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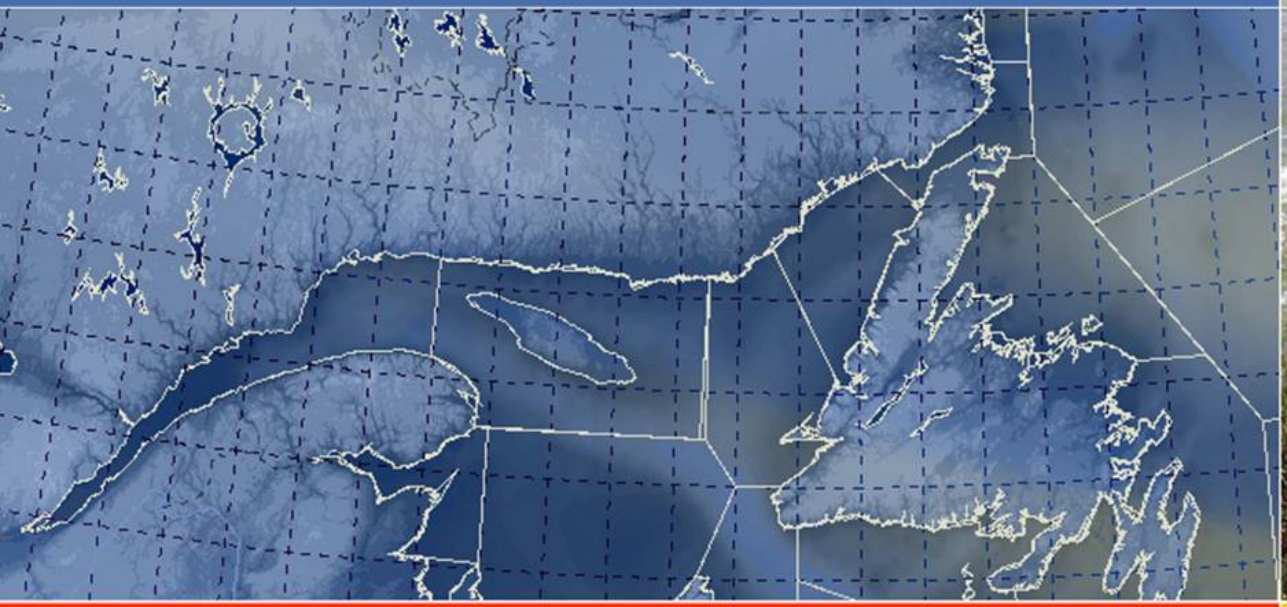
# RAPID RADIOACTIVITY ANALYSIS IN ENVIRONMENTAL SAMPLES IN RESPONSE TO EMERGENCIES USING LC-ICP-MS



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ensc chimie paris
UPMC SORBONNE UNIVERSITÉS
IRSN INSTITUT DE RADIOPROTECTION ET DE SÛRETÉ NUCLÉAIRE
UNIVERSITÉ LAVAL Département de chimie

# Objectives

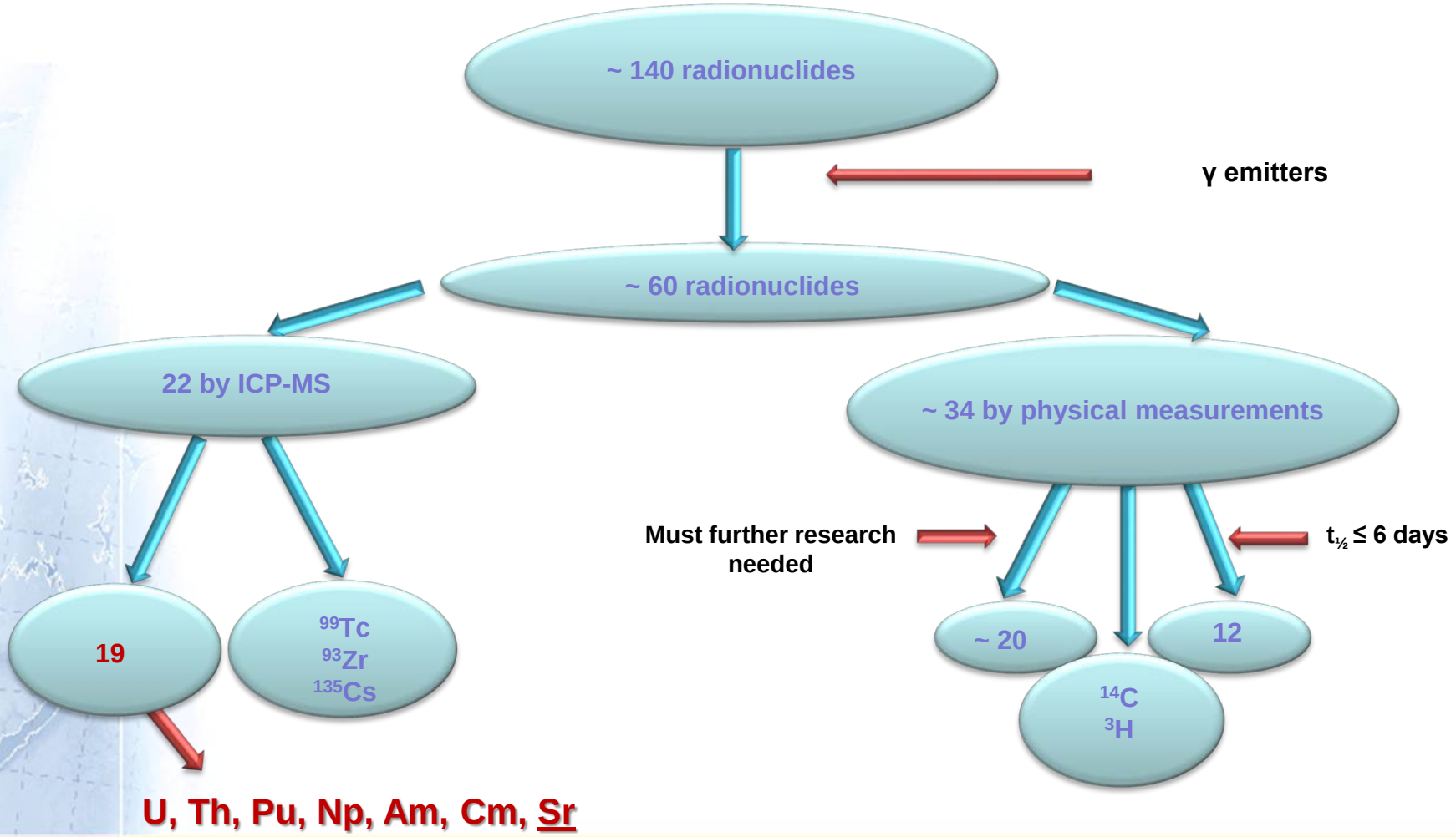
**Post-Fukushima Context ⟹ New IRSN R&D programs**

**⟹ Development of rapid methods in response to emergencies**

**Reduce the duration of radiochemical treatment and measurement of alpha and beta emitters in environmental samples**

**Several weeks ⟹ One day!**

# Radionuclides of interest in radiological emergencies



# Chromatographic separation: strategy

- **Resins: criteria of selection**
  - Affinity to the elements
  - Compatibility of the elution media with the ICP-MS
    - $\%_{acids} < 10\%$ and $\%_{salt} < 0.2\ \%$
  - Reduction of isobaric and molecular interferences
  - Minimum number of columns (previous work – 3 columns)

- **Elements: Classified according to their oxidation degrees**

**Th, Np and Pu (IV)** **Am et Cm (III)** **Sr(II)** **U(VI)**

*Major isobaric interferences*

| Isotopes | $^{90}$Sr | $^{233}$U | $^{239}$Pu | $^{241}$Pu |
|---|---|---|---|---|
| Interference | $^{90}$Zr (stable isotope ) | $^{232}$Th$^{1}$H | $^{238}$U$^{1}$H | $^{241}$Am |

# Former on-line separation

**Table 2** Protocol for the sequential separation of long-lived actinides

| | | | | Switching modules (SM) position[a] | | | | |
|---|---|---|---|---|---|---|---|---|
| Step | Time (s) | Medium | Flow rate (mL/min) | SV-1 | SV-2 | SV-3 | SV-4 | SLP[b] |
| 1 | 240 | 3M $HNO_3$ | 2.5 | On | On | On | Off | *elute* |
| 2 | 270 | 0.1M $(NH_4)_2C_2O_4$ | 1 | Off | On | Off | On | *load* |
| 3 | 120 | 0.1M $(NH_4)_2C_2O_4$ | 1 | Off | Off | On | On | *load* |
| 4 | 180 | 0.01M $(NH_4)_2C_2O_4$ | 1 | On | Off | Off | On | *load* |
| 5 | 90 | Milli-Q water | 2.5 | On | On | On | Off | *load* |
| 6 | 60 | 3M $HNO_3$ | 3 | On | On | On | Off | *load* |

[a] SV-1 to SV-4: switching valves. [b] Sample loop position, *elute* signifies that the medium is passing through the sample loop while *load* is the opposite.

| Step | Step description |
|---|---|
| 1 | 3 M $HNO_3$ is pumped through the sample loop to load the sample and rinse the residual elements from the three resins |
| 2 | 0.1 M $(NH_4)_2C_2O_4$ is pumped through U/TEVA to elute U |
| 3 | 0.1 M $(NH_4)_2C_2O_4$ is pumped through n-DGA to elute Am |
| 4 | 0.01 M $(NH_4)_2C_2O_4$ is pumped through TEVA to elute Pu |
| 5 | Milli-Q water pumped to rinse all three resins from any residual elements |
| 6 | 3 M $HNO_3$ is pumped through all three resins to pre-condition the resins for the next analysis |

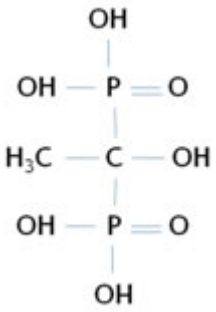
Issues:

- Sr not tested
- Th could be included but needed 6M HCl for elution (lack compatibility with ICP-MS)
- Oxalate is OK but salt deposit observable after several hours (critical in emergency response)

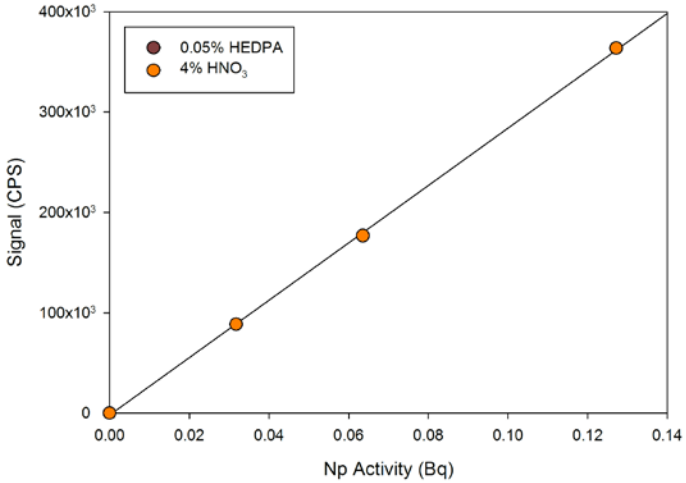
Larivière D., Benkhedda K., Kiser S., Johnson S., et Cornett R.J., (**2010**), *Analytical Methods*, 2:259-267

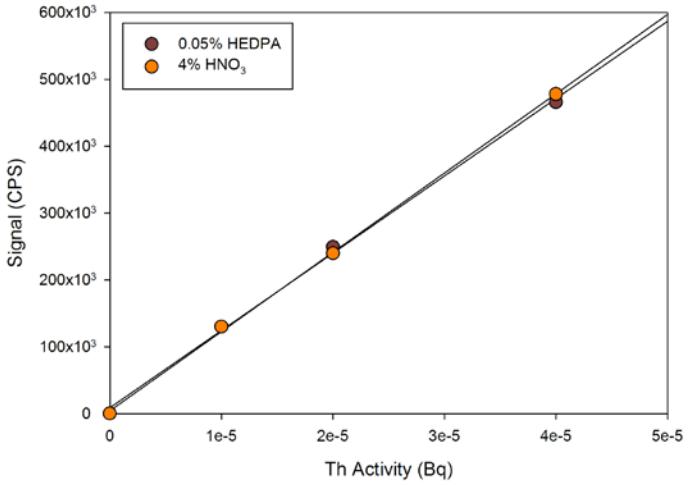
# Replacement for oxalate and HCl

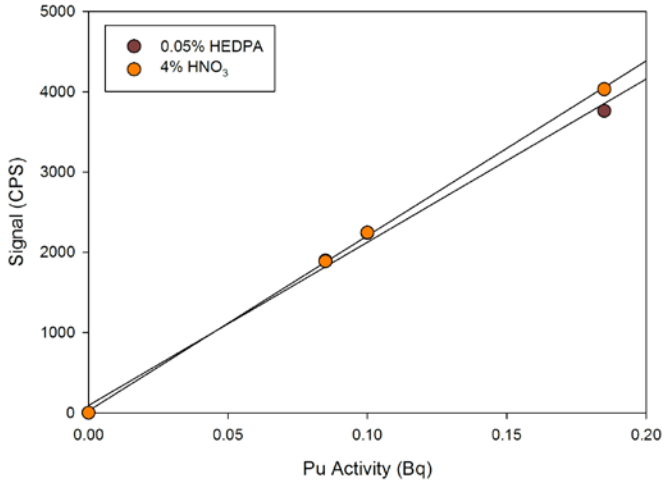
1-Hydroxyethylidene-1,1-Diphosphonic acid




*HDPA or HEDPA*

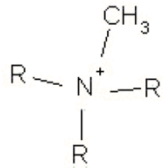


# Proposed Chromatographic separation (1/2)

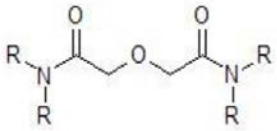
**TEVA resin**



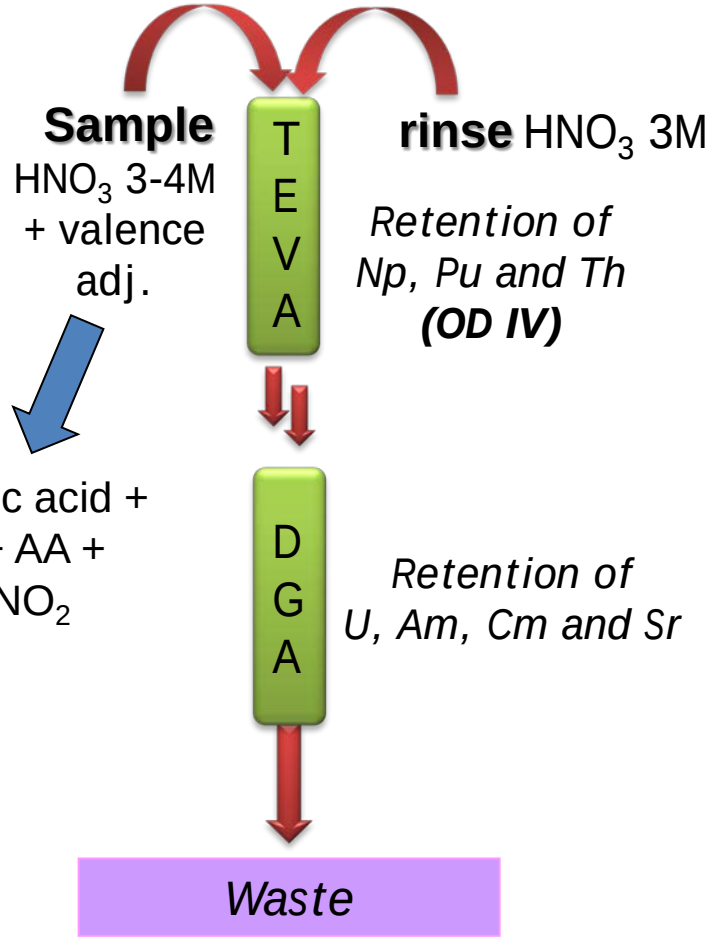
**Extractant (E):Quaternary ammonium salt**

R = $C_8H_{17}$ and $C_{10}H_{21}$

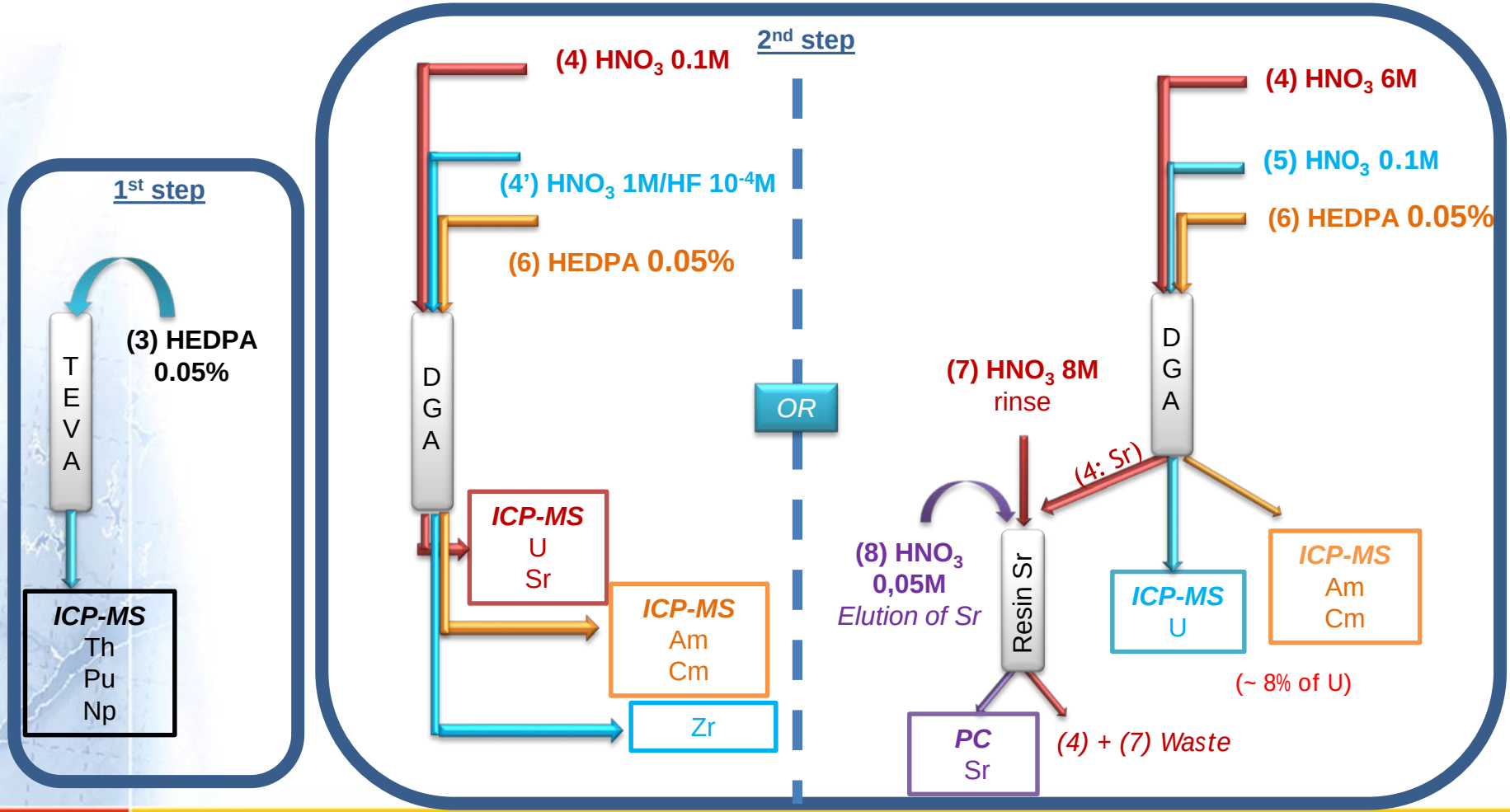
**N DGA resin**



**Extractant (E) (R=8): N,N,N',N'-tetrakis-2-ethylexyl-diglycolamide**



# Proposed Chromatographic separation (2/2)



# Chromatographic separation(2/2) – synthetic samples

## Table 1. Yield recovery (%) for radionuclides of interest

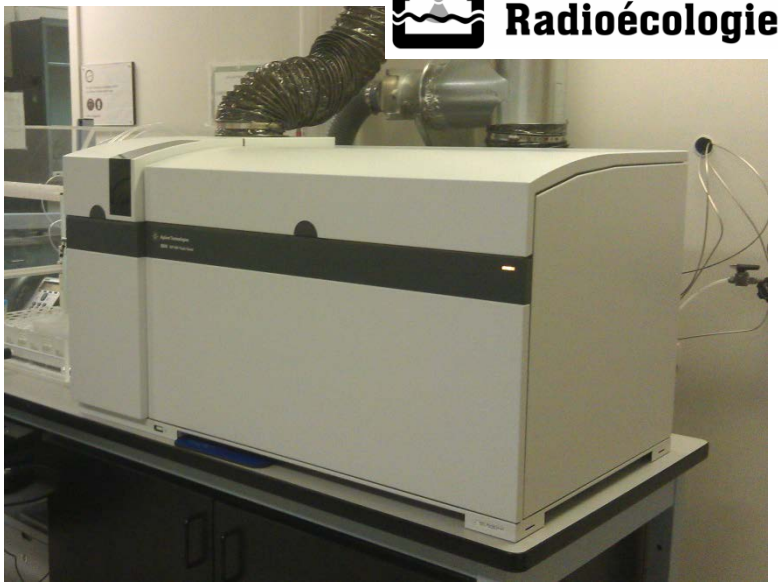
| Matrix type | TEVA | | | DGA or DGA/Sr | | | | |
|---|---|---|---|---|---|---|---|---|
| | Th | Pu | Np | U | Sr | Am | Cm | Zr |
| **Standard** | 100 | 100 | 95 | 100/90 | 95/80 | 98/98 | 95/95 | 95/95 |
| **River water** | 100 | 100 | 93 | 94/75 | 75/75 | 100/98 | 100/100 | 95/95 |
| **Sea water** | 96 | 91 | 87 | 75 | >50[a)] | 100/100 | N.P. | N.P. |
| **Standard[b)]** | 75 | 42[d)] | 45[d)] | 106/103 | 76/56 | 90/101 | N.P. | N.P. |
| **Soil[c)]** | 81 | 100 | 98 | 91/78 | N.P. | 88/103 | N.P. | N.P. |

*a) 3 mL of DGA resin used*
*b) Lithium borate fusion + HTiO coprecipitation*
*c) Lithium borate fusion + HTiO coprecipitation + PEG removal*
*d) Not enough Fe added*

**N.P. – Not performed**

# Instrumentation used


*ICP-MS:X-SERIES II (ThermoFisher)*
*Liquid chromatography (Dionex/ThermoFisher)*
*Autosampler (ThermoFisher)*

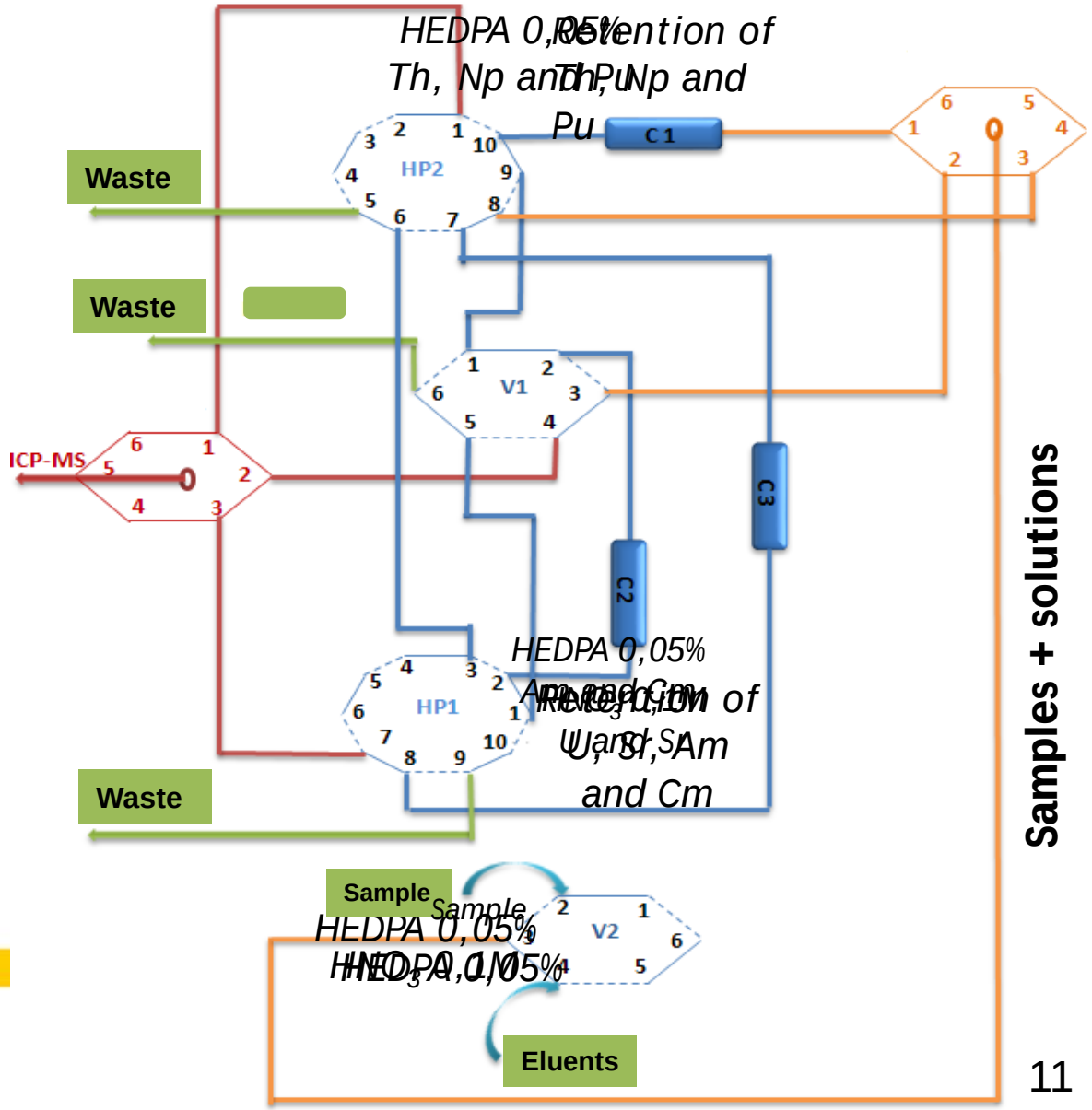


*ICP-MS: Agilent 8800 QQQ (Agilent)*
*Liquid chromatography (Dionex/ThermoFisher)*
*Autosampler (ThermoFisher)*

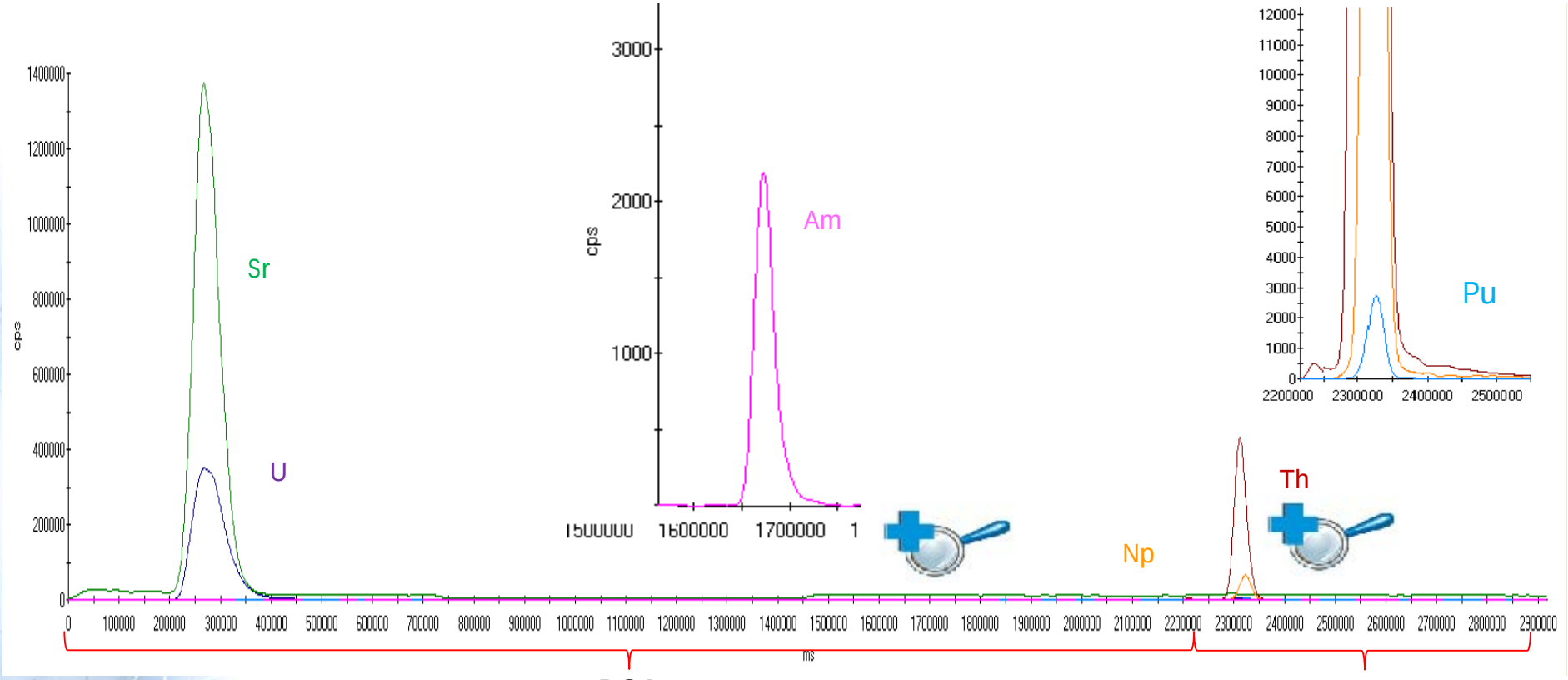
# Automated separation scheme (6 valves)

***TEVA (C1) + DGA (C2)***

1. Sample loading
2. Rinse
3. Elution of U and Sr
4. *Start measure*
5. Elution of Am and Cm
6. Elution of Th, Np and Pu



# Chromatograms - synthetic samples




**Total time (separation + measurements): 68 min (need to be optimized)**

# Figures of merit

| | U | Th | Pu | Np | Am | Sr | Cm |
|---|---|---|---|---|---|---|---|
| Gain in sensitivity | X 36 | X 36 | X 23 | X 28 | X 20 | X 29 | X 20 |

Decrease in separation time :

- from 6h30 to approximately 1h30 (I think we can do better)

Decrease in detection limits:
Approximately the same as the gain except for $^{238}U$ and $^{232}Th$

$^{90}Sr$ from 9500 Bq/kg to ~ 350 Bq/kg (with the use of the QQQ)

# Conclusions / Future research

- Unique and sequential protocol for seven elements
- Good recovery for river water / sea water / soil samples
- Automation and coupling established and validated with synthetic samples
- Reduction of the duration:
  - Several weeks ⟹ **~ 1 hour**
- Reduction of the duration of digestion (alkaline fusion and coprecipitation)
- Adaptation of the protocol to other environmental samples: milk, sediment, air filter
- Validation of the automation and on-line coupling with environmental SRM

# Acknowledgements

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