FACULTY OF ENGINEERING AND ARCHITECTURE

DEPARTMENT OF MATERIALS, TEXTILES AND CHEMICAL ENGINEERING
LABORATORY FOR CHEMICAL TECHNOLOGY (LCT)

Micro Teaching

ESR 10

Chemical recycling of plastic waste by reactor and catalyst engineering

Bahman Goshayeshi
9 September 2020

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Prof. dr. Angeliki Lemonidou

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Overview

- Background
- Plastic recycling
- Pilot plant steam cracking
- Vortex reactors

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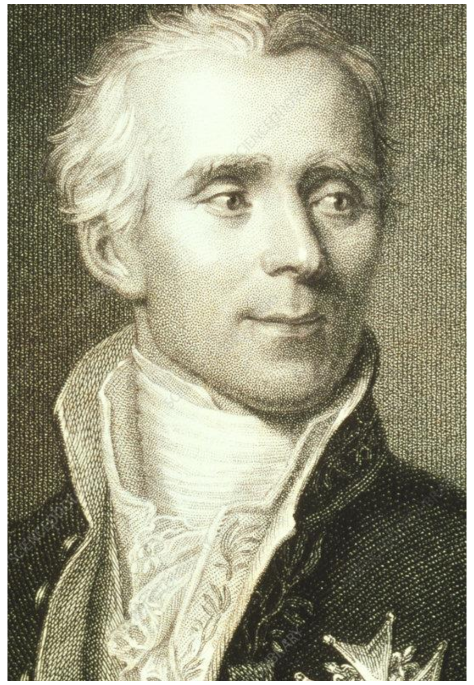
C-PlaNeT
CIRCULAR PLASTICS NETWORK FOR TRAINING

Background

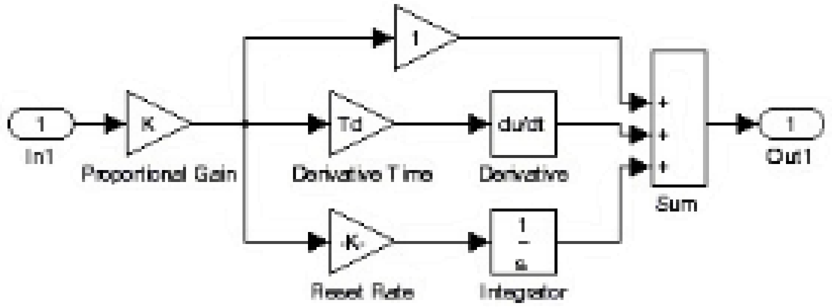
Background

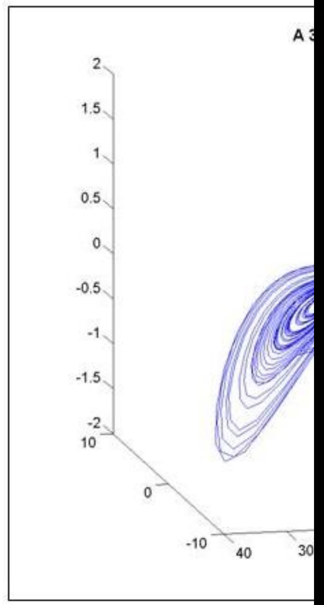
Master’s degree in chemical engineering

- Process control and simulation



Pierre-Simon Laplace





Background

Master's thesis:

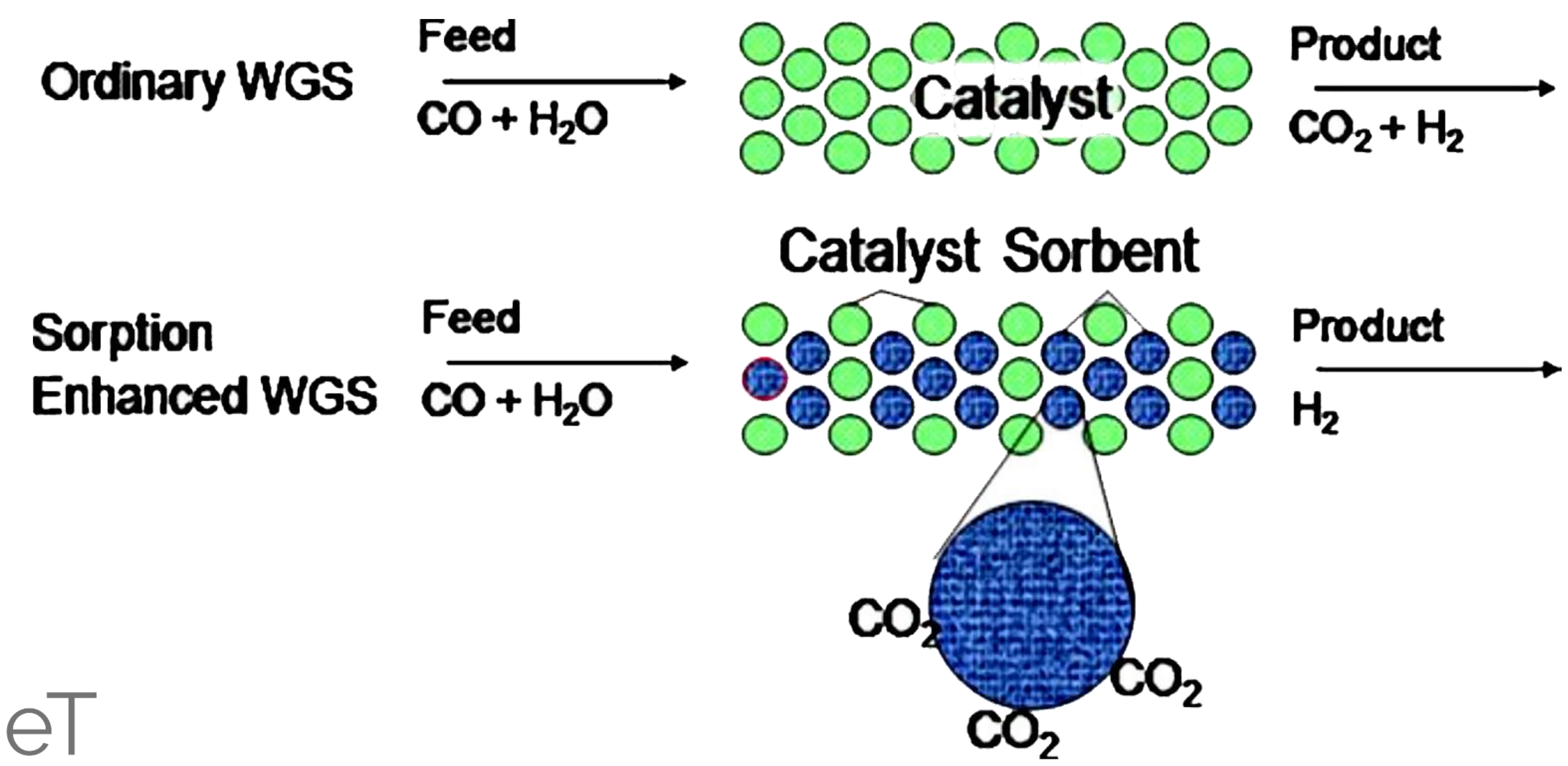
Dynamic modeling and simulation of integrated pre-combustion CO_2 capture based on SEWGS technology in natural gas combined cycle

Sorption Enhanced Water Gas Shift (SEWGS)

Water gas shift reaction : $\mathrm{CO}+\mathrm{H_2O} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2}$ $\quad -\Delta H^0_{298} = 41 kJ/mol$

Advantages:

- **Process simplification**
- **High H_2 and CO_2 recovery**
- **Better heat integration**
- **Lower steam usage**



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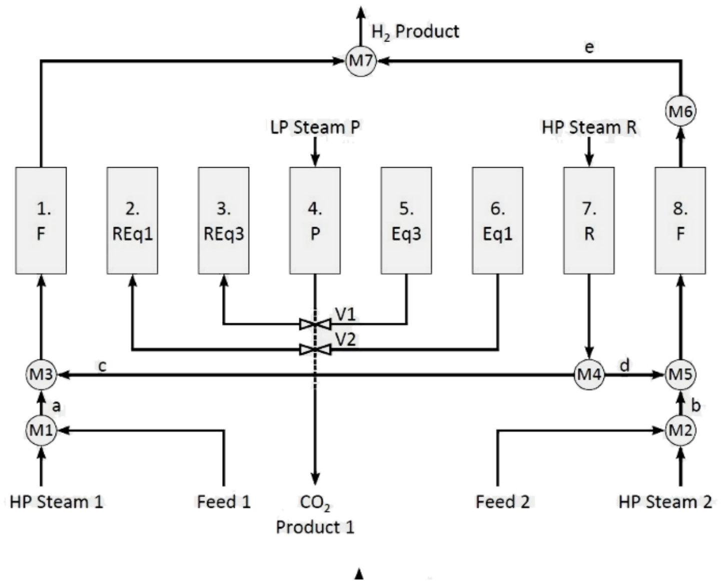
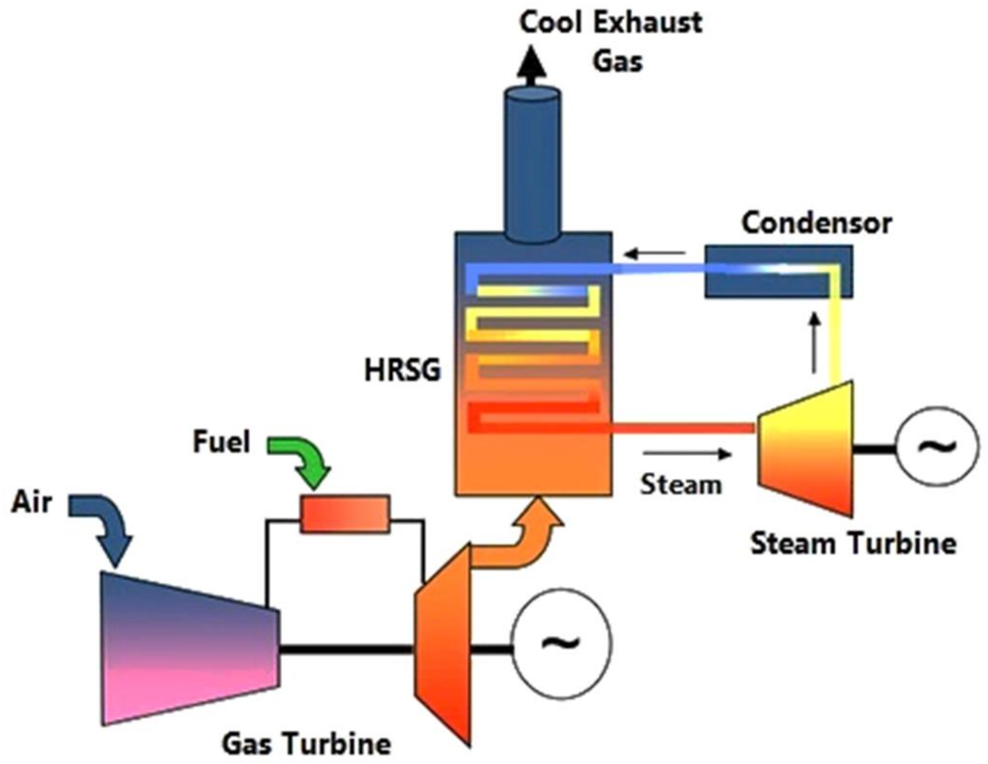
Background



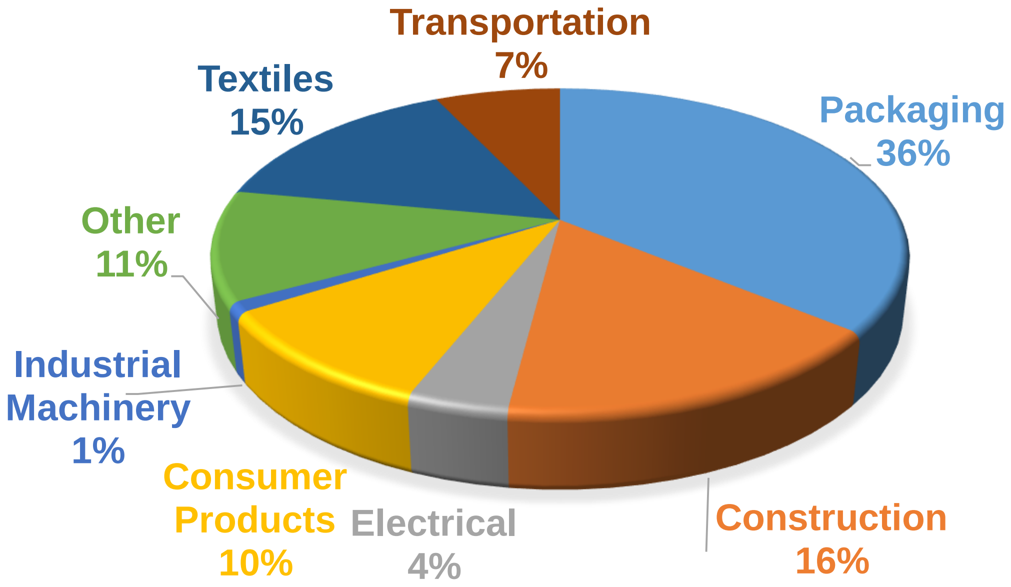


Storage

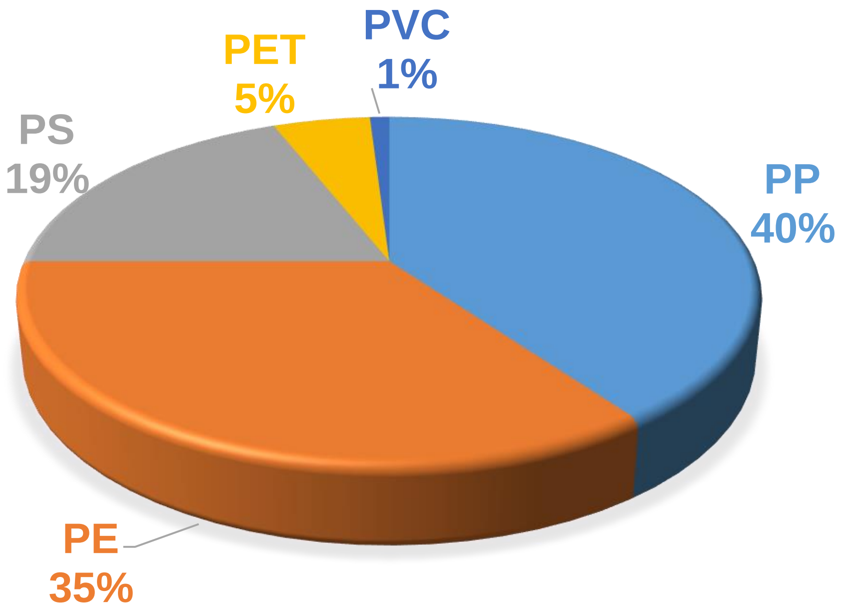
Plastic recycling

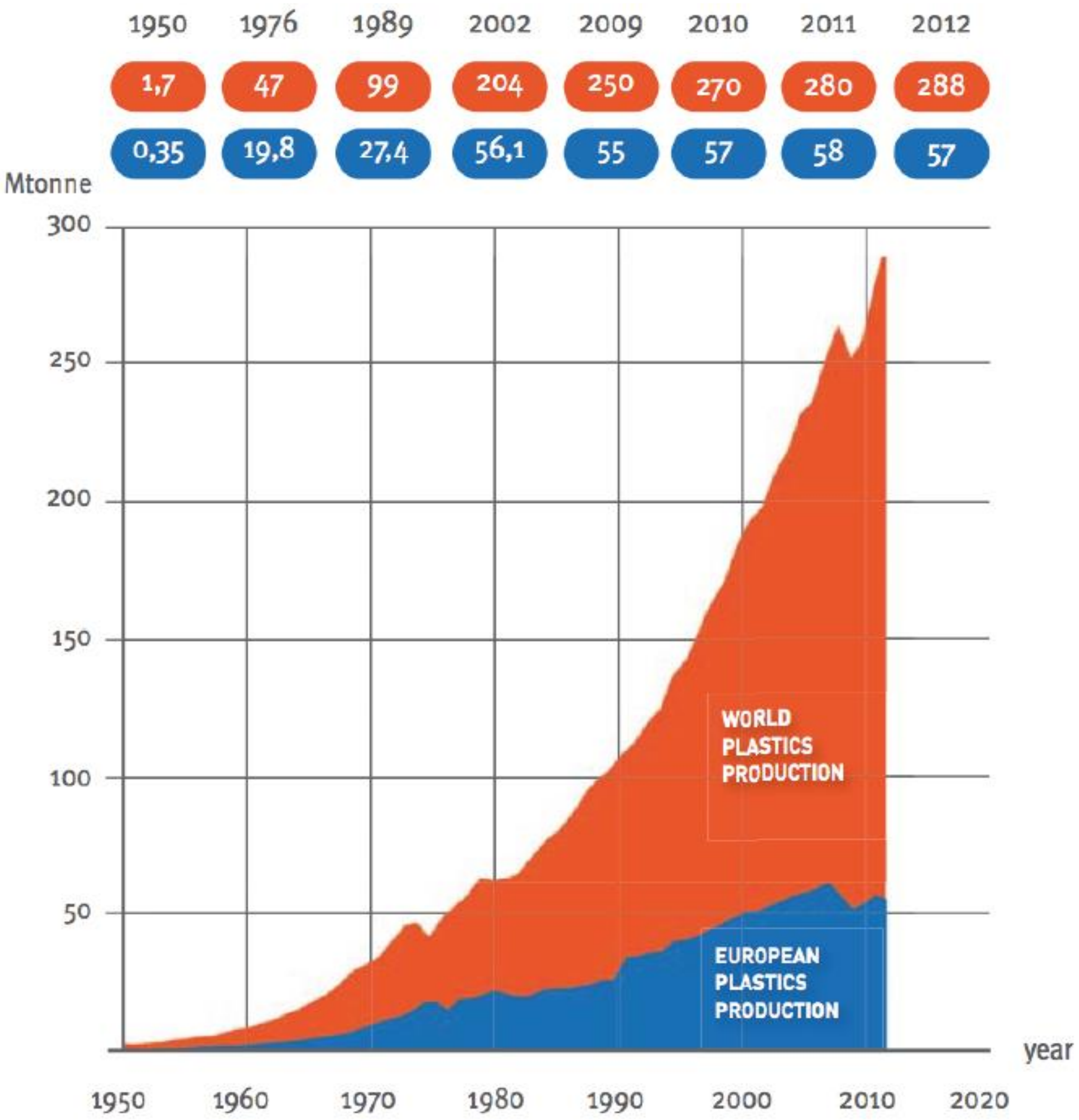
Solid plastic waste

- **Plastic Consumption**
  Europe, USA, China, India
  2002-2014



- **Plastic Waste Composition (wt.%)**
  local material recovery facility
  Bizkaia, Spain





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The plastic waste problem

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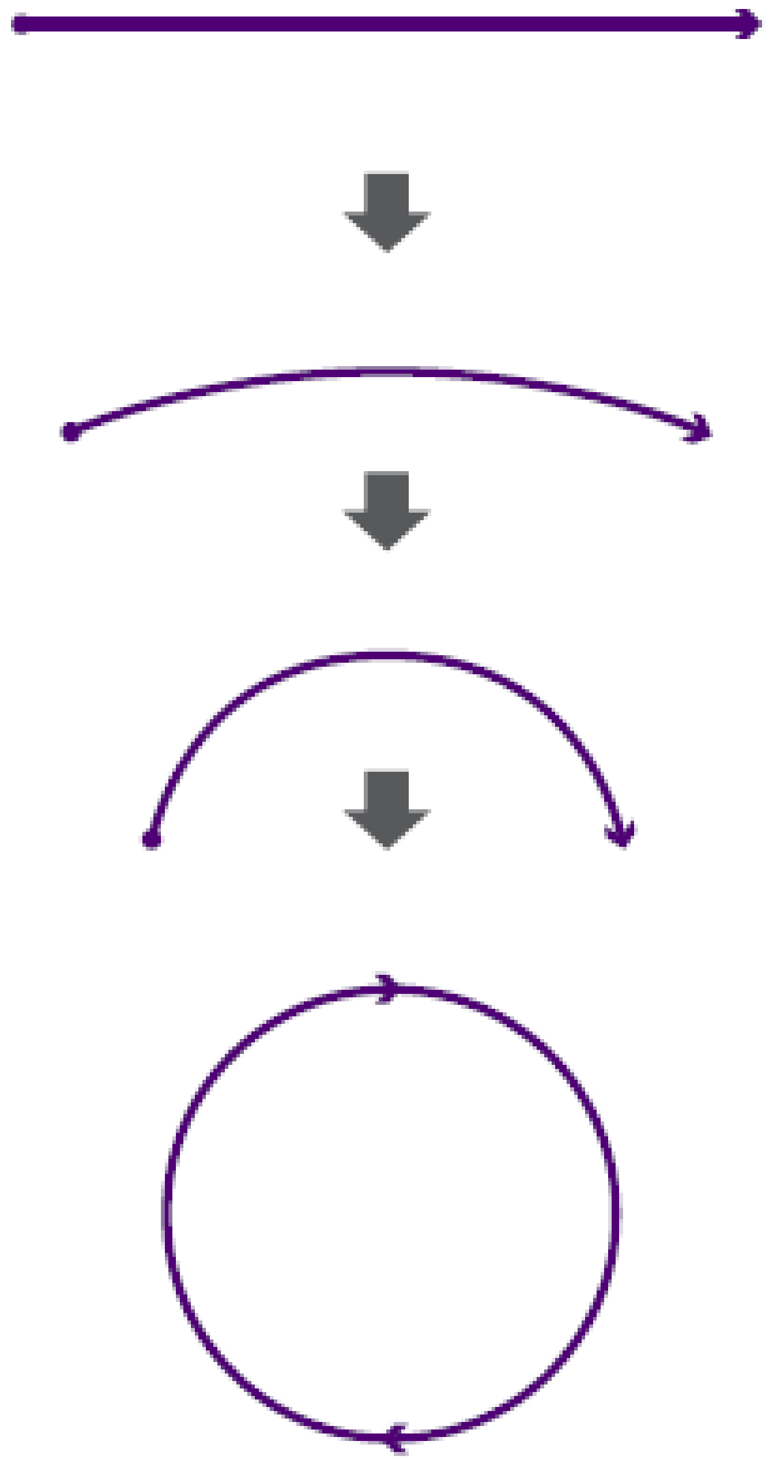
Times are changing

- ❖ A circular economy helps enable ideal resource recovery
- ❖ Decrease dependency on oil and gas



Linear model

- Disposal of molecules at end of lifecycle (landfill, etc.)
- Unmanaged CO_2 emissions

Increasingly “bent” model

- Partially renewable feedstocks and energy
- Some level of product reuse and recycling
- Energy recovery

Circular model (total recovery)

- Full reuse of molecules – with or without modifications of molecular bonds
- Climate neutrality

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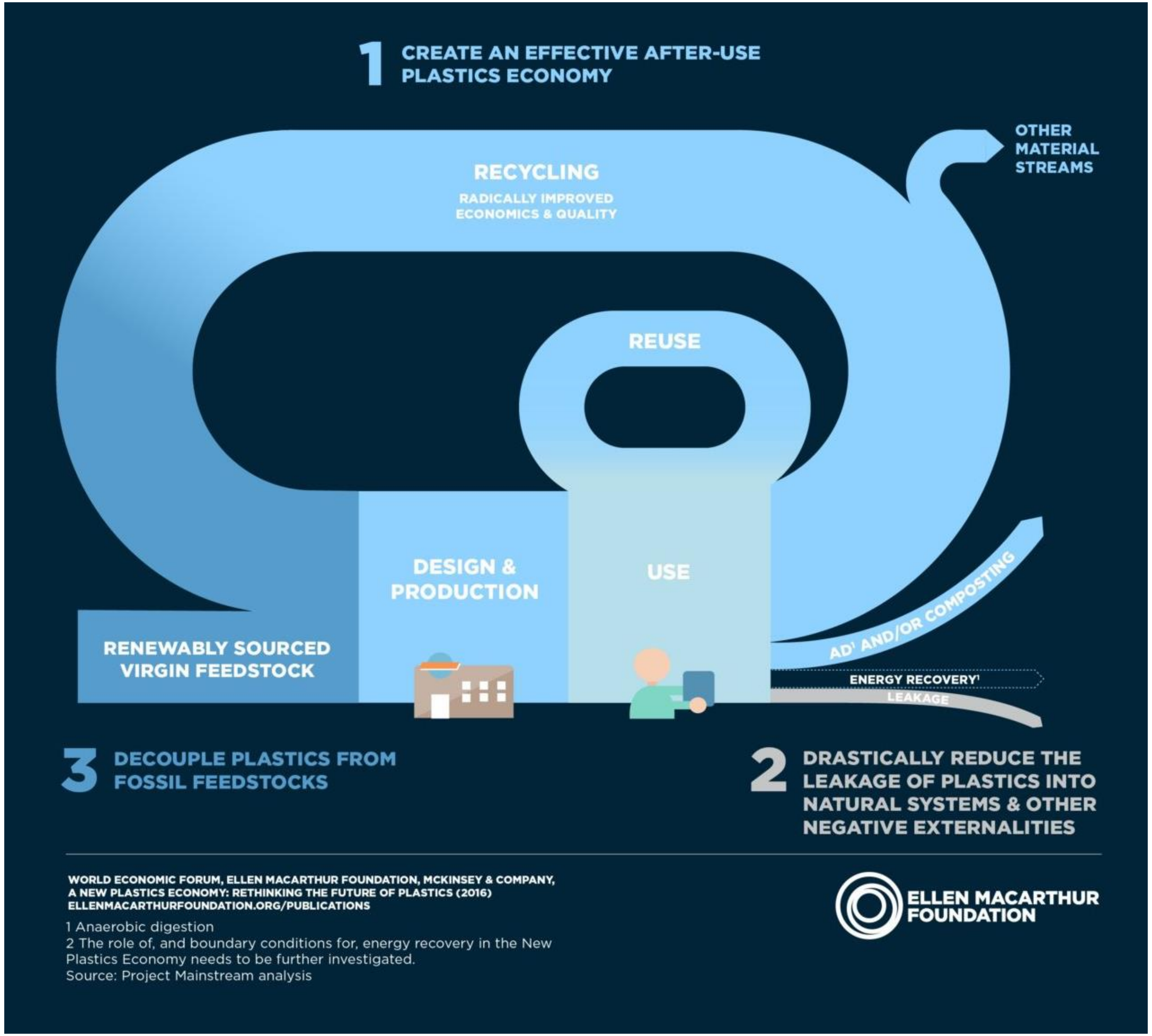
The new plastics economy



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Always look at the global recycling picture

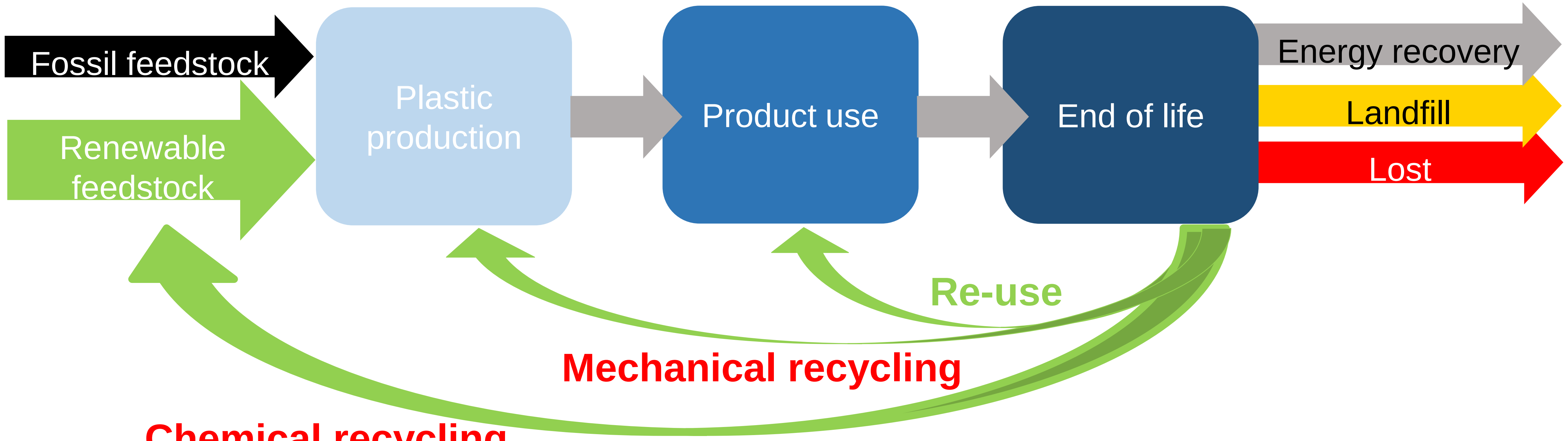
The best strategy will be a combined strategy:

1. Mechanical recycling

- Collection, sorting, washing, grinding and reprocessing
- Not possible for all waste streams

2. Thermochemical recycling (pyrolysis and gasification)

- Conversion into base chemicals, similar to virgin materials
- No extra risk for (food) safety (similar as for virgin materials)



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Pyrolysis of plastic waste

Thermal degradation of long-chain polymers

– **Catalytic pyrolysis**
  - With presence of catalyst
– **Thermal pyrolysis**
  - Without presence of catalyst

Products:

- Liquids (condensable vapors or oil)
- Solids (char)
- Gases (non-condensables)

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Why did Chemical Recycling not fly in 90’s?

- The main **challenge** for chemical recycling is:
  - Stable and continuous feed supply
  - Making a profit => simpler (less equipment) is better
  - Corrosion, because of poor separation
  - Finding the most suitable reactor technology with maximum selectivity.
  - Optimizing the technology in a way that it is least affected by changing process conditions and feedstock variation.

Facilities

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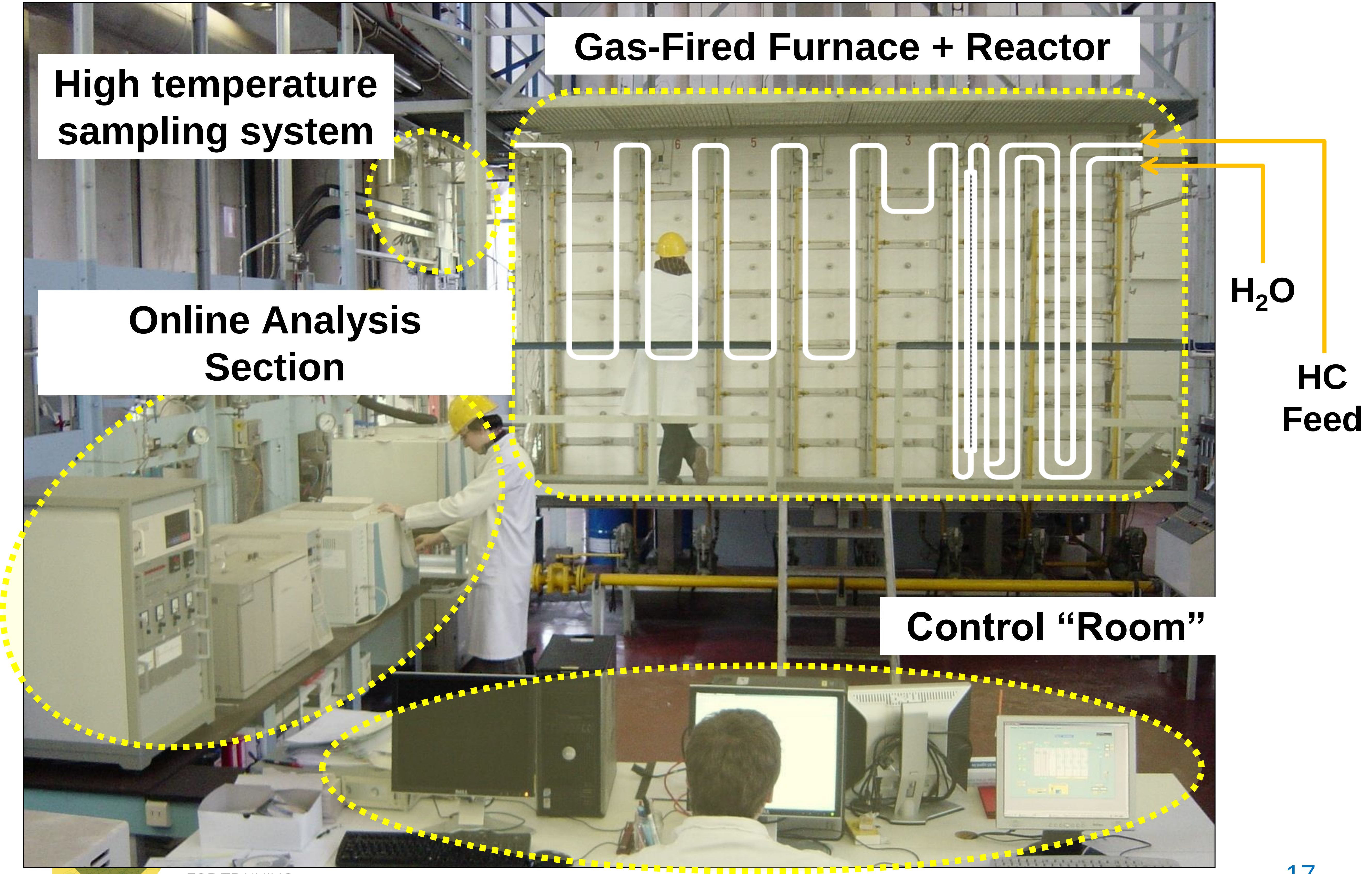
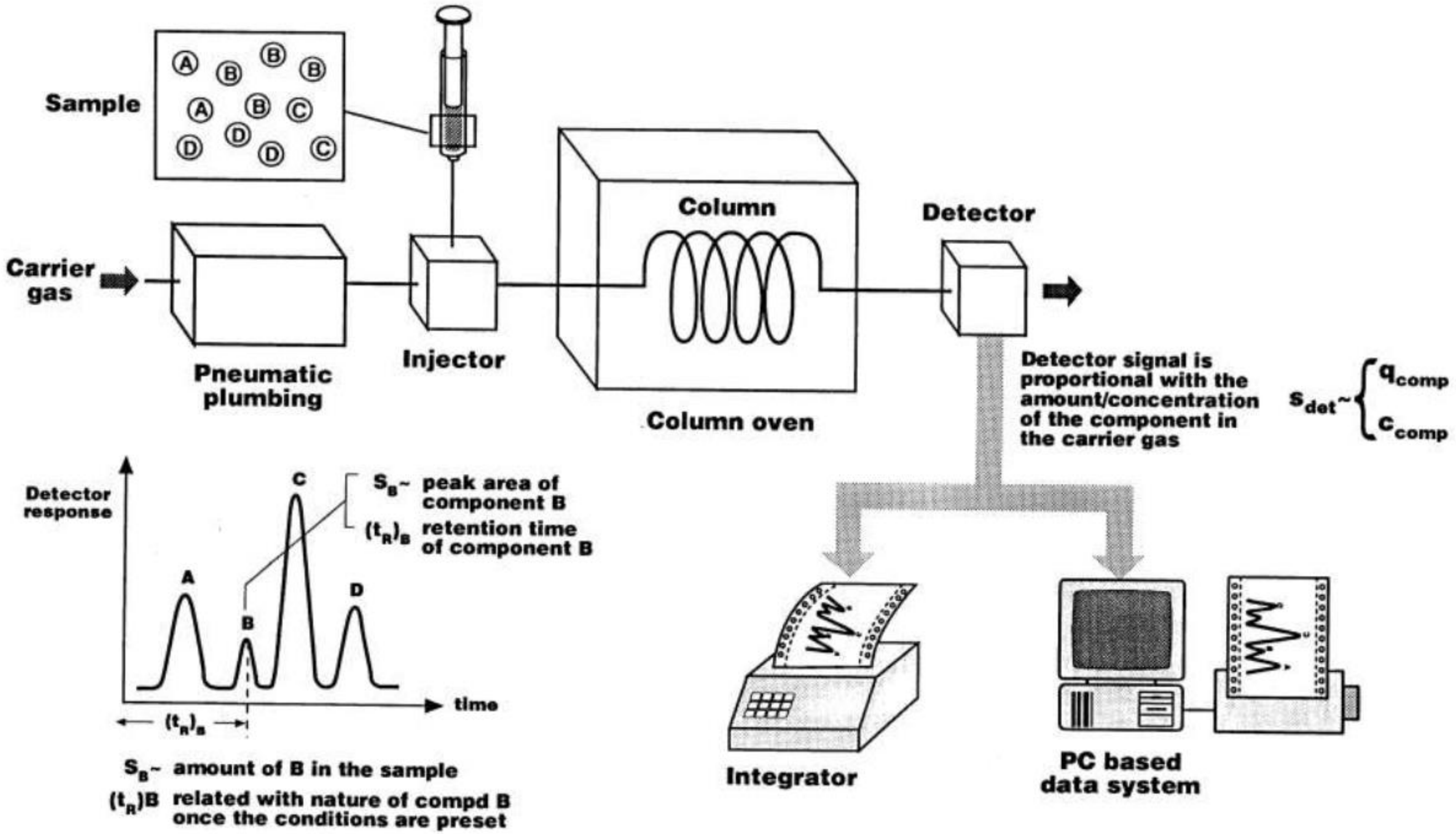
Pilot plant steam cracking

Steam cracking pilot plant



What is chromatography?



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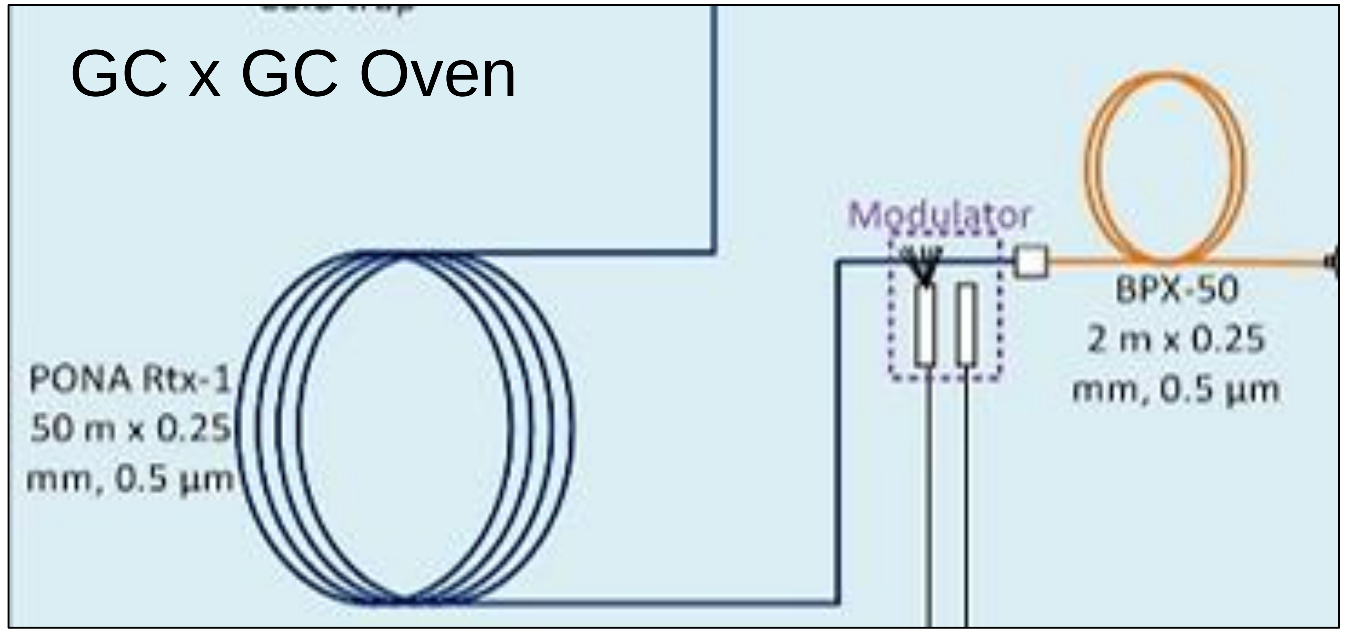
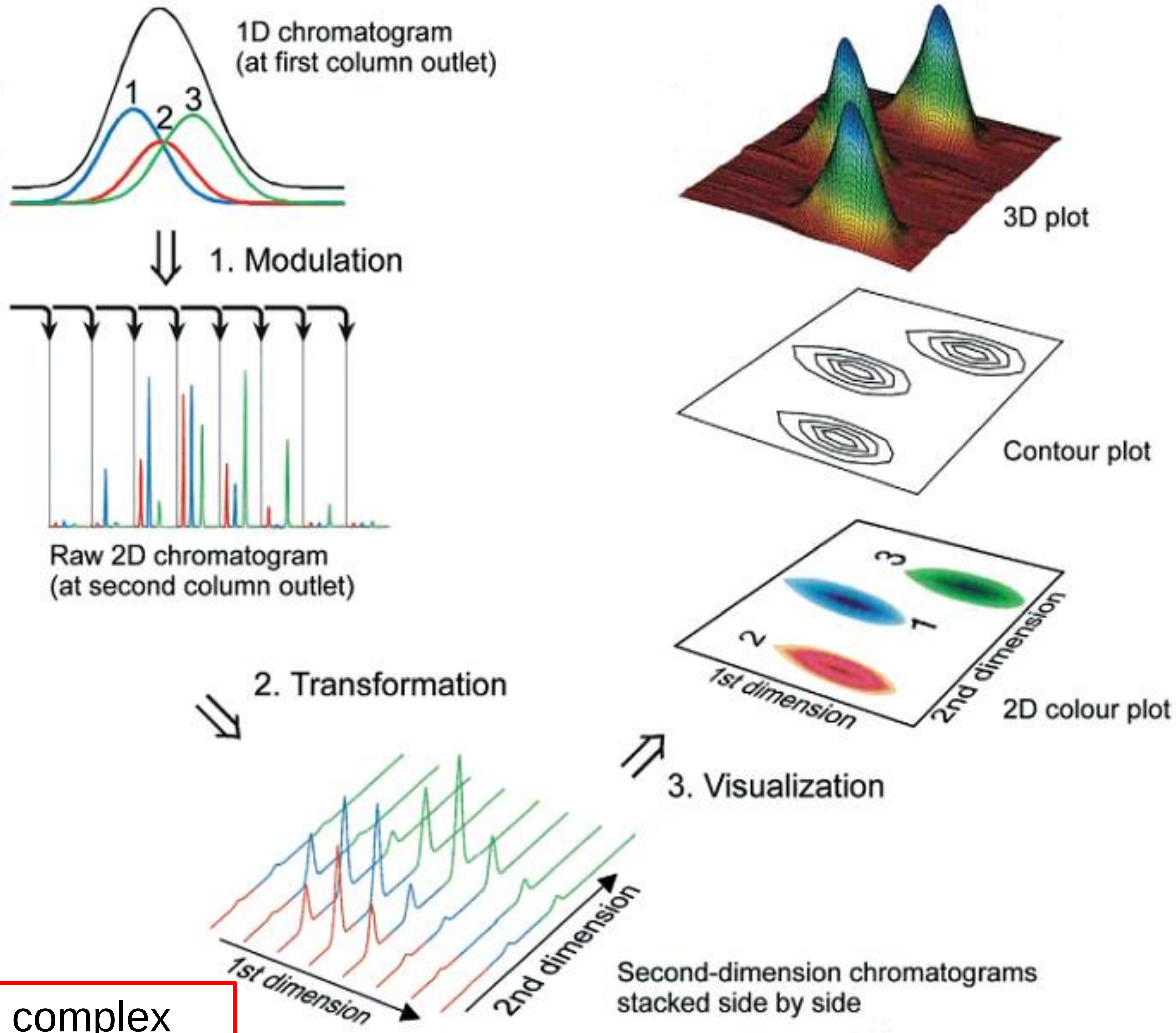
GC x GC Principle



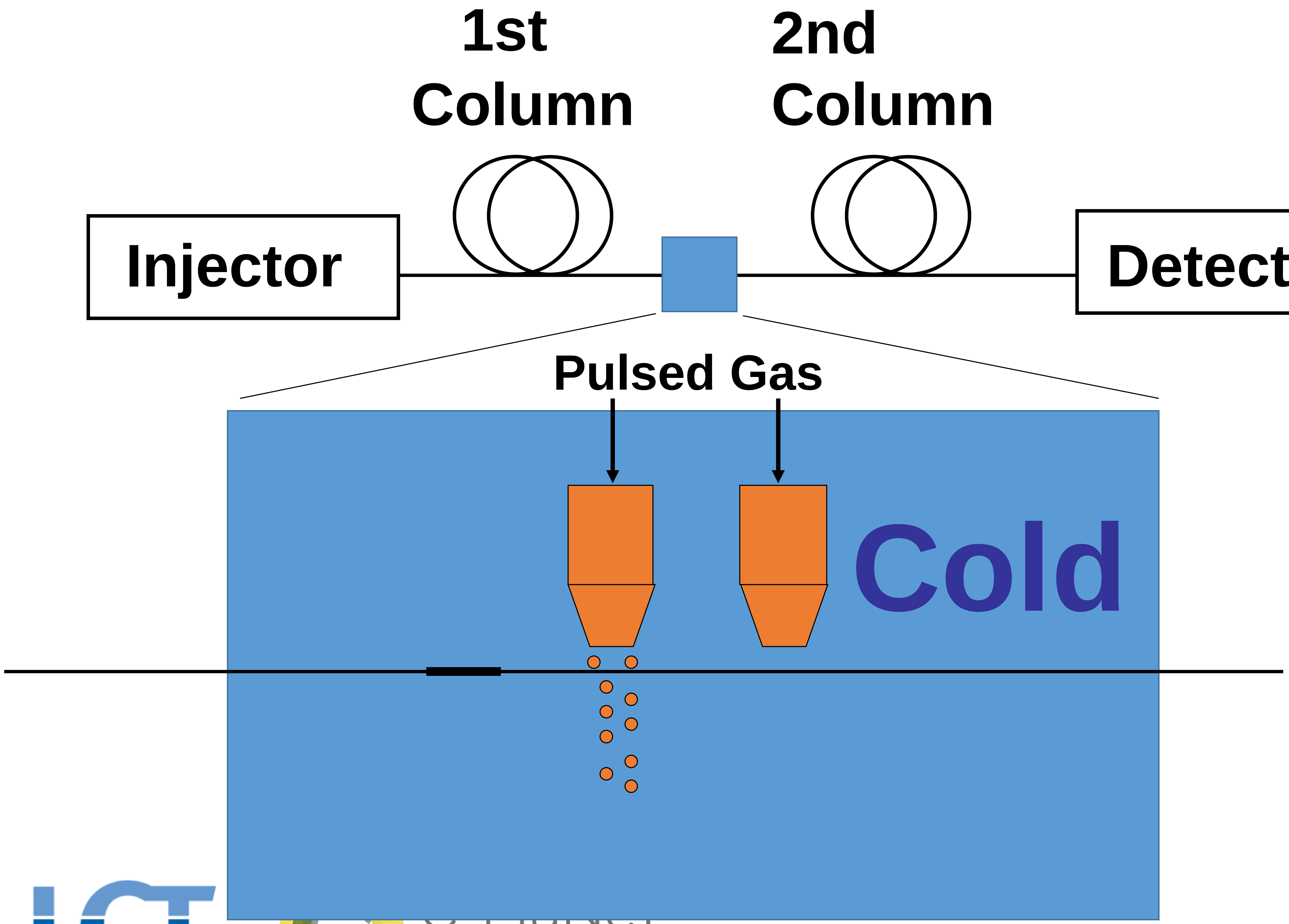
Liquid CO_2

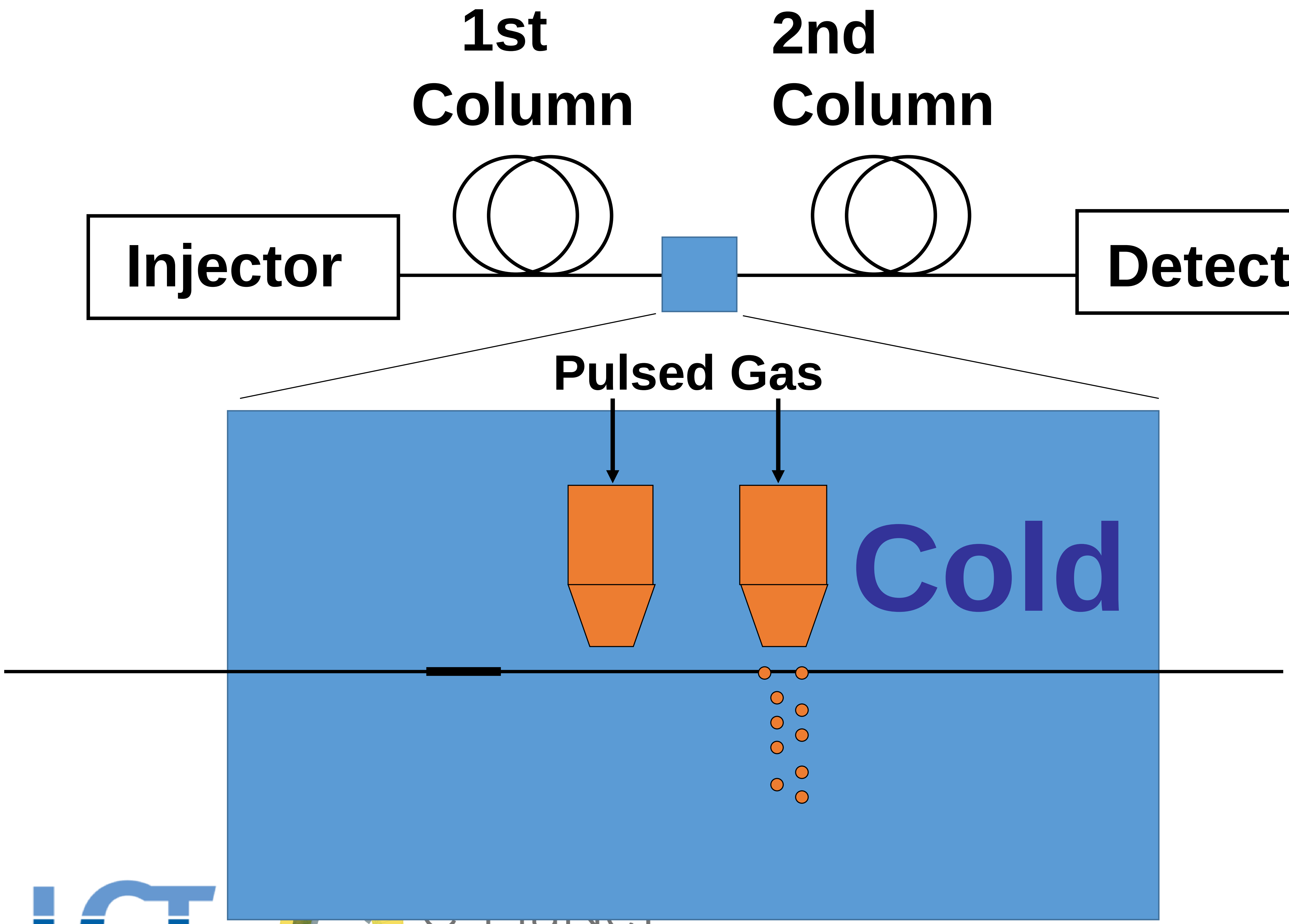
- Analytes are separated using two different columns with two different stationary phases.
- The modulator quickly traps, then "injects" the analytes from the first dimension column onto the second dimension.
- This process creates a retention plane of the 1st dimension separation x 2nd dimension separation.



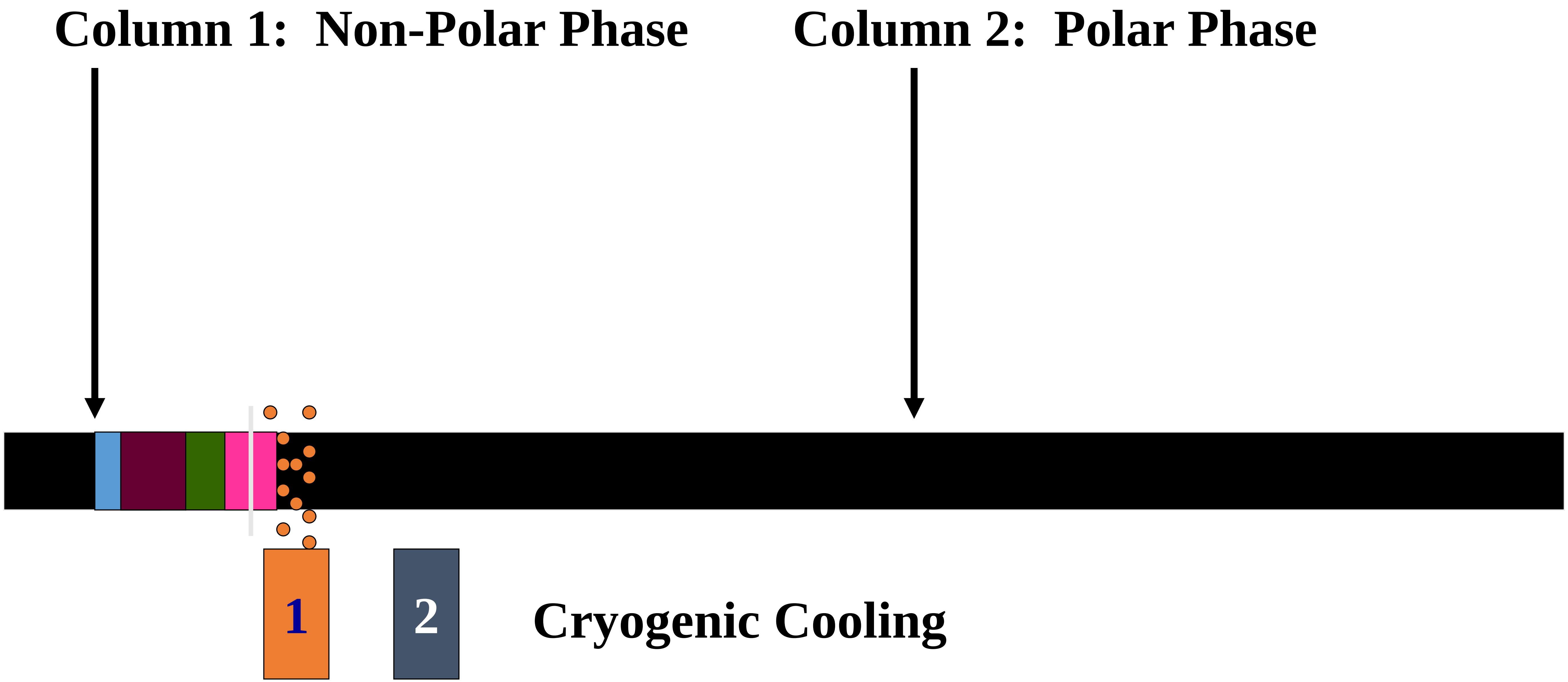
Highly beneficial to analyze complex samples

Dalluge, Beens, & Brinkman (2003), Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool. Journal of Chromatography A. 69-108


1st
Column
2nd
Column
Injector
Detector
Pulsed Gas
Cold


1st
Column
2nd
Column
Injector
Detector
Pulsed Gas
Cold

Comprehensive GCxGC



Analytes Partially Resolved on Column 1

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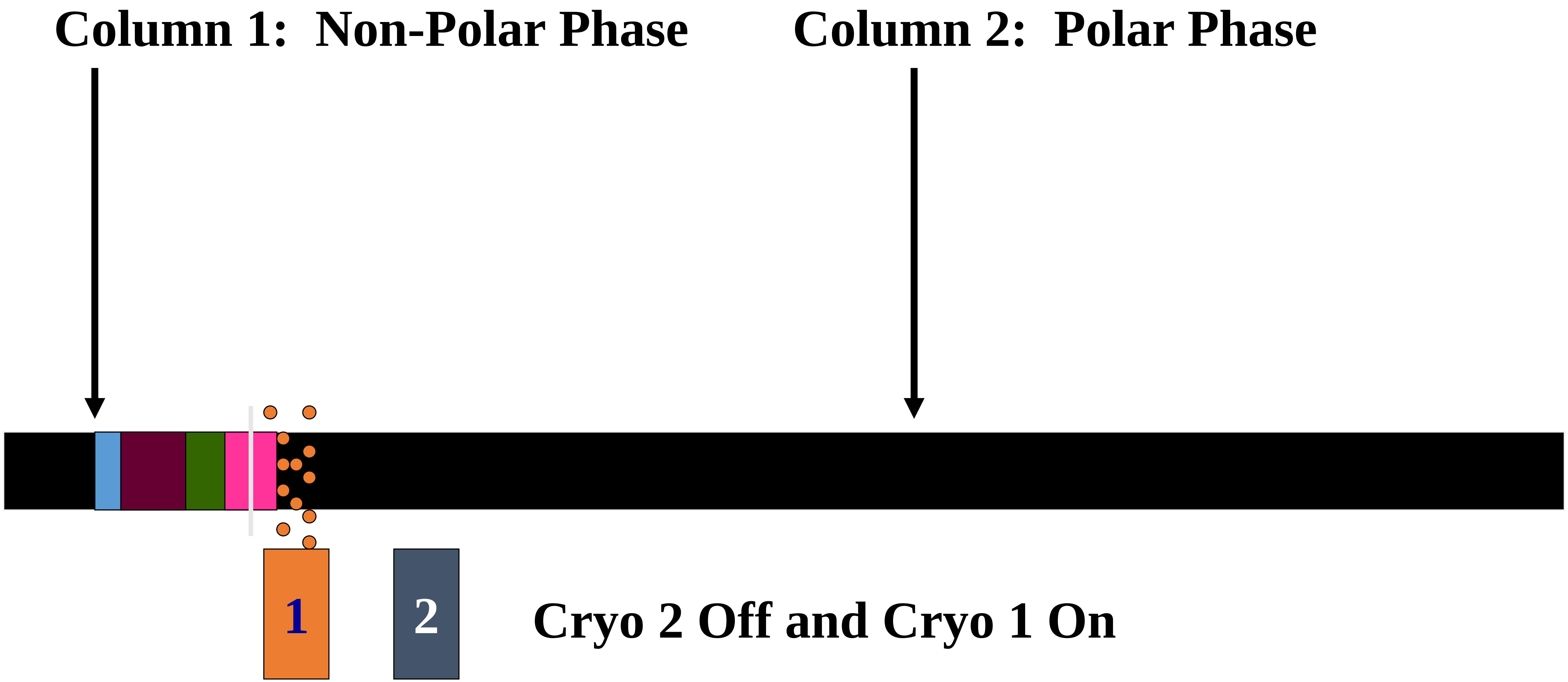

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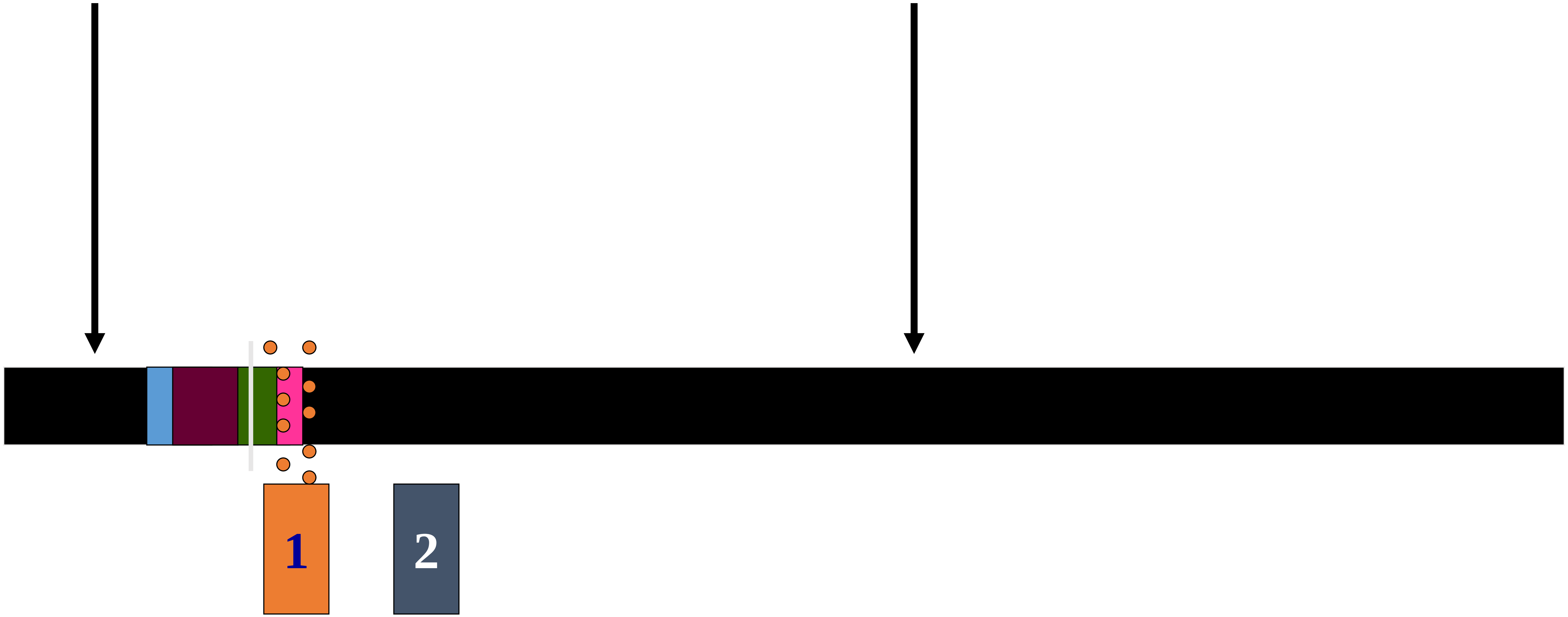
Column 1: Non-Polar Phase **Column 2: Polar Phase**



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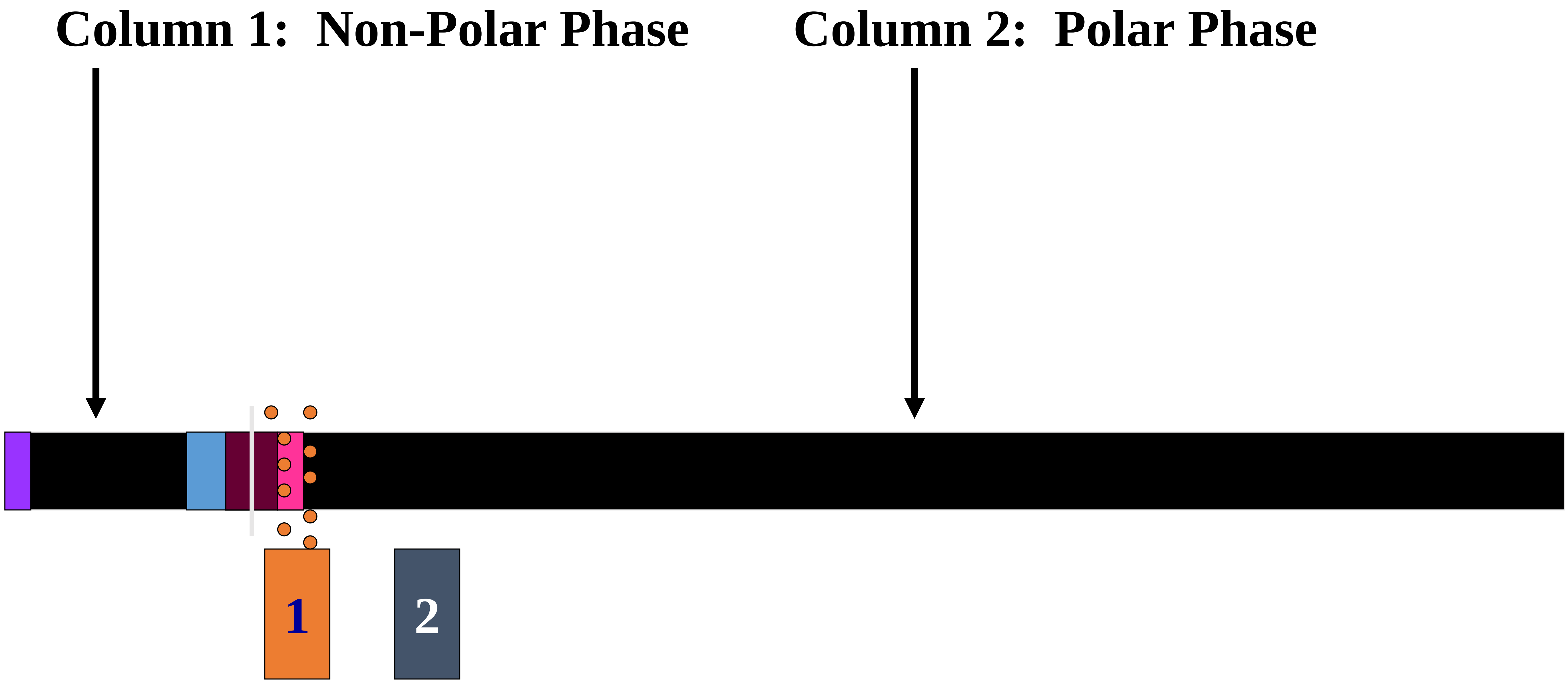
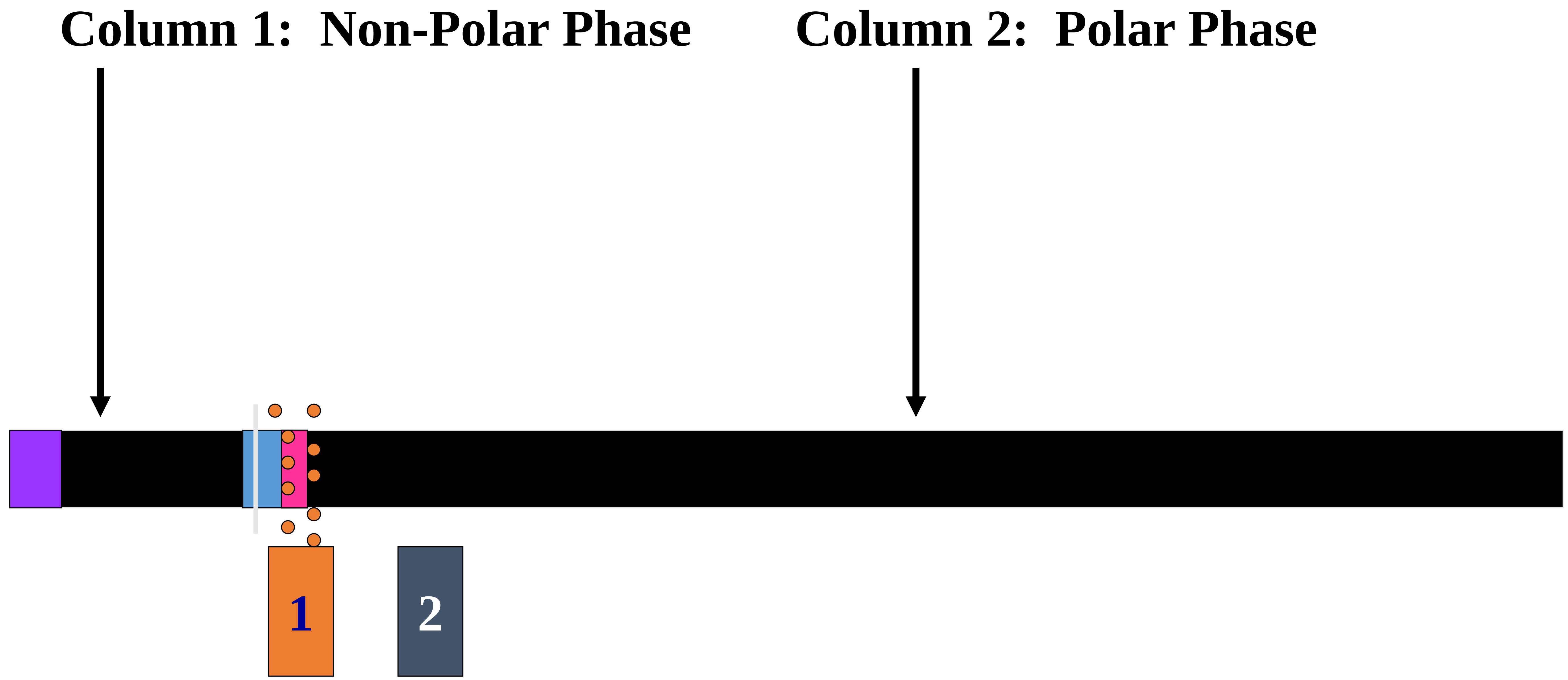
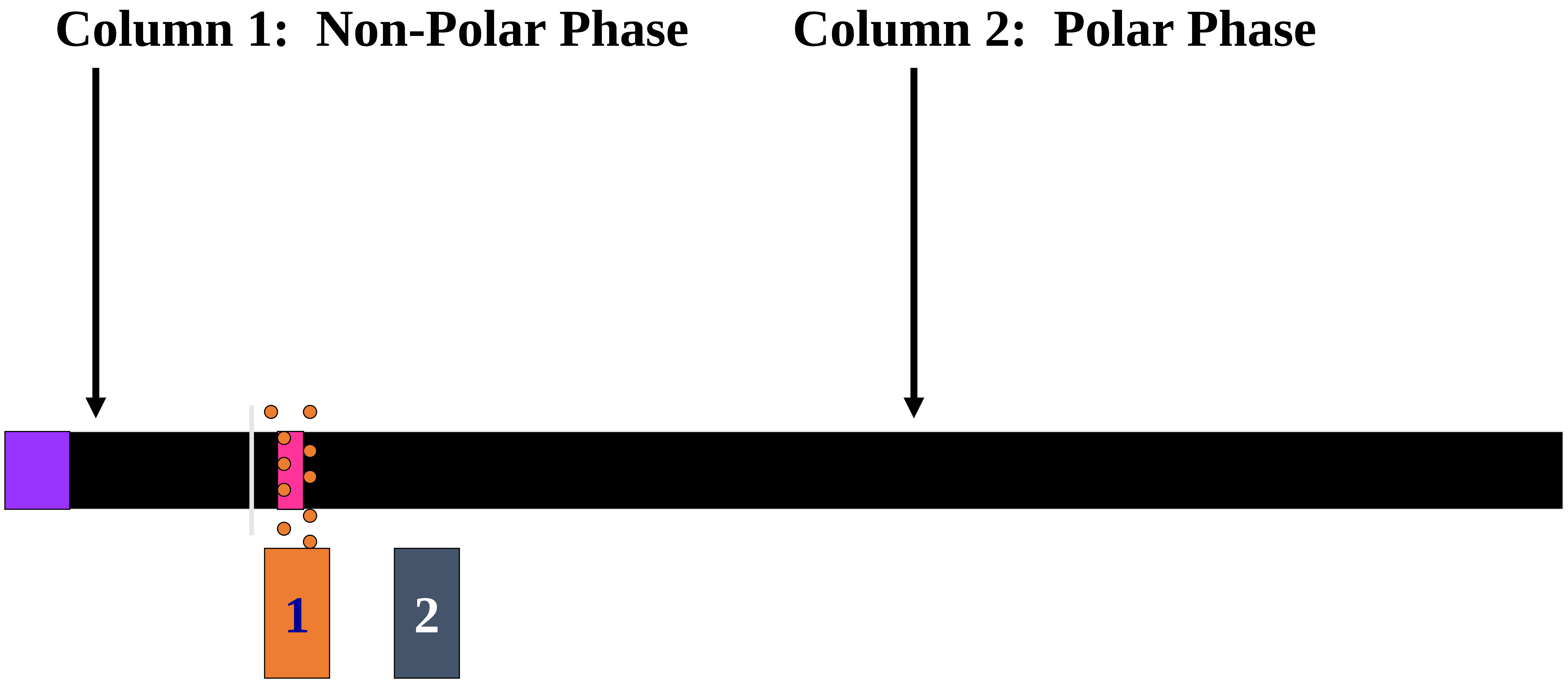


Comprehensive GCxGC



Comprehensive GCxGC



Analytes Trapped on Stage 1 of the Thermal Modulator

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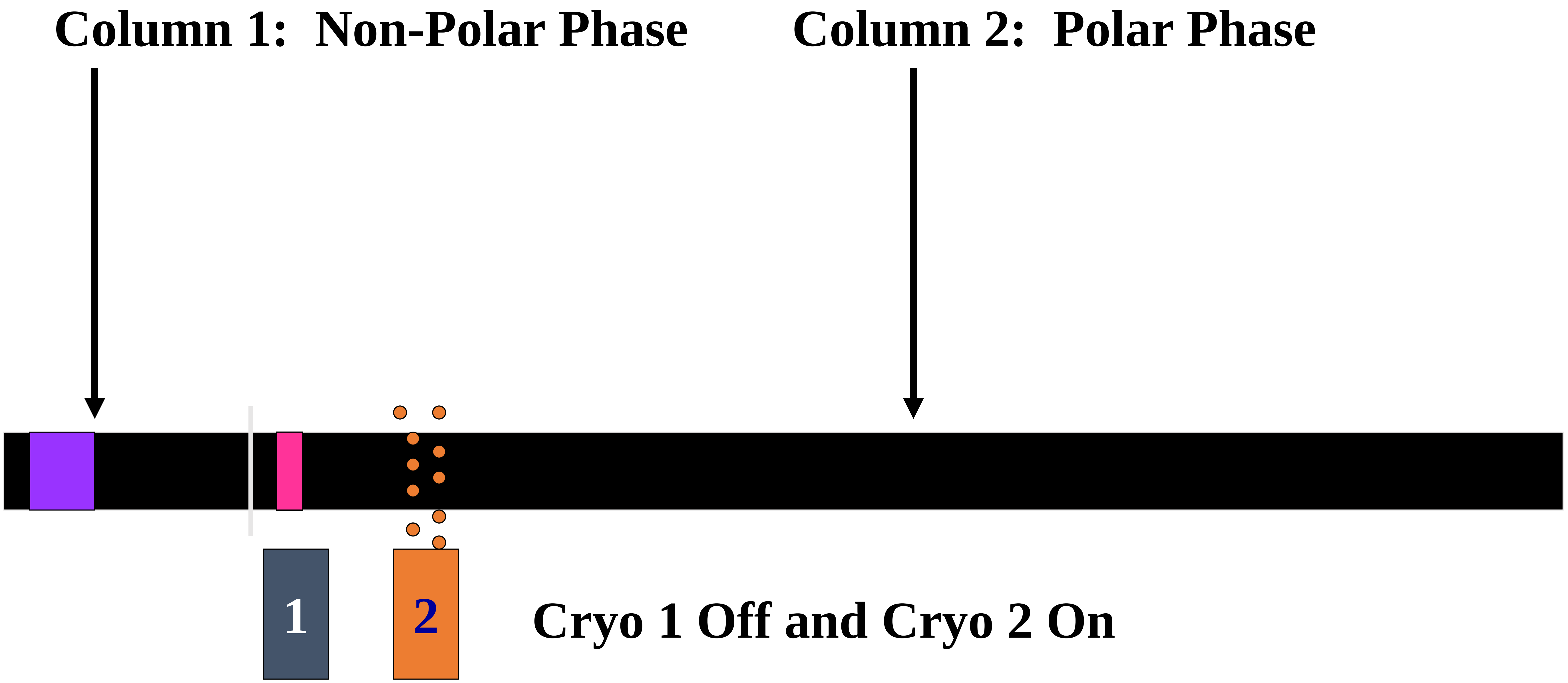
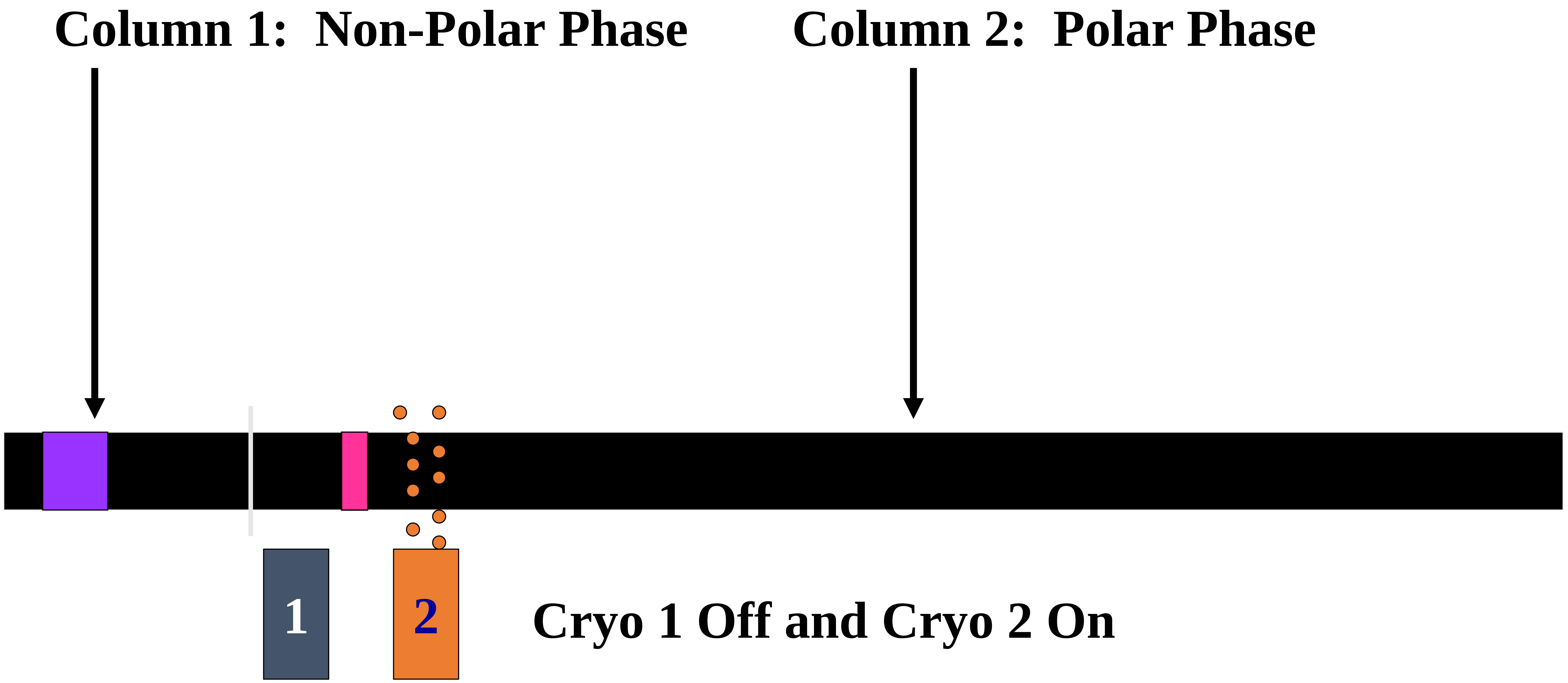
Comprehensive GCxGC



Analytes Released to Stage 2 of the Thermal Modulator

Comprehensive GCxGC



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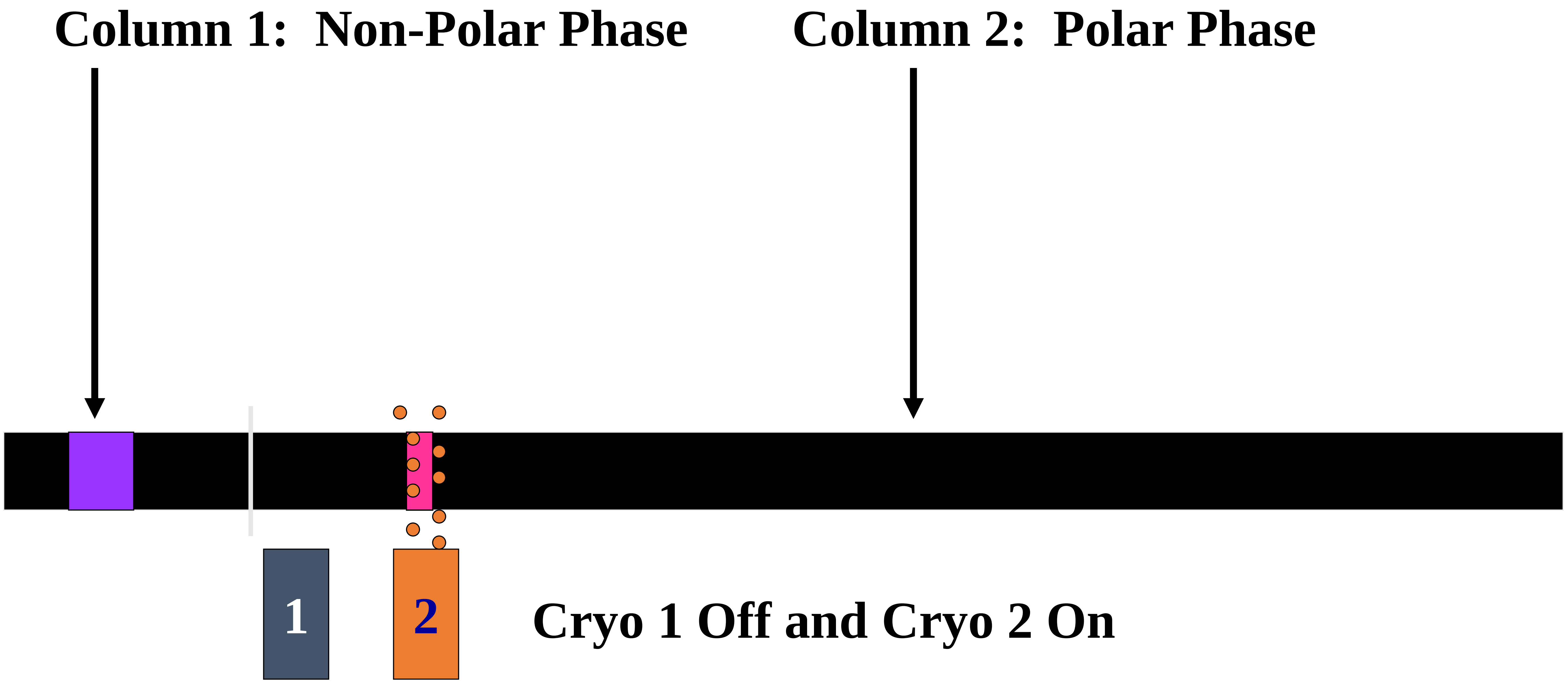
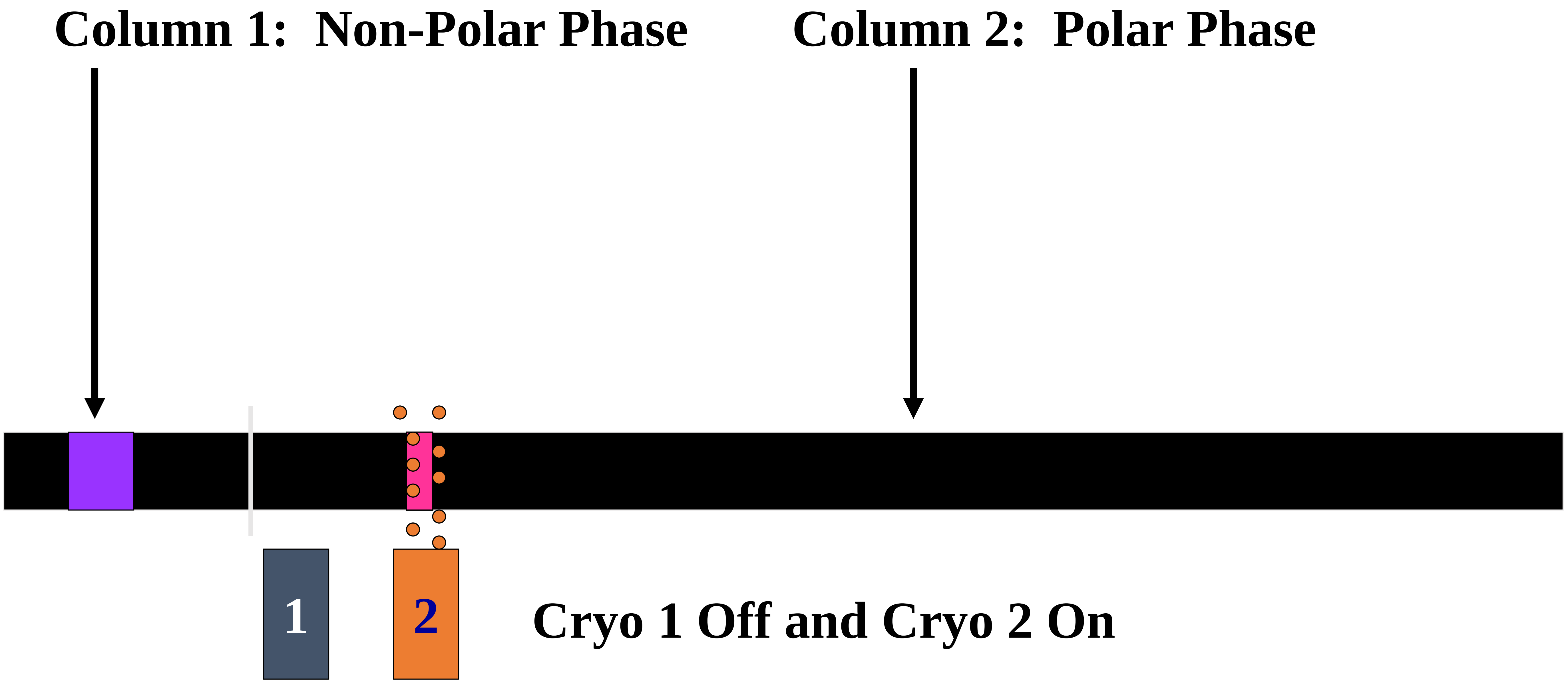
Comprehensive GCxGC

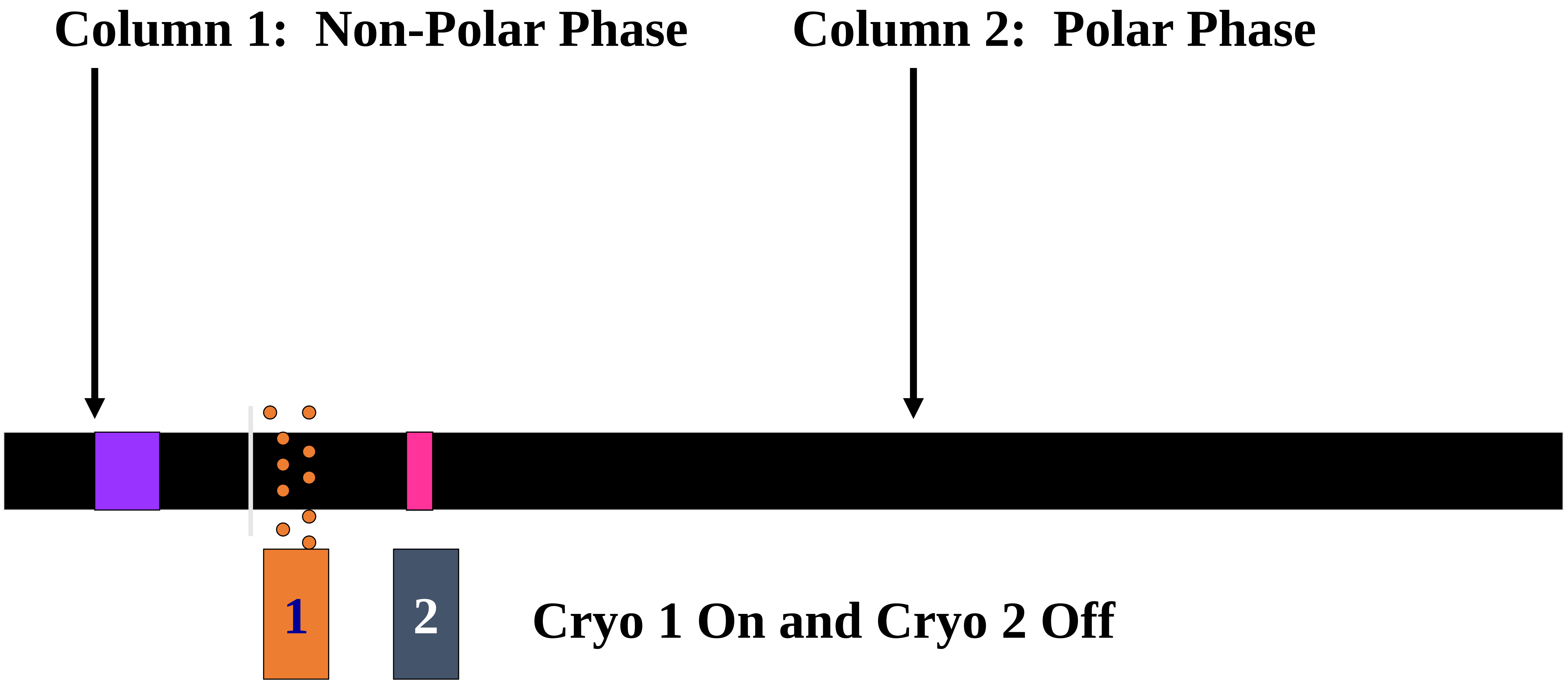


Comprehensive GCxGC



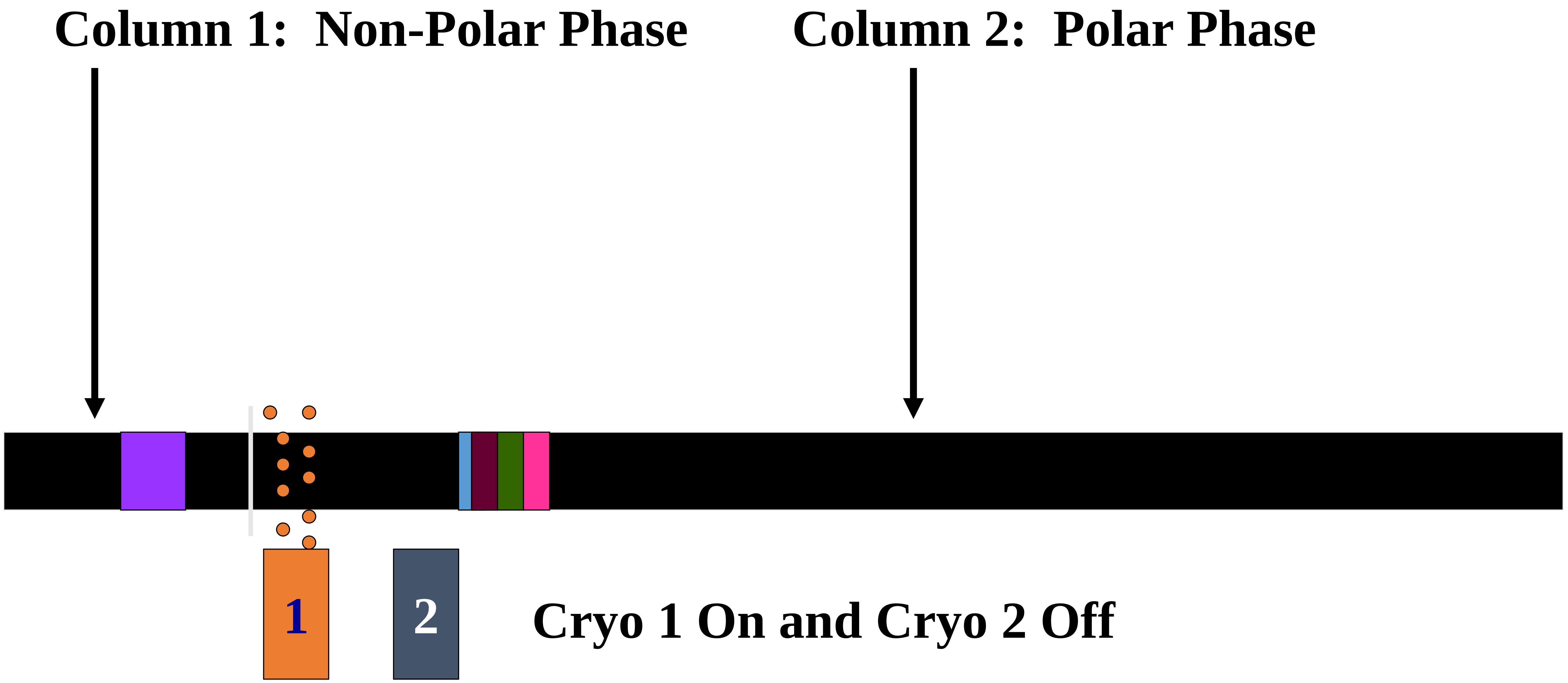
Analytes Trapped on Stage 2 of the Thermal Modulator

Comprehensive GCxGC



Analytes Released to Column 2

Comprehensive GCxGC



Analytes Separate on Column 2

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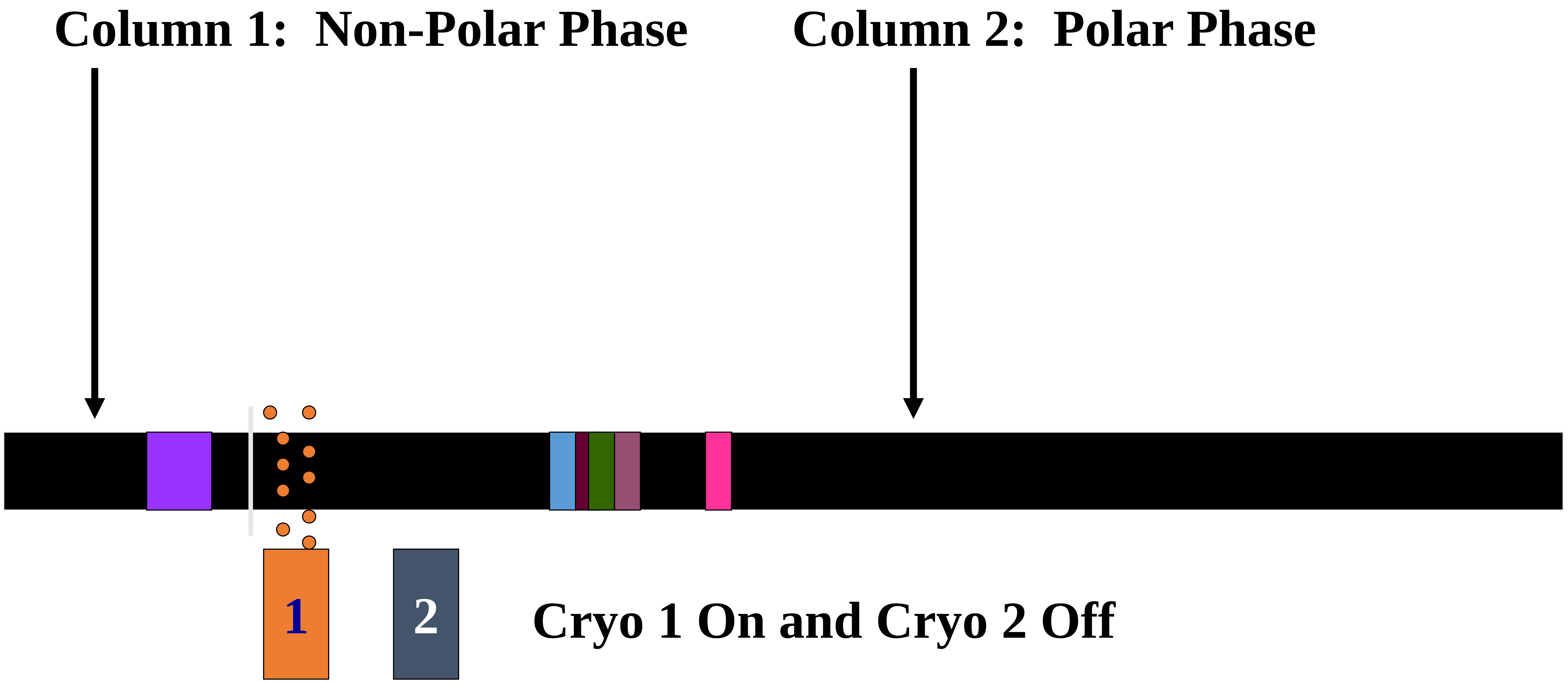
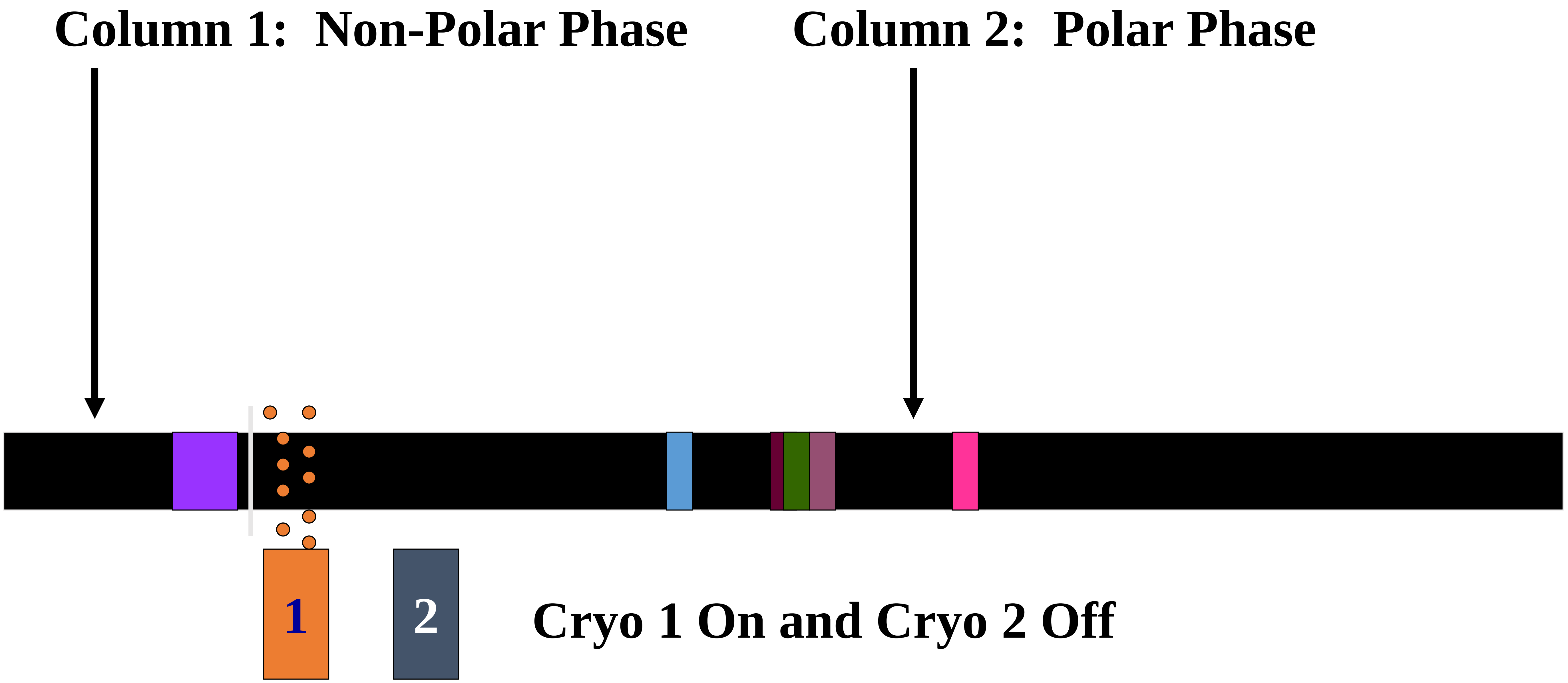
Comprehensive GCxGC



Analytes Separate on Column 2
Next Bands Enter the Thermal Modulator

Comprehensive GCxGC



Analytes Separate on Column 2

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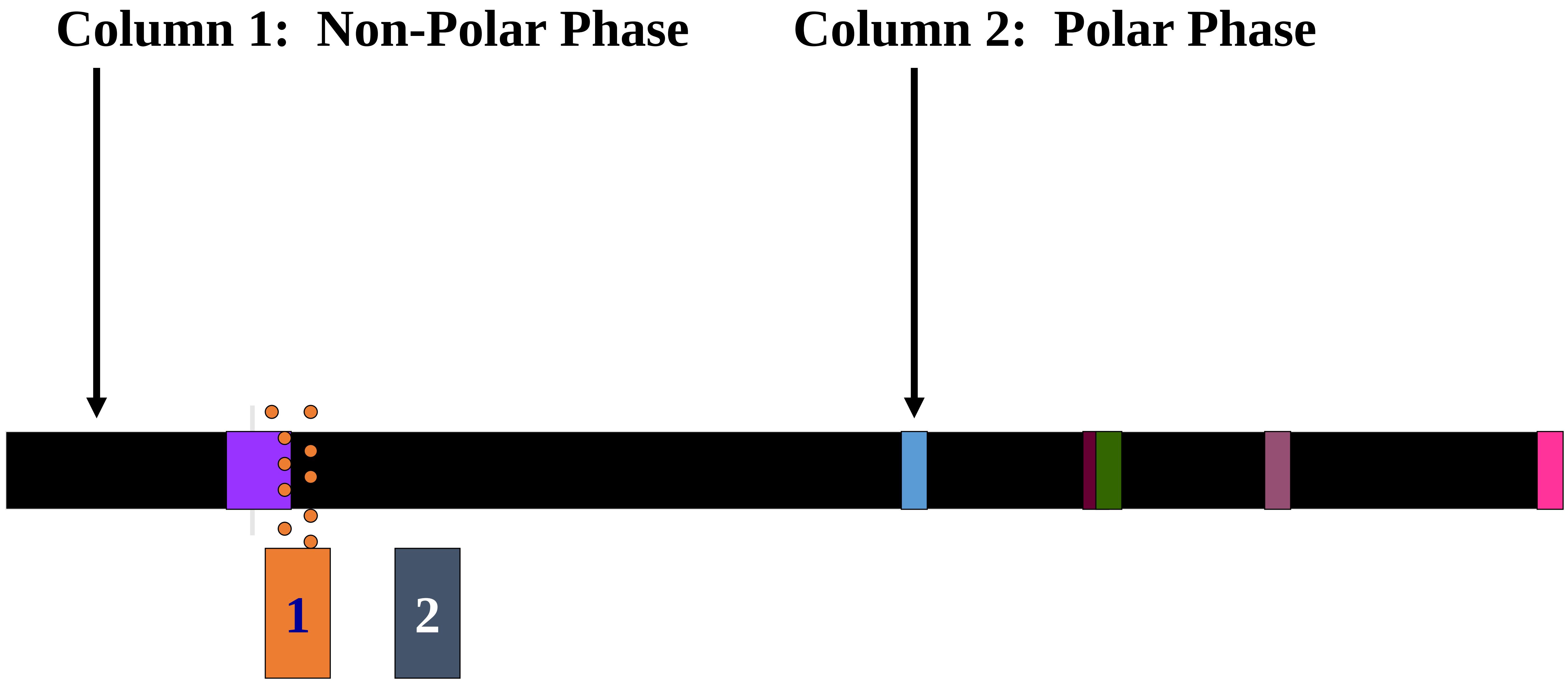
Comprehensive GCxGC



Analytes Separate on Column 2

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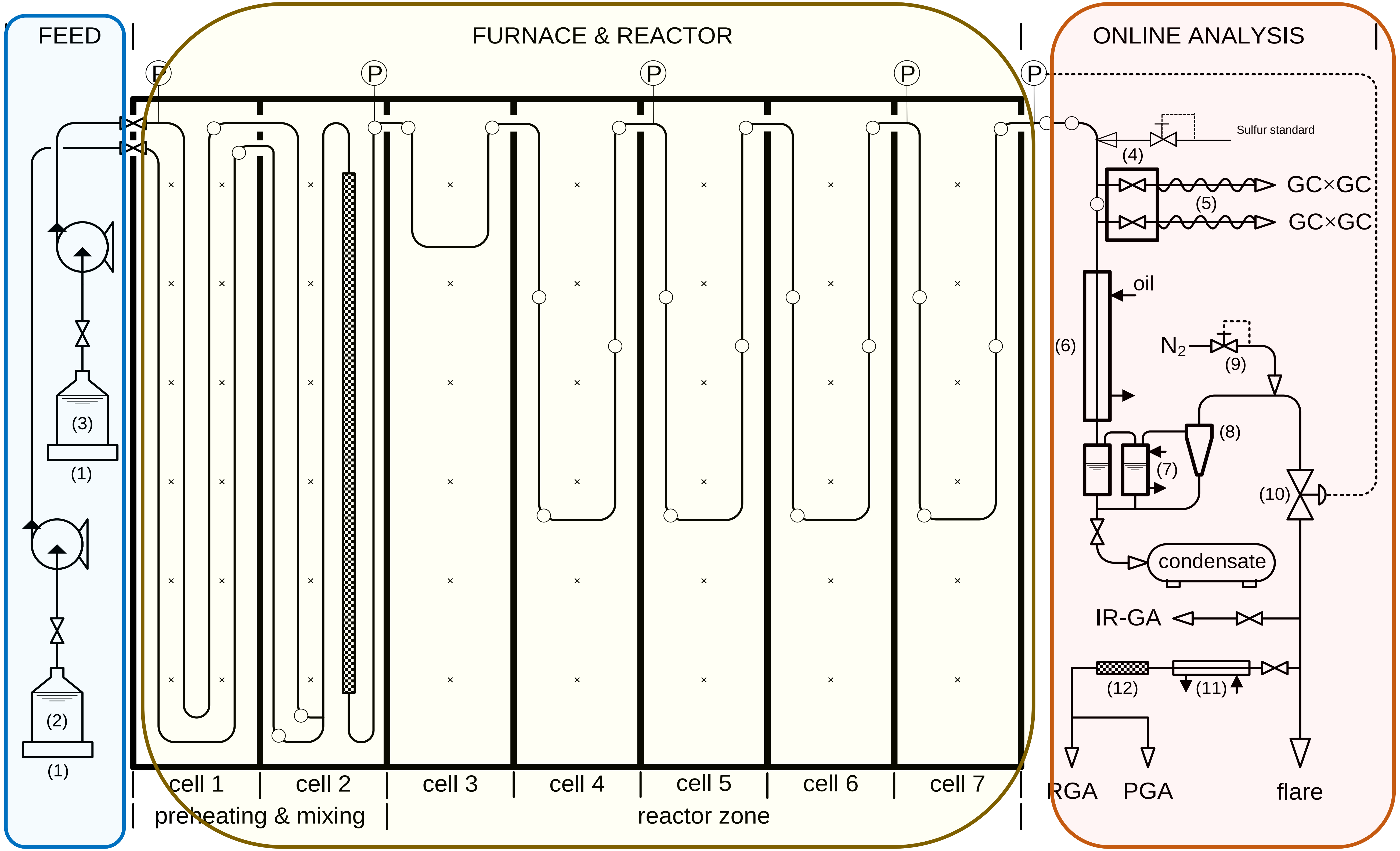
Comprehensive GCxGC

Analytes Separate on Column 2

GC×GC advantages

- Improved Chromatographic Resolution
- Increased Peak Capacity
- Enhanced Signal to Noise
- More accurate qualitative and quantitative info
- More Information per Analyzed Sample



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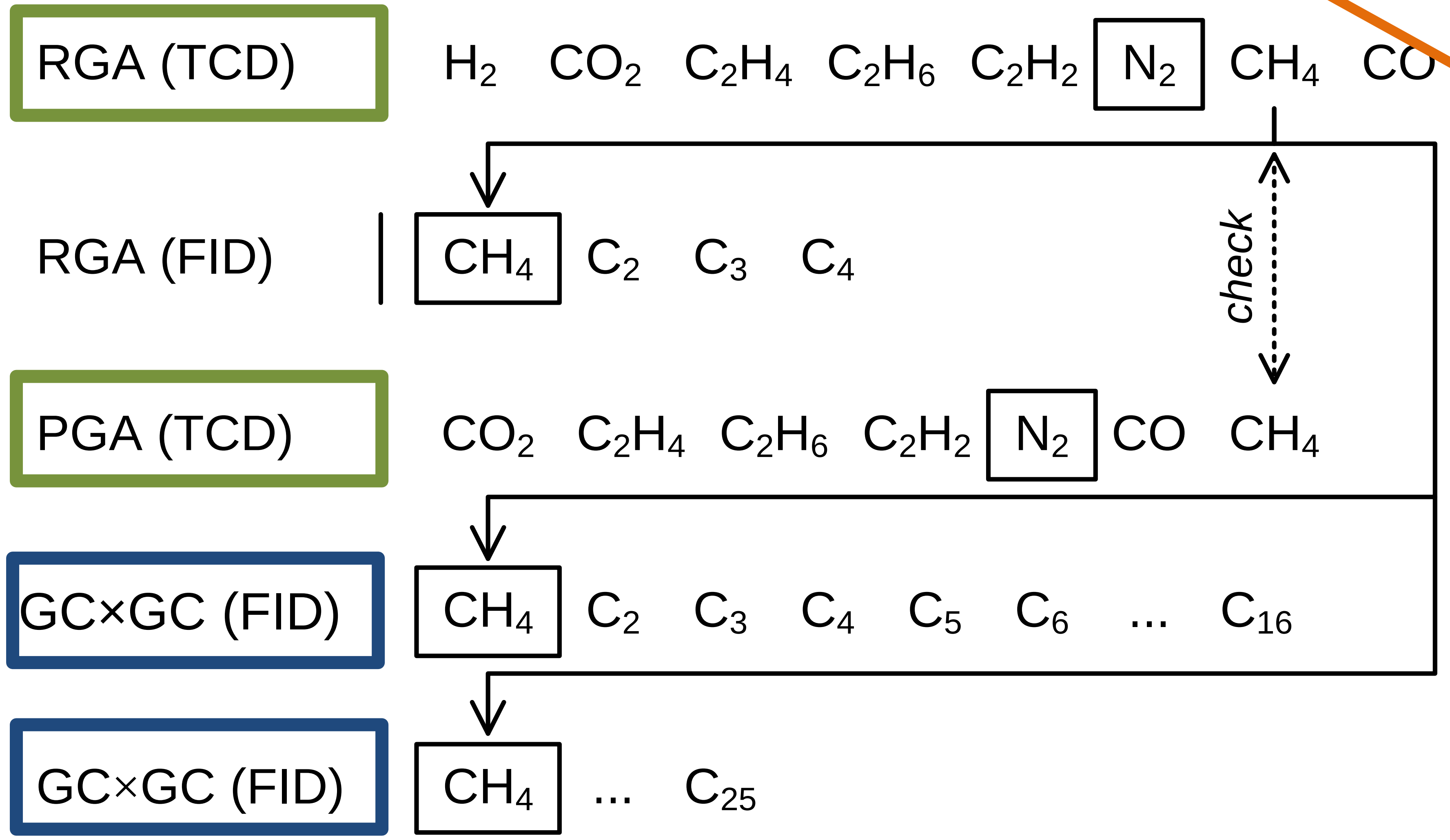
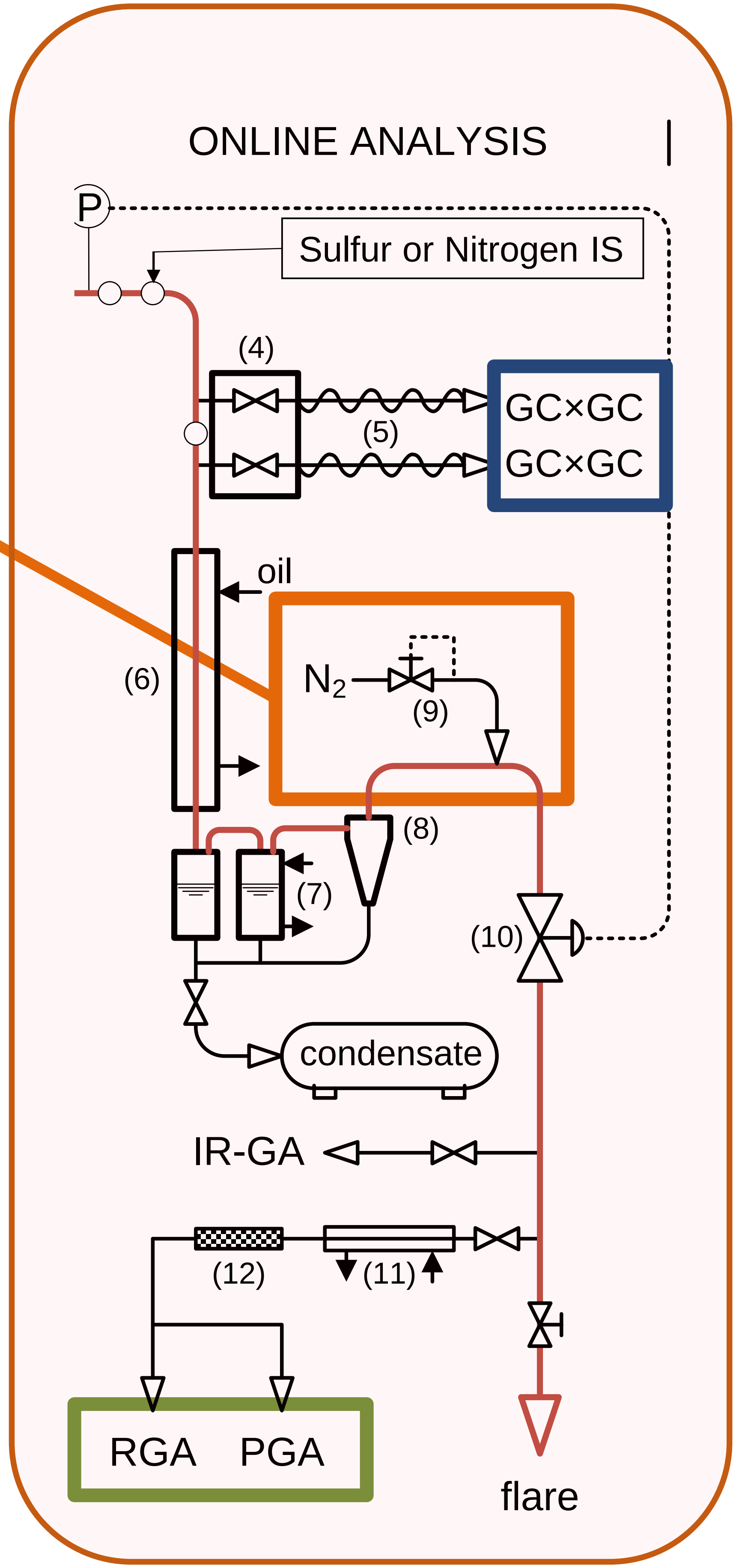
Universal On-line quantification

Nitrogen = Internal Standard





Methane = Reference Component

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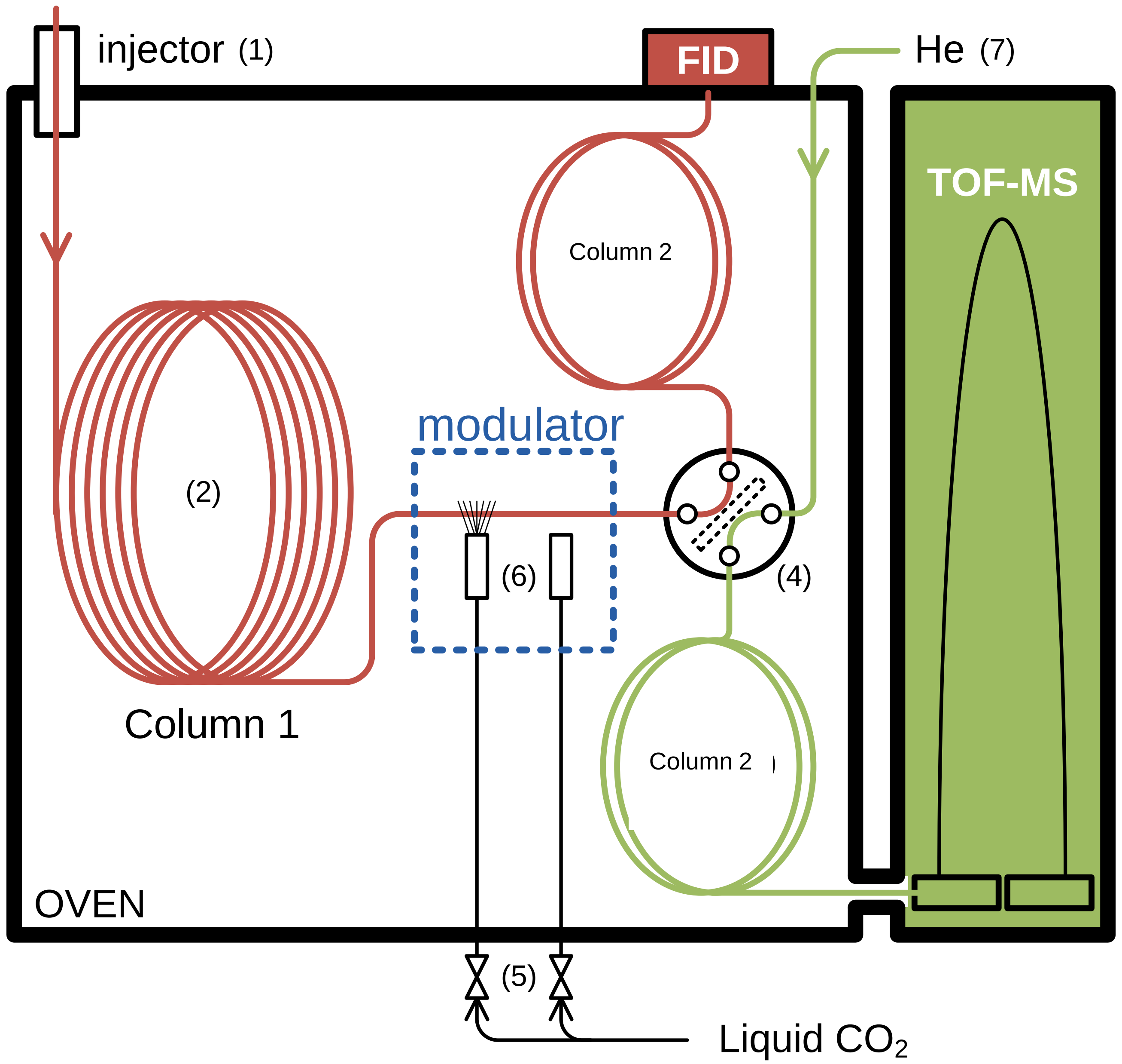
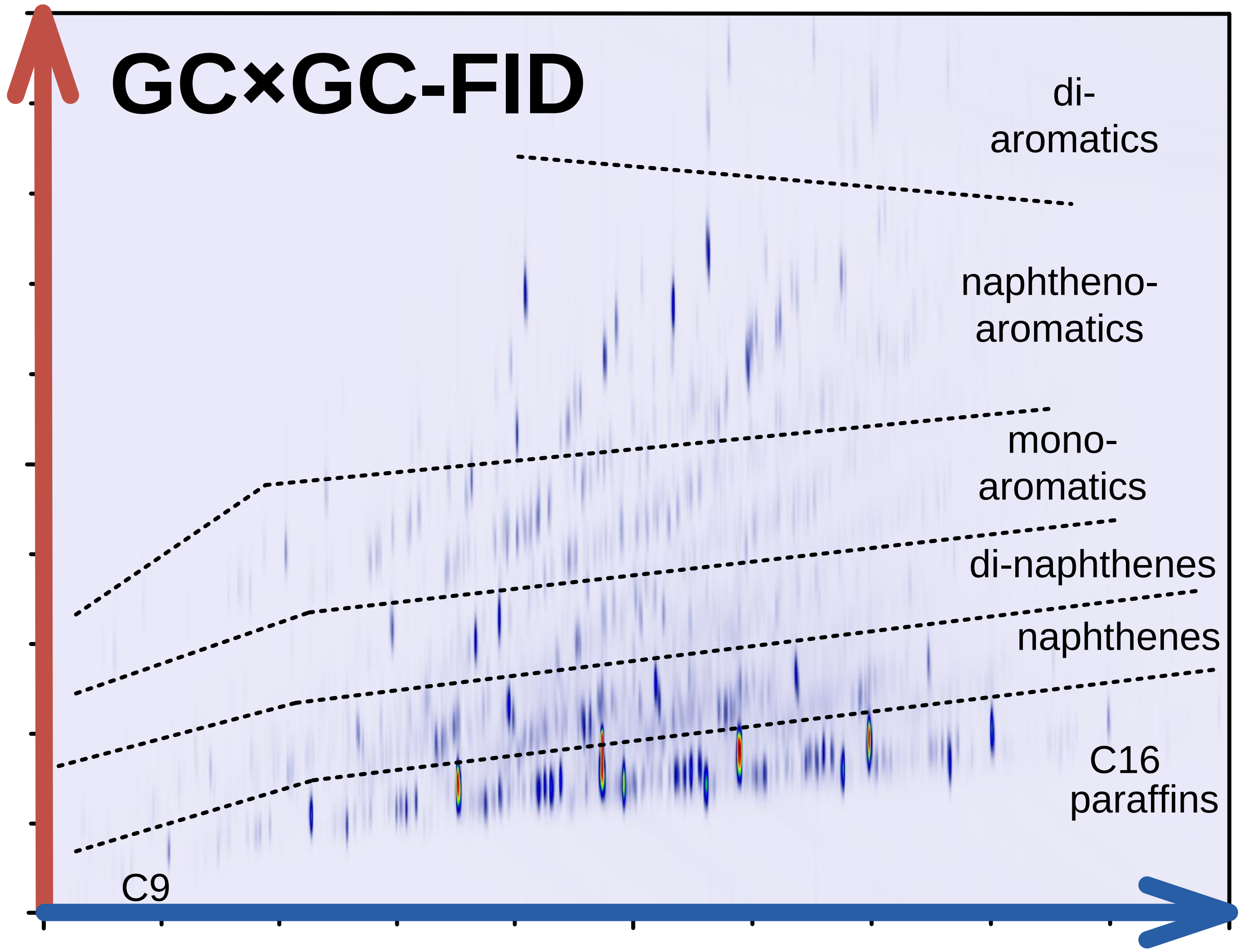
Comprehensive 2D Gas Chromatography: GCxGC



Van Geem K.M. et al., J. Chrom. A. 2010

Comprehensive 2D Gas Chromatography: GCxGC



2D contour plot

↓

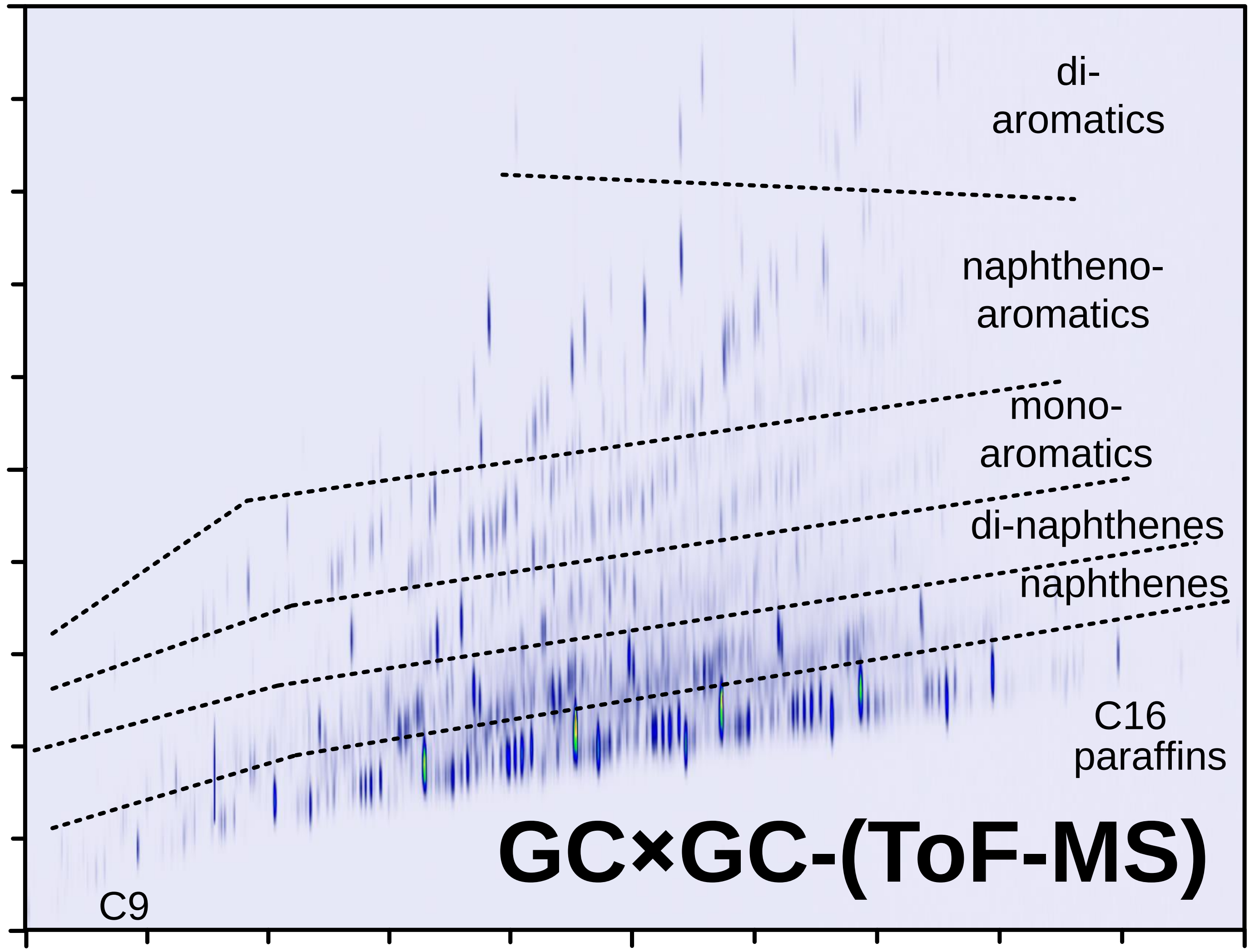
Straightforward
group-type analysis

Combining MS and FID

Confident peak identification

+

Accurate quantification



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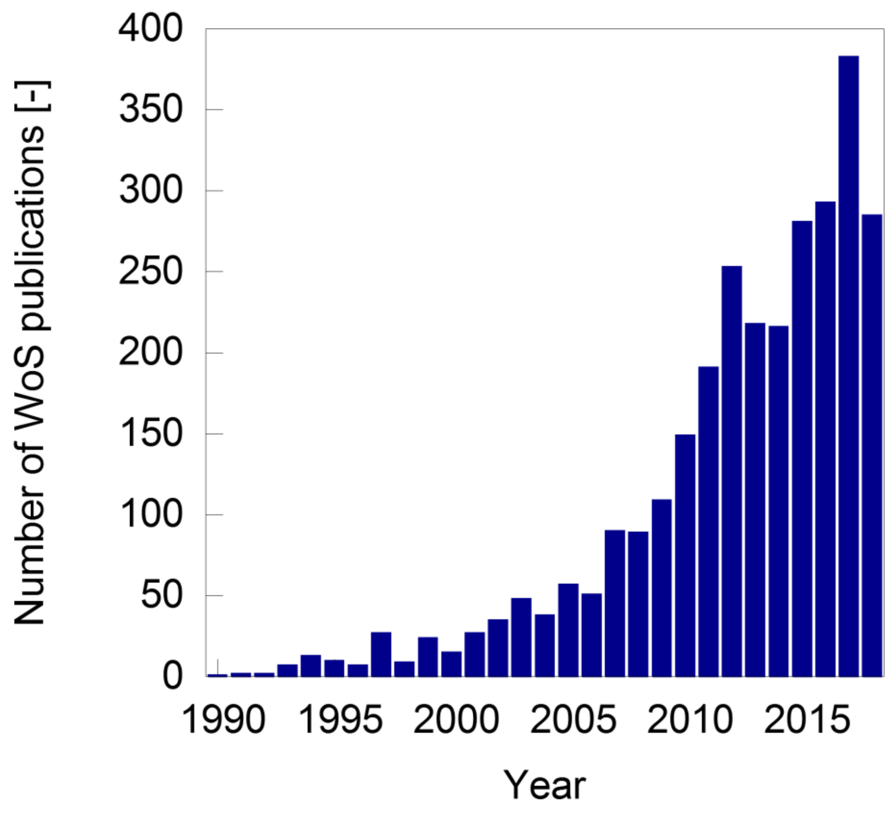
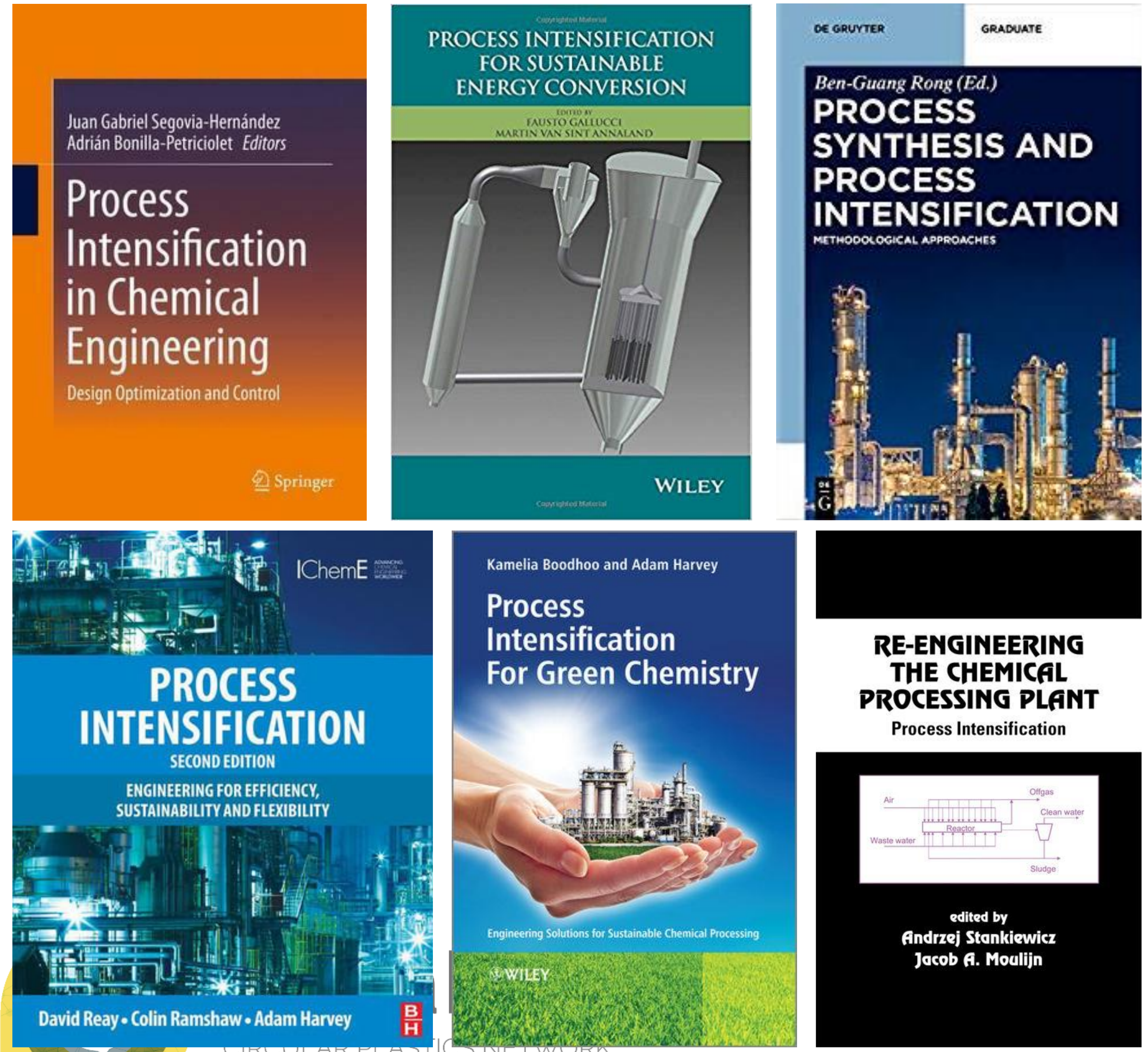
Vortex reactors

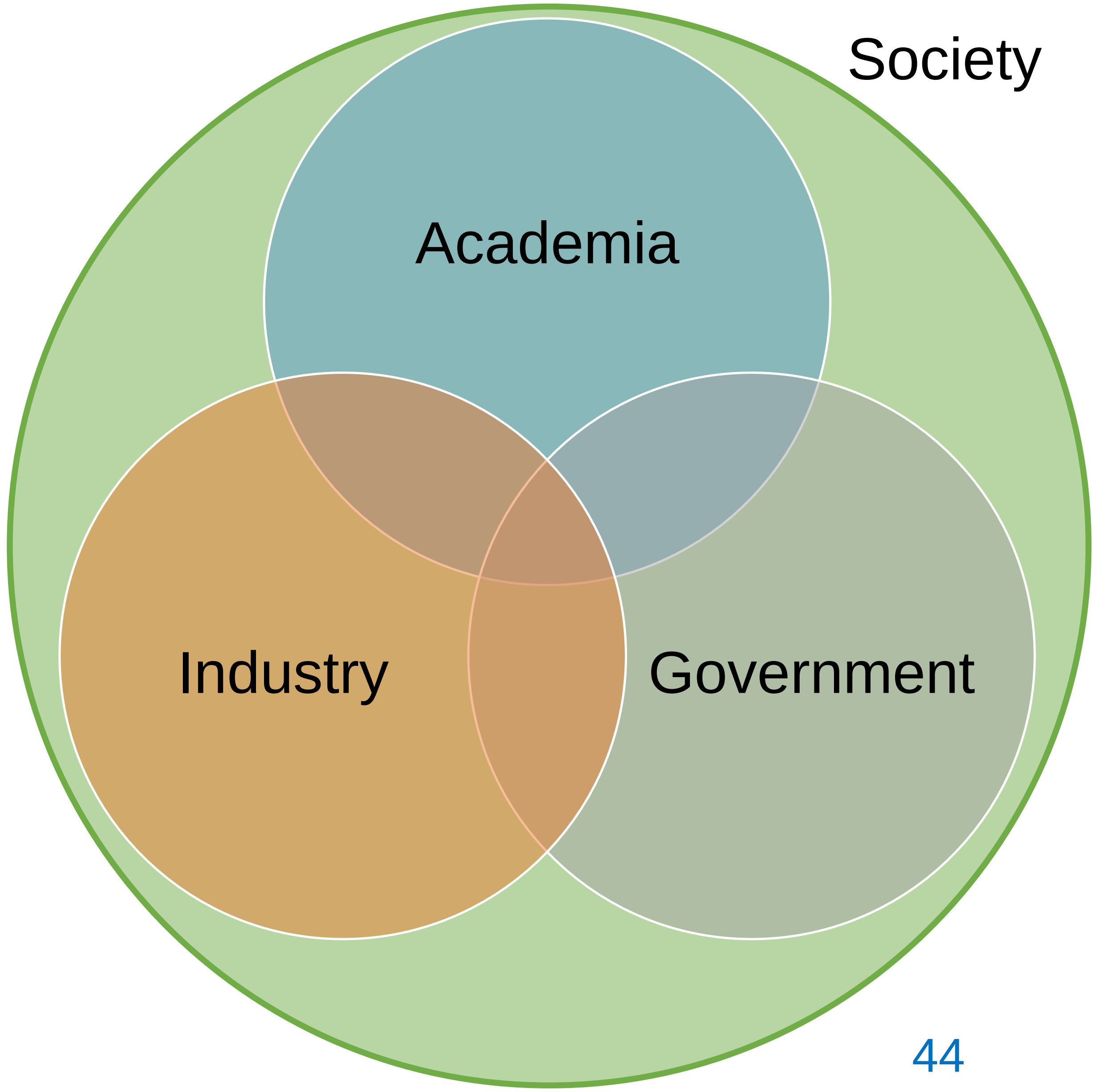
Process intensification – what?

"any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology"

A. Stankiewicz, J. Moulijn



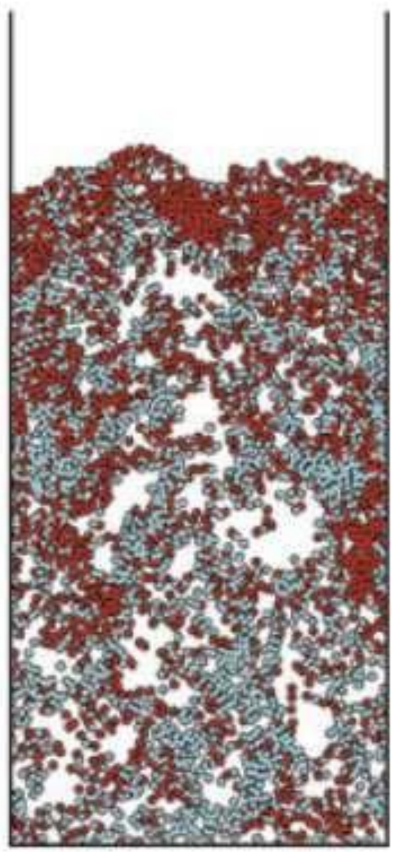




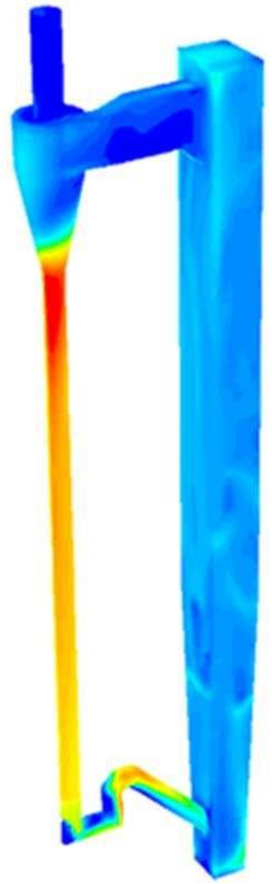
Stankiewicz, A. I.; Moulijn, J. A., Process Intensification: Transforming Chemical Engineering. Chemical Engineering Progress 2000, 22.
https://www.ugent.be/csc/en

Fluidized bed reactors

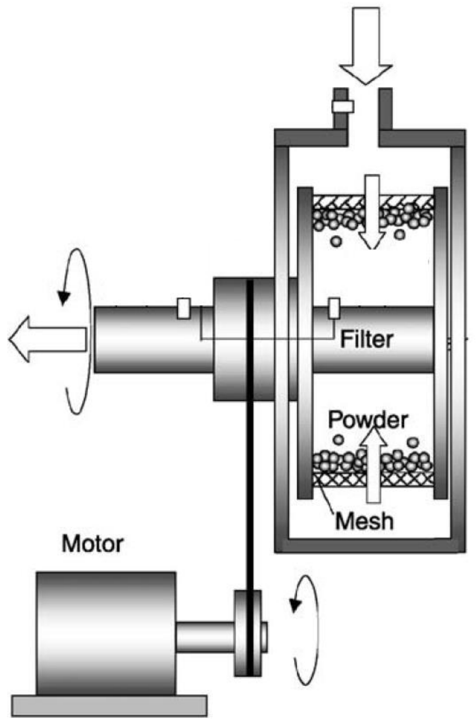
Conventional Fluidized Bed [1]



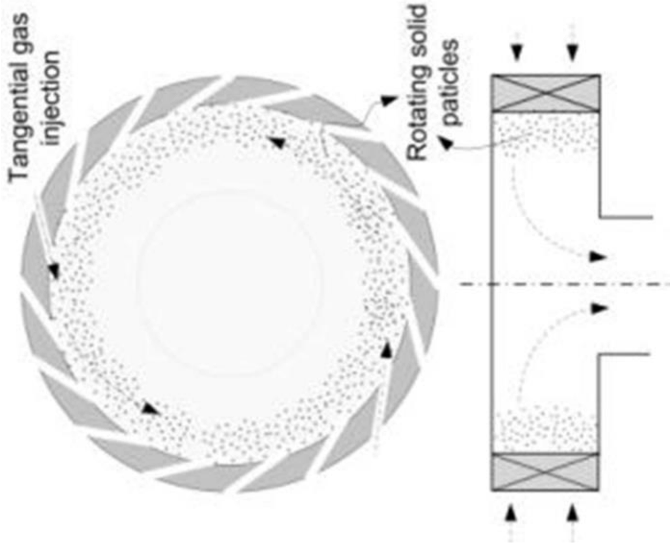
Circulating Fluidized Bed [2]



Conventional Rotating Fluidized Bed [3]



Gas/Solid Vortex Reactor



gravitational technologies

centrifugal technologies

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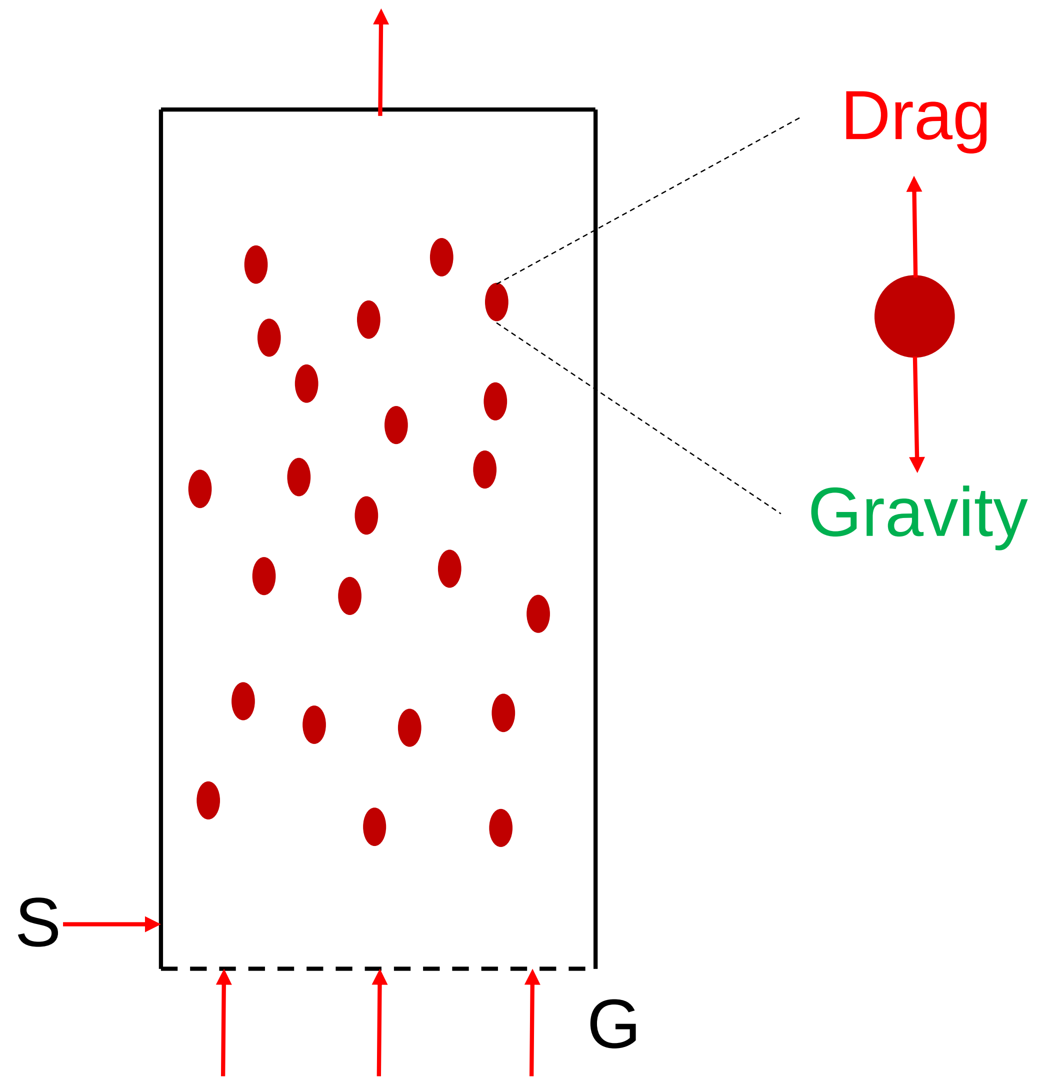
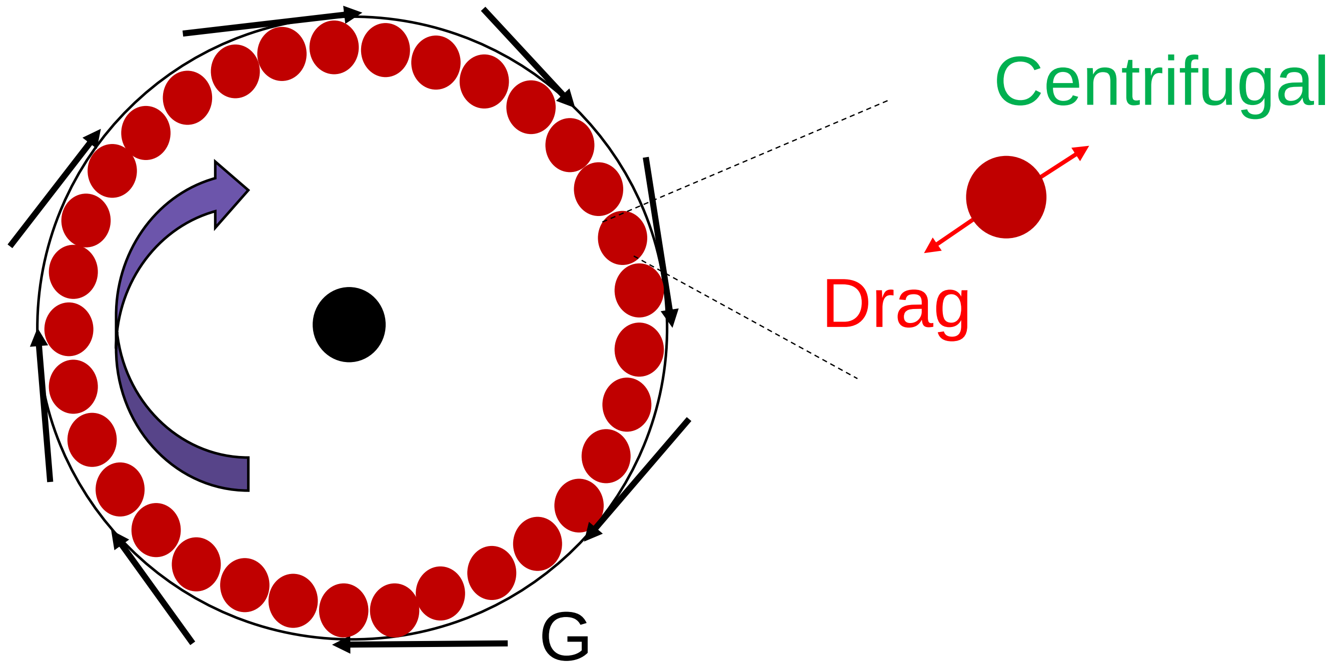
1. van Hoef et al., Ann. Rev. Fluid Mech. 40 (2008) 47-70
2. http://www.fluidcodes.co.uk/fbed.html
3. adapted from Watano et al., Powder Tech.131 (2003) 250-255

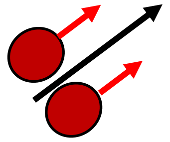
What are the Vortex Reactors?

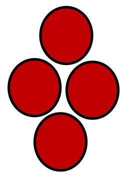
Rotating fluidized bed reactor in *a static geometry*





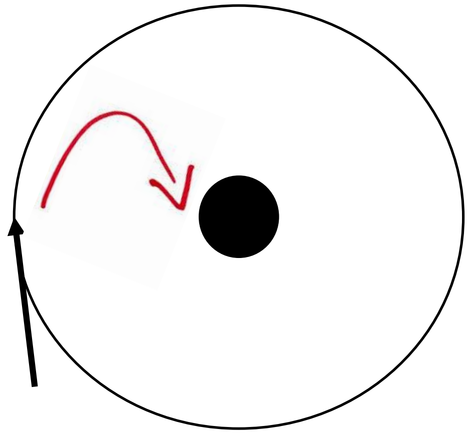
Gas-Solid slip velocities





Packed beds

Short Gas Residence time



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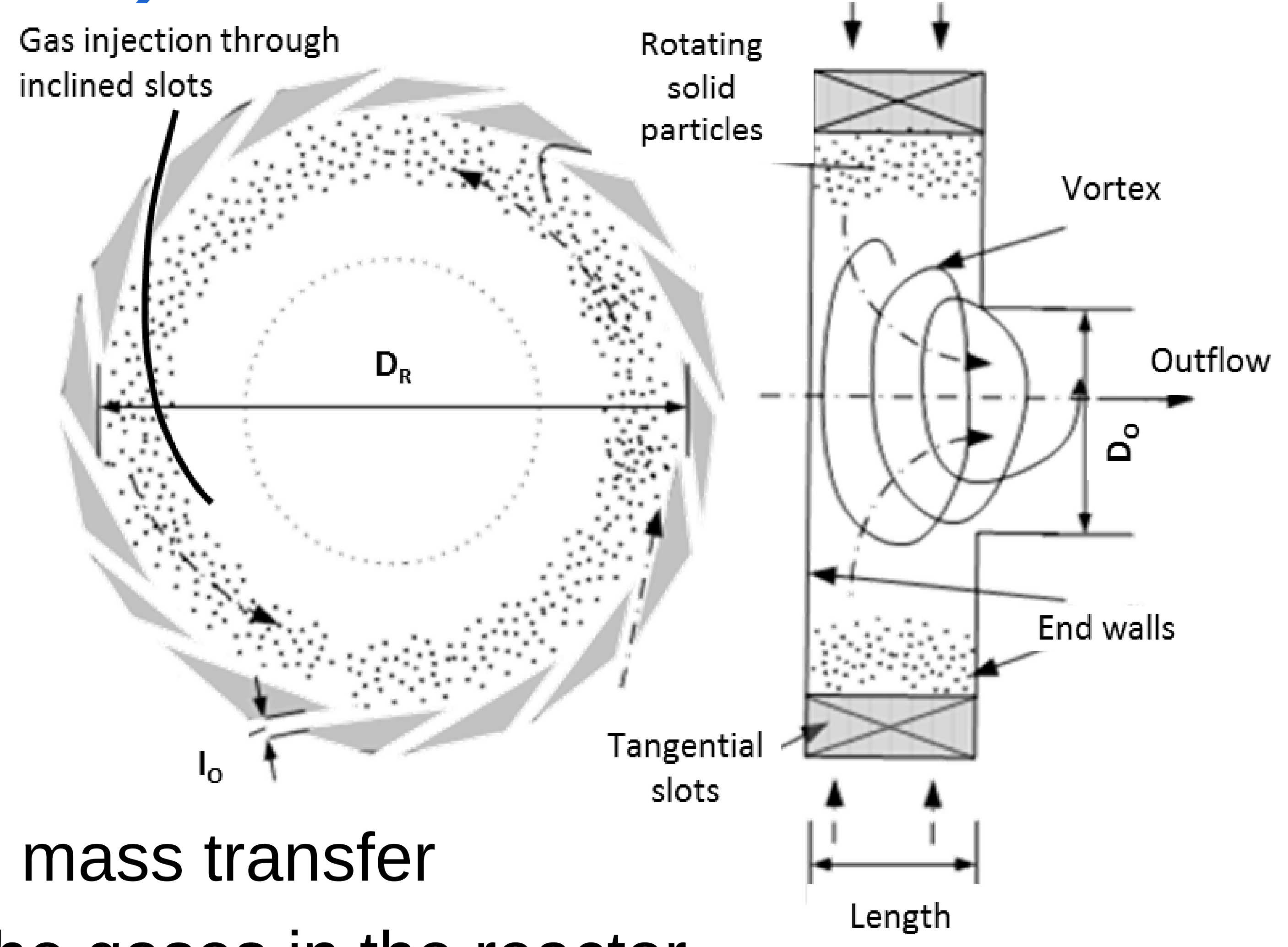
Process intensification in terms of heat & mass transfer

CIRCULAR PLASTICS NETWORK FOR TRAINING

Gas-solid vortex reactor (GSVR)



- Dense particle bed → reduced reactor volume
- High gas feed flow rates → shorter gas residence time
- Higher gas-solid slip velocity → better gas-solid heat and mass transfer
- Gas phase has plug flow behavior → no back-mixing of the gases in the reactor
- High effective thermal conductivity in the solid bed → uniform temperature in the solid bed

Momentum, heat and mass transfer intensification

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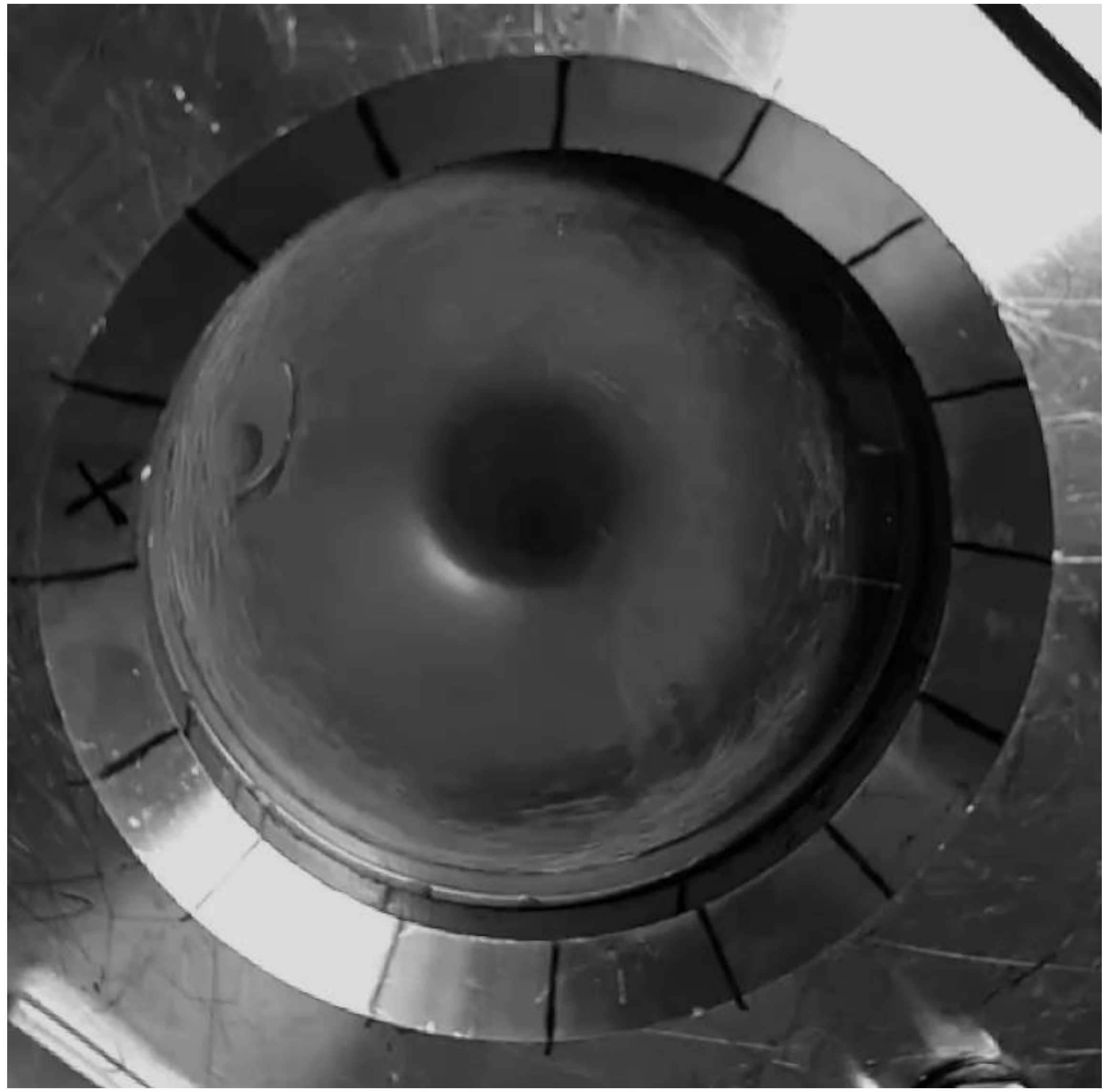
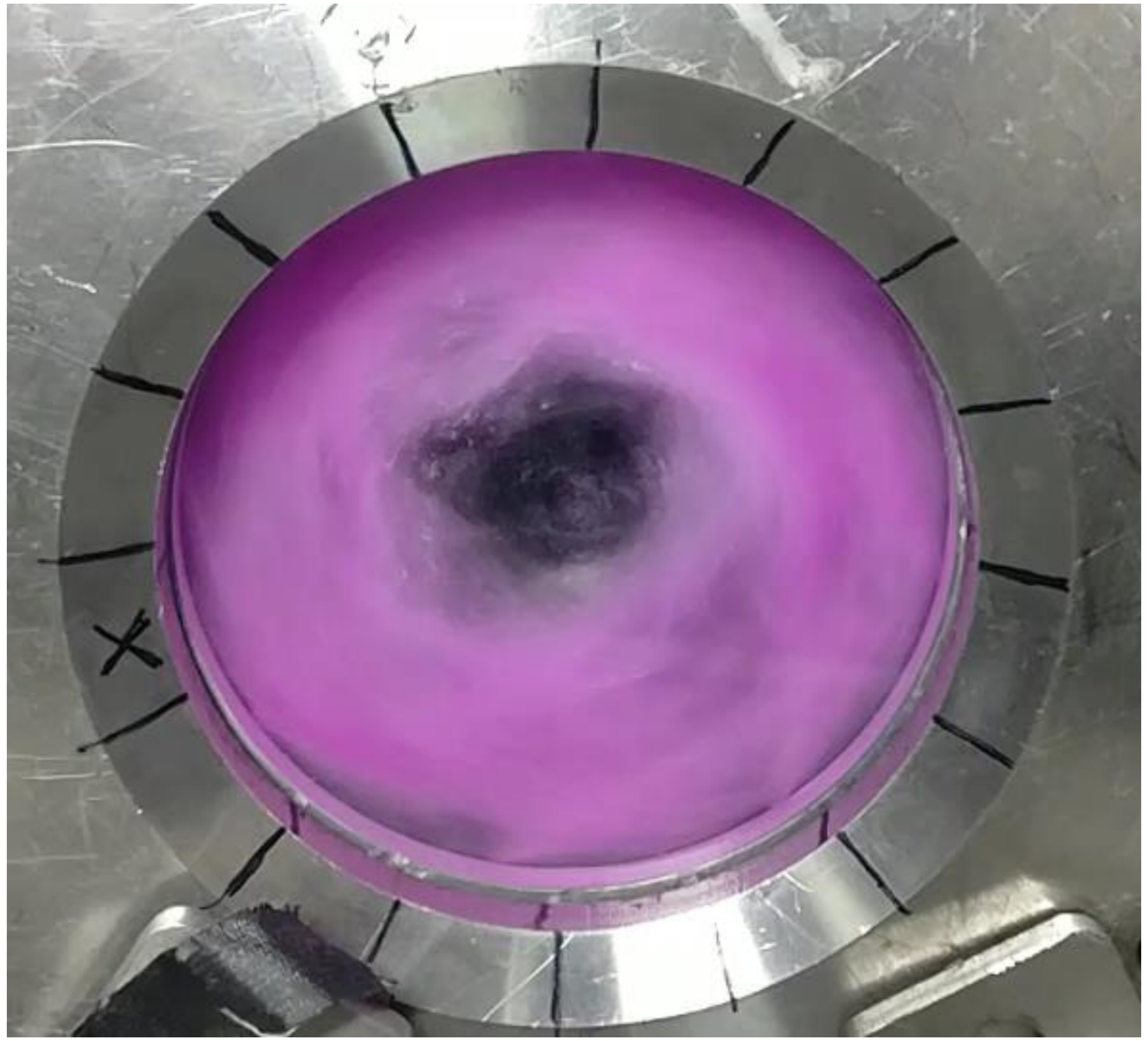
LCT DRIVING CHEMICAL TECHNOLOGY

C-PlaNeT CIRCULAR PLASTICS NETWORK FOR TRAINING

GSVR & GLVR

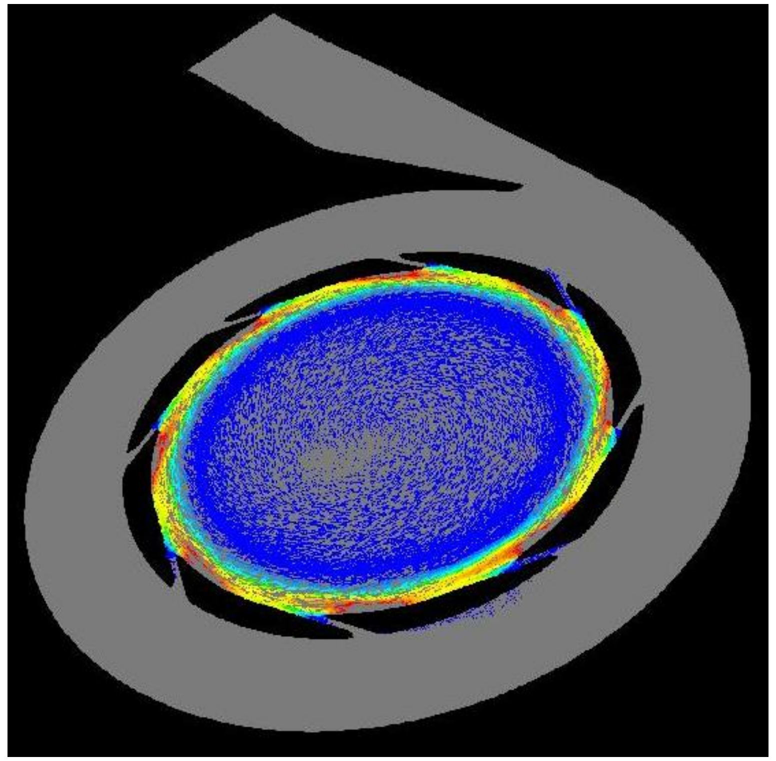


Gas-Solid Vortex Reactor

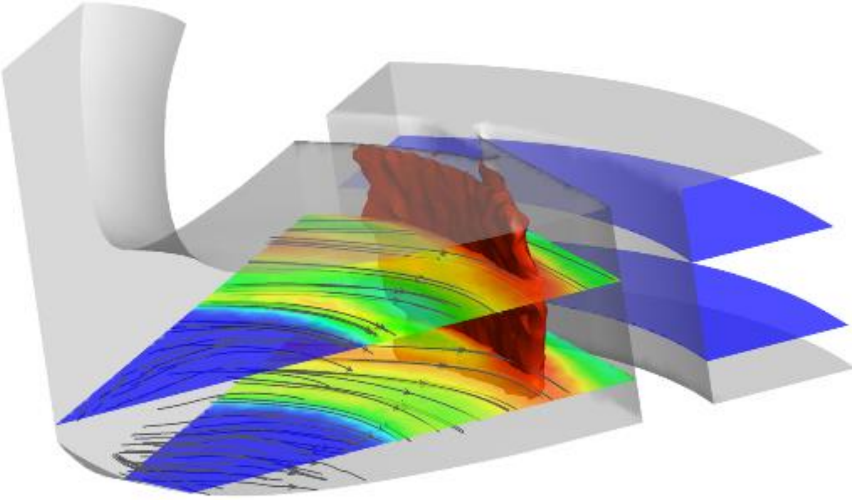


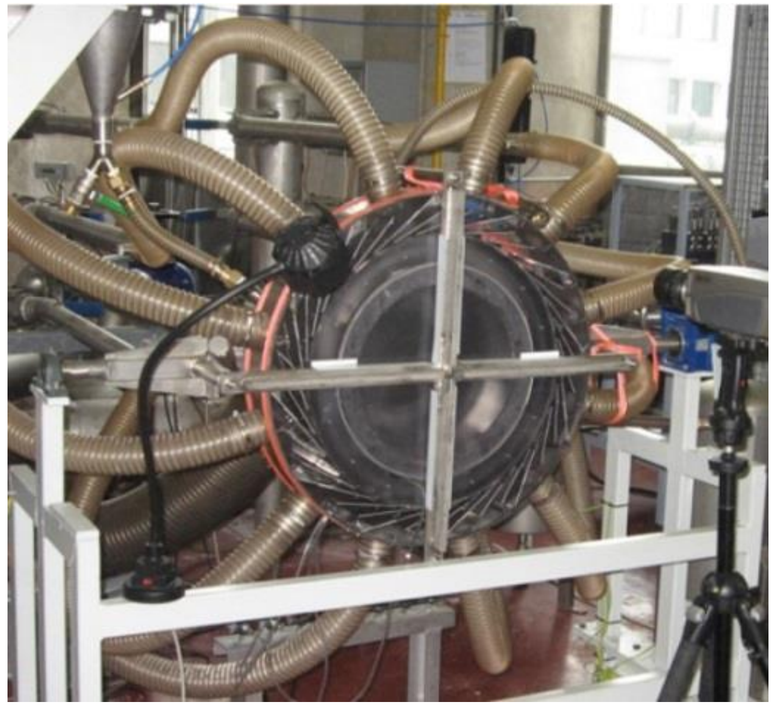
Gas-Liquid Vortex Reactor

GSVR Research @ LCT

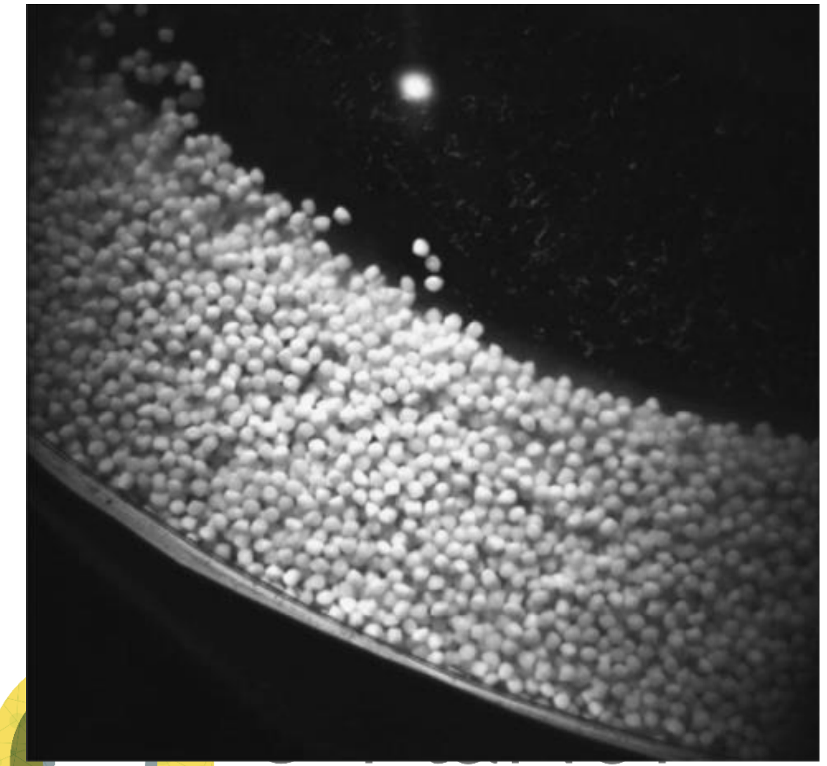


CFD

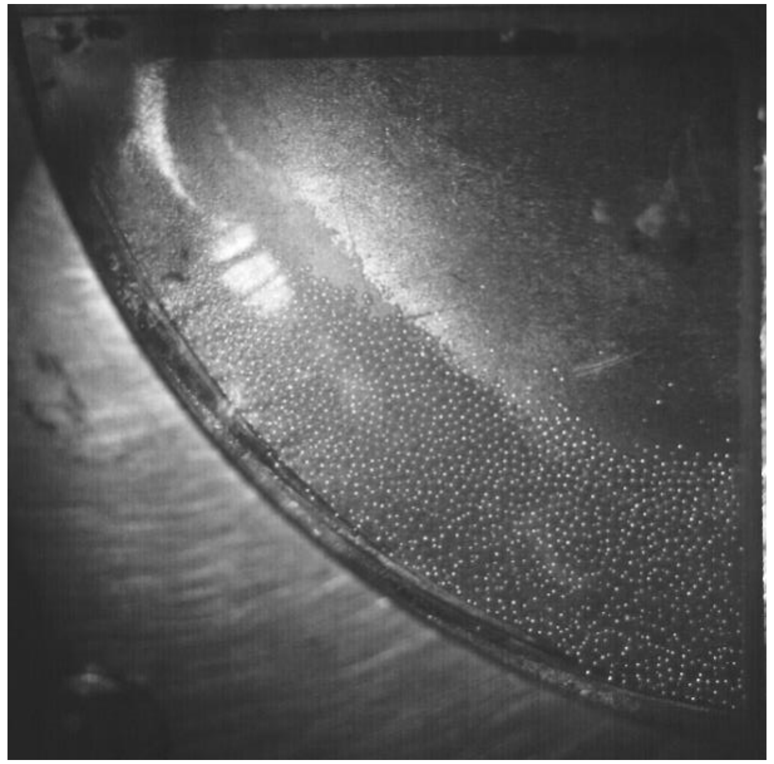


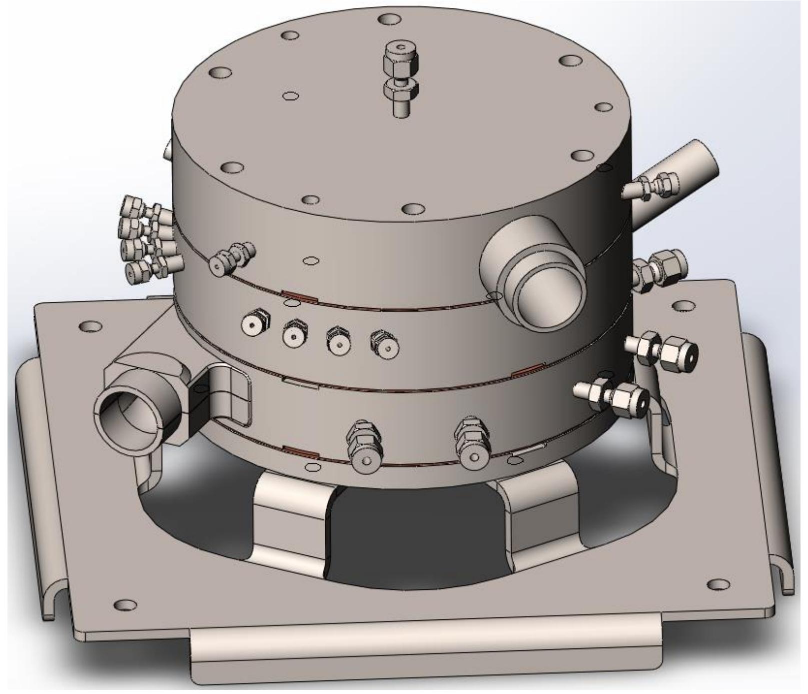


Cold-Flow GSVR

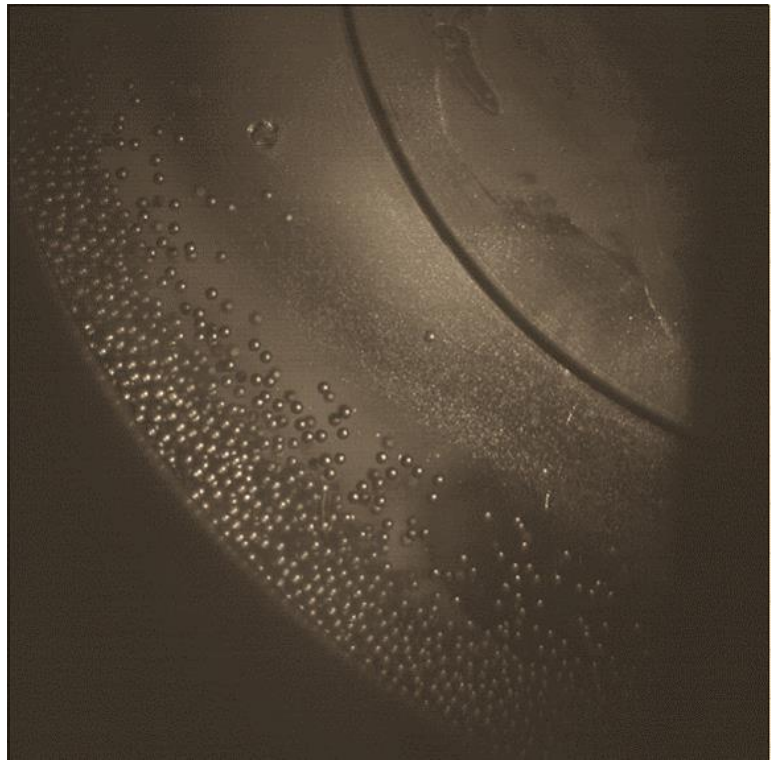


Hot-Flow GSVR





Reactive GSVR



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CIRCULAR PLASTICS NETWORK FOR TRAINING

Vortex Reactors Infrastructure @ LCT

	Cold-flow Setup	Hot-flow Setup	Reactive Setup
Reactor Diameter [mm]	570	139	80
Length [mm]	100	25	15
Exhaust Diameter [mm]	150	40	20
Number of Slots [-]	32	8,16	16,12,8
Slot Width [mm]	2,6	0.5,0.6,1	0.45,0.6,0.95
Max Solid loading [g]	2000 – 5000	100 – 200	20 – 30
Materials tested [-]	PVC, PTFE, HDPE, FCC,…	HDPE, Pine, Al, Al_2O_3,…	Poplar, Pine, Al, Al_2O_3, SiC, …
Gas Heater [-]	X	✔ (~ 200 °C)	✔ (~ 1000 °C)
Gas Flow [Nm3/h]	360 - 1800	40 - 600	15 – 60

- High frequency (10 Hz) pressure and temperature sensors
- High accuracy mass flow controllers for all the gases.

TRL 4/5
Research → Demonstration

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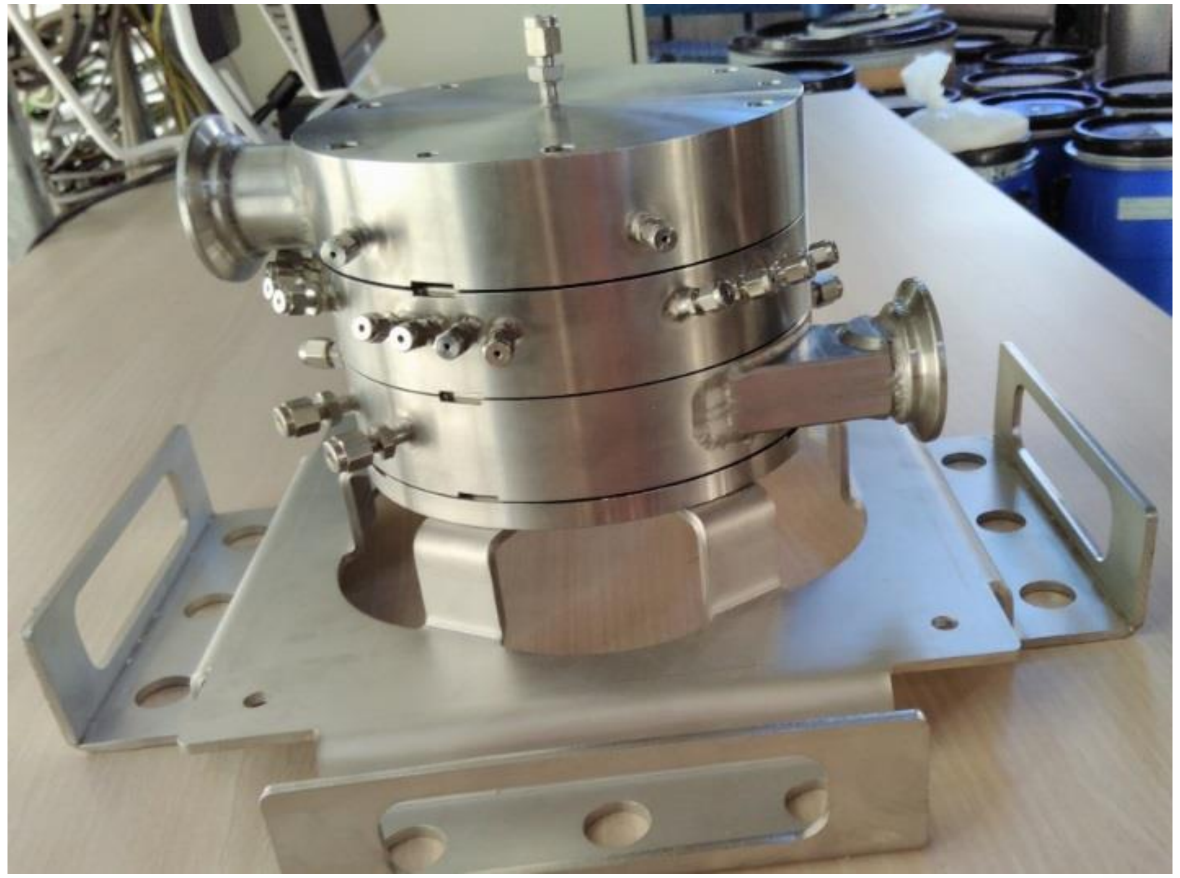
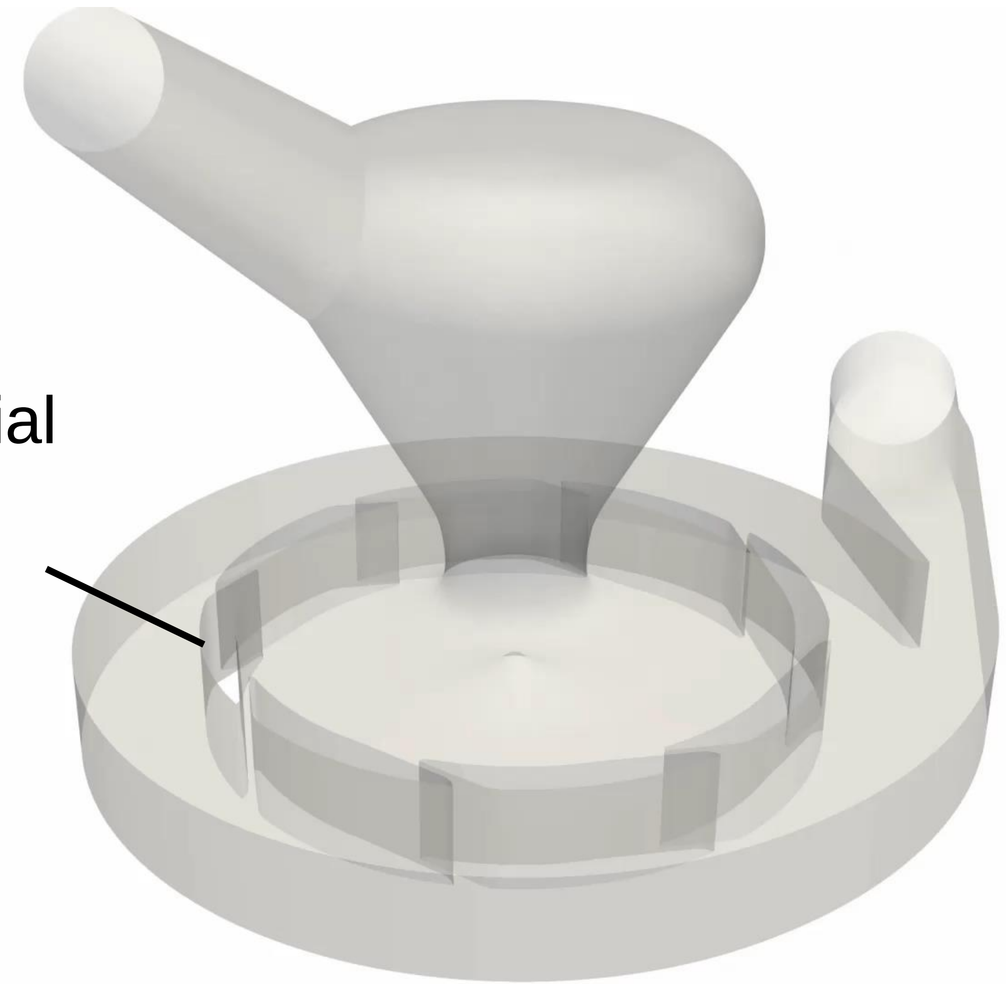
C-PlaNeT CIRCULAR PLASTICS NETWORK FOR TRAINING

Reactive Gas-Solid Vortex Reactor (GSVR)





Tangential gas injection slots

Rotating bed in Vortex reactor

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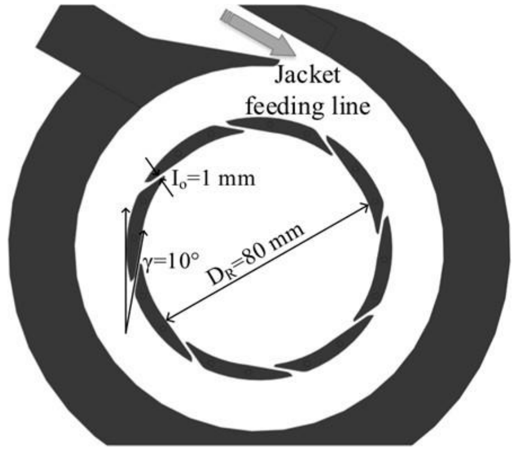
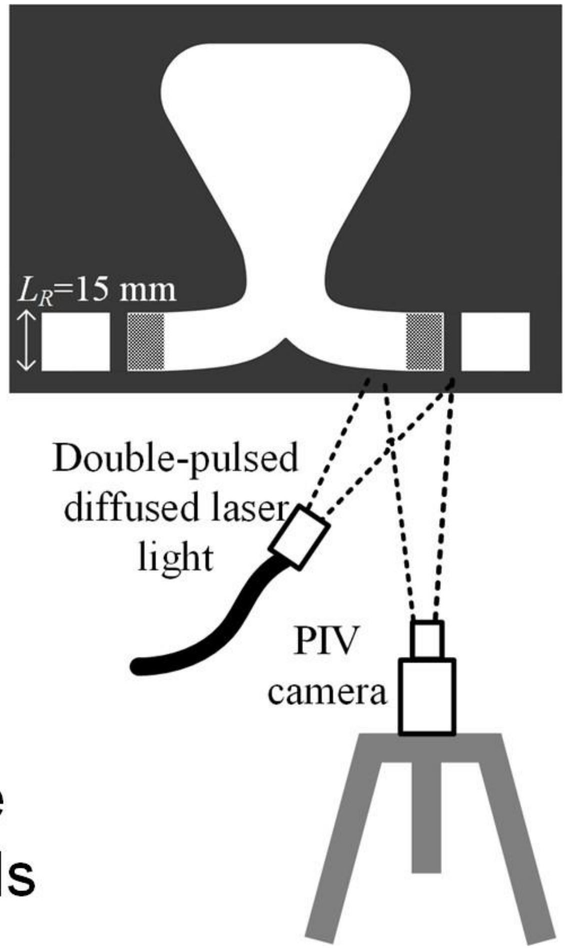
Cold-flow CFD model validation

EXPERIMENT

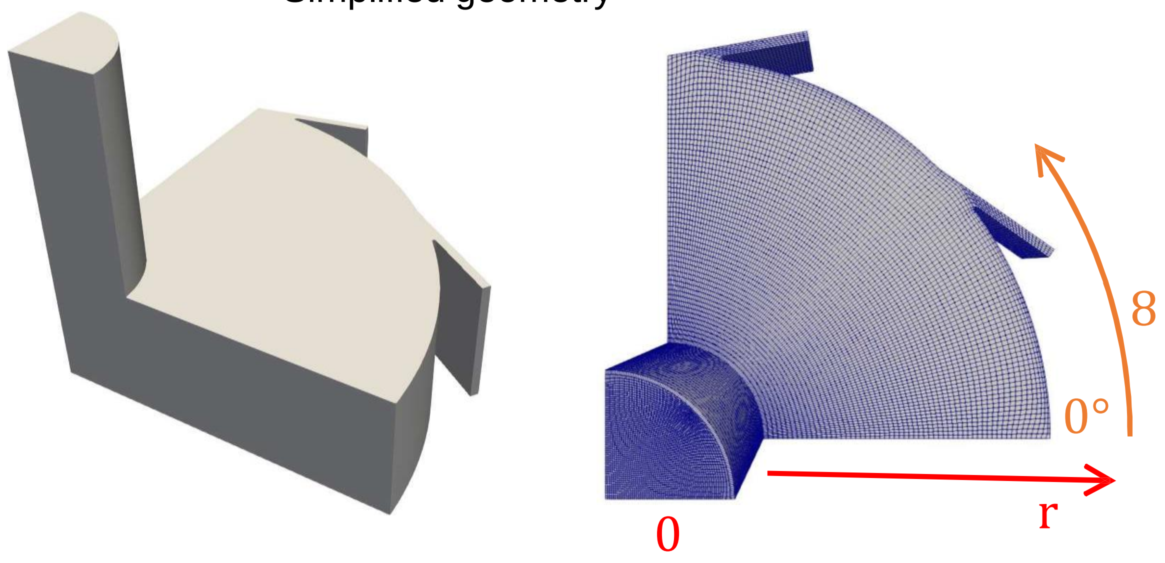




Particle image velocimetry (PIV)
Measuring particle velocity profile to validate e hydrodynamic mod els

CFD MODEL

Simplified geometry



- OpenFOAM
- Euler-Euler model with KTGF closures

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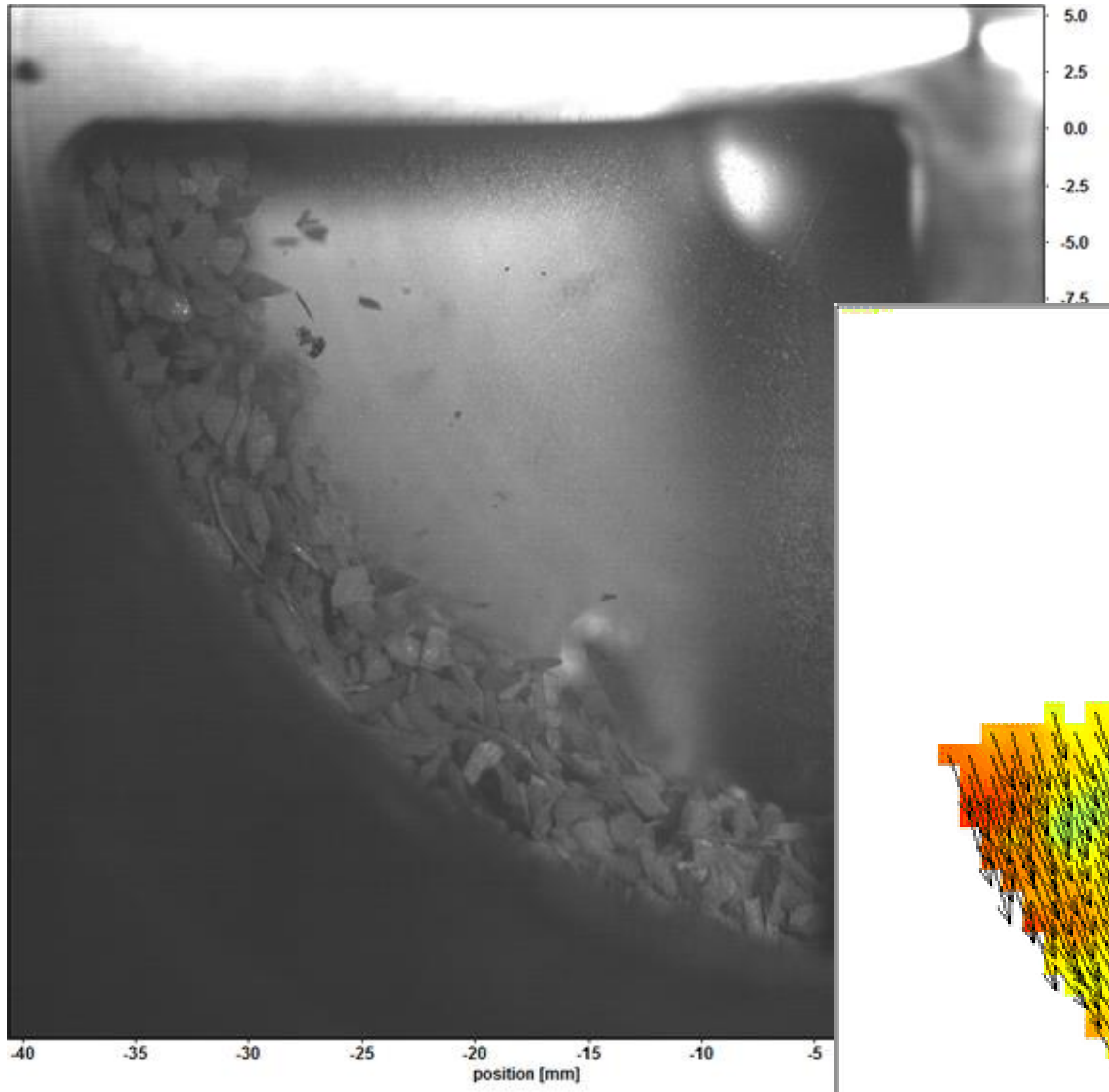
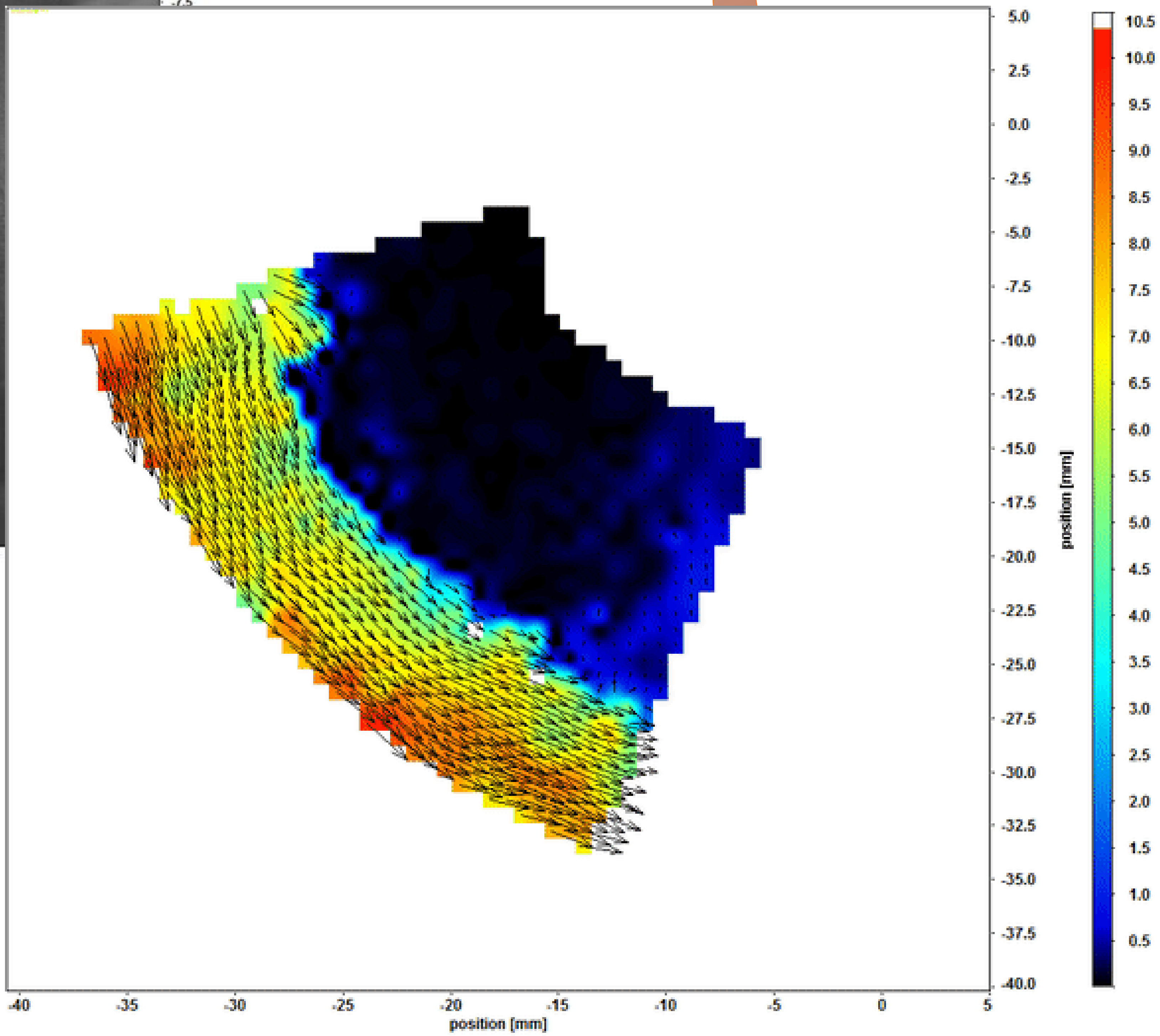
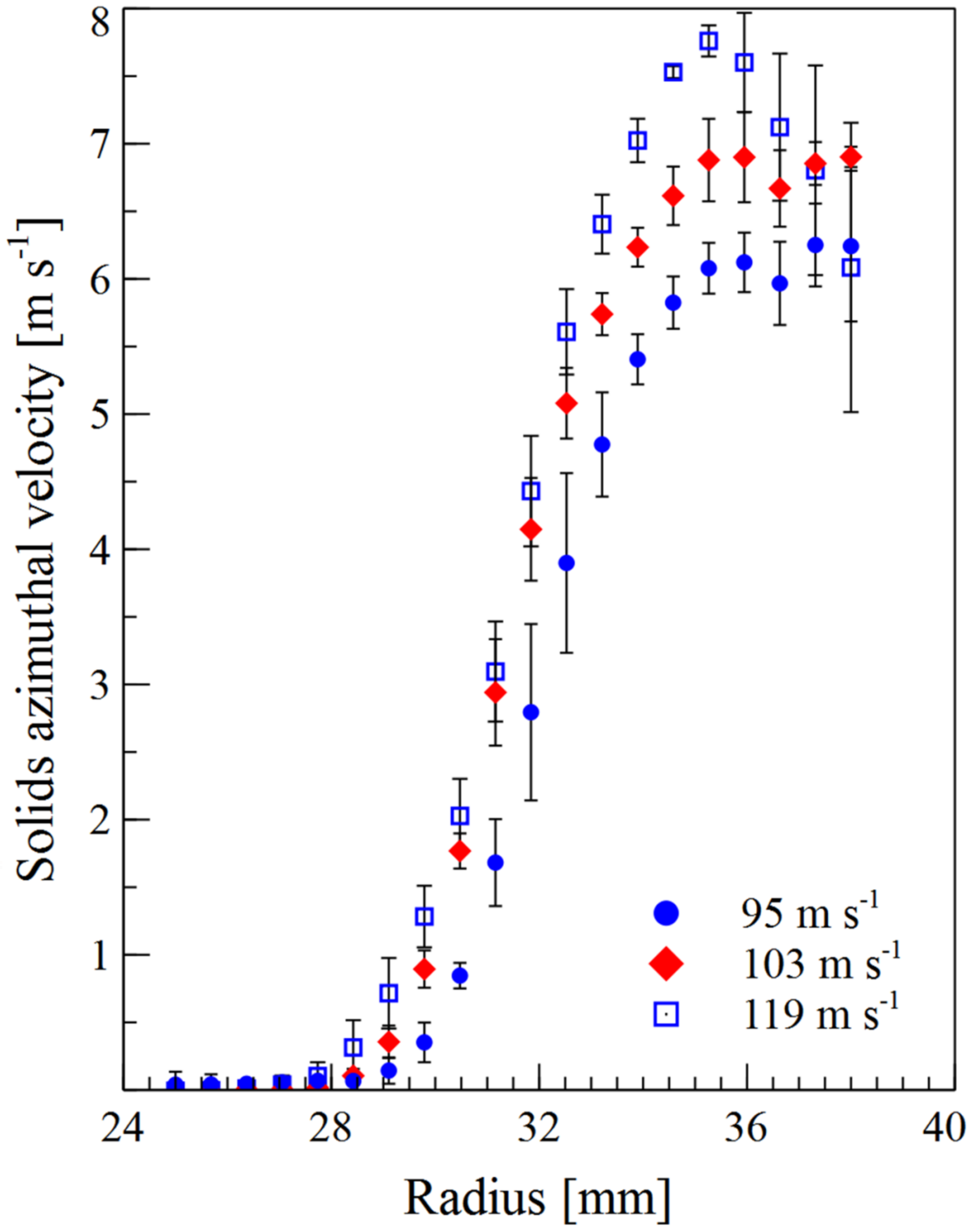
Cold flow testing and data acquisition



Particle image velocimetry





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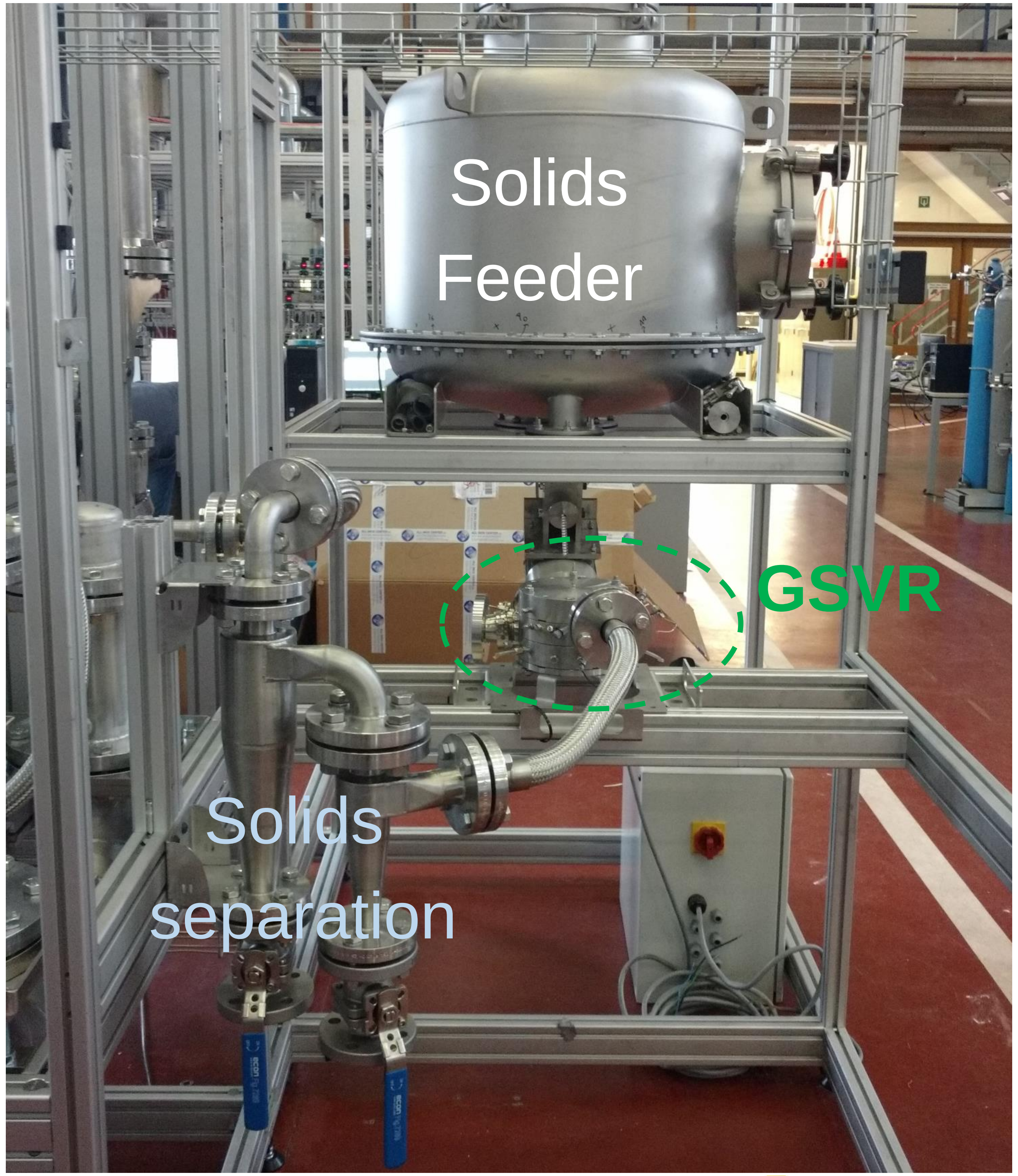
Gonzalez-Quiroga et al., *Chem. Eng. J.* **329** 198, 2016

GSVR setup



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GSVR[1] operational range & applications

Process parameter	Value
Temperature (°C)	20 - 850
Gas flow (Nm³/h)	15 - 50
Solid mass flow (Kg/h)	0.36- 1.2
Solid density (Kg/m³)	300 - 4000
Solid particle size (m)	$7 \cdot 10^{-5}$ - $3 \cdot 10^{-3}$
Solid capacity (g)	5 - 30
Liquid flow (m³/h)	$6 \cdot 10^{-3}$ - $3.6 \cdot 10^{-2}$
Gas phase residence time (s)	0.005 - 0.01

- CO_2 absorption
- Oxidative coupling of CH_4
- Biomass fast pyrolysis
- Plastic waste recycling

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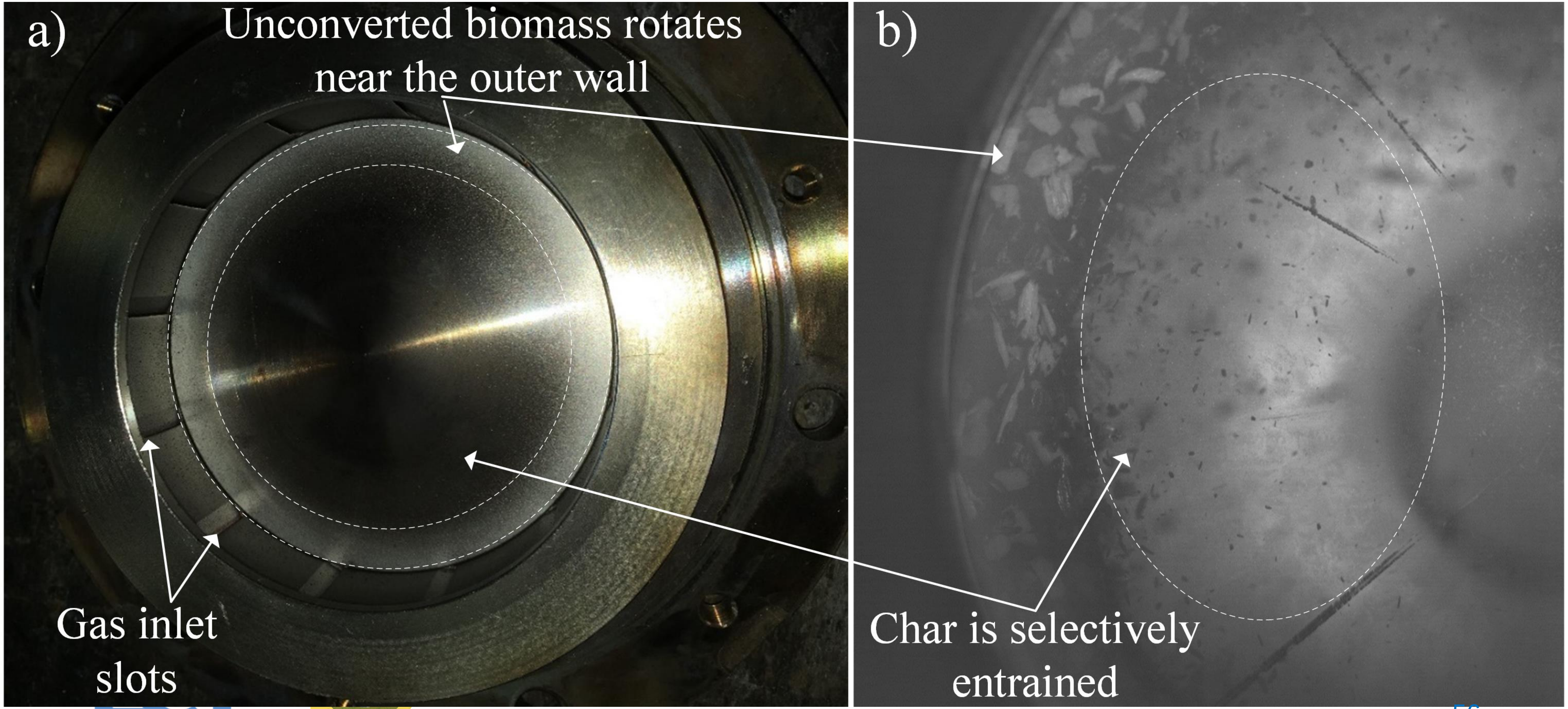
C-PlaNeT CIRCULAR PLASTICS NETWORK FOR TRAINING

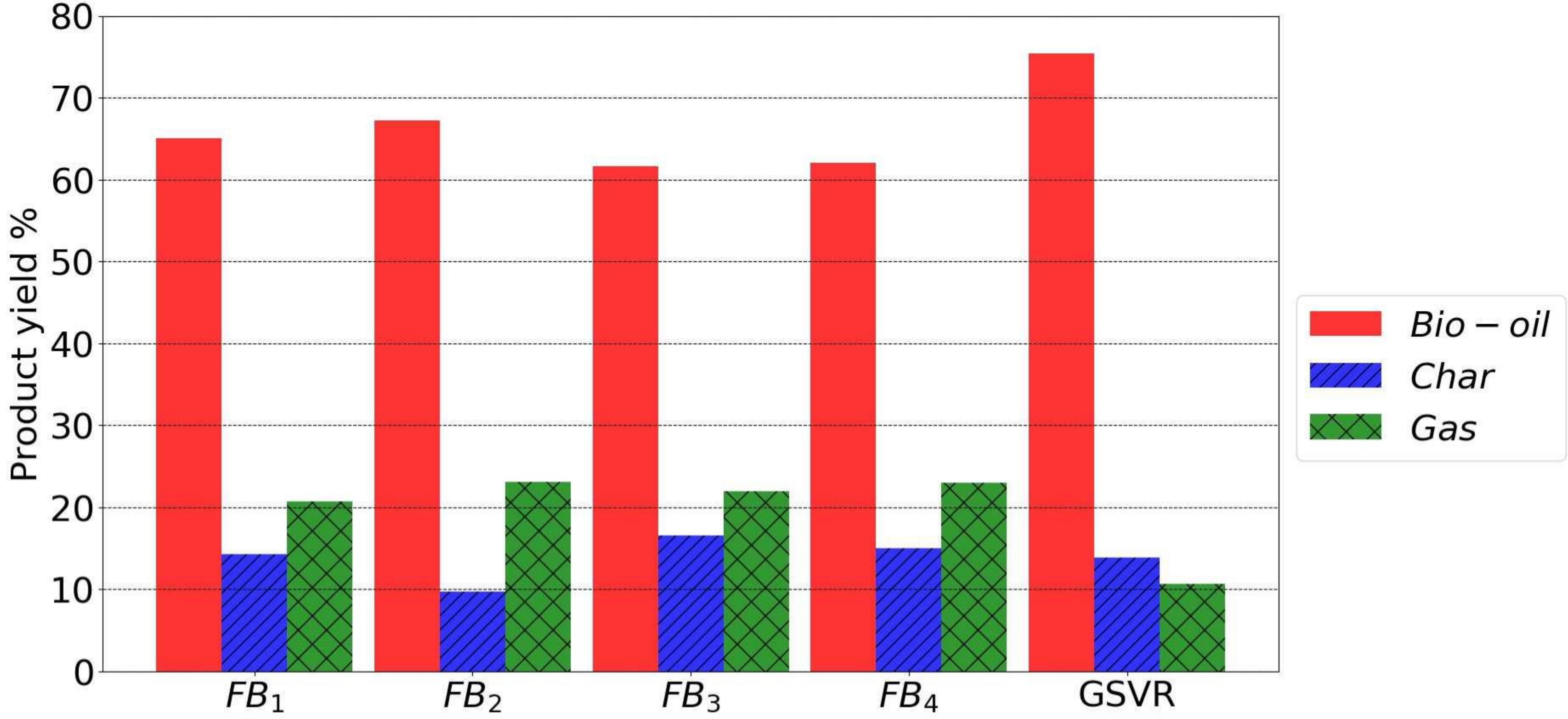
1 Reactive unit

First drop of bio-oil

- GSVR chamber after the first reactive test
- No signs of clogging of gas inlet slots or reactor exhaust



GSVR vs Conventional Fluidized-Bed reactors



FB1 - DeSisto et al. Energy Fuels (2010) 24:2646−2651
FB2 - Men et al. Bioresource Technol (2012) 111:439-446
FB3 - Kim et al. Renewable Energy (2013) 50:188-195
FB4 - Westerhof et al. Ind. Eng. Chem. Res. (2010) 49:1160-1168

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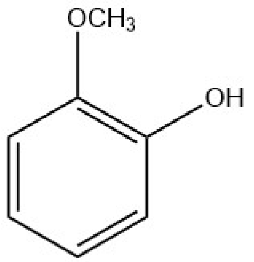
Pine Fast Pyrolysis – GCxGC oil characterization

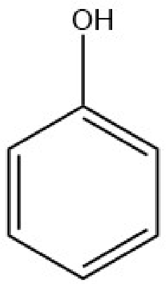
Components identified:

24 wt. % of Bio-oil

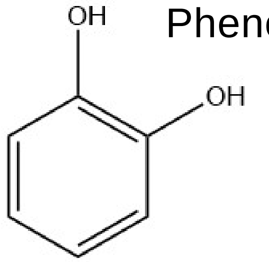
- **Non-aromatic**: 84%
- Aromatic: 16%
  - **Guaiacols** 85%
  - **Catechols** 10%
  - **Phenolics** 5%



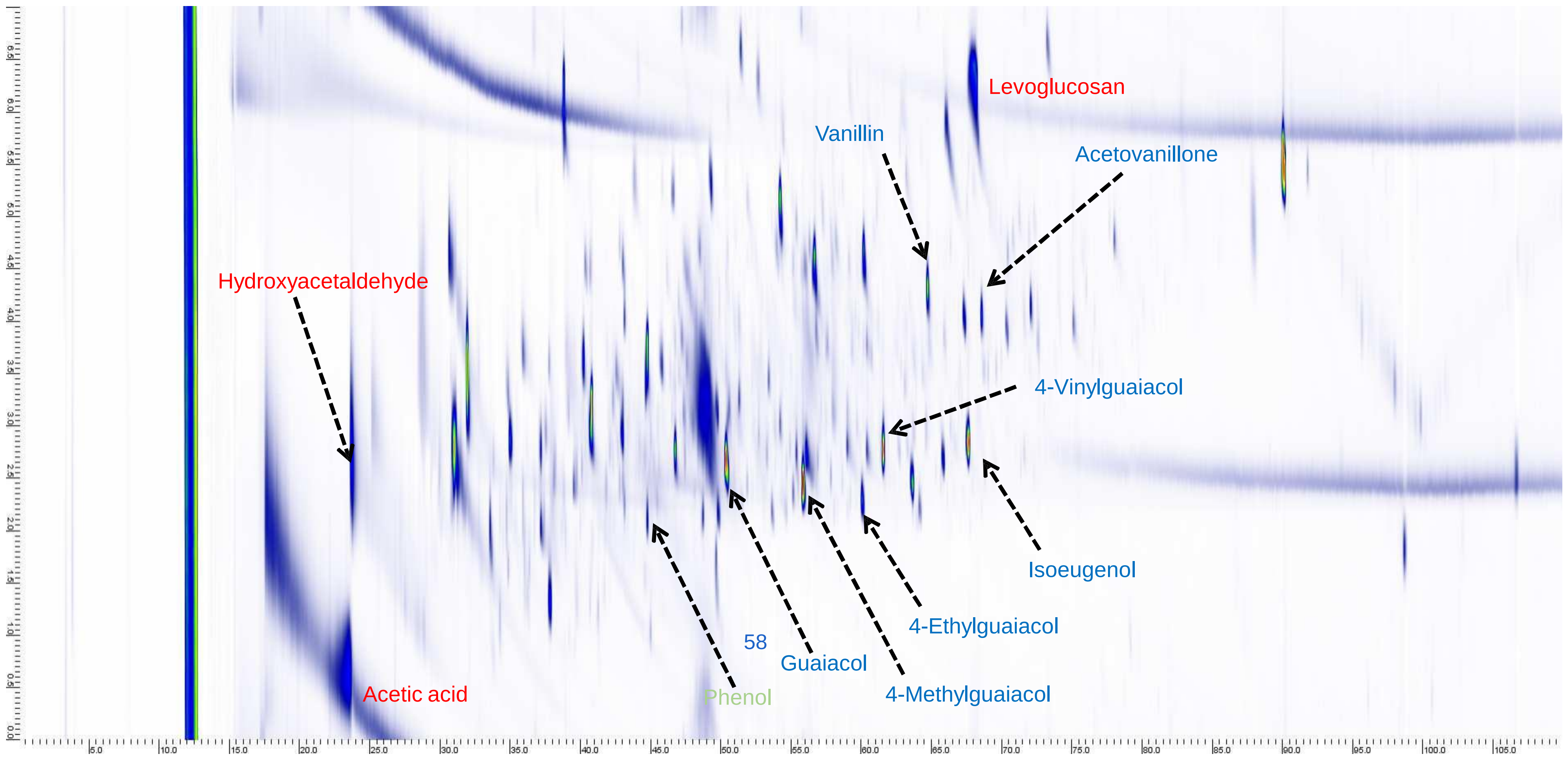
Guaiacol moiety



Phenol moiety



Catechol moiety



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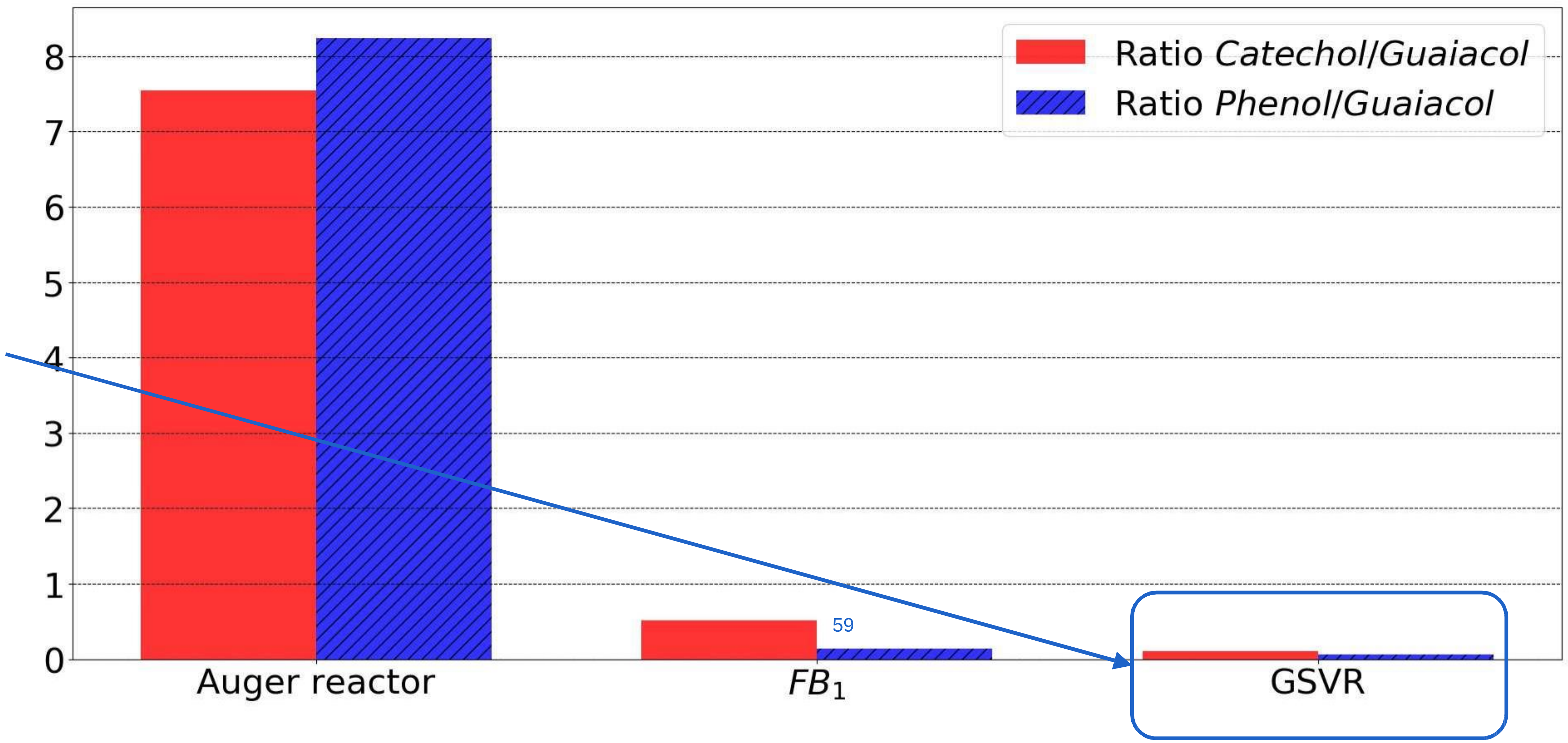
Bio oil composition: GSVR vs gravitational FBs

Reduction of secondary cracking reaction



- *Bioresource Technol. (2016) 219:371–377*
- *Energy Fuels (2010) 24:2642–2651*
- *Energy Fuels (2013) 27:4748–4759*
- *Bioresource Technol. (2010) 101:8389–8395*

Future Plan

- Vortex reactor setups (experiments and CFD)
- Catalyst synthesis at AUTH

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C-PlaNeT
CIRCULAR PLASTICS NETWORK FOR TRAINING

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