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CERN

EP-DT
Detector Technologies

ZEOLITES ABSORPTION
MEASUREMENTS AT CERN
30/04 – 13/05

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CH4 Livestock Emission Project

The *CH4 Livestock Emission* project (CH4rLiE) aims to develop a prototype to capture methane gas produced in cattle environment exploiting techniques and instruments developed for gaseous detectors used at CERN.

Absorption is achieved through porous zeolite crystals

4 types of molecular sieves with different pores size:

- Z3 - Z4 - Z5 - Z10

The best molecular sieve will be the key element of the prototype for methane gas capture

MEASUREMENTS AT CERN

Measurements at CERN (30/04 -13/05) to evaluate the absorption of molecular sieves and the efficiency of regeneration with the vacuum pump

We want to evaluate:

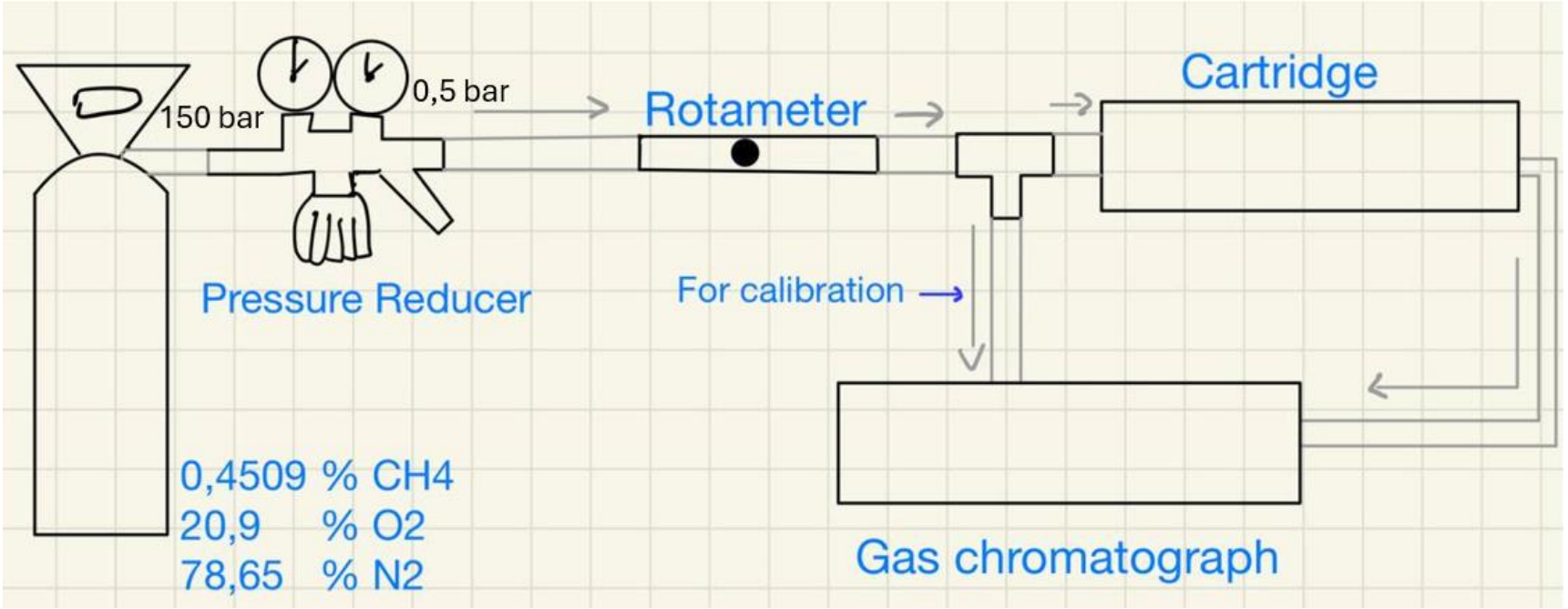
- Performance of zeolites after **high temperature** regeneration
- Performance of zeolites after regeneration with **vacuum pump**
- **Optimal time** of regeneration with vacuum pump

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

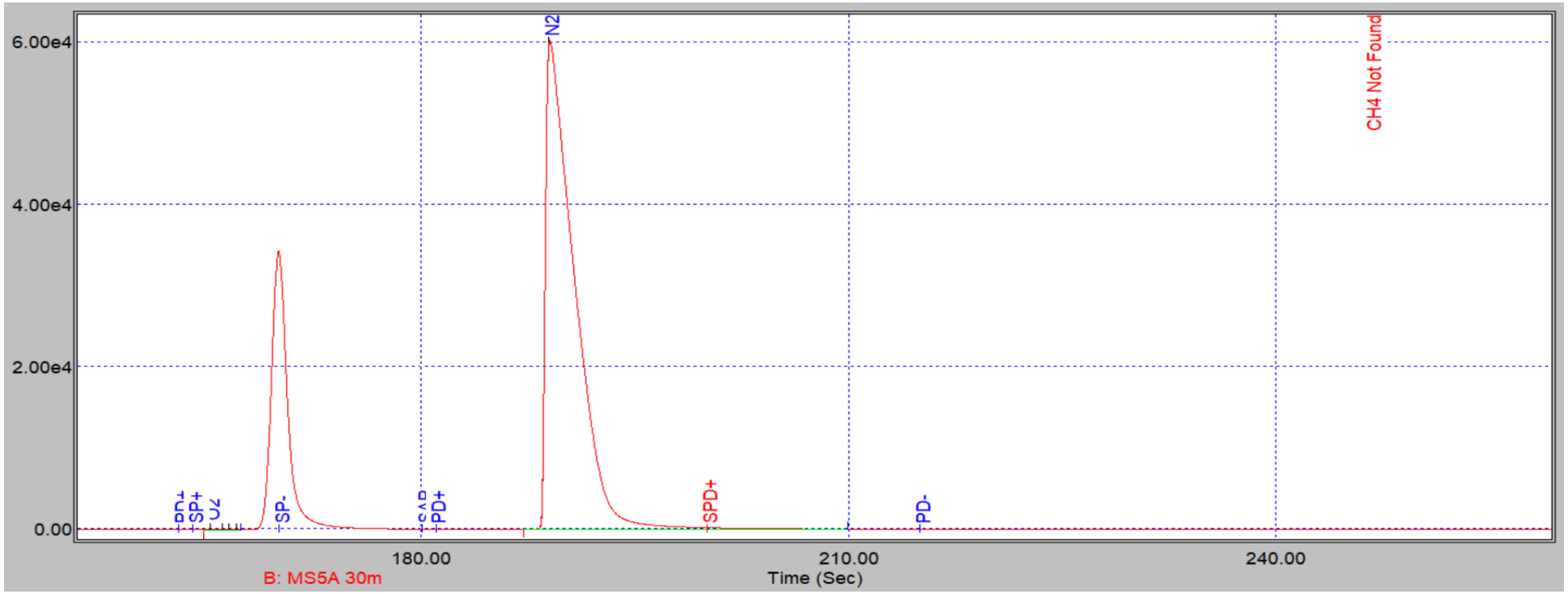


GAS CHROMATOGRAPH ANALYSIS

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

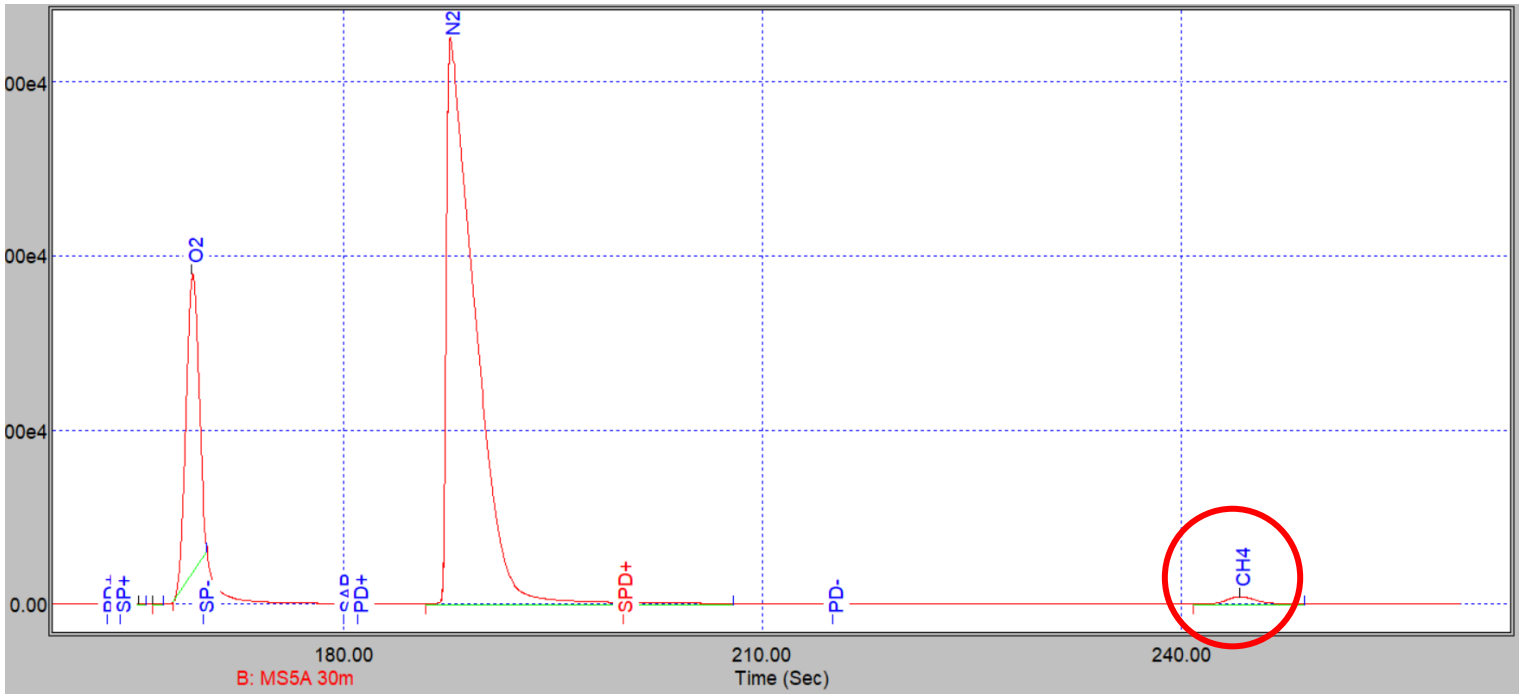
Different components → Different interactions → Different retention time

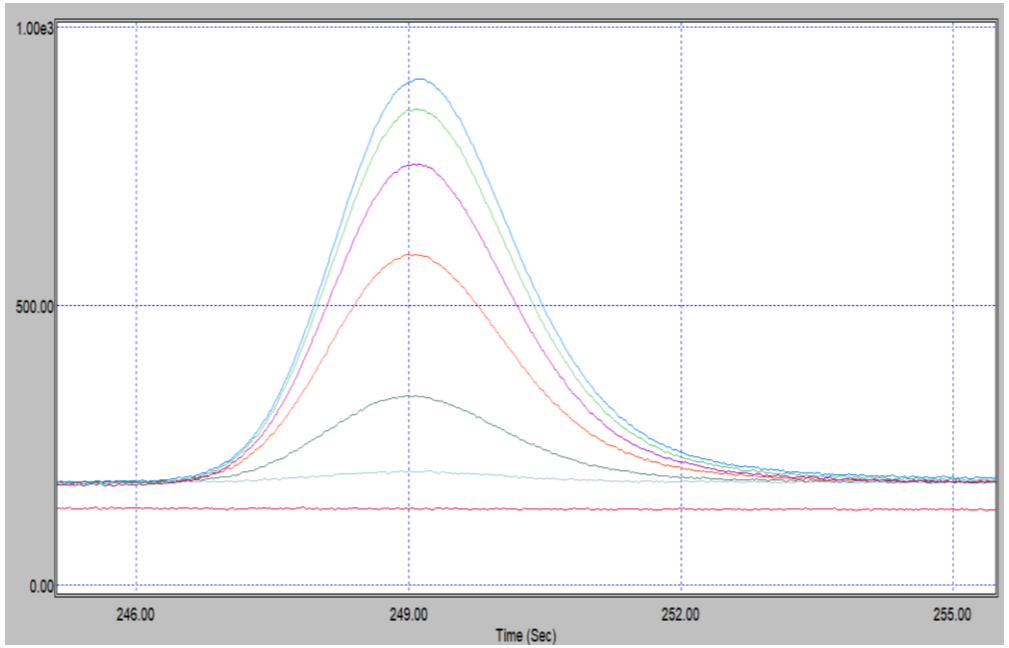
- PPU: separates air from other components
- Molecular Sieve: recognize singularly O2 and N2 and other components, it's more precise



GAS CHROMATOGRAPH ANALYSIS

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





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

When zeolites absorb methane, there is no peak

When absorption starts, the peak grows until saturation

GC CLIBRATION 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	$8{,}4 \cdot 10^{-7}$

FIRST SERIES OF MEASUREMENTS

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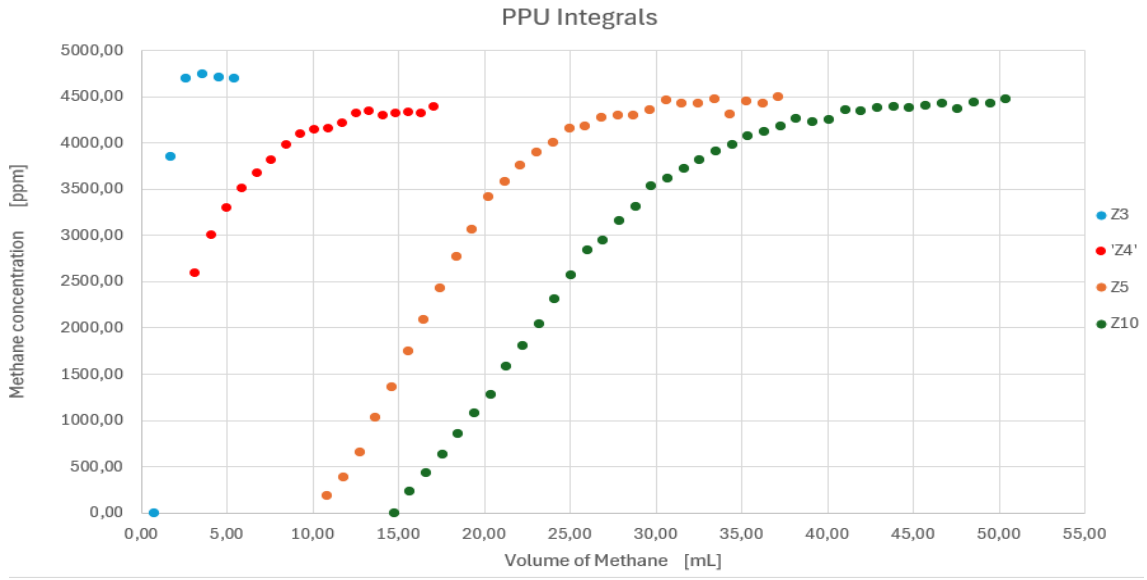
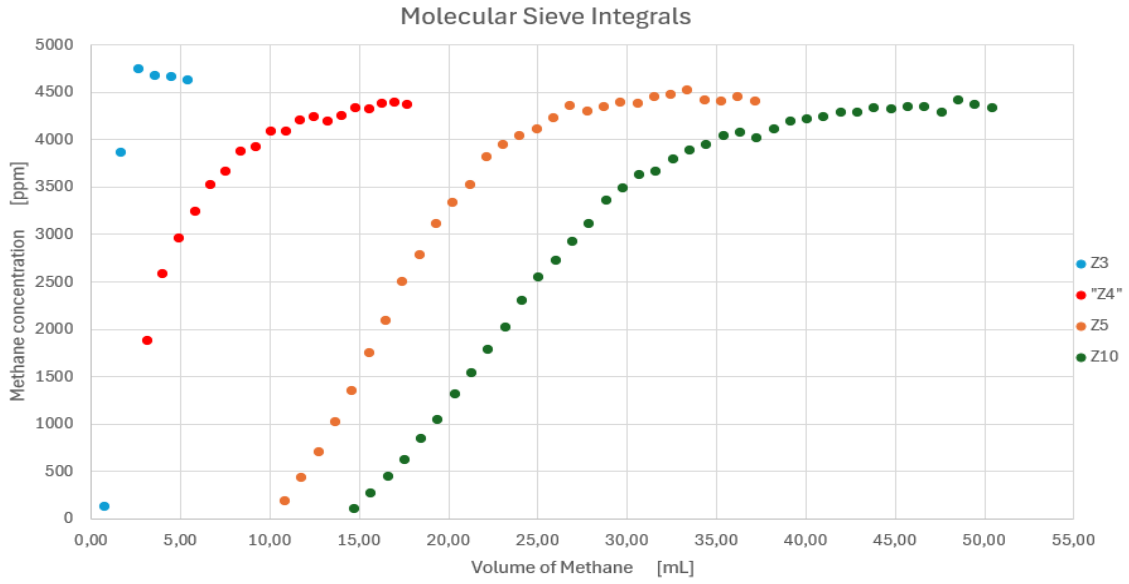
High temperature regenerated cartridges:

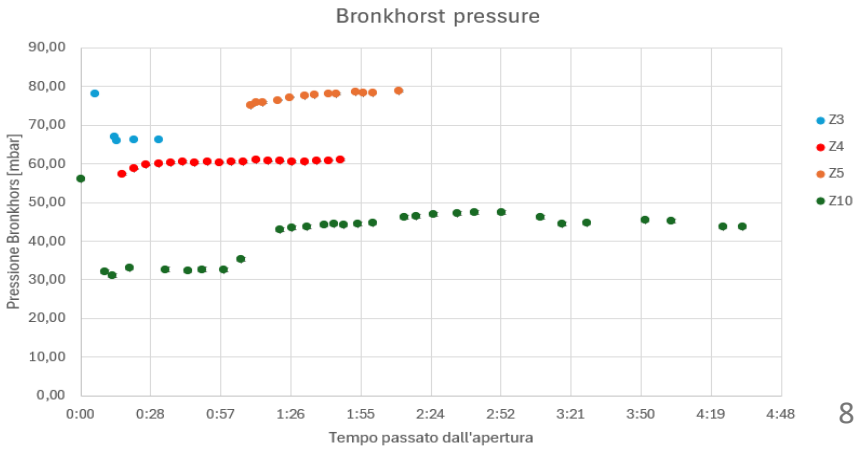




Absorbed methan before peak appearance in the chromatogram:

$Z3 = 0{,}75\ mL$ $Z4 = 3{,}13\ mL$

$Z5 = 10{,}86\ mL$ $Z10 = 14{,}73\ mL$



Overall error of 20% due to rotameter measures

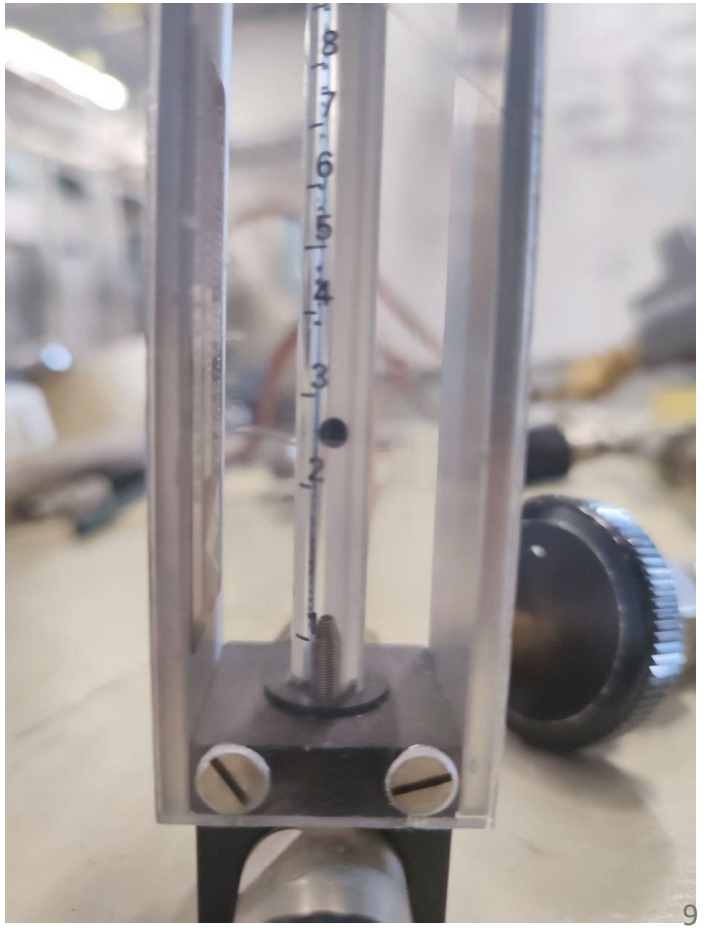
RESULTS OF FIRST WEEK

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

Z3, Z4 excluded from further measurements

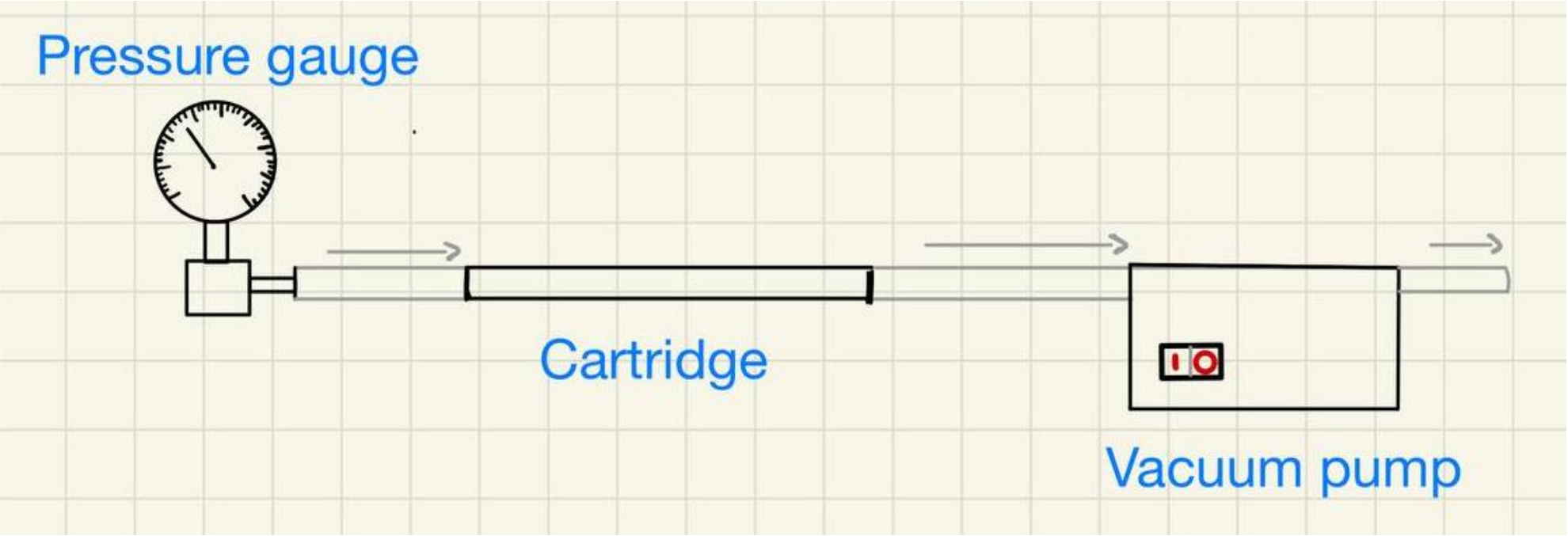
Overall error around 20% due to rotameter measures on flowed Methane.

0,5 L/h error on a 2,5 L/h measure



VACUUM PUMP REGENERATION

SETUP:



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

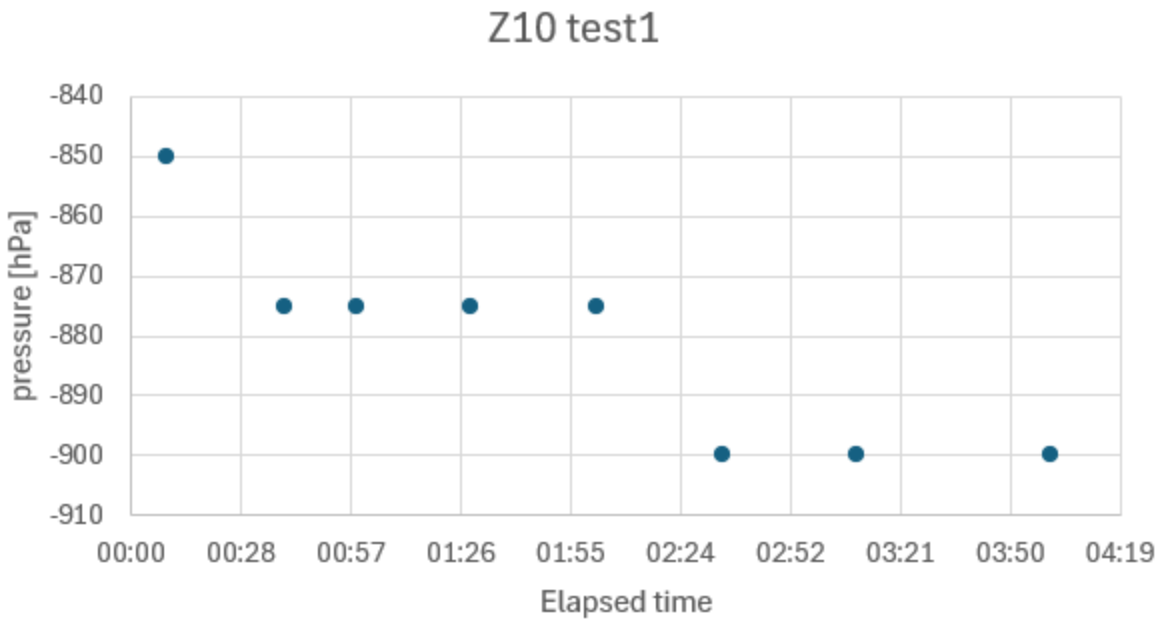
VACUUM PUMP REGENERATION

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**

At the beginning the pressure gauge was not enough sensitive to measure this changes.

Pressure range was (-1, +5)

From 09/05 we had new pressure gauge that measures in the range (-1,1) with a sensitivity of *10 mbar*



Measurements with 1° pressure gauge

LONG VACUUM REGENERATIONS

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FPA = First Peak Appearance of CH4 in the chromatogram

	Cartridge	Regeneration time	Methane before FPA	Time before FPA	Saturation methane	Saturation time	Bronkhorst pressure
*	Z5	19 h	14,6 mL	46 min	36 ÷ 40 mL	2 h 51 min	35 → 44 mbar
	Z10	17 h	11 mL	35 min	35 ÷ 39 mL	2 h 41 min	38 → 49 mbar
	Z5	4 h	13 mL	45 min	36 ÷ 39 mL	2 h 56 min	37 → 48 mbar
→	Z10	4 h	8,4 mL	30 min	30 ÷ 34 mL	2 h 45 min	38 → 49 mbar
	Z5	3 h	10 mL	40 min	30 ÷ 34 mL	2 h 50 min	38 → 48 mbar
	Z10	3 h	8 mL	40 min	30 ÷ 34 mL	2 h 45 min	45 ÷ 47 mbar
→	Z5	2h	11 mL	55 min	29,5 ÷ 33,5 mL	2 h 55 min	44 → 52 mbar

*measurements corrupted by interruptions during the flow

→ Last Z10 analysis before valve replacemente

→ Last Z5 analysis before valve replacemente

VALVE REPLACEMENT

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

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 humidity could be absorbed by the zeolites and change the absorption power

Valve

LONG VACUUM REGENERATION

$$long\ vacuum\ regeneration\ efficiency = \frac{average\ volume\ \ of\ CH4\ before\ first\ peak\ appearance\ after\ long\ vacuum\ regeneration}{volume\ of\ CH4\ before\ first\ peak\ appearance\ after\ \ high\ temperature\ regeneration}$$

$$Z5\ long\ vacuum\ regeneration\ efficiency = \frac{12{,}5\ mL}{10{,}86\ mL} \approx 112\ \%$$

$$Z10\ long\ vacuum\ regeneration\ efficiency = \frac{9{,}1\ mL}{14{,}73\ mL} \approx 64\ \%$$

Comments:

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

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

SHORT VACUUM REGENERATION

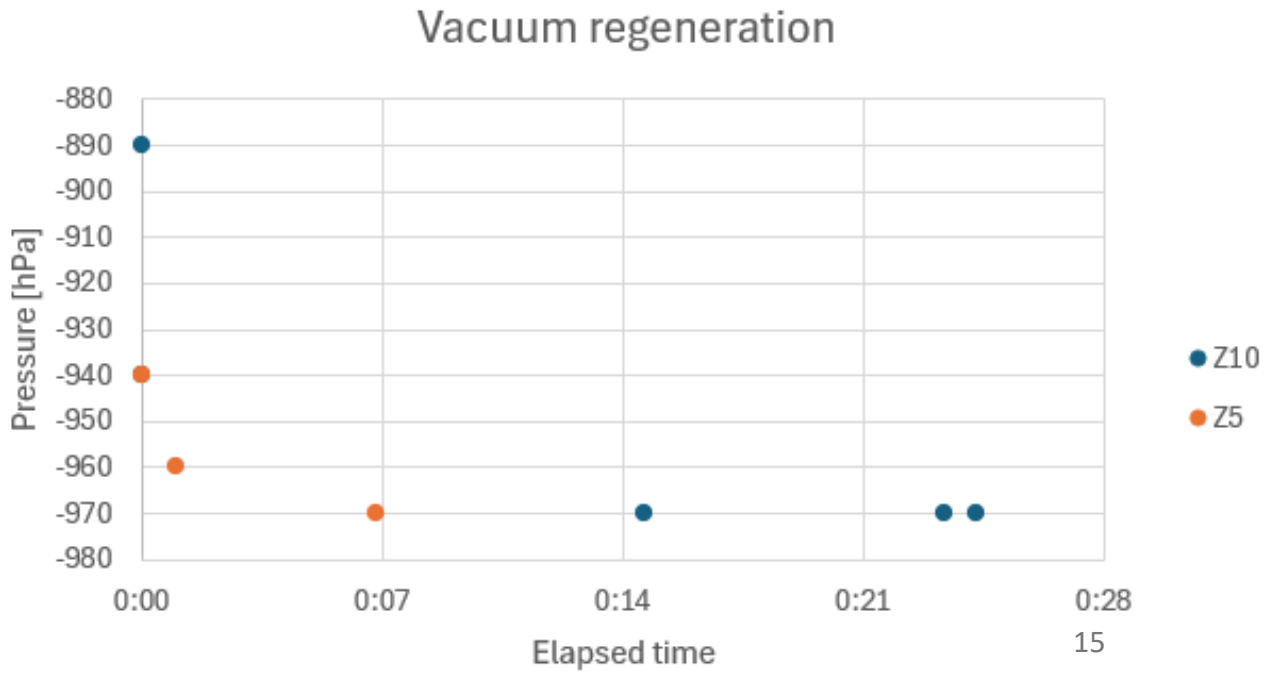
Next approach: stopping regeneration when pressure in the cartridge gets to the minimum value

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 bothcartridges.

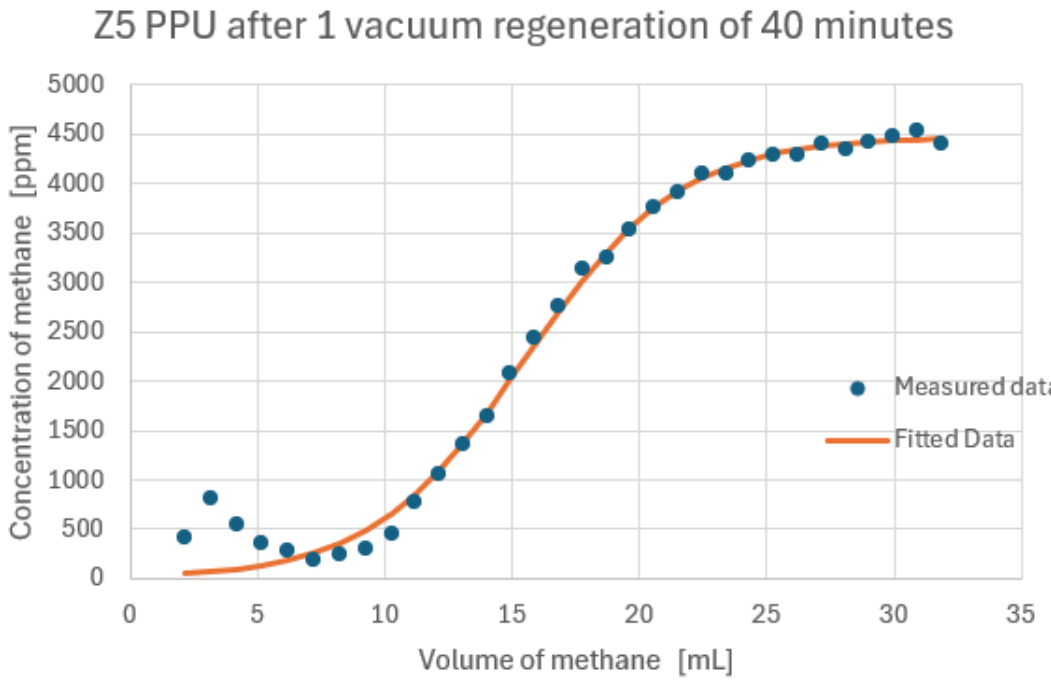
It also depends on the presence of leaks

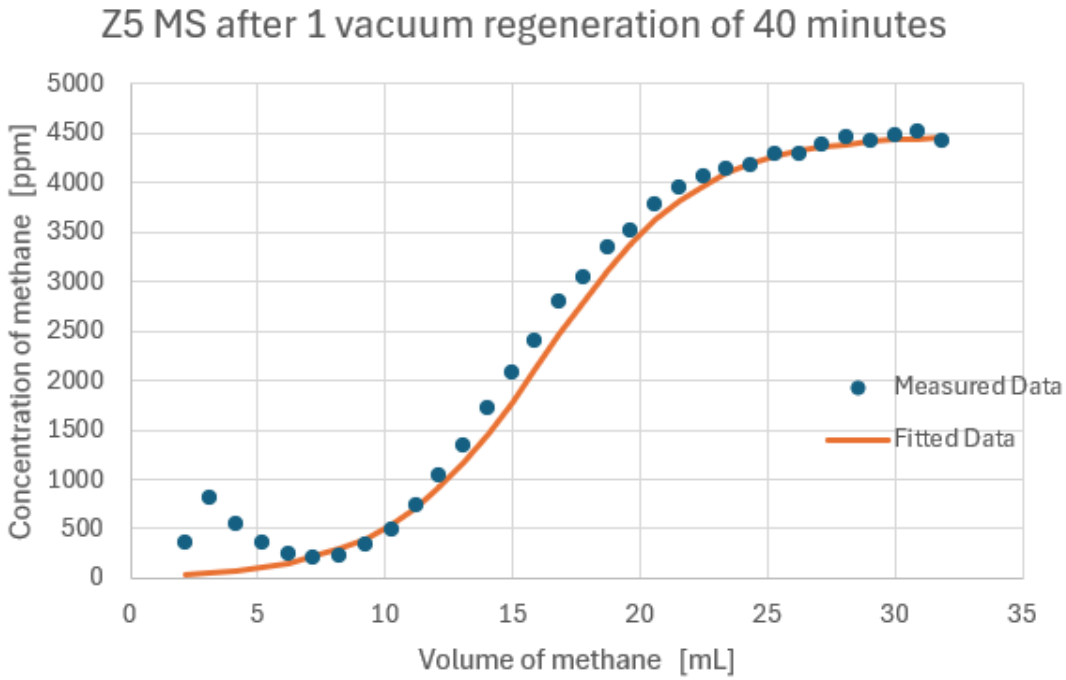


Z5 SHORT VACUUM REGENERATIONS

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

Z5 SHORT VACUUM REGENERATIONS

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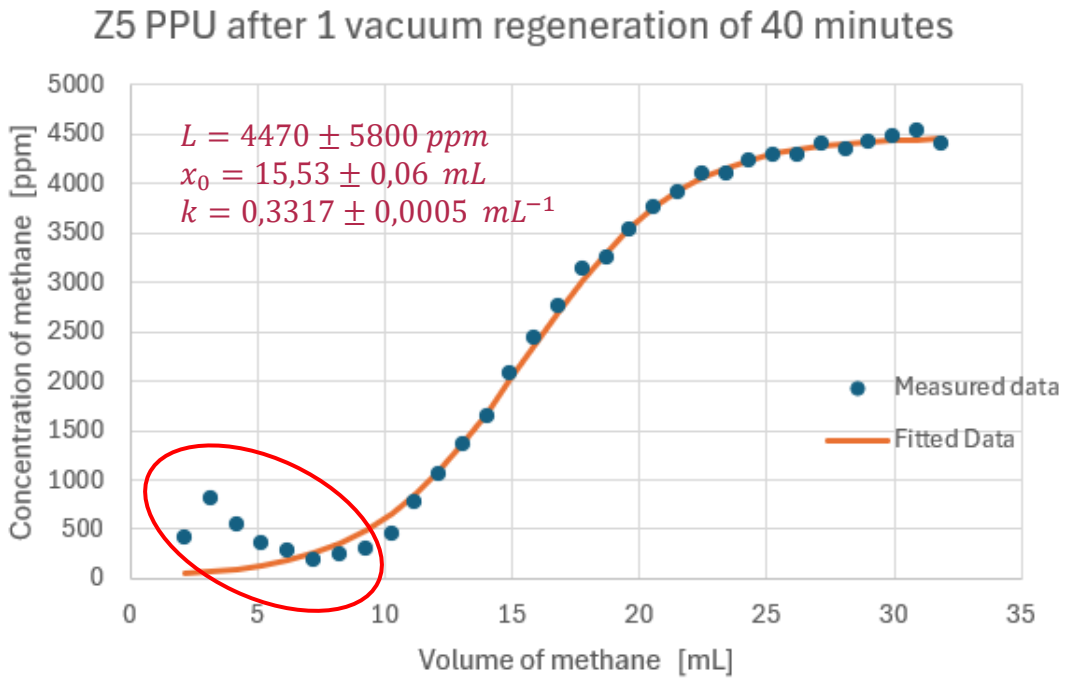
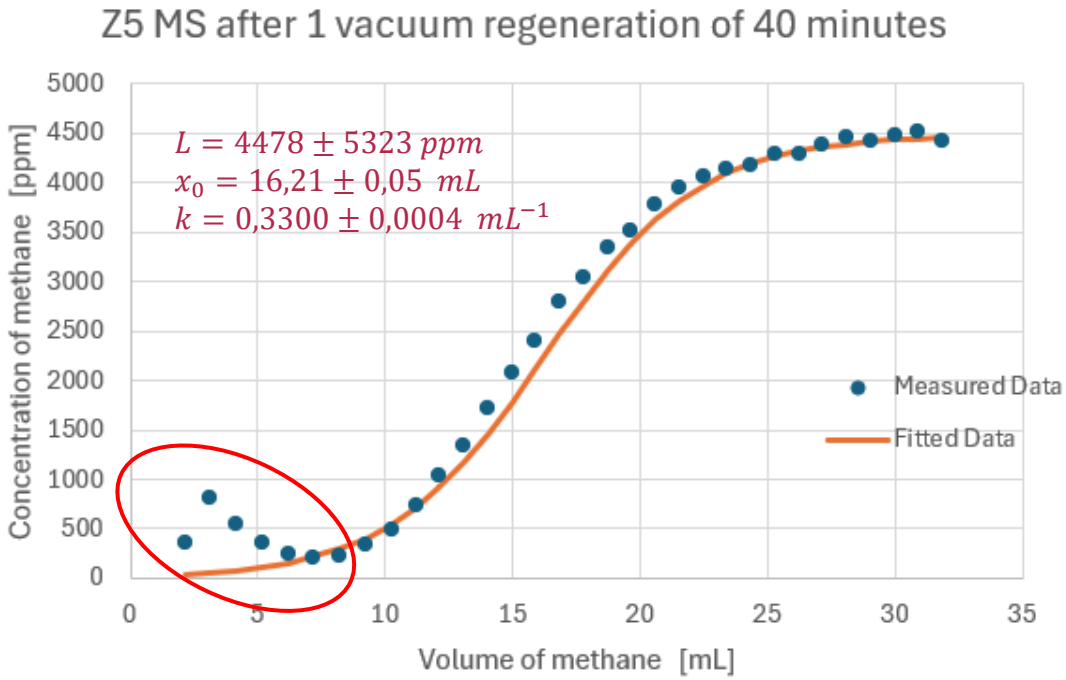


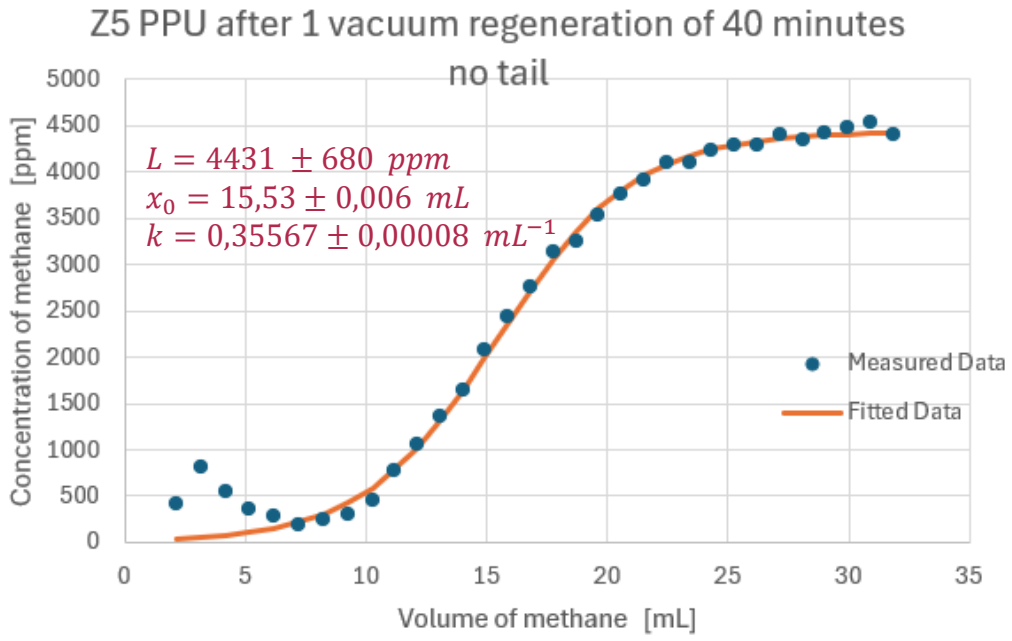


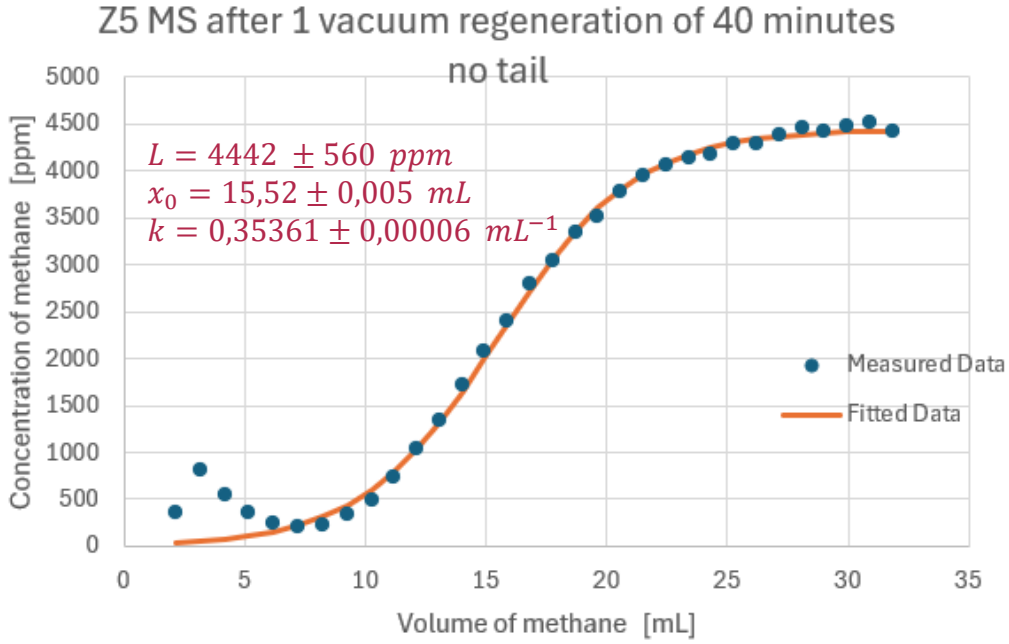
Fit function: $$\boldsymbol{sigmoid = \frac{L}{1+e^{-(x-x_0)\cdot k}}}$$

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

Z5 SHORT VACUUM REGENERATIONS

Fit without the tail points





Huge error on L

Besides the anomaly, the minimum corresponds to **7,20 mL** of methane

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

SHORT VACUUM REGENERATION

$$short\ vacuum\ regeneration\ efficiency = \frac{average\ volume\ of\ CH4\ before\ first\ peak\ appearance\ after\ short\ vacuum\ regeneration}{volume\ of\ CH4\ before\ first\ peak\ appearance\ after\ high\ temperature\ regeneration}$$

$$Z5\ short\ vacuum\ regeneration\ efficiency = \frac{8{,}64\ mL}{10{,}86\ mL} \approx 80\ \%$$

$$Z10\ short\ vacuum\ regeneration\ efficiency = \frac{6{,}35\ mL}{14{,}73\ mL} \approx 43\ \%$$

Comments:

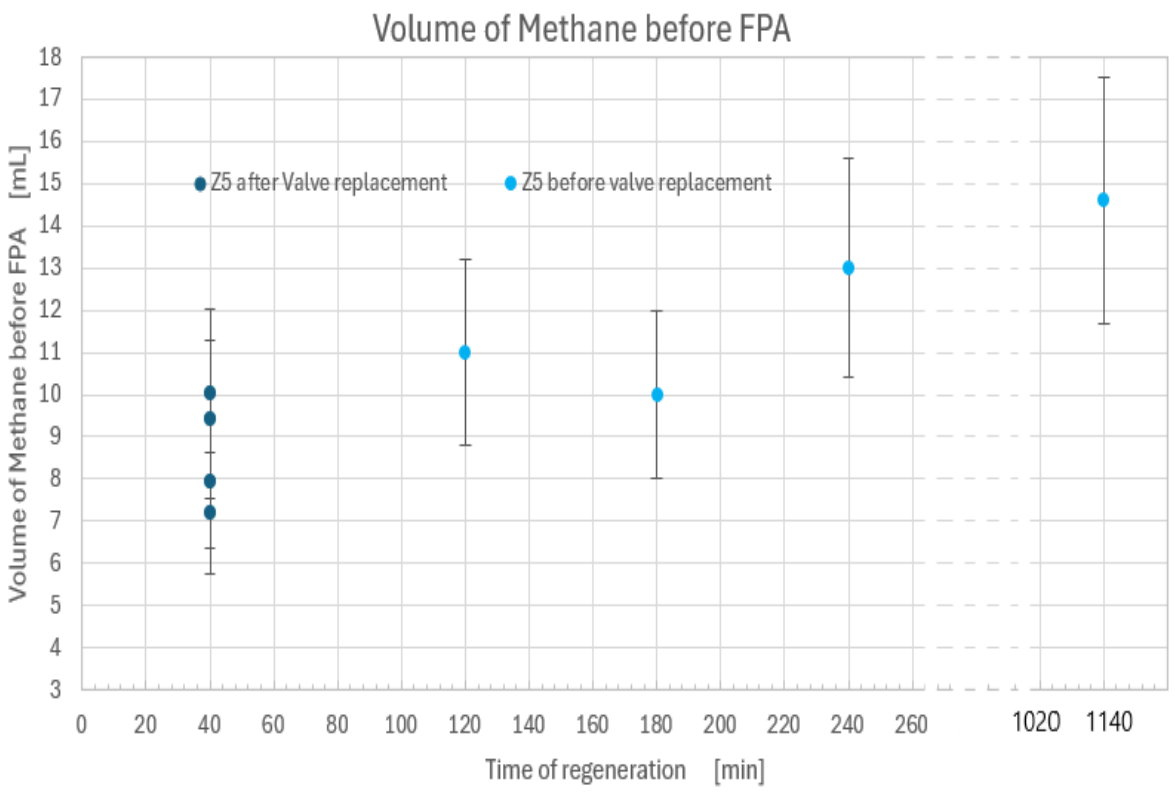
- Z5 : efficiency is a little lower, but consistent

- Z10 : irregular behaviour, efficiency drops

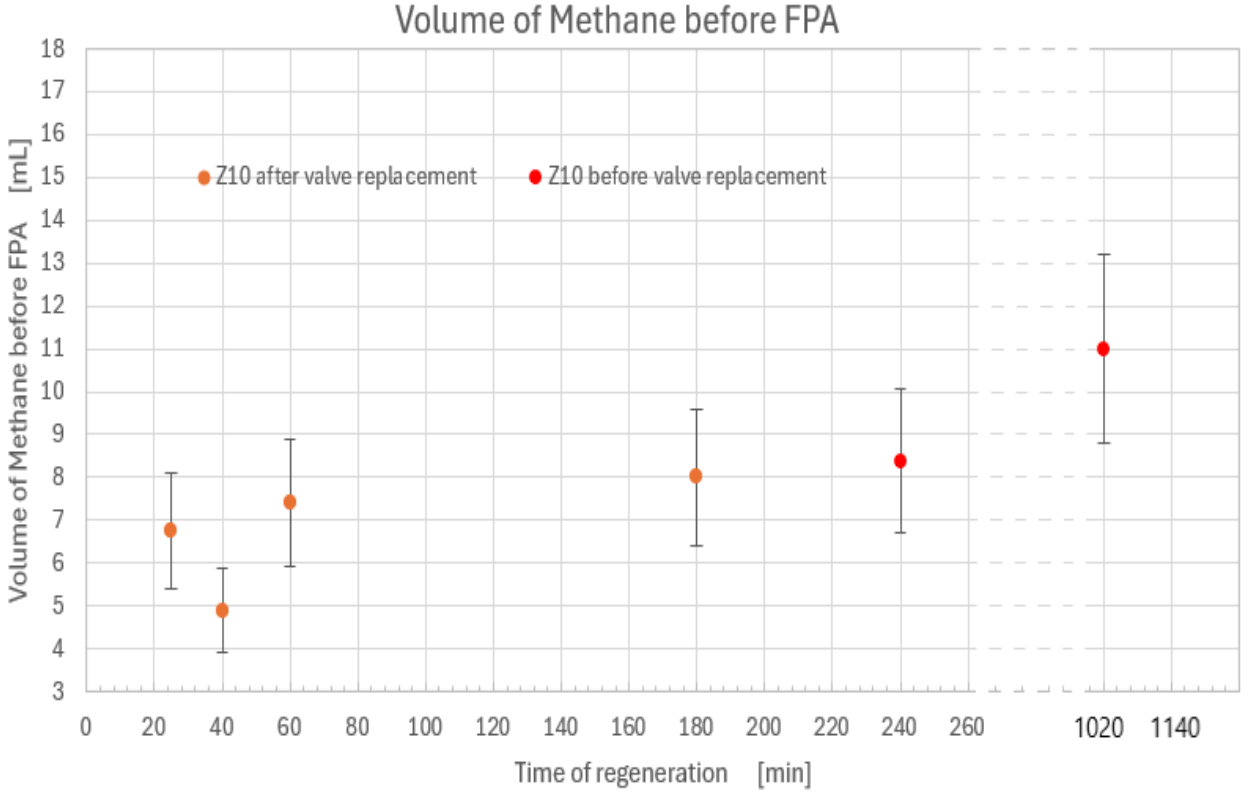
VACUUM REGENERATION SUMMARY

FPA = First Peak Appearance of CH4 in the chromatogram

Z5 :

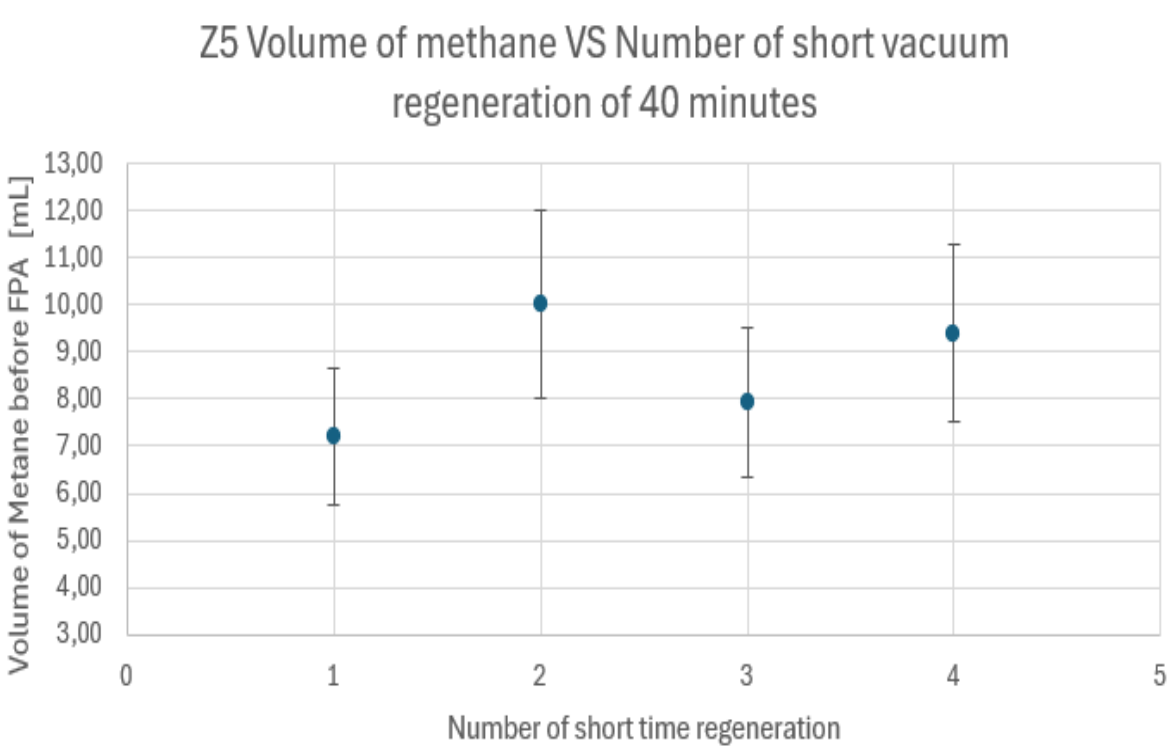


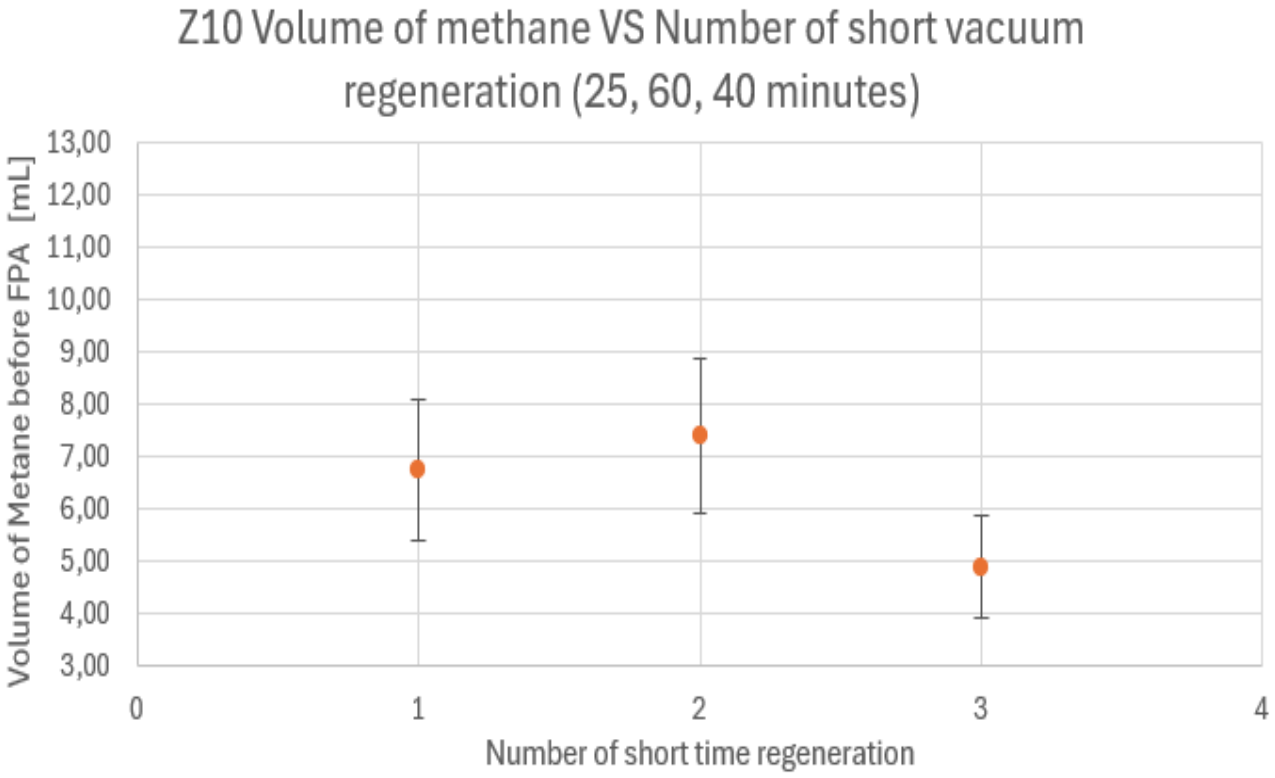
Z10 :



VACUUM REGENERATION SUMMARY

FPA = First Peak Appearance of CH4 in the chromatogram





CHEMICAL ANALYSIS

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

TGA:
- Detects change in sample mass (loss or gain)
- Detects stepwise changes in mass
- Determines temperature that characterizes a step in the mass loss or gain

DSC:
- Detects endothermic and exothermic peaks
- Determine peak areas (Transition and reaction enthalpies)
- Determine temperature that characterizes a peak or other effects
- Measures specific heat capacity

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

CHEMICAL ANALYSIS

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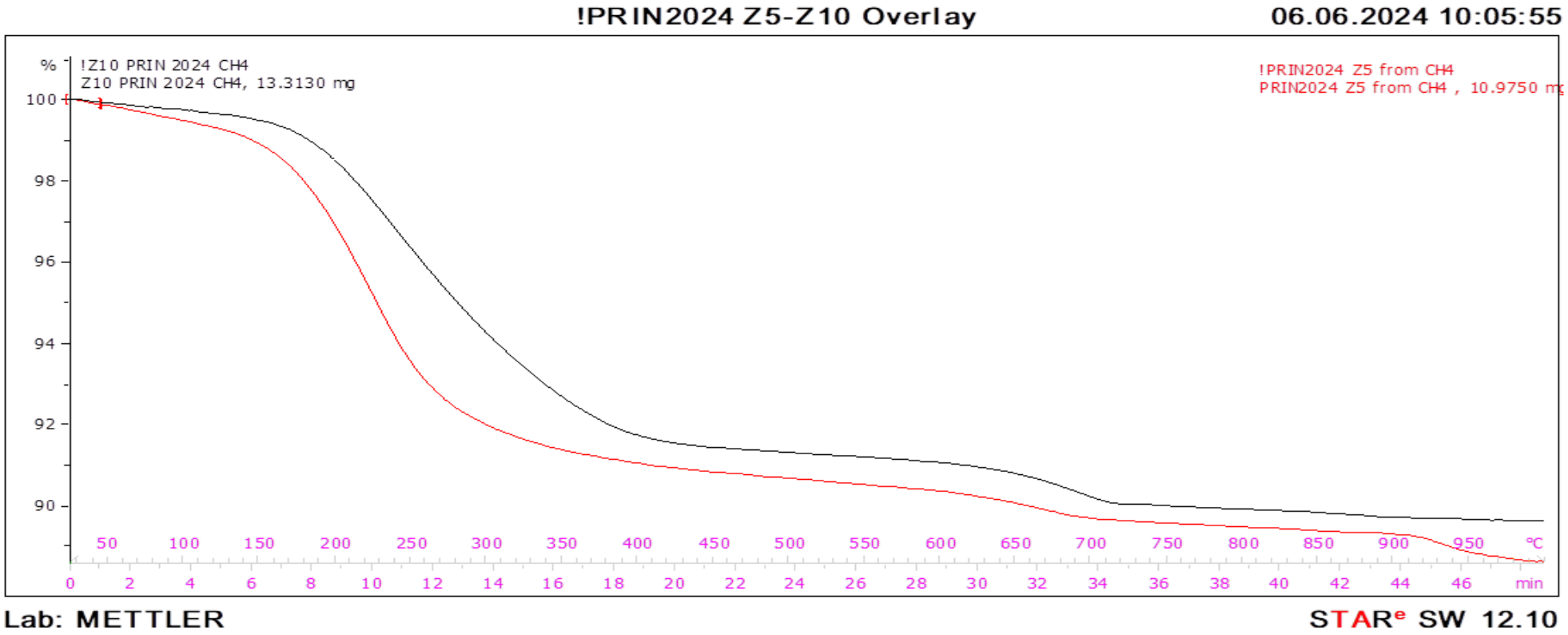
TGA:



CHEMICAL ANALYSIS

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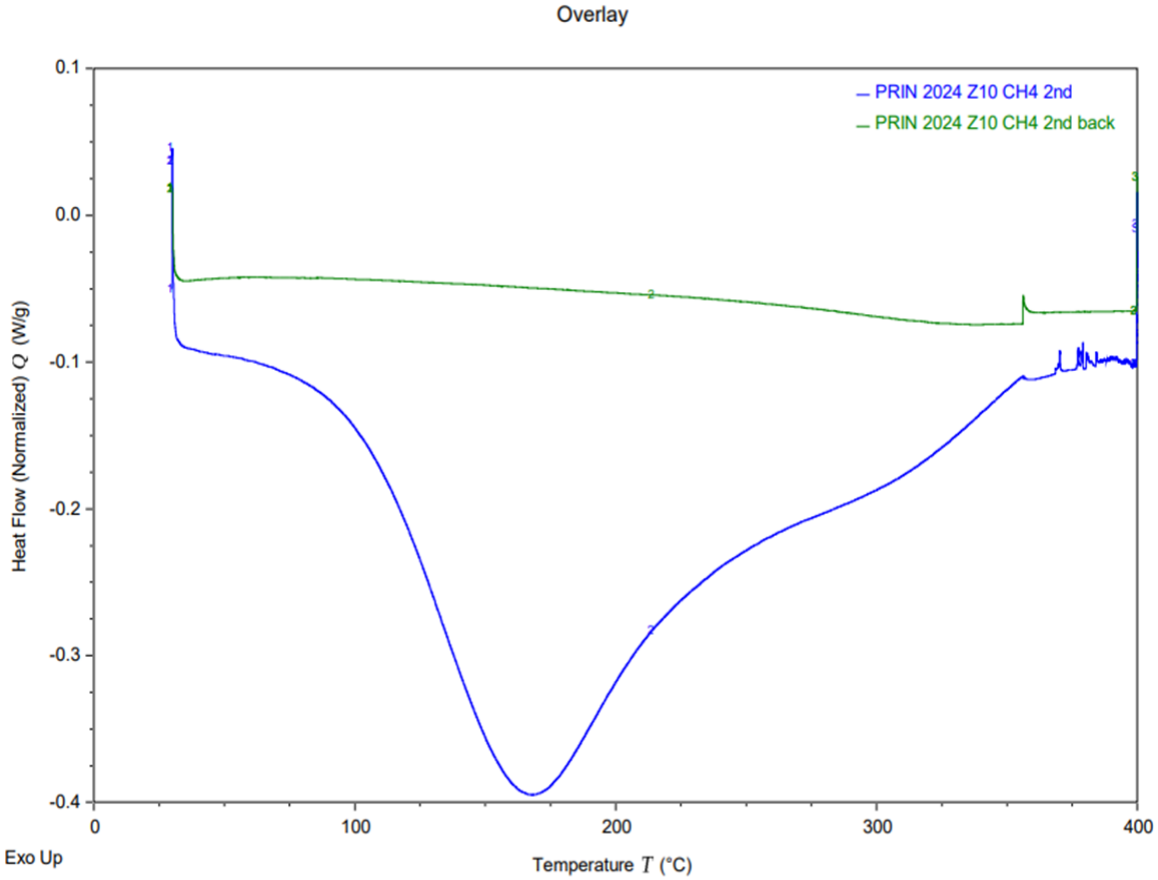
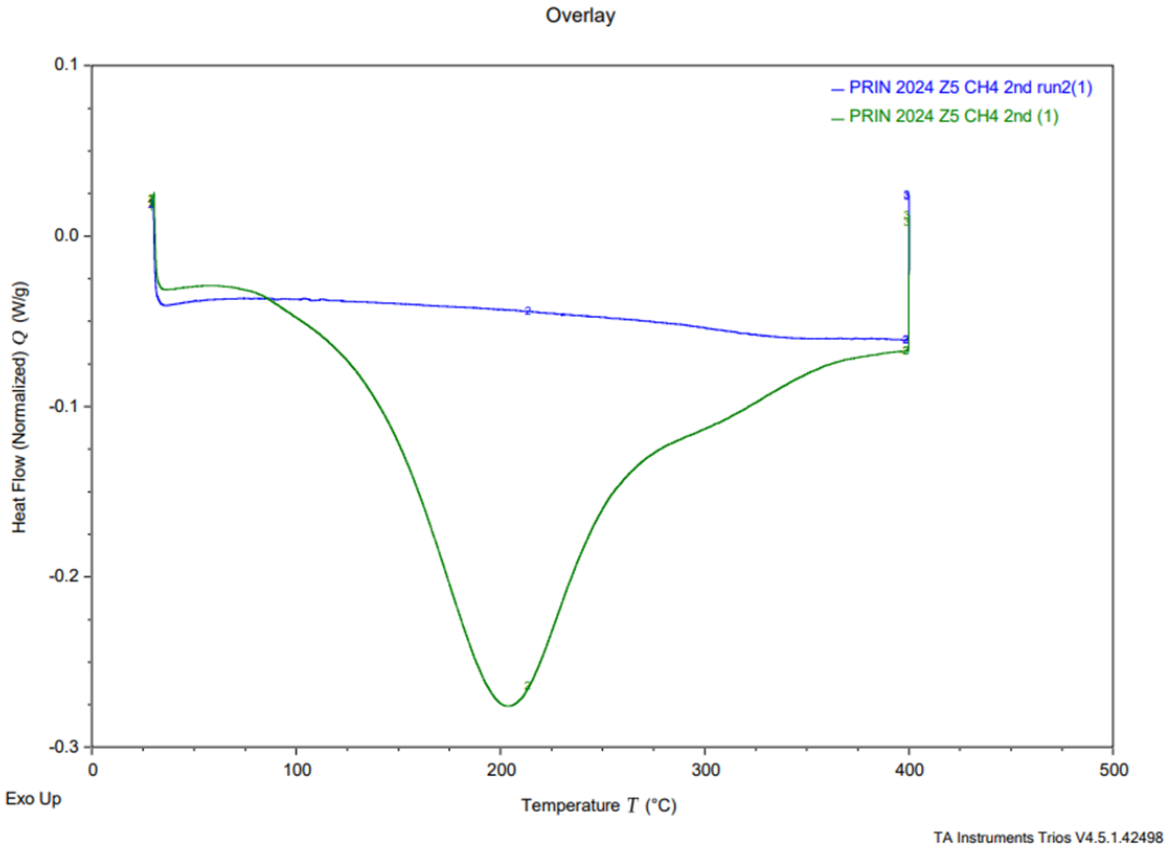
DSC:

- Z10:



- Z5:



CHEMICAL ANALYSIS

Humidity represents a problem

crystals absorbed water in two possible way:

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

CONCLUSIONS AND FURTHER EXPERIMENTS

Z3 and Z4 have lower absorption power with respect to Z5 and Z10.

Z5 has lower absorption power than Z10 when both are fully regenerated

Long regeneration with vacuum pump:

- Z5 seems fully regenerated (regeneration time > 2 h)
- Z10 absorption power decreases to ~ 65 % (regeneration time > 2 h)

Short regeneration with vacuum pump:

- Z5 absorption power decreases to ~ 80 % (regeneration time < 1 h)
- Z10 irregular behaviour, absorption power decreases to ~ 45 % (regeneration time < 1 h)

More data are needed to have statistical meaning

CONCLUSIONS AND FURTHER EXPERIMENTS

Chemical analysis shows that:

- contact with humidity is a problem
- …

Future experiments:

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

Chemical group is working on infusing Carbon – Nitrogen material in the zeolite pores to increase absorption power. The first candidates are *Urea* and *Melamine*

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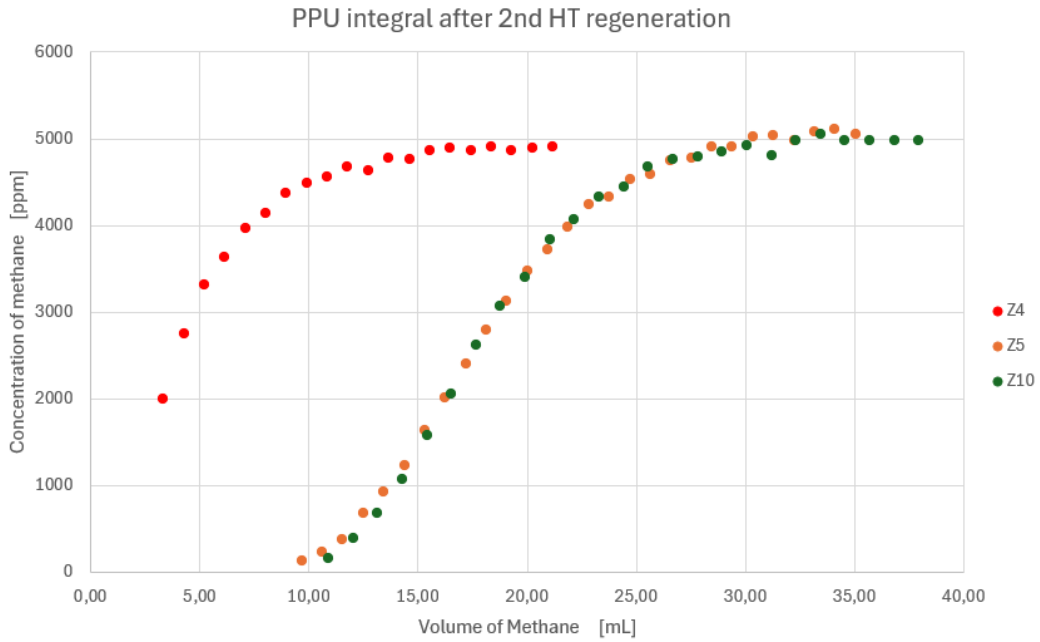
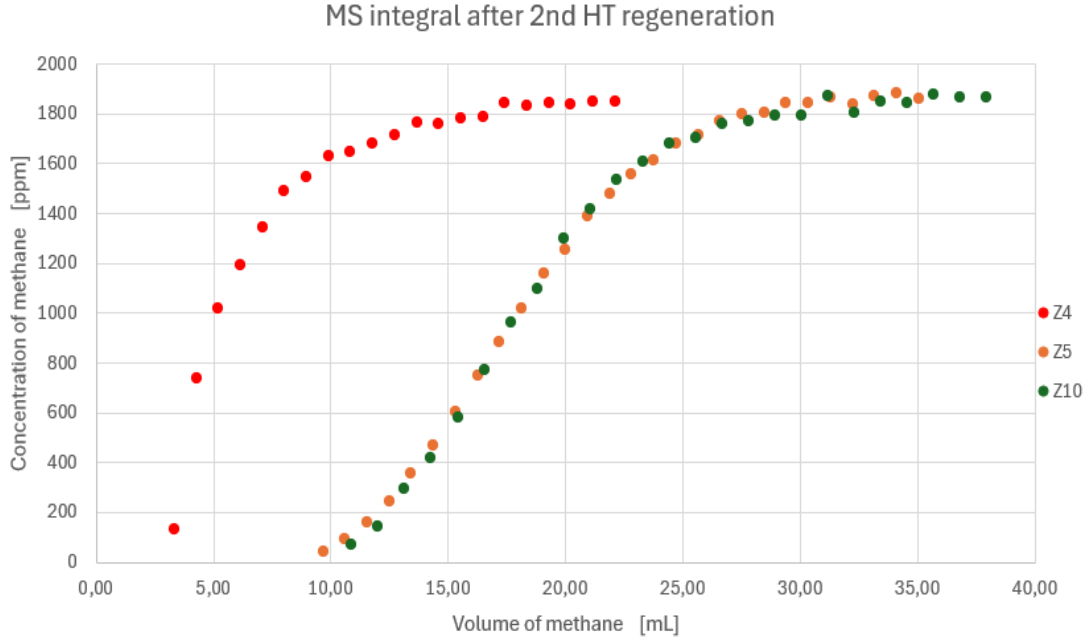
SECOND SERIES OF MEASUREMENTS

High temperature regenerated cartridges:





Absorbed methan before peak appearance in the chromatogram:

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

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

Overall error of 20% due to rotameter measures

VACUUM REGENERATION SUMMARY

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FPA = First Peak Appearance of CH4 in the chromatogram