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CH4 LIVESTOCK EMISSION
PRELIMINARY RESULTS

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CH_4 Livestock Emission Project

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The *CH_4 Livestock Emission* project (CH4rLiE) aims to develop a prototype to capture methane gas, produced in cattle environment, exploiting techniques and instruments developed at CERN and used for most gaseous detectors.

Cows produce up to 500 L per day of methane, a greenhouse gas ($GWP_{100} = 28$)

Gaseous Detectors use gas mixture containing polluting components (SF_6 , CF_4 , C_4H_{10}, ecc) that must be captured

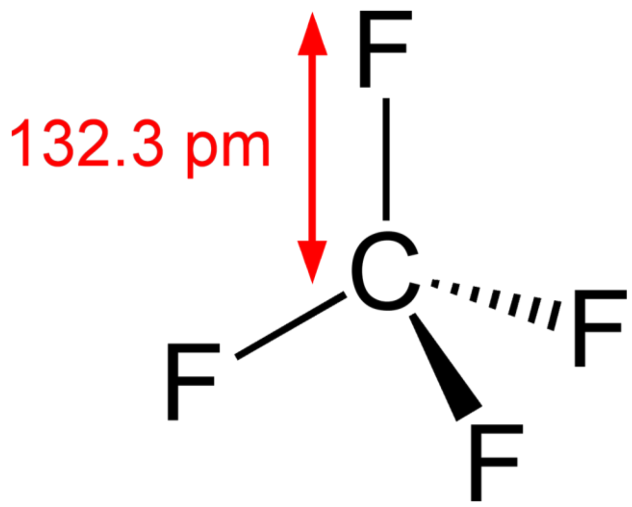
Captured methane could also be retrieved and used later for many purposes

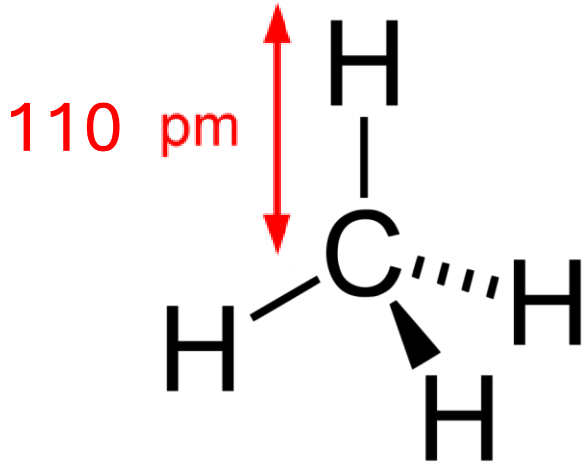
CH4 Livestock Emission Project

Recovery system for gas components are currently used at CERN for different molecules

Zeolites are used to capture CF_4 from gas mixture used in Cathode Strip Chamber (CSC) in CMS

CF_4 and CH_4 have similar structure and dimension → same adsorbent as first trial step





CH4 Livestock Emission Project

Methane capture is achieved through zeolite crystals

Zeolite : crystaline aluminosilicate, porous materials commonly used as adsorbent

Zeolites are used in many fields like horticulture, wastewater treatment or gas adsorption

In our test we used 4 types of zeolites with different pore size:

- Z3 (0.3 nm)
- Z4 (0.4 nm)
- Z5 (0.5 nm)
- Z10 (1.0 nm)

Zeolites act as adsorbent, then regeneration is needed to extract adsorbed chemical and restore the material to the empty state

PRELIMINARY MEASUREMENTS AT CERN

Measurements at CERN to evaluate the adsorption of molecular sieves and the efficiency of regeneration with the vacuum pump

We want to evaluate:

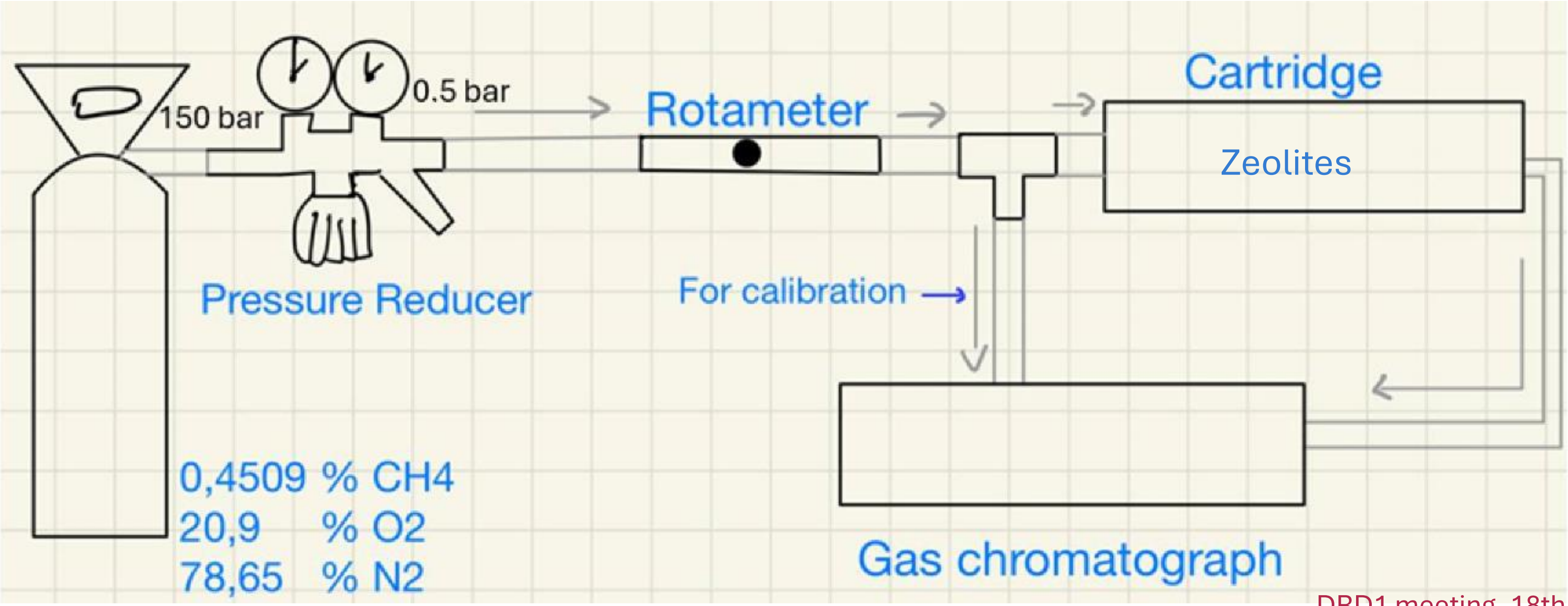
- the performance of zeolites after **high temperature** regeneration (energy consuming)
- performance of zeolites after regeneration with **vacuum pump**
- **optimal time** of regeneration with vacuum pump
- regeneration method with least **energy consumption**

MEASUREMENT SETUP

Measures with 4 different molecular sieves:

- Z3
- Z4
- Z5
- Z10

These are commercial products used in gas recovery systems for gaseous detector applied in high energy particle physics



GAS CHROMATOGRAPH ANALYSIS

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The Gas Chromatograph (GC) separates in time the signal of different components of a gas mixture

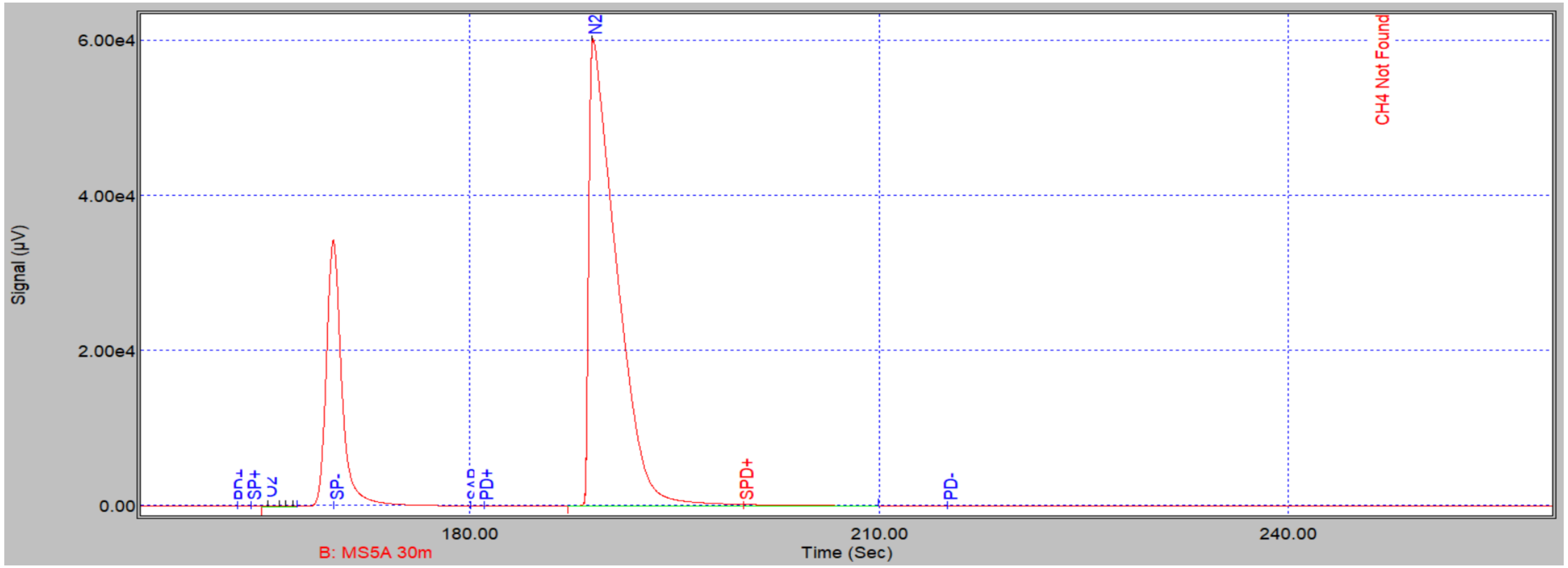
GC contains a long pipe (column) with different separation properties

Different components → Different interactions → Time separation →

→ Thermal Conductivity Detector (TCD) → Signals with different retention time

- Pressure Programming Unit (PPU): separates air from other components, short CH_4 retention time
- Molecular Sieve (MS): recognize singularly O_2 and N_2 and other components, longer CH_4 retention time

MS chromatogram:



GAS CHROMATOGRAPH ANALYSIS

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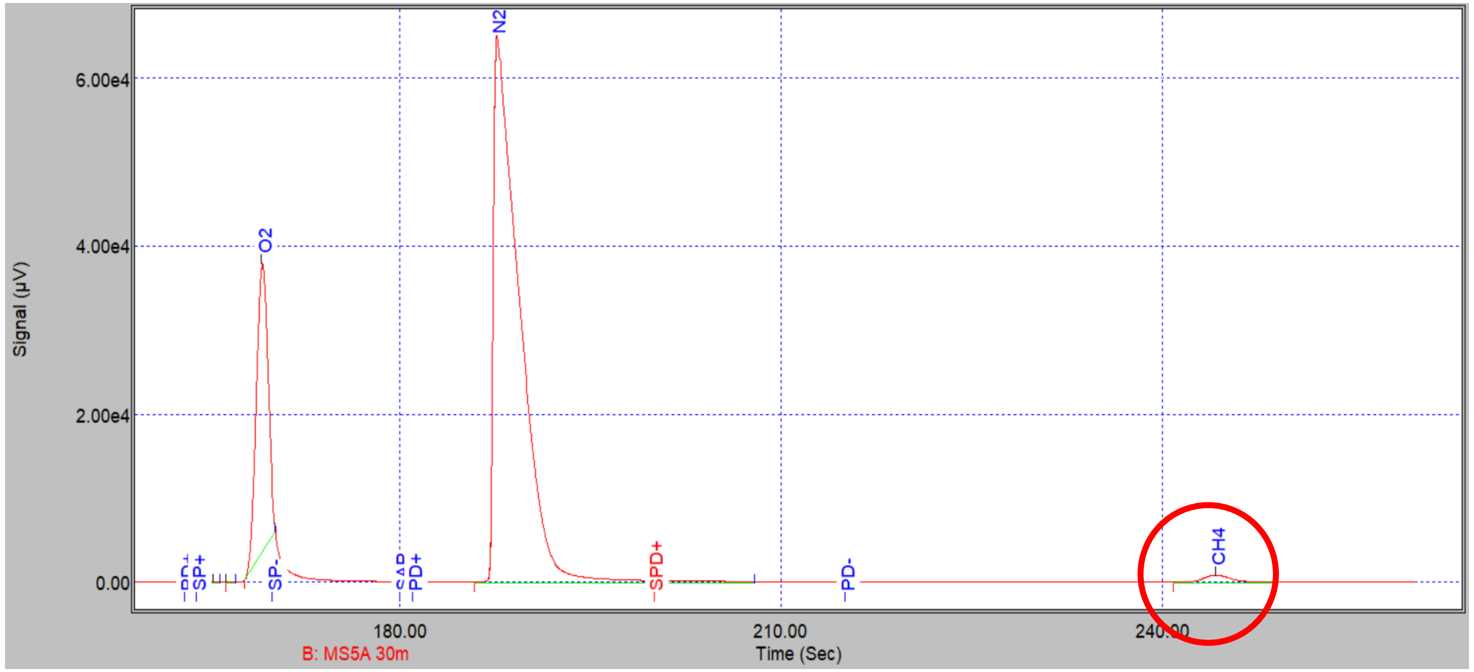
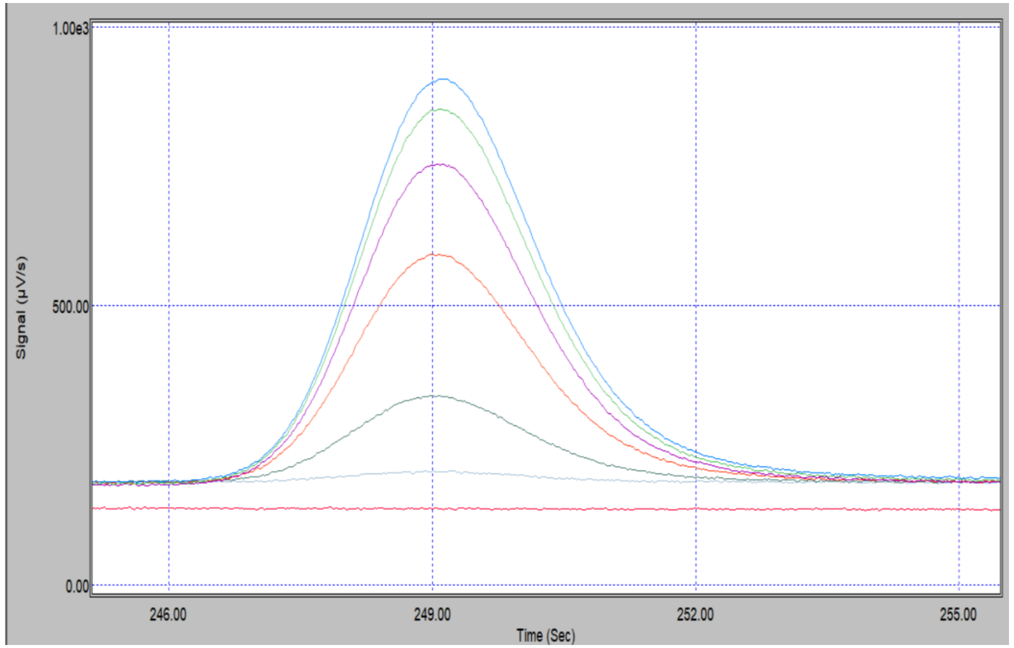
When CH4 is in the gas mixture the chromatogram shows a peak:





Area under peak is proportional to the methane concentration in the mixture

2 main phases:

- When zeolites absorb methane, there is no peak → Total adsorption, no methane escaping the cartridge
- During absorption, zeolites start to fill → the peak grows until plateau saturation

GC CALIBRATION FOR 4509 ppm METHANE

For calibration:

gas mixture with known CH_4 concentration (4509 ppm) into the GC for different value of the bronkhorst pressure (pressure regulator at entrance of GC)

With the average value on 5 measurement of PPU and MS integrals calculate the conversion factor to go from integrals to ppm

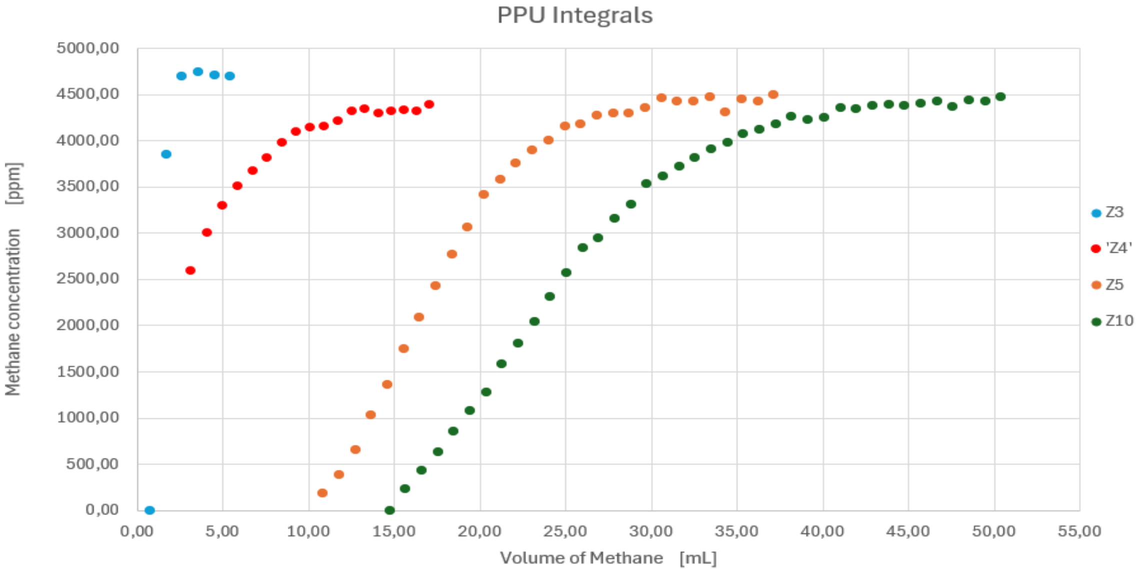
$$PPU\ Conversion\ factor = \frac{4509\ ppm}{Avg\ PPU\ integral}$$

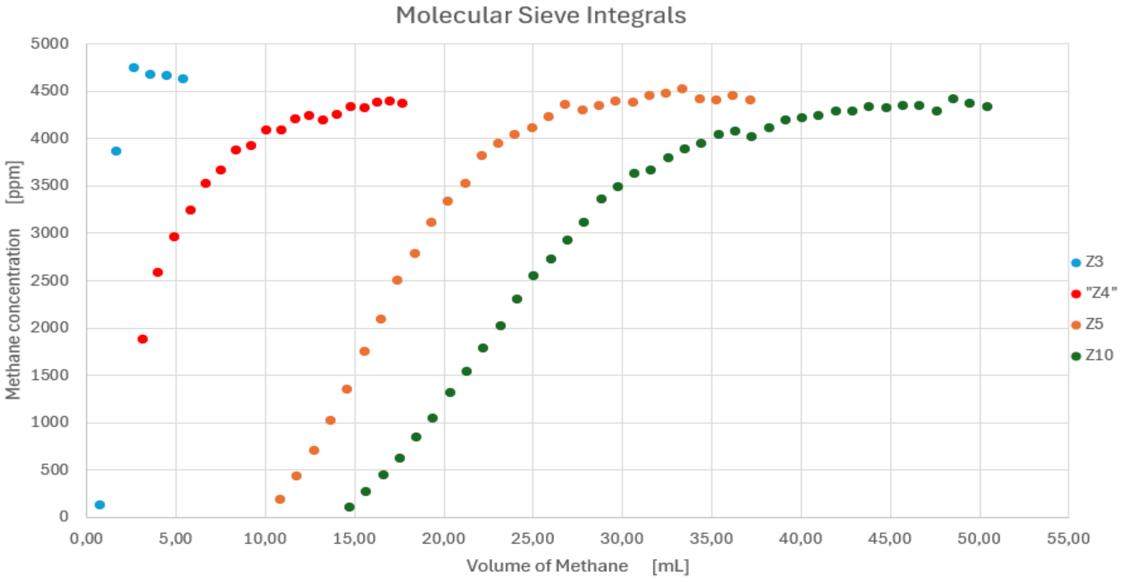
$$MS\ Conversion\ factor = \frac{4509\ ppm}{Avg\ MS\ integral}$$

Changing the bronkhorst pressure, conversion factors are almost the same

FIRST SERIES OF MEASUREMENTS

High temperature regenerated cartridges:

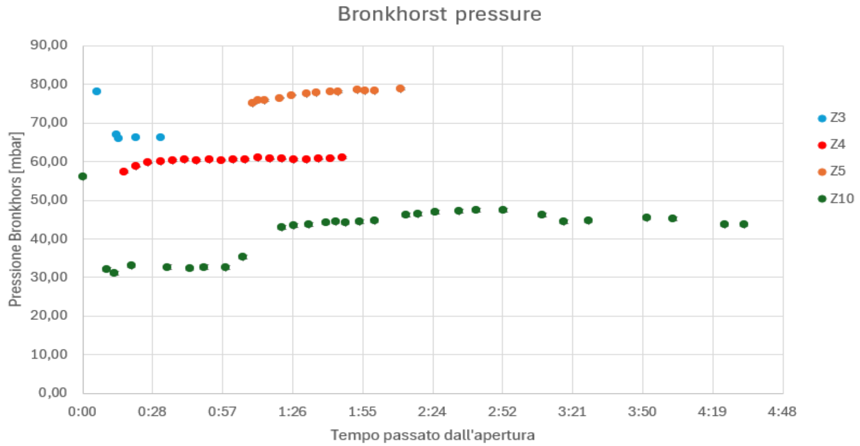




Absorbed methan before peak appearance in the chromatogram:

$Z3 = 0.75\ mL$ $Z4 = 3.13\ mL$

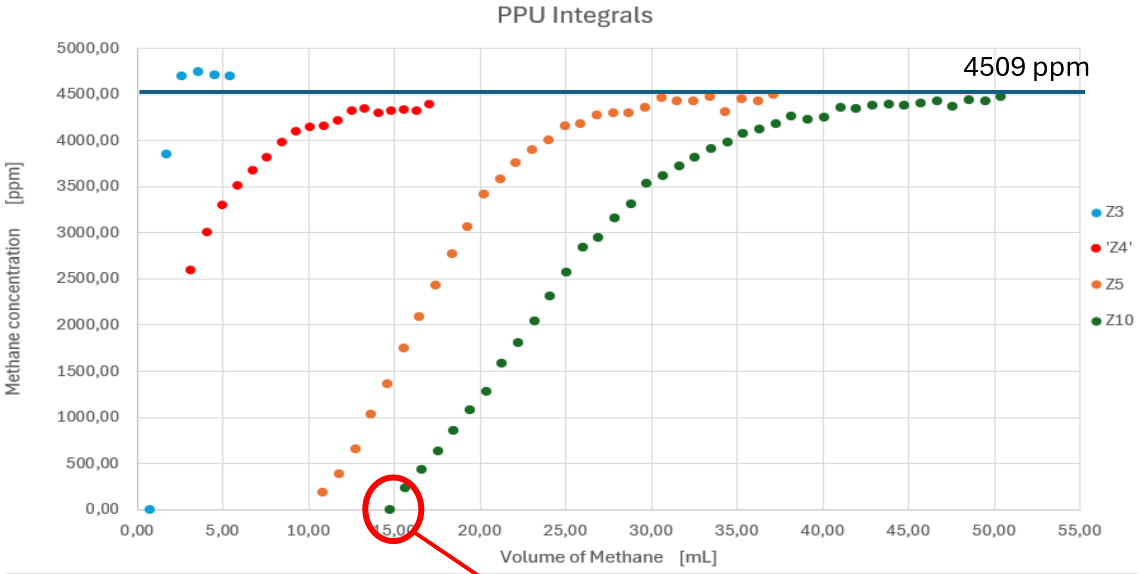
$Z5 = 10.86\ mL$ $Z10 = 14.73\ mL$

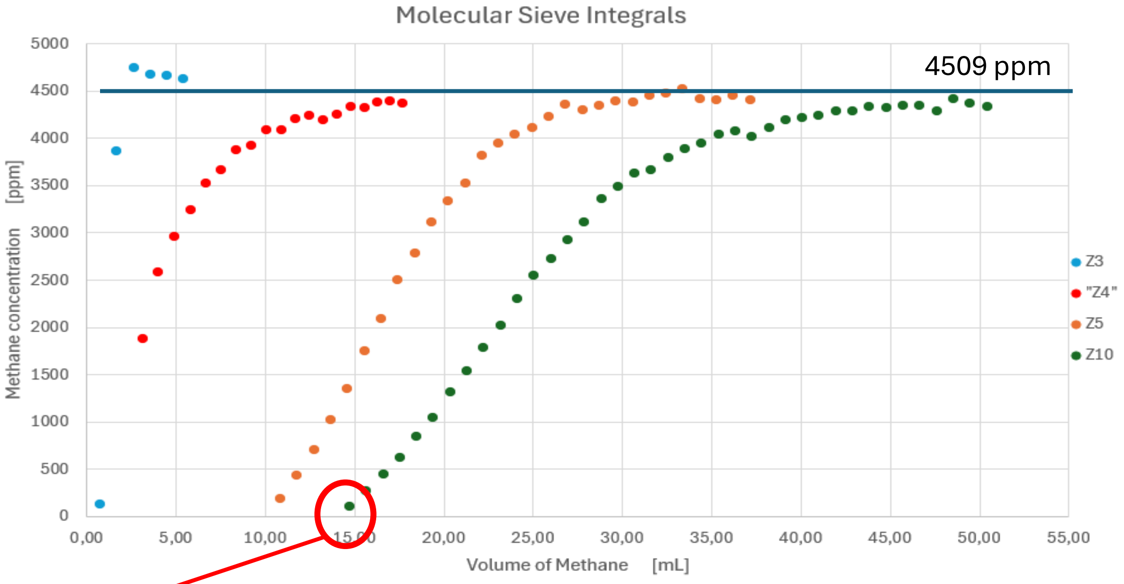


Overall error of 20% due to rotameter measures

FIRST SERIES OF MEASUREMENTS

High temperature regenerated cartridges:

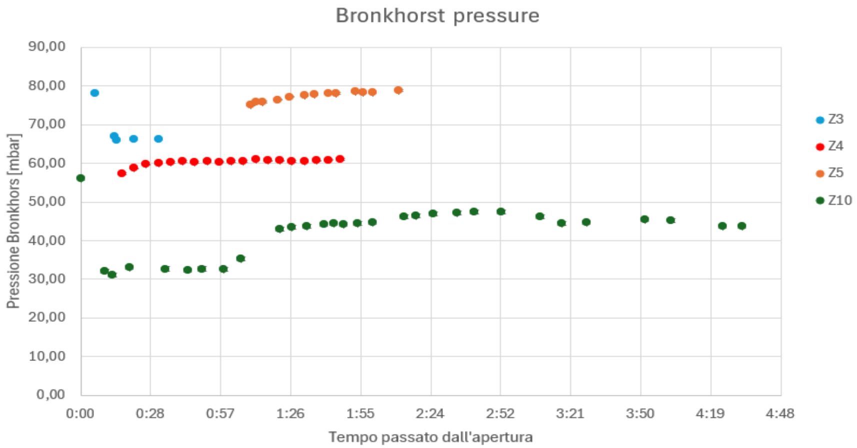




Adsorbed methan before peak appearance in the chromatogram:

$Z3 = 0.75\,mL \qquad Z4 = 3.13\,mL$

$Z5 = 10.86\,mL \qquad Z10 = 14.73\,mL$



Overall error of 20% due to rotameter measures

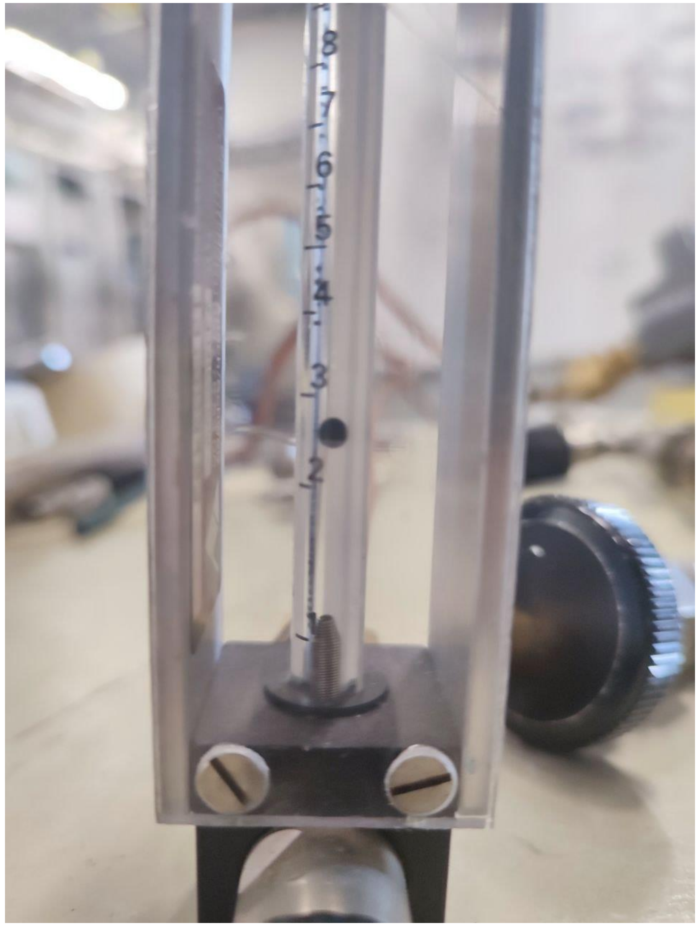
FIRST RESULTS

Performance of Z5, Z10 are much better than Z3, Z4

Z3, Z4 excluded from further measurements

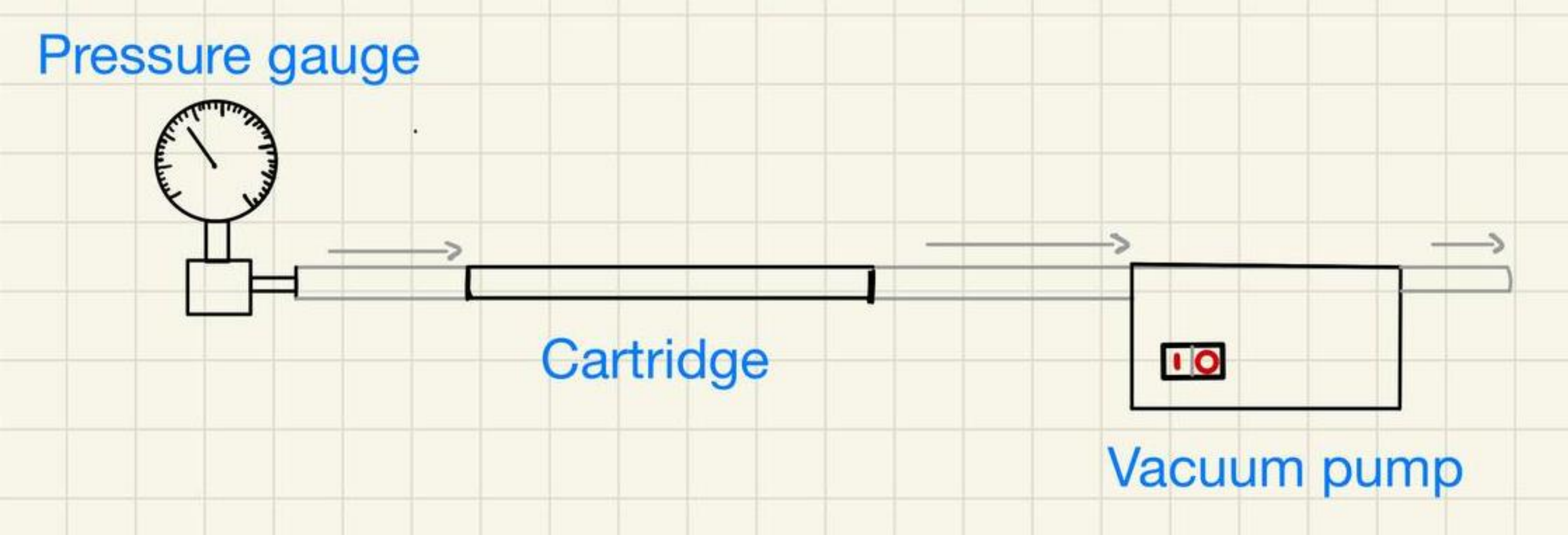
Overall error around 20% on flowed Methane due to rotameter measures.

0.5 L/h error on a 2.5 L/h measure



VACUUM PUMP REGENERATION

SETUP:



The purpose is to evaluate the regeneration power and the repeatability of regeneration with vacuum pump

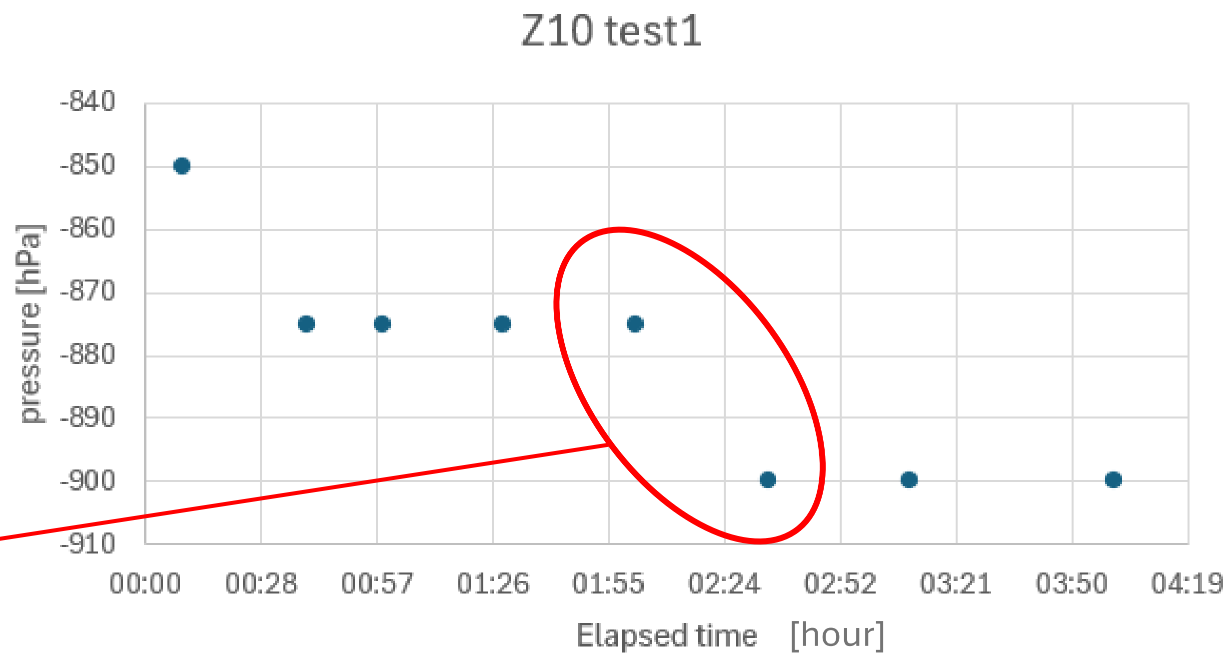
VACUUM PUMP REGENERATION

Vacuum pump regeneration can bring to less energy consumption and shorter regeneration time with respect to high temperature regeneration

After the activation of the pump the pressure goes from a *difference* of 0 with respect to the atmosphere pressure to a value between **-970 mbar** and **-960 mbar**

Measurements with 1° pressure gauge:

Low resolution on pressure gauge



This sudden change is due to low resolution
It's not a physical effect

LONG VACUUM REGENERATIONS

FPA = First Peak Appearance of CH_4 in the chromatogram

	Cartridge	Regeneration time	Methane before FPA
*	Z5	19 h	14.6 mL
	Z10	17 h	11 mL
	Z5	4 h	13 mL
→	Z10	4 h	8.4 mL
	Z5	3 h	10 mL
	Z10	3 h	8 mL
→	Z5	2h	11 mL

*measurements corrupted by interruptions during the flow

→ Last Z10 analysis before valve replacement

→ Last Z5 analysis before valve replacement

VALVE REPLACEMENT

10/05: Replacement of one valve for both Z5 and Z10 for connection problems

Z5 : valve replaced between the 2 hours vacuum regeneration and the first 40 minutes vacuum regeneration

Z10 : valve replaced between the 4 hours vacuum regeneration and the 3 hours vacuum regeneration

During the replacement (few seconds) humidity could be adsorbed by the zeolites and change the adsorption power

Valve

LONG VACUUM REGENERATION

$$long\ vacuum\ regeneration\ ratio = \frac{\begin{matrix}\boldsymbol{average}\ volume\ \ of\ CH_4\ before\ first\ peak \\ appearance\ after\ long\ vacuum\ regeneration\ \boldsymbol{on\ all\ runs}\end{matrix}}{\begin{matrix}volume\ of CH_4\ before\ first\ peak\ appearance \\ after\ \ high\ temperature\ regeneration\end{matrix}}$$

$$Z5\ long\ vacuum\ regeneration\ ratio = \frac{12.5\ mL}{10.86\ mL} \approx 112\ \%$$

$$Z10\ long\ vacuum\ regeneration\ ratio = \frac{9.1\ mL}{14.73\ mL} \approx 64\ \%$$

Comments:

- Z5 : seems to have the same performance, but the value of methane may be overestimated because of uncertainty on flux (*rotameter slightly inclined → higher flux*)

- Z10 : is not completely regenerated, it adsorbs less than what it did in previous measurements

SHORT VACUUM REGENERATION

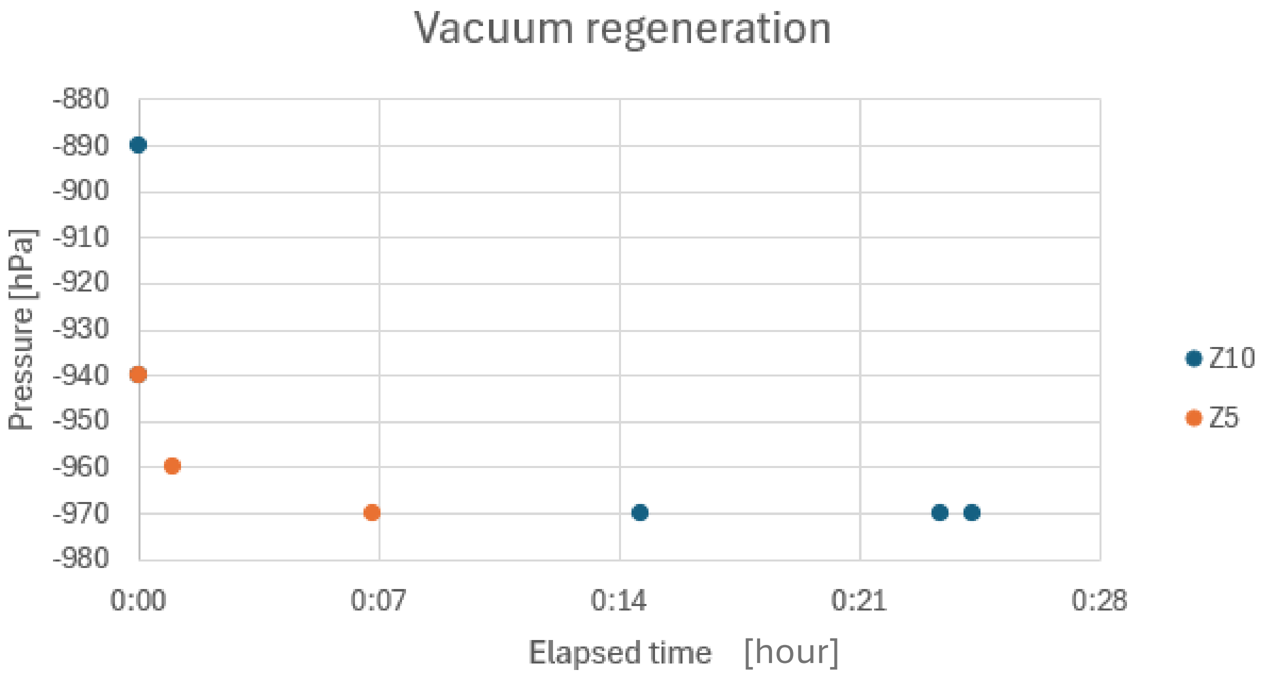
Next approach: stopping regeneration when pressure in the cartridge gets to the minimum value

Minimum value is measured with no cartridge in the setup.

Target value for pressure is between **-970 mbar** and **-960 mbar**

This target value is reached pretty soon for both cartridges.

It also depends on the presence of leaks



Z5 SHORT VACUUM REGENERATIONS

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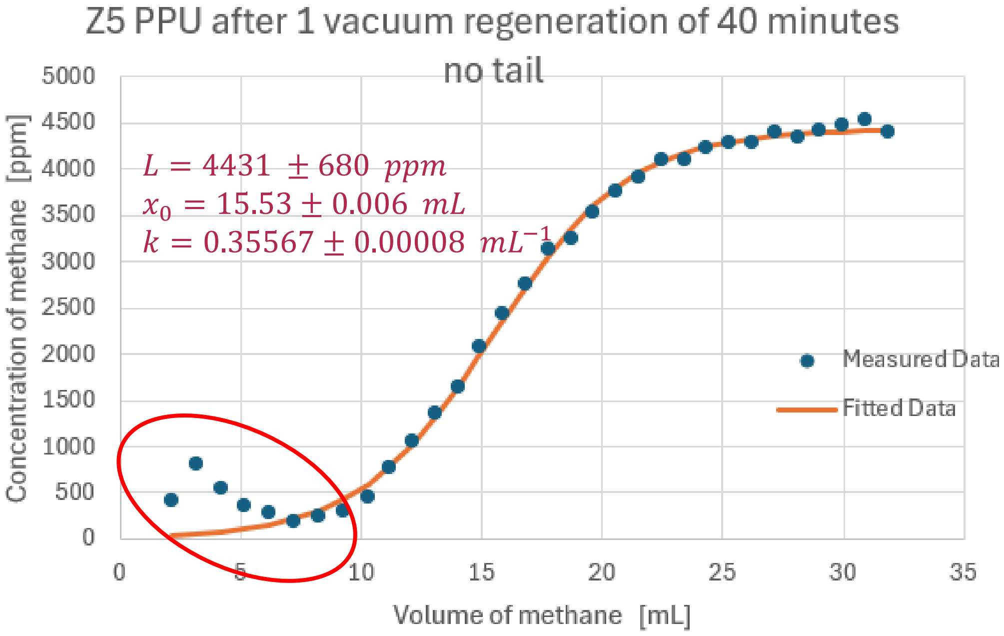
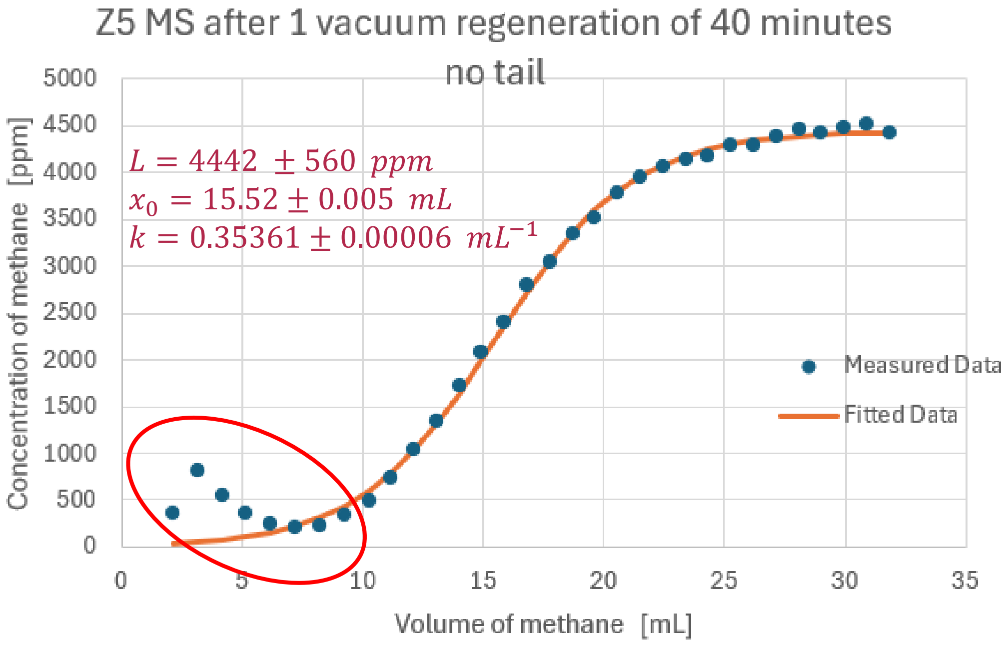
Z5 reaches the target value of pressure in 40 minutes, then it gets filled with the gas mixture

After 1° regeneration:





Fit function: $$\boldsymbol{sigmoid = \frac{L}{1+e^{-(x-x_0)\cdot k}}}$$ fit without using error on data

L = saturation level x_0 = x value to reach $\frac{L}{2}$ k = slope of the curve

Z5 SHORT VACUUM REGENERATIONS

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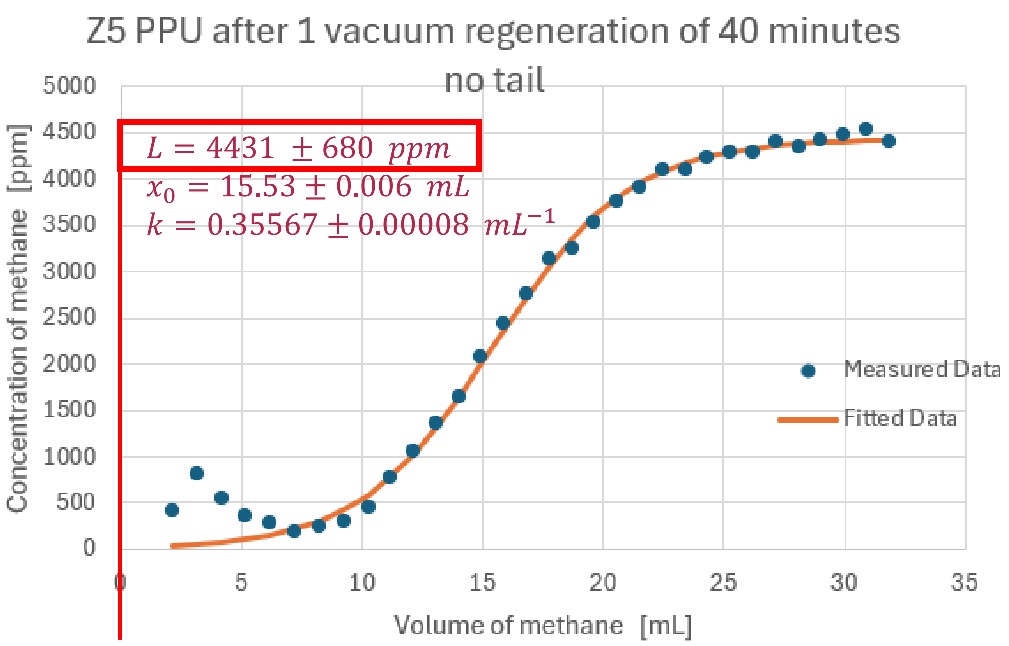
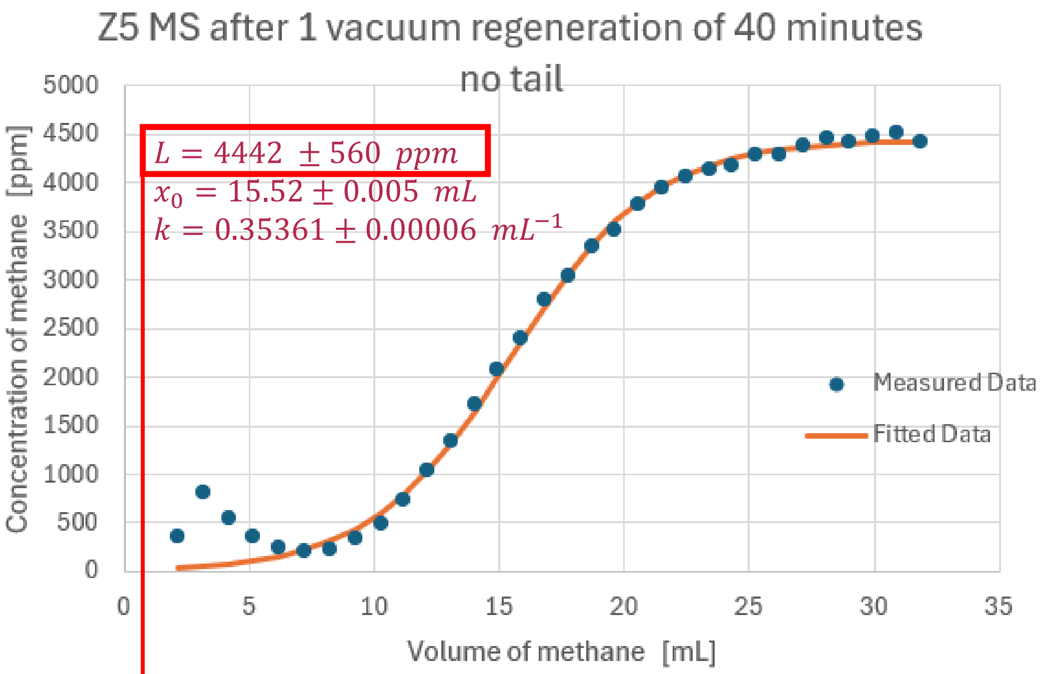
Fit without the tail points





Huge error on L

Besides the anomaly, the minimum corresponds to **7.20 mL** of methane

SUMMARY OF SHORT VACUUM REGENERATIONS

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	Regeneration	FPA / minimum
Z5	1 (40 min)	7.20 mL
	2 (40 min)	10.01 mL
	3 (40 min)	7.93 mL
	4 (40 min)	9.40 mL
Z10	1 (25 min)	6.74 mL
	2 (1 hour) *	7.40 mL
	3 (40 min)	4.90 mL

* Longer regeneration time due to leak found in the connection between the pressure gauge and the cartridge

SHORT VACUUM REGENERATION

$$short\ vacuum\ regeneration\ ratio = \frac{\begin{array}{c}\mathbf{average}\ volume\ of\ CH_4\ before\ first\ peak \\ appearance\ after\ short\ vacuum\ regeneration\ \mathbf{on\ all\ runs}\end{array}}{\begin{array}{c}volume\ of\ CH_4\ before\ first\ peak\ appearance \\ after\ high\ temperature\ regeneration\end{array}}$$

$$Z5\ short\ vacuum\ regeneration\ ratio = \frac{8.64\ mL}{10.86\ mL} \approx 80\ \%$$

$$Z10\ short\ vacuum\ regeneration\ ratio = \frac{6.35\ mL}{14.73\ mL} \approx 43\ \%$$

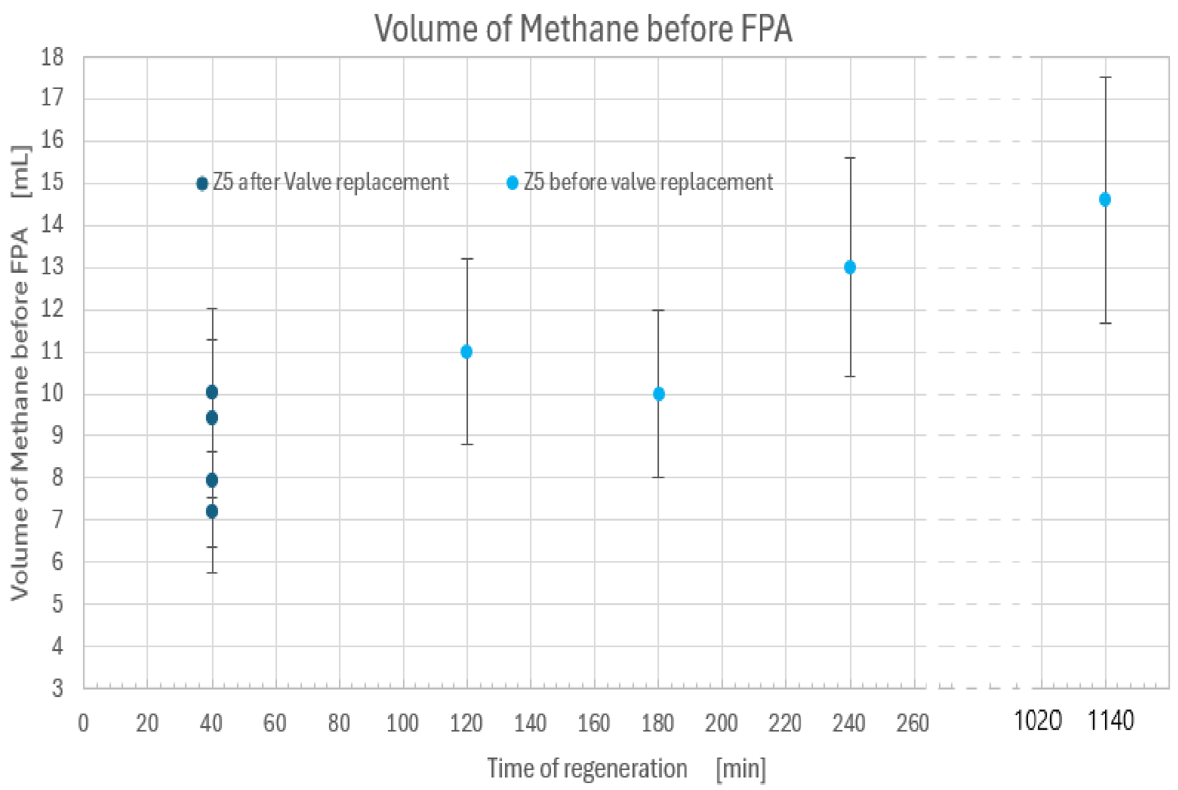
Comments:

- Z5 : the ratio is a little lower, but consistent
- Z10 : irregular behaviour, the regeneration ratio drops

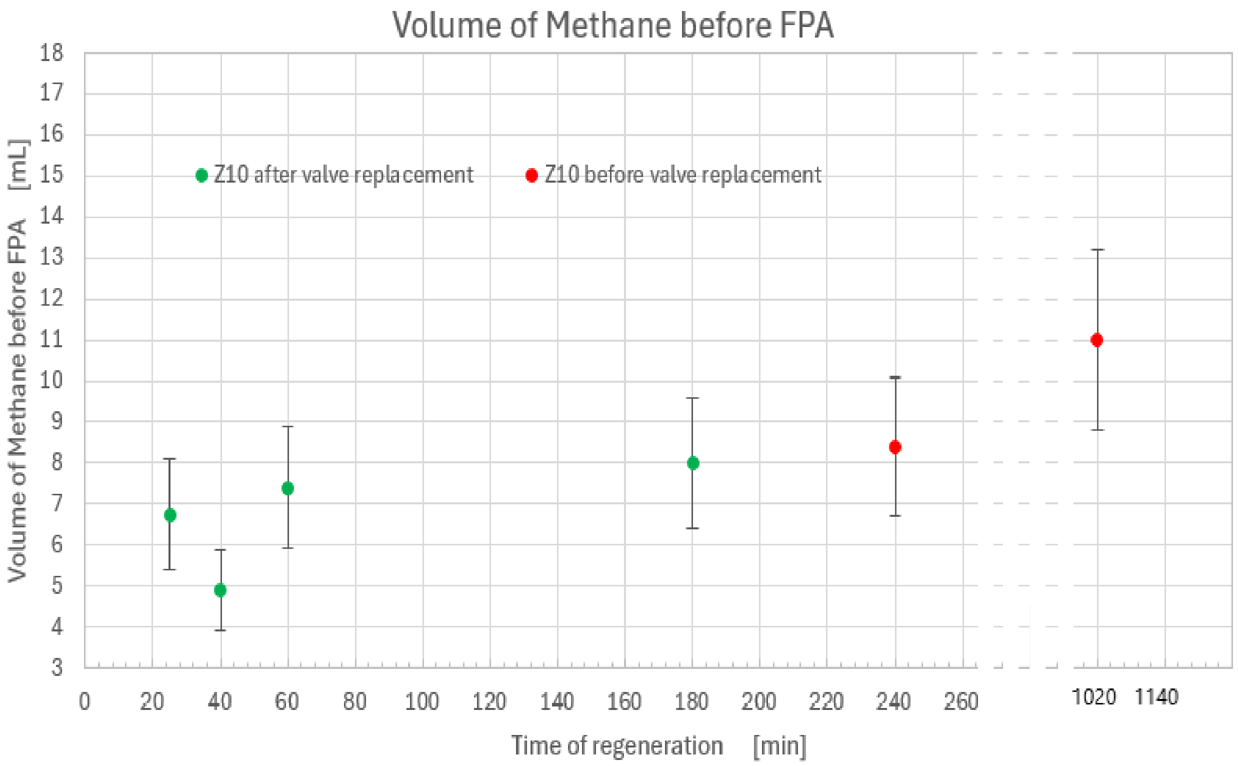
VACUUM REGENERATION SUMMARY

FPA = First Peak Appearance of CH_4 in the chromatogram

Z5 :



Z10 :



20 % error on all measurements of methane volume

VACUUM REGENERATION SUMMARY

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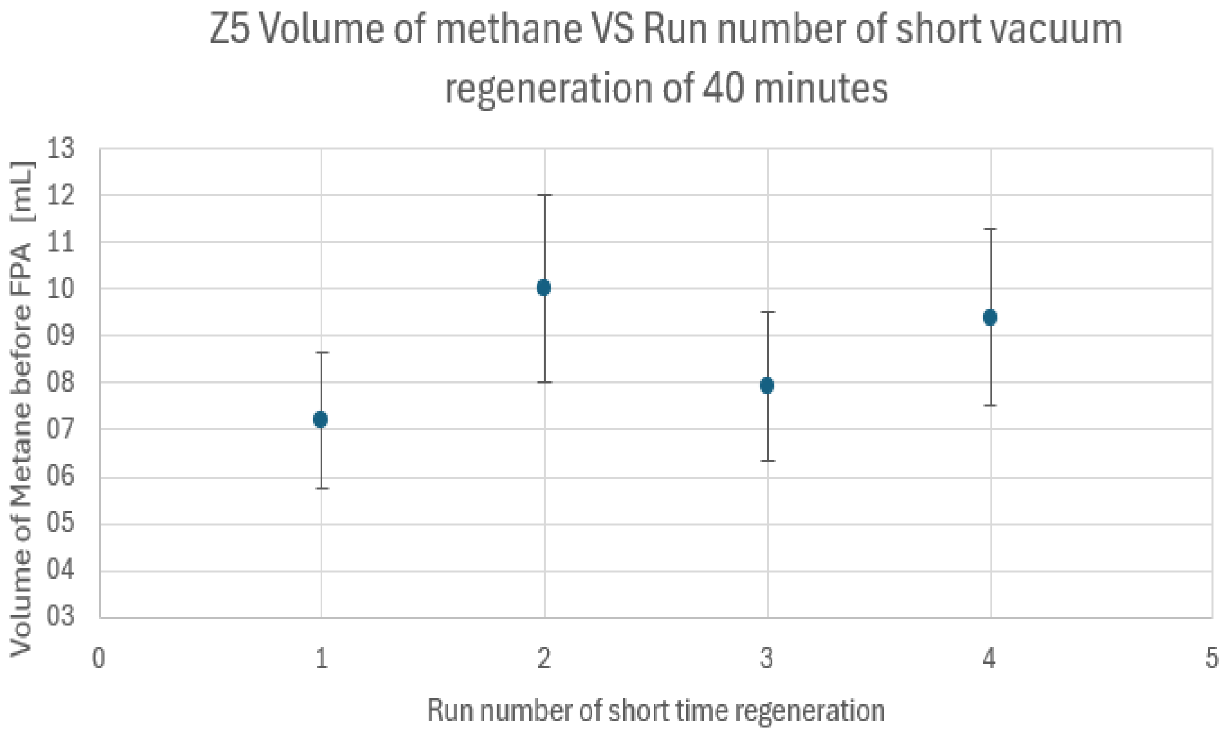
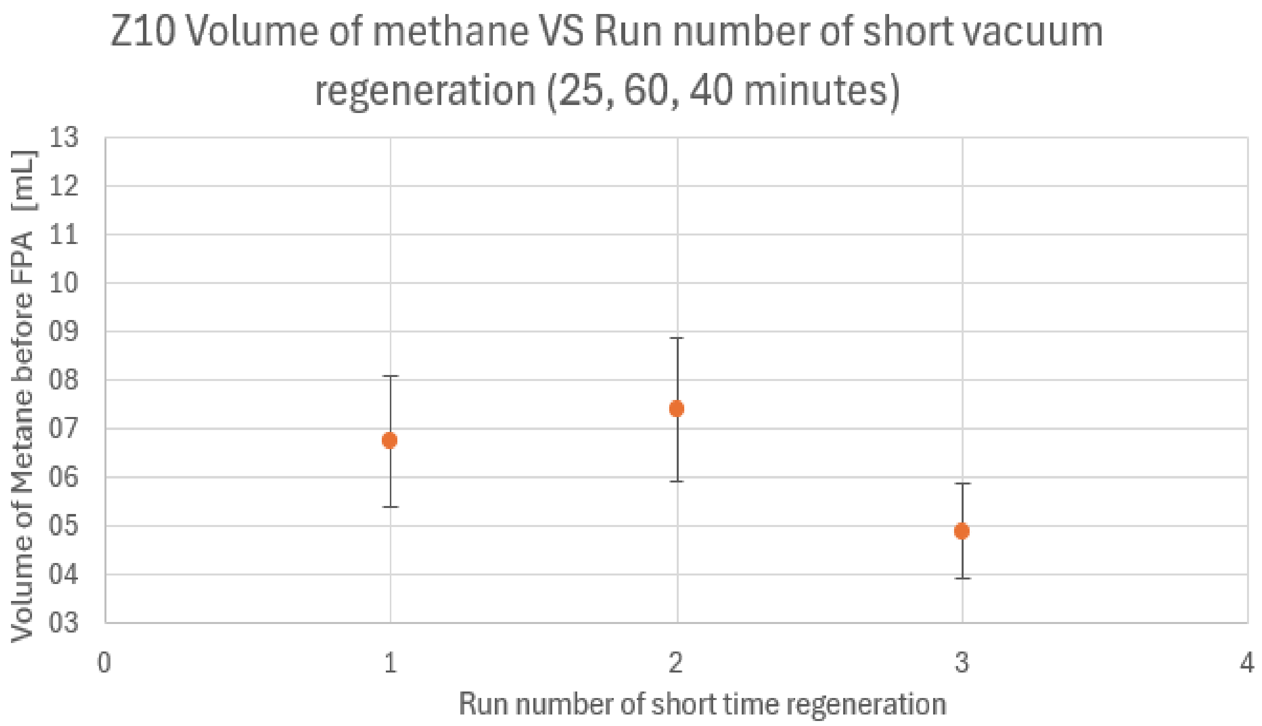
FPA = First Peak Appearance of CH_4 in the chromatogram





20 % error on all measurements of methane

CHEMICAL ANALYSIS

Z5 and Z10 containing methane has been analyzed with chemical techniques by *D. Dondi, D. Vadivel, N. Kameswaran*

Thermogravimetric Analysis (TGA)**:**

- Set heating rate on a sample in controlled atmosphere
- Detect change in sample mass (loss or gain) as a function of temperature
- Mass loss implies desorption

Differential Scanning Calorimetry (DSC)**:**

- Set heating rate on the sample and compare heat flow in the crucible containing the sample with the one from an empty crucible.
- Detects endothermic and exothermic peaks as a function of the temperature

These techniques allow to study heat flow for mass difference in the sample, with respect to Gas desorption from our adsorbent material which gives us details about the extent of gas adsorption in our material

CHEMICAL ANALYSIS

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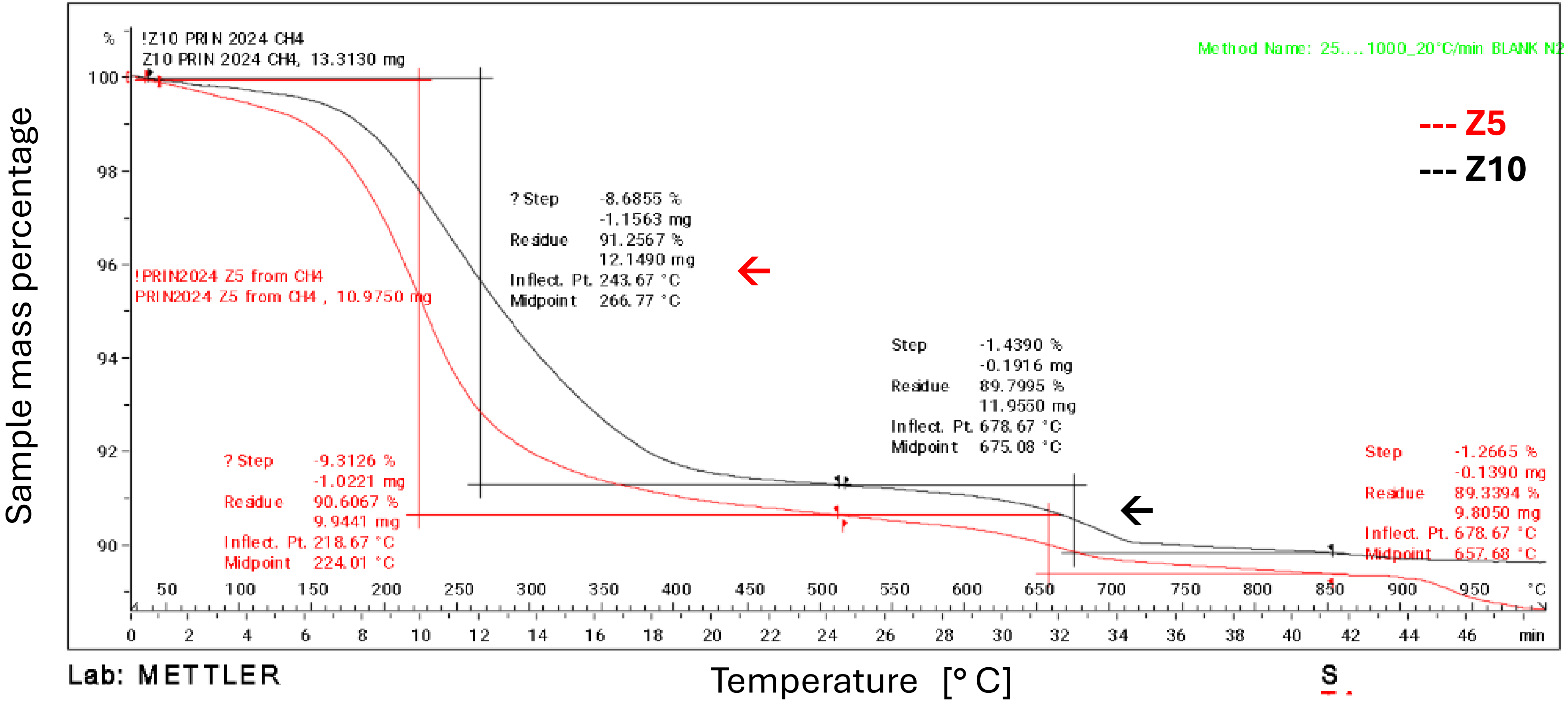
TGA 20 ° C/min:



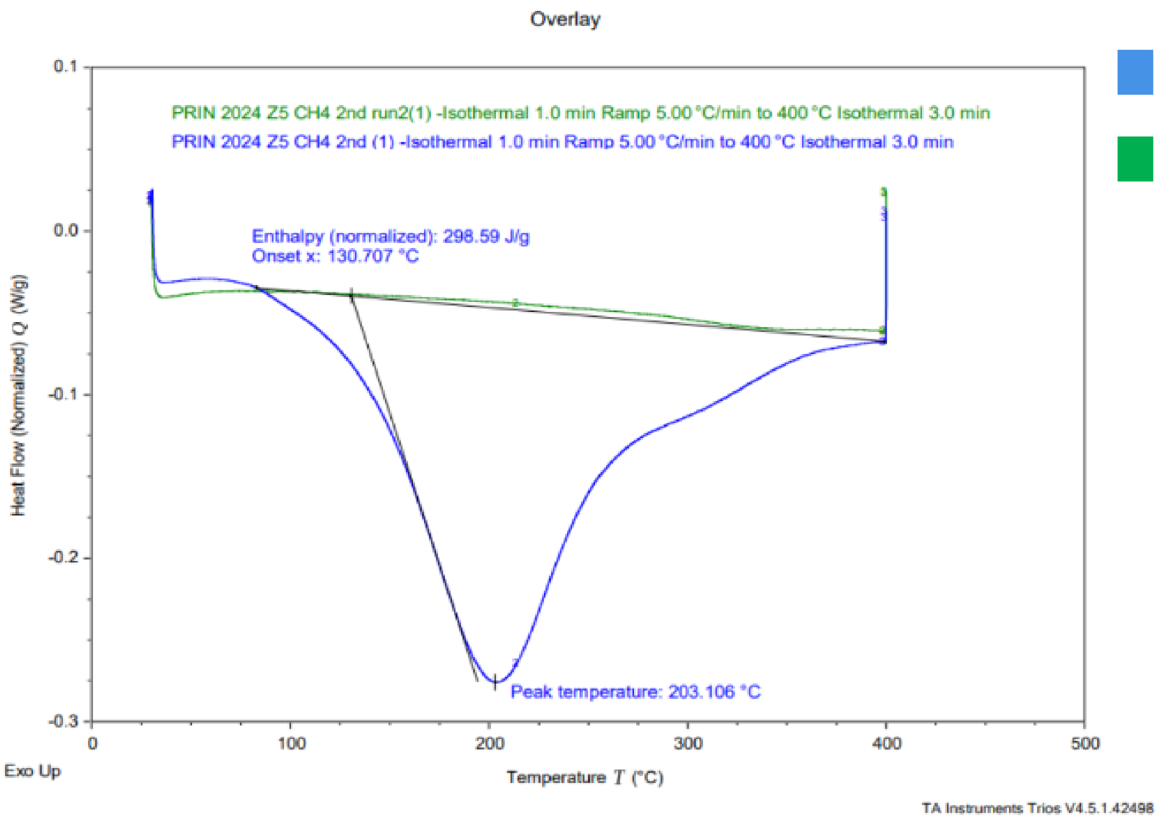
→ First weight loss due to desorption of just water or both water and CH_4

→ Second weight loss may be due to degradation of the zeolite's backbone

CHEMICAL ANALYSIS

DSC:

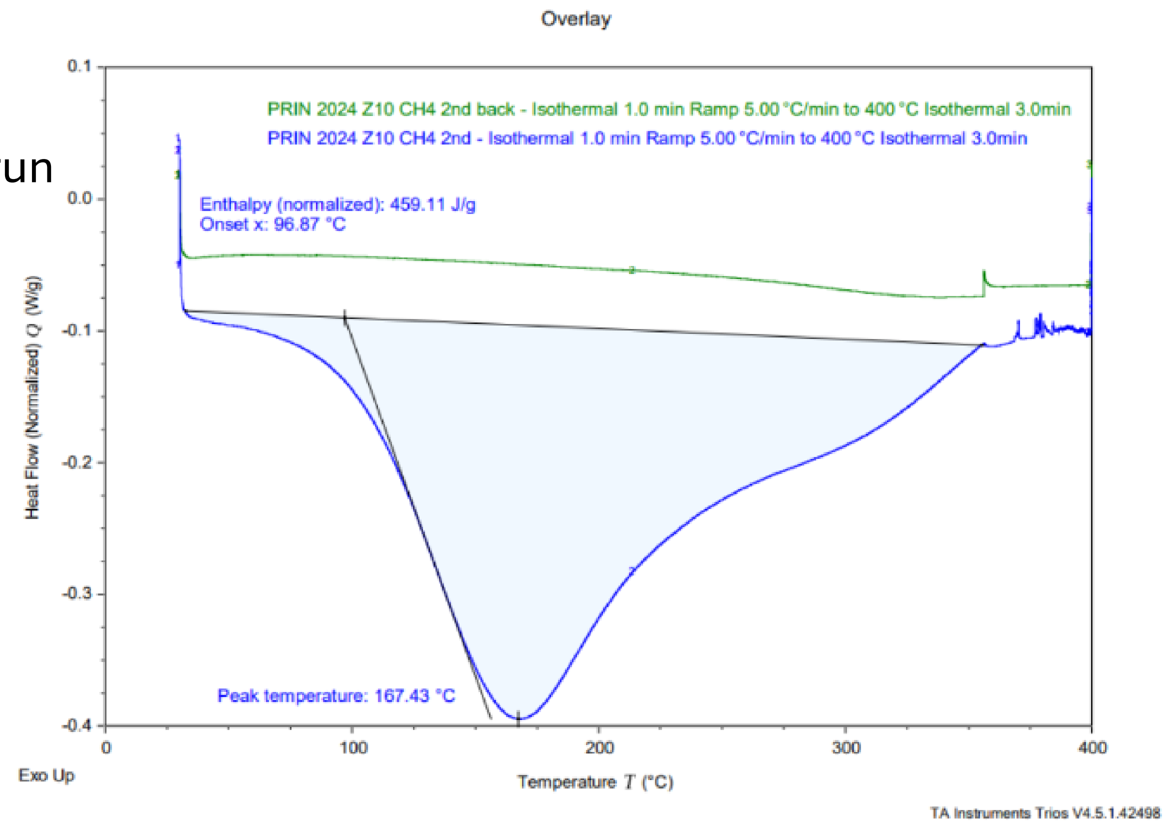
- Z5:



First run

Second run

- Z10:



Second run of the same sample without peak implies that desorption occurred as it is an irreversible process

CHEMICAL ANALYSIS: PRELIMINARY OBSERVATION

Zeolites tend to adsorb water and humidity very quickly

Humidity represents a problem, relevant also in case of few seconds opening

Crystals absorbed water in two possible way:

- Valve replacement could have let humidity spread in the cartridges
- Cartridge opening in the chemistry laboratory

From DSC it follows that desorption may be mainly of water, but more investigations are needed

PRELIMINARY CONCLUSIONS AND FURTHER EXPERIMENTS

- ❖ Z3 and Z4 have lower adsorption power with respect to Z5 and Z10.

- ❖ Z5 has lower adsorption power than Z10 when both are fully regenerated
- ❖ After long regeneration with vacuum pump: (regeneration time > 2 h)
  - Z5 seems fully regenerated
  - Z10 absorption power decreases
- ❖ After short regeneration with vacuum pump: (regeneration time < 1 h)
  - For both Z5 and Z10 adsorption power decreases

More data are needed, these are just preliminary results

PRELIMINARY CONCLUSIONS AND FURTHER EXPERIMENTS

Chemical analysis shows that:

- contact with humidity is a problem even for few seconds actions
- we can't confirm methane absorption in Z5 and Z10

Future developments:

❖ More data are needed to establish the behaviour of the zeolites after the regeneration with vacuum pump

❖ Investigating if TGA and DSC shows effects due to just water or both water and CH_4

❖ Chemistry group is preparing zeolites incorporating Carbon-based material to increase adsorption power. The first candidates are *Urea* and *Melamine*

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GC LIBRATION FOR 4509 ppm METHANE

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Bronkhorst pressure = 100 mbar

	PPU AREA	PPU CONVERSION FACTOR		MS AREA	MS CONVERSION FACTOR
AVERAGE	5080	$8{,}875 \cdot 10^{-5}$	AVERAGE	1907	$2{,}365 \cdot 10^{-4}$
DEV. STD	37	$6{,}6 \cdot 10^{-7}$	DEV. STD	11	$1{,}3 \cdot 10^{-6}$
AVG DEV. STD	16	$2{,}9 \cdot 10^{-7}$	AVG DEV. STD	4,8	$5{,}9 \cdot 10^{-7}$

Bronkhorst pressure = 60 mbar

	PPU AREA	PPU CONVERSION FACTOR		MS AREA	MS CONVERSION FACTOR
AVERAGE	5091	$8{,}858 \cdot 10^{-5}$	AVERAGE	1894	$2{,}380 \cdot 10^{-4}$
DEV. STD	46	$8{,}0 \cdot 10^{-7}$	DEV. STD	15	$1{,}9 \cdot 10^{-6}$
AVG DEV. STD	20	$3{,}6 \cdot 10^{-7}$	AVG DEV. STD	6,7	$8{,}5 \cdot 10^{-7}$

Bronkhorst pressure = 30 mbar

	PPU AREA	PPU CONVERSION FACTOR		MS AREA	MS CONVERSION FACTOR
AVERAGE	5144	$8{,}766 \cdot 10^{-5}$	AVERAGE	1932	$2{,}333 \cdot 10^{-4}$
DEV. STD	48	$8{,}3 \cdot 10^{-7}$	DEV. STD	15	$1{,}9 \cdot 10^{-6}$
AVG DEV. STD	22	$3{,}7 \cdot 10^{-7}$	AVG DEV. STD	6,9	$8{,}4 \cdot 10^{-7}$

SECOND SERIES OF MEASUREMENTS

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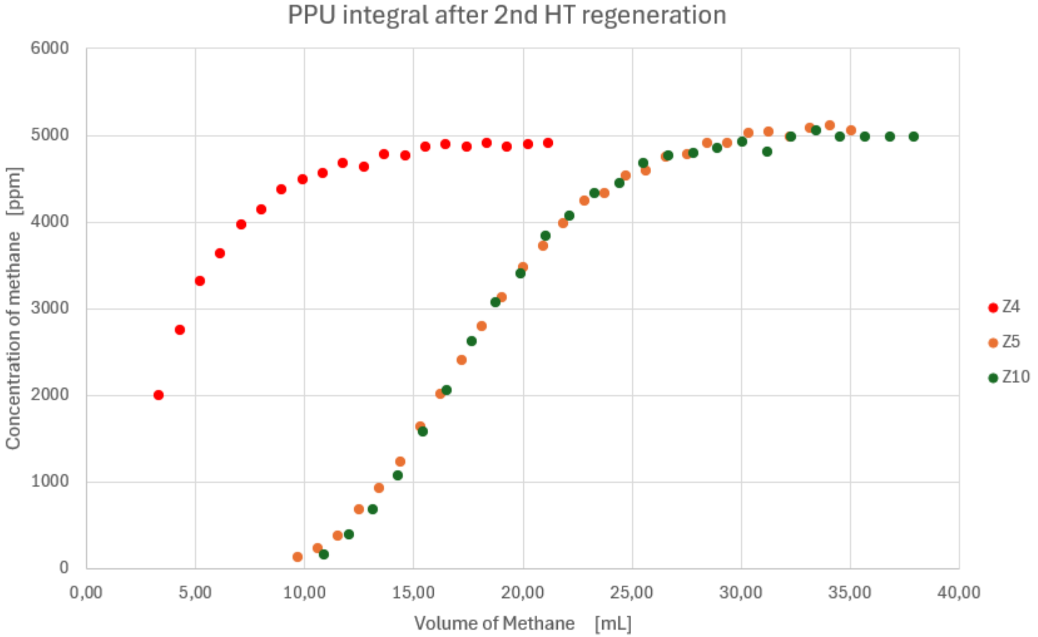
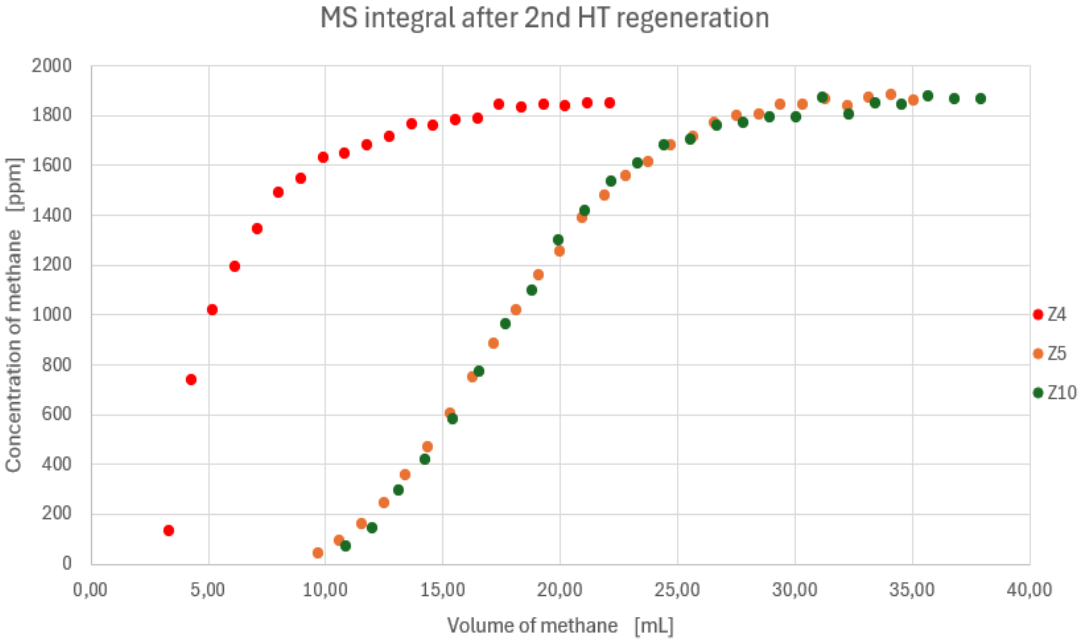
High temperature regenerated cartridges:





Absorbed methan before peak appearance in the chromatogram:

$Z3 = ---$ $\quad Z4 = 3{,}33\,mL$

$Z5 = 9{,}68\,mL$ $\quad Z10 = 10{,}90\,mL$ → Z10 not completely regenerated

Overall error of 20% due to rotameter measures

Z5 SHORT VACUUM REGENERATIONS

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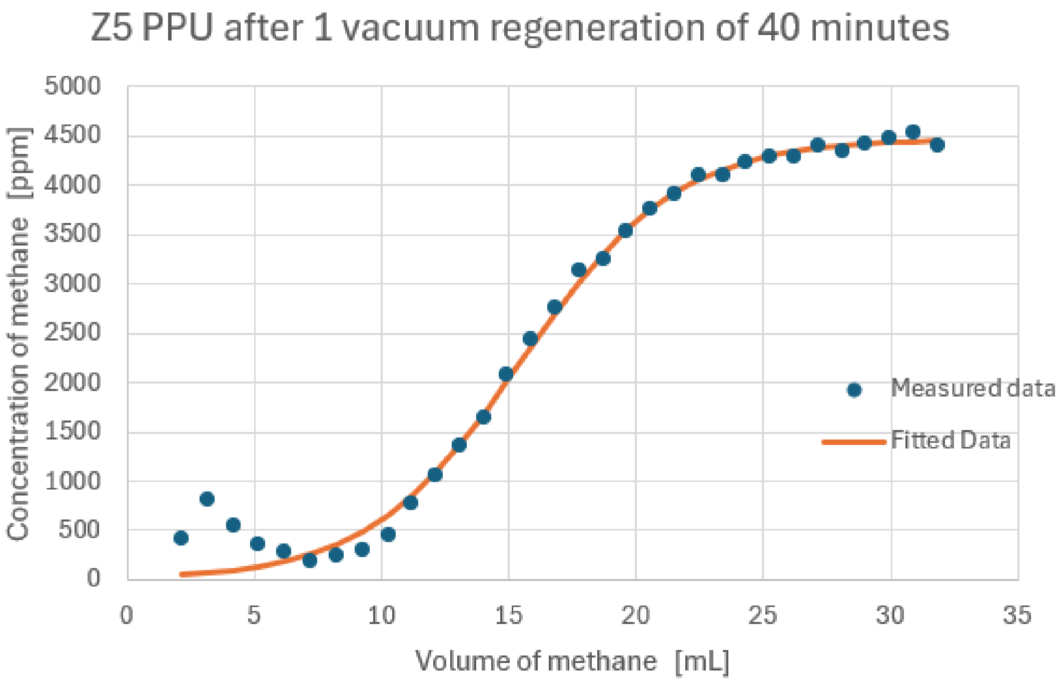
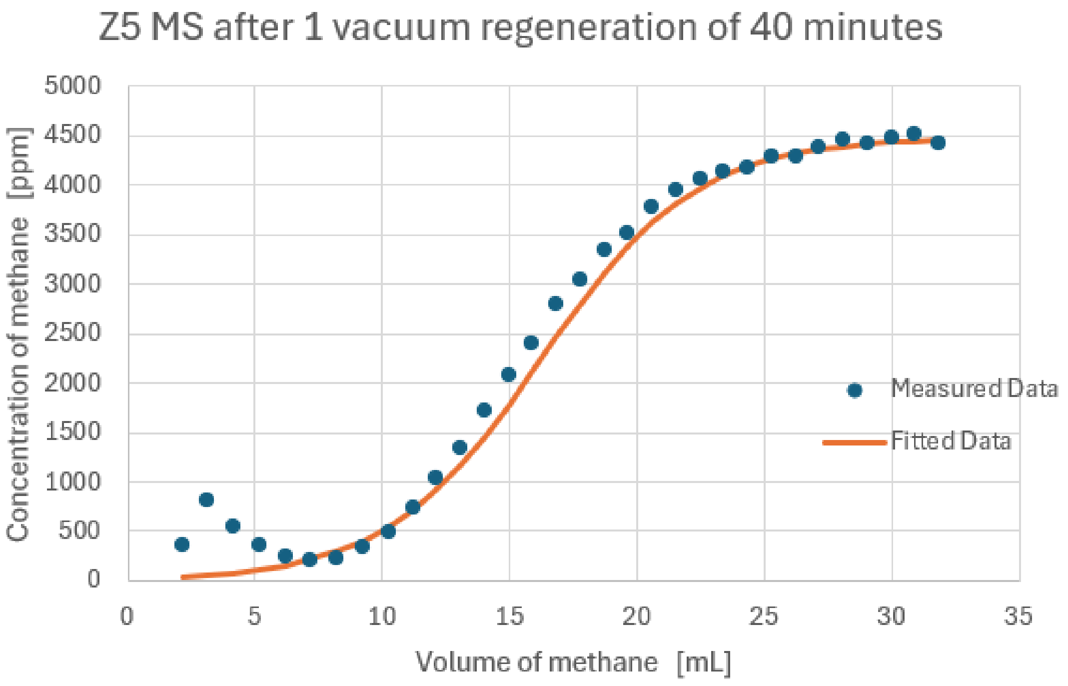
Z5 reaches the target value of pressure in 40 minutes, then it gets filled with the gas mixture

After 1° regeneration:





Fit function:

$$sigmoid = \frac{L}{1+e^{-(x-x_0)\cdot k}}$$

L = saturation level

x_0 = x value to reach $\frac{L}{2}$

k = slope of the curve

COMBINED SHORT VACUUM REGENERATIONS

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	Regeneration	FPA / minimum	$x_{0\ PPU}$ [mL]	$x_{0\ MS}$ [mL]
Z5	1 (40 min)	7.20 mL	$x_0 = 15.53 \pm 0.06$	$x_0 = 16.21 \pm 0.05$
			$x_0 = 15.53 \pm 0.006$	$x_0 = 15.52 \pm 0.005$
	2 (40 min)	10.01 mL	$x_{0\ PPU} = 16.214 \pm 0.014$	$x_{0\ MS} = 16.303 \pm 0.005$
	3 (40 min)	7.93 mL	$x_{0\ PPU} = 18.774 \pm 0.005$	$x_{0\ MS} = 18.759 \pm 0.007$
	4 (40 min)	9.40 mL	$x_{0\ PPU} = 15.82 \pm 0.03$	$x_{0\ MS} = 15.82 \pm 0.04$
			$x_{0\ PPU} = 15.798 \pm 0.006$	$x_{0\ MS} = 15.781 \pm 0.005$
Z10	1 (25 min)	6.74 mL	$x_{0\ PPU} = 16.92 \pm 0.03$	$x_{0\ MS} = 16.605 \pm 0.014$
	2 (1 hour) *	7.40 mL	$x_{0\ PPU} = 14.549 \pm 0.011$	$x_{0\ MS} = 14.456 \pm 0.008$
	3 (40 min)	4.90 mL	$x_{0\ PPU} = 16.017 \pm 0.004$	$x_{0\ MS} = 16.281 \pm 0.023$

* Longer regeneration time due to leak found in the connection between the pressure gauge and the cartridge

VACUUM REGENERATION SUMMARY

FPA = First Peak Appearance of CH_4 in the chromatogram