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Hélène Isnard, Valérie Lourenco

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Radionuclide measurements by mass spectrometry and radiometric techniques: differences and complementarities



DE LA RECHERCHE À L'INDUSTRIE

ISNARD Hélène

Laboratoire de développement Analytique Nucléaire
Isotopique et Élémentaire (LANIE)

LOURENÇO Valérie

Laboratoire National Henri Becquerel (LNHB-MA)

Direction des Energies, CEA Saclay, ISAS/DRMP/SPC/LANIE
CEA, List, Laboratoire National Henri Becquerel (LNE-LNHB)

- High precision isotopic and elemental analysis by **Mass Spectrometry**



- Fuel samples, Irradiated target,
Safeguard samples ...



- **Mass Spectrometer** instruments in glove boxes

- 2 TIMS, 2 ICPMS MC, 1 ICPMS Q



- **Separative techniques** for purification and coupling with MS



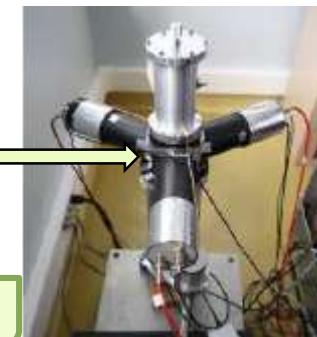
- **Triple to Double Coincidence Ratio (TDCR)**

- Primary technique based on **Liq. Scintillation Counting + a physical model** of light emission

Optical chamber



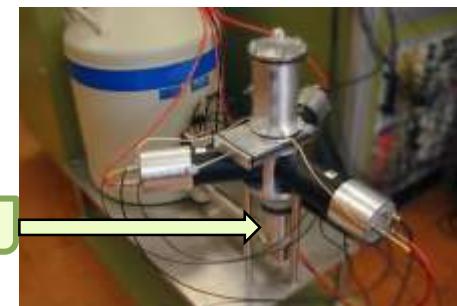
3 photomultipliers



- **$4\pi\beta\text{-}\gamma$ coincidence method**

- Primary technique coupling LSC and HPGe or NaI γ counter (no model needed)

HPGe detector



- **Other primary techniques**

Determination of half-life

Long-lived
fission products

RN	Half-life	Spike (DI)	Ref
^{93}Zr	$1,64 \pm 0,06 \times 10^6$ ans (3,6 %)	^{96}Zr	[1]
^{151}Sm *	$96,6 \pm 0,6$ ans (0,6 %)	Sm nat	[2]
^{129}I *	$16,14 \pm 0,12 \times 10^6$ ans (0,7 %)	^{127}I	[3]
^{166m}Ho *	Purification only	-	[4]

Other collaborations

RN	Goal	Purpose	Ref
^{147}Nd	Absolute gamma-ray emission intensities (neutron flux dosimeter)	Purification from ^{147}Pm	[5]

2022-2025



Development and characterisation of 2 reference materials

[1] Cassette P., Chartier F., Isnard H., ..., Bé M.M., Lépy M.C., Tartes I. *Applied Radiation and Isotopes* **68**, 122-130 (2010)

[2] Bé M.M., Isnard H., Cassette, P., Lourenço V., Nonell A., Chartier .. et al. *Radiochimica Acta* **104**, 131-139 (2015)

[3] Garcia-Torano E., Bé M.M., Bobin C., Lourenço V., Isnard H., Chartier F...et al. *Applied Radiation and Isotopes*, **140**, 157-162 (2018)

[4] Gueguen F., Isnard H., Kossert K., Nonell A., Chartier F.. et al. *Journal of Radioanalytical and Nuclear Chemistry*, **302**, 289-295 (2020)

[5] Kellett M., Bobin C., Isnard H., Lépy M.C., Lourenço V, Vio L. ... et al. *Applied Radiation and Isotopes* **166**, 109349 (2020)

* Metrology for Radioactive Waste Management (EMRP)

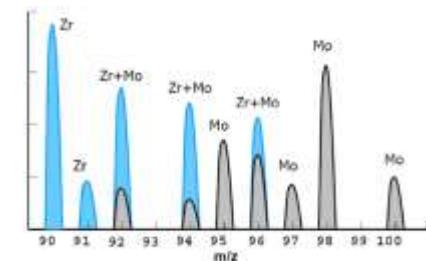


Supplementary comparisons



■ **Purification step(s)** to isolate the element of interest

- Spectral and non spectral interferences by **mass spectrometry**
- Active radionuclides for **radiometric measurements**



■ State of the art on precise **mass spectrometric** measurements

- Use of Isotope Dilution: Choice of spike
- Multicollector Mass spectrometer: TIMS or ICPMS MC (complementarities between the two techniques)

■ Link between mass and activity



$$\text{Activity (Bq} = \text{s}^{-1}) \\ n = \frac{A \cdot T_{1/2}}{N_A \cdot \ln 2} \\ \text{Amount of substance (mol)}$$



Illustration on the determination of ^{151}Sm half life

Separation step: case of ^{151}Sm

- **Sample:** Irradiated powder of a $^{149}\text{Sm}_2\text{O}_3$ (95.1%) target irradiated in a french nuclear power plant
 - **5.8 mg of Sm_2O_3** powder was irradiated and dissolved in nitric media in French installation
 - After irradiation around **400 µg** of ^{151}Sm were present

Sm	Mass (µg)	Eu	Mass (µg)	Gd	Mass (µg)
^{144}Sm	1.4				
^{147}Sm	4.7				
^{148}Sm	61				
^{149}Sm	907	-			
^{150}Sm	3238				
^{151}Sm	402	^{151}Eu	10		
^{152}Sm	296	^{152}Eu	0.3	^{152}Gd	0.2
		^{153}Eu	70		
^{154}Sm	14	^{154}Eu	16	^{154}Gd	5
		^{155}Eu	5	^{155}Gd	3
				^{156}Gd	2
				^{157}Gd	0.1

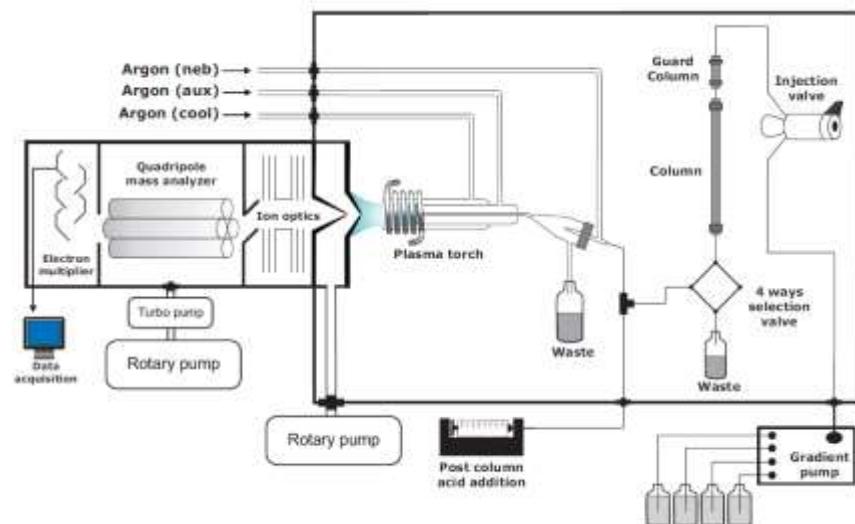
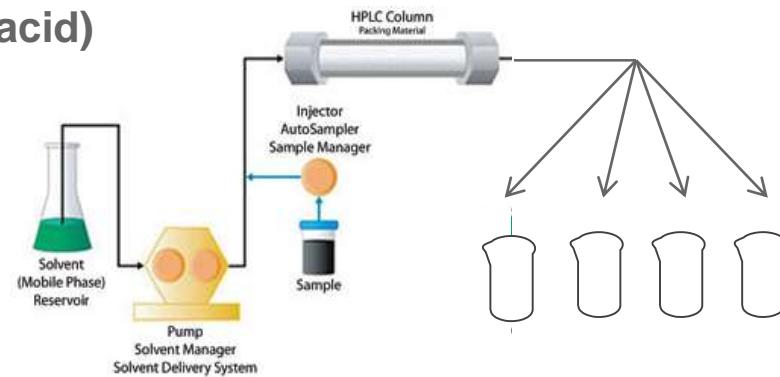
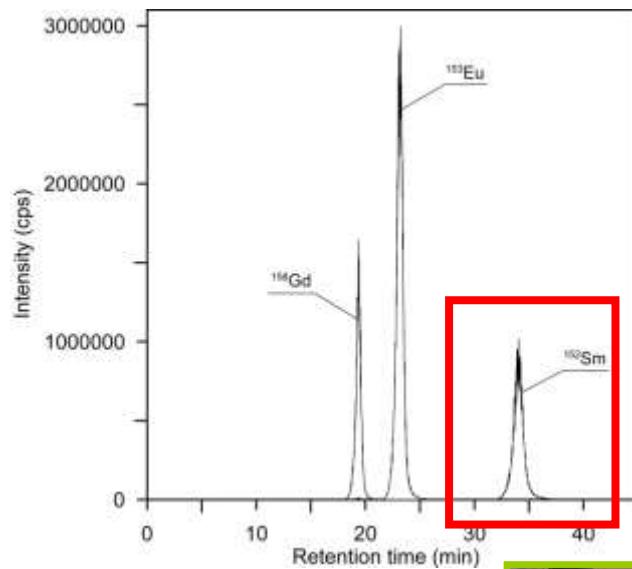
- ➡ Level of purification different for Mass Spectrometry and radiometry
- ➡ Addition of Ho used as a carrier element (no interferences)

Separation step: case of ^{151}Sm

■ Separation by **High Performance Liquid Chromatography** (HPLC)

Use of HMBA acid (hydroxy methylbutyric acid)

Coupling with Q ICP-MS



→ Same chromatographic separation
for purification of Ho and Nd

Mass Spectrometric measurements: Isotope Dilution

Choice of the Spike

Use of NIST SRM 3147a: uncertainty 0.15 % at $k=1$

$$C_s = C_{sp} \times \frac{m_{sp}}{m_s} \times \frac{M_s}{M_{sp}} \times \frac{(150)_{sp}}{(150)_s} \times \frac{\left(\frac{152}{150}Sm\right)_{sp} - \left(\frac{152}{150}Sm\right)_{mix}}{\left(\frac{152}{150}Sm\right)_{mix} - \left(\frac{152}{150}Sm\right)_s}$$

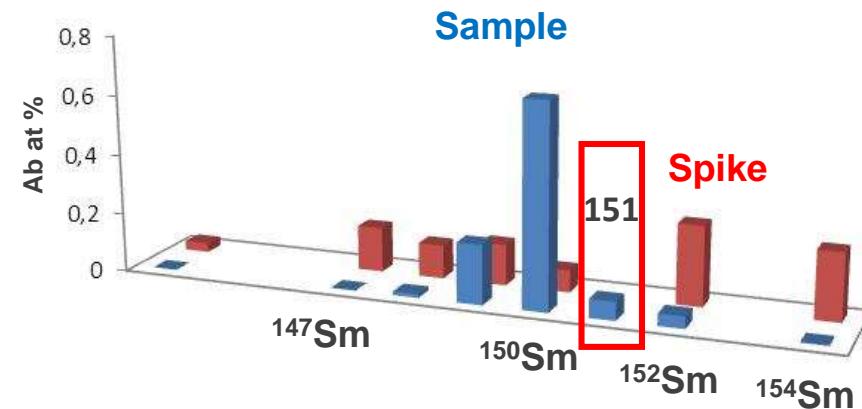
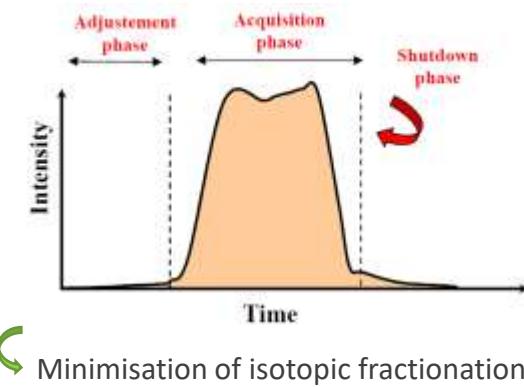


Table 1: Comparison of the recommended and measured isotopic ratios for the NIST SRM 3147 certified natural samarium solution.

	IUPAC	$u(x)$ in % ($k = 1$)	This work $u(x)$ ($k = 1$)
$^{144}\text{Sm}/^{150}\text{Sm}$	0.416(5)	1.2%	0.4194(4)
$^{147}\text{Sm}/^{150}\text{Sm}$	2.031(13)	0.6%	2.037(4)
$^{148}\text{Sm}/^{150}\text{Sm}$	1.523(7)	0.5%	1.526(1)
$^{149}\text{Sm}/^{150}\text{Sm}$	1.873(5)	0.3%	1.874(1)
$^{152}\text{Sm}/^{150}\text{Sm}$	3.625(11)	0.3%	3.614(2)
$^{154}\text{Sm}/^{150}\text{Sm}$	3.083(20)	0.7%	3.068(3)

Determination by **TIMS** using total evaporation method *
[Fiedler et al. \(1995\) IJMS, 146/147, 91-97](#)
[Richter et al. \(2011\) JAAS, 26, 550](#)



Mass Spectrometric measurements: Isotope Dilution metrologic approach

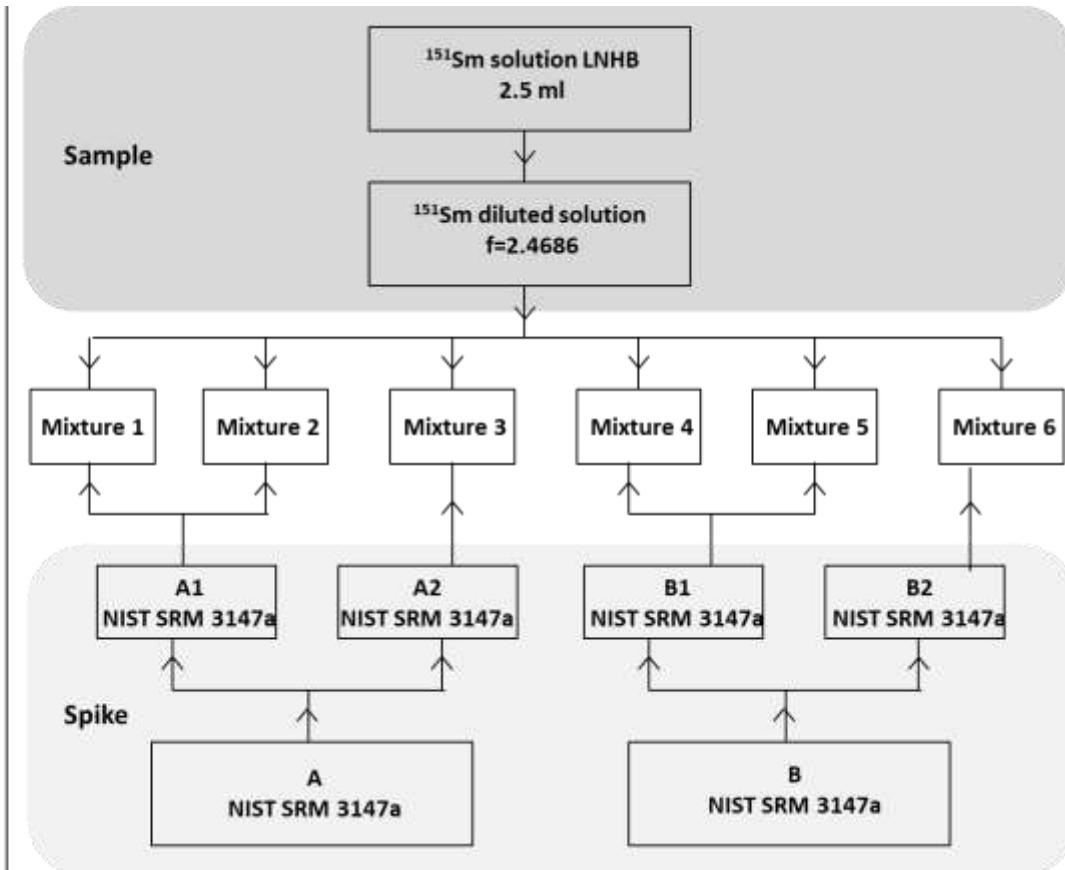
^{151}Sm solution sent by LNHB

Diluted ^{151}Sm solution

Mixtures Sample-Spike for ID

NIST SRM 3147a diluted

NIST SRM 3147a



Sample concentration $[^{151}\text{Sm}] (\mu\text{g g}^{-1})$

Mixture 1	0.08524(26)
Mixture 2	0.08524(26)
Mixture 3	0.08516(26)
Mixture 4	0.08530(26)
Mixture 5	0.08533(26)
Mixture 6	0.08527(26)
Mean	0.08526

Uncertainty fractions %

C_{Sp}	17.52
m_{Sp}	0.03
m_S	3.60
Atomic masses	-
$(^{151}\text{Sm}/^{150}\text{Sm})_S$	8.08
$(^{151}\text{Sm}/^{150}\text{Sm})_{Sp}$	39.91
$(^{149}\text{Sm}/^{150}\text{Sm})_{Mix}$	30.86

Table 6: Final results for the activity concentration A , as reported by the participants. The stated uncertainties u are combined standard uncertainties ($k = 1$).

Participant	A in kBq g^{-1}	u in kBq g^{-1}	Measurement method
PTB	79.41	0.59	CIEMAT/NIST
PTB	79.04	0.56	TDCR
PTB	79.22	0.41	Final result
LNE-LNHB	77.87	0.41	TDCR and final result
IRMM	78.5	0.4	CIEMAT/NIST
IRMM	78.86	0.40	TDCR
IRMM	78.7	0.4	Final result
POLATOM	79.51	0.48	TDCR and final result
CMI	77.9	0.93	TDCR and final result
SMU	80.247	0.376	TDCR and final result

Measurements by liquid scintillation counting (TDCR, CIEMAT/NIST)

Table 7: ^{151}Sm half-life and uncertainty from the literature and this work.

Reference	$T_{1/2}$ (a)	Uncertainty (a)
Flynn et al. [19] (1965)	87	9
Reynolds et al. [20] (1968)	93	8.6
Ming He et al. [21] (2009)	96.6	2.4
This work (2015)	94.6	0.6

4-fold Reduction !

- Publication of a **new value for the half-life of ^{151}Sm with a significantly reduced uncertainty (0.6%)**
- Resulted in a **new recommended value for the half-life of ^{151}Sm with a 10-fold reduced uncertainty (0.6%) compared to the previous one (6.7 %)**

Thanks for your attention



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