



ERA14: 14TH INTERNATIONAL SYMPOSIUM ON NUCLEAR & ENVIRONMENTAL RADIOCHEMICAL ANALYSIS



DE LA RECHERCHE À L'INDUSTRIE

**Is it possible to measure Sr-90 in radioactive waste
without harmful chemical reagents?**

ERA 14 – September 15th 2022

Céline GAUTIER - DES/ISAS/DPC/SEARS/LASE

Strontium-90 is a major fission product so it is often analyzed in radioactive waste. As a pure β -emitter, it has to be isolated from matrix and interferences before its nuclear measurement.

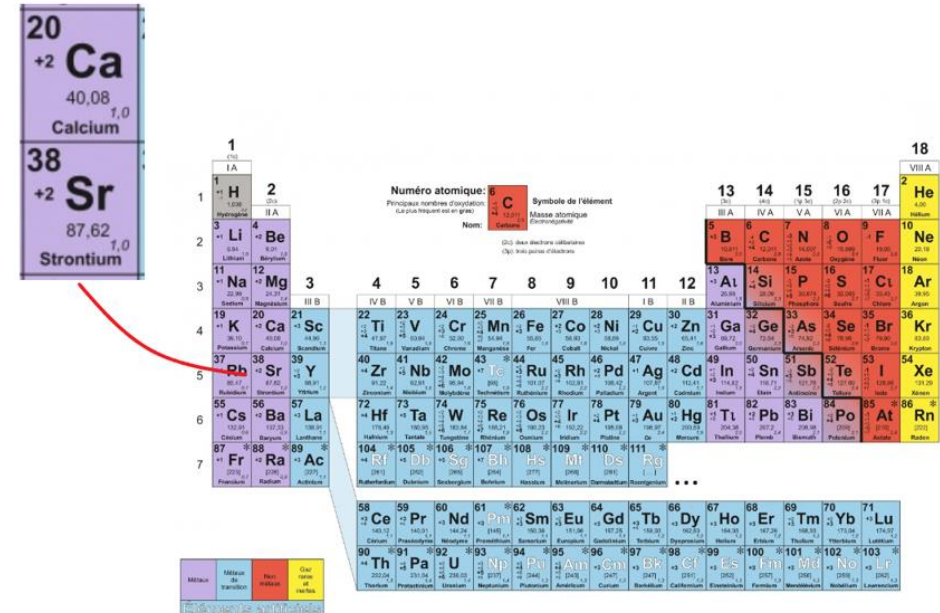
➔ **Radiochemical purification**

Sr-90



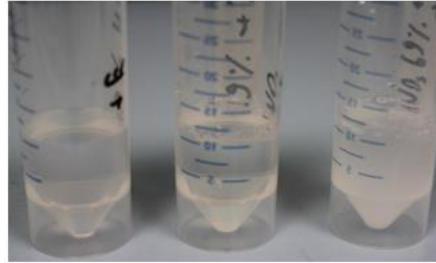
It decays to Yttrium-90

RN	Reporting threshold (Bq/g) → Maximum activity (Bq/g) for French surface disposal facility (ANDRA Specifications: ACO.SP.ASRE.99.002/D)
${}^{90}\text{Sr}$	$1 \rightarrow 6 \times 10^6$



Precipitation based on nitric acid

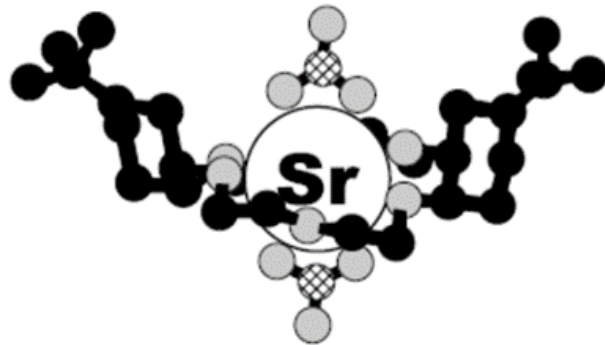
Method 1



Proportional counter

Extraction chromatography based on Sr-resin[®]

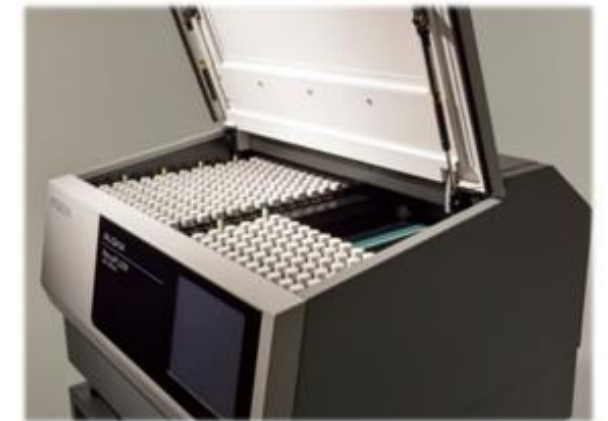
Method 2



Triskem[®]: Product Sheet, Sr-Resin[®]



Dietz et al. 2004



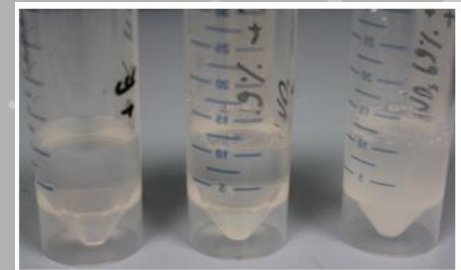
Liquid scintillation counter

⇒ **Implementation of toxic reagents for both methods incompatible with ISO 45001 and REACH* regulation: fuming nitric acid and scintillation cocktails**



*Registration, Evaluation and Authorisation of Chemicals

Precipitation method based on nitric acid: method 1



Sample + Stable Sr carrier

↓ Addition of *fuming nitric acid*

Precipitation of strontium (x2):
recovery of precipitate by
centrifugation and dissolution in water



Ca



↓ Addition of *ammonia*

Recovery of strontium in supernatant
after filtration

↓ Addition of *ammonium oxalate*

Precipitation of strontium oxalate

Sr yield by
gravimetry

^{90}Sr activity by
proportional
counter

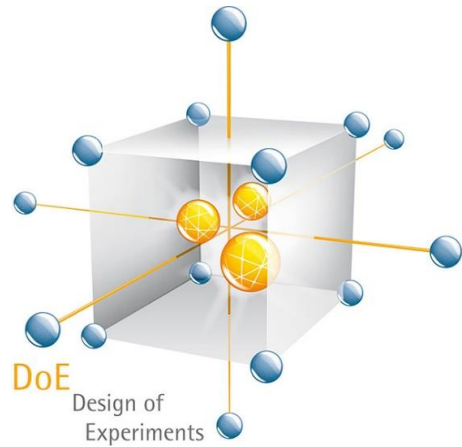


Publication	Fuming nitric acid (>82%)	Concentrated nitric acid
Glendenin (1945)	~80%	
Beaufait (1952)	~60-80%	
Martell (1956)	75%	
Sunderman (1957)	~60%	
Bayhurst (1958)	~80%	
Goldin (1959)		70%
Johns, EPA (1975)	~75%	
Krieger, EPA (1980)		70%
IAEA (1989)	66%	
Bojanowski (1990)		60-70%
Sajeniouk (2005)		
Letho (2011)	70%	
CEA (2012)	~75-80%	
Qiao, interlaboratory (2017)	65-70%	65-70%

⇒ No consensus towards the appropriate concentration of nitric acid to use !

⇒ Is fuming nitric acid really essential?

⇒ **Design of experiment methodology: optimization of processes with a minimum of experiments**



1/ Identification of 5 parameters with potential influence:

- Concentration of nitric acid: c_{HNO_3}
- Total volume of solution: V_{tot}
- Sr mass: m_{Sr}
- Ca mass: m_{Ca}
- Waiting time for precipitation: T

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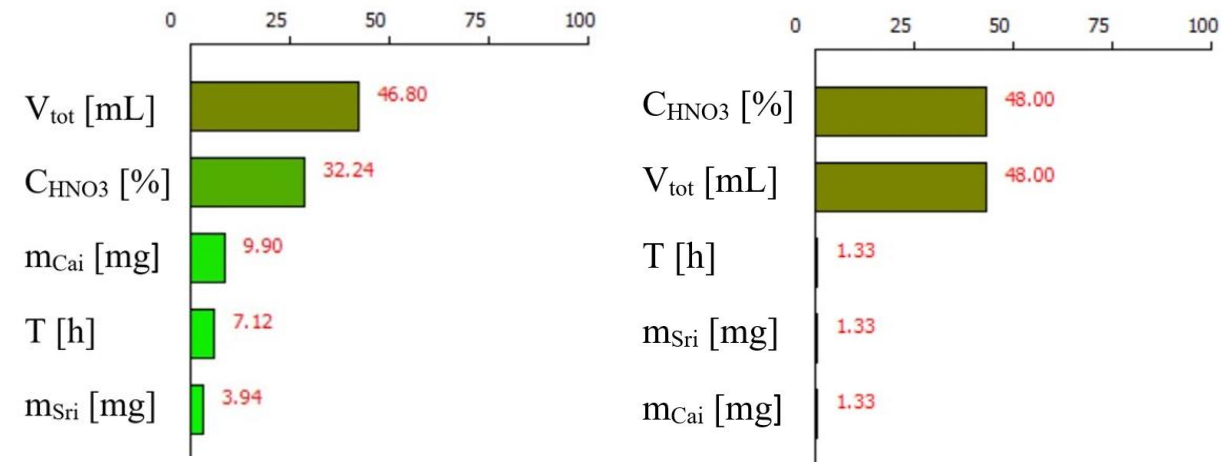
2/ Plackett-Burman Design: parameter screening

8 experiments, study of 2 responses



[%] Sr precipitate

[%] Ca precipitate



Influent parameters:

Nitric acid concentration C_{HNO_3} and total volume of solution V_{tot}

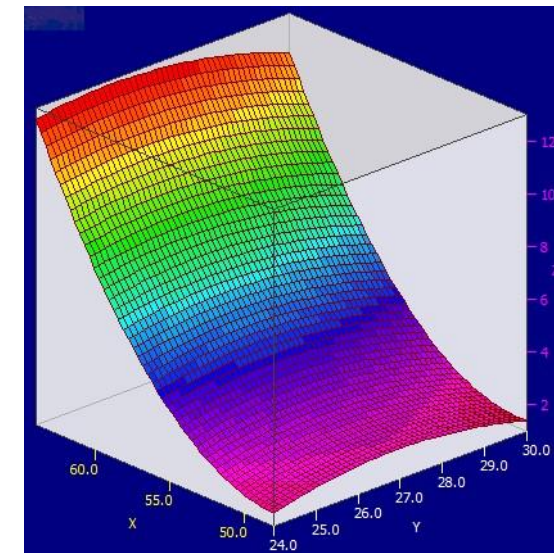
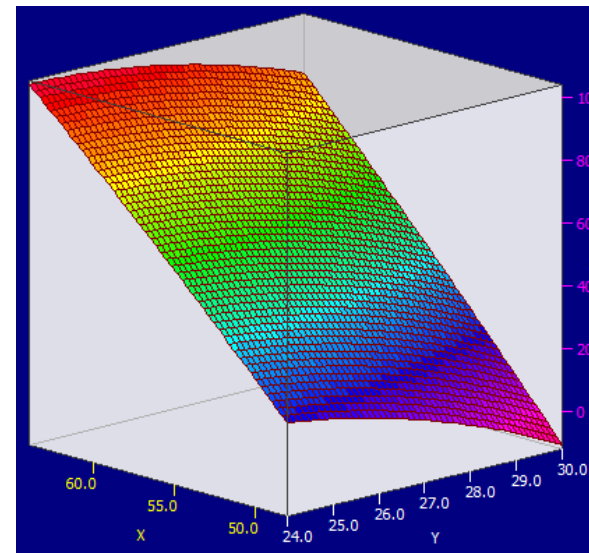
3/ Box-Behnken Design: optimization of influent parameters

10 experiments, study of 2 responses

[%] Sr precipitate

[%] Ca precipitate

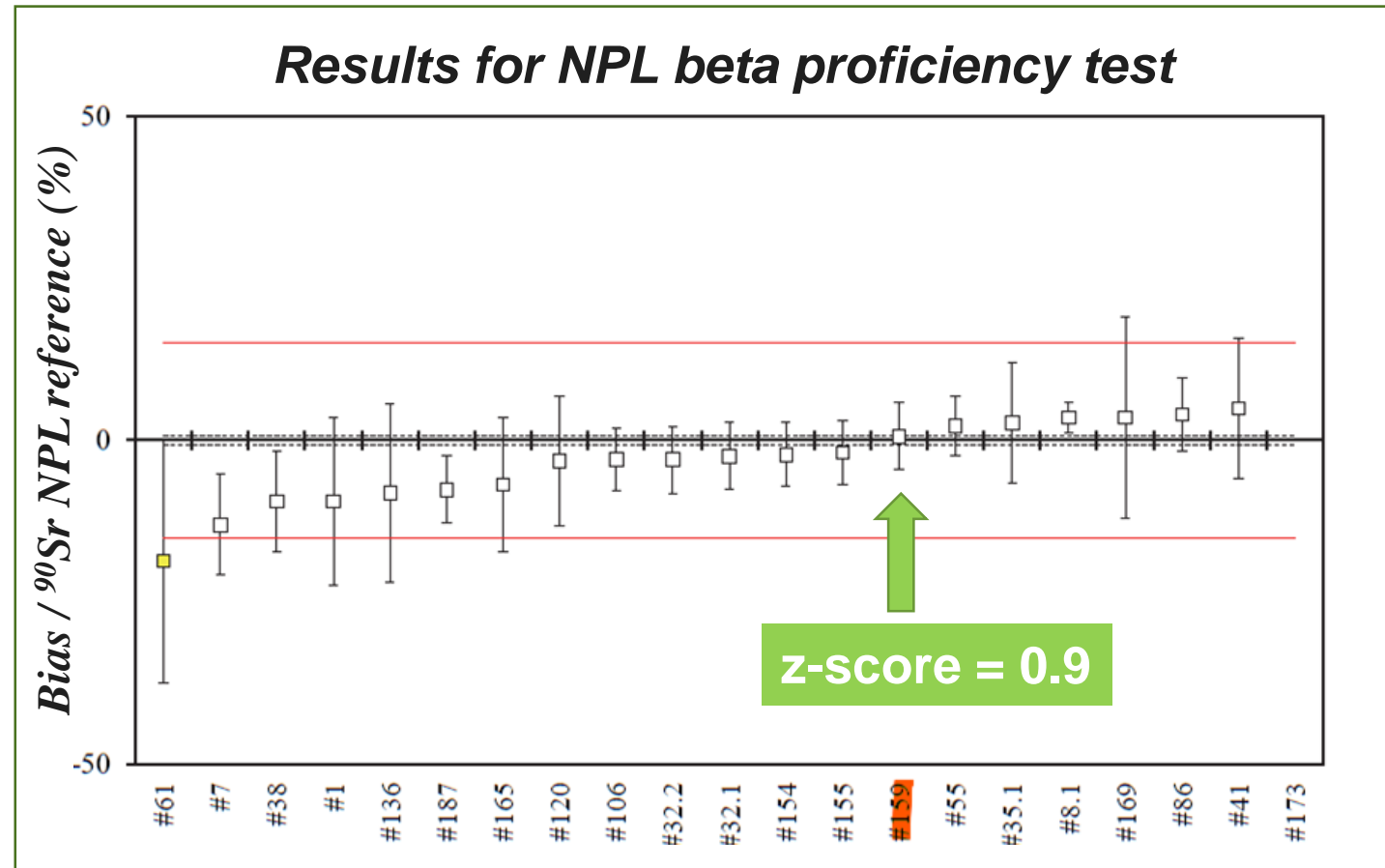
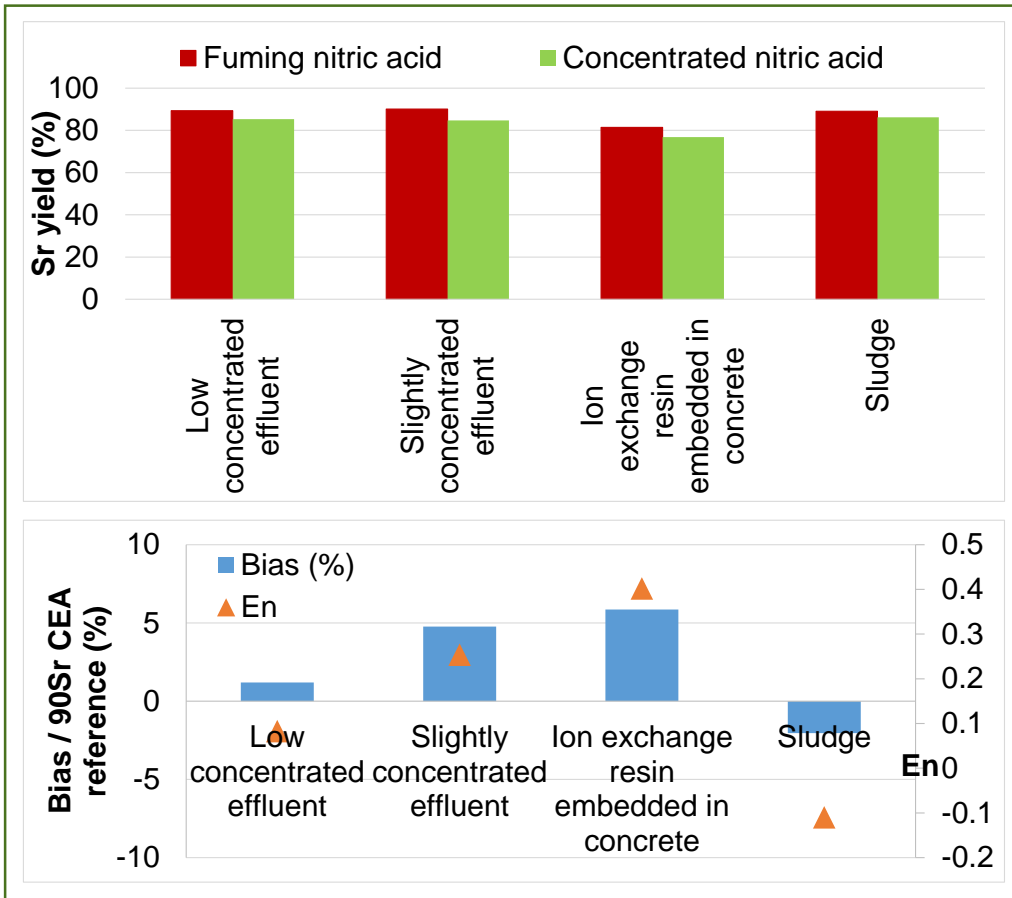
As a function of nitric acid concentration X [%] and solution volume Y [ml]



Optimal values: $C_{\text{HNO}_3} = 63 \%$ and $V_{\text{tot}} = 26 \text{ mL}$

E. Baudat et al., Journal of Radioanalytical and Nuclear Chemistry 328 (2021) 637-650

4/ Application to real nuclear waste samples and comparison to CEA reference method



Similar separation yields and bias < 10 % ⇒ validation of the new method based on concentrated nitric acid



Extraction chromatography method based on plastic scintillation: method 2

Sample + Stable Sr carrier

↓ Addition of *ammonia*

Recovery of strontium in supernatant

↓ Addition of *sodium carbonate*

Precipitation of strontium carbonate

↓ Deposition on *Sr-resin®* column

Dissolution in 6 M HNO₃

Washing with 4 M HNO₃

Sr elution with 0.02 M HNO₃

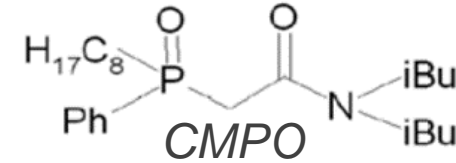
Sr yield by
ICP-AES

⁹⁰Sr activity
by LSC

**Loss of Sr for samples with HF
at ammonia precipitation step**



Implementation of TRU-resin® column

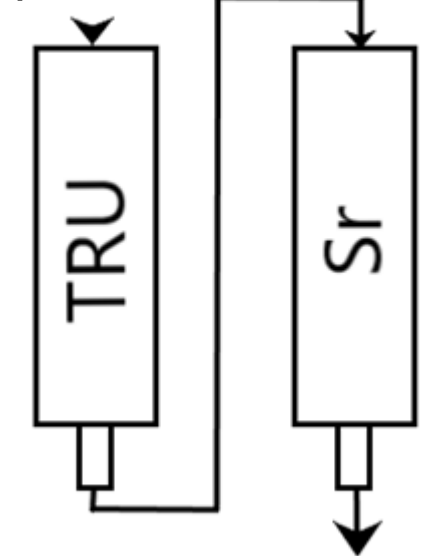


Triskem® :
Product Sheet, TRU-Resin®

Sample + stable Sr carrier:
1/ Evaporation and dissolution
in 10 mL HNO₃ 6M

2/ Sample
deposition

3/ Washing
4/ Sr elution

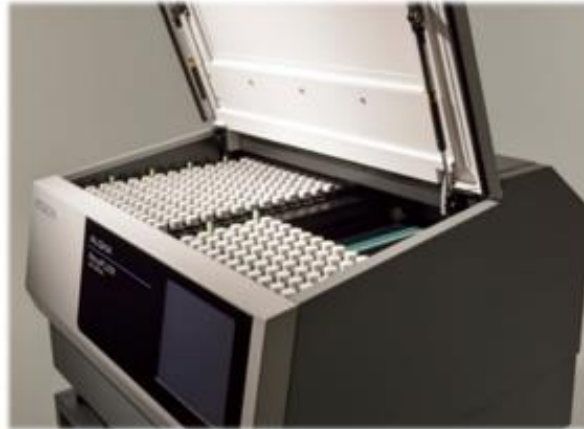


5) Sr fraction

Validation on real
nuclear waste samples
with Sr yield of ~ 90 %



Addition of liquid scintillation cocktail



Liquid scintillation cocktail:

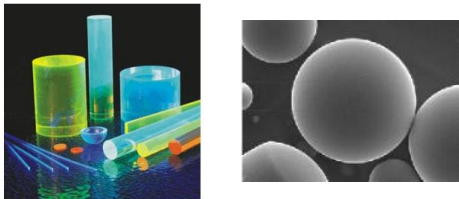
TOXIC → included in the european REACH* regulation

*Registration, Evaluation and Autorisation of CHemicals

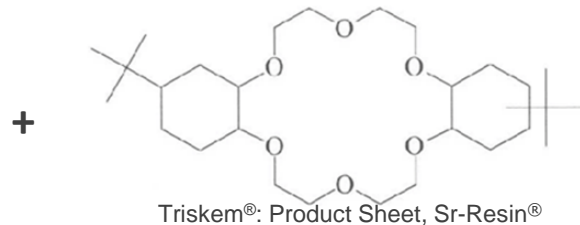


Alternative: plastic scintillation using Sr PS-Resin

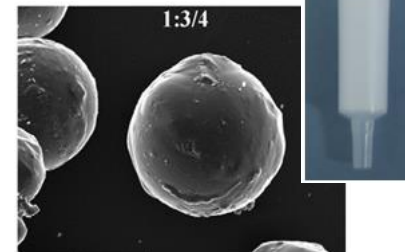
beads of scintillating plastic



Extractant selective for Sr



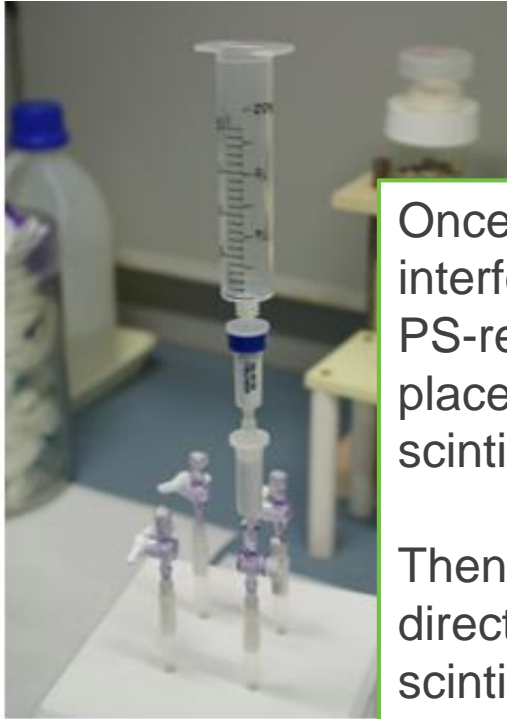
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H. Bagán et al., *Analytica Chimica Acta* 686 (2011) 50-56,
<https://doi.org/10.1016/j.aca.2010.11.048>

- No Sr elution
- Supplementary washing with 6M LiNO₃
- Indirect determination of Sr yield
- Plastic scintillation
 → **No liquid scintillation cocktail**

Sr PS-Resin method:



Once Sr fixed and interferences discarded, PS-resin cartridge is placed in a standard scintillation flask.

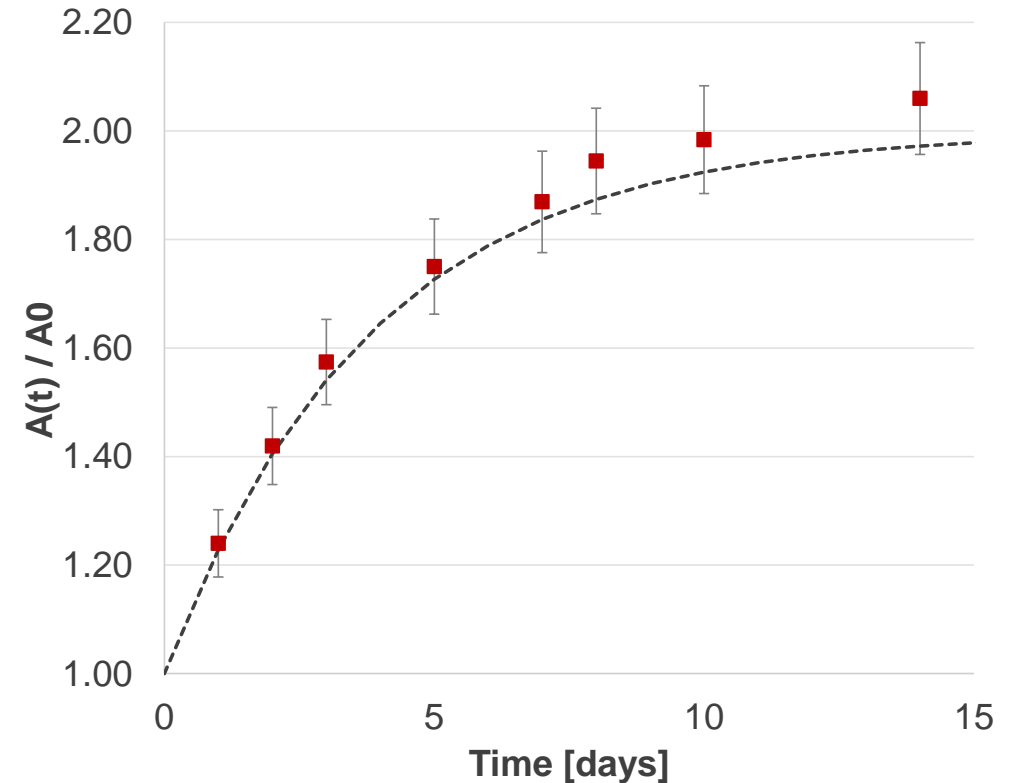
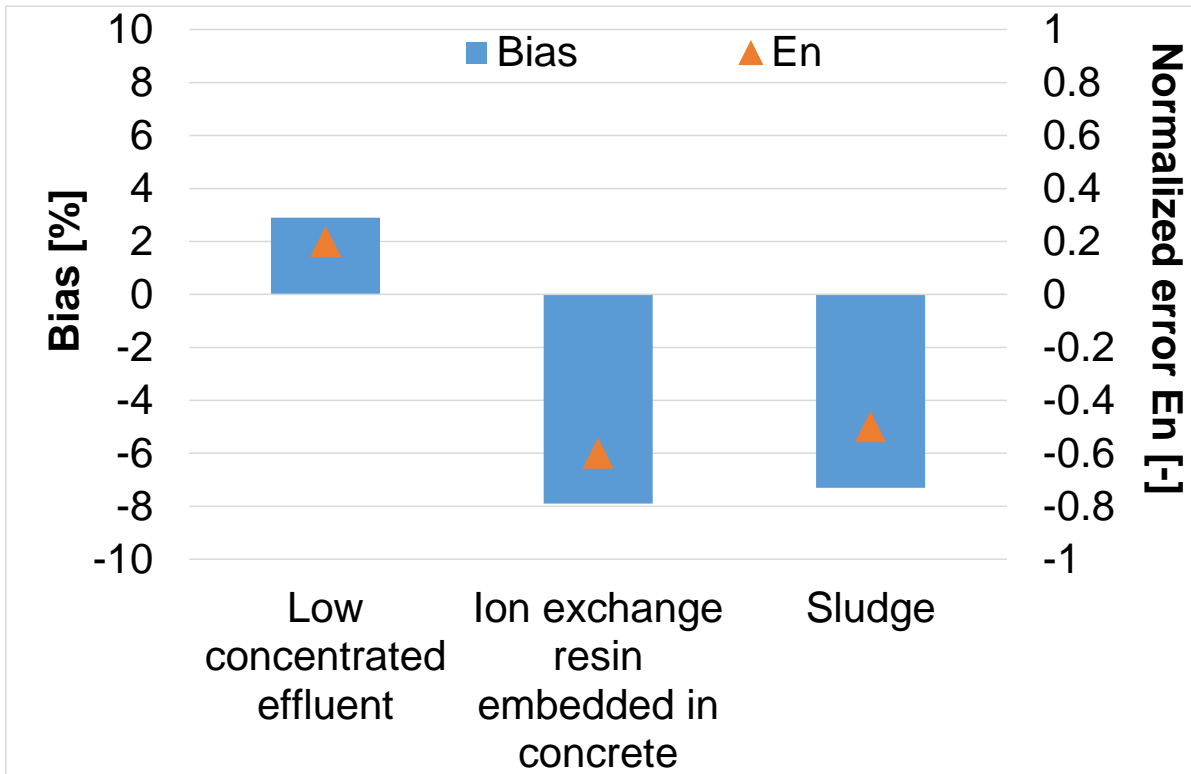
Then it is closed and directly placed in the scintillation counter for nuclear measurement.



	Sr-resin [®] + LSC	Sr PS-resin
Sr yield [%]	90 ± 9	70 ± 11
Counting efficiency [%]	99 ± 1	90.4 ± 0.4

Similar separation yields and counting efficiencies

Application to real nuclear waste samples and comparison to CEA reference method



- Validation of the Sr PS-resin method by comparison with CEA reference values of real samples (bias < 10 % and $E_n < 1$)
- Possible verification of ^{90}Y regrowth with Sr PS-Resin for selectivity check

Conclusions and prospects

➤ Method based on nitric acid:

- **Successful replacement of fuming nitric acid by concentrated nitric acid**
- Validation on real radioactive waste samples with a better selectivity and a similar recovery in comparison to the method based on fuming nitric acid

➤ Method based on Sr PS-resin:

- **Elimination of liquid scintillation cocktail without loss of counting efficiency**
- Validation on real radioactive waste samples with the same selectivity and satisfying recovery (70 %) in comparison to the method based on Sr-resin[®] and LSC



⇒ It is possible to measure accurately ^{90}Sr in nuclear waste without toxic reagent !

Prospects:

- Implementation of design of experiment methodology to optimize radiochemical procedures with a minimum of experiments
- Use of plastic scintillation for other radionuclides, for example ^{99}Tc

The CEA logo consists of the lowercase letters 'cea' in a white, rounded, sans-serif font. A horizontal green line is positioned below the letters. The logo is centered within a red square.

Thank you for your attention

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E. Baudat, C. Colin, E. Laporte, M. Balandras, E. Destrel, P. Fichet
from CEA

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for their contribution for works on PS resins



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