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

Hélène Isnard, Valérie Lourenco

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ISNARD Hélène

Laboratoire de développement Analytique Nucléaire Isotopique et Elémentaire (LANIE)

LOURENÇO Valérie

Laboratoire National Henri Becquerel (LNHB-MA)

DE LA RECHERCHE À L'INDUSTRIE

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

CEA Saclay: LANIE and LNHB

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

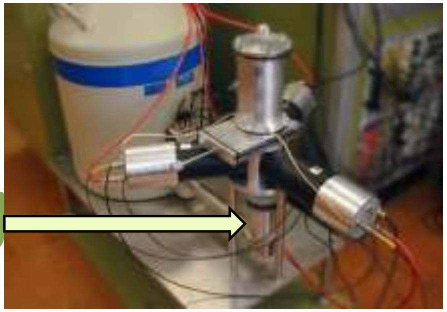
  - Fuel samples, Irradiated target, Safeguard samples …

- **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 **L**iq. **S**cintillation **C**ounting + a <u>physical model</u> of light emission

- **4πβ-γ coincidence method**
  - Primary technique coupling LSC and HPGe or NaI γ **counter** (no model needed)



- **Other primary techniques**

Applications and collaborations between LANIE and LNHB

Determination of **half-life**

Long-lived fission products

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

* **Metro**logy for **R**adioactive **W**aste **M**anagement (EMRP)

3 EURAMET

Supplementary comparisons

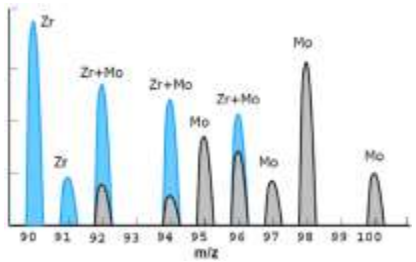
Other collaborations

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

2022-2025 MetroPOEM Development and characterisation of 2 reference materials

[1] Cassette P., Chartier F., Isnard H., …, Bé M.M., Lepy 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)

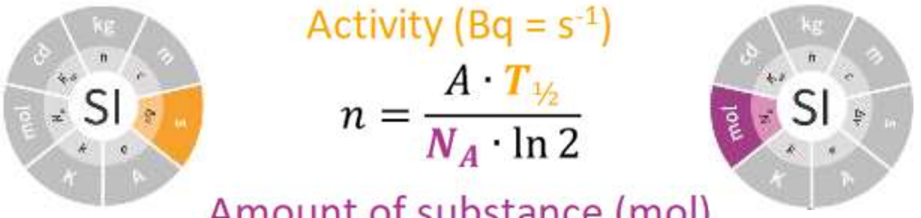
Requirements to perform precise mass spectrometric and radiometric measurements



- **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



$$n = \frac{A \cdot T_{1/2}}{N_A \cdot \ln 2}$$

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

- **Sample**: Irradiated powder of a $^{149}Sm_2O_3$ (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

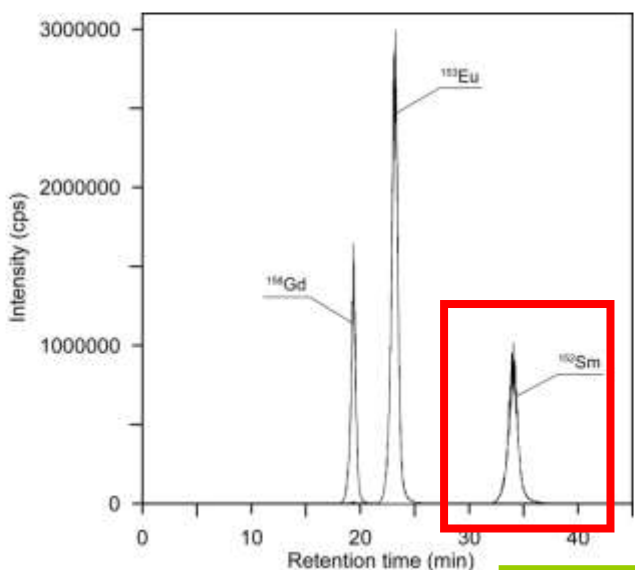
Sm	Mass (µg)	Eu	Mass (µg)	Gd	Mass (µg)
^{144}Sm	1.4				
^{147}Sm	4.7				
^{148}Sm	61				
^{149}Sm	907	-			
^{150}Sm	3238				
^{151}Sm	402	^{151}Eu	10		
^{152}Sm	296	^{152}Eu	0.3	^{152}Gd	0.2
		^{153}Eu	70		
^{154}Sm	14	^{154}Eu	16	^{154}Gd	5
		^{155}Eu	5	^{155}Gd	3
				^{156}Gd	2
				^{157}Gd	0.1

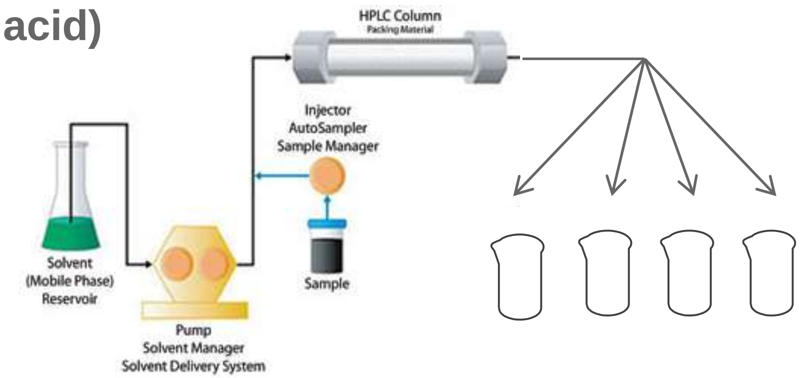
➡ Level of purification different for Mass Spectrometry and radiometry

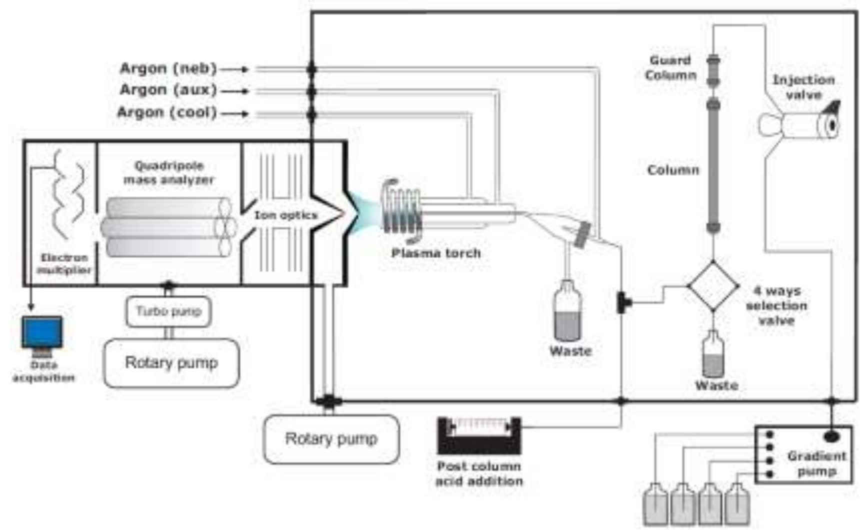
➡ Addition of Ho used as a carrier element (no interferences)

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

Choice of the **Spike**

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

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

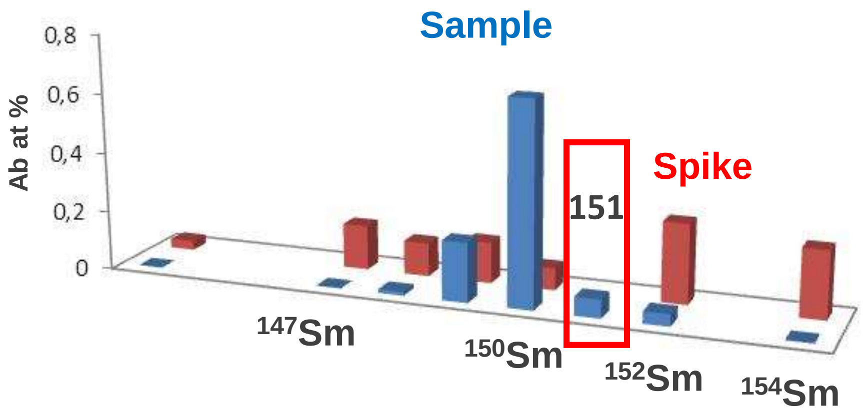
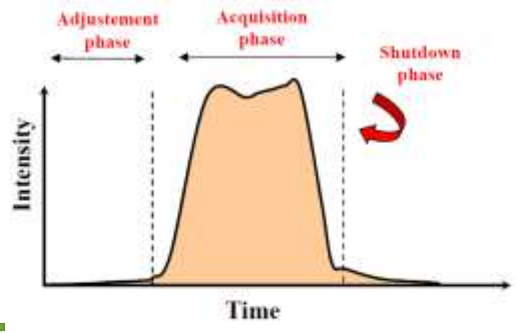


Table 1: Comparison of the recommended and measured isotopic ratios for the NIST SRM 3147 certified natural samarium solution.

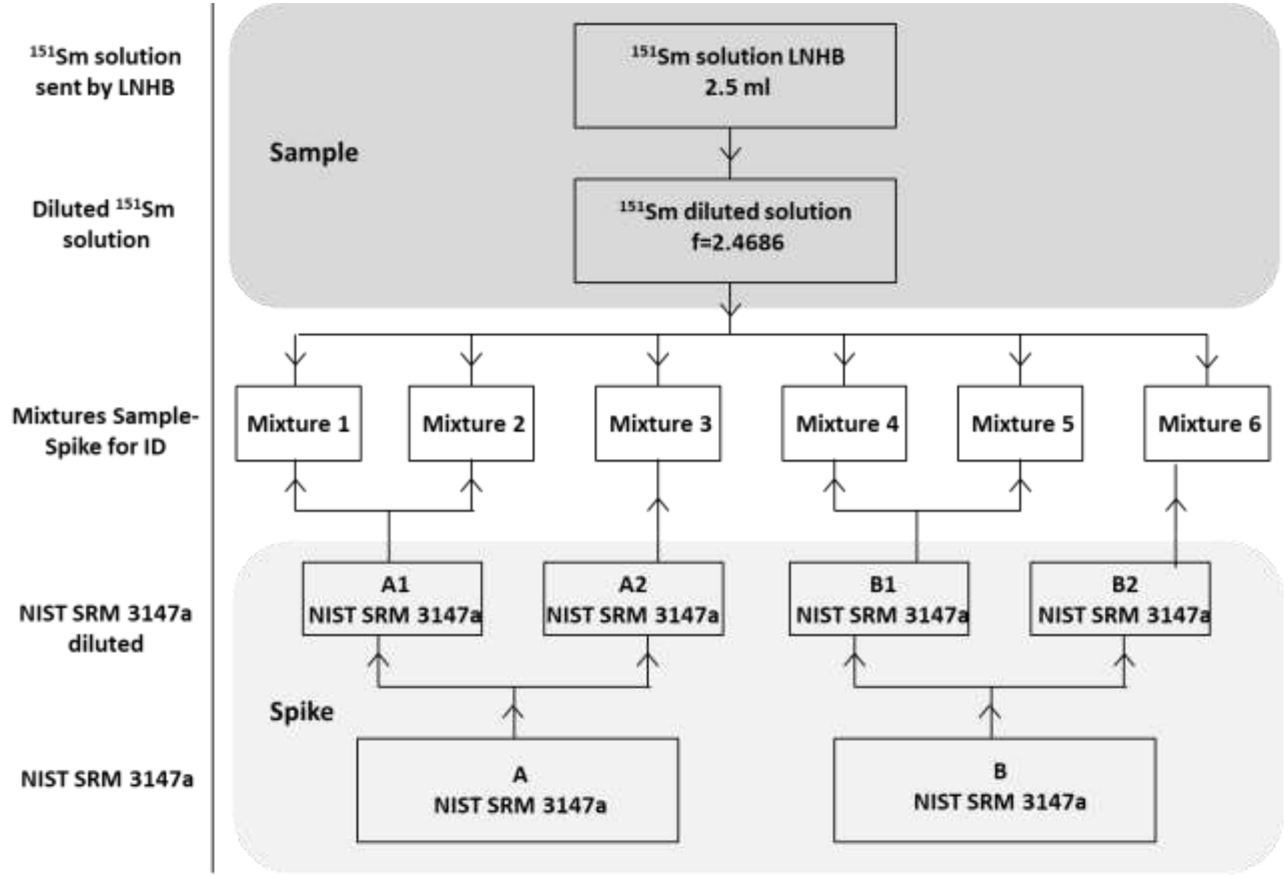
	IUPAC	$u(x)$ in % (k = 1)	This work $u(x)$ (k = 1)
$^{144}Sm/^{150}Sm$	0.416(5)	1.2%	0.4194(4)
$^{147}Sm/^{150}Sm$	2.031(13)	0.6%	2.037(4)
$^{148}Sm/^{150}Sm$	1.523(7)	0.5%	1.526(1)
$^{149}Sm/^{150}Sm$	1.873(5)	0.3%	1.874(1)
$^{152}Sm/^{150}Sm$	3.625(11)	0.3%	3.614(2)
$^{154}Sm/^{150}Sm$	3.083(20)	0.7%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



Minimisation of isotopic fractionation

Mass Spectrometric measurements: Isotope Dilution metrologic approach



	Sample concentration $[^{151}Sm]$ ($\mu g\ g^{-1}$)
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}	$\boxed{17.52}$
m_{Sp}	0.03
m_S	3.60
Atomic masses	–
$(^iSm/^{150}Sm)_S$	8.08
$(^iSm/^{150}Sm)_{Sp}$	$\boxed{39.91}$
$(^{149}Sm/^{150}Sm)_{Mix}$	$\boxed{30.86}$

Improvement on the ^{151}Sm half life

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
$\boxed{\text{This work (2015)}}$	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

MERCI