of Pu-239, as the major component.

The characterization of the uranium isotopic abundance in the MP4 CRM involved determining three isotope ratios expressed in relation to U-235 major isotope and in terms of mol/mol.

A total of five laboratories measured the U isotopic composition of the MP4 CRM during the ILC. The laboratories performed analyses through TIMS, ICP-MS, or High-resolution ICP-MS (HR-ICPMS), resulting in the attribution of five laboratory codes. The mean values of their results and with the associated uncertainties are provided in Table 8.

As the time lag between the dates of analysis and the reference date did not exceed six months, and the radioactive

Table 7 Am mass fraction measurement results for material characterization expressed in $\mu\text{g/g}$

Sample ID	Lab code/method	w_{Am} ($\mu\text{g/g}$) (*)
X066	1-ID-TIMS	98.3(1.9)
X066	2-Gamma spectr	99.8(2.0)
X050-X121-X145	3-ICP-AES	86.8(5.8)
X080-X101-X172	4-Gamma spectr	101.4(3.4)
X126-X150	5-Gamma spectr	97(10.7)
X126-X150	6-Alpha spectr	97.4(16.1)
Consensual value for characterization		
$(w_{\text{Am}})_{\text{char}}$ value	$\mu\text{g/g}$	99.3
Uncertainty	$\mu\text{g/g}$ ($k=2$)	1.3
Rel. uncertainty	($k=2$)	1.3%

(*) The value in italics was considered as an outlier and was not taken into account in a first approach

Values are averages of replicate measurements for one or several pieces for a laboratory and an associated method. The numbers in parentheses are expanded uncertainties ($k=2$) corresponding to the last two digits of the mass fraction. Consensual value for characterization is given at the end of the table. All reported values are decay corrected to the reference date of June 30th 2023

half-lives of U isotopes are greater than 245,000 years, no corrections for decay were applied.

The experimental results for the, $n(^{234}\text{U})/n(^{235}\text{U})$, and $n(^{236}\text{U})/n(^{235}\text{U})$ isotope ratios are presented in Fig. 5 relative to the weighted mean of all the results. The weighted mean of the analyses, presented as the red line with its coverage interval (red band) was taken as the consensual value for the $n(^{234}\text{U})/n(^{235}\text{U})$, and $n(^{236}\text{U})/n(^{235}\text{U})$ isotope ratios in the MP4 CRM (Table 8).

In the case of the $n(^{238}\text{U})/n(^{235}\text{U})$ isotopic ratio, no consensus between the analysis results could be found as the results were highly disparate. As such, in accordance with all the involved laboratories, only the analysis value with the lowest value and uncertainty has been retained to characterize the $n(^{238}\text{U})/n(^{235}\text{U})$ ratio in MP4 (Table 8). The laboratory involved in this measurement implemented a particularly careful U/Pu separation procedure on a UTEVA resin column, minimizing external uranium contamination.

The U isotopic ratios consensual values for material characterization are shown in Table 8 as well as their expanded uncertainty in both absolute and relative terms ($k=2$).

Uranium mass fraction measurement

The U mass fraction in MP4 was measured by three different techniques; ID-TIMS, ICP-MS, and HR-ICPMS, leading to the attribution of four different laboratory codes. The measurement results are shown in Table 9 and have been plotted in Fig. 6.

The experimentally measured values for the U mass fraction are presented by ascending value in Fig. 6. The consensus value for the U mass fraction in MP4, determined by the DL weighted mean approach is also presented in Fig. 6 as the solid red line with the red band representing its coverage interval ($k=2$).

The consensual value for the mass fraction of U in the MP4 CRM is reported in Table 9 with its expanded uncertainty in absolute and relative terms ($k=2$).

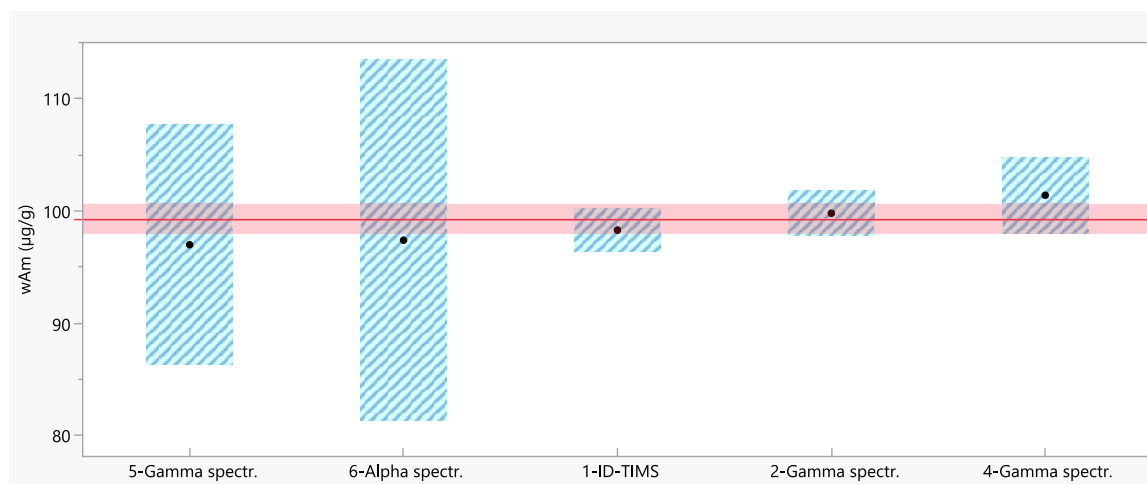


Fig. 4 Am mass fraction data for individual measurements with their coverage intervals (in hatched form, $k=2$). The red solid line represents the consensual mean value and the red shaded area delineates its

coverage interval ($k=2$). All values are decay corrected to a reference date of June 30th 2023

Table 8 U isotope ratio measurement results for material characterization expressed in mol/mol. Experimental values are averages of replicate measurements for one or several pieces for a laboratory and an associated method. The numbers in parentheses are expanded

uncertainties ($k=2$) corresponding to the last two digits of the isotopic ratio values. Consensual values are shown at the end of the table. All reported values are given for the reference date of June 30th 2023

Sample ID	Lab code/method	$n(^{234}\text{U})/n(^{235}\text{U})$	$n(^{236}\text{U})/n(^{235}\text{U})$	$n(^{238}\text{U})/n(^{235}\text{U})$
X050-X121-X145	1-ICPMS		<i>0.0586(76)</i>	
X066	2-TIMS	0.003908(24)	0.06187(24)	<i>0.00105(22)</i>
X055	3-TIMS	0.003904(20)	0.061887(62)	0.000623(32)
X080-X101-X172	4-HR-ICPMS	0.003917(33)	0.0621(29)	<i>0.0648(63)</i>
X126-X150	5-TIMS	<i>0.00350(16)</i>	0.0614(11)	<i>0.0375(33)</i>
Consensual value for characterization				
Value	mol/mol	$3.908 \cdot 10^{-3}$	$6.1886 \cdot 10^{-2}$	$6.23 \cdot 10^{-4}$
Uncertainty	mol/mol ($k=2$)	$0.014 \cdot 10^{-3}$	$0.0060 \cdot 10^{-2}$	$0.32 \cdot 10^{-4}$
Rel. Uncertainty	($k=2$)	0.36%	0.10%	5.1%

(*Values in italic were considered as outliers and were not taken into account for the determination of the characterization consensual value

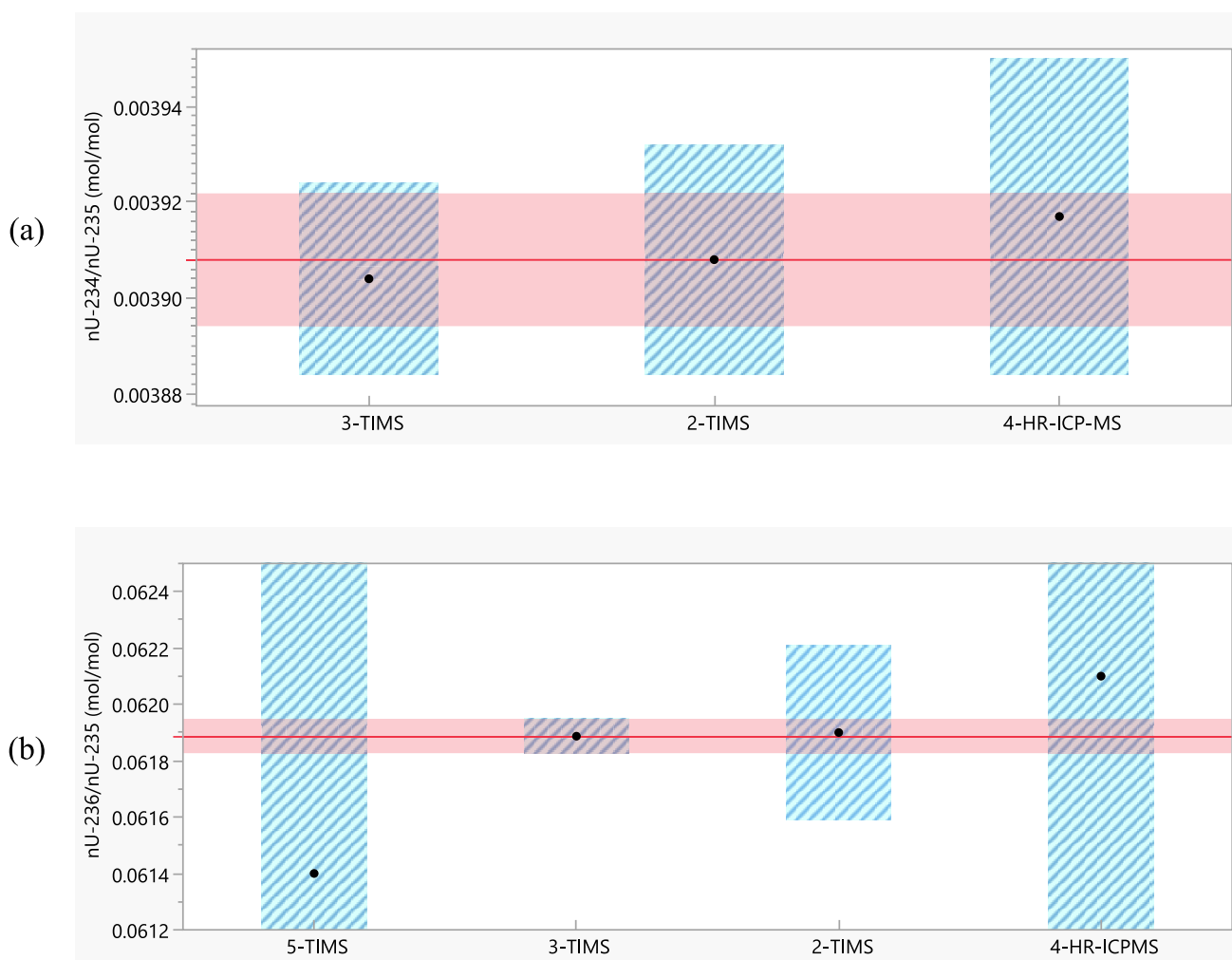


Fig. 5 Uranium isotope amount ratio data for individual measurements and their coverage intervals (in hatched form, $k=2$). The red solid lines represent consensual mean values calculated for each isotope ratio estimated by the weighted mean approach. The shaded area

delineates the coverage interval ($k=2$) for the mean value. Reference date is June 30th 2023. **a** U-234/U-235; **b** U-236/U-235

Table 9 U mass fraction measurement results for material characterization expressed in $\mu\text{g/g}$

Sample ID	Lab code/method	w_U ($\mu\text{g/g}$)
X066	1-ID-TIMS	842(11)
X050-X121-X145	2-ICPMS	952(29)
X080-X101-X172	3-HR-ICPMS	918(14)
X126-X150	4-ID-TIMS	874(18)
Consensual value for characterization		
$(w_U)_{\text{char}}$ value	$\mu\text{g/g}$	896
Uncertainty	$\mu\text{g/g}$ ($k=2$)	47
Rel. uncertainty	($k=2$)	5.2%

Values are averages of replicate measurements for one or several pieces for a laboratory and an associated method. The numbers in parentheses are the expanded uncertainties with a coverage factor of 2 corresponding to the last two digits of the mass fraction. Consensual value is given at the end of the table. All reported values are decay corrected to the reference date of June 30th 2023

Carbon and oxygen mass fraction measurements

The carbon mass fraction in MP4 was measured by three laboratories using the combustion technique and leading to the attribution of three laboratory codes. Table 10 presents the results of the analyses performed.

The experimentally measured values for the C mass fraction are presented in Fig. 7 along with their coverage intervals (in hatched form, $k=2$). The weighted mean was determined by applying the DL theory to the three results provided by the laboratories and has been drawn

as a horizontal red line on the same graph as well as its coverage interval (red shaded area). The coverage intervals of individual results are then reinterpreted according to DL theory and are drawn on the same graph as a blue shaded coverage interval.

From the analysis results, the DL weighted mean presented in Fig. 7 was taken as the consensual value for the mass fraction of C in MP4. This consensual value is reported in Table 10 as well with its expanded uncertainty in absolute and relative terms ($k=2$).

Oxygen mass fraction measurement

Determination of the consensus value for the O mass fraction, w_O , was based on the mean of six results reported by a single laboratory which used inert gas fusion technique. Table 11 summarizes these measurements and their interpretation. The weighted mean according to DL theory gives the best estimate of the mean, since the τ dark uncertainty term is greater than 0 and is very high compared with the uncertainty of the measurements. The results are very scattered indeed, indicating a high degree of heterogeneity with regard to the presence of oxygen in the material or, more likely, on the surface of the material in the form of an oxide. This heterogeneity term is taken into account in the τ factor and enables us to estimate the uncertainty of the consensus mean, taking all contributions into account.

The experimentally measured values for the O mass fraction in MP4 are presented in Fig. 8 in relation to their DL

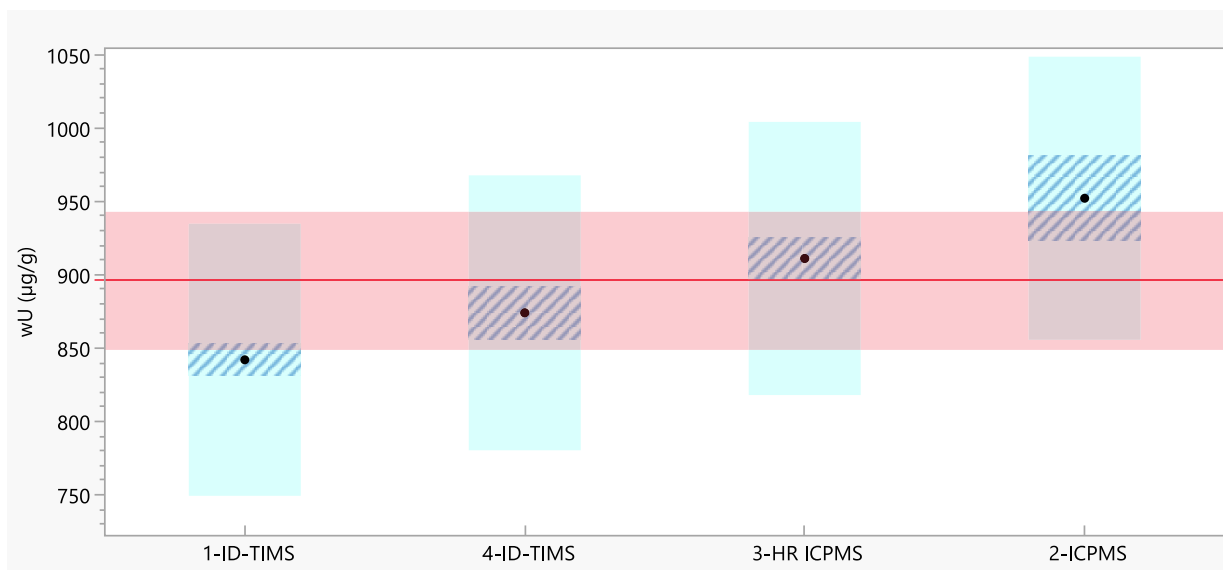


Fig. 6 Uranium mass fraction data for individual measurements with their coverage intervals (in hatched form, $k=2$) overlaid by the DL coverage intervals (in light blue shaded form, $k=2$). The solid line in red represents the consensual mean value calculated by the DL

weighted mean approach. The shaded area in red delineates the coverage interval ($k=2$) for the mean value. All values are decay corrected to a reference date of June 30th 2023

Table 10 C mass fraction measurement results for material characterization expressed in $\mu\text{g/g}$

Sample ID	Lab code/method	w_C ($\mu\text{g/g}$)
X099-X125-X174	1-C analyser	48(12)
X095-X181	2-C analyser	60(19)
X071-X119-X142	3-C analyser	42(11)
Consensual value for characterization		
$(w_C)_{\text{char}}$ value	$\mu\text{g/g}$	47.7
Uncertainty	$\mu\text{g/g}$ ($k=2$)	9.0
Rel. uncertainty	($k=2$)	19%

Values are averages of two or three measurements. The numbers in parentheses are expanded uncertainties with coverage factor of 2 corresponding to the last two digits of the mass fraction. Consensual value for characterization is reported at the end of the table

weighted mean (solid red line) with its associated coverage interval at $k=2$ (red band).

Metallic impurity mass fraction measurement

The analysis of the non-actinide metallic impurities in MP4 was carried out by three laboratories and concerned the eight metallic elements—Al, Cu, Ga, Mo, Ni, Pb, Ta, W—detected in significant quantities in the material after metal casting (based on post-fabrication analyses). Three laboratory codes were thus attributed for the analyses of the non-actinide metallic impurities in MP4, the measurement results are presented in Table 12.

From the results in Table 12, it can be seen that the mass fractions of Cu and Mo were reported to lie below the detection limit by every laboratory. In the case of Ta,

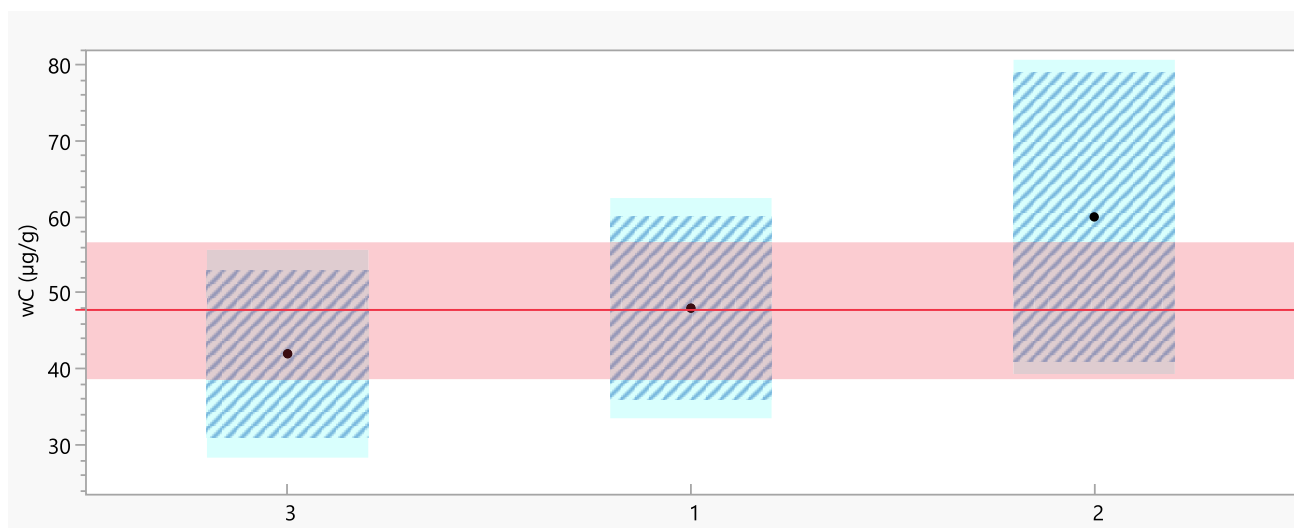


Fig. 7 Carbon mass fraction data for individual measurements with their coverage interval (in hatched form, $k=2$) overlaid by the DL coverage interval (blue shaded form, $k=2$). The red solid line repre-

sents the consensual mean value calculated by the DL weighted mean approach. The red shaded area delineates the coverage interval ($k=2$) for the mean value

Table 11 O mass fraction measurement results for material characterization expressed in $\mu\text{g/g}$

Oxygen mass fraction	Reference unit	Mean $\mu\text{g/g}$	Uncertainty ($k=2$) $\mu\text{g/g}$	Consensual mean expression from DL weighted mean approach ($\mu\text{g/g}$)
w_O	X 042	320	21	(179 ± 75)
	X 046	220	22	
	X 062	210	22	
	X 065	130	22	
	X 147	86	24	
	X 149	110	23	

In the last column, the mean value obtained by the DL approach with its expanded uncertainty

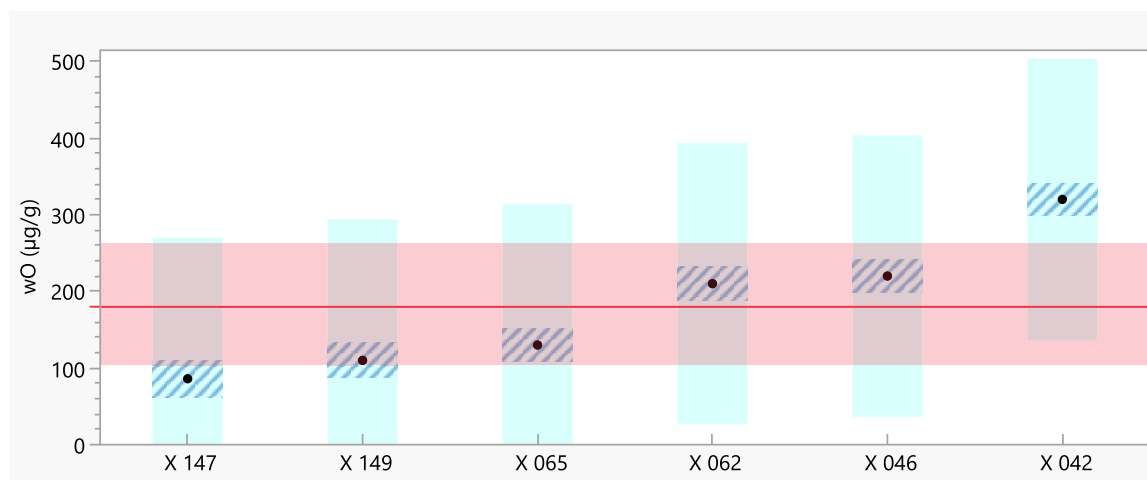


Fig. 8 Oxygen mass fraction data for individual measurements with their coverage interval (in hatched form, $k=2$) overlaid by the DL coverage interval (blue shaded form). The red solid line represents the

consensual mean value. The red shaded area delineates the coverage interval ($k=2$) for the mean value

the analysis values can be seen to be particularly disparate. As such, the choice was made to retain solely the mean Ta analysis value reported by laboratory one in light of the fact that it was the result of three independent and very repeatable measurements.

Following the results reported in Table 12, the consensus values were determined for the mass fraction of the six metallic impurities, w_{Mi} , present above the detection limit. w_{Mi} was therefore based on either a single result, a pair of results averaged arithmetically, or a triplet of results averaged according to the DL approach. The consensual values thus determined are presented in the same table in combination with their absolute and relative expanded uncertainties ($k=2$).

A comparison of the consensual values for characterization with the post fabrication analyses performed by the CEA Valduc in Table 13 shows a good coherence between the two series of results, especially for Ta. Only Cu and Mo are no longer significantly detected. Their presence in the post fabrication samples at significant level could be explained by analytical pollution.

The sum of the mass fractions of the non-metallic impurities in MP4 can be expressed as a single consensual value, W_{Mi} , which is the sum of the individual impurity values with its standard uncertainty defined as the root of the squared sum of the individual standard uncertainties. This consensual value of the mass fraction of non-actinide metallic impurities in MP4 is reported in the end of Table 12 with its expanded uncertainty in both absolute and relative terms ($k=2$).

Plutonium mass fraction measurements

The determination of the consensus value for the mass fraction of Pu in MP4, w_{Pu} , was based on the expression of the average of six results from:

- Five direct determinations of w_{Pu} by CPC or ID-TIMS,
- A single indirect determination of w_{Pu} .

The indirect determination of w_{Pu} was based on the measurement of the sum of the impurities, considered exhaustive, at the reference date and the following calculation of the complementary value (Eq. 7):

$$w_{Pu}^{indirect} = 1 - \sum_i w_{impurities} \quad (7)$$

The standard uncertainty associated with this indirect determination is equal to the root of the squared sum of the measurement standard uncertainties for each impurity. This uncertainty calculation is detailed in Table 14 with the final expression of the Pu mass fraction from indirect calculation:

These analyses resulted in the attribution of six laboratory codes. Table 15 summarizes the results for direct and indirect measurements of the Pu mass fraction in MP4.

The results of the six different laboratory codes used to determine W_{Pu} through both direct and indirect means are graphically displayed in Fig. 9 in ascending order in combination with the weighted mean of these results with

Table 12 Metallic impurity mass fraction measurement results for material characterization expressed in µg/g

Sample ID	Lab code /method	W _{Al} (µg/g)	W _{Cu} (µg/g)	W _{Ga} (µg/g)	W _{Mo} (µg/g)	W _{Ni} (µg/g)	W _{Pb} (µg/g)	W _{Ta*} (µg/g)	W _W (µg/g)
X050-X121-X145	1-ICPAES	30.3(5.8)	< 10	10.5(5.8)	< 10	10.0(5.8)	14(10)	397(23)	14.7(5.8)
X066	2-ICPAES/MS	< 100	< 4	11.1(2.4)	< 0.6	13.8(6.9)	< 20	24(12)	14.5(3.1)
X080-X101-X172	3-ICP-MS	< 100	< 100	12.4(0.6)	< 10	< 100	< 10	90(37)	2.3(1.1)
Consensual value for characterization for individual impurity									
Value	µg/g	30.3		11.9		11.9	14	397	14.6
Uncertainty	µg/g (k=2)	5.8		1.7		4.5	10	23	3.3
Rel. uncertainty	(k=2)	19%		14%		38%	71%	6%	23%
Consensual value for characterization for total impurities									
W _{Mi} Value	µg/g			480					
Uncertainty	µg/g (k=2)			23					
Rel. uncertainty	(k=2)			4.8%					

(*)Values in italic were considered as outliers and were not taken into account for the determination of the characterization consensual value

Values are averages of replicate measurements for one or several pieces for a laboratory and an associated method. The numbers in parentheses are expanded uncertainties (k=2) corresponding to the last two digits of the mass fraction. Mass fraction consensual values are given at the end of the table for each impurity detected above detection limit and for the sum of all impurities

Table 13 Comparison of post-fabrication and post-conditioning metallic impurity mass fraction measurements

Post fabrication analysis	w (µg/g)	Uncertainty (k=2) (µg/g)	Post conditioning analysis	w (µg/g)	Uncertainty (k=2) (µg/g)
Al	22	10	Al	30.3	6
Cu	16	10	Cu	< 3	
Ga	12	10	Ga	11.9	1.7
Mo	45	10	Mo	< 10	
Ni	11	10	Ni	11.9	4.5
Pb	29	10	Pb	14	10
Ta	382	38	Ta	397	23
W	12	10	W	14.6	3.3
			W _{Mi}	480	26

Table 14 Pu mass fraction indirect determination

	w (µg/g)	Uncertainty (k=2) (µg/g)
U	896	47
Am	99.3	1.3
C	47.7	9.0
O	179	75
metal i	480	26
sum	1702	93
Date	30/06/2023	
w _{Pu}	998.298	g/kg
Uncert. (k=2)	0.093	g/kg

its coverage interval as determined according to the DL weighted mean approach.

The final consensual value for W_{Pu} in the MP4 CRM was taken to be the DL weighted mean of the six (direct and indirect) analysis results. This consensual value is reported in Table 15 with its expanded uncertainty (k=2) in both absolute and relative terms:

Determination of the certified values and demonstration of their traceability

General considerations on the expression of the reference values and their uncertainties

Following the determination of the consensual values for the characterization of MP4, the chosen properties were certified according to the procedures laid out in the ISO 33405 standard⁸. In this standard, a certified value, *y_{ref}*, is established

Table 15 Pu mass fraction measurement results for material characterization expressed in g/kg

Sample ID	Lab code/method	wPu (g/kg)
X066	1-CPC	997.94(74)
X80-X101-X172	2-ID-TIMS	996.5(1.7)
X066	3-ID-TIMS	997.8(3.0)
23 samples	4-indirect measurement	998.298(93)
X126-X150	5-CPC	997.90(78)
X126-X150	6-ID-TIMS	997.95(57)
Consensual value for characterization		
(w _{Pu}) _{char} value	g/kg	998.06
Uncertainty	g/kg ($k=2$)	0.33
Rel. uncertainty	($k=2$)	0.033%

Values are averages of replicate measurements for one or several pieces for a laboratory and an associated method. Number in parentheses are expanded uncertainties ($k=2$) corresponding to the last two digits of the mass fraction values. All reported values are decay corrected to the reference date of June 30th 2023

based on analyses that are traceable to the International System (SI) of Units and is taken to be equal to the characterization consensus value, y_{char} , plus any errors related to heterogeneity, δ_{hom} , or material instability, δ_{lts} (Eq. 8):

$$y_{ref} = y_{char} + \delta_{hom} + \delta_{lts} \quad (8)$$

In the case of the MP4 CRM, the material is known to be homogeneous both in terms of isotopic composition and mass fractions, such that $\delta_{hom} = 0$. Furthermore, as the material is characterized for a given date, its instability does not need to be taken into account whilst expressing certified values ($\delta_{lts} = 0$), such that (Eq. 9):

$$\text{for MP4, } y_{ref} = y_{char} \quad (9)$$

In terms of the uncertainty on the reference value, it follows that, by applying the GUM [33], the variance of a reference value is equal to the sum of the variances of characterization, homogeneity and long-term stability (Eq. 10):

$$u_{ref}^2 = u_{char}^2 + u_{hom}^2 + u_{lts}^2 \quad (10)$$

Pu isotope amount ratio reference values and their derived values

In the case of the Pu isotope amount ratios, the Pu in MP4 is considered homogeneous in terms of isotopic composition. Meaning that the homogeneity standard uncertainty between pieces can be considered equal to zero (Eq. 11):

$$u_{hom} = 0 \quad (11)$$

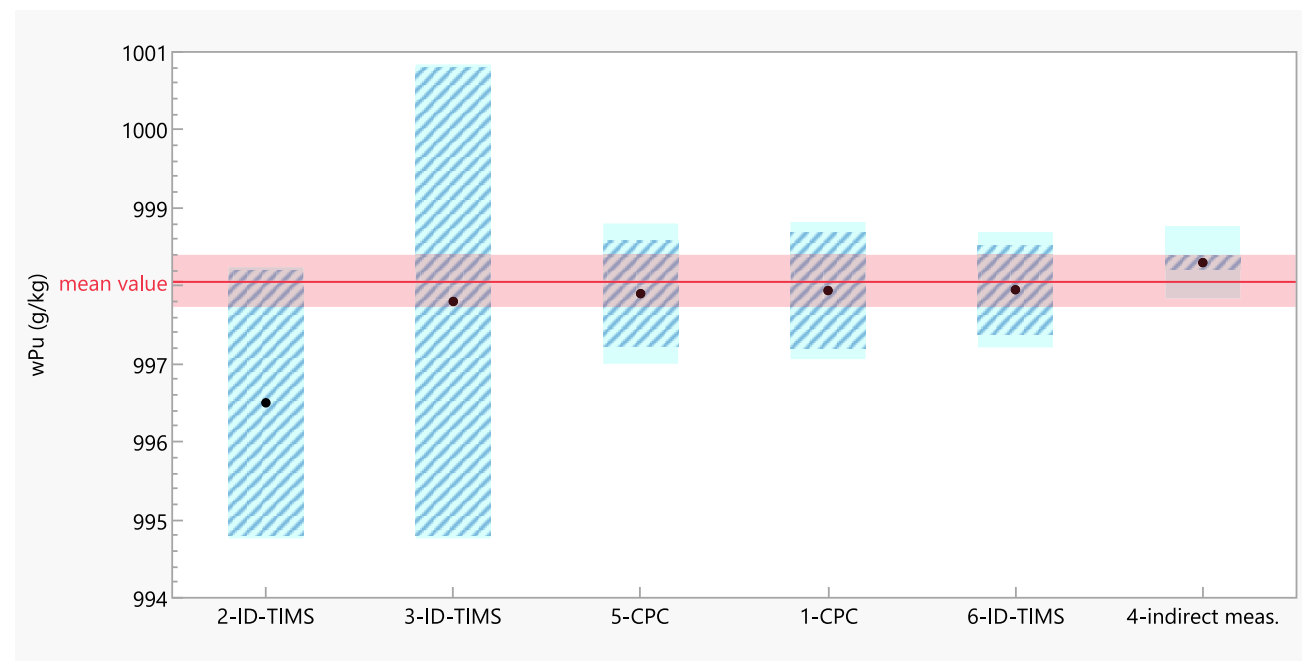


Fig. 9 Plutonium mass fraction individual measurements with their coverage interval (in hatched form, $k=2$) overlaid by the DL coverage interval (blue shaded form, $k=2$). The solid line represents

the consensual mean value calculated by the DL weighted mean approach. The red shaded area delineates its coverage interval ($k=2$). All values are decay corrected to a reference date of June 30th 2023

For isotope ratios, the long-term stability (l_{ts}) of matter is described by the physical laws of radioactive decay of Pu isotopes which parameters are known with great accuracy. It follows that the long-term uncertainty associated with the physical behavior of matter is very low and can be neglected (Eq. 12):

$$u_{l_{ts}} \approx 0 \quad (12)$$

It thus follows that the uncertainty of the certified Pu isotope ratios in MP4 can be expressed as (Eq. 13):

$$u_{ref} = u_{char} \quad (13)$$

The certified values of Pu isotope ratio and isotopic abundance can thus be found in Tables 16 and 17 with their expanded uncertainties derived from the determinations of the characterization values.

The reference value of the Pu molar mass at the reference date of June 30th 2023 was calculated from the molar masses of Pu isotopes taken from the most recent 32 and Pu isotopic abundance from Table 17:

$$M_{Pu} = (239.06880 \pm 0.00089) \text{ g/mol } (k = 2)$$

The SI traceability of the measurements used to establish the reference values of Pu isotope ratios was guaranteed by the use of CRMs (traceable to the SI) for the calibration of the measuring devices of all the laboratories involved in the certification (see Table 5).

Pu mass fraction reference value

The reference value of the Pu mass fraction, w_{Pu} , is expressed in g/kg for the reference date of June 30th 2023.

Since MP4 material is considered to be homogeneous, the reference value of the Pu mass fraction for a given date is equal to the consensus characterization value determined from the ILC (Eq. 14):

$$y_{ref} = y_{char} \quad (14)$$

In terms of uncertainty, previous experience on MP2 CRM which has been equivalently packaged in double sealed ampoules under an inert atmosphere, the variance linked to the Pu's long-term stability can be neglected. Consequently, the expression of the variance of the reference value is expressed as (Eq. 15):

$$u_{ref}^2 = u_{char}^2 + u_{hom}^2 \quad (15)$$

The homogeneity studies performed on the material (see section dedicated to material homogeneity of the present paper) allowed to determine the heterogeneity factor in the variance of w_{Pu} as:

Table 16 Reference values of Pu isotope ratios for MP4 CRM

Pu isotope ratio	Certified value [mol/mol]	Uncertainty ($k = 2$) [mol/mol]
30/06/2023		
$n(^{238}\text{Pu})/n(^{239}\text{Pu})$	0.0000137	0.0000012
$n(^{240}\text{Pu})/n(^{239}\text{Pu})$	0.0168114	0.0000023
$n(^{241}\text{Pu})/n(^{239}\text{Pu})$	0.00002796	0.00000046
$n(^{242}\text{Pu})/n(^{239}\text{Pu})$	0.00000616	0.00000019

Table 17 Reference value of Pu isotopic abundance for MP4 CRM

Pu isotopic abundance	Certified value [mol/mol]	Uncertainty ($k = 2$) [mol/mol]
30/06/2023		
$n(^{238}\text{Pu})/n(\text{Pu})$	0.0000135	0.0000012
$n(^{239}\text{Pu})/n(\text{Pu})$	0.9834203	0.0000026
$n(^{240}\text{Pu})/n(\text{Pu})$	0.0165327	0.0000023
$n(^{241}\text{Pu})/n(\text{Pu})$	0.0000275	0.00000045
$n(^{242}\text{Pu})/n(\text{Pu})$	0.00000606	0.00000019

$$u_{hom} = 100 \mu\text{g/g}$$

It follows from this that the variance on the reference value is:

$$u_{ref}^2 = 165^2 + 100^2$$

which corresponds to a standard uncertainty equal to:

$$u_{ref} = 192 \mu\text{g/g} = 0.192 \text{ g/kg}$$

Thus, the expression of the reference value of the Pu mass fraction at the reference date of June 30th 2023 is:

$$w_{Pu} = (998.06 \pm 0.38) \text{ g/kg } (k = 2)$$

Traceability of this reference value to the SI is also guaranteed through the use of CRMs traceable to the SI (list given in Table 5).

Sample mass reference value

The mass of each piece of MP4 was measured very accurately after stripping and drying in a nitrogen-inert glove box before immediate conditioning in a double glass ampoule sealed under argon gas.

For this specific operation, the CEA Valduc used a METTLER XPR2 class I balance suitable for low-mass weighing (capacity 2.1 g, resolution 1 μg). Weighing

uncertainty was estimated using French committee for accreditation (COFRAC) reference document [34].

The mean value of the mass of a piece of MP4 is around 350 mg.

The expanded uncertainty on the masses is ($k=2$):

- 20 µg for pieces in the 100-500 mg range
- 50 µg for pieces in the 500-1000 mg range

To achieve a certified mass for the MP4 samples, the mass measured by the CEA Valduc was corrected for the effects of the buoyancy of the nitrogen atmosphere in order to express each sample's true mass. The buoyancy-corrected mass thus corresponds to the reference value of the piece's mass. Table 18 shows the examples of measured mass before and after correction for nitrogen buoyancy with their expanded uncertainties ($k=2$).

The SI traceability of each certified mass was ensured by calibrating the balance with SI traceable COFRAC-certified ZWIEBEL calibration weights.

U, Am and C mass fraction reference values

As for the Pu mass fraction, the reference values of the mass fractions of U, Am, and C were taken to equal the consensual values determined by the ILC and with a variance equal to the sum of the characterization and homogeneity variances. Table 19 summarizes the different components used for the calculations as well as the final expression of the reference values and their expanded uncertainties ($k=2$) for w_U , w_{Am} , and w_C .

Traceability to the SI was guaranteed by the use of CRMs traceable to the SI (list given in Table 5).

U isotope amount ratio reference values

The U of the MP4 material is considered to be homogeneous in terms of isotopic composition, which means that the uncertainty of homogeneity between pieces is zero. Furthermore, as the physical laws describing the radioactive decay of U and Pu isotopes are very accurate, the uncertainty about long-term stability was not taken into account for the reference values. Only two U isotopic ratios could be accurately characterized as the measurement of the U-238/U-235 isotope ratio is interfered

Table 19 U, Am and C mass fraction reference values in MP4 metal (at the date of June 30th 2023 for U and Am)

	y_{char} µg/g	u_{char} µg/g ($k=1$)	u_{hom} µg/g ($k=1$)	y_{ref} µg/g ($k=2$)
w_U	896	23.5	11.5	(896 ± 53)
w_{Am}	99.3	0.65	1.5	(99.3 ± 3.3)
w_C	48	4.5	2.8	(48 ± 11)

by the Pu-238 signal in mass spectrometry leading to highly scattered results.

As such, only the U-234/U-235 and U-236/U-235 ratios were expressed as reference values and are given in Table 20.

Traceability to the SI for the measurement of U isotope ratios is justified through the use of CRMs traceable to the SI (list given in Table 5).

Indicative values

During the MP4 production and certification processes, some properties could not be certified and it was thus chosen to report these values in the MP4's certificate as purely indicative values which are provided only for information purposes and are not guaranteed by the CRM's certificate.

The indicative values concern the U-238/U-235 isotope ratio, some metallic impurities amount contents and Am isotopic composition. Those values were not certified as they were not determined by consensus (in the case of Ta mass fraction quantity), or the uncertainty was too large (in the case of W and Ga) or the uniqueness of the determination prevented the value from being certified (in the cases of the U-238/U-235 isotope ratio for U and in the case of the isotope ratios for Am).

Isotope ratio of U-238 to U-235

The value of the U-238/U-235 ratio is taken equal to the value measured by laboratory three, which is the laboratory that returned the result with the lowest value and uncertainty.

$$\left(\frac{n_{238U}}{n_{235U}} \right)_{\text{indic.}} = (6.23 \pm 0.32)10^{-4} \text{ mol/mol } (k=2)$$

Table 18 Examples of MP4 pieces certified masses

Ampoule number	Mass after etching (mg)	Mass corrected for N ₂ buoyancy (mg)	Uncertainty (mg) ($k=2$)	Rel. uncertainty ($k=2$) (%)
X126	330.174	330.146	0.020	0.0061
X100	523.505	523.460	0.050	0.0096

Table 20 Reference values of U isotopic ratios for MP4 CRM

U isotope amount ratio		
30/06/2023	Certified value [mol/mol]	Uncertainty ($k=2$) [mol/mol]
$n(^{234}\text{U})/n(^{235}\text{U})$	0.003908	0.000014
$n(^{236}\text{U})/n(^{235}\text{U})$	0.061886	0.000060

Table 21 Indicative value of U isotopic abundance for the MP4 CRM

U isotopic abundance		
30/06/2023	Indicative value [mol/mol]	Uncertainty ($k=2$) [mol/mol]
$n(^{234}\text{U})/n(\text{U})$	0.003665	0.000013
$n(^{235}\text{U})/n(\text{U})$	0.937712	0.000061
$n(^{236}\text{U})/n(\text{U})$	0.058031	0.000056
$n(^{238}\text{U})/n(\text{U})$	0.000593	0.000030

Uranium isotopic abundance and uranium molar mass

On the basis of all the isotope ratio values, it was therefore possible to express the U isotope abundance as presented in Table 21.

The indicative value of U molar mass at the reference date of June 30th 2023 is calculated from the molar masses of U isotopes taken from the most recent literature [32] and U isotopic abundance of Table 21.

$$M_U = (235.100 \pm 0.021) \text{ g/mol } (k = 2)$$

Ga, Ta and W mass fractions

The indicative values for the mass fractions of Ga and W are provided in Table 22. Although these results arise from a consensus of two or three measurements, they are particularly small values with high relative uncertainties, which makes them incompatible with a reference value.

The indicative value for the Ta mass fraction is also given in Table 22. Although the value is both large and consistent

Table 22 Ta, W and Ga mass fraction indicative values in MP4 metal

	$y \pm U(y) \mu\text{g/g } (k=2)$
w_{Ta}	(397 ± 23)
w_{W}	(14.6 ± 3.3)
w_{Ga}	(11.9 ± 1.7)

Table 23 Indicative value of Am isotopic composition for MP4 CRM

Am isotope ratio	
30/06/2023	Indicative value [mol/mol]
$n(\text{Am-242 m})/n(\text{Am-241})$	$< 5 \cdot 10^{-5}$
$n(\text{Am-243})/n(\text{Am-241})$	$< 5 \cdot 10^{-5}$

with post-fabrication analyses, it is not a consensus value between different laboratories. It was thus chosen not to use the Ta mass fraction as a reference value.

Am isotope ratios and molar mass

The isotopic composition of Am was characterized by one laboratory using TIMS, with the communication of detection limit values for isotopic ratios relative to the major isotope, Am-241. In the absence of consensus with other measurements from other laboratories the Am isotope ratio values were considered as indicative values (Table 23).

Indicatively, the isotopic abundance of Am-241 could therefore be taken to be at least 99.99%:

$$\frac{n_{\text{Am241}}}{n_{\text{Am}}} > 0.9999$$

In the absence of quantitative measurements of Am isotopes other than Am-241, the indicative value for the molar mass of Am was taken to be equal to that of the Am-241 isotope [32].

$$M_{\text{Am}} = (241.0568273 \pm 0.0000024) \text{ g/mol } (k = 2)$$

MP4 /MP2 material comparison

One of the reasons for the production of MP4 was to replace in the long term the CETAMA's MP2 plutonium metal CRM. As such, following certification, the characteristics of the two materials were compared. Table 24 presents a comparison of the main characteristics of the MP4 and MP2 CRMs at the date of June 30th 2023 (the certification date of MP4). From this comparison, a number of significant elements can be observed:

Firstly, MP4 samples can be seen to have a certified mass approximately 30% lower than that of the MP2 ingots. As previously described, this lower mass is believed to be an asset for the handling and commercialization activities connected to the CRM.

It can be further seen that the two materials display a similar mass fraction (and associated uncertainty) of Pu in

Table 24 Comparison of MP4 and MP2 characteristics in mass, actinide and impurities mass fractions)

MP4 versus MP2	Unit	MP4	MP2 from certificate	MP2 updated
piece mass	mg	~ 350 ± 0.020 certified	~ 500 ± 0.012 certified	
Pu mass fraction w_{Pu}	g/kg	998.06 ± 0.38 30/06/2023 certified	999.6 ± 0.4 1/01/1988 certified	998.0 ± 0.4 30/06/2023 certified
U mass fraction w_{U}	µg/g	896 ± 52 30/06/2023 certified	95 ± 10 1/01/1988 indicative	1160 ± 10 30/06/2023 indicative
Am mass fraction w_{Am}	µg/g	99.3 ± 3.3 30/06/2023 certified	155 ± 14 1/01/1988 indicative	635 ± 14 30/06/2023 indicative
C mass fraction w_{C}	µg/g	48 ± 11 30/06/2023 certified	nc	
Metal impurities mass fraction	µg/g	Ga, Ta, W indicative	nc	
Am isotopic composition	mol/mol	> 99.99% Am-241 indicative	nc	

MP4 and MP2 *i.e.* close to (998.0 ± 0.4) g/kg at the date of June 30th 2023.

In terms of the U mass fraction, it can be seen that on June 30th 2023 the certified U content of MP4 (896 ± 47) µg/g ($k=2$) was lower than the indicative–non certified—U content of MP2 (1160 ± 34) µg/g ($k=2$).

MP4 further provides a mass fraction of Am content in the CRM which is both certified and significantly lower (99.3 ± 3.3 µg/g versus 635 ± 14 µg/g) when compared to the indicative mass fraction of Am in MP2 at the same date.

In addition to providing certified values for the mass fractions of U and Am (which are only indicative in MP2), MP4 is also certified for the mass fraction of C content unlike MP2.

Finally, MP4 provides the indicative values for both the mass fractions of some metallic impurities as well as for

the isotopic composition of Am, with Am-241 purity being greater than 99.99%.

A greater understanding of the two different CRMs can be obtained by observing the Pu isotopic ratios of the two materials. Table 25 compares MP4 and MP2 Pu isotopic composition in terms of isotope ratios and isotopic abundances.

The first observation that can be made from Table 25 is that MP4 shows a significant decrease in the proportions of some isotopes when compared to MP2. Consequently, the proportion of Pu-239 isotope is higher for MP4 than for MP2, with values of 98.34% and 97.77% respectively. Most notably, between the two CRMs the proportion for each of the Pu-241 and Pu-242 isotopes has been divided tenfold, whilst that of the Pu-238 isotope has been divided threefold.

In terms of uncertainties, at equivalent levels, the uncertainty in the determination of the Pu-240 to Pu-239 isotope

Table 25 Comparison of MP4 and MP2 Pu isotopic composition

MP4			MP2		
Isotope amount ratio			Isotope amount ratio		
30/06/2023	Certified value [mol/mol]	Uncertainty ($k=2$) [mol/mol]	12/03/2001	Certified value [mol/mol]	Uncertainty ($k=2$) [mol/mol]
$n(^{238}\text{Pu})/n(^{239}\text{Pu})$	$1.37 \cdot 10^{-5}$	$1.2 \cdot 10^{-6}$	$n(^{238}\text{Pu})/n(^{239}\text{Pu})$	$3.32 \cdot 10^{-5}$	$4.1 \cdot 10^{-7}$
$n(^{240}\text{Pu})/n(^{239}\text{Pu})$	$1.68114 \cdot 10^{-2}$	$2.3 \cdot 10^{-6}$	$n(^{240}\text{Pu})/n(^{239}\text{Pu})$	$2.24374 \cdot 10^{-2}$	$9.9 \cdot 10^{-6}$
$n(^{241}\text{Pu})/n(^{239}\text{Pu})$	$2.796 \cdot 10^{-5}$	$4.6 \cdot 10^{-7}$	$n(^{241}\text{Pu})/n(^{239}\text{Pu})$	$2.980 \cdot 10^{-4}$	$1.7 \cdot 10^{-6}$
$n(^{242}\text{Pu})/n(^{239}\text{Pu})$	$6.16 \cdot 10^{-6}$	$1.9 \cdot 10^{-7}$	$n(^{242}\text{Pu})/n(^{239}\text{Pu})$	$7.09 \cdot 10^{-5}$	$7.1 \cdot 10^{-7}$
Isotopic abundance			Isotopic abundance		
30/06/2023	Certified value $100 \times$ [mol/mol]	Uncertainty ($k=2$) $100 \times$ [mol/mol]	12/03/2001	$100 \times$ [mol/mol]	Uncertainty ($k=2$) $100 \times$ [mol/mol]
$n(^{238}\text{Pu})/n(\text{Pu})$	0.00135	0.00012	$n(^{238}\text{Pu})/n(\text{Pu})$	0.003241	0.000040
$n(^{239}\text{Pu})/n(\text{Pu})$	98.34203	0.00026	$n(^{239}\text{Pu})/n(\text{Pu})$	97.76705	0.00098
$n(^{240}\text{Pu})/n(\text{Pu})$	1.65327	0.00023	$n(^{240}\text{Pu})/n(\text{Pu})$	2.19364	0.00094
$n(^{241}\text{Pu})/n(\text{Pu})$	0.00275	0.000045	$n(^{241}\text{Pu})/n(\text{Pu})$	0.02914	0.00017
$n(^{242}\text{Pu})/n(\text{Pu})$	0.000606	0.000019	$n(^{242}\text{Pu})/n(\text{Pu})$	0.006929	0.000069
	Molar mass			Molar mass	
	239.06880 ± 0.00089 g/mol			239.074888 ± 0.000011 g/mol	

Table 26 Comparison of MP4 and MP2 U isotopic composition

MP4			MP2		
Isotope amount ratio (*)			Isotope amount ratio (*)		
30/06/2023	Certified/indicative val [mol/mol]	Uncertainty ($k=2$) [mol/mol]	20/02/2006	Indicative value [mol/mol]	Uncertainty ($k=2$) [mol/mol]
$n(^{234}\text{U})/n(^{235}\text{U})$	3.908 10^{-3}	1.4 10^{-5}	$n(^{234}\text{U})/n(^{235}\text{U})$	<i>9.005 10^{-3}</i>	<i>3.8 10^{-6}</i>
$n(^{236}\text{U})/n(^{235}\text{U})$	6.1886 10^{-2}	6.0 10^{-5}	$n(^{236}\text{U})/n(^{235}\text{U})$	8.2571 10^{-2}	2.8 10^{-5}
$n(^{238}\text{U})/n(^{235}\text{U})$	<i>6.32 10^{-4}</i>	<i>3.2 10^{-5}</i>	$n(^{238}\text{U})/n(^{235}\text{U})$	N/A (set to 0)	
Isotopic abundance (*)			Isotopic abundance (*)		
30/06/2023	Indicative value 100 \times [mol/mol]	Uncertainty ($k=2$) 100 \times [mol/mol]	20/02/2006	Indicative value 100 \times [mol/mol]	Uncertainty ($k=2$) 100 \times [mol/mol]
$n(^{234}\text{U})/n(\text{U})$	<i>0.3665</i>	<i>0.0013</i>	$n(^{234}\text{U})/n(\text{U})$	0.82495	0.00036
$n(^{235}\text{U})/n(\text{U})$	93.7712	0.0061	$n(^{235}\text{U})/n(\text{U})$	91.6107	0.0022
$n(^{236}\text{U})/n(\text{U})$	5.8031	0.0056	$n(^{236}\text{U})/n(\text{U})$	7.5644	0.0024
$n(^{238}\text{U})/n(\text{U})$	<i>0.0593</i>	<i>0.0030</i>	$n(^{238}\text{U})/n(\text{U})$	N/A	
Molar mass (235.100 ± 0.021) g/mol			Molar mass (235.111416 ± 0.000026) g/mol		

(*) values in italics are only indicative

ratio is a factor of 3 lower between MP4 and MP2. This lower uncertainty is undoubtedly the fruit of the interlaboratory comparison certification process.

Concerning U isotopic composition, Table 26 presents the comparison between the MP4 and MP2 CRMs.

The first observation from the data present in Table 26 is that MP2, unlike MP4, was not characterized in terms of U-238. This element signifies that the MP2 isotopic abundance values for U isotopes other than 238 are likely positively biased.

The second salient point from Table 26 is that the proportions of U-234 and U-236 are higher in MP2 than in MP4. This is a direct consequence of the fact that the proportions of the parent isotopes Pu-238 and Pu-240 are also higher in MP2 than in MP4.

As a result of this isotopic distribution, the proportion of the U-235 isotope is higher in MP4 than in MP2, with respective values of 93.8 and 91.6%.

Conclusion

The production and certification of the MP4 plutonium metal CRM represents the realization of a project that has been more than 10 years in the making. Through extensive research, investments, and international collaborations MP4 was developed as a successor to the CETAMA's MP2 CRM which was certified more than 30 years ago.

The certification process for MP4 was finalized through the organization of an interlaboratory comparison involving eight expert laboratories attached to European (JRC), international (IAEA) or national (CEA) institutions. This shared

effort enabled to certify reference values for the MP4 material in terms of sample mass, Pu isotopic composition and Pu mass fraction, as previously done for MP2. In addition to these values, MP4 was also certified in four new quantities; the U, Am, and C mass fractions, as well as some U isotope ratios which were added to the material's certificate. Furthermore, indicative values for the isotopic ratio of U-238 to U-235 as well as the isotopic composition of Am and the mass fractions of some metallic impurities (Ga, Ta, and W) are given in the certificate, contributing to a complete and exhaustive understanding to the newly created CRM.

MP4 is therefore not only a worthy successor to the CETAMA's MP2 CRM, but it also represents a new Pu metal CRM in its own right. As a material MP4 which can boast a high Pu mass fraction of over 998 g/kg, a Pu-239 isotopic abundance of over 98.3%, and a particularly low Am mass fraction of less than 100 $\mu\text{g/g}$, MP4 is a unique material of its kind which will be of major importance for nuclear safeguards and material accountancy.

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Declarations

Conflict of interest Sébastien Picart, Marielle Crozet, Giacomo Canciani, Ygor Davrain, Caroline Bertorello, Danièle Cardona, Guillaume

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Human/animal rights This article does not contain any studies with human or animal subjects performed by any of the authors.

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