Measurements of long-lived ^{121m}Sn and ^{126}Sn nuclides in Low and Intermediate Level Nuclear Waste

Céline Gautier, J.-P. Degros, M. Coppo, P. Fichet, F. Goutelard, R. Brennetot

Measurements of long-lived Sn-121m and Sn-126 nuclides in Low and Intermediate Level Nuclear Waste

C. Gautier[1], J.P. Degros[1], M. Coppo[1], P. Fichet[1], F. Goutelard[2] and R. Brennetot[1]

[1]Operator Support Analyses Laboratory, Atomic Energy Commission, CEA Saclay, DEN/DANS/DPC/SEARS/LASE, Building 459, PC171, 91191 Gif-sur-Yvette Cedex, FRANCE
celine.gautier@cea.fr
[2]CEA/DEN/MAR/DEIM/Nuclab, Atomic Energy Commission, CEA Marcoule, Building 109, BP 17 171, 30207 Bagnols-sur-Ceze, FRANCE

MARC X — METHODS & APPLICATIONS OF RADIOANALYTICAL CHEMISTRY — KAILUA-KONA, HAWAII, USA • APRIL 12-17, 2015

10th International Conference on Methods and Applications of Radioanalytical Chemistry, USA, April 12-17, 2015

Context

In France, nuclear waste are managed by the National Radioactive Waste Management Agency (ANDRA). Several repository sites have been built in order to accommodate nuclear waste packages. One is dedicated to waste containing short-lived radionuclides with radioactivity at Low and Intermediate Level. Criteria for 143 radionuclides have been defined by ANDRA which guarantees the safety of the facility. Among this long list, Sn-121m and Sn-126 have to be declared as soon as their activities are over 10E-3 Bq/g [1]. Both tin isotopes are fission products obtained according to thermal fission yields of 0.00003 % and 0.06 %, respectively. Sn-121m can also be produced by activation of tin present as an additive in zircaloys and as an impurity in inconels and steels used in the nuclear industry. Sn-121m decays with a half-life of 55 years whereas Sn-126 is a very long-lived radionuclide with a half-life estimated at around 10E5 years. Because of the long half-life and the unknown impact of high energy gamma emissions of Sn-126, ANDRA allows a very low Sn-126 activity limit (2.7 Bq/g) in waste packages. Due to their potential low activities in nuclear wastes, both tin nuclides need to be separated from the matrices and concentrated through chemical separations prior to any measurement.

Radiochemical protocol

➲ **Q ICPMS (Elan DRCe, Perkin Elmer):**

- Measurement of ^{126}Sn activity

$$A(^{126}Sn) = \frac{N \times \ln 2 \times [^{126}Sn]_{ICPMS}}{M \times T_{196\,000\ years}\ [2]}$$

Digestion after addition of a few µg of natural tin carrier and ^{113}Sn spiker

Co-precipitation with $Al(OH)_3$ / Dissolution in 8M HCl

Preliminar separation on anion exchange AG1X8 resin

Co-precipitation with MoS_3 / Dissolution in 69% HNO_3 + HCl

Selective step **Ethylation in acetic acid buffer ⇨ $SnEt_4$**

Purification of the organic phase on Silicagel column

Back-extraction of Sn via degradation of tetra-ethyl Sn

Co-precipitation with $Al(OH)_3$ / Dissolution in 6M HCl

Final purification on anion exchange AG1X4 resin with Ultrex reagents (0.5M HNO_3 + 0.01M HF)

Purification/ separation steps

Q ICPMS	γ Spectrometry	γ Spectrometry
^{126}Sn	^{113}Sn (392 keV)	^{121m}Sn (37 keV)

➲ **Gamma spectrometer (Ge detector, Ortec GMX-15185):**

- Measurement of ^{121m}Sn activity
- Measurement of ^{113}Sn activity for the determination of the radiochemical separation yield

⇨ **Radiochemical yield: 30% up to 70% depending on the matrix**

Validation

In-house tin standards preparation

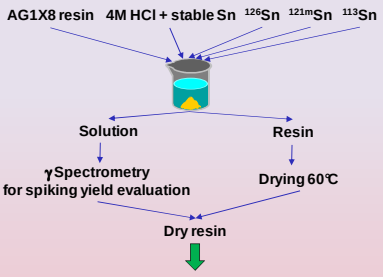
No availability of commercial ^{121m}Sn and ^{126}Sn sources

Application to radioactive zircaloys ⇨ in-house ^{121m}Sn source

Application to spent nuclear fuel dissolution solutions ⇨ in-house ^{126}Sn source

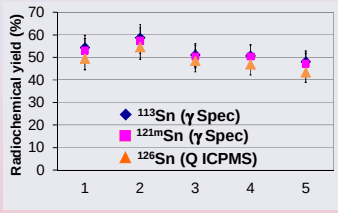
Spiking of ion exchange resins with ^{113}Sn*, ^{121m}Sn, ^{126}Sn sources

*(*CERCA commercial source)*



5 aliquots of spiked resin for radiochemistry

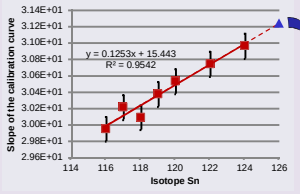
Results of 5 radiochemical replicates



⇨ **Same radiochemical yields whatever the studied tin isotopes**

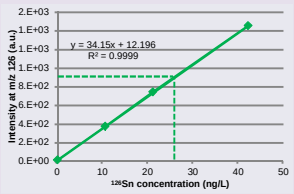
Determination of ^{126}Sn activity

❖ **Method 1:** Extrapolation of the slope of the ^{126}Sn calibration curve from other natural tin isotopes



$$[^{126}Sn] = \frac{\text{Intensity at m/z 126}}{\text{Extrapolated slope at m/z 126}}$$

❖ **Method 2:** ^{126}Sn calibration curve obtained from the in-house ^{126}Sn source



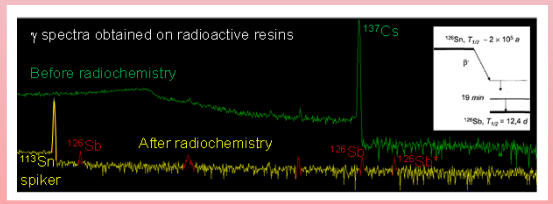
$$[^{126}Sn] = \frac{\text{Intensity at m/z 126} - \text{Intercept}}{\text{Slope at m/z 126}}$$

	[126Sn] (ng/L) obtained from Method 1	[126Sn] (ng/L) obtained from Method 2	Difference (%)
Sample 1	36.2	36.7	-1.4
Sample 2	12.3	11.7	4.8

⇨ **No significant difference between the two methods**

Applications

Real matrices: radioactive steels and ion-exchange resins



	121mSn activity (Bq.g-1)
Steels	50 → 1000

	126Sn activity (Bq.g-1)
Resins	0.1 → 10

Conclusions

A radiochemical protocol was developed on synthetic samples to separate tin from various matrices and concentrate it prior to any nuclear or mass spectrometry measurements. As no ^{121m}Sn or ^{126}Sn sources are commercially available, the protocol was first applied to zircaloys and spent nuclear fuel dissolution solutions to obtain in-house standards. The radiochemical procedure was validated subsequently on ion exchange resins spiked with ^{113}Sn, ^{121m}Sn and ^{126}Sn. The developed radiochemical procedure enables to measure ^{121m}Sn and ^{126}Sn in Low and Intermediate Level Nuclear Waste with detection limits of 20 Bq/g and 0.02 Bq/g respectively.

[1] ANDRA, Spécifications d'acceptation des colis de déchets radioactifs au centre de l'Aube - Spécification technique générale, ACO.SP.ASRE.99.001 indice D, 2014.
[2] P. Bienvenu et al., Determination of ^{126}Sn half-life from ICP-MS and gamma spectrometry measurements, Radiochim. Acta 97, 687-694 (2009)