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Determination of carbon-14 source term in French SIERS

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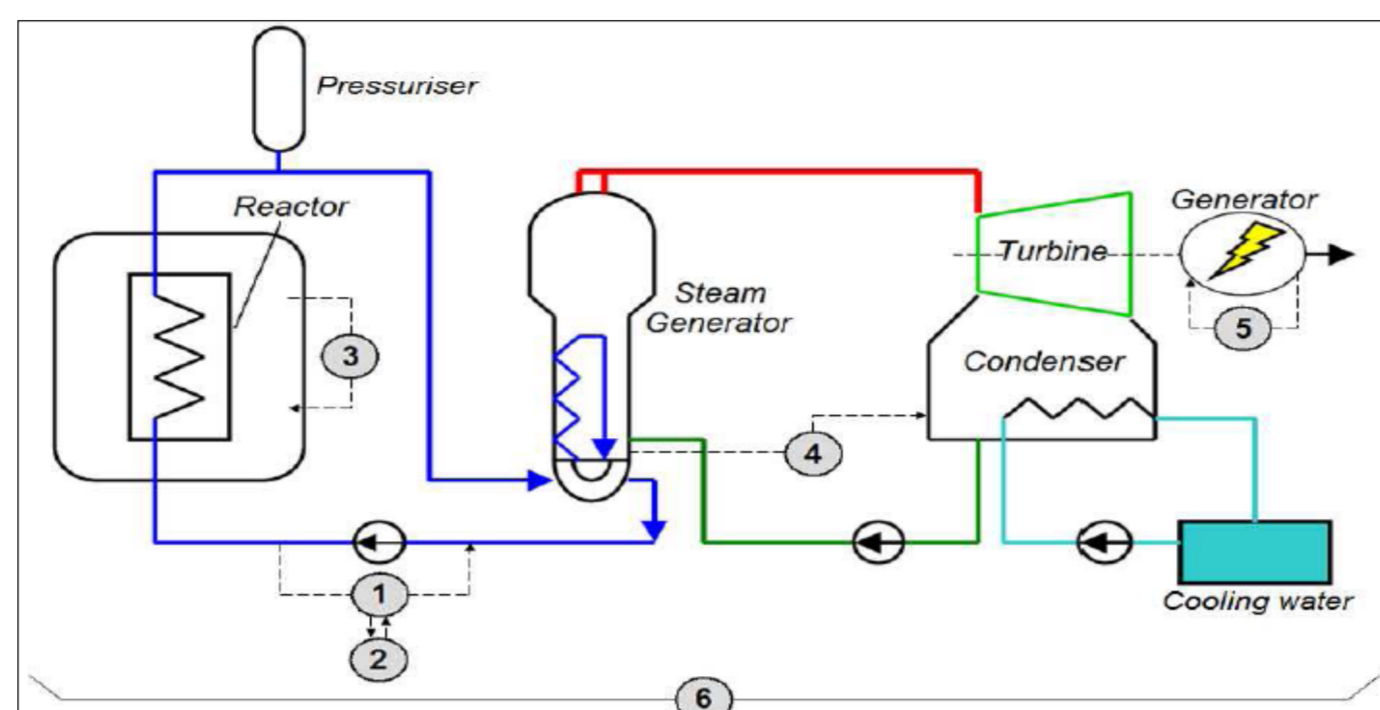
Introduction / Context

This poster presents the methodologies and results of experiments carried out on the spent ion exchange resins (SIERS) from EDF PWR (pressurized water reactor) at the Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA beneficiary N°4) within the framework of the European program Carbon-14 Source Term (CAST) Work Package 4. The studies concern both carbon-14 measurements and its speciation (inventory) and the measurement of organic molecules issued from extraction experiments on SIERS.

Origin of spent ion exchange resins

Ion Exchange Resins (IERS as combination of cationic, anionic and/or mixed bed resins) are used for **purification of the various circuits in various operating history.**

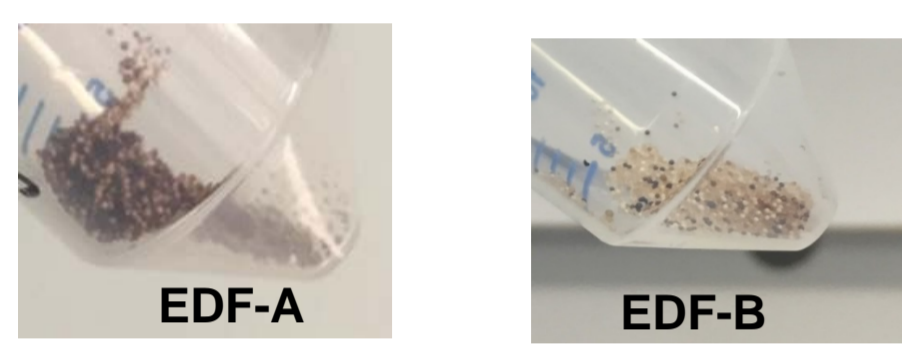
	Cationic resins	Anionic resins
Polymer	polystyrene DVB	polystyrene DVB
Functional group	Sulphonic acid	Trimethylammonium
Ionic shipped	⁷ Li ⁺ (primary circuit) H ⁺ (others circuit)	OH ⁻
Impurity	Nuclear grade	Nuclear grade



General location of the key purification systems in EDF PWR

Spent ion exchange resins samples

Name of the sample	Power reactor unit (MWt)	Type of fuel	Sampling date	Received date	Mass (g)	Dose rate
EDF-A	1450	UOX	01/2014	06/2014	10	15 µSv/h (10g)
EDF-B	1300	UOX	11/2014	02/2015	4*10	300 µSv/h (10g)



Sampling of SIERS (~10g) are performed during this process and transferred to CEA laboratory

Samples are representatives of the waste before conditioning (not of the "packaged waste")
Samples are made of SIERS from different circuits depending on the sampling campaign

Origin of SIERS

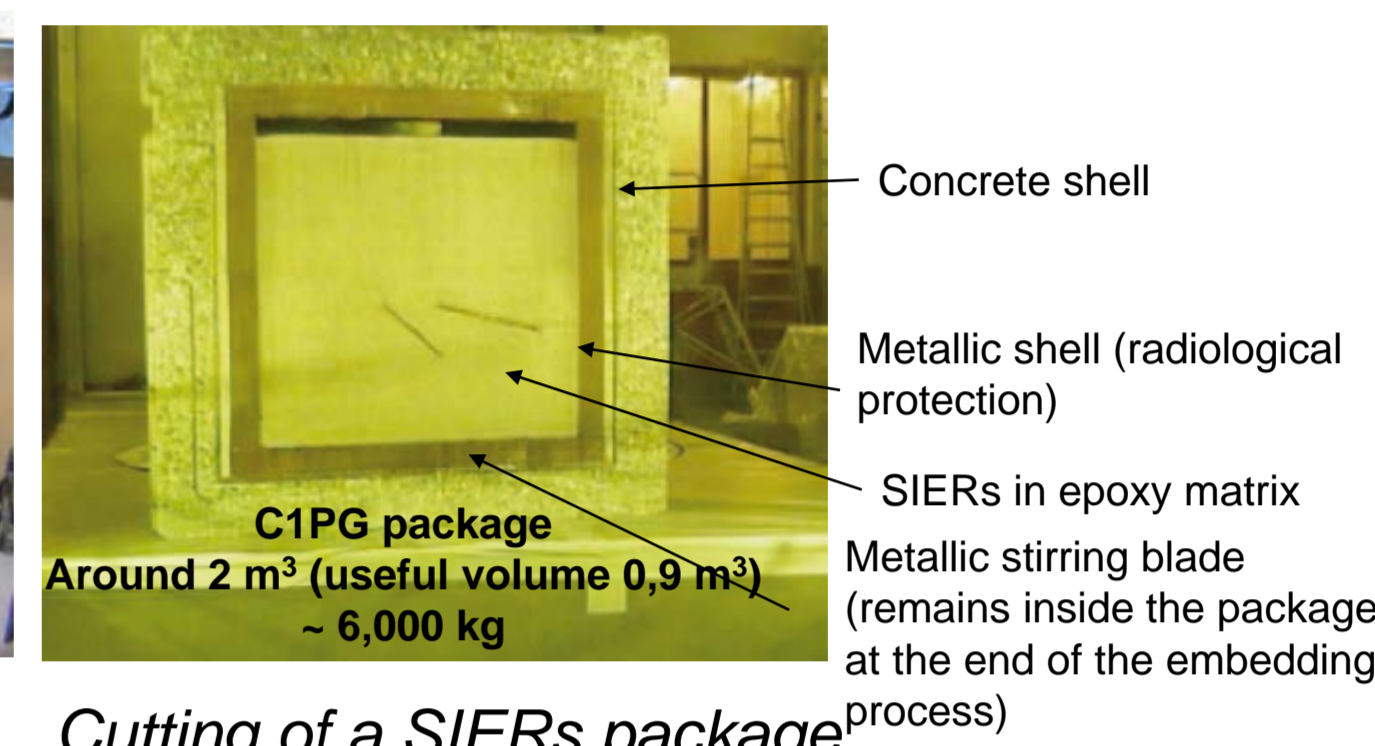
SIERS management in France

EDF operates 58 PWR in France. Spent Ion Exchange Resins (SIERS) are discharged under water and stored before final conditioning. Discharge conditions criteria are usually **chemical or radiochemical saturation, maximum service lifetime...**

- EDF-SIERS are classified as **Low and Intermediate level Short Lived waste (LILW-SL)**
- Contain short-lived radionuclides, such as cobalt-60, and may also contain strictly limited amounts of long-lived radionuclides such as **carbon 14.**
- **Are disposed off at the Andra CSFMA surface waste disposal facility after packaging**

SIERS packaging "Mercure" process conditioning

280-360 kg of wet SIERS are embedded in an epoxy resin (400 to 680 kg)
 Total mass of waste package : 6000 kg



Mobile unit on EDF site

Cutting of a SIERS package

Determination of ¹⁴C source term (WP4 Task 4-2)

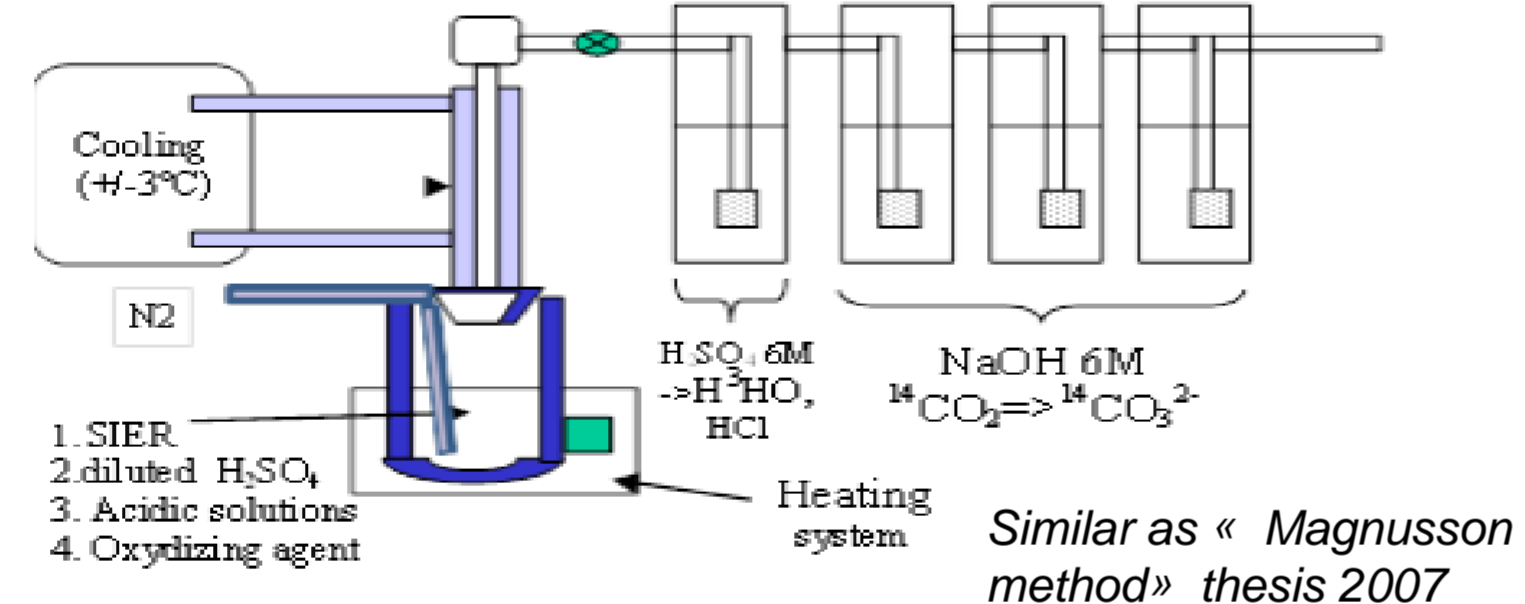
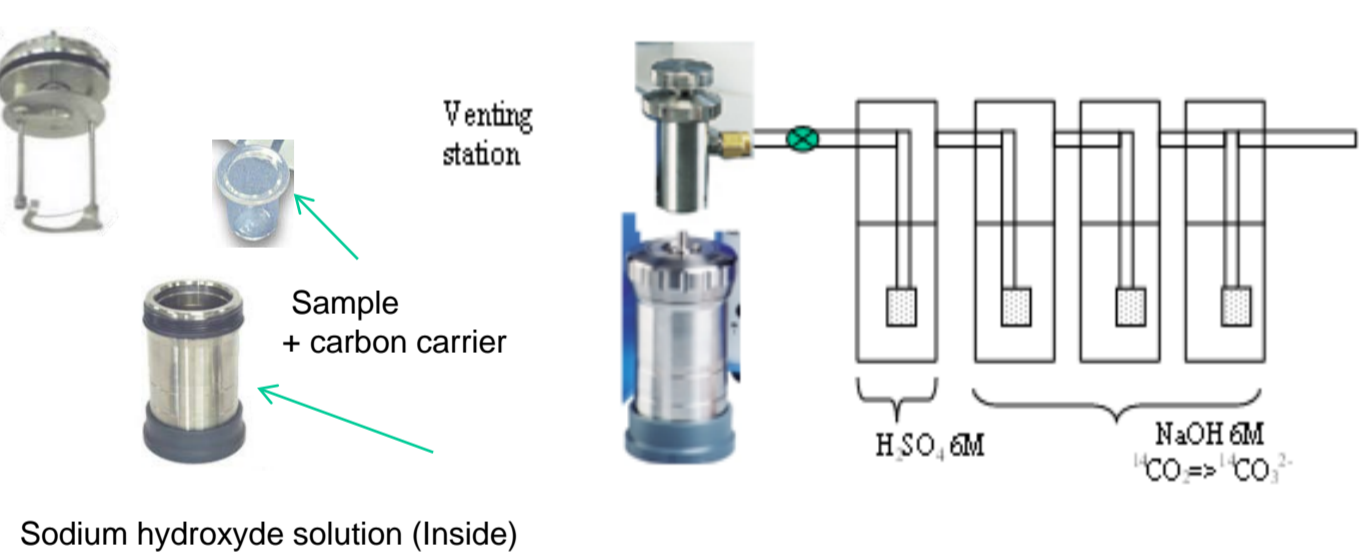
Analytical methodologies were developed on virgin IER for the measurement of total carbon 14 and speciation

Total ¹⁴C by combustion with O₂

- IER (0.2 to 0.5 g) mixed with carrier (graphite)
- Combustion under O₂ (25 bars)
- CO₂ produced by mineralization :
 - trapped in NaOH solution as CO₃²⁻ in the mineralization device during combustion and cooling
 - to achieve the recovery of ¹⁴C, the mineralization system is degassed in a venting station and the gases are flushed into NaOH bubblers

Speciation of ¹⁴C by acidic mineralization

- IER (0.2 to 0.5 g) spiked by carbonate solution
- First step : measurement of mineral ¹⁴C
 - Acidification by H₂SO₄
 - Degassing under N₂ and vacuum into NaOH bubblers
 - Measurements of CO₃²⁻ carrier (recovery) and ¹⁴C
- Second step : measurement of organic ¹⁴C
 - Concentrated acid (H₂SO₄/HNO₃) with oxidant (H₂O₂)
 - Degassing under N₂ and vacuum reflux into NaOH bubblers
 - Measurement ¹⁴C



Optimizations performed on virgin resins spiked with ¹⁴C as carbonate and/or glucose

Combustion with O ₂	Acidic dissolution method	¹⁴ C minéral	¹⁴ C organique
¹⁴ C recovery	¹⁴ C recovery and selectivity		
> 95%	¹⁴ C mineral	> 95 %	< 3 %
	¹⁴ C organic	< 6 %	> 90 %

Application on SIERS

Sample	Type	Total ¹⁴ C Combustion (Bq.g ⁻¹)	Total ¹⁴ C Acidic dissolution (Bq.g ⁻¹)	Difference (Bq.g ⁻¹)
EDF-A	Wet	5570 ± 430	5610 ± 430	40
EDF-B	Wet	2125 ± 200	1612 ± 150	513

EDF-A sample : similar results
 EDF-B sample : inconsistent results

Two analytical methodologies are needed to check the accuracy of measurements
Application on drying SIERS show that some inconsistent results were obtained

Results

Sample	State	Total ¹⁴ C (Bq.g ⁻¹)	Mineral form	Organic form
EDF-A	Wet	5570 ± 430	77 %	23 %
EDF-B	Wet	2125 ± 200	Can not be determined (*)	

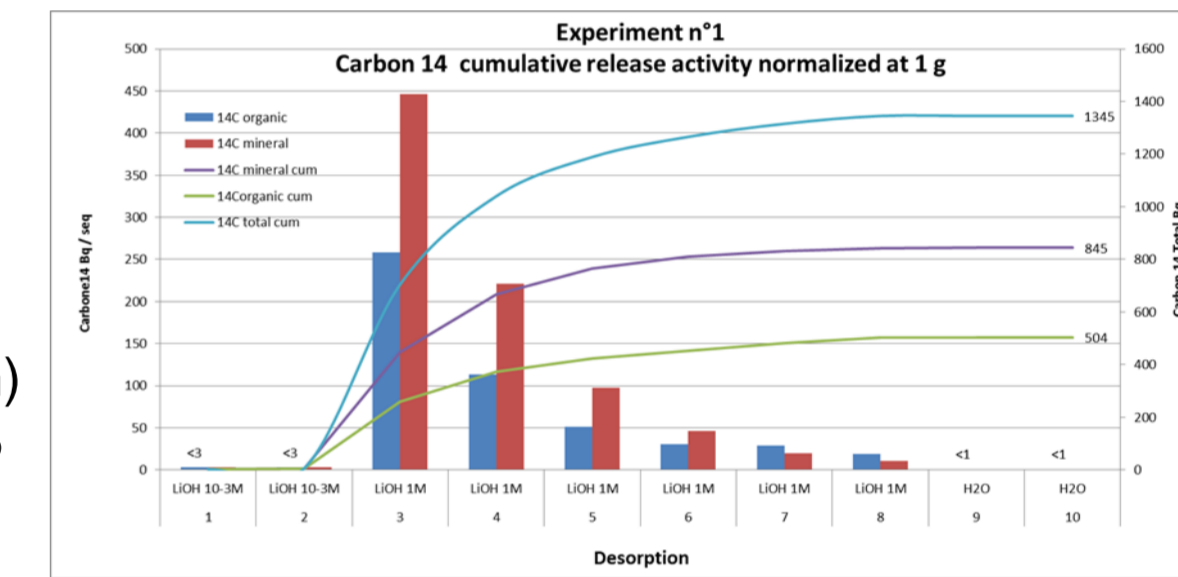
Total carbon determined by combustion - Speciation determined by acidic dissolution

- problem is identified in the case of drying => more experiments are needed
- Samples representativeness is questioned => a statistical approach is needed to take into account the origin of the SIERS (various campaigns)

Desorption experiments (WP4 Task 4-3)

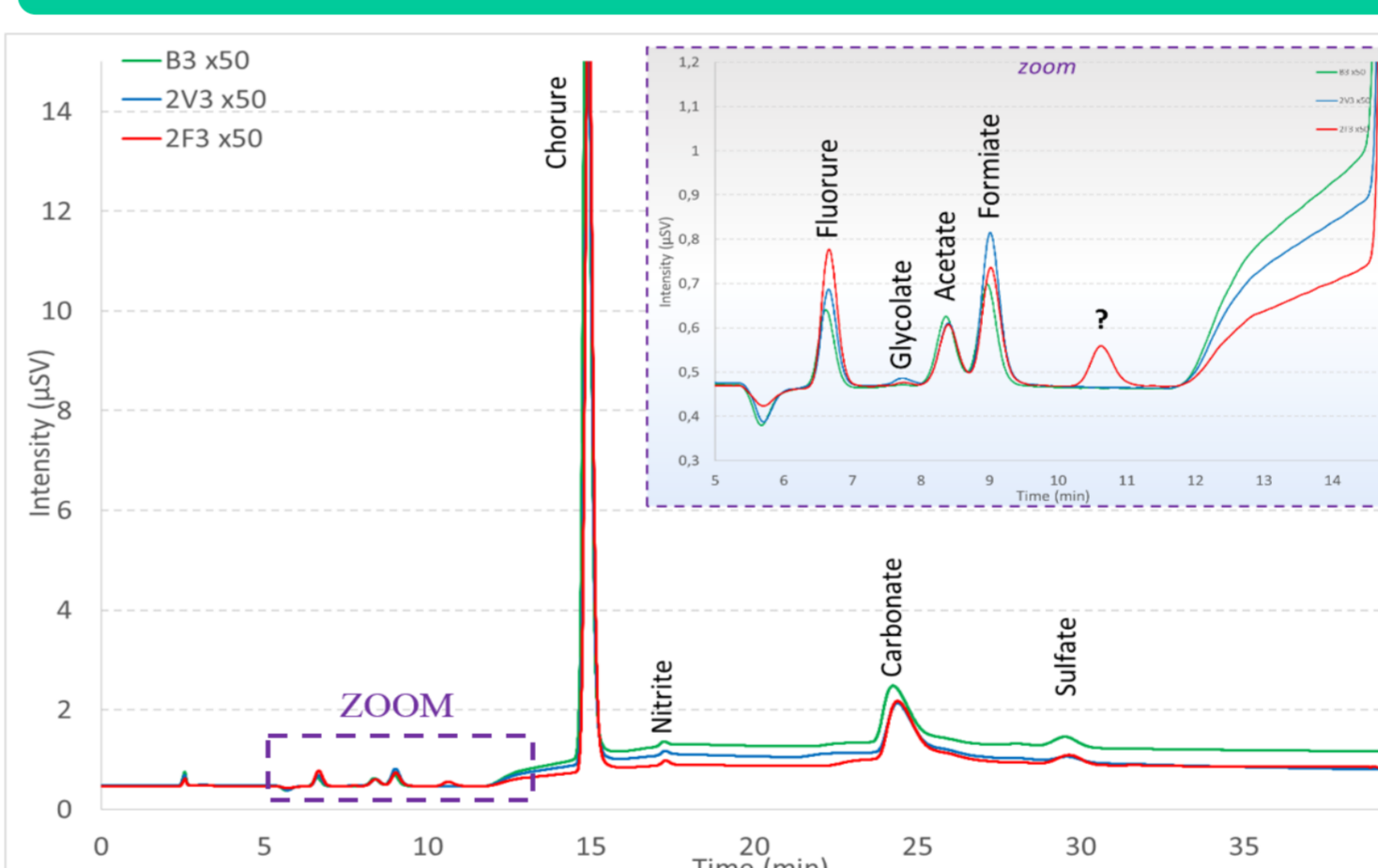
Desorption experiments performed to identify organic compounds fixed on the SIERS

- Experimental methodology
 - Desorption ~1 g of wet SIERS by 10 ml of LiOH 10⁻³ up to 1 Mol/l
- Carbon 14 results
 - ~ 10 % of ¹⁴C remains in SIERS after desorption experiment (in organic form)
 - Desorption ¹⁴C balance (~ 1400 Bq/g) does not fit with total carbon 14 (2125 Bq/g with the combustion method) → **carbon 14 loss in the gas phase ?**

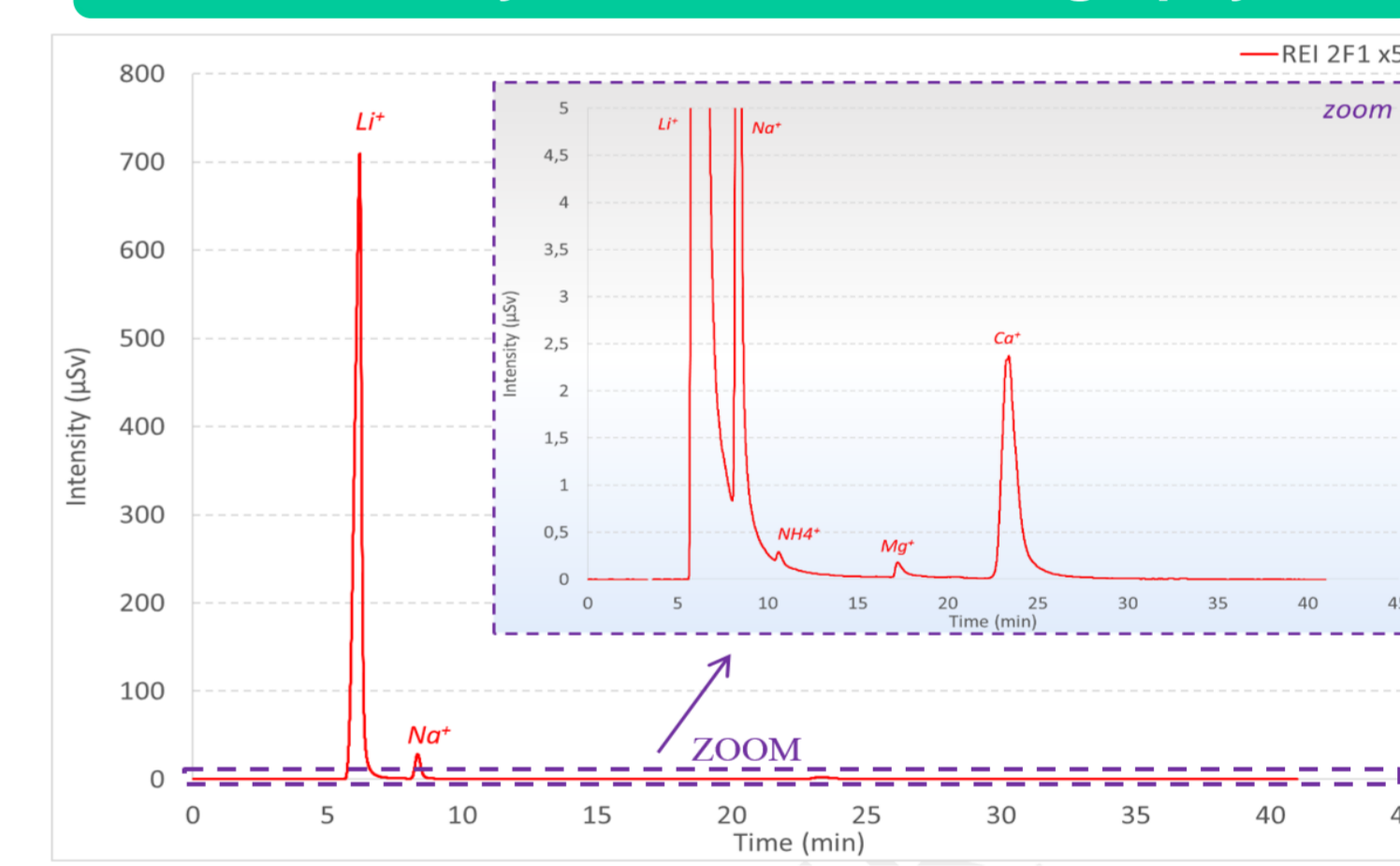


Analytical development and sample analysis for the determination of the hydro soluble organic compounds

Carboxylic acids by anionic chromatography



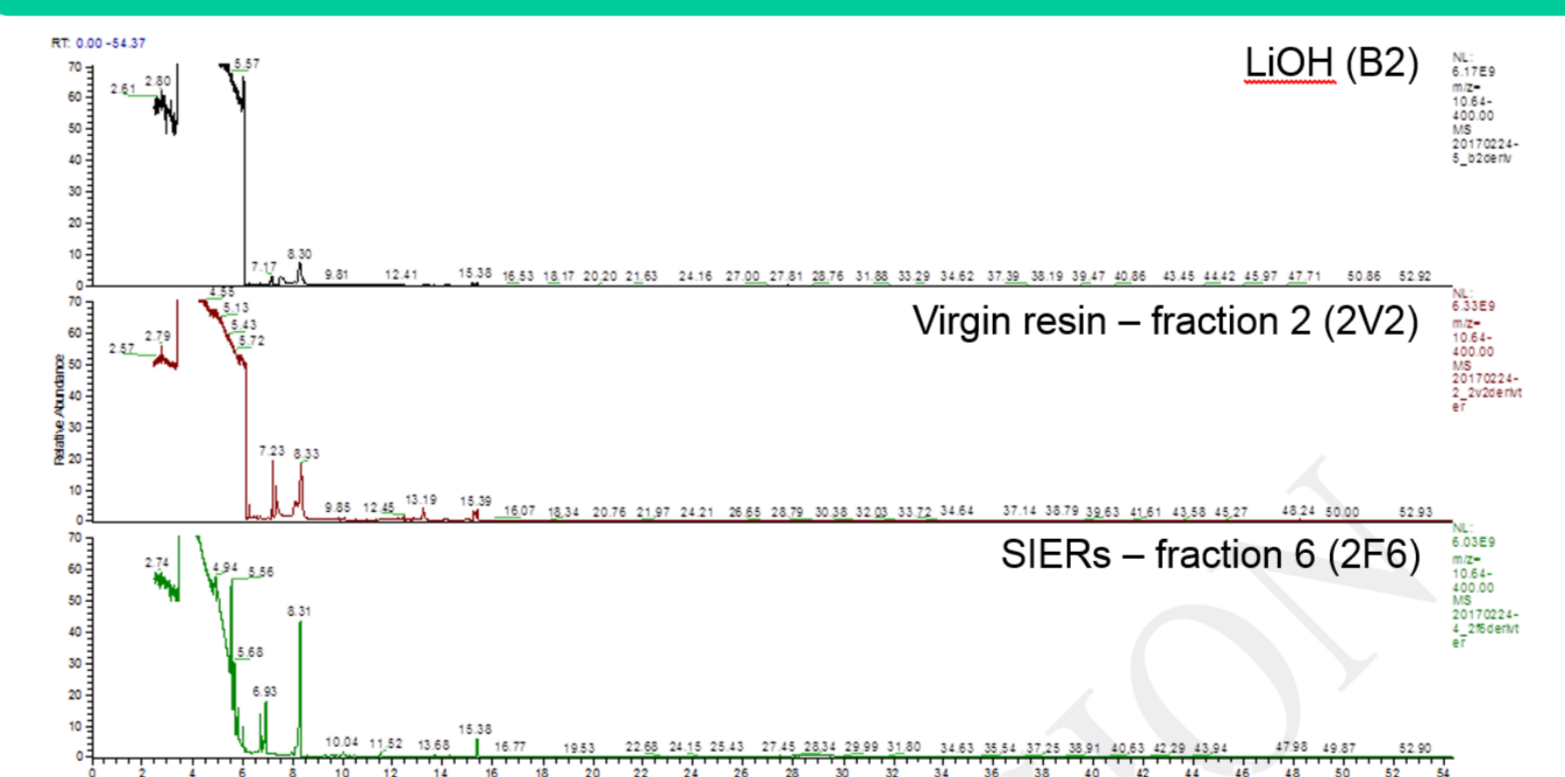
Amines by cationic chromatography



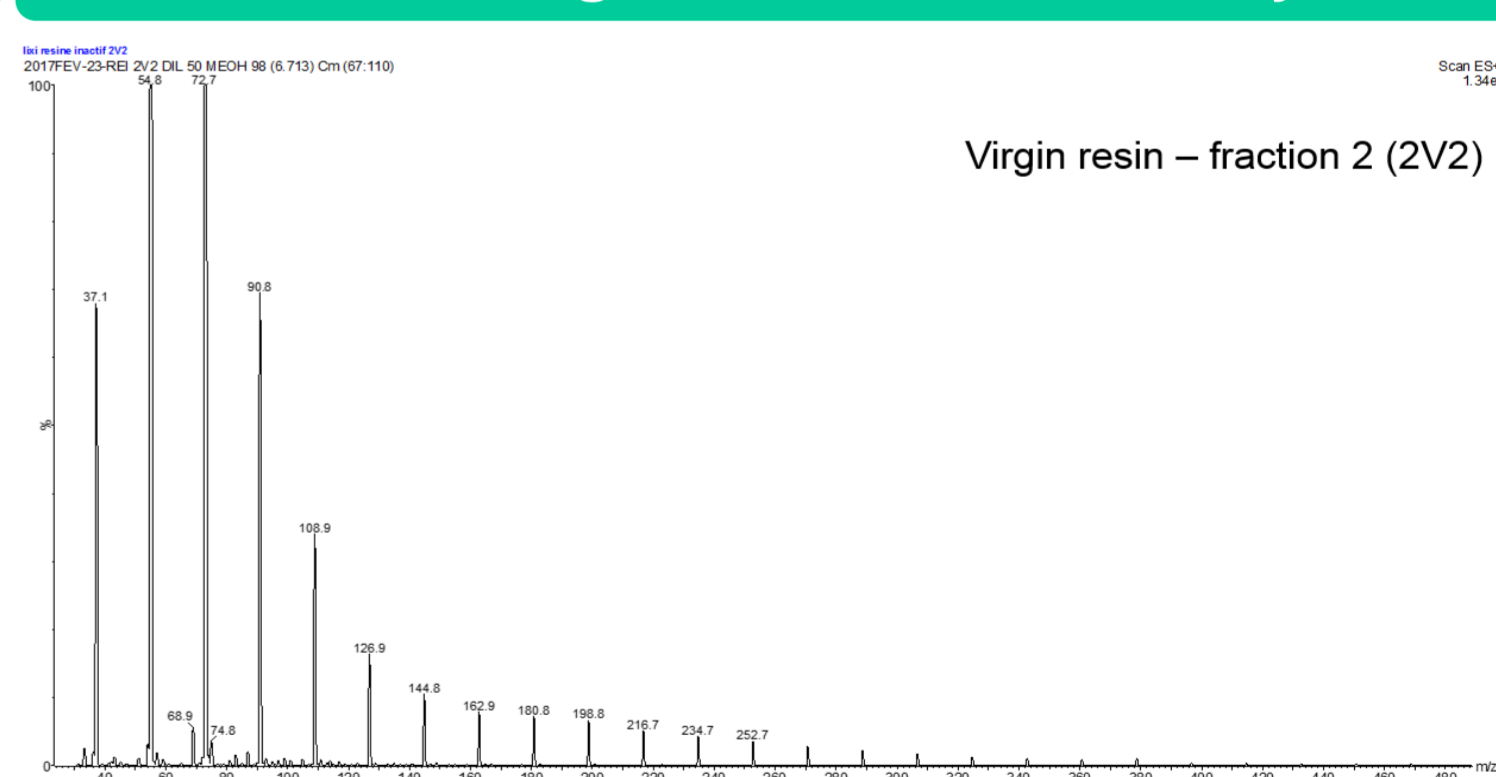
Acetate & formiate detected in LiOH solutions (contamination), only glycolate come from resin desorption (< 8 mg_{acid}.L⁻¹)

No amine detected with the developed method, no chemical degradation of functional groups observed in these conditions

Low molecular weight volatile molecules by GC-MS



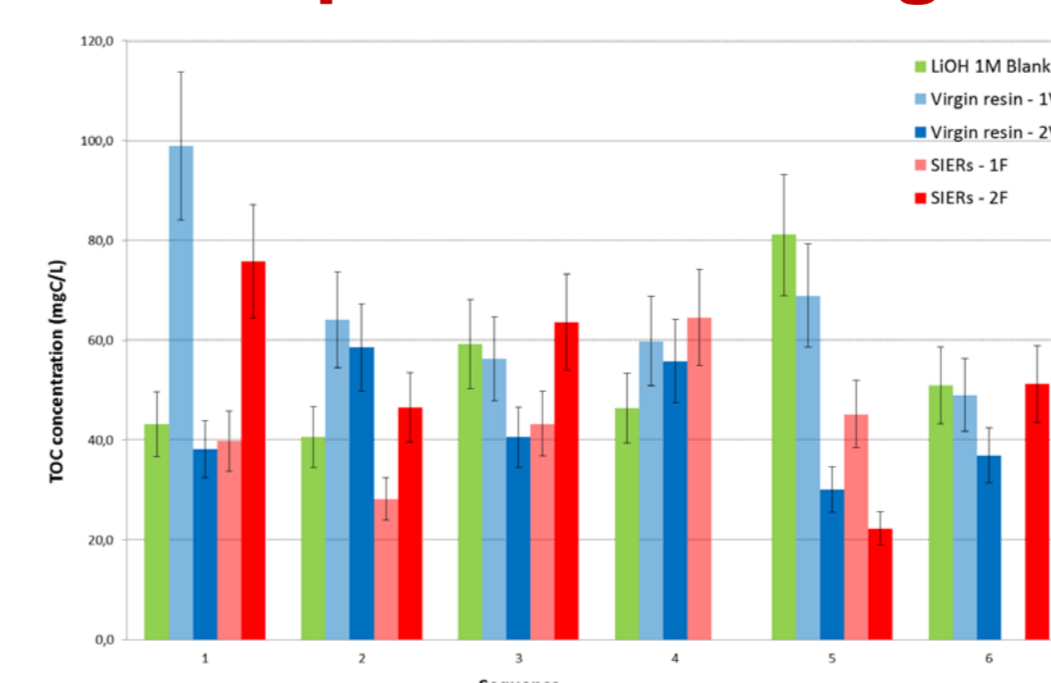
Molecules with higher molecular mass by ESI-MS



Derivatization reaction performed to improve volatile organic compounds identification, nothing detected on resin desorption

LiOH matrix but no organic compound with higher molecular weight in solution is detected (probably salts hide signal)

Interpretation of organic carbon speciation in resin desorption solutions



- Carbon Organic mass balance is calculated
- ≈ 12 % is identified in LiOH "blank", virgin resins and SIERS solutions.
- Only one organic compound identified in resin desorption solutions at very low concentration ≈ 1 % of Total Organic Carbon (TOC).
- Identified carboxylic acids do not complete the carbon mass balance, even in LiOH solution. So, other molecules are in solution.

Contamination in LiOH makes difficult the determination of organic molecules in resin desorption solutions.

* GC-MS : Gas Chromatography - Mass Spectrometry - ESI-MS : Electrospray - Mass Spectrometry

Conclusion / Future works

Task 4-2 : Aim of the project achieved

Two analytical methodologies were developed for total ¹⁴C and speciation measurement and applied on real samples (Dry/Wet)

Results show

That it is difficult to compare different wet SIERS (H₂O content variability / analytical problems) - ¹⁴C speciation on one sample showing ~75 % of mineral carbon

But question remain about the representativeness of the results

=> Statistical approach needed

Task 4-3 : Aim of the project achieved

Desorption experiments permit to obtain aqueous solutions containing ¹⁴C in organic form for the determination of the hydro soluble organic compounds

Measurements with different techniques were used

Results show

One organic compound representative of resin desorption is observed but doesn't complete the total carbon organic mass balance ≈ 1 % of TOC identified