Johnson Matthey
Inspiring science, enhancing life

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

The impact of PM on coated catalytic GPF structures investigated by Spatially resolved Mass Spectrometry (SPACI-MS)

JM: Aldo Lanza, Ryutaro Sato, Tim Watling, Djamela Bounechada, Andrew York
Prague: Miroslav Blazek, Petr Koci

Particulate matter filtration flows, 17th December 2024

Catalysing the net zero transition

Our aspiration is to lead across our four businesses

Clean Air	Catalyst Technologies	Hydrogen Technologies
Leading in autocatalyst markets	#1 in syngas-based chemicals and fuels technology	Market leader in performance components for fuel cells and electrolysers

PGM Services
(Platinum Group Metals Services)

#1 recycler of PGMs[1]

JM

1. Iridium, palladium, platinum, rhodium and ruthenium.

Emission Control Research

JM Technology Centre UK

Clean air’s applications

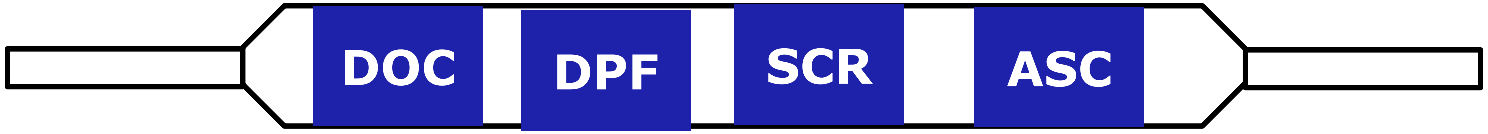
Automotive (catalytic converters)

Heavy Duty

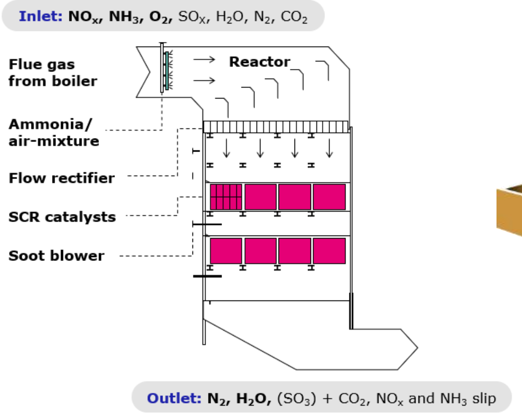
Light Duty

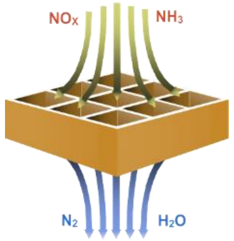
Gasoline internal combustion engines

Diesel (and H_2) internal combustion engines

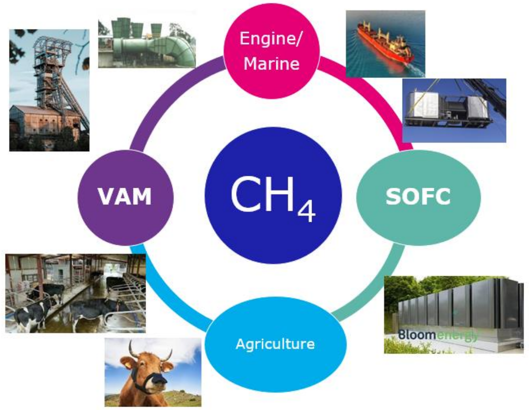


CASolutions

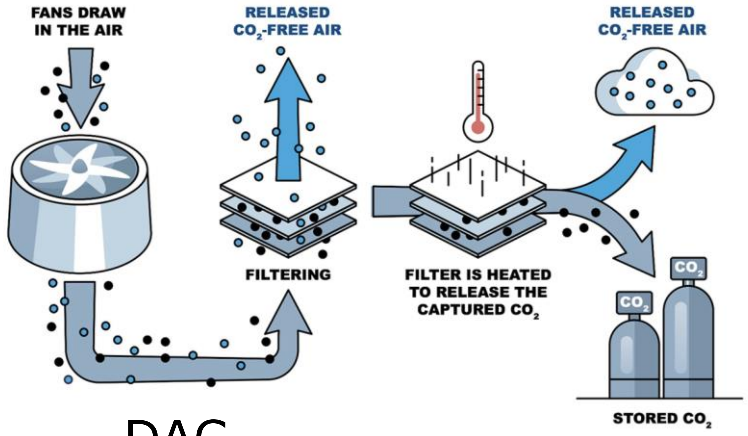




Power generation



Methane control



DAC

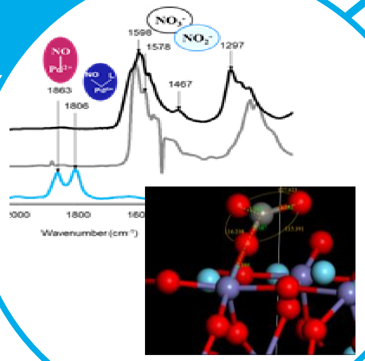
JM

Emissions Control Research – current portfolio

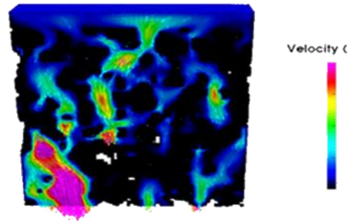
An integrated science & engineering approach underpins our research

Catalysis Science

New catalytic components
New materials
Catalyst preparation
Catalyst testing
Mechanism
Atomistic Modelling
Advanced Characterisation

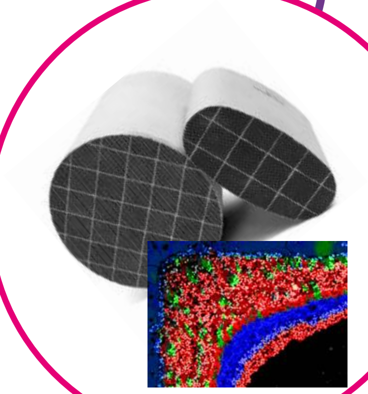


Reaction Engineering



Kinetic modelling
Reaction mechanism
Diffusion & Porosity
Structural Characterisation & Modelling

Process Research

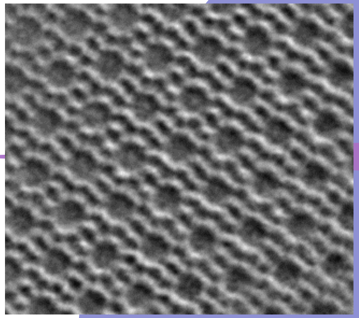


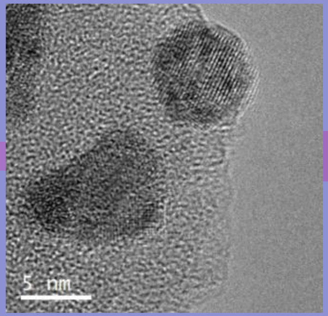
Process science understanding
Formulations
Characterisation
New coating concepts
Process control

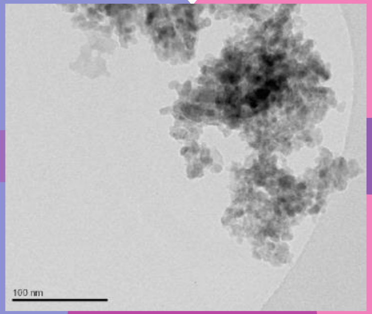
The data included herein were collected in a JM laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing.
The data do not represent a guarantee that the tested catalyst system will pass the relevant emissions legislation.

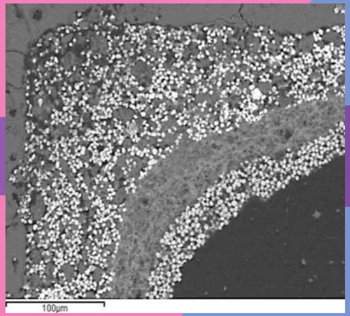
Research Challenges – across the length scales

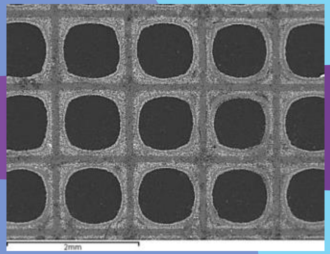
pm | nm | μm | 100s μm | mm | cm











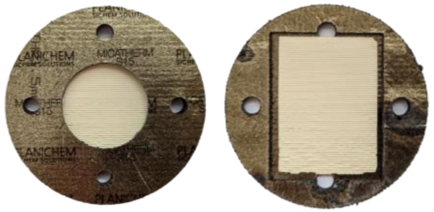
Product Research
New Catalytic Components
New materials
Mechanisms
Advanced Characterisation

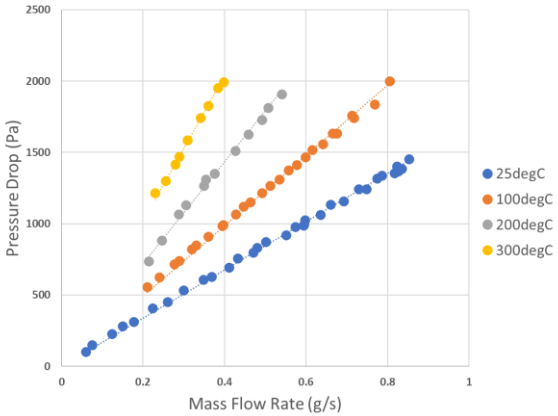
Process Research
Process Understanding
Formulations
New Coating Concepts

Reaction Engineering
Kinetic Modelling
Diffusion & Porosity
Structural characterisation & modelling

Academic collaborations during the years enabled us to understand our products

PhD Project: Direct Filter Wall Permeability Measurement





Coventry University

Several PhD projects on catalytic particles of filters

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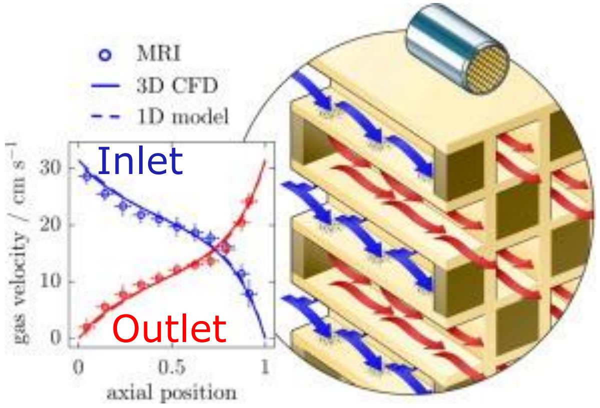
http://dx.doi.org/10.1016/j.ces.2022.117876
http://dx.doi.org/10.1016/j.fuel.2023.129603

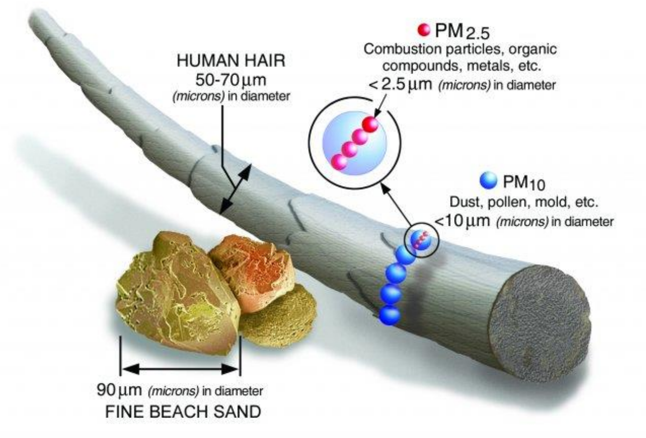
And more: MRI to validate flow inside channels

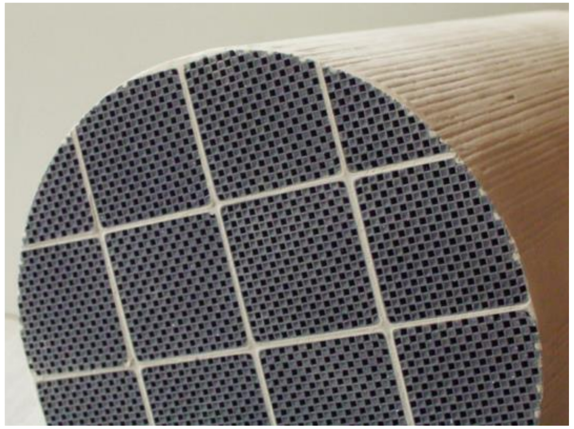


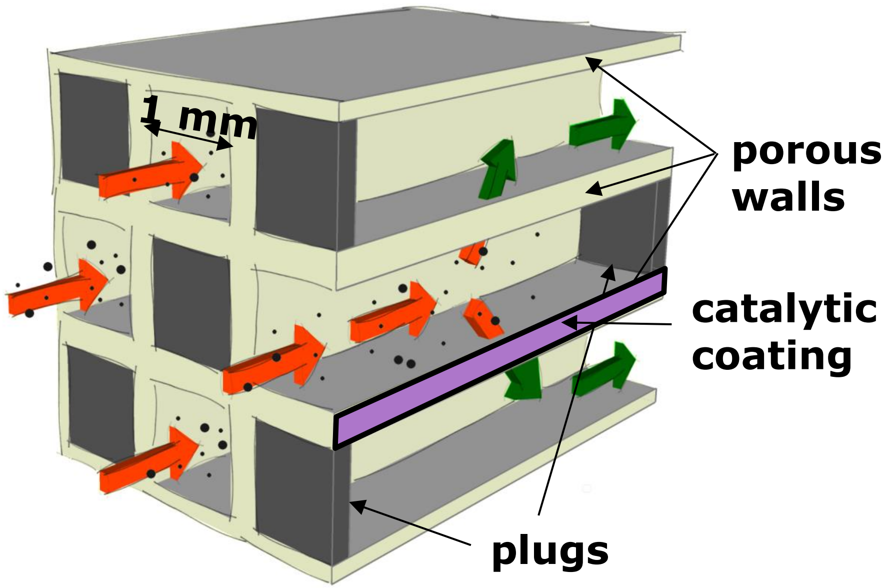
https://www.sciencedirect.com/science/article/abs/pii/S0009250919306700

Monolithic filter structure

- Diesel particulate filter – **DPF**
- Gasoline particulate filter – **GPF**



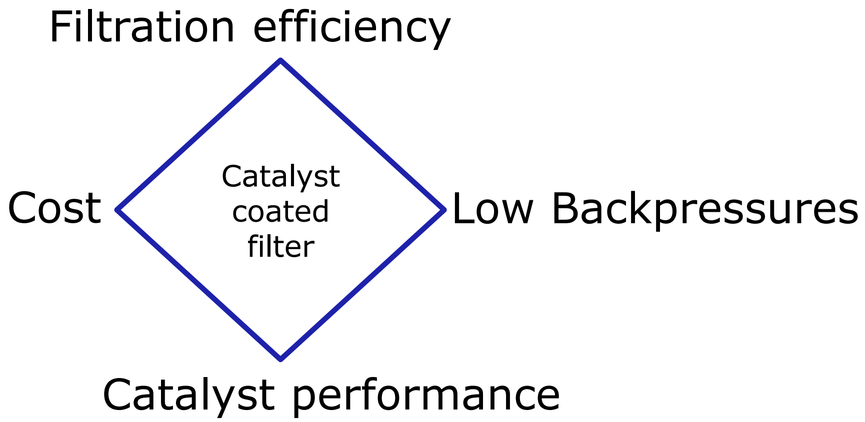




Catalytic coating of a filter

+ Reduction of size and cost, lower heat loss

– Higher pressure drop



Gasoline internal combustion engines

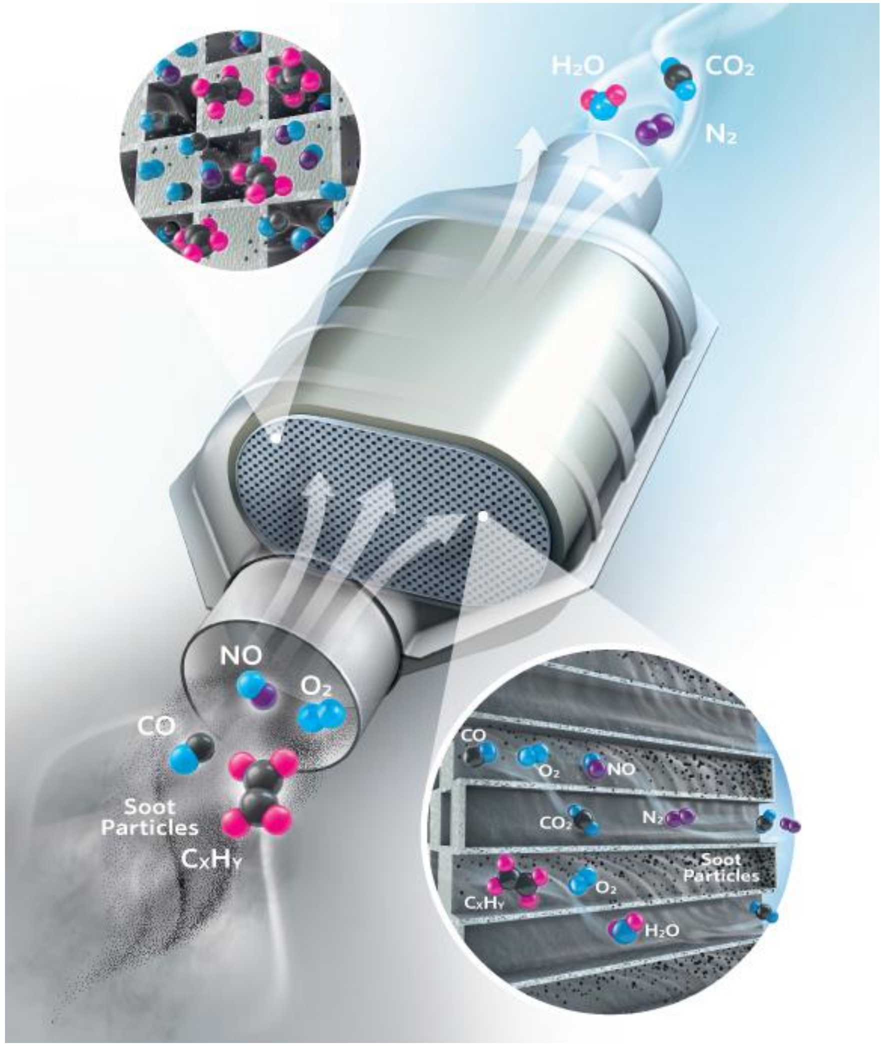
Three-Way Filter (TWF®)

Gasoline particulate filter (GPF) with a JM catalyst coating.

- Reduction of particle number up to 99%

  - [CO] + $O_2 \rightarrow CO_2$
  - [HC] + $O_2 \rightarrow CO_2 + H_2O$
  - [NO_x] + $H_2 \rightarrow N_2 + H_2O$

Composition: Typically precious metals (Pd, Pt or Rh) with alumina and rare earth oxide, coated on filter substrate.



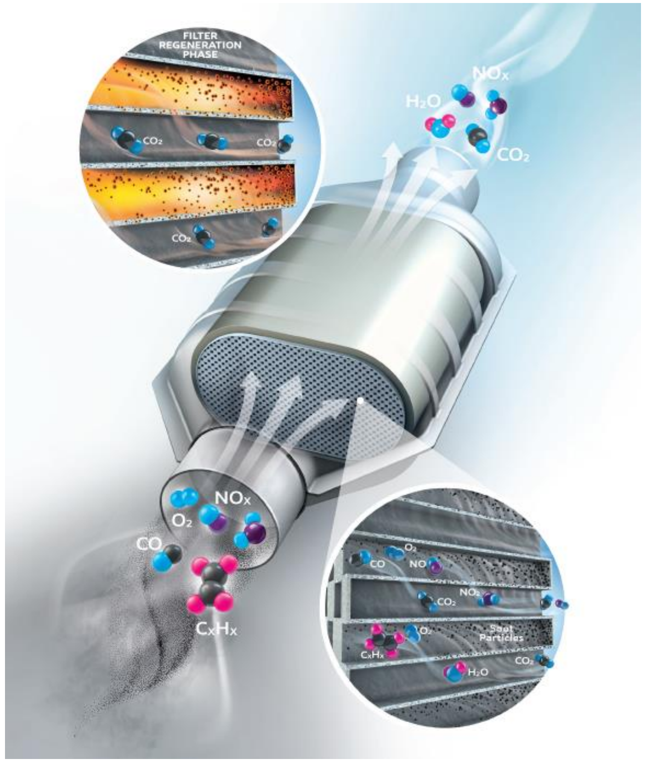
Coated filters for diesel: Diesel particulate filter (DPF)

Catalysed soot filter (CSF)

- Traps particulates and catalyses the oxidation of gaseous emissions:

  $CO + ½\,O_2 \rightarrow CO_2$

  $[HC] + O_2 \rightarrow CO_2 + H_2O$
- Pd/Pt active component



Selective Catalytic Reduction Filter® (SCRF®)

- Combines SCR on a DPF
- Traps particulates and catalyses the reduction of NOx (with urea addition):

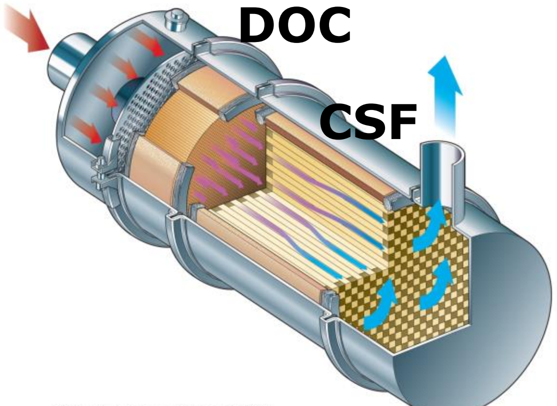
  $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

  $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$

  $8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$
- Cu-Zeolite

Remove soot by oxidation with O_2

- Soot removal by oxidation with O_2
  - Requires high temperature (500°C)
  - Need to avoid excessive heat generation and filters melting
- Soot removal by oxidation with NO_2
  1. $2NO + O_2 \rightarrow 2NO_2$
  2. $2NO_2 + C \rightarrow CO_2 + 2NO$
  3. $NO_2 + C \rightarrow CO + NO$
  - Reaction at lower temperature (200°C)
  - Requires appropriate NO_x/PM
  - Temperature more typical of exhaust, continuous regeneration
  - Common for heavy duty diesel



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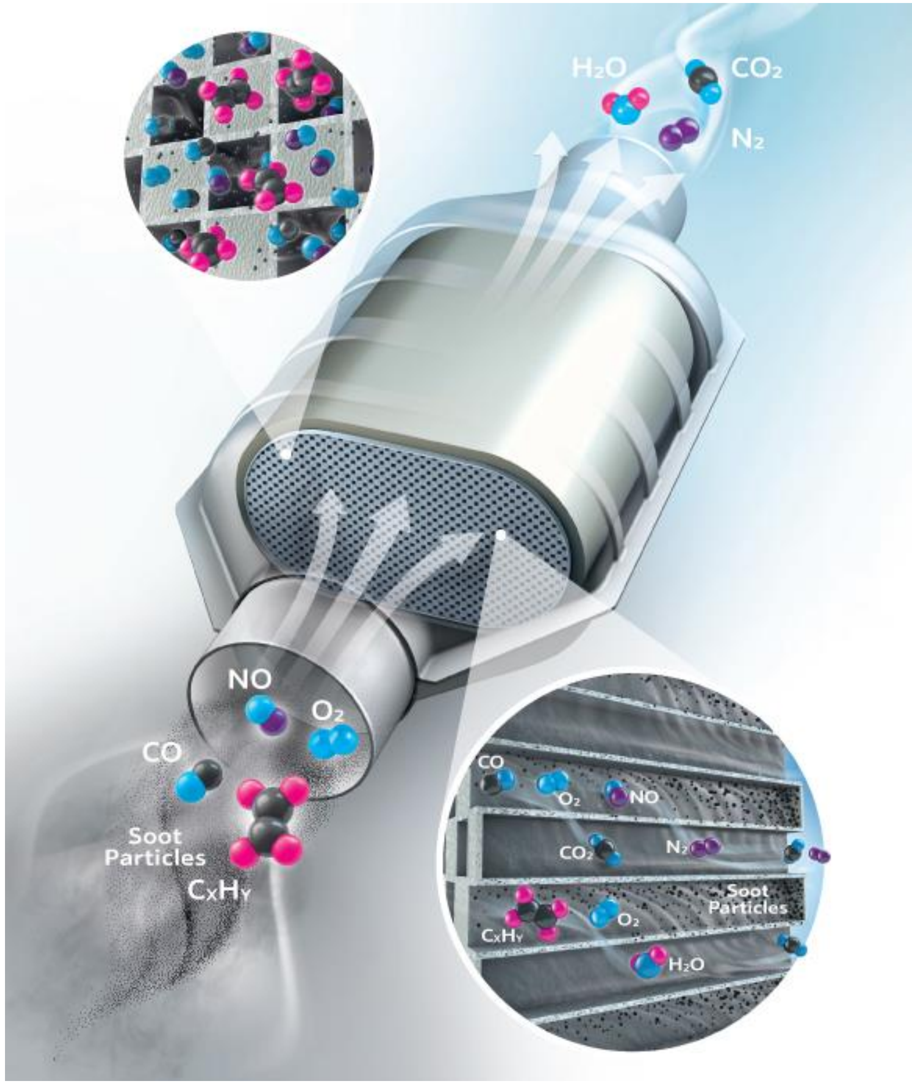
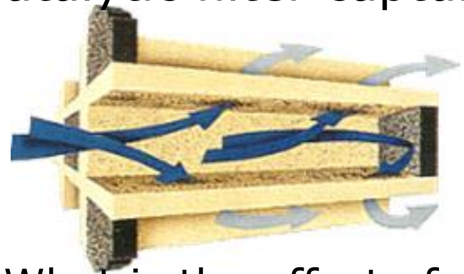
Effect of soot deposition on Particulate filters

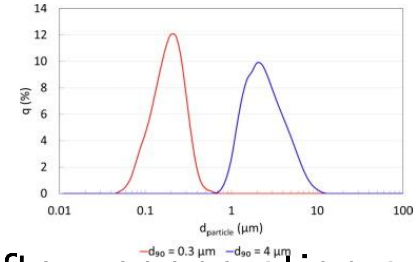
Helps understands how soot is acting

SV = 100 000 h^{-1}, C8H18 = 100 ppm, O_2 = 5 %, Ar



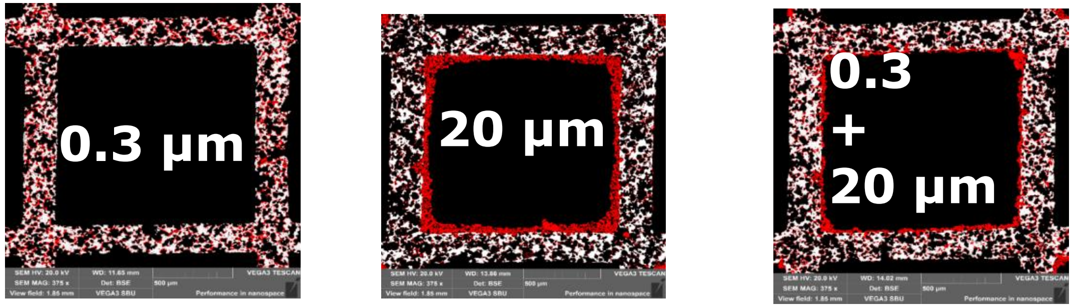
- Catalytic filter capture soot and are reactive





- What is the effect of soot and after regeneration and on catalyst activity?
- Coating with different controlled particle size distribution (d_{90})

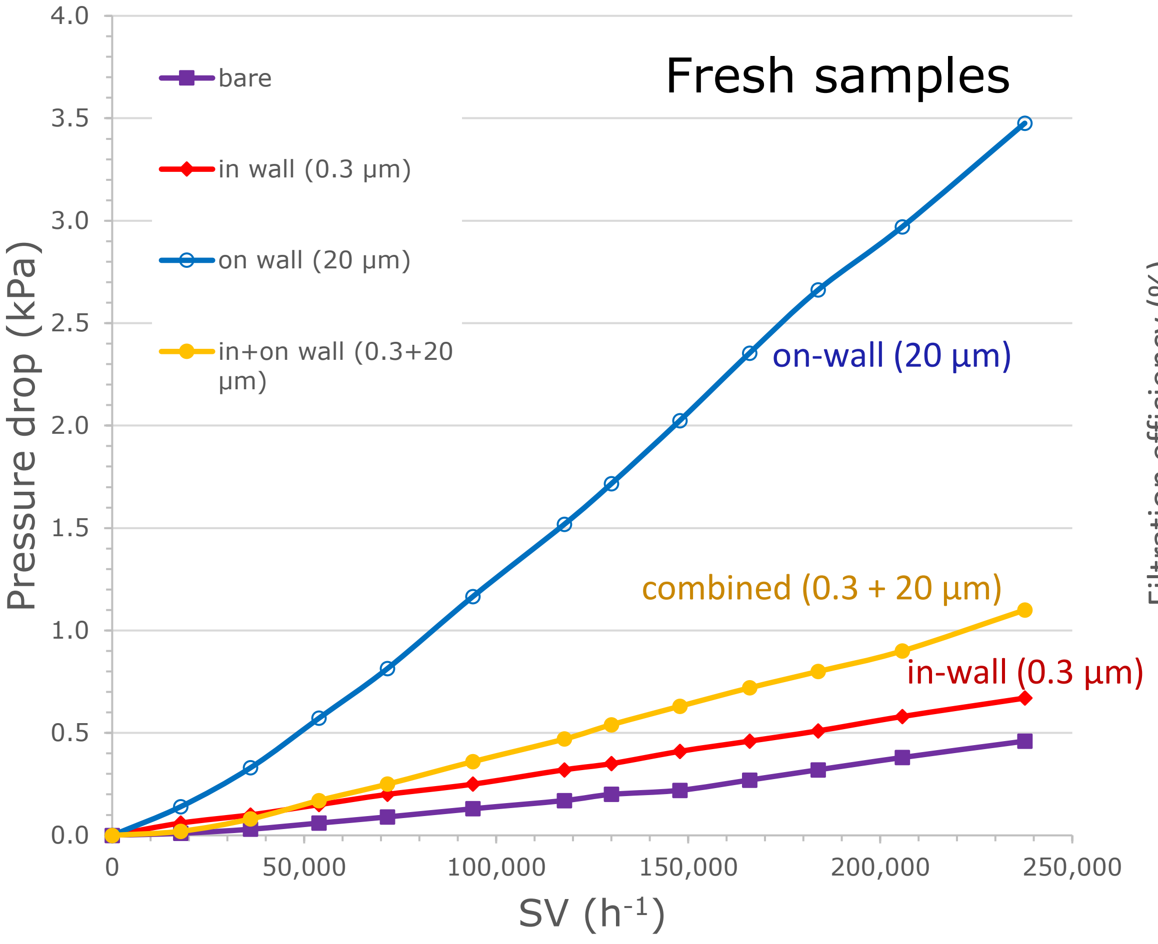
In-wall **on-wall** **in+on-wall**

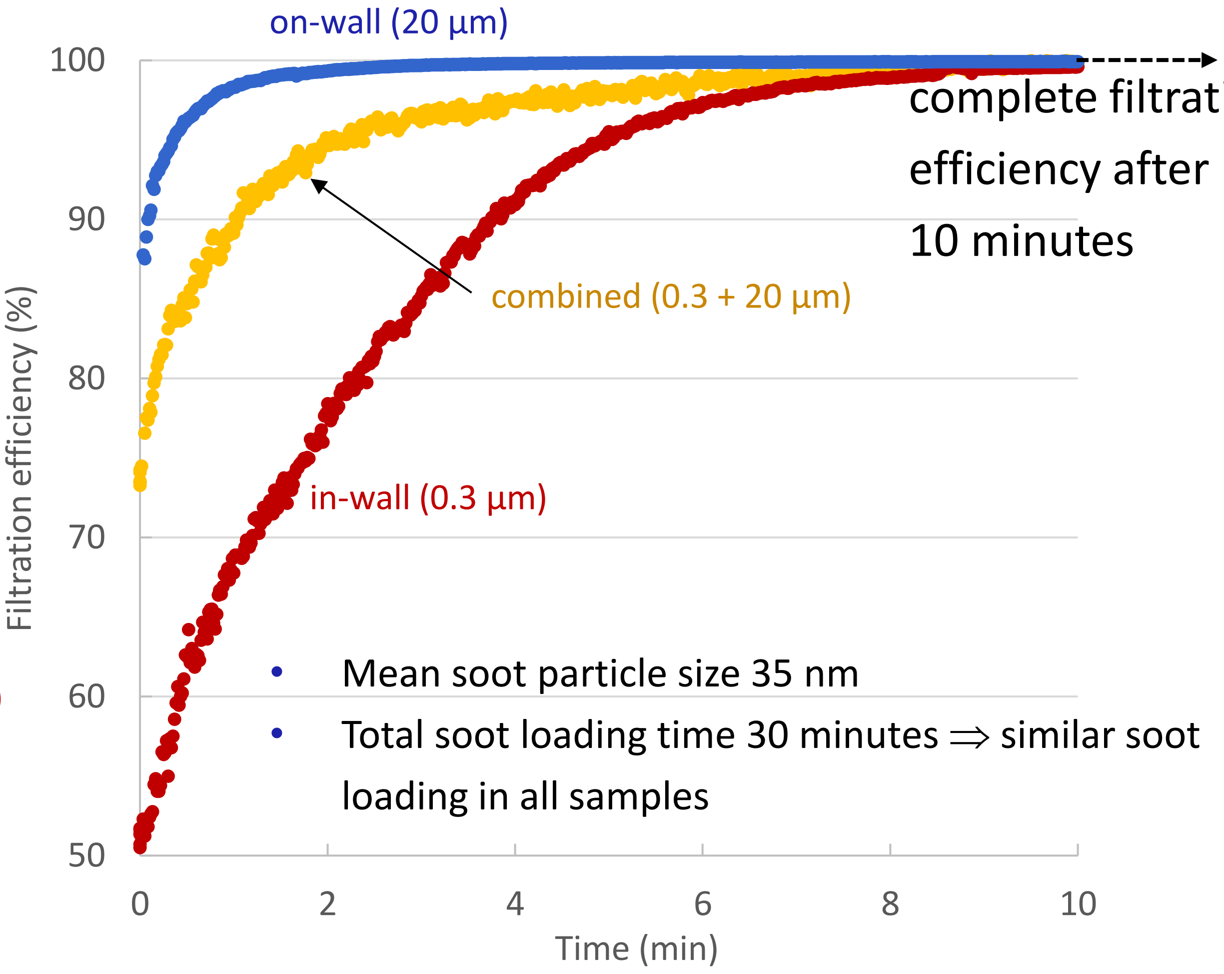


- Tests:
  - Pressure drops
  - Filtration efficiency
  - Activity tests: fresh, soot-deposited, regenerated
  - Regeneration: 600C with 10-20%O_2

With: M. Blazek (Prague), P. Koci (Prague), A. P. York

Backpressures



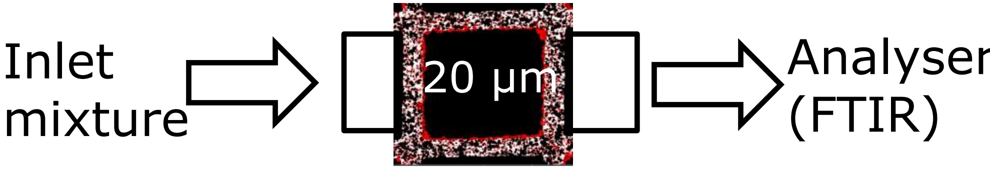


complete filtration efficiency after 10 minutes

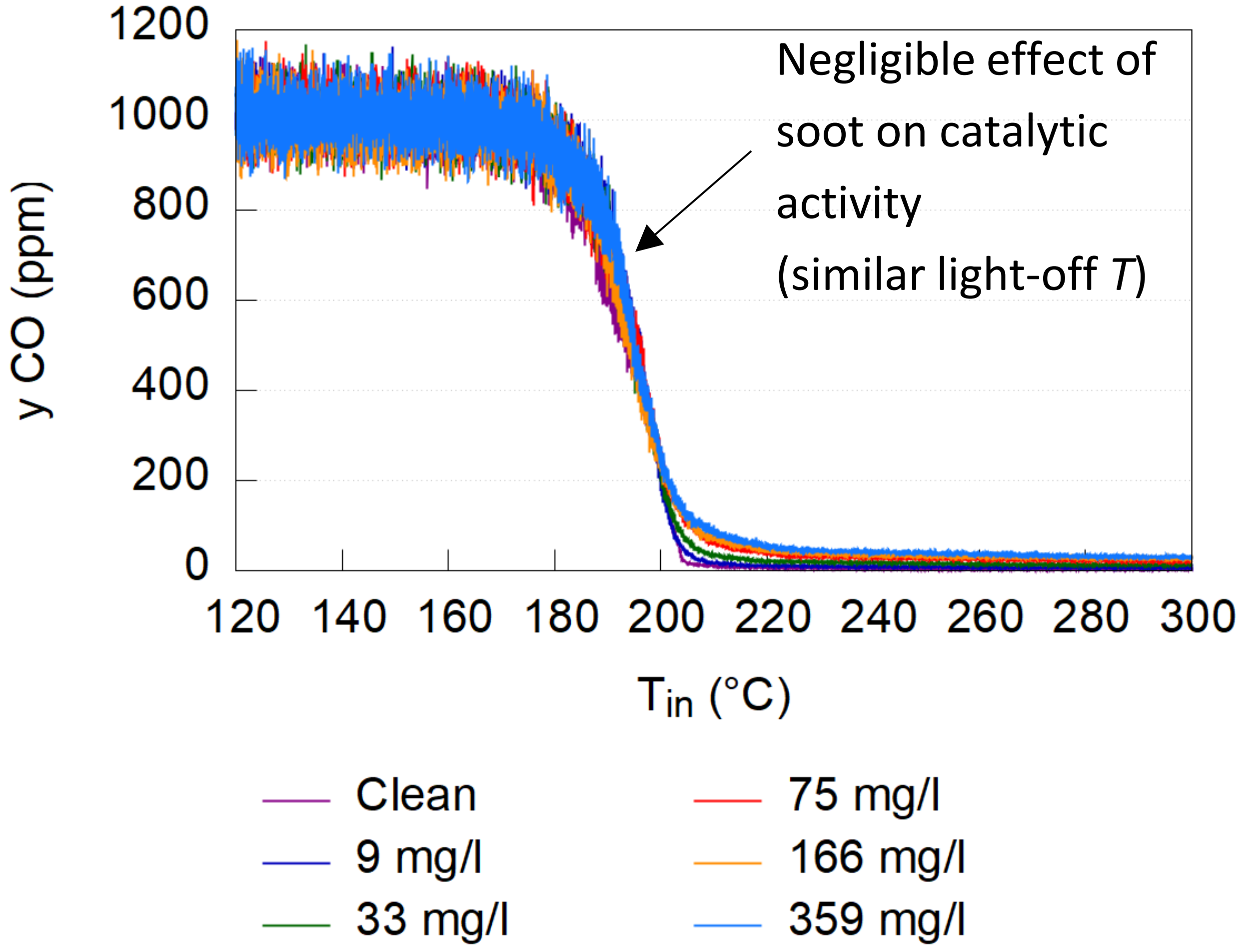
- Mean soot particle size 35 nm
- Total soot loading time 30 minutes ⇒ similar soot loading in all samples

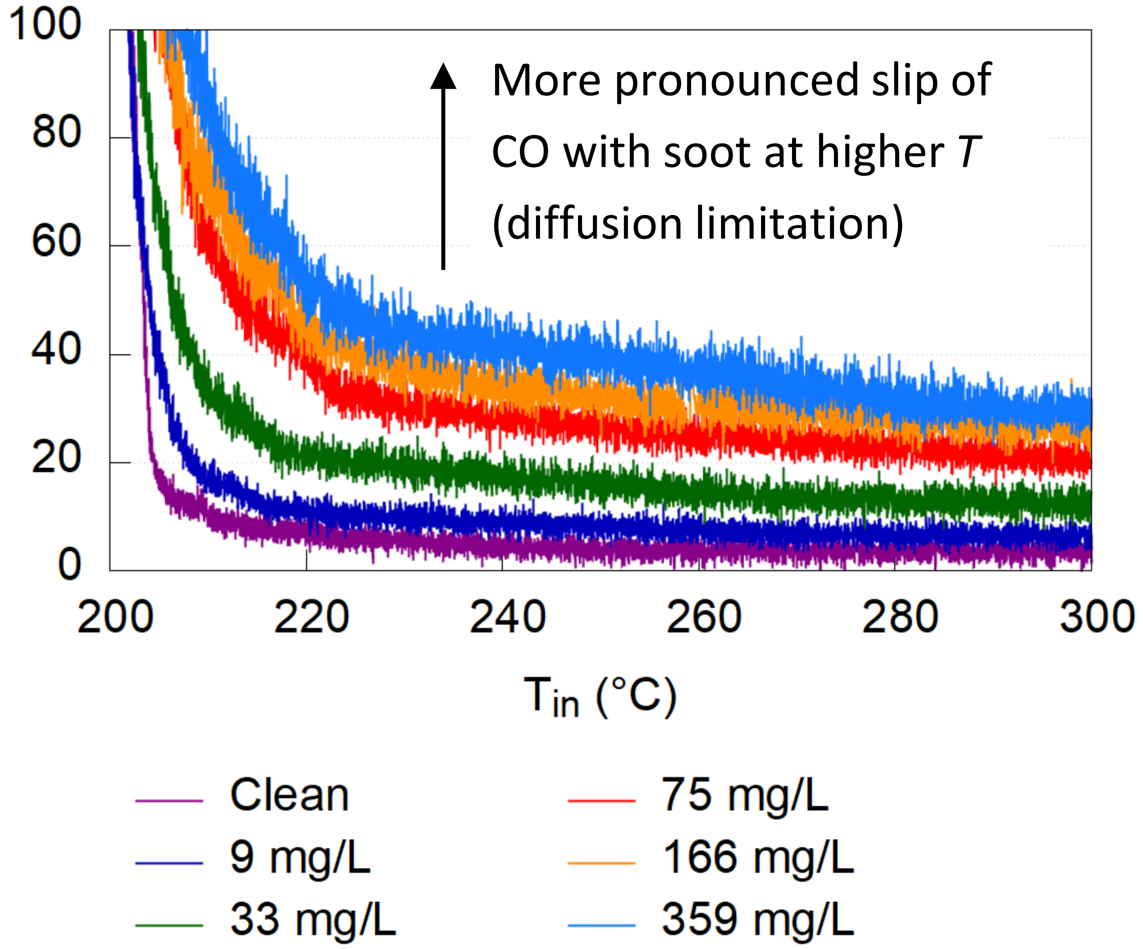
Let's look at catalyst activity

Impact of soot on CO light-off activity



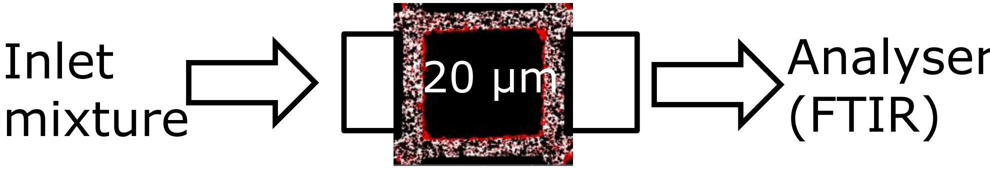
On-wall sample **High** gas flowrate (GHSV = 200 000 h^{-1}) 1000 ppm CO + 5 % O_2





CO slips depending on loaded soot

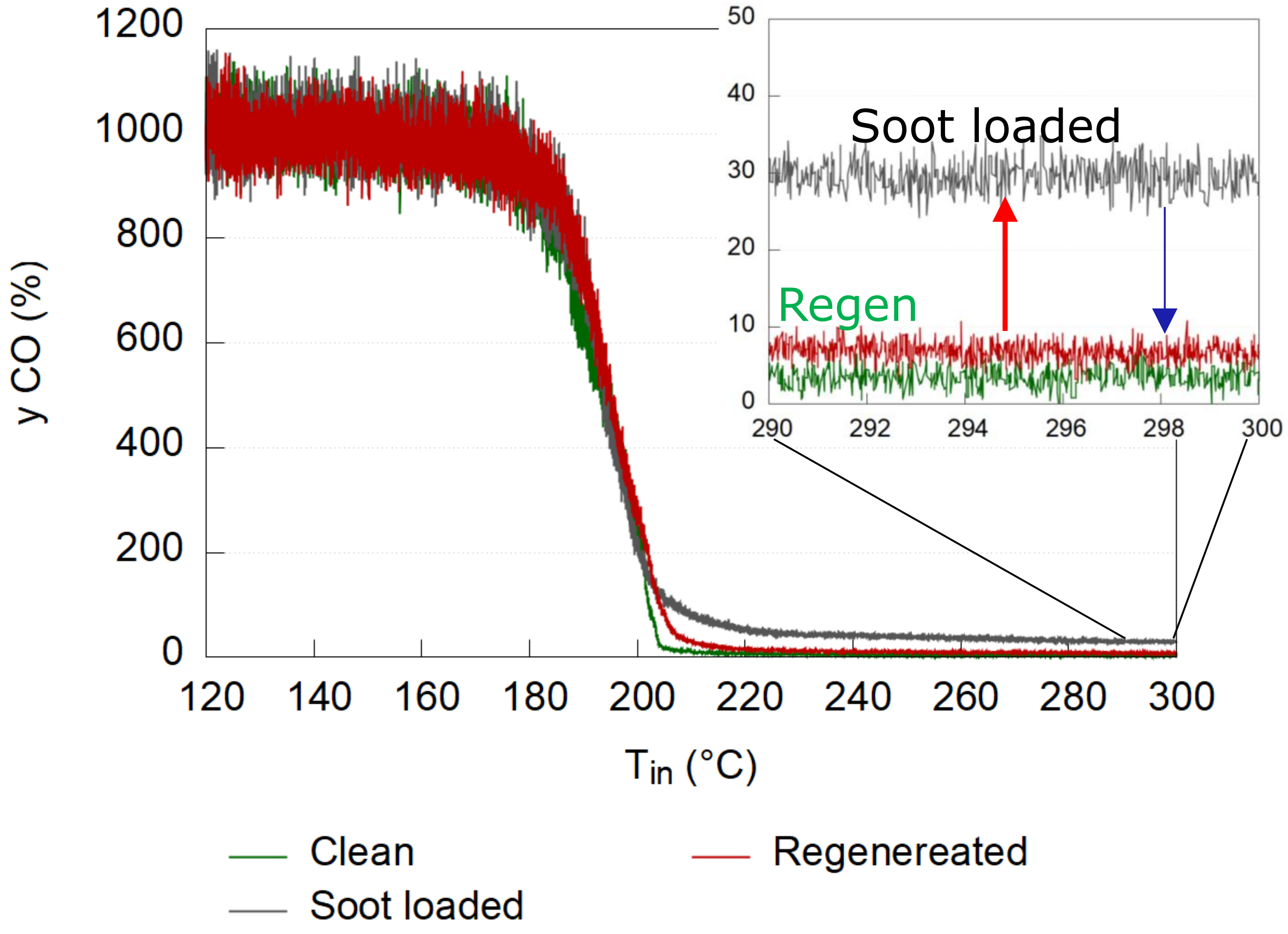
Impact of soot on CO light-off activity



On-wall sample

High gas flowrate (GHSV = 200 000 h^{-1})

1000 ppm CO + 5 % O_2



Increased slip of CO with soot at higher *T* (diffusion limitation)

Diffusion limitation decreased back after burning out soot at 600°C in air

How can we understand better the effect of the coating inside the filter?

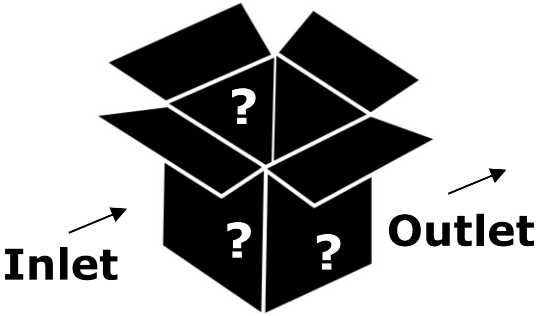
Why SPACI-MS?

Kinetic study and quantification of the exhausts along the monolith channel

Investigation on PBR

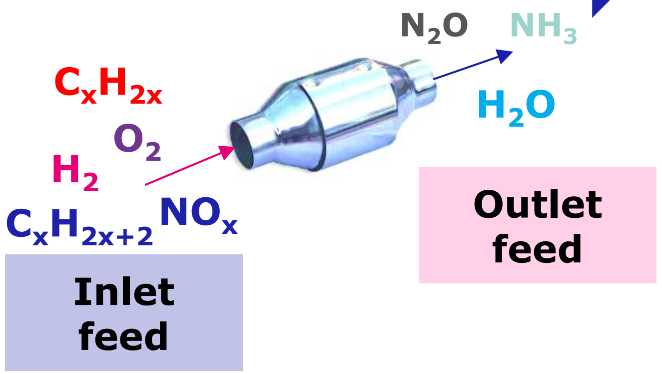
Intrinsic Kinetics and redox properties (Powders)

Monolith shows mixed chemical-diffusive regime (Structured catalyst)

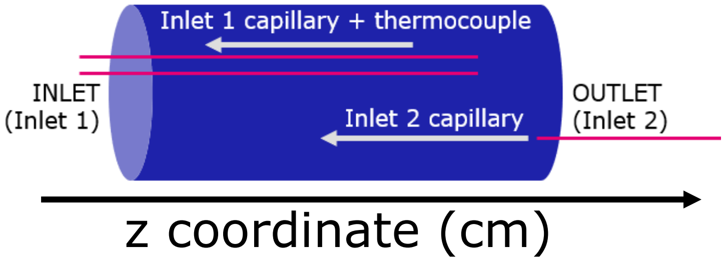


Traditional investigations focus on measuring inlet to outlet exhausts

What about understanding along the channel?



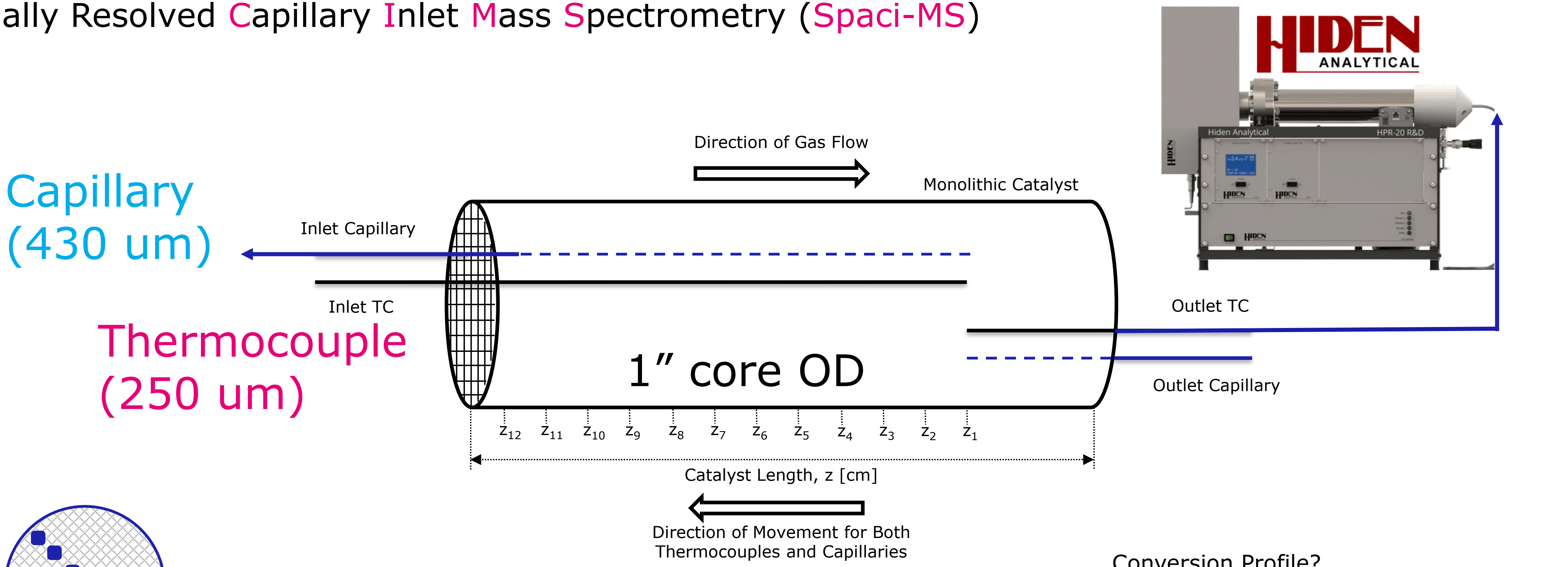
SPACI-MS

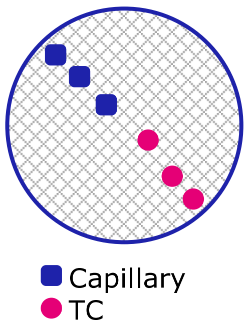


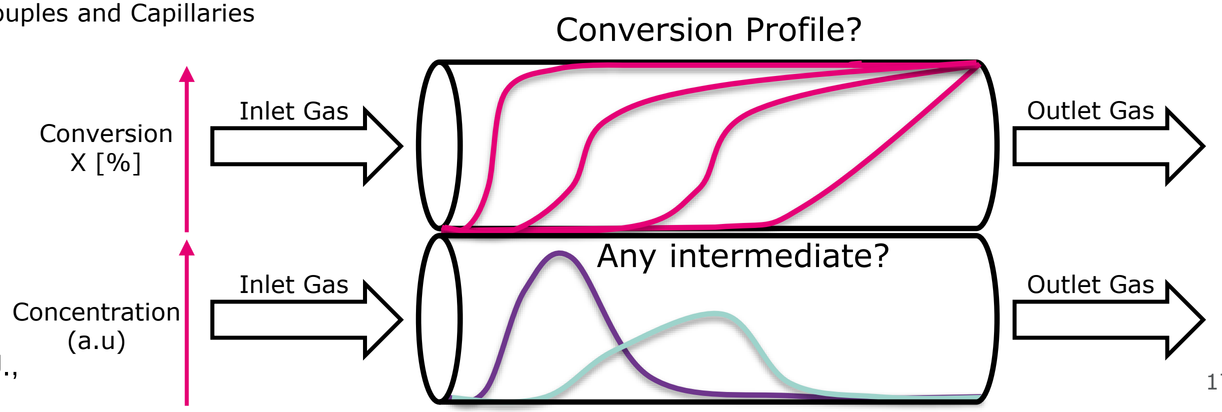
- Spatially resolve the development of products along the channels
- Real-scale conditions
- Gives info for modelling
- Transient and steady state data

An Introduction to the Spaci-MS Rig

Spatially Resolved Capillary Inlet Mass Spectrometry (Spaci-MS)







Partridge W.P., Storey J.M.E., Lewis S.A., Smithwick R.W., DeVault G.L., Cunningham M.J., Currier N.W. & Yonushonis T .M. Journal of Fuels & Lubricants, 109, 2983-2991 (2000).

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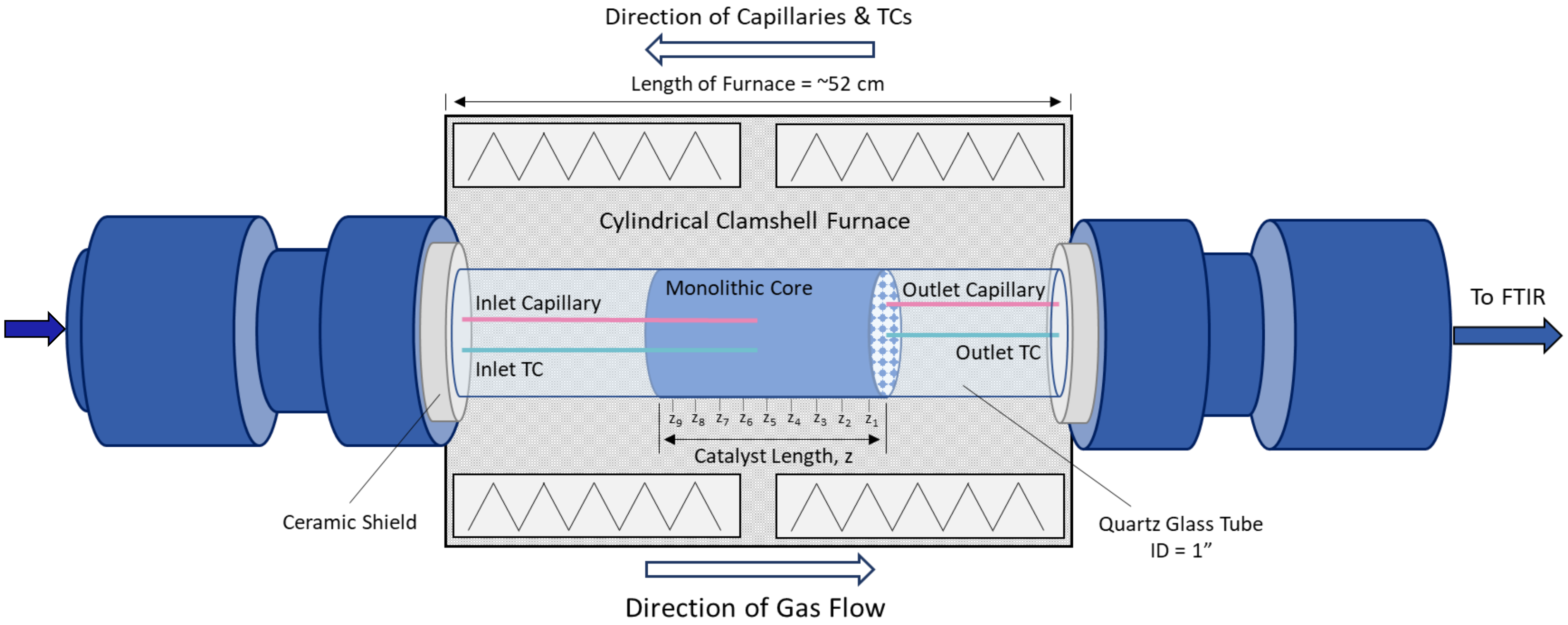

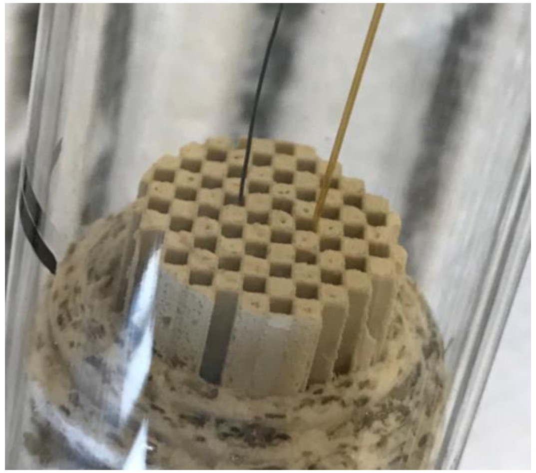

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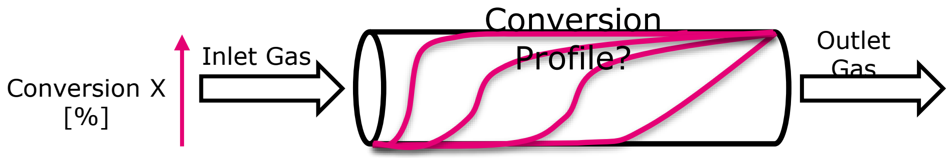

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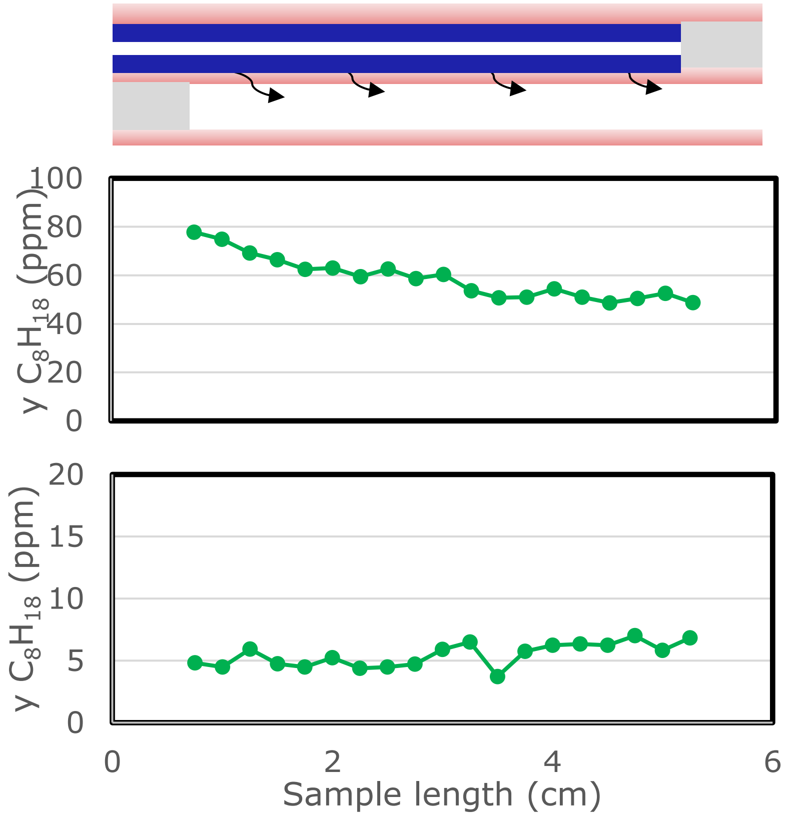
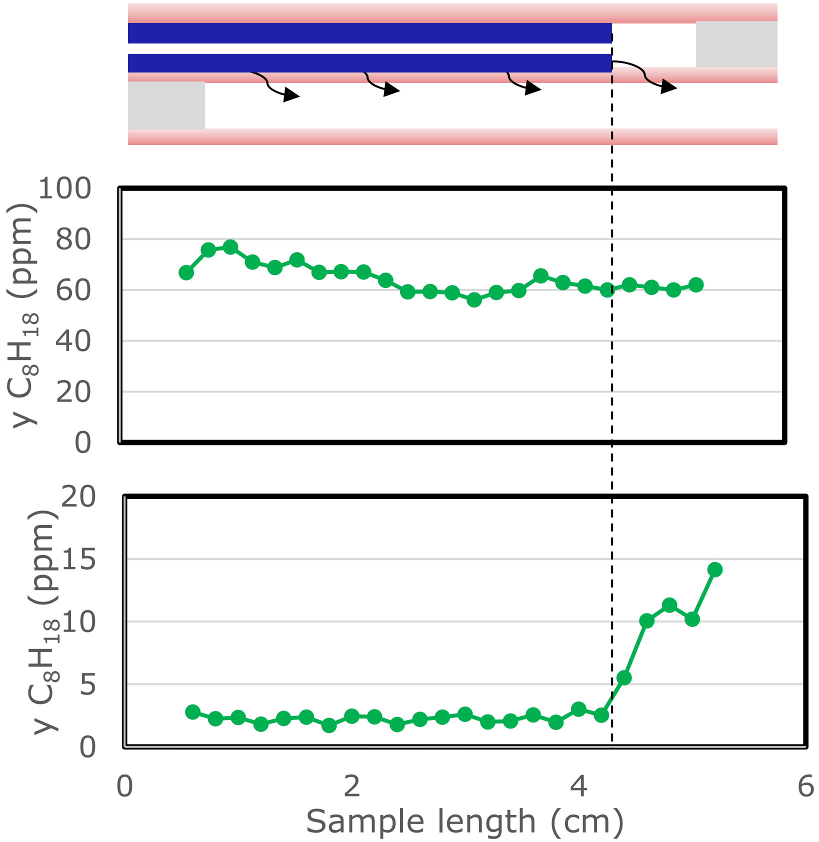
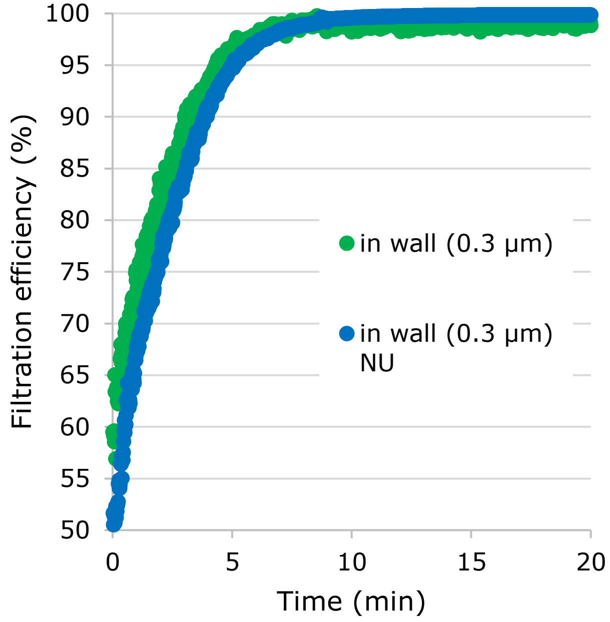
Some feature of Spaci for filters: measure on partial coating







- Provided understanding on the coating length
- Shows clearly how non-uniform coating allow slips from outlet channel
- What about the soot loading on different size?

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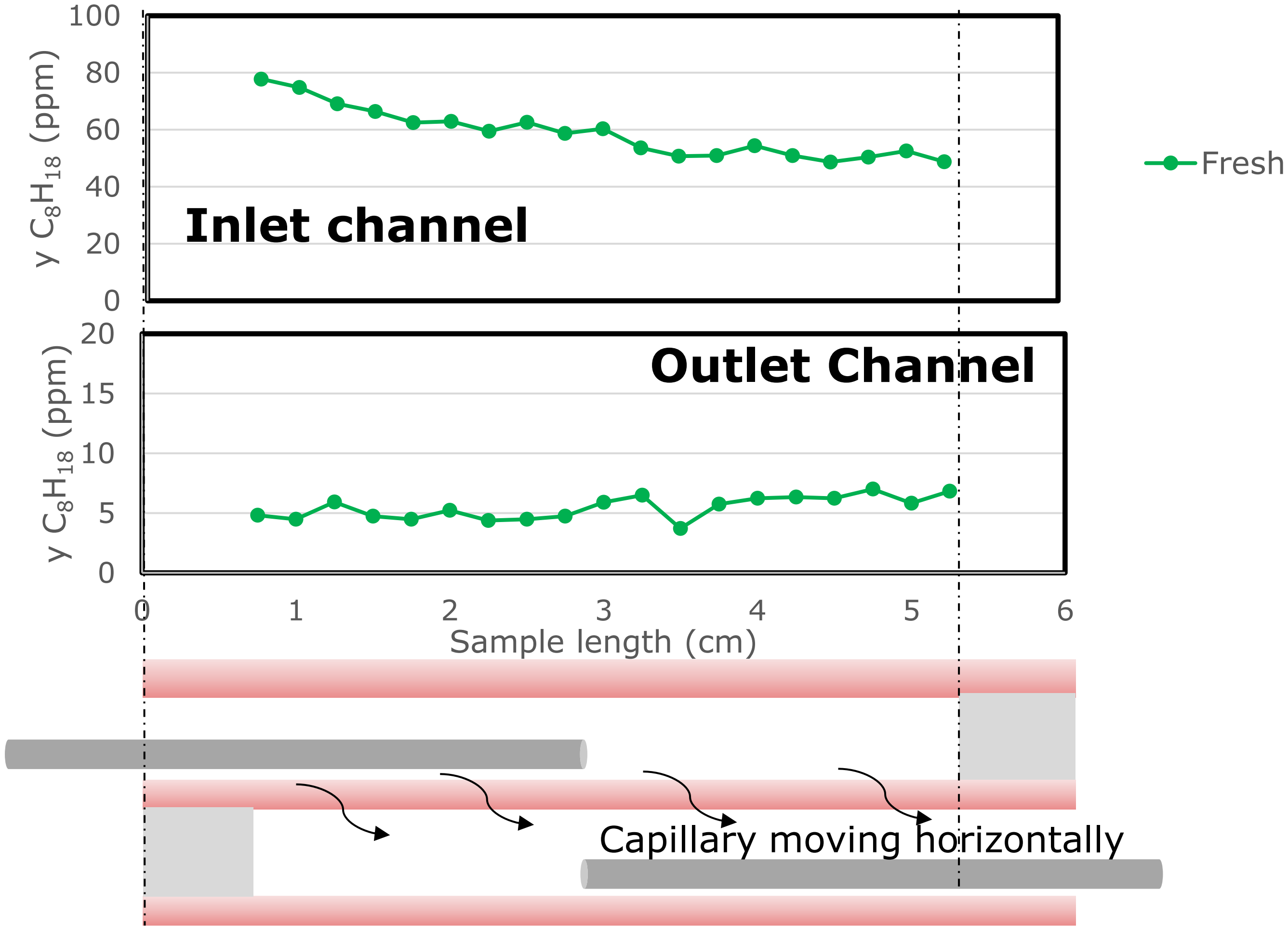
Effect of soot deposition on Particulate filters

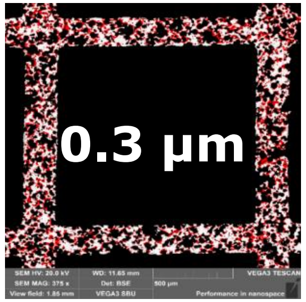
Helps understands how soot is acting

SV = 100 000 h^{-1}, C8H18 = 100 ppm, O_2 = 5 %, Ar

In-wall coating - 0.5%Pt/alumina



- In-wall coating shows completion of reaction along outlet channel



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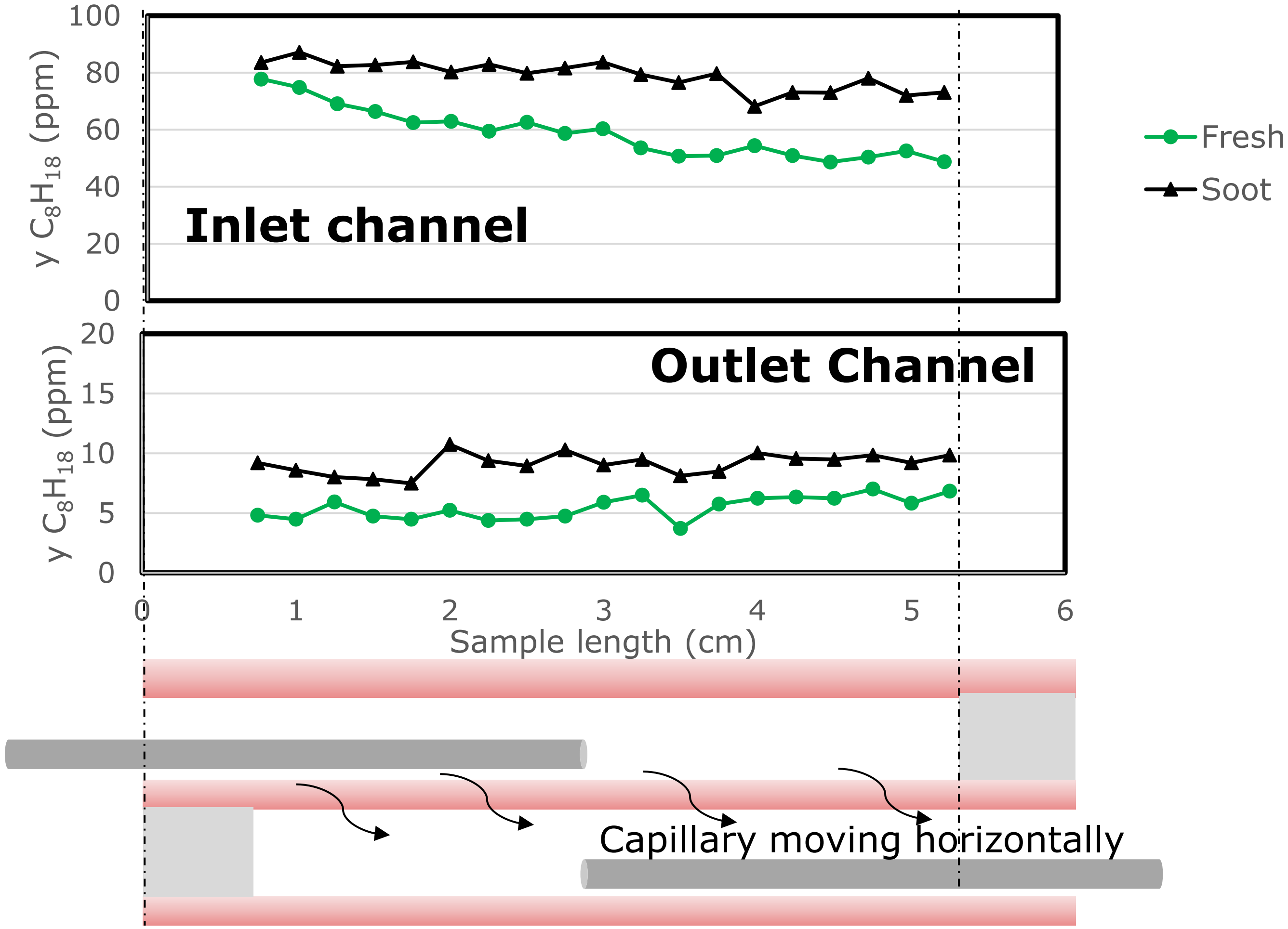
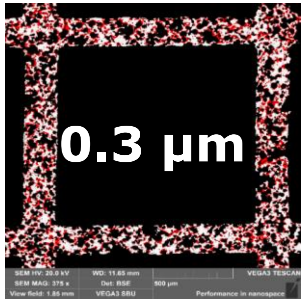


- In-wall coating shows completion of reaction along outlet channel
- When soot loaded, activity lowers along both channels



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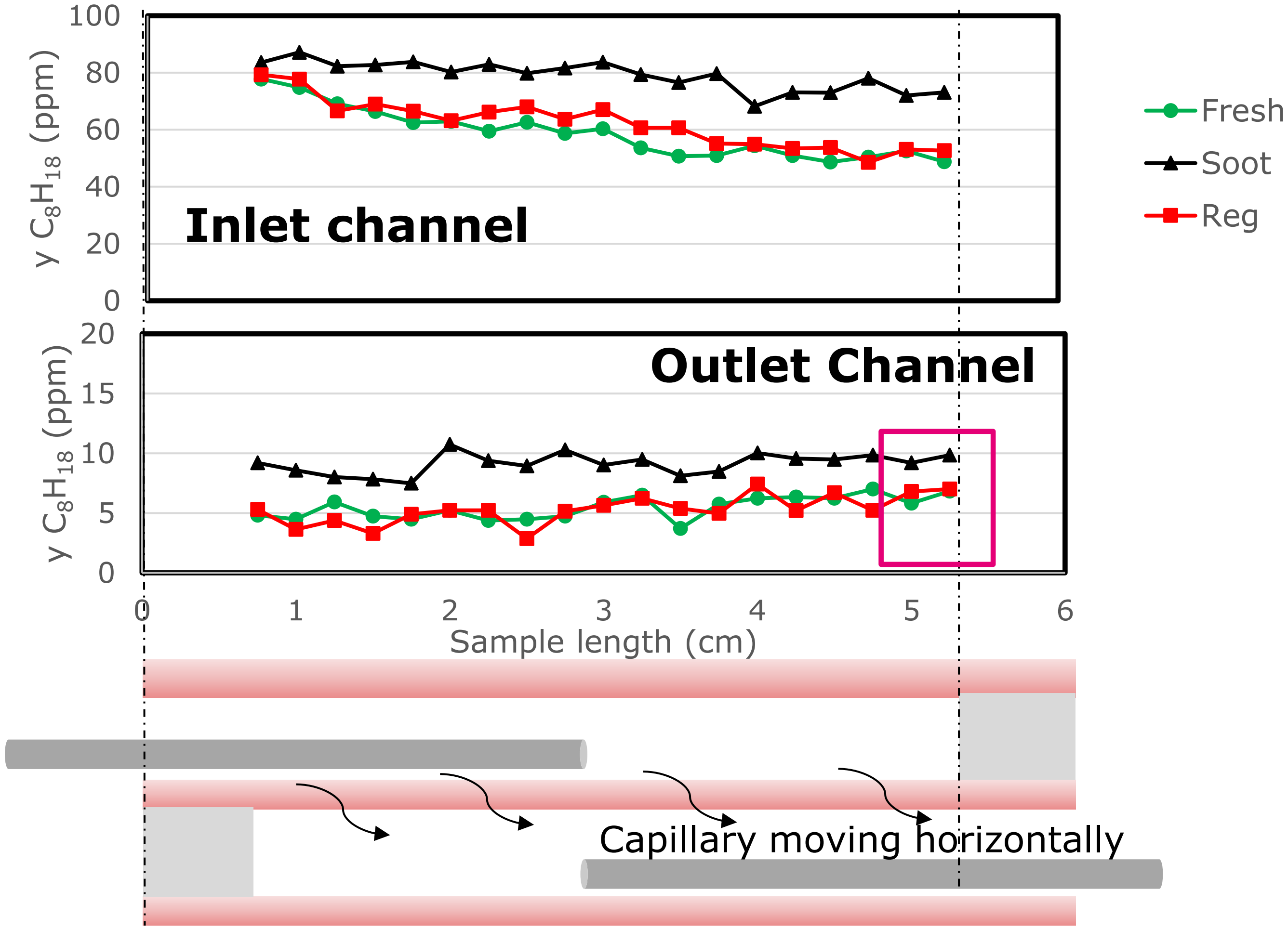
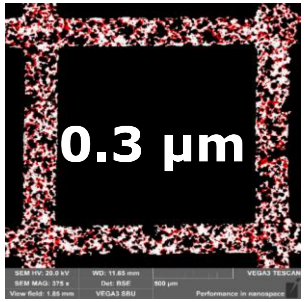


- In-wall coating shows completion of reaction along outlet channel
- When soot loaded, activity lowers along both channels
- Regeneration shows full recovery of activity



JM

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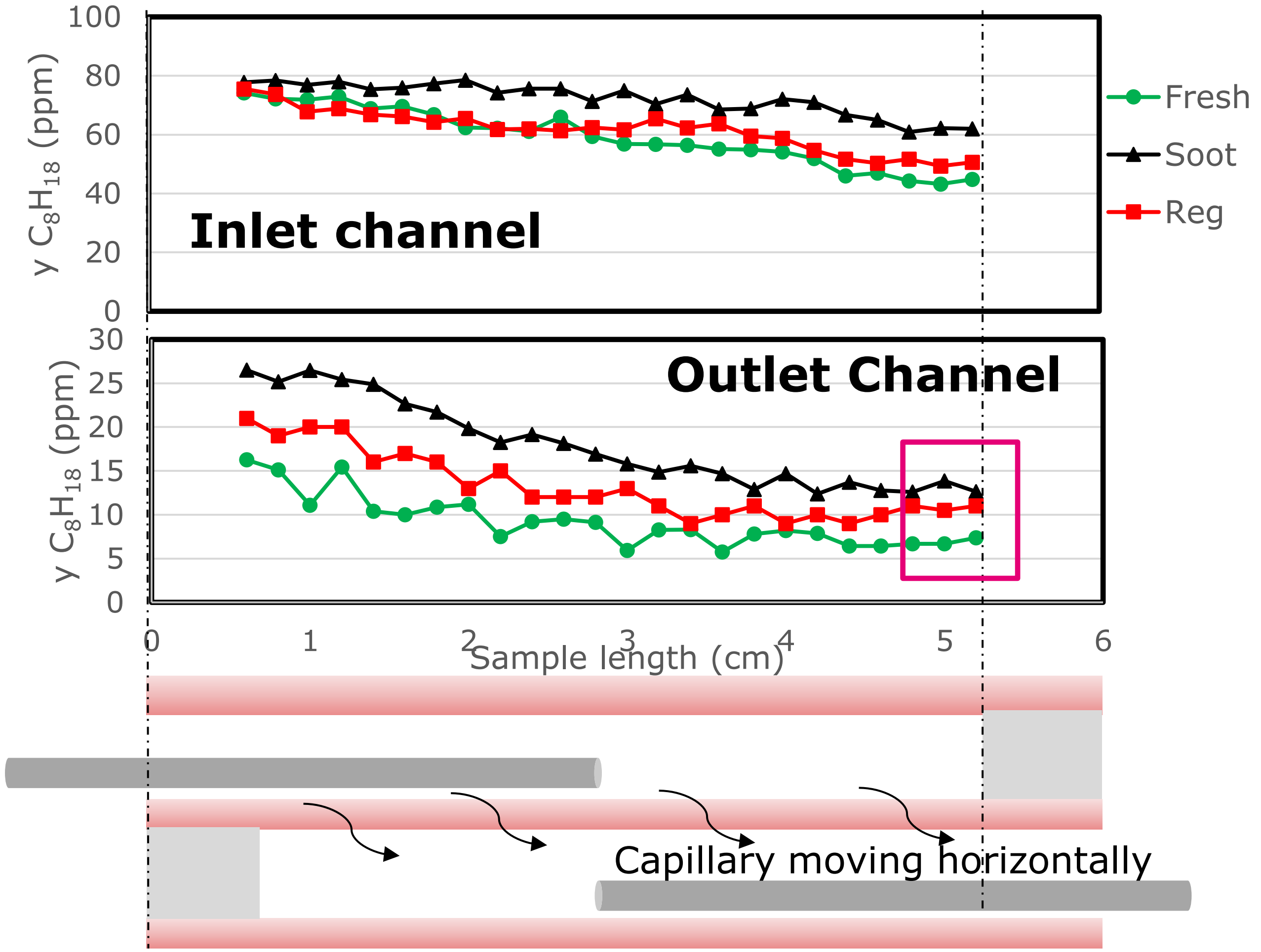
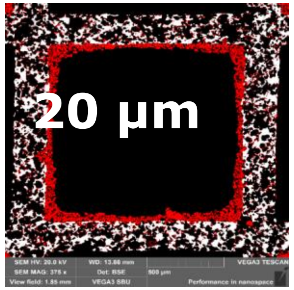


- On-wall coating shows higher HC slip
- When soot loaded, less HC consumption
- Regeneration shows acceptable recovery



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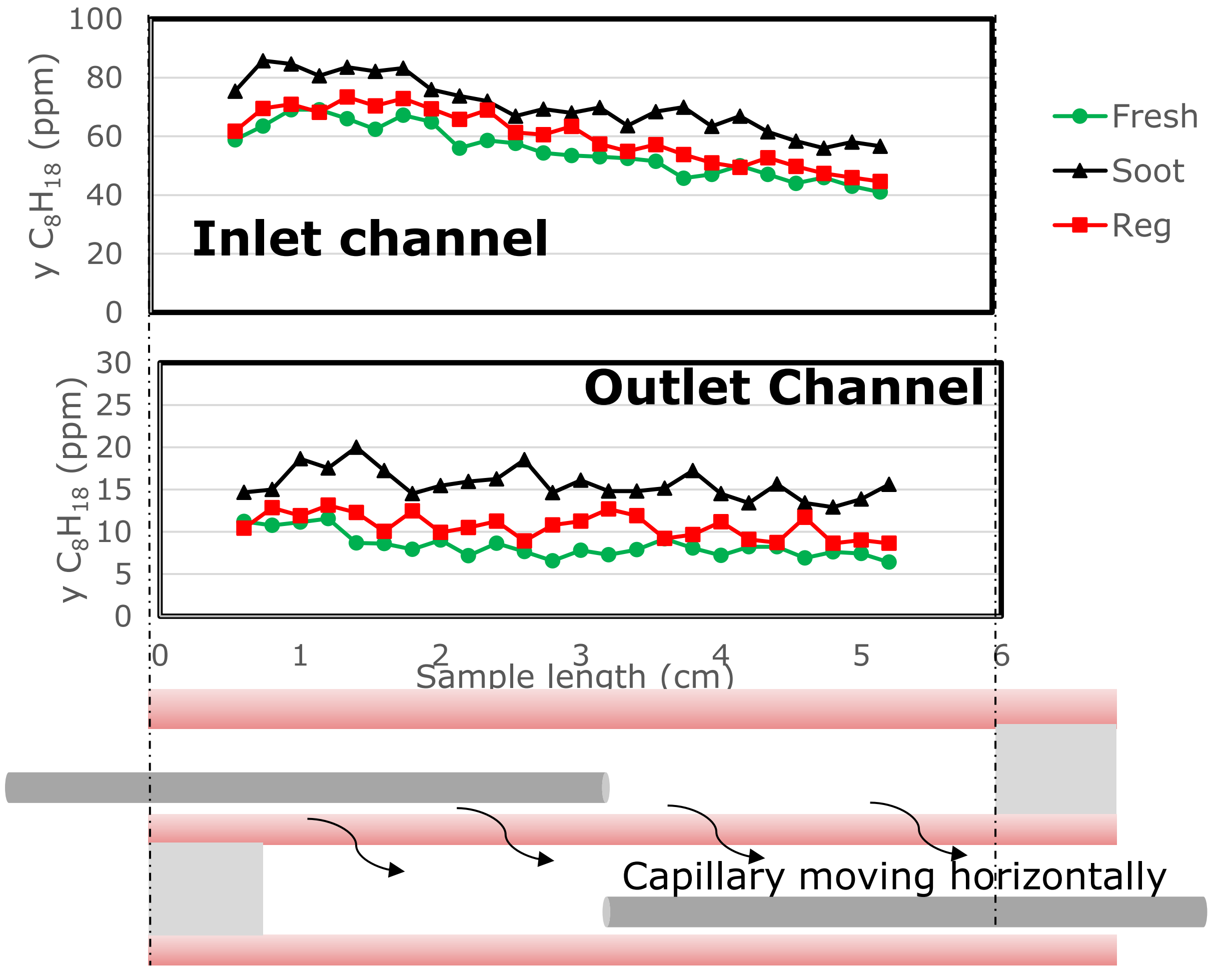
Effect of soot deposition on Particulate filters

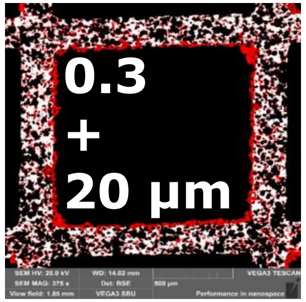
Helps understands how soot is acting

SV = 100 000 h^{-1}, C8H18 = 100 ppm, O_2 = 5 %, Ar

In+on-wall coating - 0.5%Pt/alumina



- Combined coating showed similar slips as on-wall
- When soot loaded, less HC consumption
- Regeneration shows important recovery



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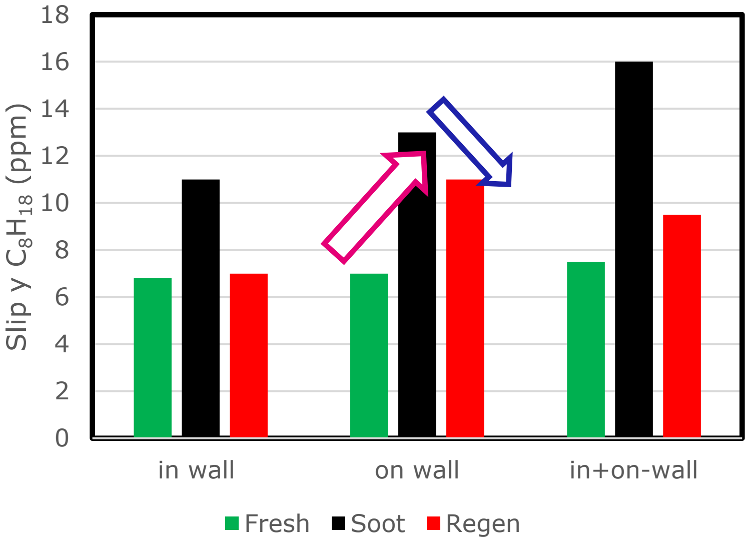
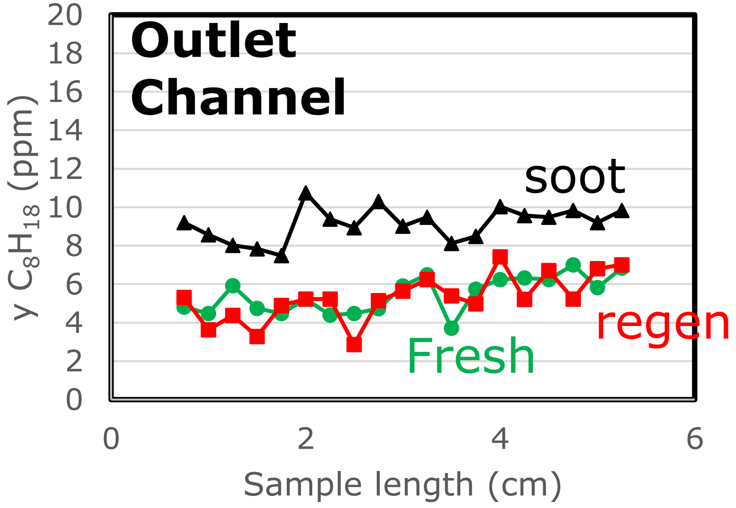
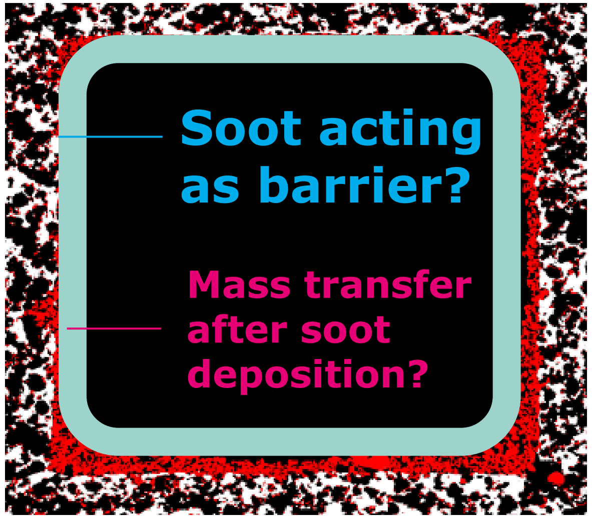
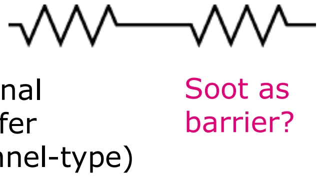
Summary

- SPACI-MS data powerful as tool to visualise deactivation on filters









What’s next
- Model Spaci results
- Decouple activity and external limitations

- Regeneration showed important catalytic activity recovery
- Soot possibly acting as additional external limitations
- Modelling can help decouple kinetics from external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SIMULATED CO LIGHT-OFF CURVES WITH SOOT

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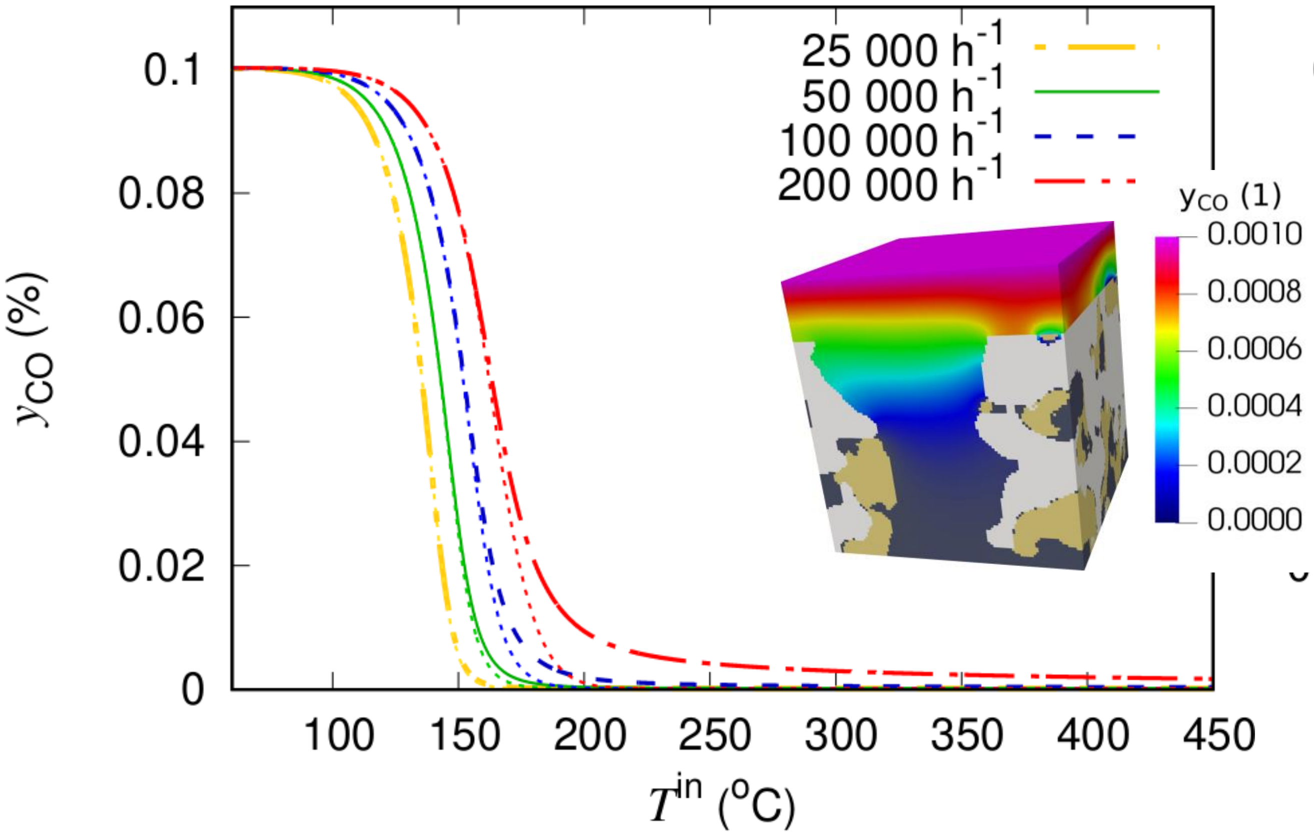
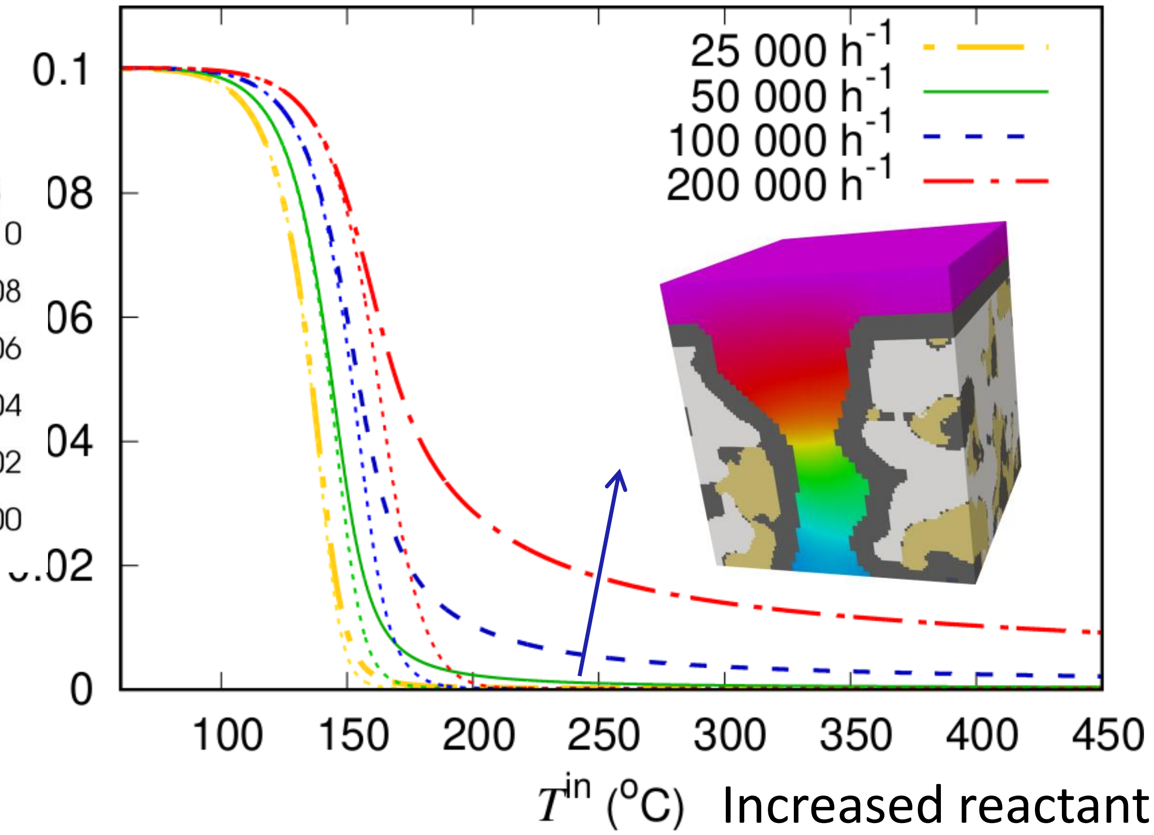
Initial diffusion limitation in **free pores**

Increased diffusion limitation due to **deposited soot**





Increased reactant slip with soot at high flow rates

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