Contribution of an Inter-laboratory Comparison to the Certification of the STAM/IRMM-0243 ^{243}Am Spike Reference Material

ID39

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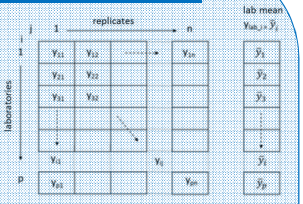
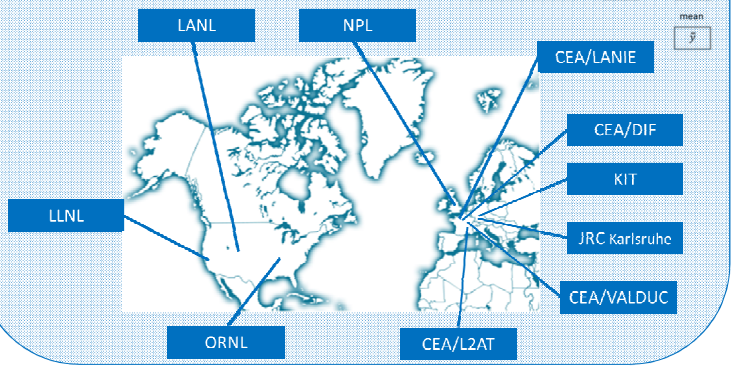
Following the expression of the need for an americium (Am) standard and particularly for one with a certified americium 243 (^{243}Am) content in 2009 and thereafter by the International Atomic Energy Agency (IAEA), the Commissariat à l'Energie Atomique (CEA) et aux Energies Alternatives/ Direction de l'Energie Nucléaire of Marcoule and the Joint Research Center of the European Commission in Geel carried out a collaborative project to produce a Certified Reference Material (CRM) enriched in ^{243}Am. In parallel to the certification process and prior to the issuing of the material certificate, CEA's Commission d'ETAblissement des Méthodes d'Analyse organized an inter-laboratory comparison using that same material as the test sample. The objectives of the inter-laboratory comparison to assess the measurement capabilities in the field and to confirm the provisional certified values for the amount contents of ^{243}Am, ^{241}Am, total Am, the isotopic composition and the molar mass of Am have been demonstrated. Furthermore, the inter-laboratory comparison enabled to derive an indicative value for the $n(^{242m}\text{Am})/n(^{243}\text{Am})$ isotope amount ratio.

Interlaboratory Comparison (ILC) : PROFICIENCY TEST (PT) & VALIDATION of the provisional certified values

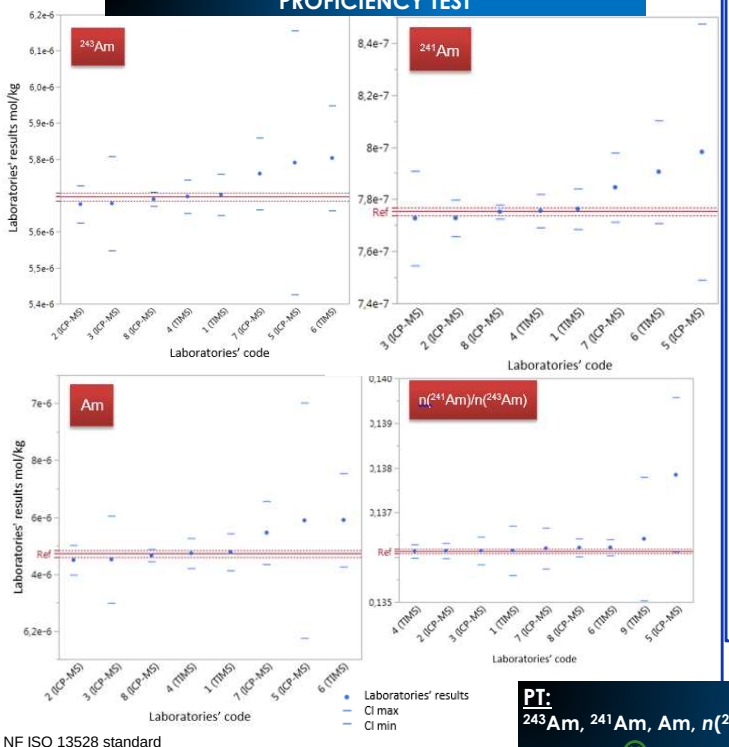
- 5 measurands:

^{243}Am amount content (mol.kg^{-1})
^{241}Am amount content (mol.kg^{-1})
Am total amount content (mol.kg^{-1})
$n(^{241}\text{Am})/n(^{243}\text{Am})$ amount ratio (mol.mol^{-1})
$n(^{242m}\text{Am})/n(^{243}\text{Am})$ amount ratio (mol.mol^{-1})





PROFICIENCY TEST



NF ISO 13528 standard

$$D_i\% = \frac{(y_{lab\_i} - y_{pt})}{y_{pt}}\% \qquad z_i = \frac{(y_{lab\_i} - y_{pt})}{s_{pt}} \qquad \zeta_i = \frac{(y_{lab\_i} - y_{pt})}{\sqrt{u^2(y_{lab\_i}) + u^2(y_{pt})}}$$

	Lab code	U%	zeta score	z score (robust)		Lab code	U%	zeta score	z score (robust)
^{243}Am	1 (TIMS)	0.11	0.2	0.1	^{241}Am	1 (TIMS)	0.12	0.2	0.1
	2 (ICP-MS)	-0.35	-0.8	-0.3		2 (ICP-MS)	-0.34	-0.7	-0.3
	3 (ICP-MS)	-0.32	-0.3	-0.3		3 (ICP-MS)	-0.35	-0.3	-0.3
	4 (TIMS)	0.019	0.0	0.0		4 (TIMS)	0.022	0.0	0.0
	5 (ICP-MS)	1.7	0.5	1.6		5 (ICP-MS)	2.9	0.9	2.3
	6 (TIMS)	1.9	1.5	1.8		6 (TIMS)	2.0	1.5	1.6
	7 (ICP-MS)	1.1	1.3	1.1		7 (ICP-MS)	1.2	1.4	0.9
	8 (ICP-MS)	-0.11	-0.6	-0.1		8 (ICP-MS)	-0.023	-0.1	0.0
Am	Lab code	D%	zeta score	z score (robust)	$n(^{241}\text{Am})/n(^{243}\text{Am})$	Lab code	D%	zeta score	z score (robust)
	1 (TIMS)	0.09	0.2	0.1		1 (TIMS)	0.031	0.1	0.1
	2 (ICP-MS)	-0.35	0.8	0.3		2 (ICP-MS)	0.0082	0.1	0.1
	3 (ICP-MS)	-0.32	-0.3	-0.3		3 (ICP-MS)	0.0061	0.1	0.1
	4 (TIMS)	0.019	0.0	0.0		4 (TIMS)	0.00009	0.0	0.0
	5 (ICP-MS)	1.8	0.6	1.7		5 (ICP-MS)	1.3	2.0	13.6
	6 (TIMS)	1.8	1.4	1.7		6 (TIMS)	0.062	0.9	0.7
	7 (ICP-MS)	1.1	1.3	1.1		7 (ICP-MS)	0.048	0.3	0.5
	8 (ICP-MS)	-0.094	-0.5	-0.1		8 (ICP-MS)	0.059	0.8	0.6
						9 (TIMS)	0.20	0.4	2.2

VALIDATION of the provisional certified values

The external check of the characterization values obtained by the JRC-Geel during the material certification process, was obtained by estimating the compatibility (E_n) for each of the characterized values with the best estimator for the corresponding measurand from the results of the inter-laboratory comparison.

$$E_n = \frac{y_{estim} - y_{char}}{\sqrt{u^2(y_{estim}) + u^2(y_{char})}}$$

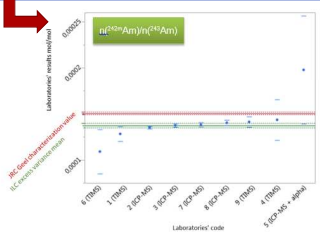
1) calculate the initial values for y* and s* by: y* = median of y_{lab_i}
2) calculate the robust standard deviation s* as s* = 1.483 median of $|y_{lab\_i} - y^*|$
3) update the values for y* and s* as follows.
- calculate: $\varphi = 1.5\ s^*$
- for each value y_{lab_i}, calculate: $\tilde{y}_i = \begin{cases} y^* - \varphi & y_{lab-i} < y^* - \varphi \\ y^* + \varphi & y_{lab-i} > y^* + \varphi \\ y_{lab-i} & \text{otherwise} \end{cases}$
4) calculate the new values for x* and s* by $y^* = \sum_{i=1}^{p} \tilde{y}_i \cdot y_i^* \cdot \phi$ and $s^* = 1{,}134 \sqrt{\frac{p}{(p-1)} \sum_{i=1}^{p} (\tilde{y}_i - y^*)^2 \cdot (p-1)}$

y_{estim}

$$y_w = \sum_{i=1}^{p} w_i \cdot y_{lab-i} \qquad w_i = \frac{1/u^2(y_{lab\_i})}{\sum_{i=1}^{p} \left[1/u^2(y_{lab\_i})\right]}$$

$$y_{\widetilde{w}} = \sum_{i=1}^{p} \widetilde{w}_i \cdot y_{lab-i} \qquad \widetilde{w}_i = \frac{1/(u^2(y_{lab\_i}) + \lambda)}{\sum_{i=1}^{p} \left[1/(u^2(y_{lab\_i}) + \lambda)\right]}$$

		robust mean	weighted mean			excess variance mean			
		U% (k=2)	value	U (k=2)	U% (k=2)	lambda	value	U (k=2)	U% (k=2)
^{243}Am	x_{ILC}	0,91%	5,693	0,016	0,27%	0	_	_	_
	En	1,1	-0,5			_	_	_	_
^{241}Am		U% (k=2)	value	U (k=2)	U% (k=2)	lambda	value	U (k=2)	U% (k=2)
	x_{ILC}	1,1%	0,7756	0,0022	0,28%	0	_	_	_
	En	1,1	0,1			_	_	_	_
Am		U% (k=2)	value	U (k=2)	U% (k=2)	lambda	value	U (k=2)	U% (k=2)
	x_{ILC}	0,92%	6,469	0,018	0,27%	0	_	_	_
	En	1,1	-0,3			_	_	_	_
$n(^{241}\text{Am})/n(^{243}\text{Am})$		U% (k=2)	value	U (k=2)	U% (k=2)	lambda	value	U (k=2)	U% (k=2)
	x_{ILC}	0,077%	0,136178	8,05E-05	0,059%	0	_	_	_
	En	1,6	0,8			_	_	_	_
$n(^{242m}\text{Am})/n(^{243}\text{Am})$		U% (k=2)	value	U (k=2)	U% (k=2)	lambda	value	U (k=2)	U% (k=2)
	x_{ILC}	5,6%	0,0001367	0,00000090	0,66%	6,92E-12	0,0001373	0,0000024	1,8%
	En	-3,2	-16			-9,4			



PT:

^{243}Am, ^{241}Am, Am, $n(^{241}\text{Am})/n(^{243}\text{Am})$:

✓ z score: ☺ 91% (32/35), 😐 6% (2/35), ☹ 3% (1/35).

✓ ζ score: ☺ 100%

The proficiency of the labs was demonstrated.

$n(^{242m}\text{Am})/n(^{243}\text{Am})$: the characterization value could not be used as an assigned value.

Validation:

^{243}Am, ^{241}Am, Am, $n(^{241}\text{Am})/n(^{243}\text{Am})$: the characterization values have been confirmed by the weighted means.

$n(^{242m}\text{Am})/n(^{243}\text{Am})$: The provisional certified value was rejected. The excess variance weighted mean is the best estimator ⇒ indicative value

Measurand	Certified value
^{243}Am	(5.696 ± 0.011) [nmol/g(solution)] (k=2)
^{241}Am	(0.7754 ± 0.0015) [nmol/g(solution)] (k=2)
Am	(6.472 ± 0.012) [nmol/g(solution)] (k=2)
$n(^{241}\text{Am})/n(^{243}\text{Am})$	(0.136138 ± 0.000054) [mol/mol] (k=2)
Measurand	**Indicative value**
$n(^{242m}\text{Am})/n(^{243}\text{Am})$	(0.0001373 ± 0.0000024) [mol/mol] (k=2)

M. Crozet, D. Roudil, C. Maillard, C. Rivier, R. Jakopič, Y. Aregbe, S. Richter, A. Fankhauser, "Contribution of an interlaboratory comparison to the certification of the STAM/IRMM-0243 ^{243}Am Spike Reference Material", submitted to JRNC in July 2018, under review