# $^{89}Sr/^{90}Sr$ determination in milk in emergency situations by using PSresins

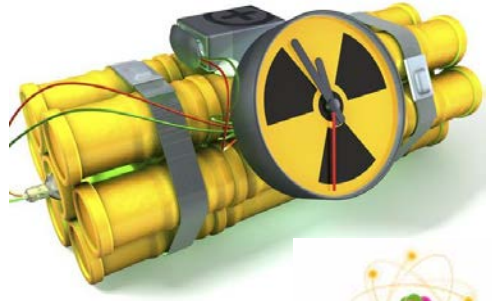
**Marina Sáez-Muñoz** [1)], Héctor Bagán [2)], Alex Tarancón [2)], José F. García [2)], Josefina Ortiz [1)], Sebastián Martorell [1)]

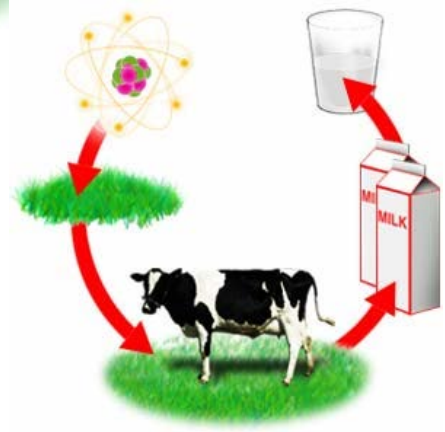
[1)] Laboratorio de Radiactividad Ambiental, MEDASEGI Research Group, Universitat Politècnica de València, Camino de Vera s/n, 46022, Valencia, Spain

[2)] Departament de Química Analítica, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain

Corresponding author's e-mail: **masaemuo@etsii.upv.es**

# Background






- Need for rapid radiochemical methods → **Emergency situations**
  - Nuclear accidents
  - Radiological Dispersal Devices (RDDs): Dirty bombs
- Radiostrontium: **$^{89}$Sr, $^{90}$Sr**
  - Environmental samples: **Milk**
  - **(Euratom) 2016/52**: Dairy products → Radiostrontium: 125 Bq/kg
- Rapid methods:

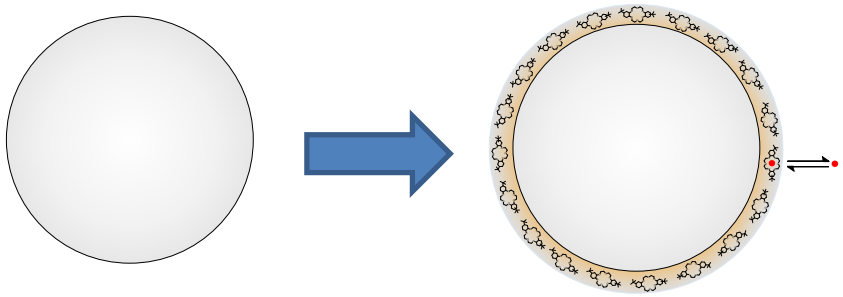
| Procedure | Reference | Sample | $Sr^{2+}$ carrier | Recovery ± SD % (RSD) | Relative Bias $^{90}$Sr | Relative Bias $^{89}$Sr | LD | Time |
|---|---|---|---|---|---|---|---|---|
| IAEA/AQ/27, 2013 | ISSN 2074–7659 | 0.25 L | 10 mg | 73 ± 14.6 (20%) | 3.3 ± 6.7 % | 0.5 ± 1.1 % | 2-4 Bq/L | 7 – 8 h |
| Kabai et al., 2011 | DOI:10.1016/j.scitotenv.2011.09.052 | 0.1 L | 10 mg | 93.5 ± 6.6 (7%) | - | - | 0.8 Bq/L | 7 – 8 h |
| Maxwell et al., 2009 | DOI: 10.1007/s10967-008-7368-3 | 0.1 L | 4.19 mg | 75.1 ± 17 (23%) | 3.19% ± 14.9% | - | 0.5 Bq/L | 7 – 8 h |

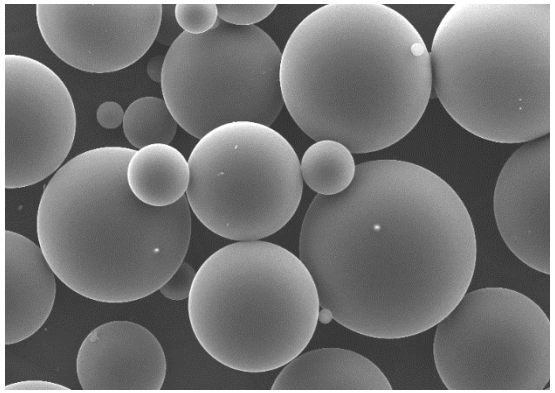
**$^{89}$Sr/$^{90}$Sr determination in milk in emergency situations by using PSresins.**

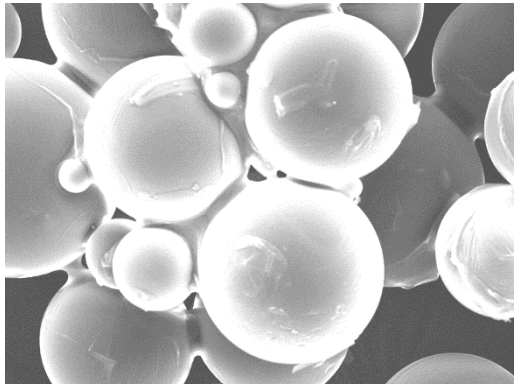
M. Sáez-Muñoz, H. Bagán, A. Tarancón, J.F. García, J. Ortiz, S. Martorell

# Approach → PSresins

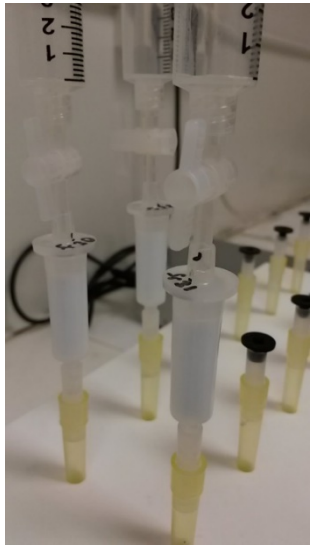
- PSm + selective extractant (DtBuCH18C6)

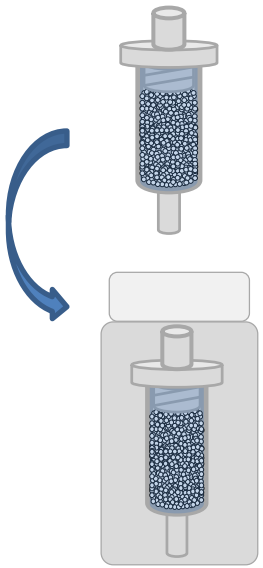






- Advantages:
  - Separation/Measurement preparation→ One single step
  - **Time reduction**
  - Less steps
  - No production of mixed waste





**$^{89}$Sr/$^{90}$Sr determination in milk in emergency situations by using PSresins.**

M. Sáez-Muñoz, H. Bagán, A. Tarancón, J.F. García, J. Ortiz, S. Martorell

# Objective

- Development of a rapid procedure for radiostrontium determination in milk in emergency situations by using PSresins.
  - ✓ Optimization of PSresin conditions.
  - ✓ Study of the pre-treatment steps.
  - ✓ Development of a calibration system for radiostrontium by PSresin separation.
  - ✓ Validation of the method with spiked milk samples and reference materials.

# PSresin separation procedure adaptation

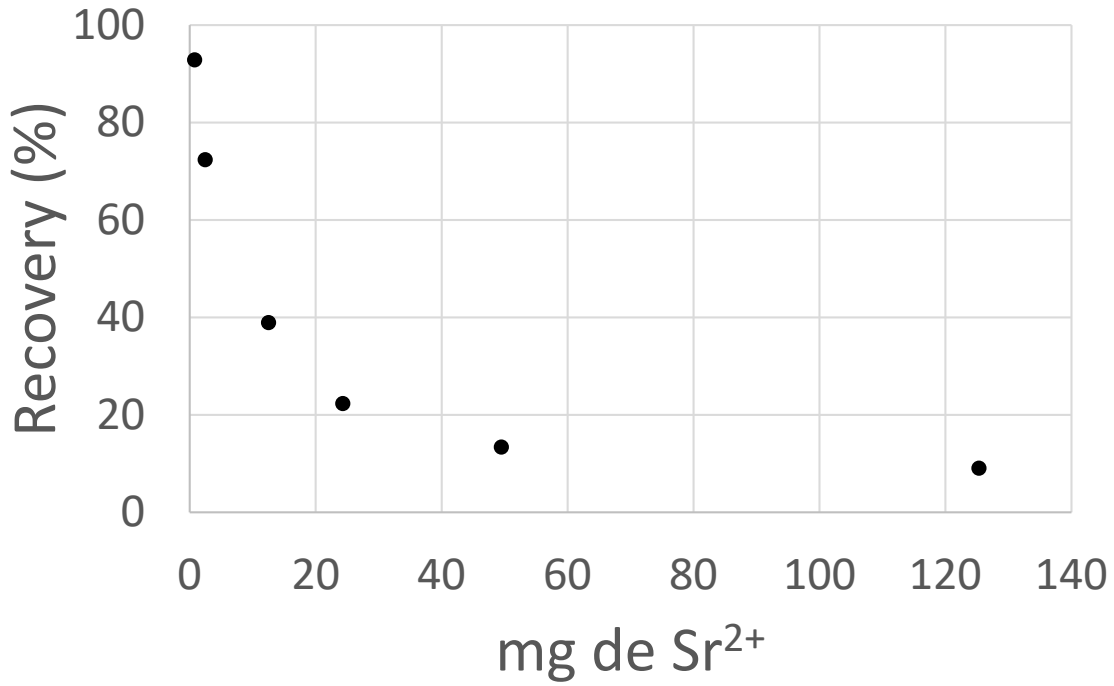
- Radiostrontium separation and measurement in a single step using plastic scintillators plus selective extractants. Application to aqueous sample analysis. Analytica Chimica Acta, 686, 1-2, 50–56, 2011.

| Conditions | 1st paper | Actual study |
|---|---|---|
| Diameter PSm | 180 µm | 60 µm |
| Psresin | 3 g | 1 g |
| Proportion PSm:extractant | 1:1/4 | 1:1/8 |
| Support | 6mL PE vial | 2mL cartridge |
| $Sr^{2+}$ carrier | 0.1 mg | 1 mg |
| Separation conditions | 1) 5mL 6M $LiNO_3$ | 1) 2mL 6M $HNO_3$ |
| | 2) 10mL sample (6M $LiNO_3$) | 2) 10mL sample (6M $HNO_3$) |
| | 3) 4x 5mL 6M $LiNO_3$ | 3) 2x 2mL 6M $HNO_3$ |
| | | 2x 2mL 6M $LiNO_3$ |

| | |
|---|---|
| Recovery | 100% |
| Efficiency $^{90}Sr$ | 83.4 ± 0.2% |

| | |
|---|---|
| Recovery | 93 ± 2% |
| Efficiency $^{90}Sr$ | 94 ± 4% |

# Recovery actual study

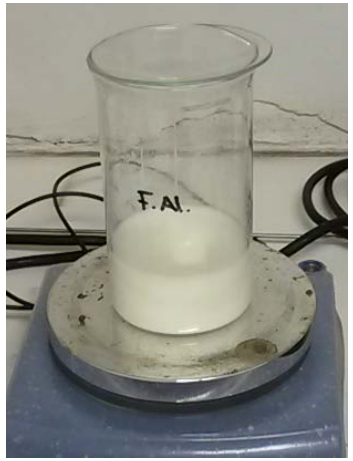



- Recovery decreases with the amount of $Sr^{2+}$ carrier
- Work with 5 mg of $Sr^{2+}$ carrier (50-60%) to minimize relative errors due to $Sr^{2+}$ in milk.
- Milk samples → Increase PSresin amount from 1g to **1.5g**

# Method for Sr isotopes determination in milk

| | |
|---|---|
| Sampling (100mL milk) | |
| $Sr^{2+}$ carrier (5 mg) + homogenization | 0.5 h |
| Extraction (TCA) | 1 h |
| Precipitation (oxalates) | 1 h |
| PSresin | **1 h** |
| Measurement (Quantulus 1220) | 1 h |
| Results | 0.5 h |
| | **Total 5 h** |

# Sample pre-treatment



Sampling (100mL milk)

↓

$Sr^{2+}$ carrier (5 mg) + homogenization

↓

Extraction (TCA)
Filtration

→ Fat and proteins

Na, K, P, Ca, Mg, Sr ($^{90}Y$)

↓

Precipit.-centrifugation (oxalates)
Dissolution in 6M $HNO_3$

→ Na, K, P, Mg

Ca, Sr ($^{90}Y$)

↓

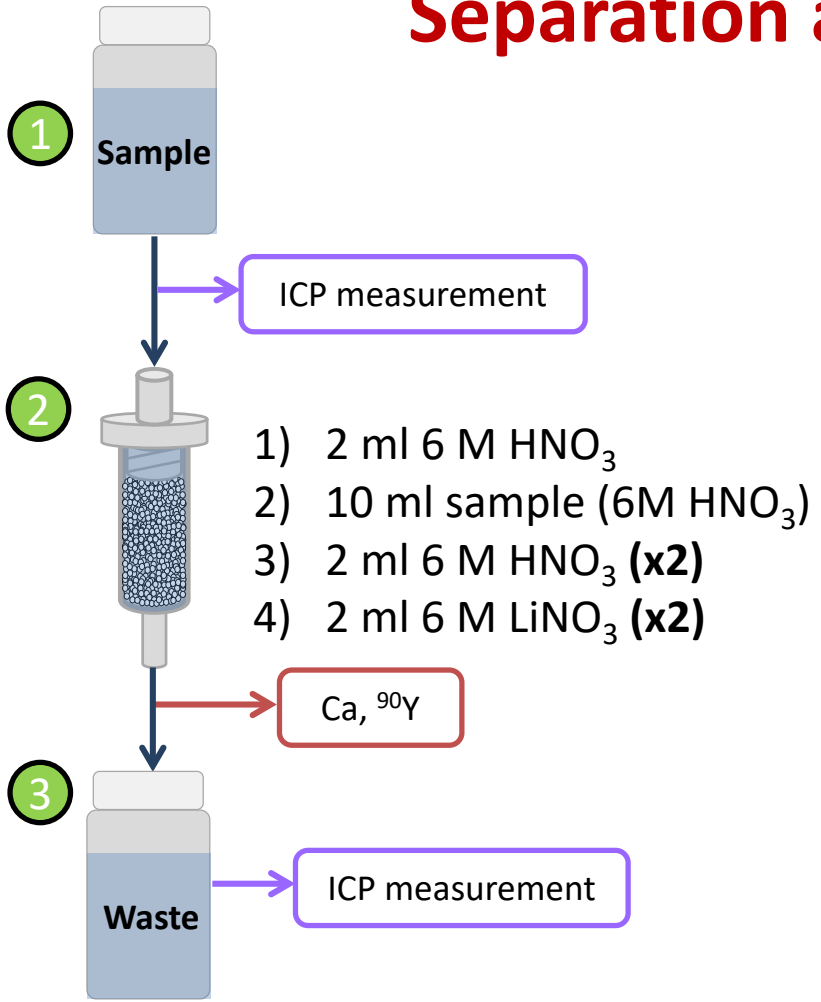
| 50 mL TCA | 75 mL TCA | 100 mL TCA |
|---|---|---|
| 99 ± 1% | 98 ± 1% | 101 ± 4% |

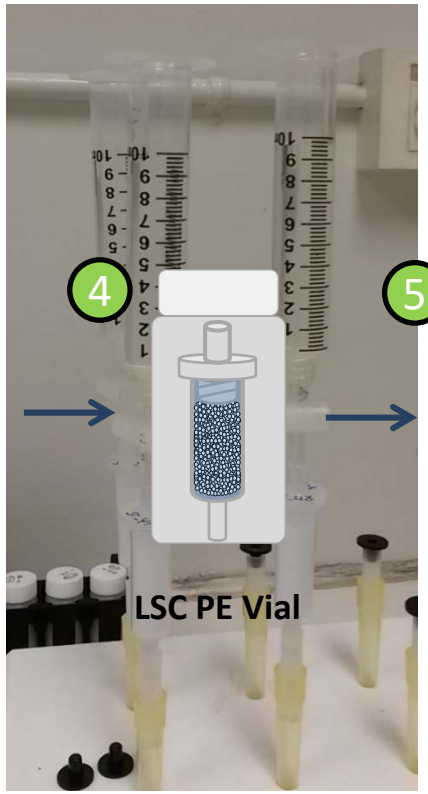
| 1g oxalic acid | 2g oxalic acid | 5g oxalic acid |
|---|---|---|
| 94 ± 2% | 97 ± 2% | 93 ± 4% |

**$^{89}Sr/^{90}Sr$ determination in milk in emergency situations by using PSresins.**

M. Sáez-Muñoz, H. Bagán, A. Tarancón, J.F. García, J. Ortiz, S. Martorell

# Separation and measurement





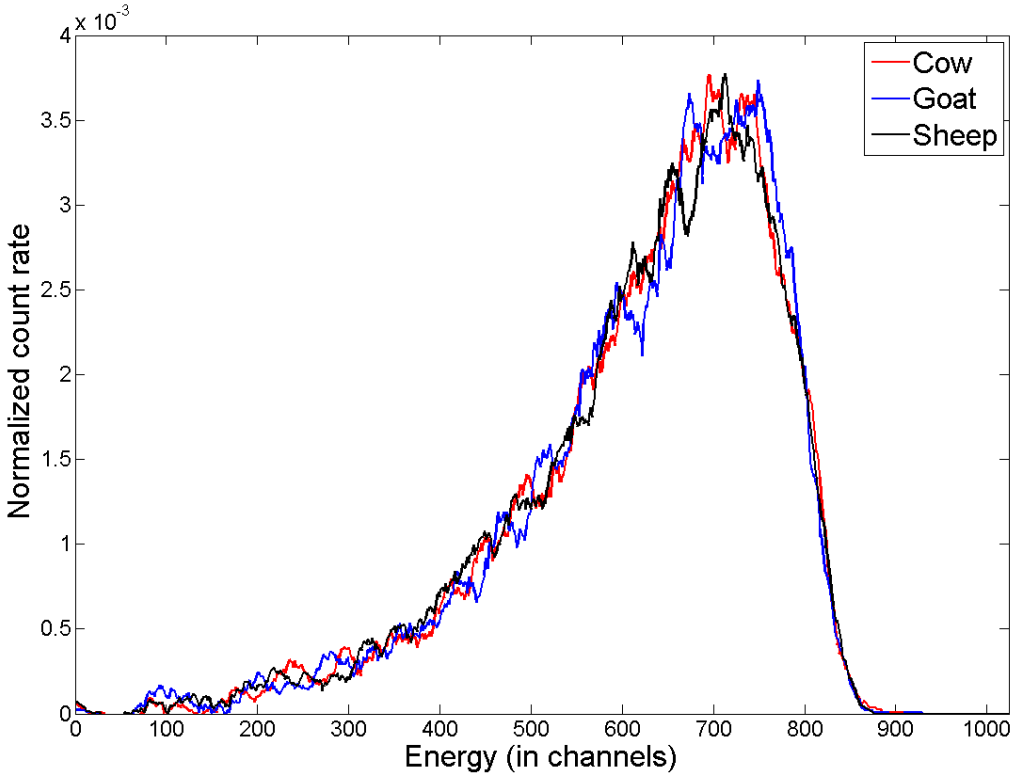

**$^{89}Sr/^{90}Sr$ determination in milk in emergency situations by using PSresins.**

M. Sáez-Muñoz, H. Bagán, A. Tarancón, J.F. García, J. Ortiz, S. Martorell

# Spectral analysis

- Different milk samples (cow, goat, sheep), fat content (whole, semi-skimmed, skimmed), milk treatment (UHT, pasteurized, raw milk, etc.)
- Different sample pre-treatment (TCA, oxalic acid)
- Average SQP(E) = 787 ± 9 (n=27)
- Same position of the spectra

**$^{89}$Sr in different milk samples**



# Window calibration system

| Calibration standards | $^{90}$Sr | $^{89}$Sr |
|---|---|---|
| Stable Sr (mg) | 3, 4, 5, 6, 7 | 3, 4, 5, 6, 7 |
| Average SQP(E) | 789 ± 8 | 791 ± 4 |
| Average Efficiency (%) | 82.2 ± 6.7 | 88.9 ± 4.0 |

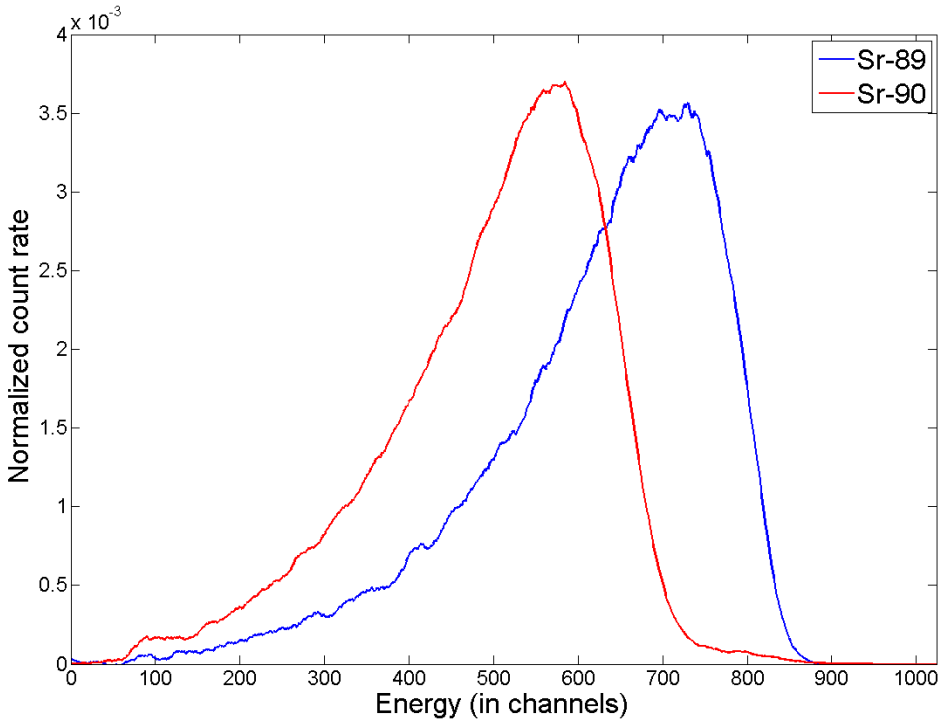
- $^{89}$Sr window (channel 740-900) → k = 0.209

$$cpm\ (^{89}Sr) = \frac{cpm\ (channel\ 740 - 900)}{k}$$

- $^{90}$Sr window (total window)

$$cpm\ (^{90}Sr) = cpm(total\ window) - cpm(89Sr)$$

**$^{89}$Sr and $^{90}$Sr spectra**



UNIVERSITAT POLITÈCNICA DE VALÈNCIA

UNIVERSITAT DE BARCELONA

LSC 2017 COPENHAGEN

# Application to milk samples




## Animal

- Cow
- Goat
- Sheep

## Treatment

- Powder
- UHT
- Pasteurized
- Raw milk

## Fat content

- Whole (3.6g/100mL)
- Semi-skimmed (1.6g/100mL)
- Skimmed (0.3g/100mL)

## Reference material

- IAEA-473, milk powder



**$^{89}$Sr/$^{90}$Sr determination in milk in emergency situations by using PSresins.**

M. Sáez-Muñoz, H. Bagán, A. Tarancón, J.F. García, J. Ortiz, S. Martorell

# Application

| Type of milk | Pre-treatment Recovery (%) | Column Recovery (%) | Total Recovery (%) |
|---|---|---|---|
| Cow (x7) | 93.0 ± 2.9 (3%) | 69.1 ± 2.0 (3%) | 64.3 ± 3.4 (3%) |
| Sheep (x4) | 93.6 ± 6.1 (6%) | 64.3 ± 2.7 (3%) | 60.3 ± 6.0 (10%) |
| Goat (x4) | 96.2 ± 2.7 (3%) | 69.6 ± 1.8 (3%) | 66.9 ± 3.1 (3%) |
| Semi-skimmed | 86.5 | 71.7 | 62.0 |
| Skimmed | 90.2 | 71.1 | 64.1 |
| Powder (x2) | 95.3 % ± 1.3 (1%) | 68.3 ± 0.5 (1%) | 65.1 ± 1.4 (2%) |
| Pasteurized | 94.8 | 68.2 | 64.7 |
| Reference material (x3) | 91.2 ± 2.4 (3%) | 78.4 ± 1.5 (2%) | 71.5 ± 1.6 (2%) |
| | | | |
| Total samples | 93.3 ± 3.7 (4%) | 69.7 ± 4.3 (6%) | 65.0 ± 4.5 (7%) |

| Type of milk | Activity $^{90}Sr$ (Bq/L) | Activity $^{89}Sr$ (Bq/L) | Prop. $^{90}Sr$: $^{89}Sr$ | Relative bias $^{90}Sr$ + $^{89}Sr$ (%) | Relative bias $^{90}Sr$ (%) | Relative bias $^{89}Sr$ (%) |
|---|---|---|---|---|---|---|
| Reference material IAEA-473 | 209 ± 5 (k=1) | - | 1:0 | - | 0,4 | - |
| Reference material IAEA-473 | 209 ± 5 (k=1) | - | 1:0 | - | -0,8 | - |
| Reference material IAEA-473 | 209 ± 5 (k=1) | - | 1:0 | - | -1,4 | - |
| Cow/whole/UHT | 27 | - | 1:0 | - | 1,9 | - |
| Cow/whole/UHT | - | 15 | 0:1 | - | - | -15,8 |
| Cow/whole/UHT | 27 | 27 | 1:1 | -1,4 | 13,2 | -15,5 |
| Sheep/semi-skimmed/UHT | 27 | 27 | 1:1 | 6,9 | 5,1 | 8,7 |
| Goat/semi-skimmed/UHT | 27 | 27 | 1:1 | 6,1 | 27,7 | -16,1 |
| Cow/semi-skimmed/UHT | 27 | 27 | 1:1 | 4,7 | 6,4 | 2,9 |
| Cow/skimmed/UHT | 27 | 27 | 1:1 | 6,4 | 11,5 | 1,0 |
| Cow/whole/powder | 27 | 27 | 1:1 | 2,0 | 8,5 | -4,7 |
| Cow/whole/pasteurized | 27 | 27 | 1:1 | 2,8 | 7,6 | -2,1 |
| Cow/whole/UHT | 12,5 | 27 | 1:2 | 0,2 | 2,3 | -0,7 |
| Sheep/semi-skimmed/UHT | 12,5 | 27 | 1:2 | 19,5 | 56,0 | 1,9 |
| Goat/semi-skimmed/UHT | 12,5 | 27 | 1:2 | 5,5 | 19,3 | -1,6 |
| Cow/whole/UHT | 12,5 | 125 | 1:10 | -5,9 | 122,9 | -21,6 |
| Sheep/semi-skimmed/UHT | 12,5 | 125 | 1:10 | -6,4 | 36,3 | -11,6 |
| Goat/semi-skimmed/UHT | 12,5 | 125 | 1:10 | -6,3 | 74,4 | -16,1 |

## $^{89}Sr/^{90}Sr$ determination in milk in emergency situations by using PSresins.

M. Sáez-Muñoz, H. Bagán, A. Tarancón, J.F. García, J. Ortiz, S. Martorell

# Conclusions

- **PSresins** can be used for **radiostrontium** separation in **milk** in **emergency situations**
- Less steps: separation/measurement preparation in **one single step**
- **Reduction of time** compared to other rapid procedures to **5 h**
- **Reproducible** and **good total recovery** (65.0 ± 4.5 %) for **different types of milk** (fat content, type of animal, treatment, etc.)
- **Windows calibration procedure:** good results for total $^{89}Sr$ + $^{90}Sr$ activity and samples with similar $^{89}Sr$ and $^{90}Sr$ activities.
- Further work: assay other calibration procedures and adaptation to other matrices

# Acknowledgements

- Ministerio de Economia y Competitividad (MINECO) for financial support under CTM2014-02020
- Agència de Gestió d'Ajuts Uiversitaris i de Recerca (AGAUR) for financial support under 2014-SGR-1277.
- Universitat Politècnica de València for PhD grant.
- Carles Mir from "La Rosita" for supplying some of the milk samples.


# Thank you for your attention

**$^{89}Sr/^{90}Sr$ determination in milk in emergency situations by using PSresins**

**Marina Sáez-Muñoz [1)],** Héctor Bagán [2)], Alex Tarancón [2)], José F. García [2)], Josefina Ortiz [1)], Sebastián Martorell [1)]

[1)] Laboratorio de Radiactividad Ambiental, MEDASEGI Research Group, Universitat Politècnica de València, Camino de Vera s/n, 46022, Valencia, Spain

[2)] Departament de Química Analítica, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain

Corresponding author's e-mail: **masaemuo@etsii.upv.es**

# Background

- (Euratom) 2016/52: maximum permitted levels of radioactive contamination of food and feed following a nuclear accident or any other case of radiological emergency
  - Dairy products → Radiostrontium: 125 Bq/kg

# ICP

| | leche | | | | | | |
|---|---|---|---|---|---|---|---|
| **Type of milk** | mg/kg Ca | mg/Kg Mg | mg/kg Zn | mg/kg K | mg/kg Na | mg/kg P | mg/kg Sr |
| **Nata Cow/whole/UHT** | 1030,52 | 92,11 | 4,30 | 1407,17 | 419,71 | 685,65 | 0,52 |
| **Nata Sheep/semi-skimmed/UHT** | 1634,80 | 145,23 | 5,66 | 1049,91 | 1038,28 | 1439,48 | 2,65 |
| **Nata Goat/semi-skimmed/UHT** | 1123,60 | 122,34 | 4,16 | 1738,14 | 605,12 | 871,22 | 0,41 |
| **Nata Cow/whole/pasteurized** | 1049,38 | 95,70 | 4,17 | 1439,07 | 388,25 | 643,18 | 0,73 |
| **Nata Goat/animal** | 1250,71 | 108,86 | 4,42 | 1371,13 | 343,82 | 696,84 | 2,51 |

## Cow/whole/UHT

| | mg/kg Ca | mg/Kg Mg | mg/kg Zn | mg/kg K | mg/kg Na | mg/kg P |
|---|---|---|---|---|---|---|
| **FB1-Nata** | 1164,02 | 104,89 | 5,11 | 1568,39 | 469,05 | 777,56 |
| **FA1-Nata** | 1192,31 | 106,80 | 5,12 | 1614,08 | 475,14 | 792,63 |
| **FA2-Nata** | 1152,80 | 101,38 | 4,70 | 1571,67 | 459,83 | 750,58 |
| **FB1** | 1002,91 | 1,37 | 0,48 | 8,80 | 11,75 | - |
| **FA1** | 1009,31 | 1,58 | 0,49 | 8,90 | 10,51 | - |
| **FA2** | 1035,58 | 1,27 | 0,39 | 14,36 | 16,36 | - |
| **W.FB1** | 861,09 | 1,27 | 0,39 | 7,07 | 14,30 | 6,01 |
| **W.FA1** | 833,02 | 1,73 | 0,45 | 7,96 | 15,44 | 8,00 |
| **W.FA2** | 856,15 | 1,36 | 0,44 | 12,59 | 20,82 | 8,73 |

| **% oxalate remove** | | | | | |
|---|---|---|---|---|---|
| **Ca** | Mg | Zn | K | Na | P |
| **13,8%** | 98,7% | 90,6% | 99,4% | 97,5% | 100,0% |
| **15,3%** | 98,5% | 90,5% | 99,4% | 97,8% | 100,0% |
| **10,2%** | 98,7% | 91,7% | 99,1% | 96,4% | 100,0% |

| **% column retention** | | | | | |
|---|---|---|---|---|---|
| **Ca** | Mg | Zn | K | Na | P |
| **14,1%** | 6,9% | 19,3% | 19,7% | -21,7% | |
| **17,5%** | -9,3% | 8,2% | 10,6% | -46,8% | |
| **17,3%** | -7,0% | -13,6% | 12,3% | -27,2% | |

**$^{89}Sr/^{90}Sr$ determination in milk in emergency situations by using PSresins.**

M. Sáez-Muñoz, H. Bagán, A. Tarancón, J.F. García, J. Ortiz, S. Martorell