Multidimensional Gas Chromatography (MDGC)

○ What is the two dimensional GC?

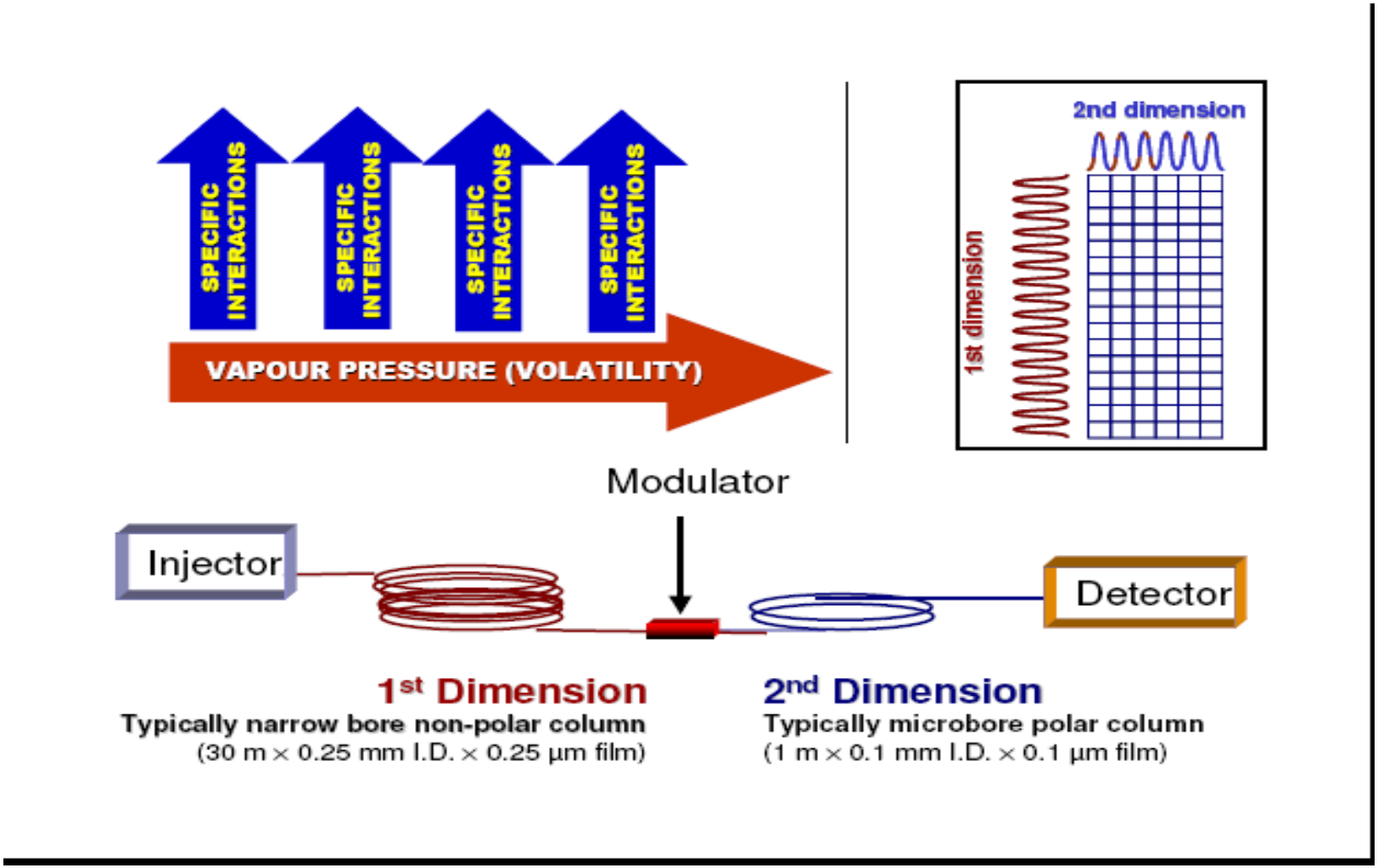
✓Two dimensional GC is new mode of high resolution .

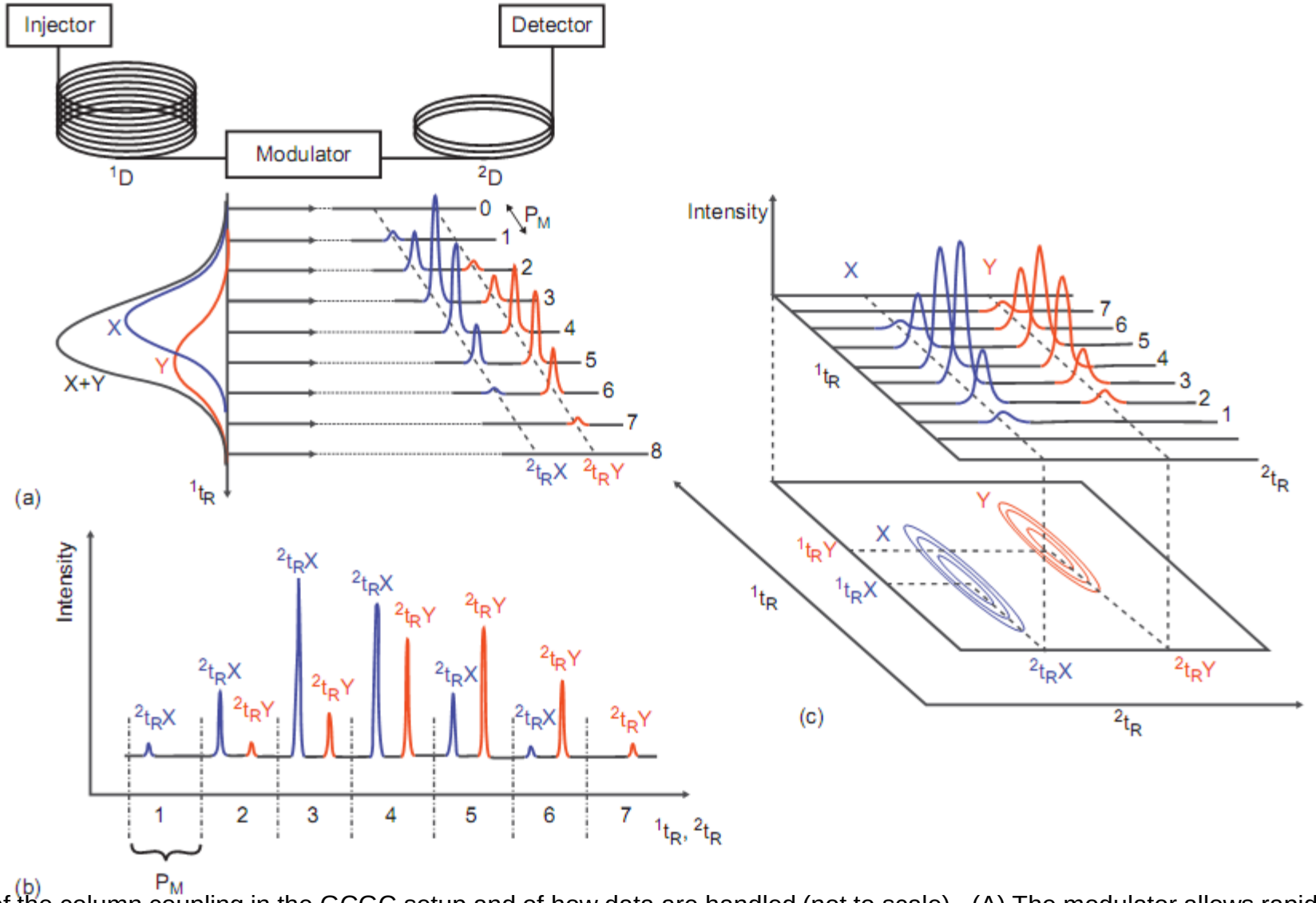
✓It is consisting of, two coupled columns with complementary separation mechanism.

✓ Ensuring a high degree of orthogonality.

✓ Interfaced using a two stage thermal modulation .

✓ Developed solute-selection heart-cutting techniques.


SPECIFIC INTERACTIONS
SPECIFIC INTERACTIONS
SPECIFIC INTERACTIONS
SPECIFIC INTERACTIONS
VAPOUR PRESSURE (VOLATILITY)
2nd dimension
1st dimension
Modulator
Injector
Detector
1st Dimension
Typically narrow bore non-polar column
(30 m × 0.25 mm I.D. × 0.25 µm film)
2nd Dimension
Typically microbore polar column
(1 m × 0.1 mm I.D. × 0.1 µm film)

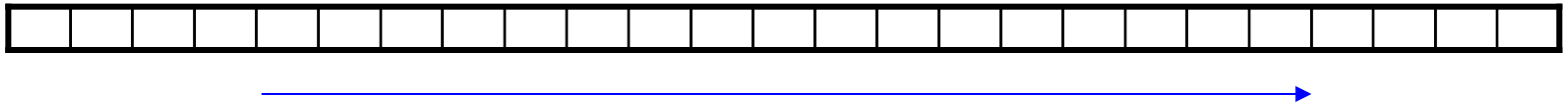


Scheme of the column coupling in the GCGC setup and of how data are handled (not to scale) . (A) The modulator allows rapid sampling of the analytes eluting out of 1D and reinjection in 2D. The modulation process is illustrated for two overlapping compounds (X and Y) coming out of 1D at a defined first-dimension retention time (1 tR). As the modulation process occurs during a defined PM, narrow bands of sampled analytes are entering 2D and appear to have different second-dimension retention times (2 tRX and 2 tRY). (B) Raw data signal as recorded by the detector through the entire separation process. (C) Construction of the two-dimensional contour plot from the collected high-speed secondary chromatograms of (B), in which similar signal intensities are connected by contour lines.

1D-versus 2D-chromatography

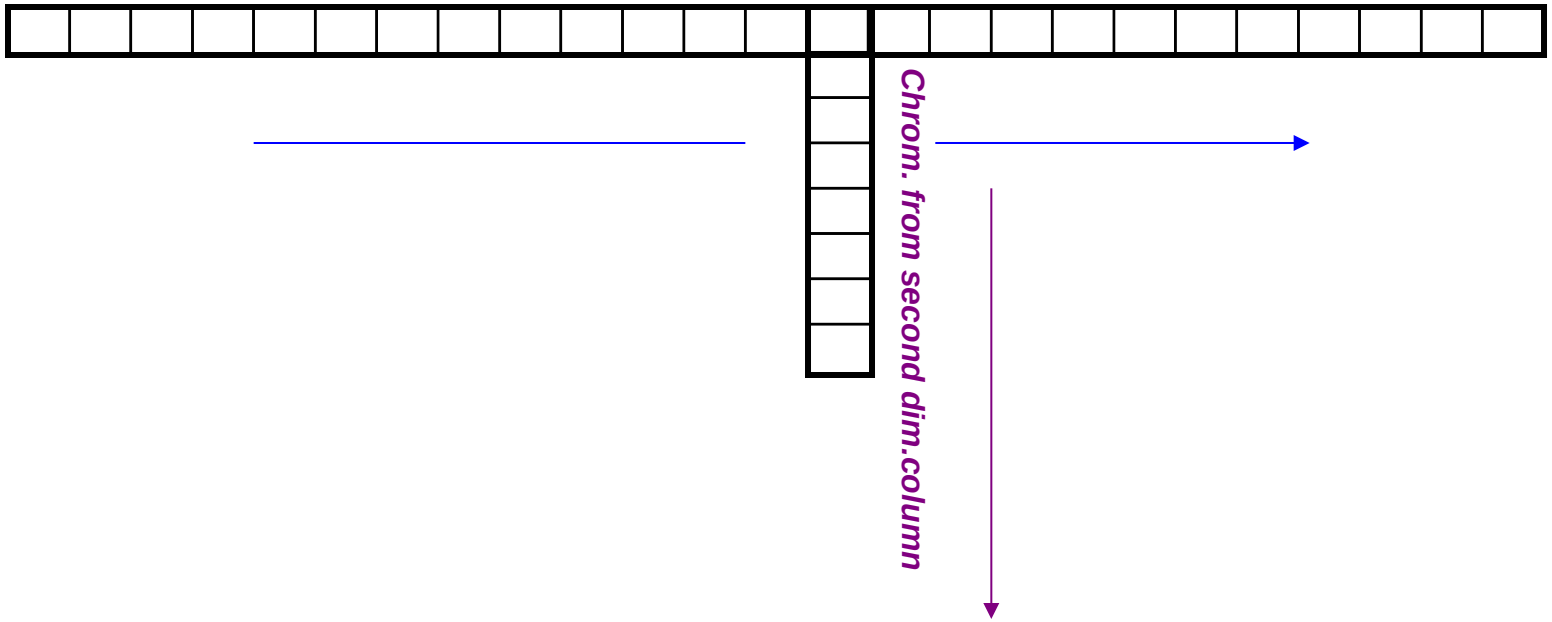
Normal 1D-chromatography

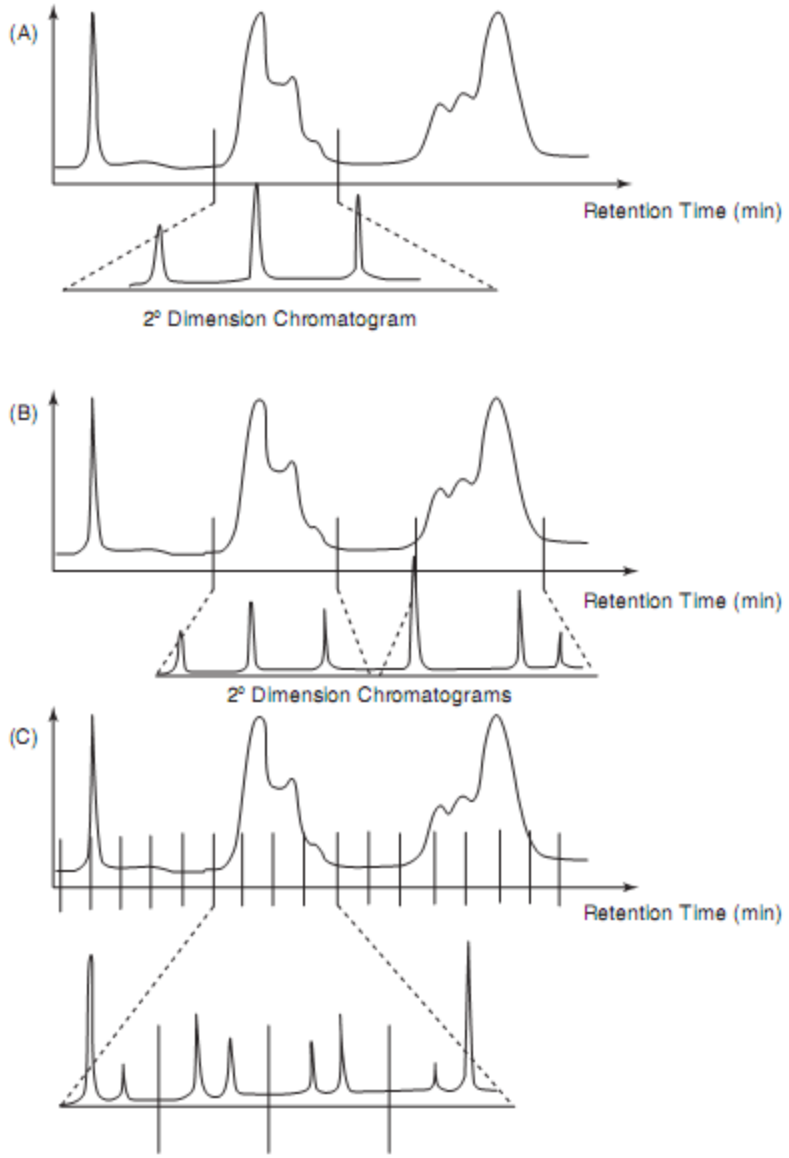
Chromatogram from first dim. column



Heart-cut 2D-chromatography

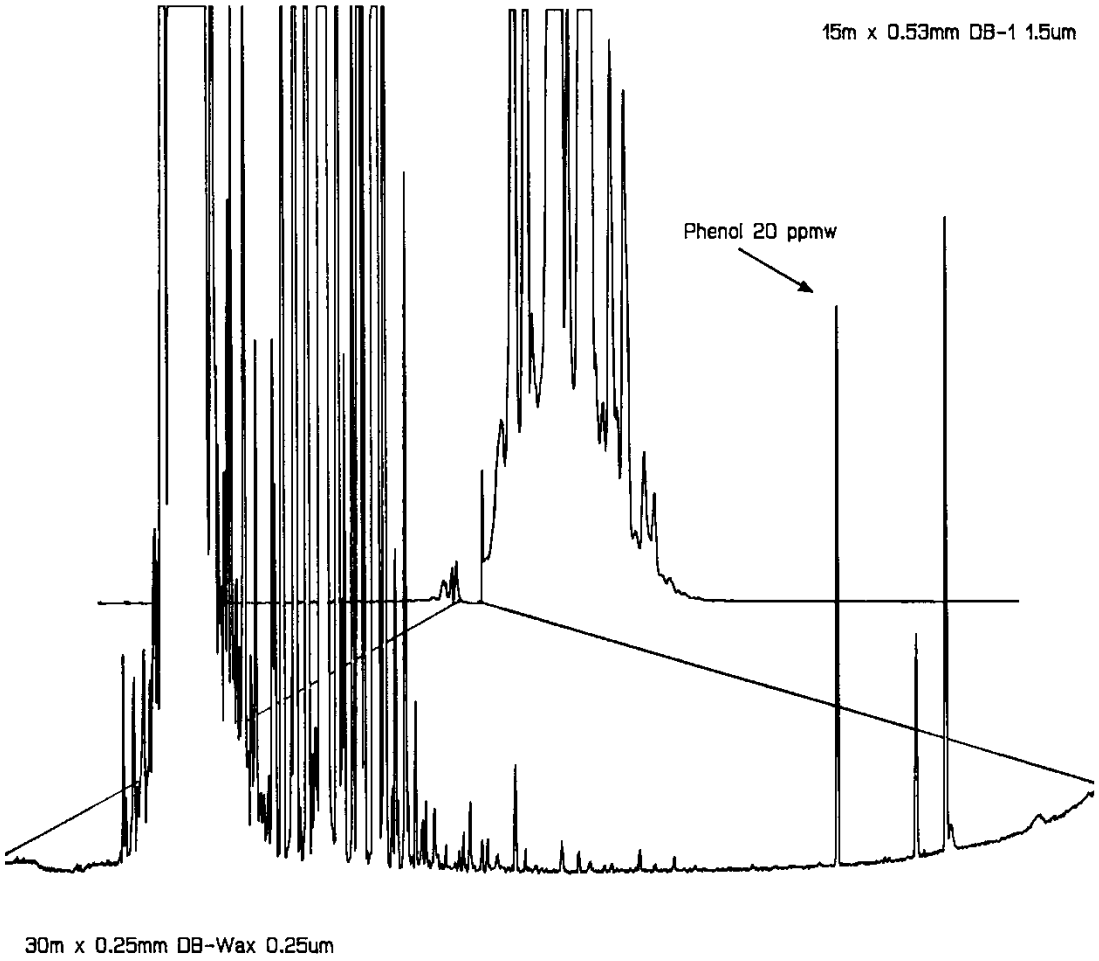
Chromatogram from first dim. column





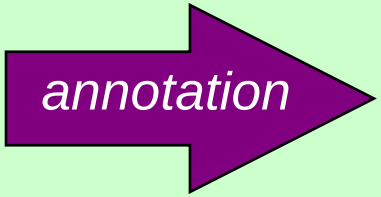
(A) single heart-cut GC analysis, where a large portion of the effluent from the primary column with coelutions is diverted to the second-dimension column and separated over an extended period of time. (B) Dual heart-cut GC analysis, where two regions with coelutions are diverted to the second- dimension column, but with less time to perform each separation. (C) Comprehensive two-dimensional GC analysis occurs when the size of the sequential heart cuts is very short, as are the second-dimension chromatograms.

Two-dimensional separation through heart-cut (GC-GC)



Conventional MDGC

Heart-cut technique



GC-GC

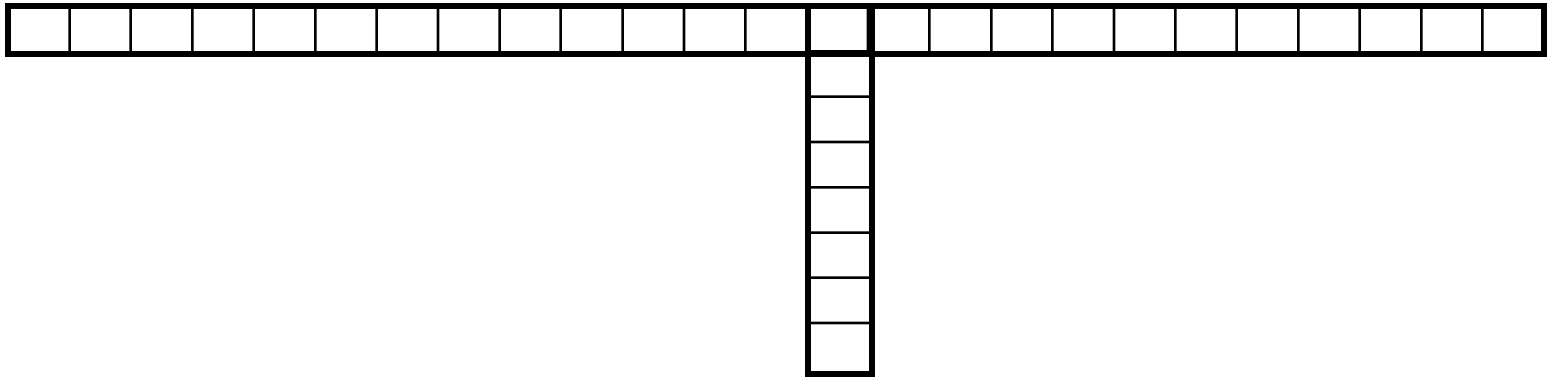
Only few fractions of the sample are separated on the second dimension

Comprehensive 2DGC – What is it?

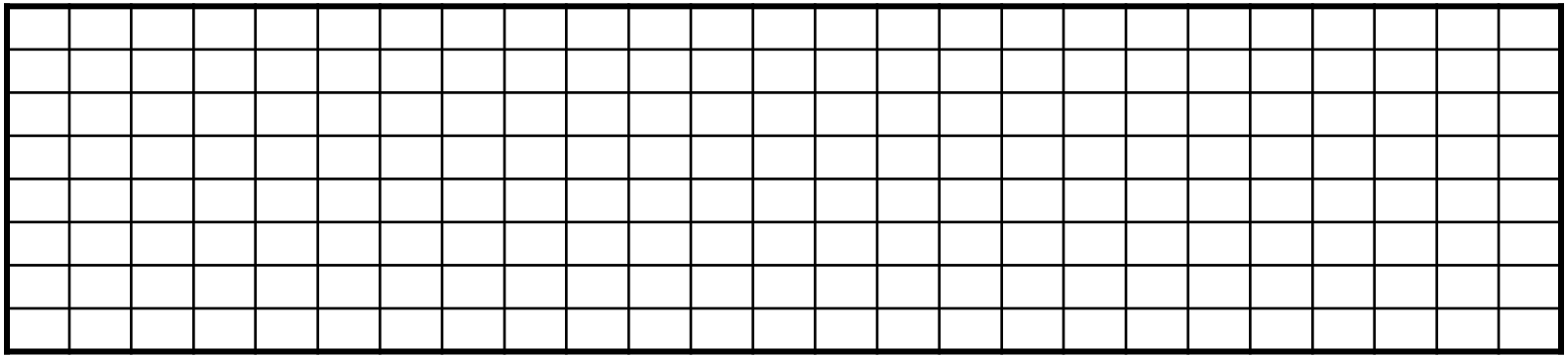
A much larger number of fractions from the first column is sent to a second column, so that the entire sample is submitted practically at the same time to both separations

Normal chromatography

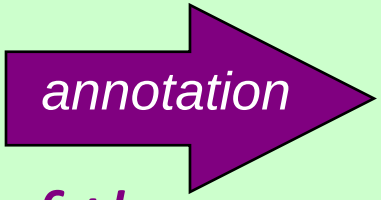
Heart-cut 2D chromatography



Comprehensive 2D chromatography



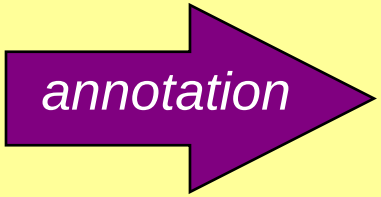
Conventional MDGC
Heart-cut technique



GC-GC

Only few fractions of the sample are separated on the second dimension

Comprehensive
2D-GC

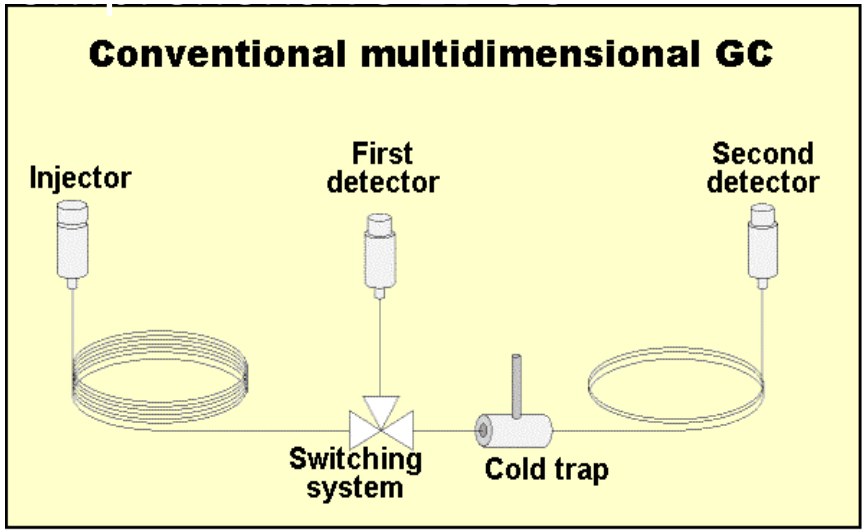


GCxGC

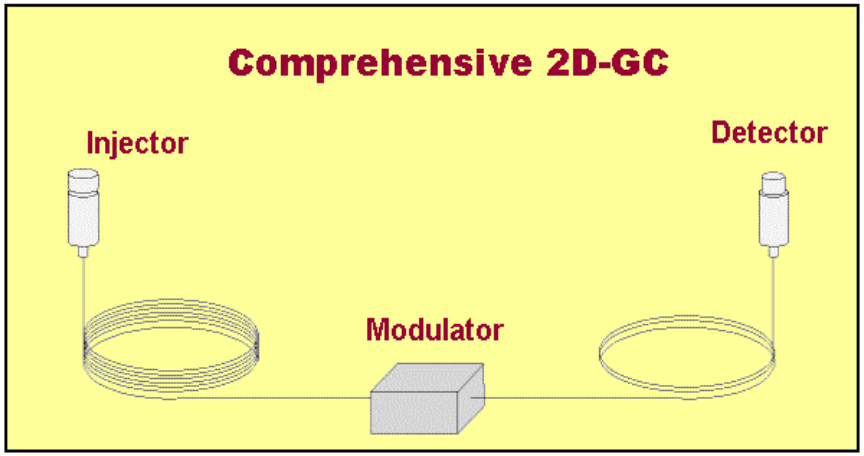
The entire sample is separated on both dimensions

Any analytical range of a given sample is sacrificed

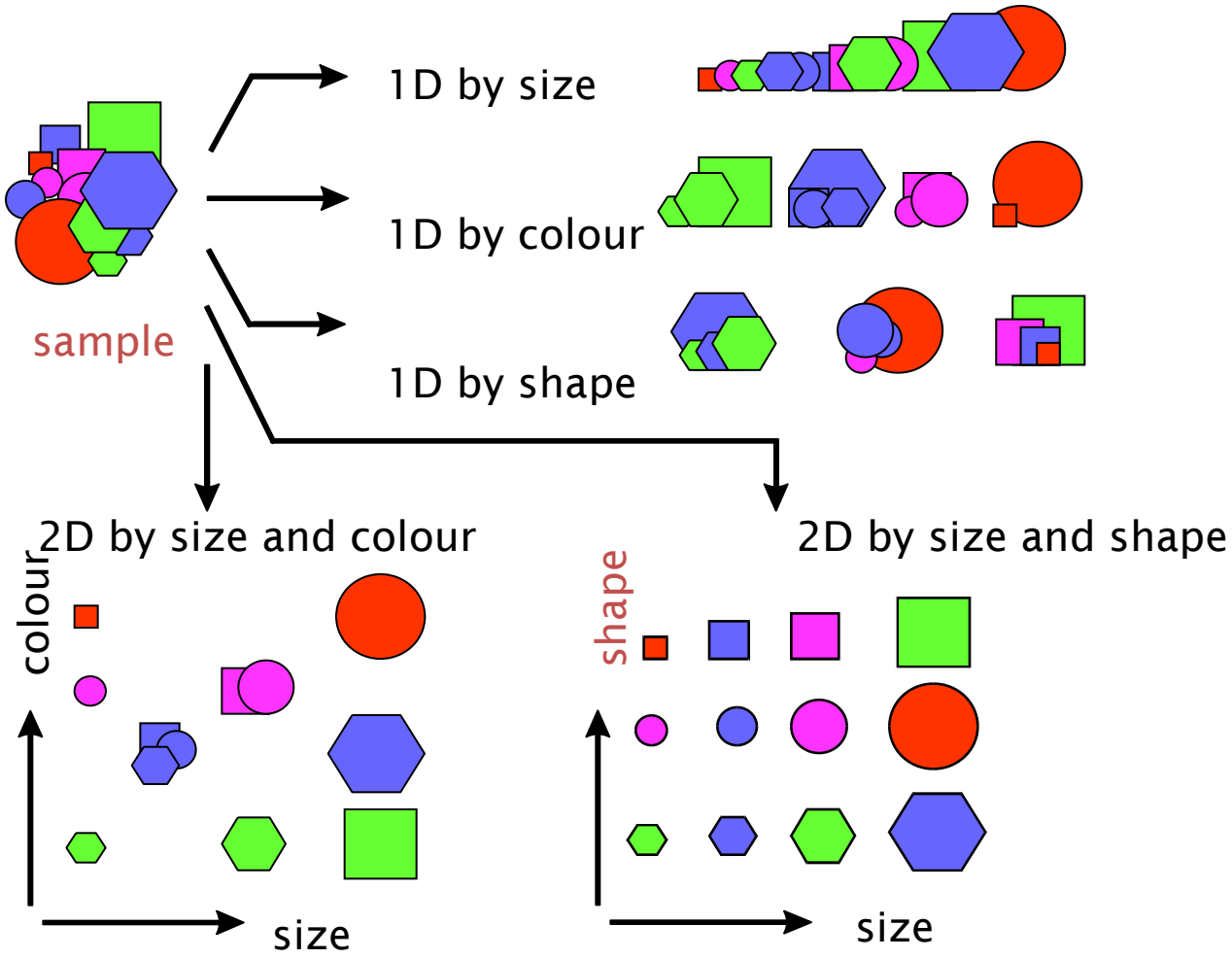
In the conventional MDGC only a part of the peaks is transferred for further separation into the second column



In comprehensive 2DGC each peak is sliced and fully transferred for further separation into the second dimension column

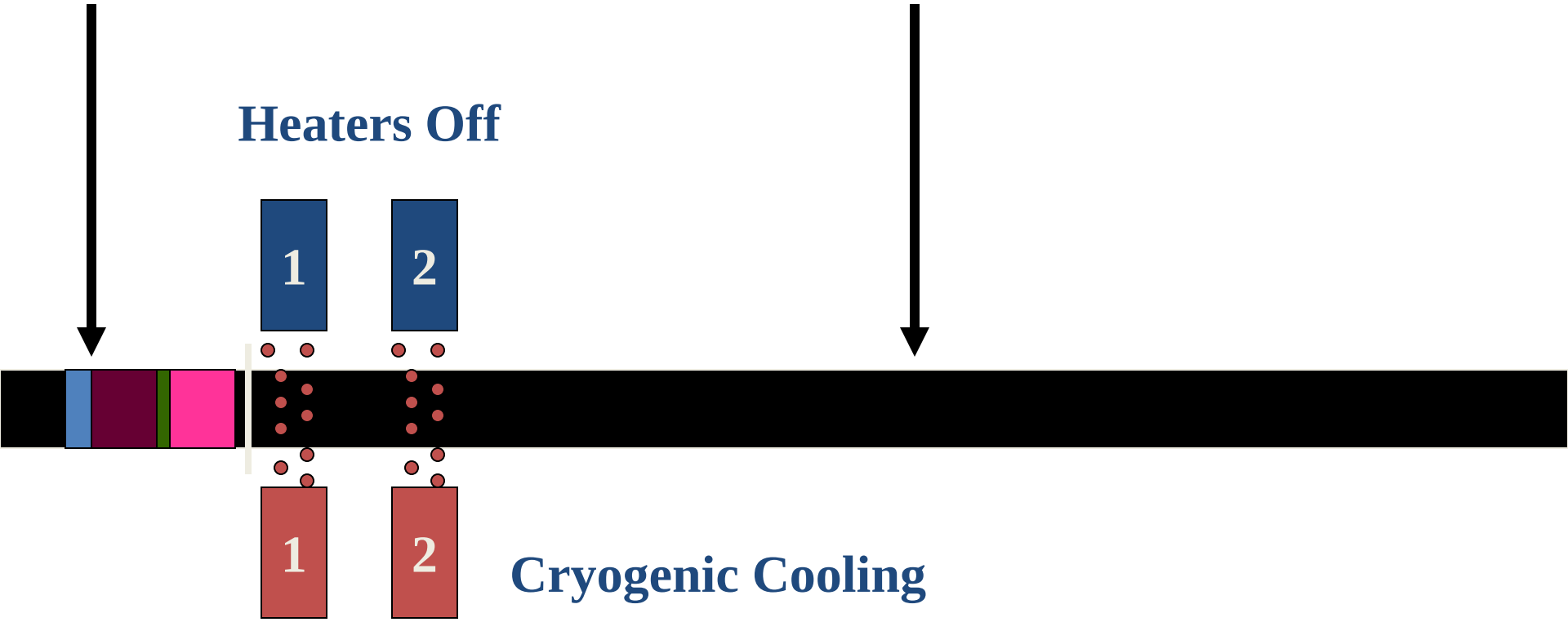


The use of sample dimensionality



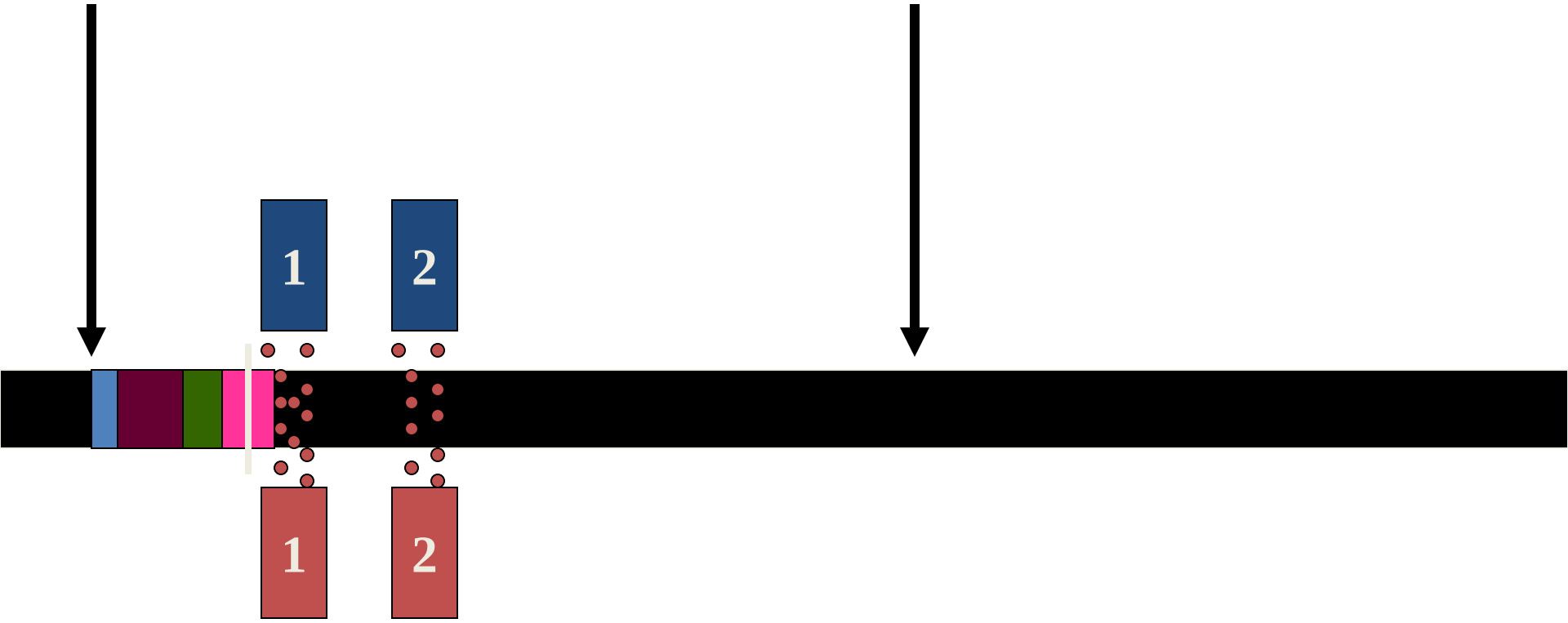
Comprehensive GCxGC

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

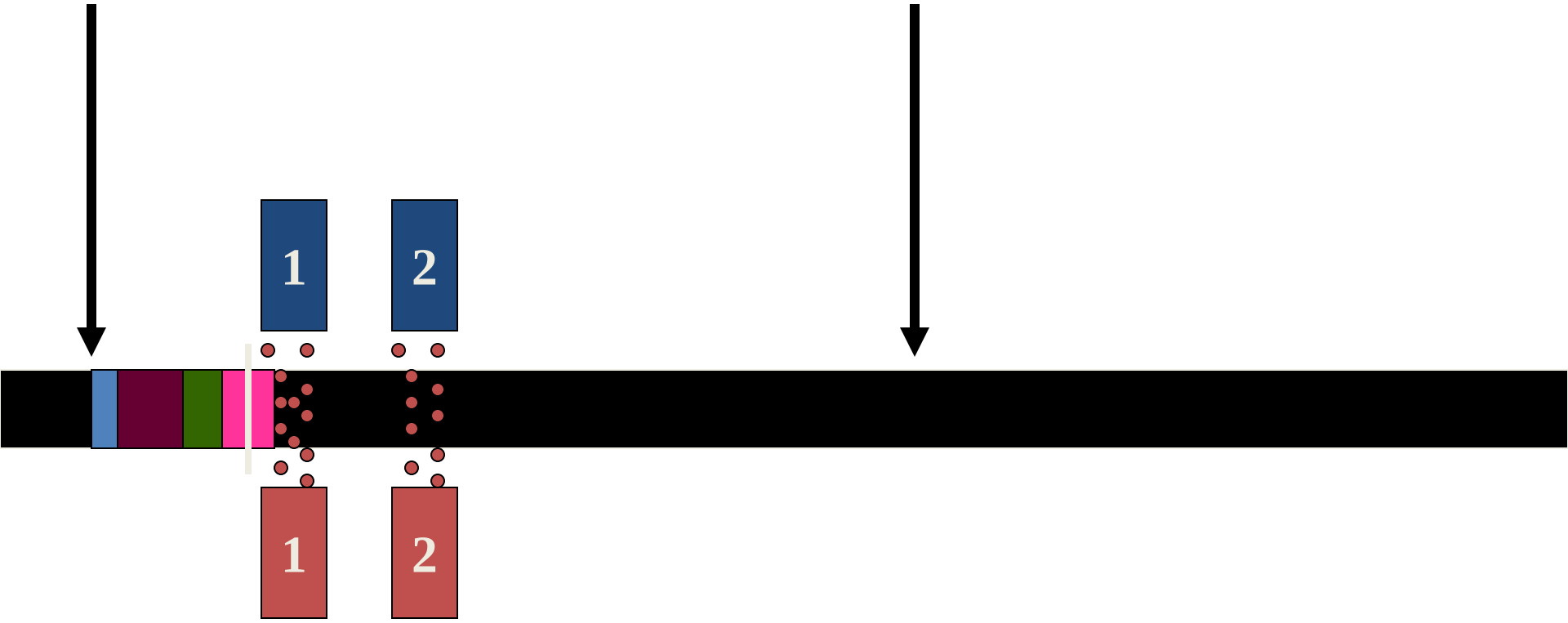


Analytes Partially Resolved on Column 1

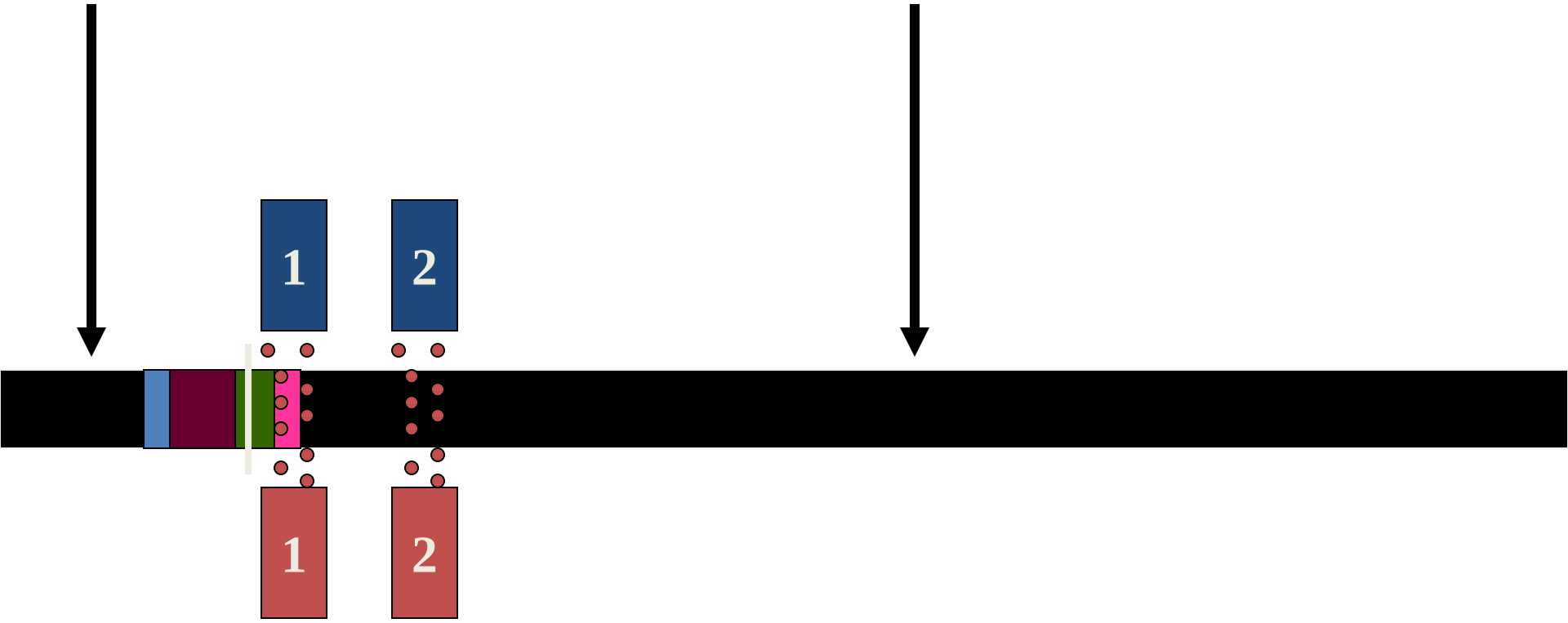
Column 1: Non-Polar Phase **Column 2: Polar Phase**



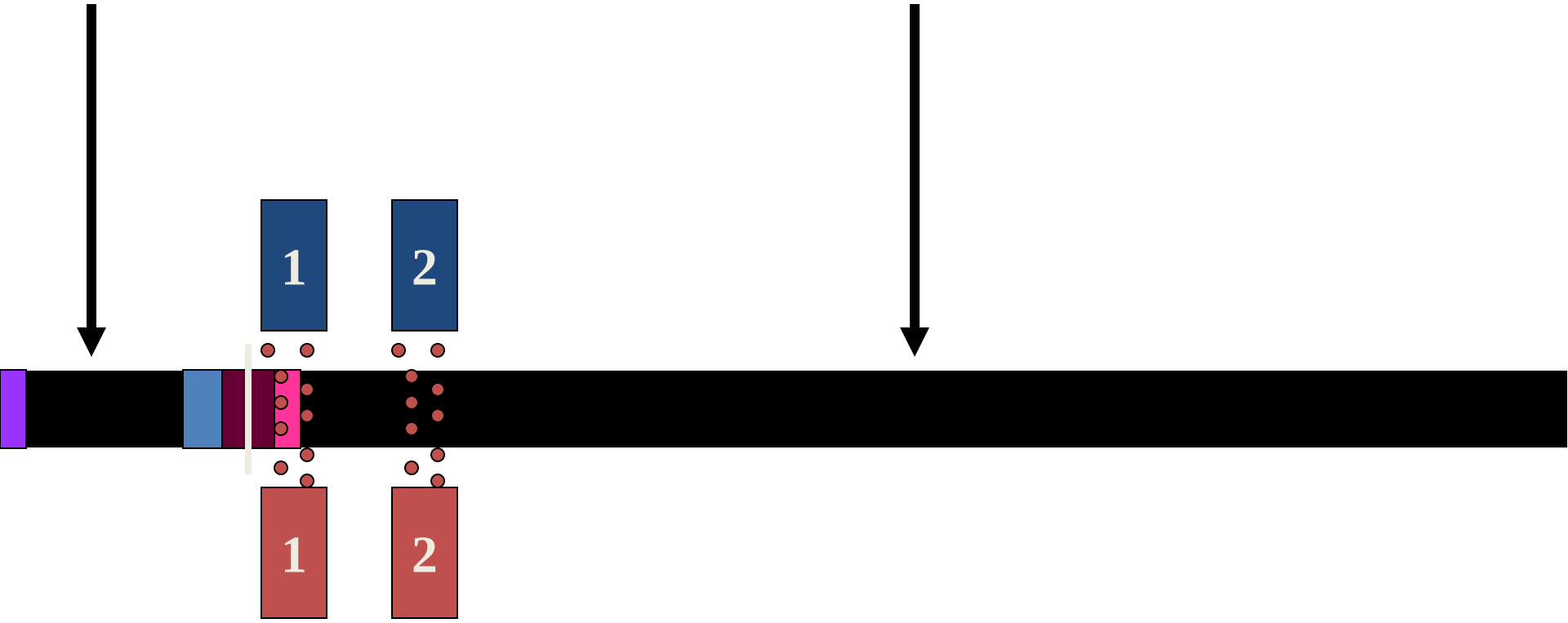
Column 1: Non-Polar Phase **Column 2: Polar Phase**



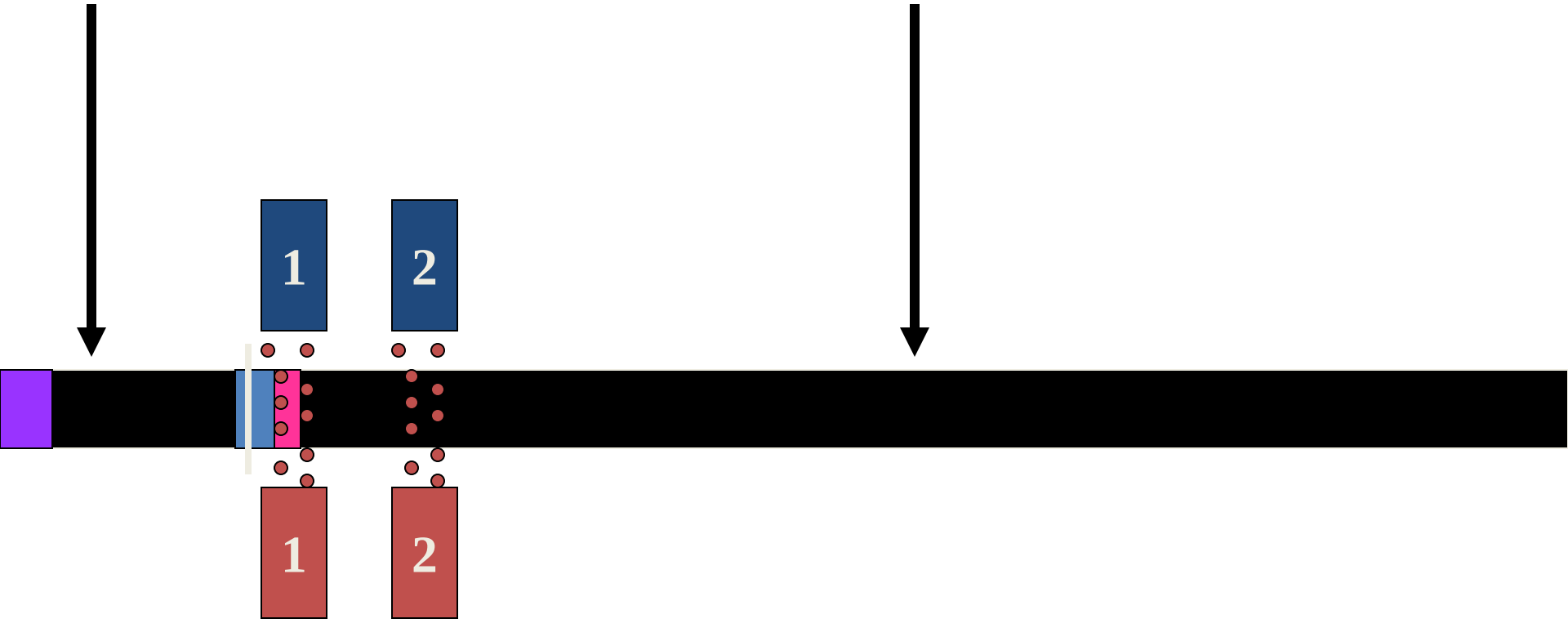
Column 1: Non-Polar Phase **Column 2: Polar Phase**

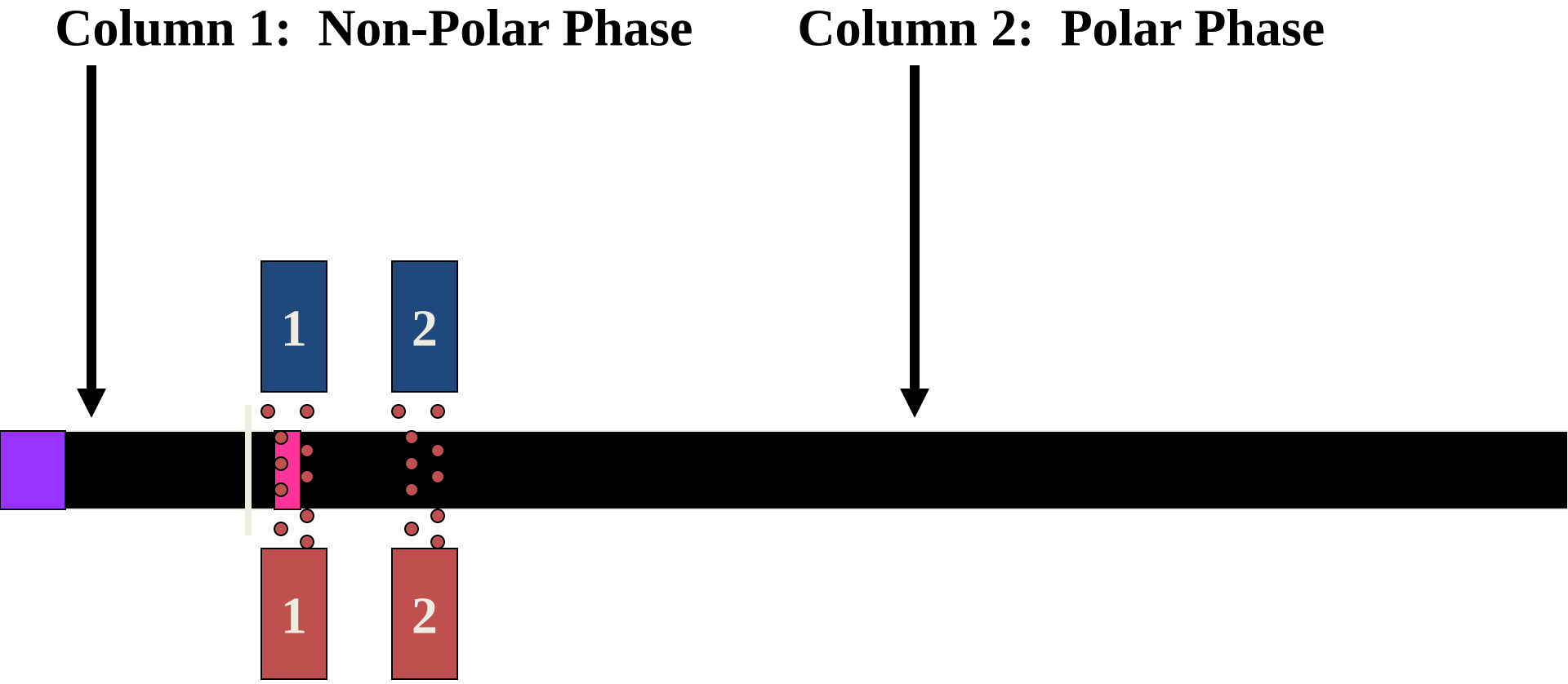


Column 1: Non-Polar Phase **Column 2: Polar Phase**

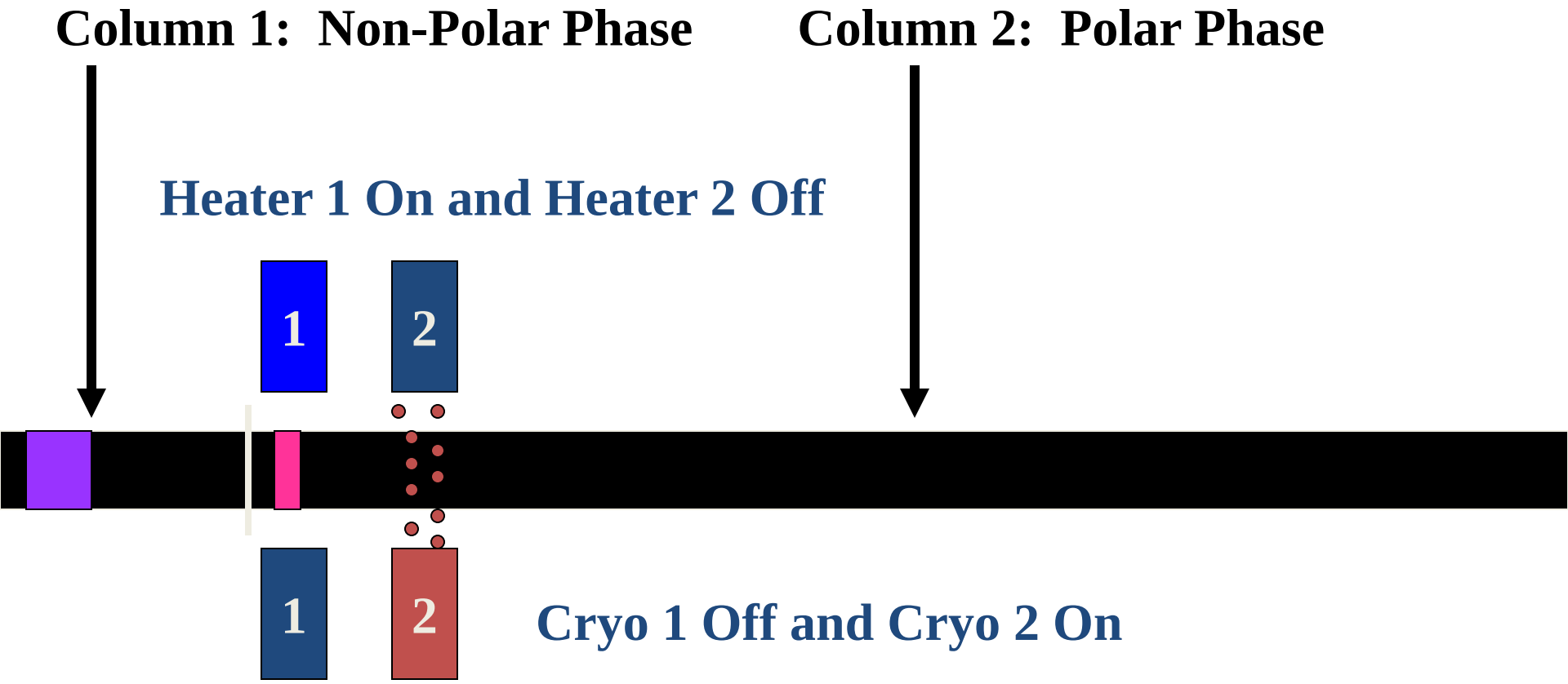


Column 1: Non-Polar Phase **Column 2: Polar Phase**

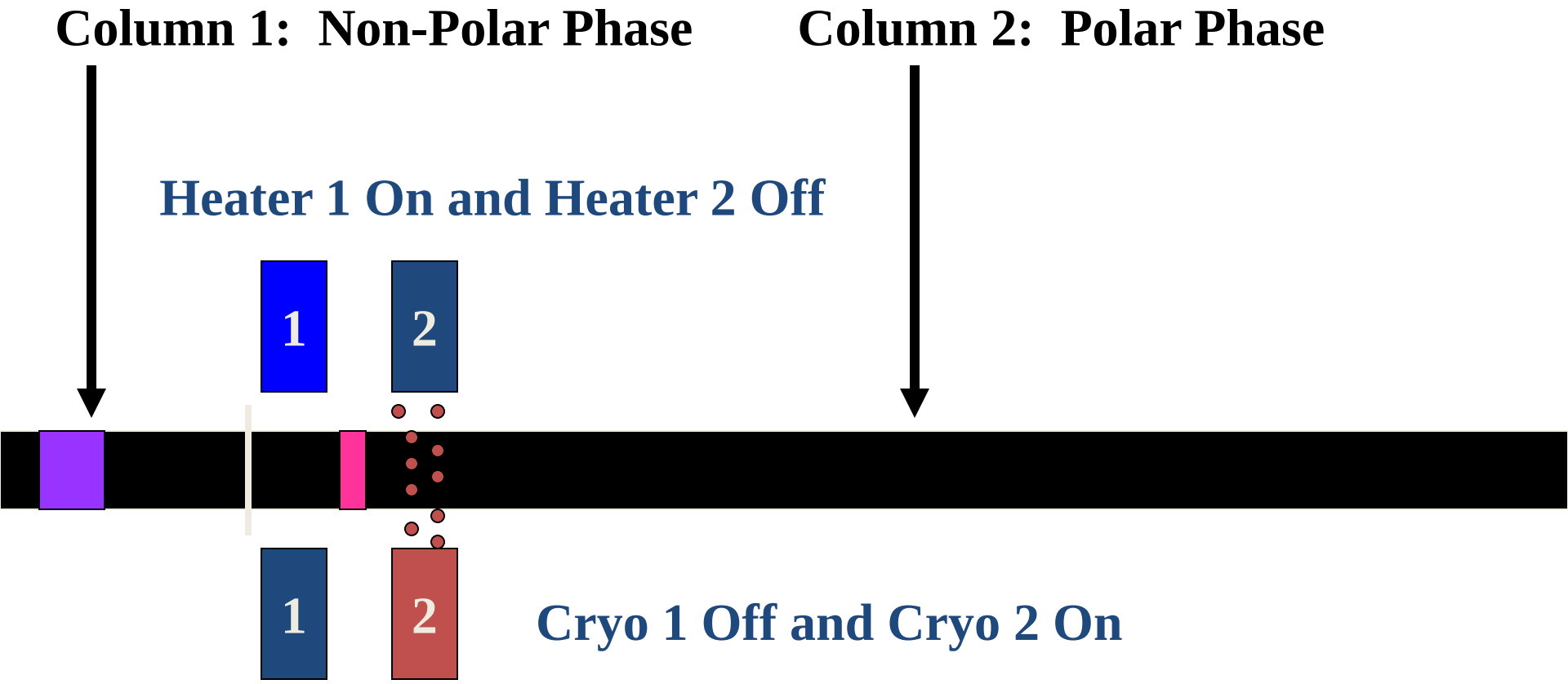


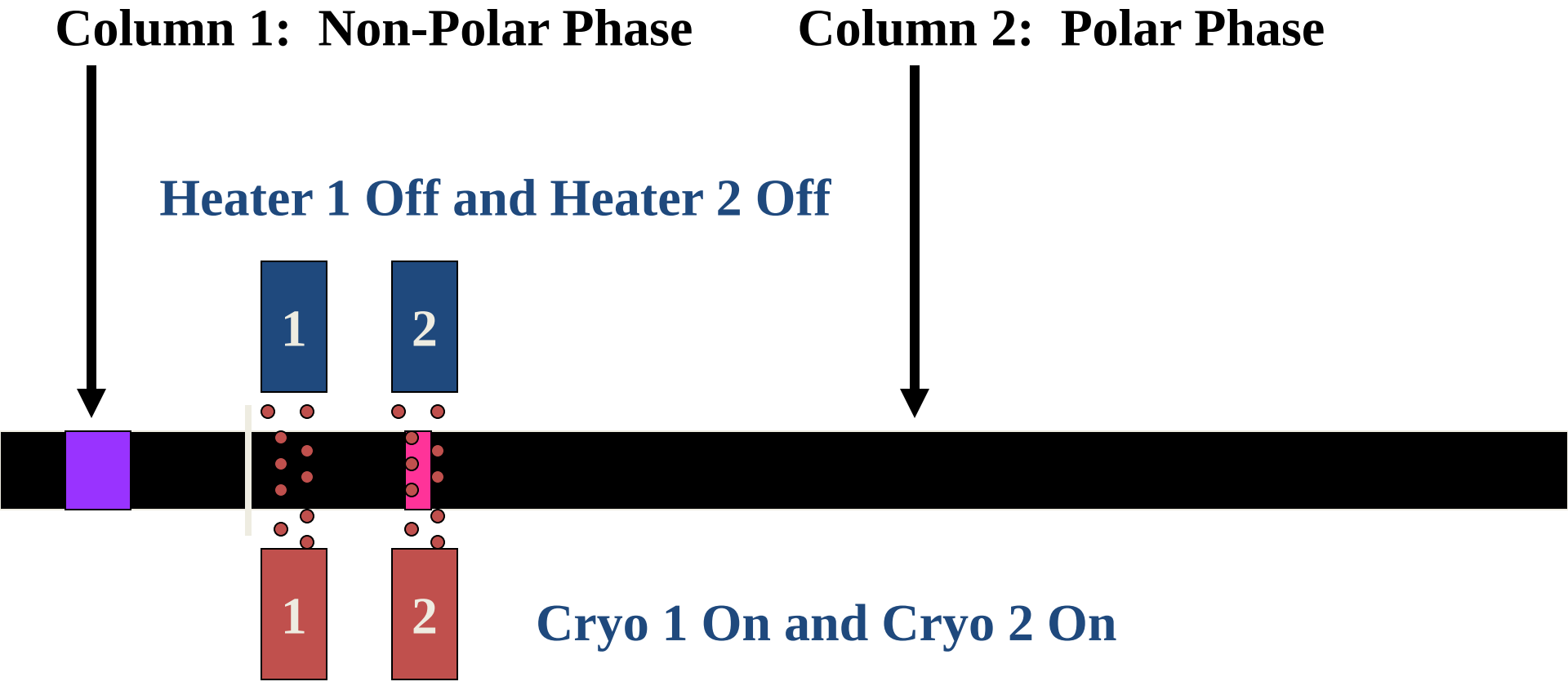


Analytes Trapped on Stage 1 of the Thermal Modulator

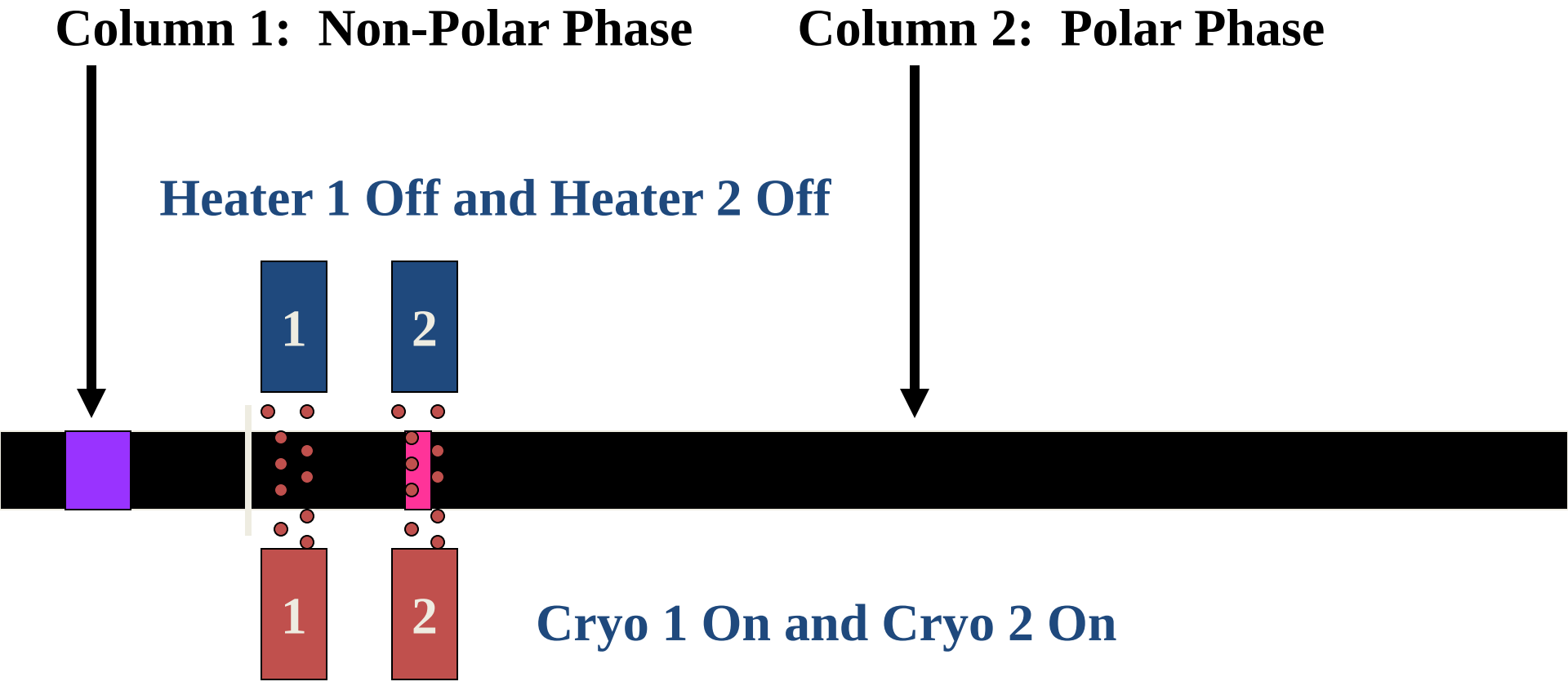


Analytes Released to Stage 2 of the Thermal Modulator

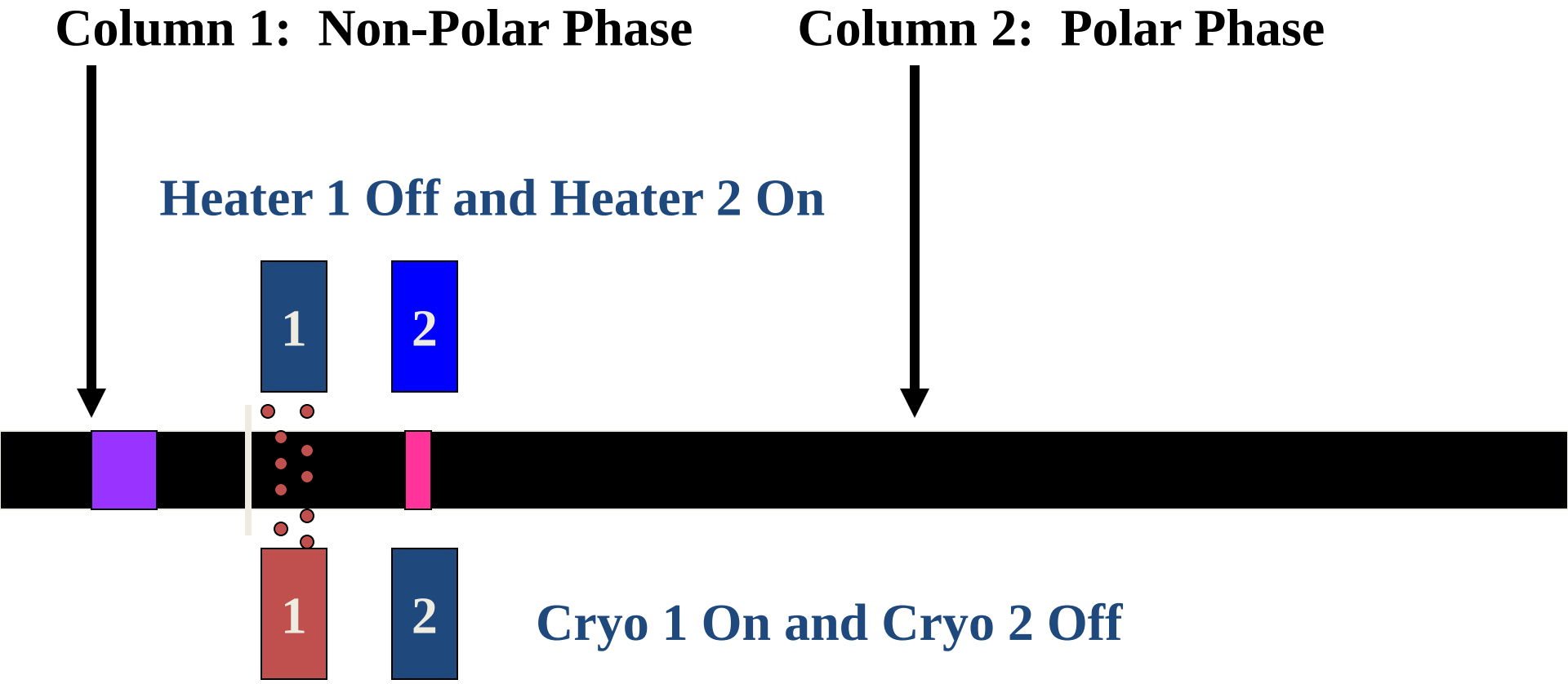

Column 1: Non-Polar Phase
Column 2: Polar Phase
Heater 1 On and Heater 2 Off
1
2
1
2
Cryo 1 Off and Cryo 2 On



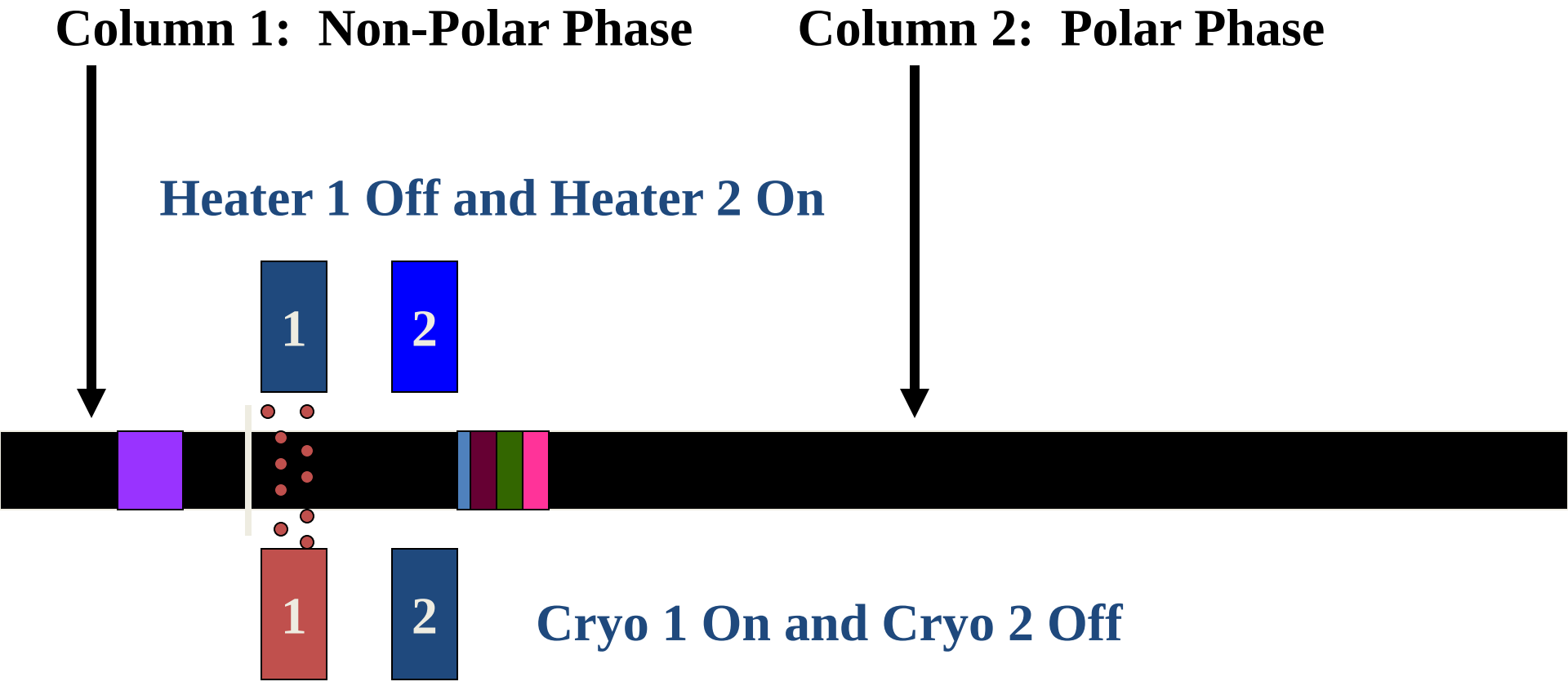
Stage 1 Returns to Thermal Trapping Mode



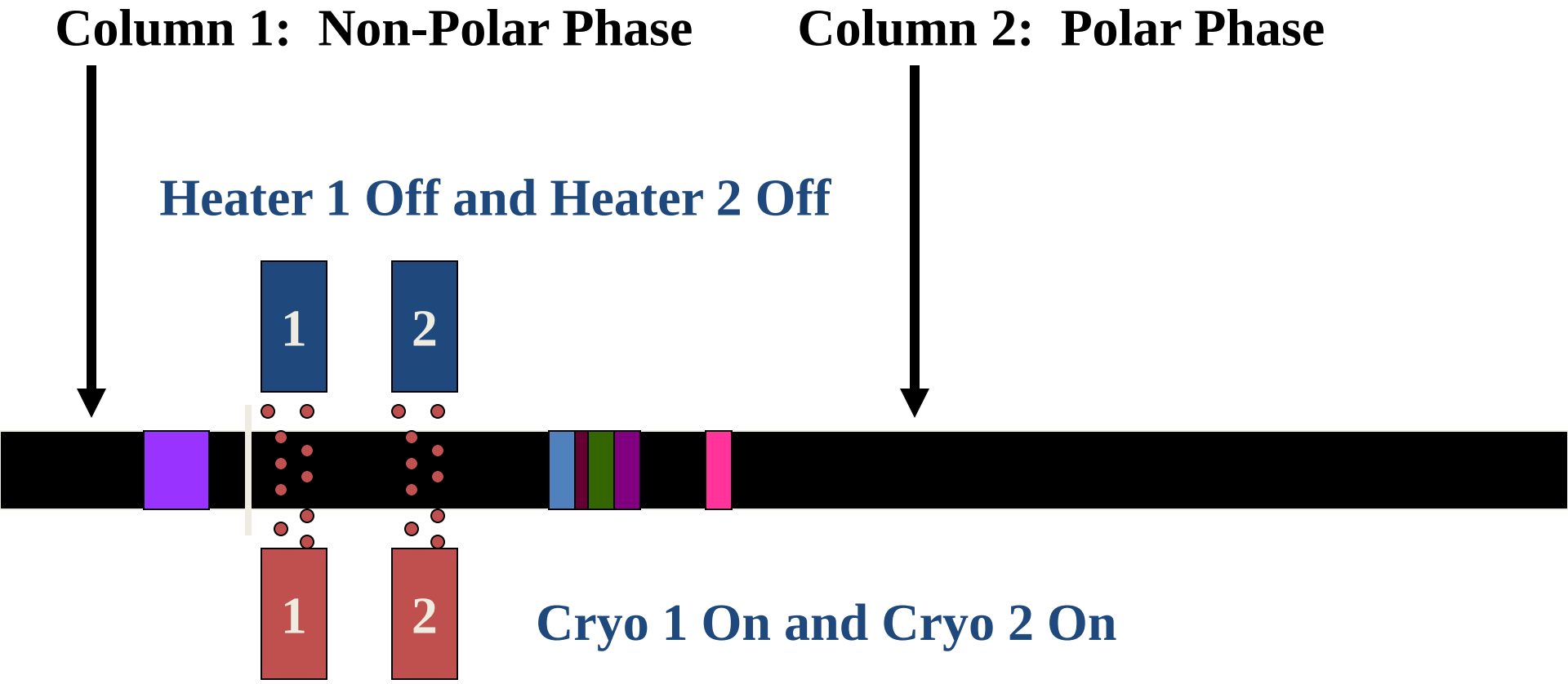
Analytes Trapped on Stage 2 of the Thermal Modulator



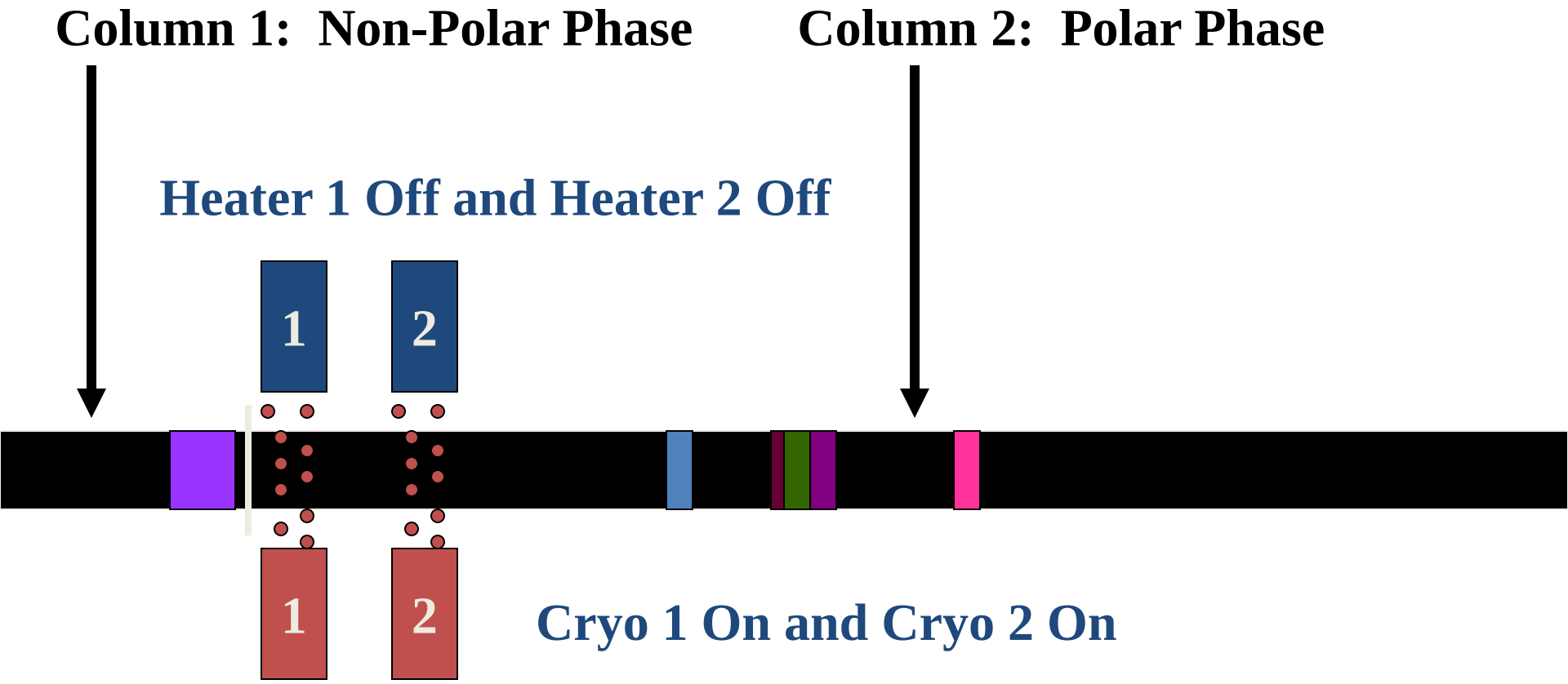
Analytes Released to Column 2



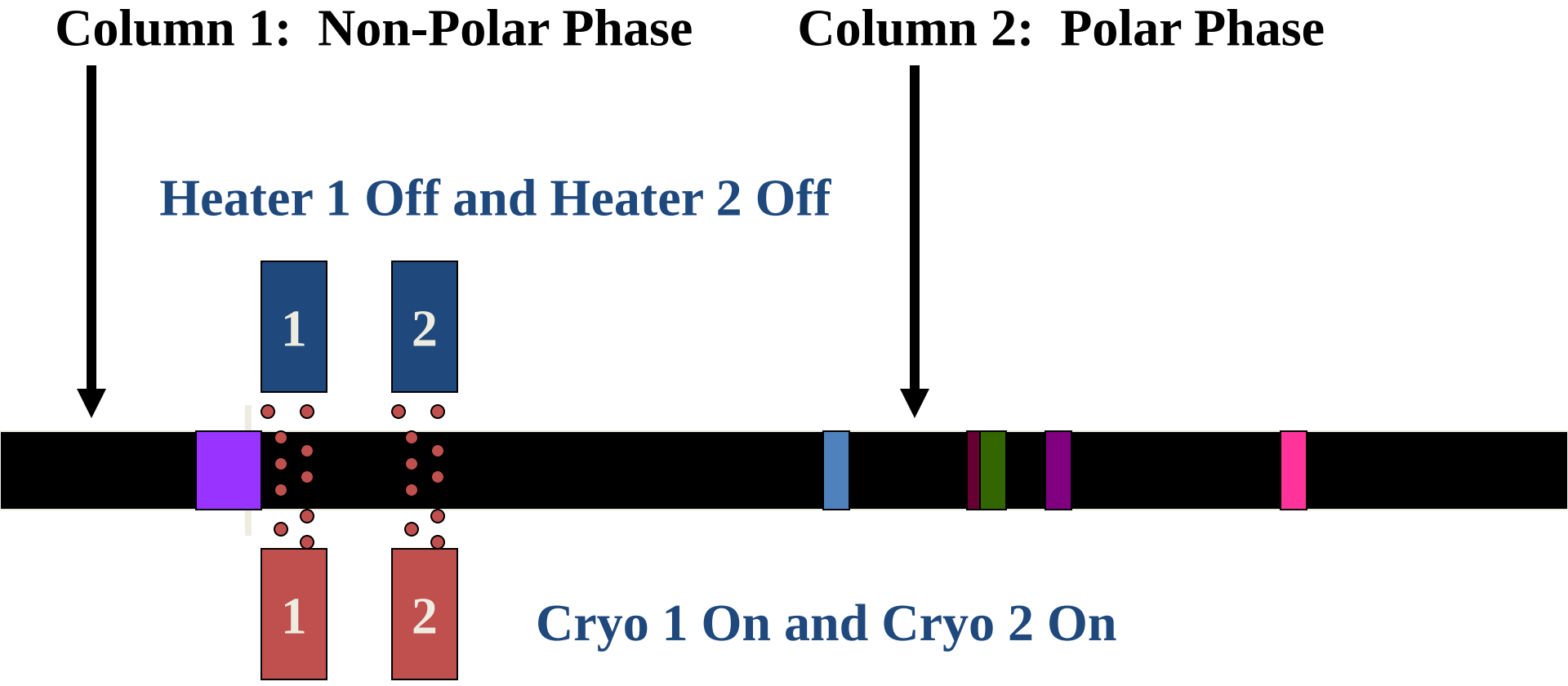
Analytes Separate on Column 2



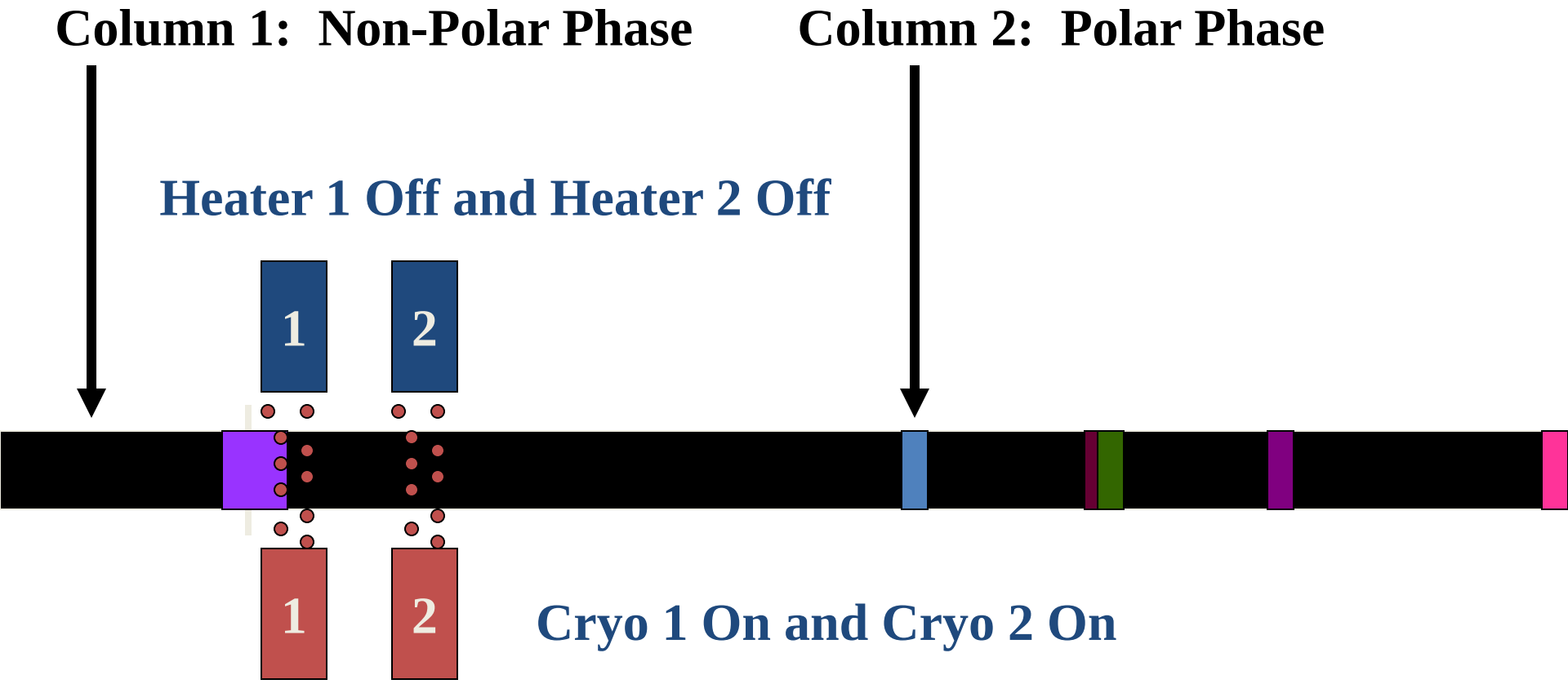
Analytes Separate on Column 2
Next Bands Enter the Thermal Modulator



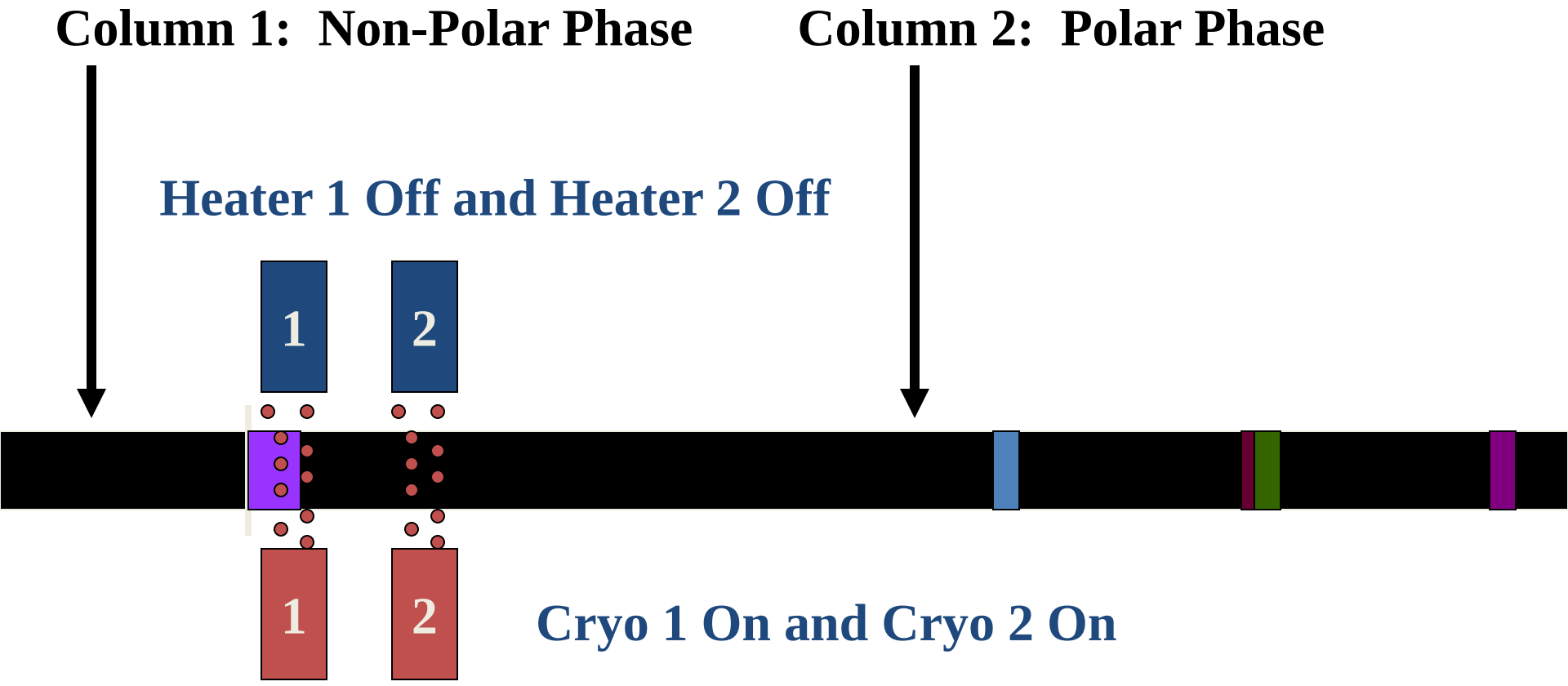
Analytes Separate on Column 2



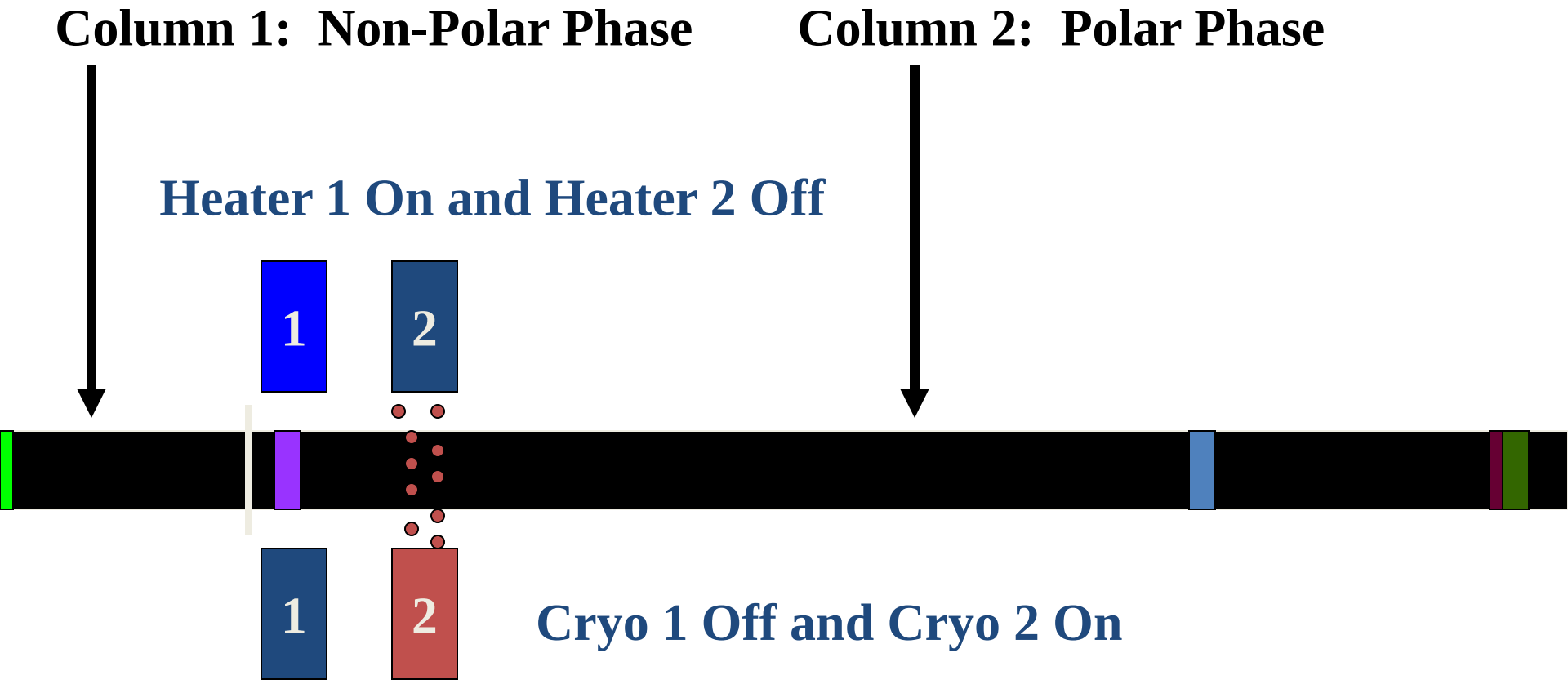
Analytes Separate on Column 2



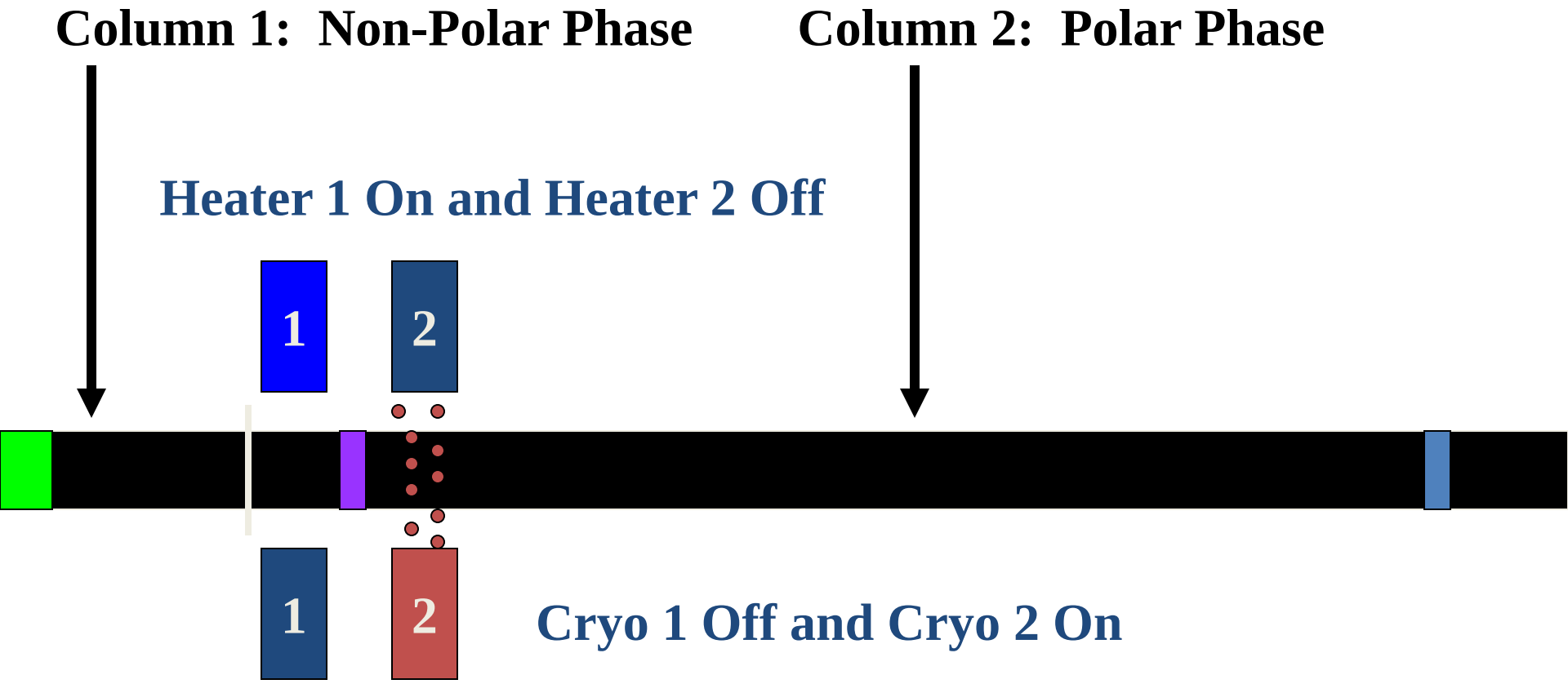
Analytes Separate on Column 2



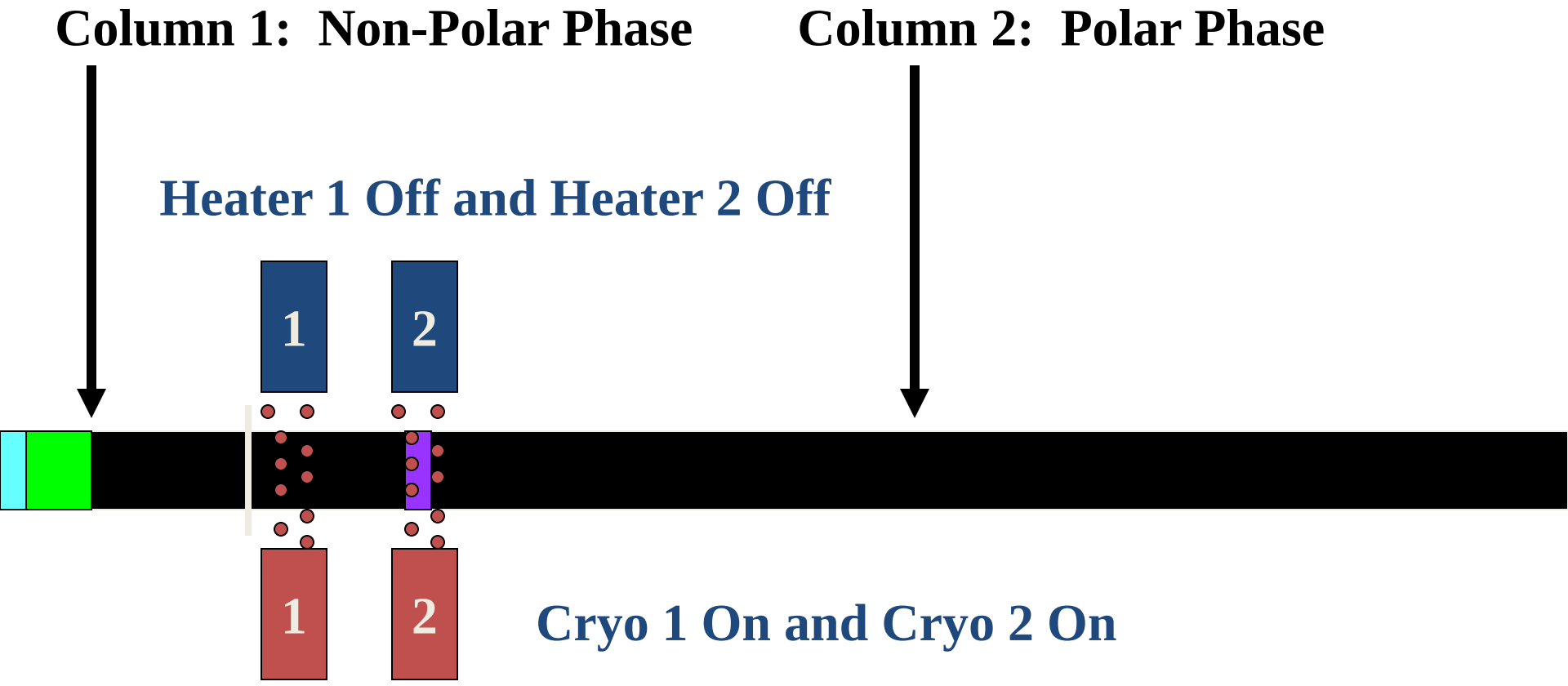
Analytes Separate on Column 2



Analytes Separate on Column 2



Analytes Separate on Column 2



Next Second Dimension Separation Ready to Begin

Orthogonality in GCxGC

"The absence of a correlation between

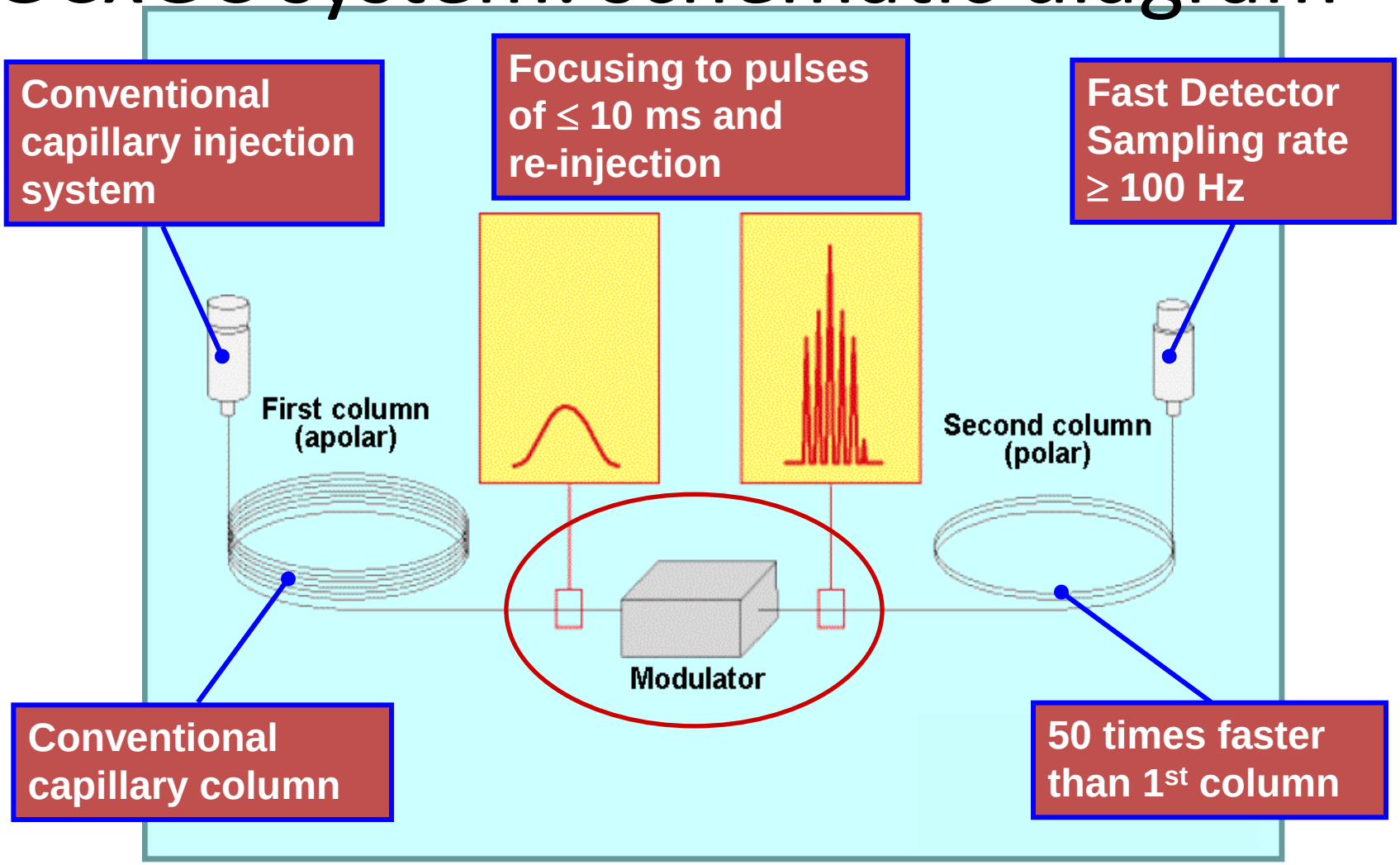
retention behaviour on the two dimensions"

First column : non-polar,
boiling point separation

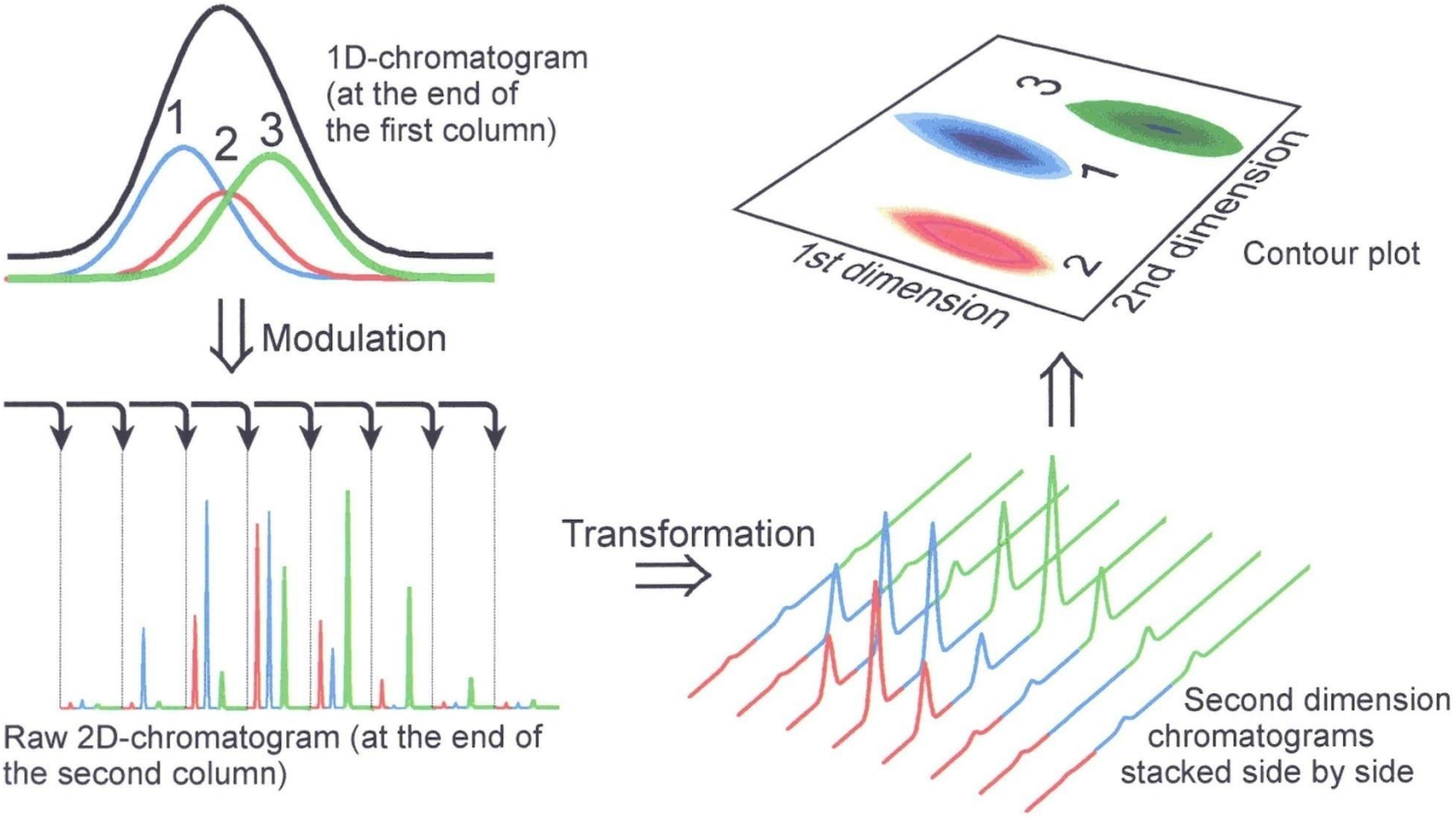
Second column: (medium) polar or shape selective,
polarity/shape selectivity separation

So, first and second separation independent: orthogonal

GCxGC system: schematic diagram



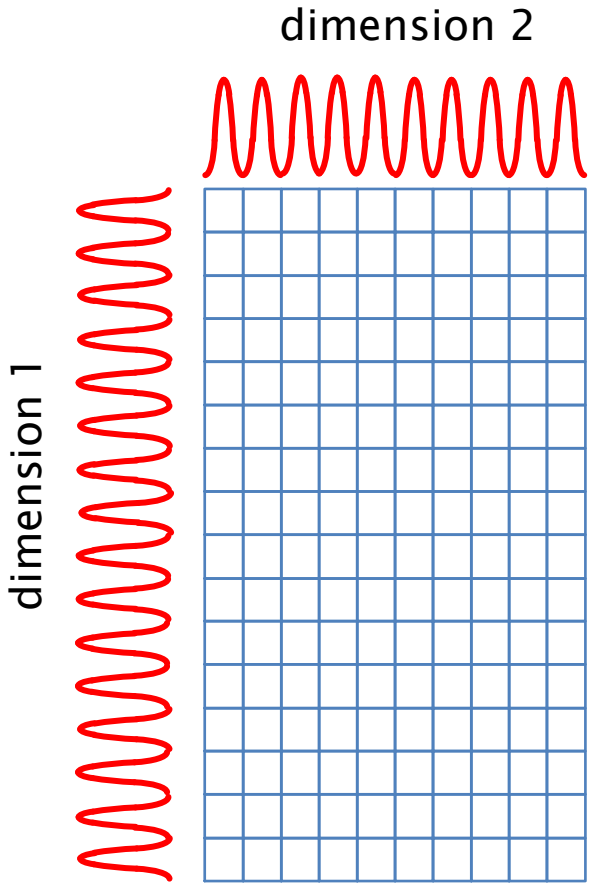
Data conversion for visualization



Advantages of Comprehensive 2D GC

1. The Separation Power of GCxGC is considerably higher than conventional capillary GC
2. GCxGC offers better sensitivity than conventional capillary GC due to the focusing effect of the modulation.
3. GCxGC separation permits better peak identification compared with conventional capillary GC as the peak elution is characterised by a couple of retention times
4. GCxGC generates structured chromatograms which make the technique more suitable for sample screening than conventional capillary GC as it gives considerably more information about the sample in comparable analysis times
5. GCxGC Technique is compatible with all type of injection systems and sample handling techniques used in GC because the first column is conventional.
6. GCxGC is simple to interface with TOF MS leading to an exceptionally powerful GC/MS system able to separate and identify the most complex samples.
7. GCxGC reduces the need of complex sample preparation procedures as the separation power of the technique is so large to eliminate the interferences critical in conventional GC separations.

Enormous separation power :**huge peak capacity** (number of peaks able to be separated by the system)



(peak capacity ~ n_1 x n_2)

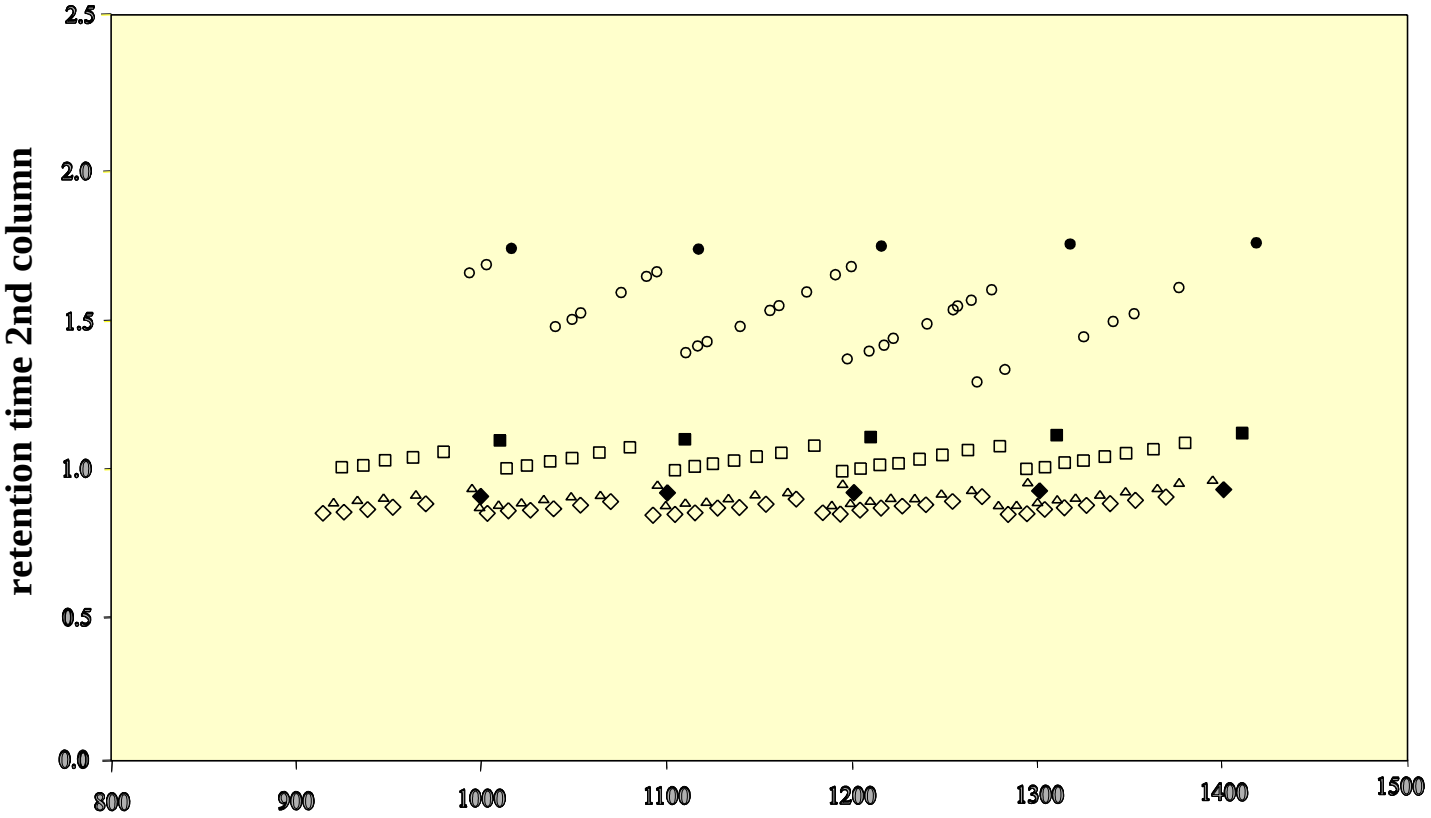
"normal"capillary column n = 1100

2nd dimension fast GC column n = 35

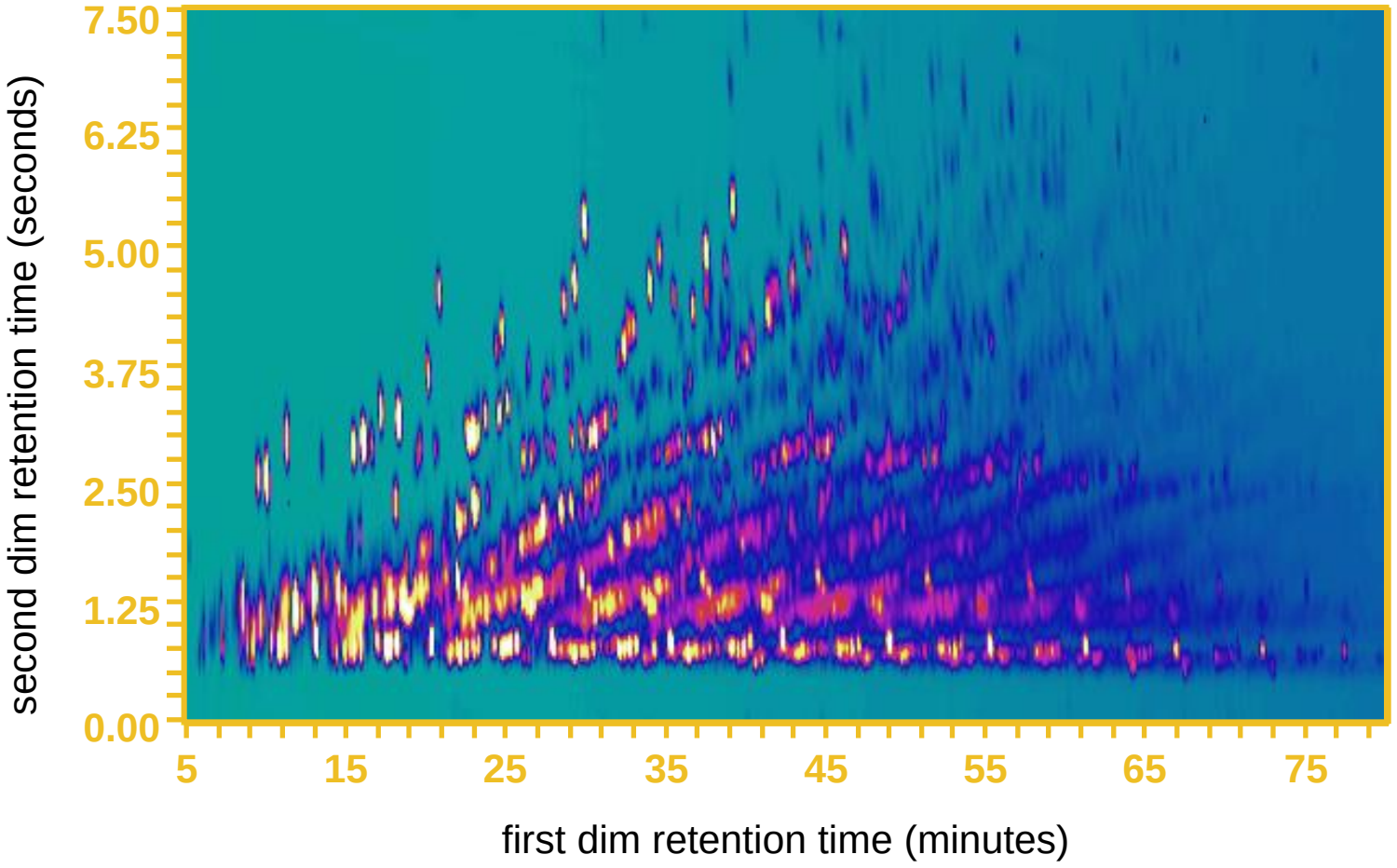
→ **Conventional Multidimensional GC**
n = 1100 + 1100 = 2200

→ **Comprehensive 2D GC**
n_{GCxGC} = 1100 x 35 = 38.000

Structured chromatograms

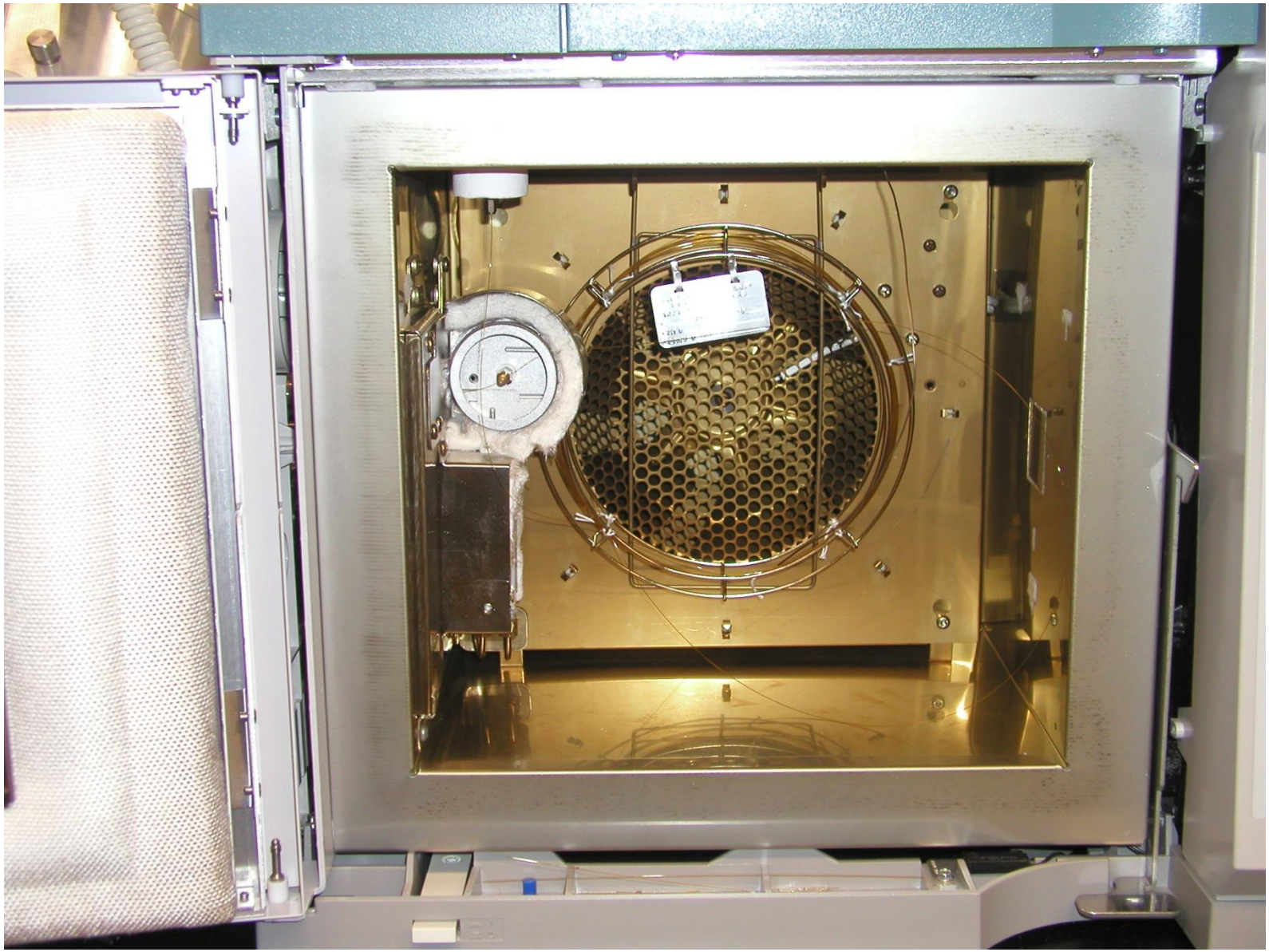


Structured chromatograms

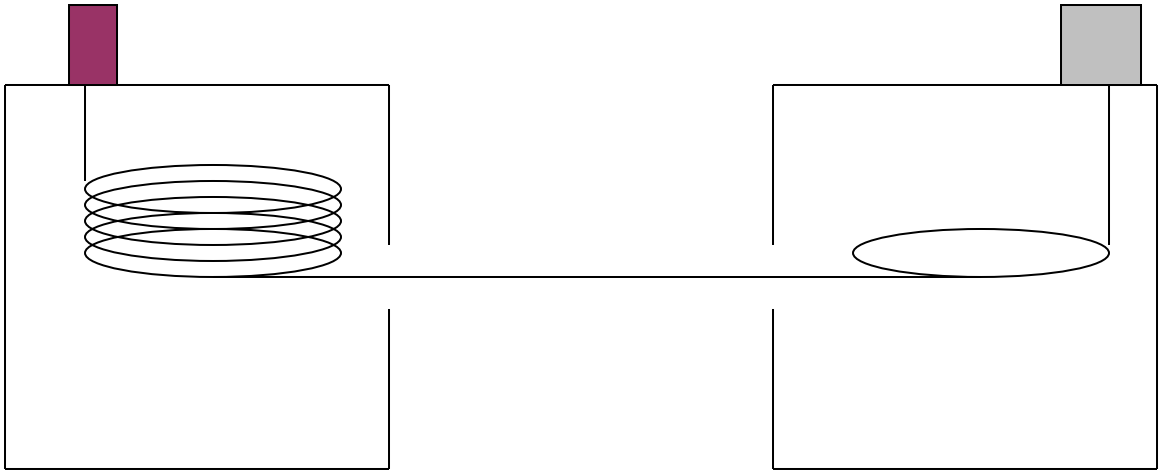


Instrumentation

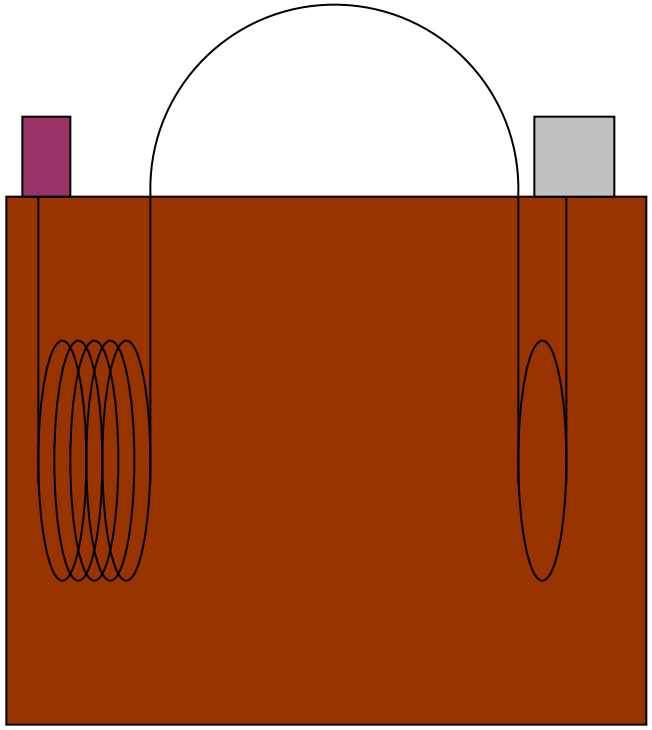
GC oven including second oven for second column



Dual-Oven



Single-Oven



Columns

- Characteristics of two columns :

  - The first column

Non-polar ,dimensions: 15-30m × 0.25-0.32 mm I.D. ×0.1 µm dm, stationary phase (100% methylpolysiloxan or 5% pheneylene and 95% methylsiloxan)
Time of separation : 45-120 min

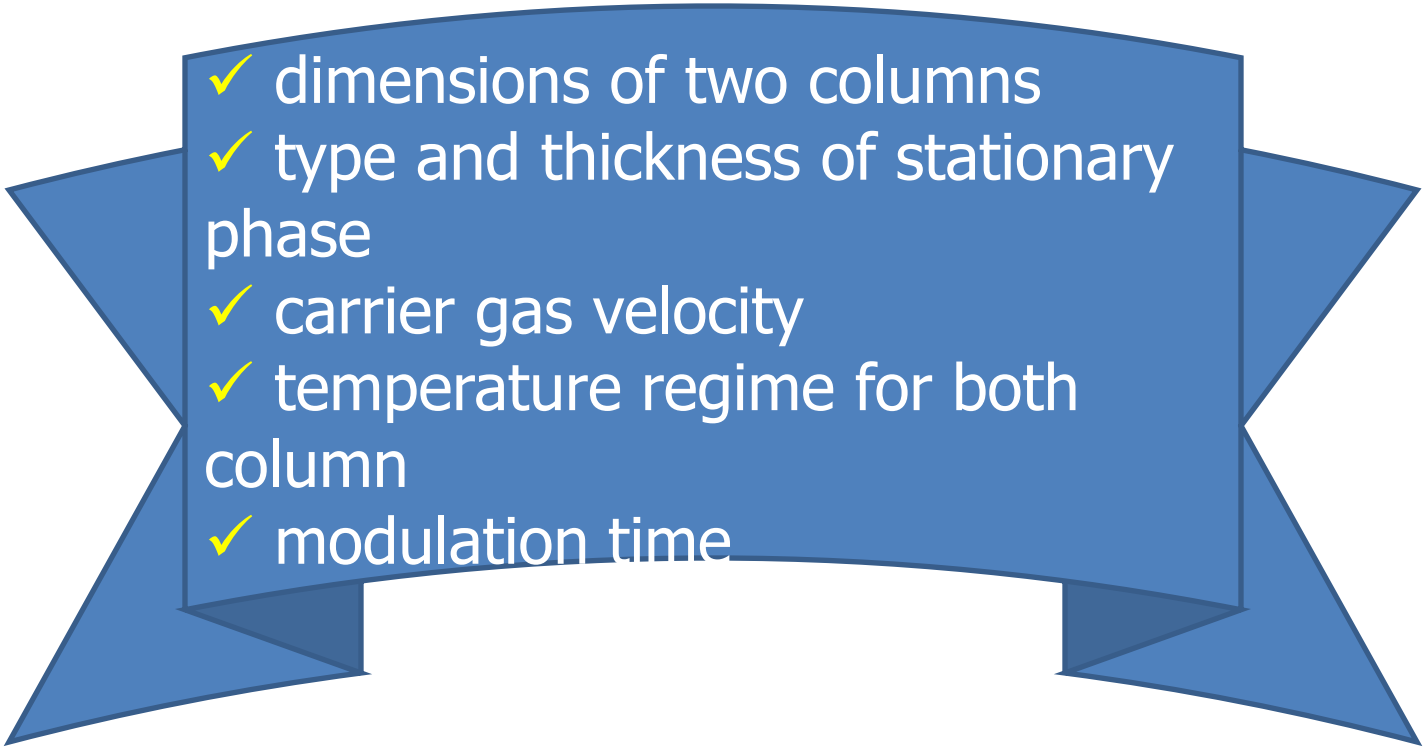
Columns

The second column

polar, dimensions: 1-2 m × 0.1 mm I.D. ×0.1 µm dm, stationary phase (35-50% phenylene and 50-65% dimethylpolysiloxan-carbowax-carboran-cyanoporopyl)
Time of separation : 1-10 s

Columns

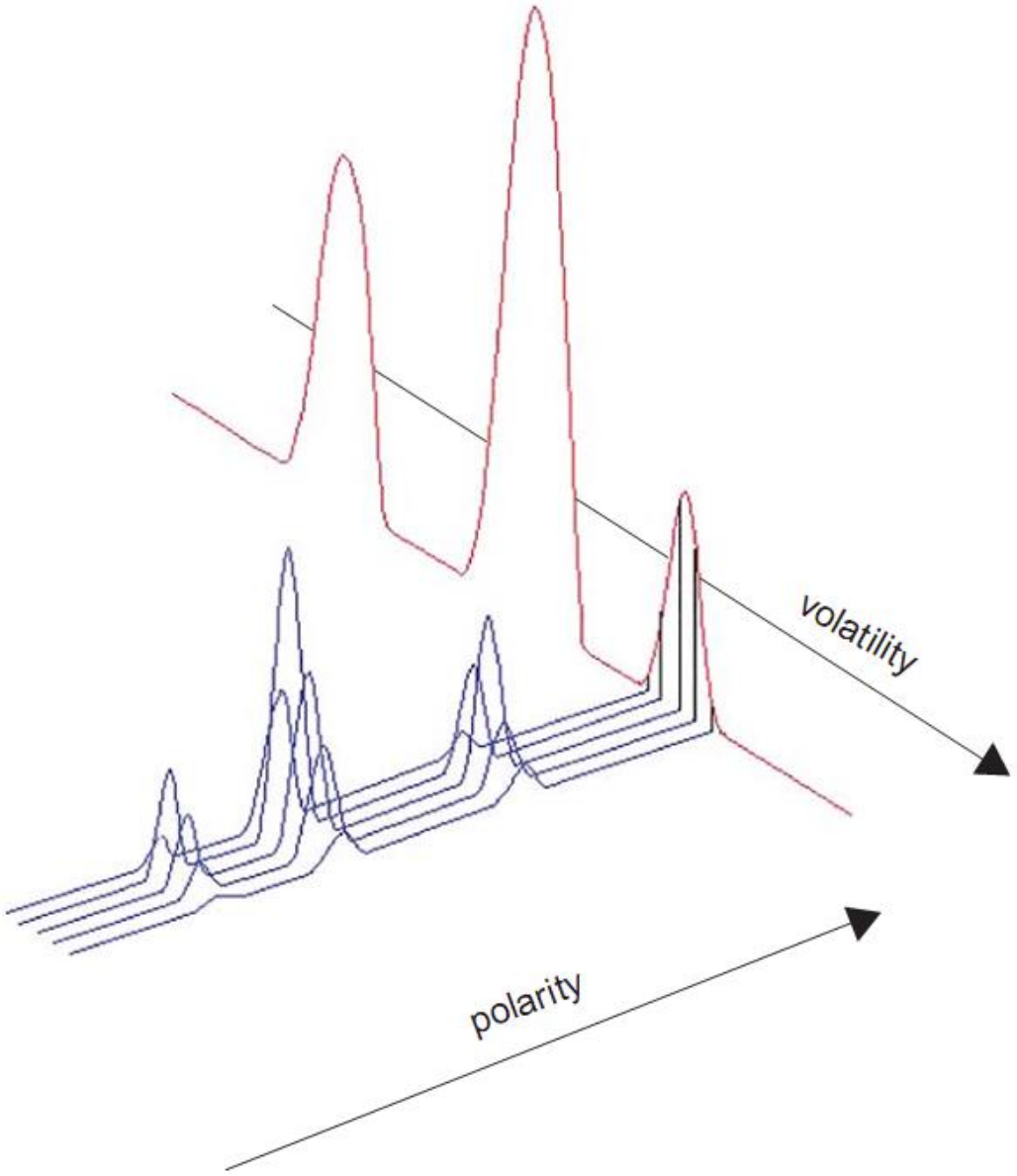
- Most important parameters in fluencing the overall separation :



Columns

Orthogonality:

- ✓ Orthogonality is achieved by varying the retention of the second column as a function of progress of the first column separation.
- ✓ The most important benefit of orthogonality made of ordered structure.
- ✓ If the first column non-polar and the second column polar "orthogonality " realize
- ✓ To achieve orthogonality, 1D column has to be non-polar.



Orthogonality in GC×GC.

Columns

Peak capacity :

✓ The limitation of 1D-GC as a peak capacity is obvious in separating complex mixture.
✓ The peak capacity is: The number of peaks that can be separated with $R_s = 1$.
✓ Peak capacity of the first column are the same in 1D-GC.
✓ Peak capacity of the second column are much more than that of the first column.

Columns

Linear velocity :

The first column  30 cm /s

The second column  100 cm /s

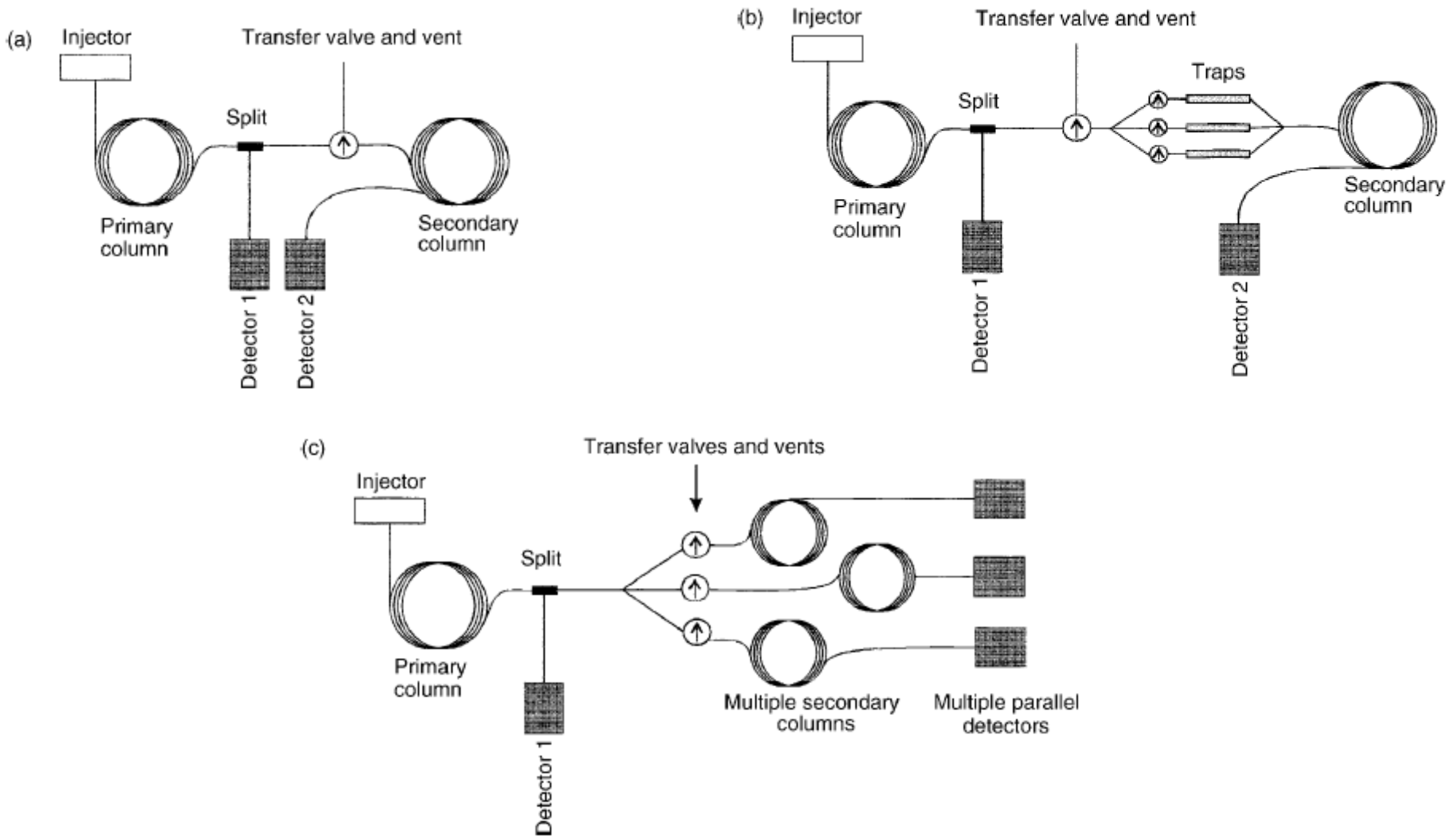
	Selective	Comprehensive
2D GC	Heart-cut GC-GC	GCxGC

Heart-cut

The most basic classification of GC couplings is into off-line and on-line interfacing.

Off-line is described as the manual collection of effluent from a column prior to manual re-injection to a second column. significant problems in handling volatile species, the reproducibility of manual handling of samples is poor and automation is clearly not practical.

on-line interfacing is performed within a sealed analytical system. This is enabled by the automatic diverting of column flows via mechanical or pressure-driven switching devices.



Two-dimensional gas chromatography instrumental configurations: (a) direct transfer heart-cut configuration; (b) multiple parallel trap configuration; (c) multiple parallel column configuration.

Interfacing unit

range from relatively simple manually operated valves, to more complex but flexible computer pressure and flow control systems.

mechanical valve: This mode of operation highlights a major limiting factor in two dimensional gas chromatography–that peak widths introduced to the second column from the first will critically limit the peak capacity of the second column. This arises since the peak width eluting from the primary column must be less than the peak width resulting from second column unless a refocusing or zone compression is performed.

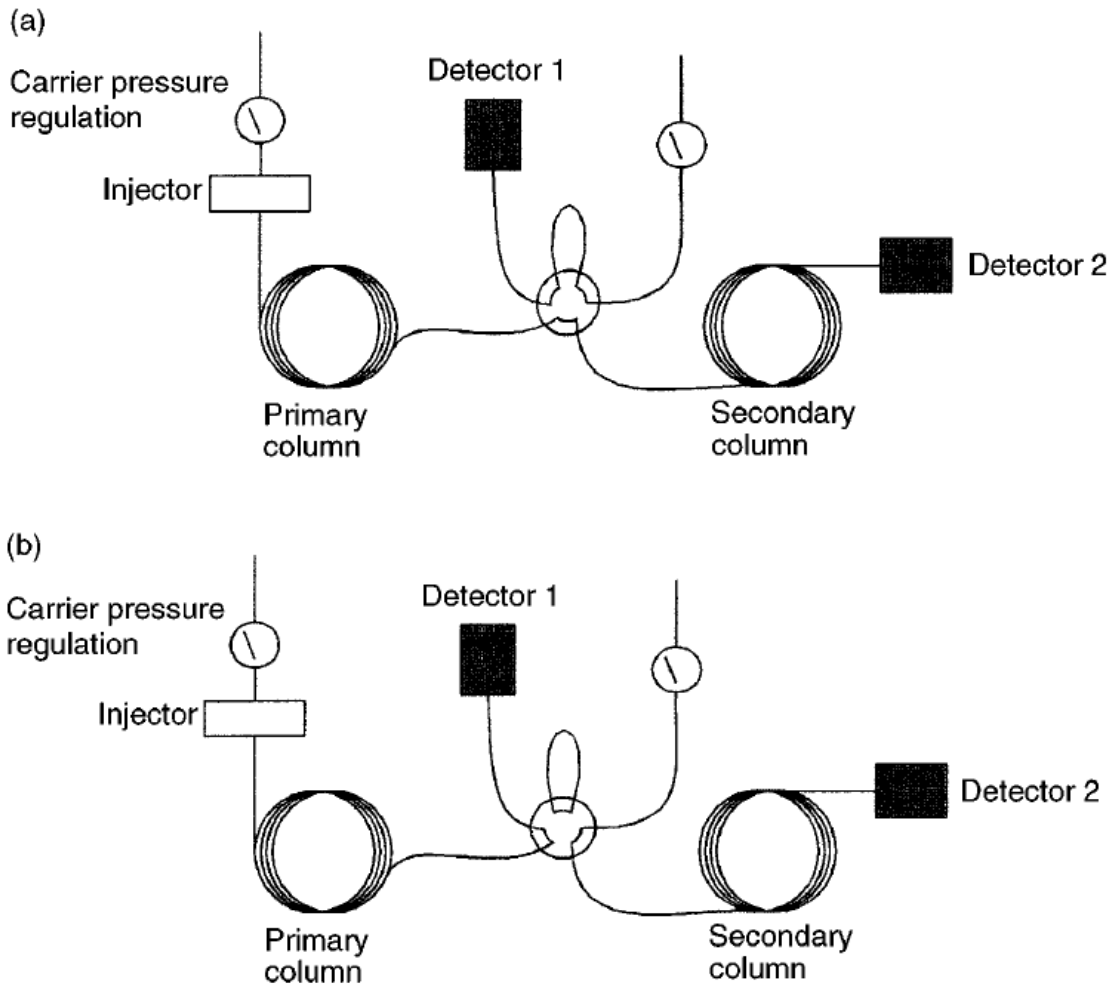
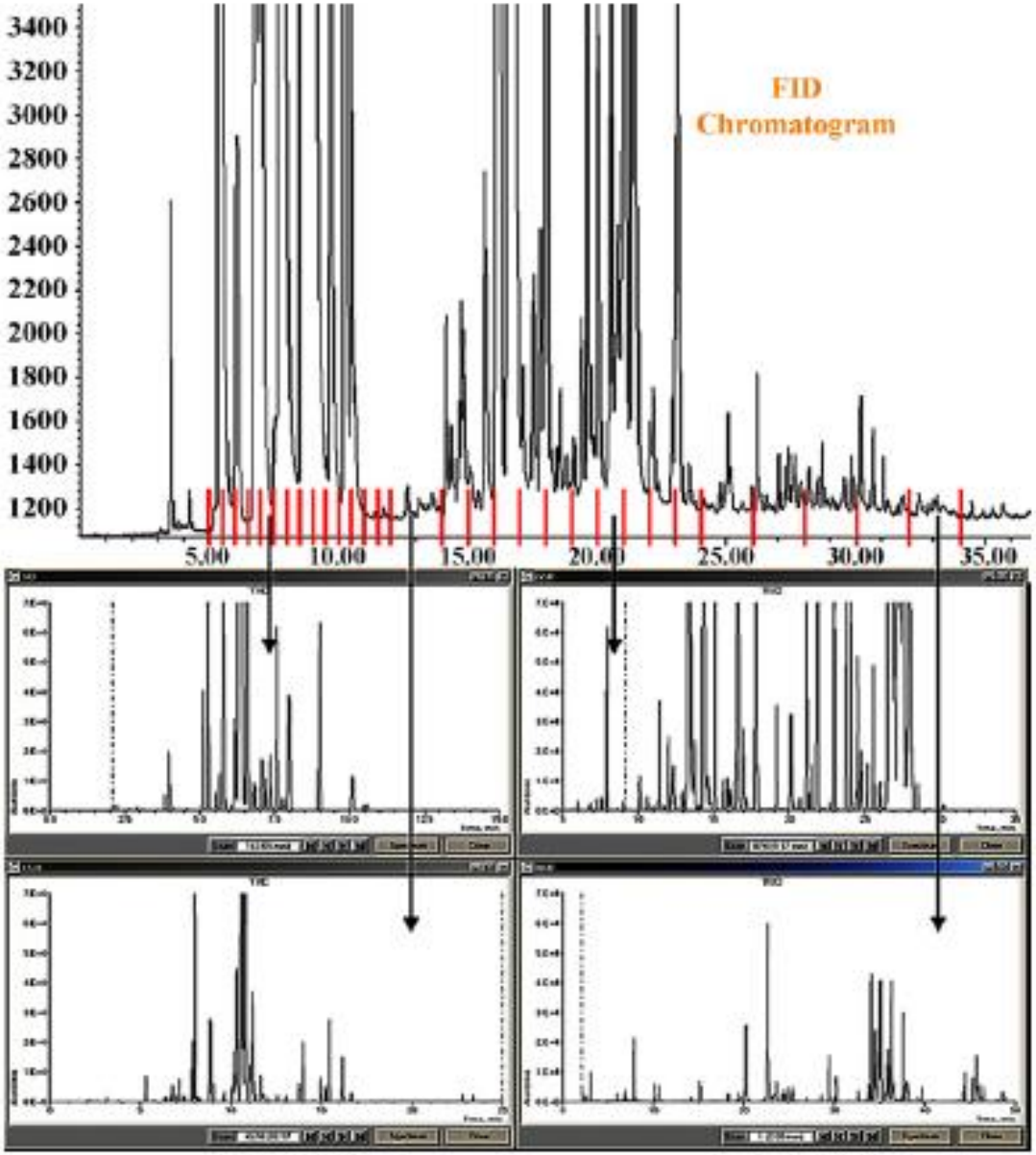
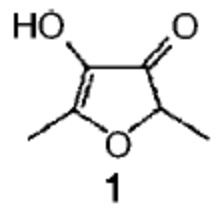


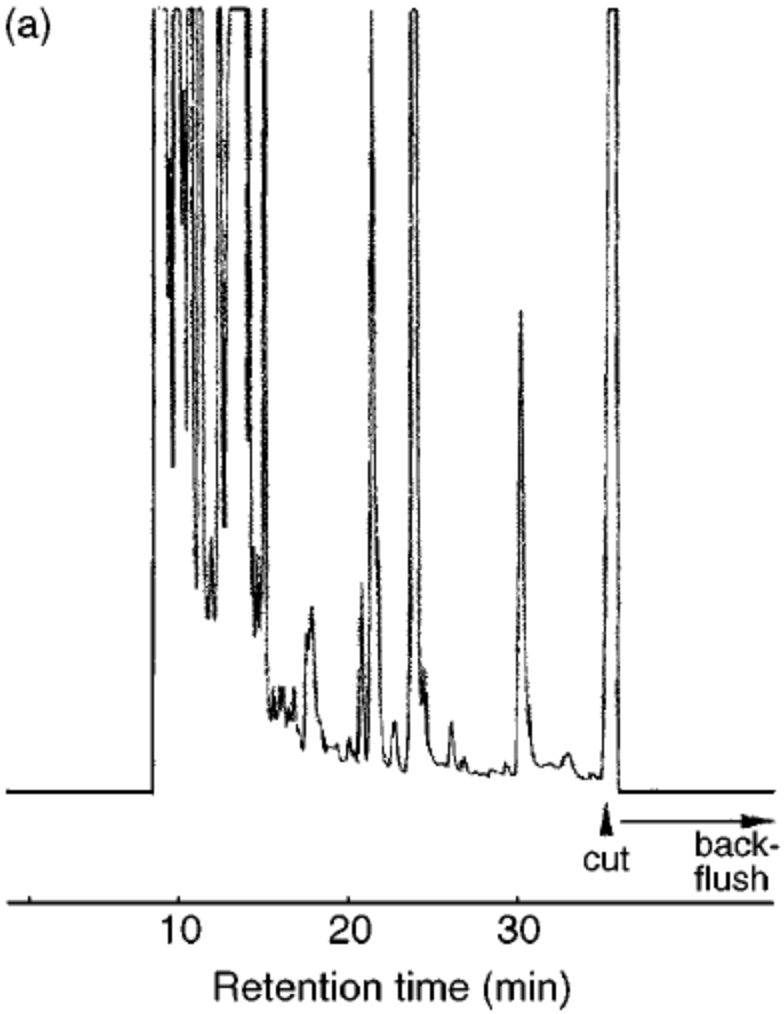
Figure 3.2 Valve switching interfaces in (a) heart-cut position and (b) primary column monitor/secondary column analyse position.

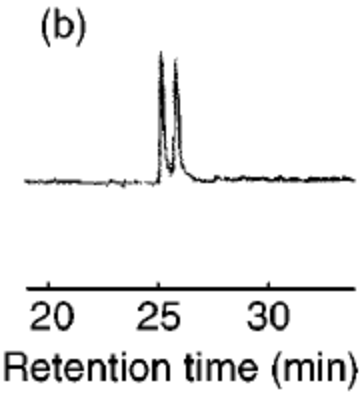

FID
Chromatogram
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
5,00
10,00
15,00
20,00
25,00
30,00
35,00



1

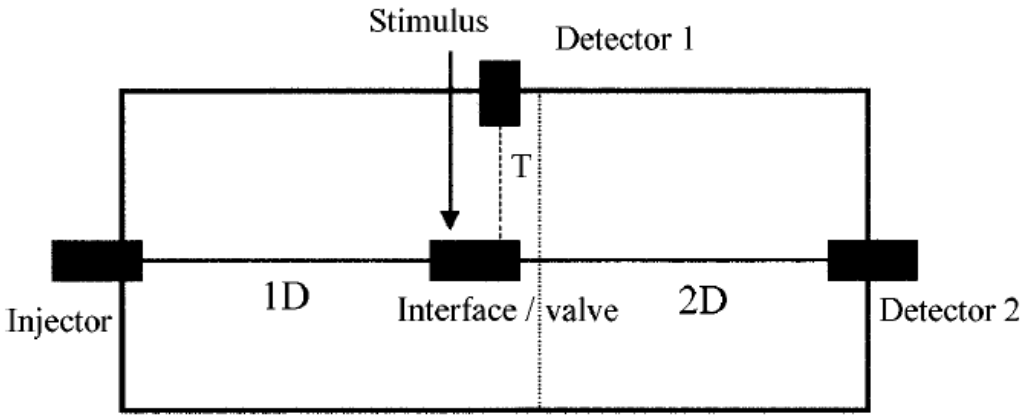
2,5-dimethyl-4-hydroxy-3[2H]-furanone obtained from a ‘strawberry’ tea,





Comprehensive Gas Chromatography

The comprehensive GC GC experiment is also defined as a system that allows ***all of the sample*** from the first column to be analysed on the second column. The key to the experiment is the technical achievement of the interface between the two dimensions



Orthogonallity

Provided that the response bases of both dimensions are sufficiently different, then an orthogonal analysis results. If the mechanism of the two dimensions are similar, then we might propose that some degree of correlation exists, and this may reduce the identification power of the multidimensional analysis.

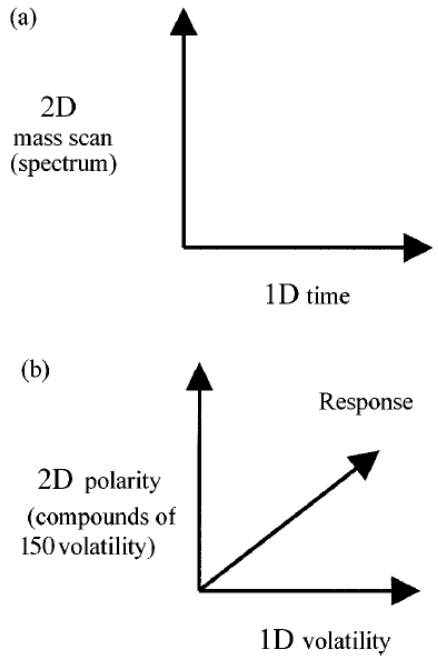
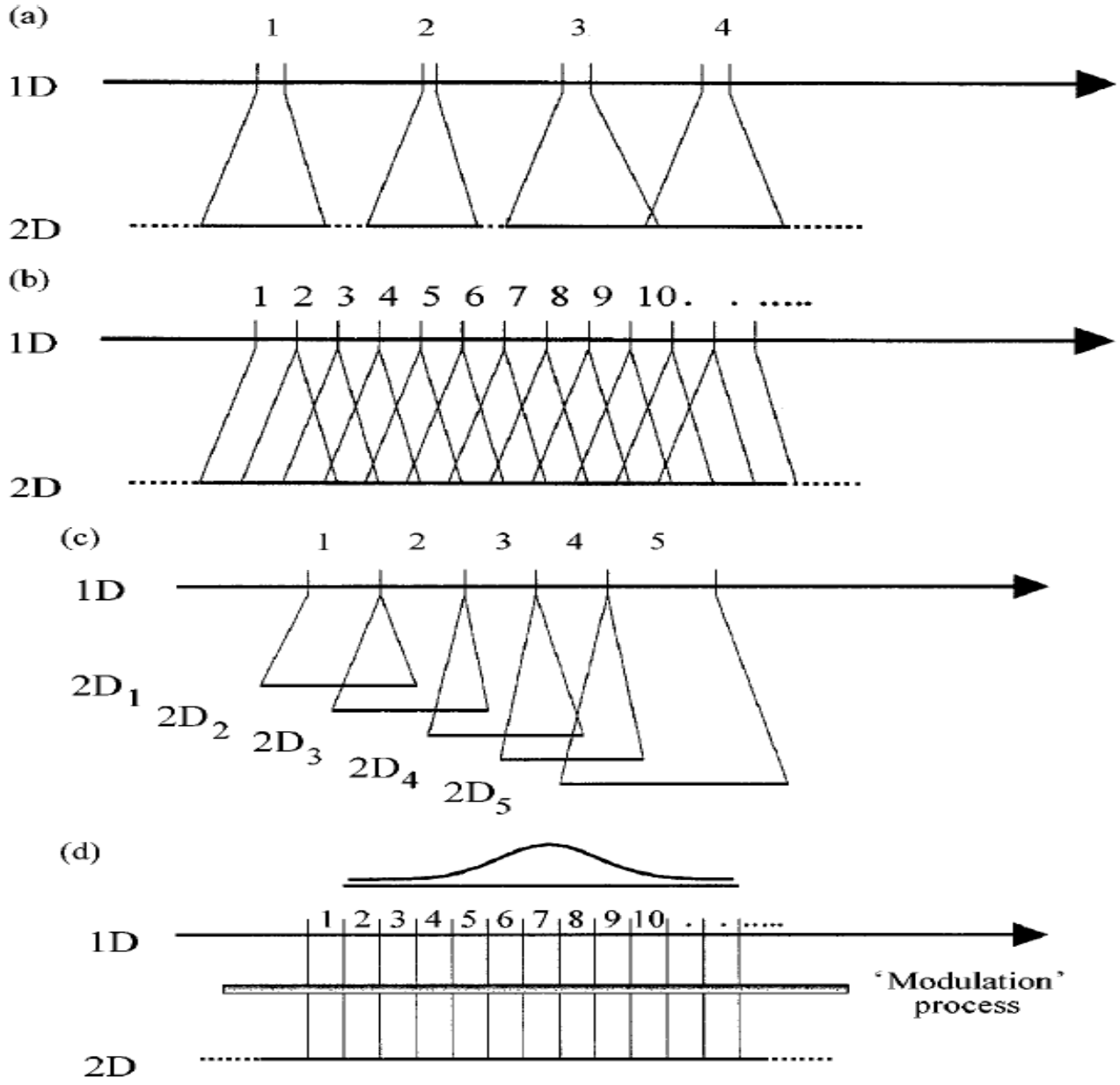
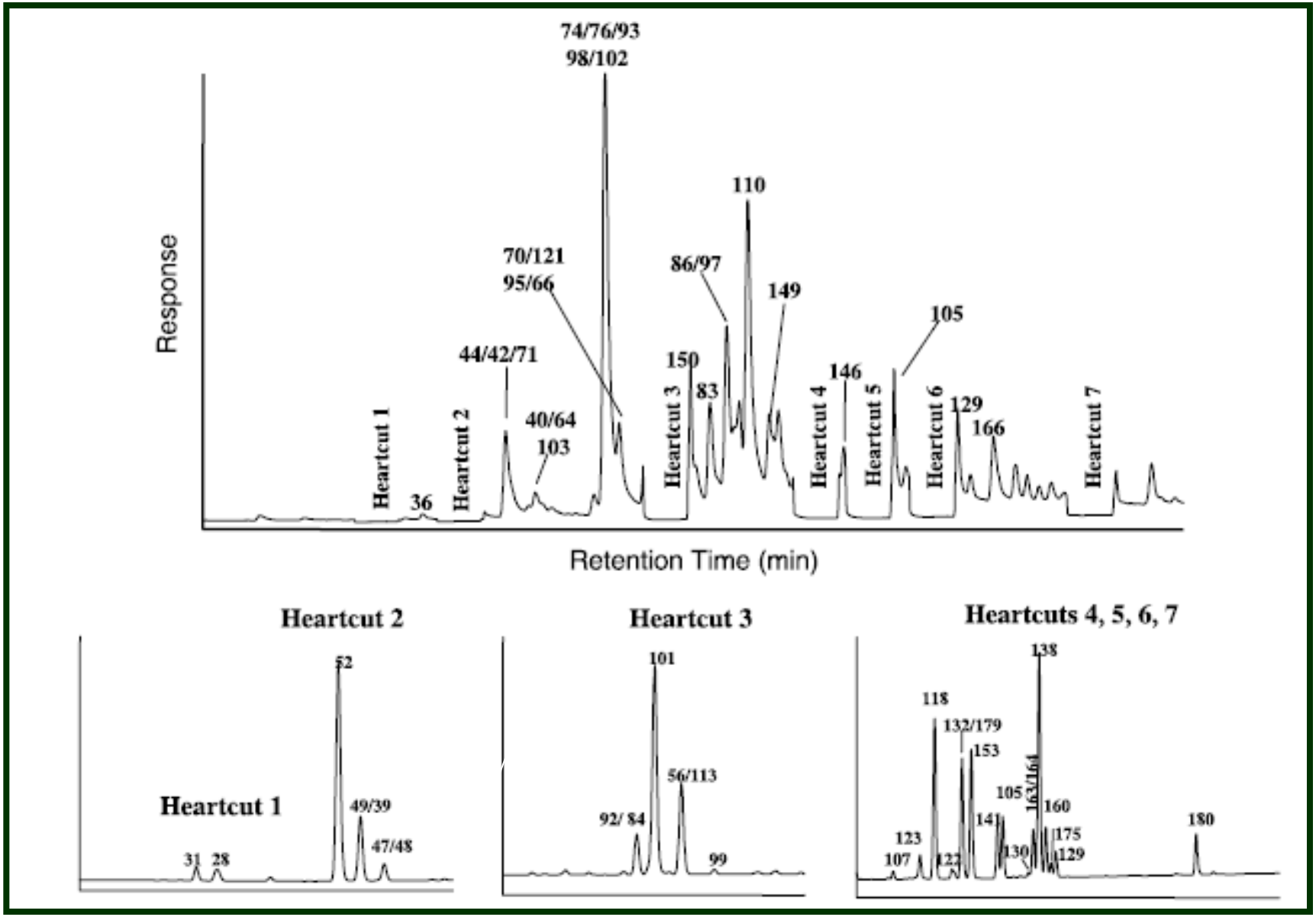


Figure 4.11 (a) Representation of GC–MS as a two-dimensional analysis method. (b) Representation of GC × GC as a two-dimensional separation, with separation mechanisms based of different chemical properties in each dimension.


(a)
1
2
3
4
1D
2D
(b)
1 2 3 4 5 6 7 8 9 10 . . ..
1D
2D
(c)
1
2
3
4
5
1D
2D1
2D2
2D3
2D4
2D5
(d)
1 2 3 4 5 6 7 8 9 10 . . ..
1D
2D
'Modulation' process



Clinica Chimica Acta 328 (2003) 1 –19 GC16

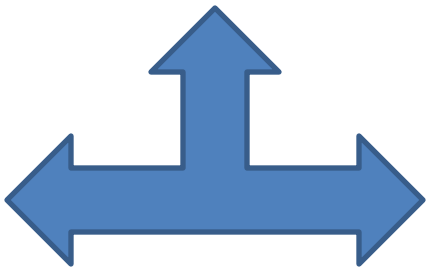
Modulator

Modulator

- Independent of its design, a modulator must serve three functions:

To accumulate or trap small adjustment fractions

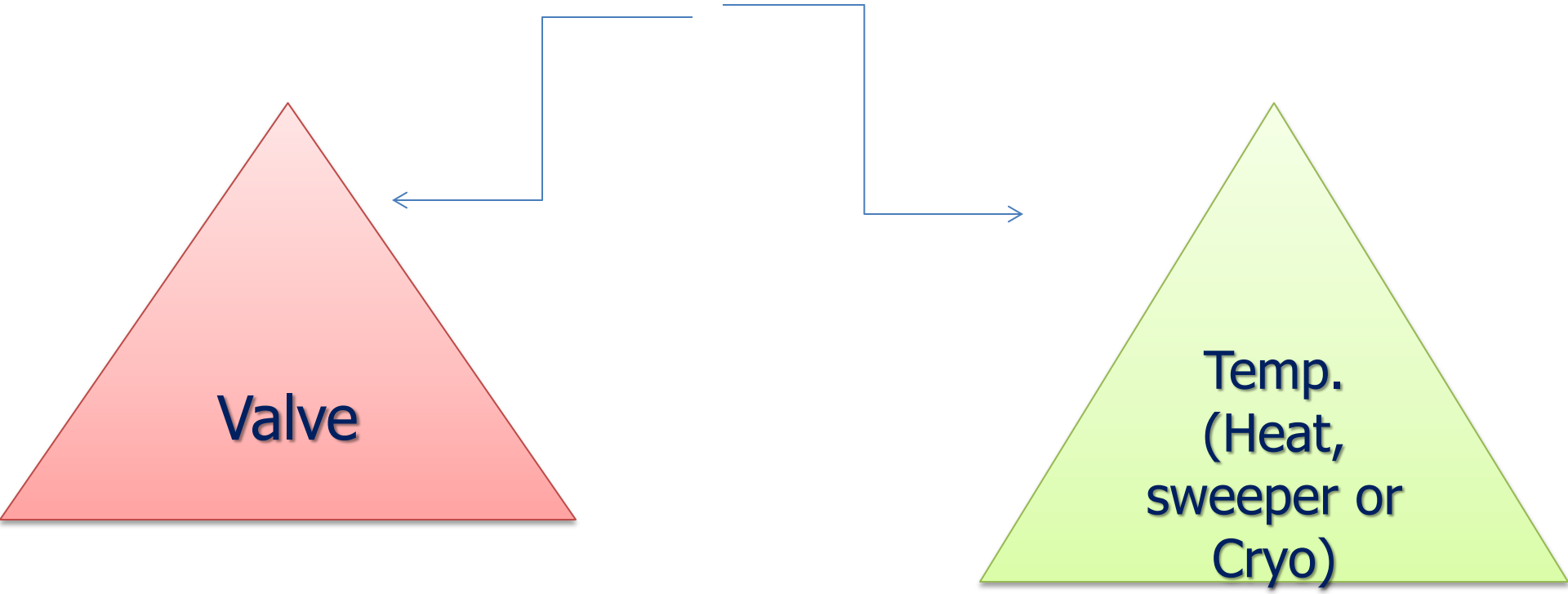
To focus the trapped fractions



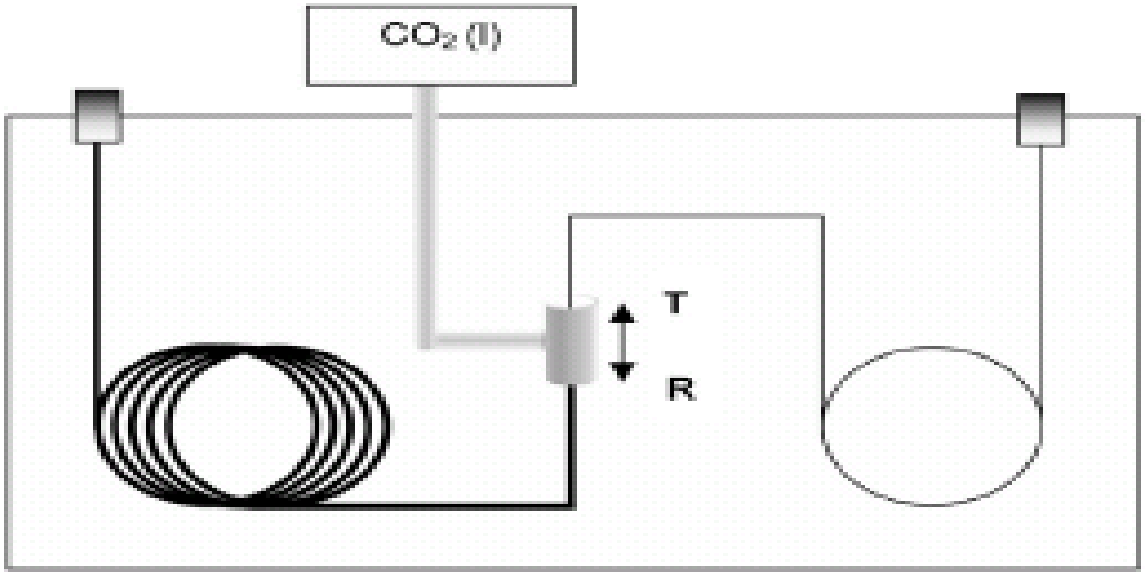
To inject as narrow pulse into 2D column

Modulator

Three usual applied modulators



Modulator



Cryogenic

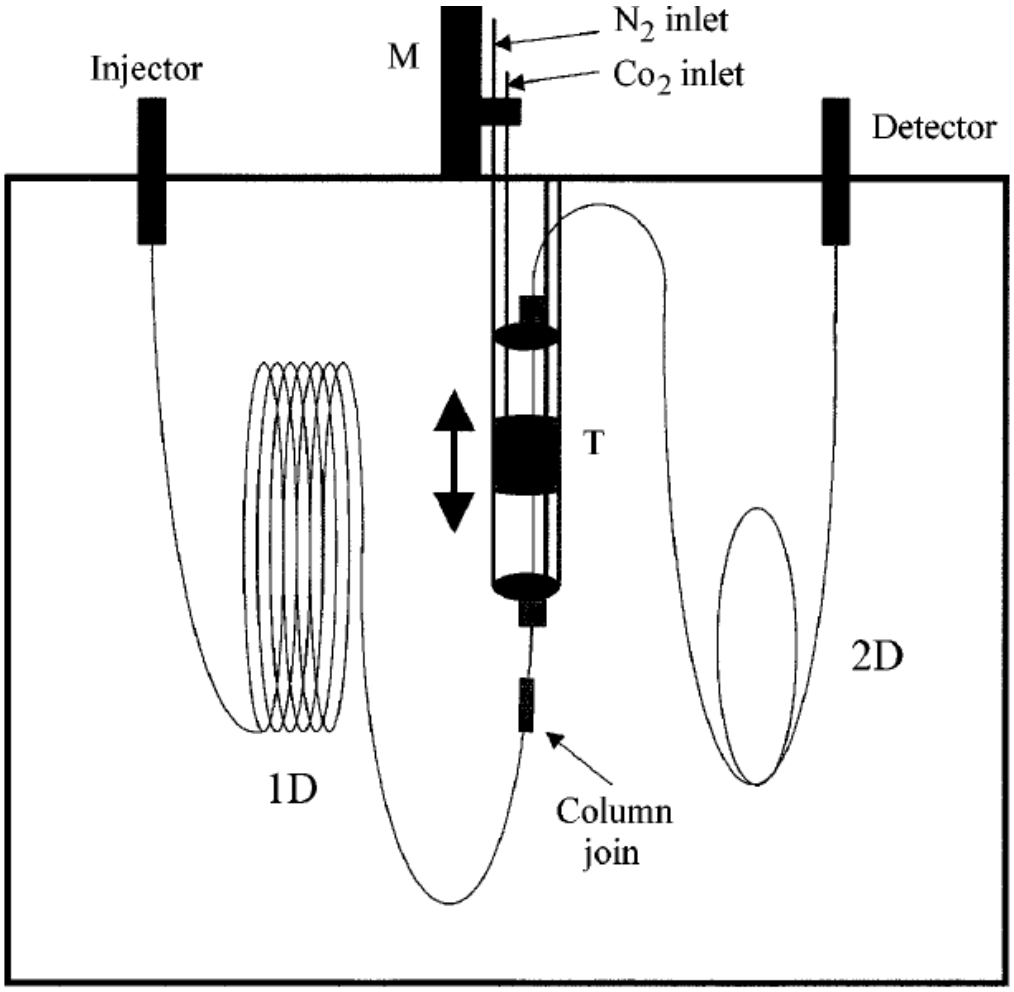
Modulator

Another modulators are:

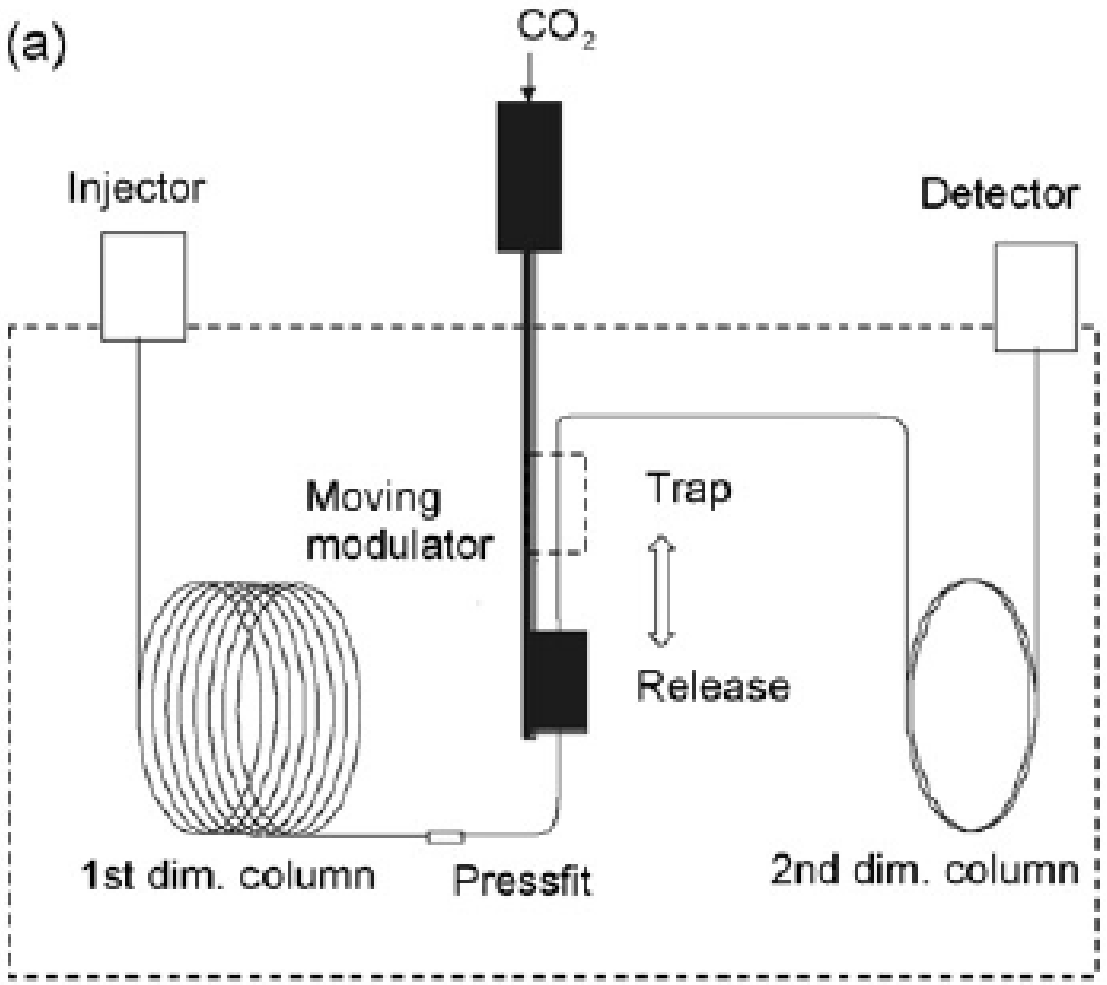
- ✓ four – jet cryogenic N_2
- ✓ Two-jet cryogenic CO_2(liquid)
- ✓ single –jet ,dual stage cryogenic CO_2(gas) / N_2
- ✓ single-jet, single stage cryogenic CO_2 (liquid)

- ✓ Diaphragm valve
- ✓ Differential flow

cryogenic system

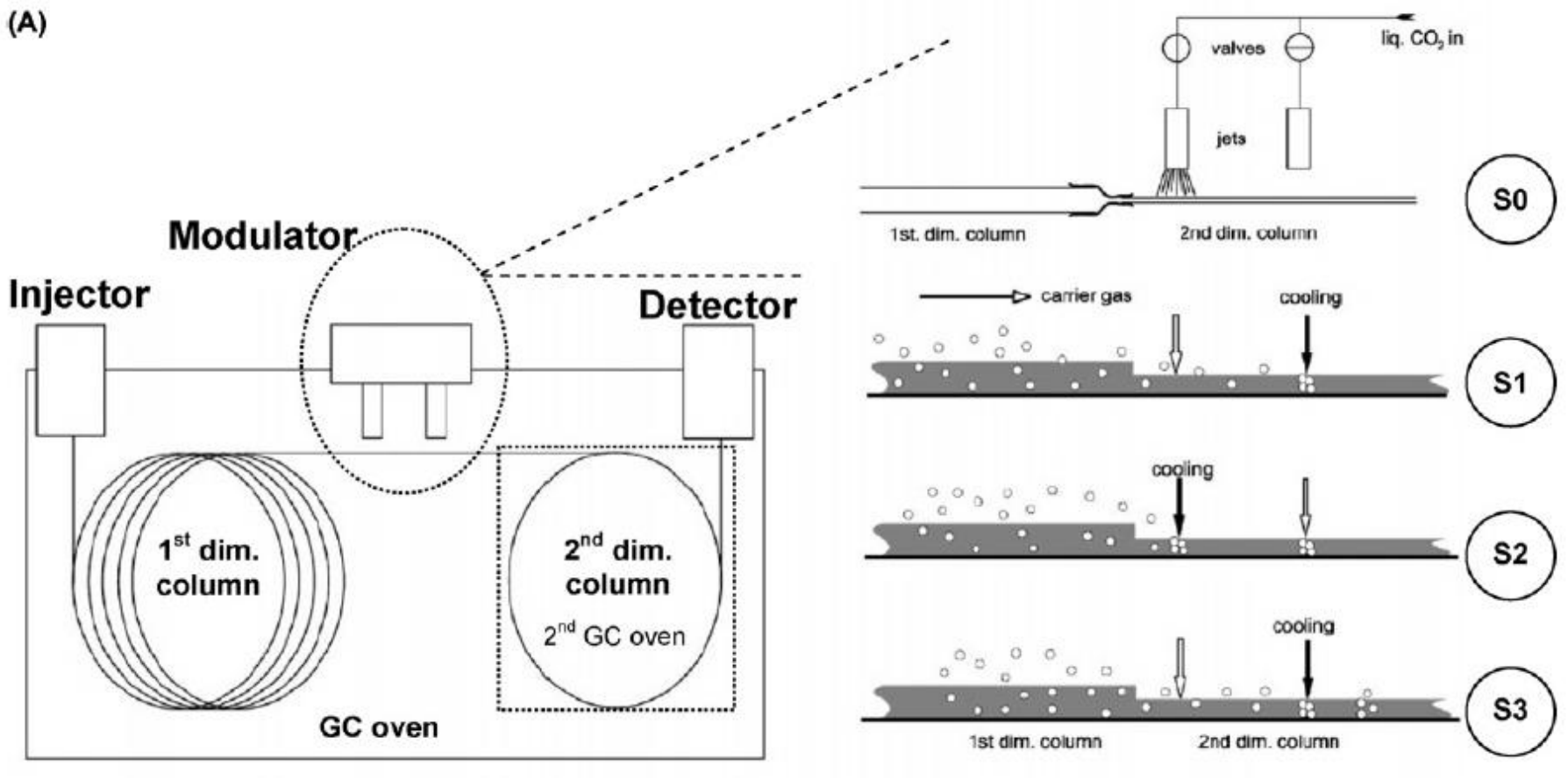


longitudinal modulating cryogenic system (LMCS)



M. Adahchour, J. Beens, U.A.Th. Brinkman *Journal of Chromatography A*, 1186 (2008) 67–108

This modulator uses expanding liquid carbon dioxide for trapping and focusing of the analytes in the first centimetres of the second-dimension column.



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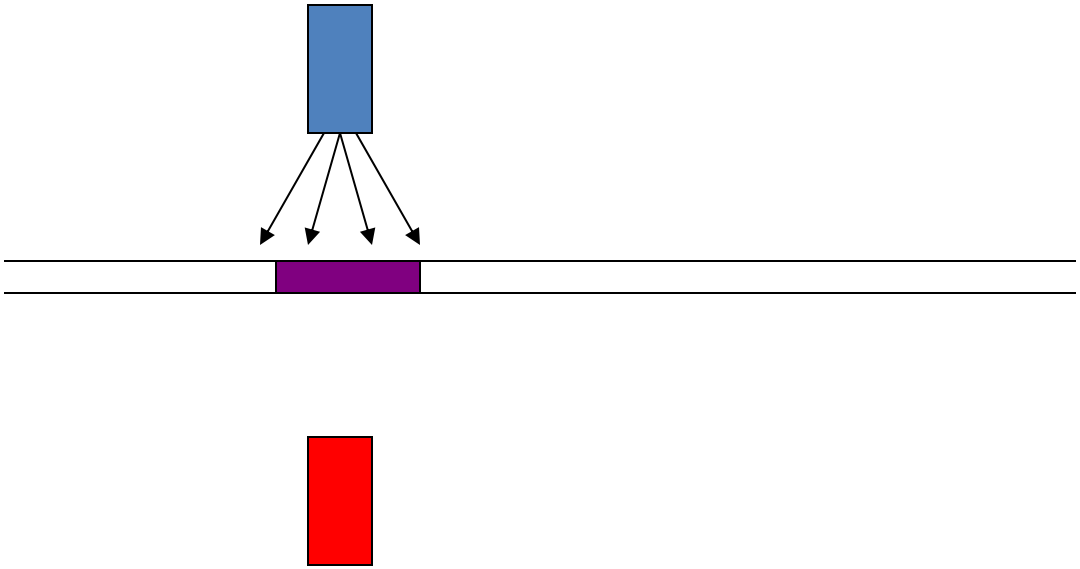
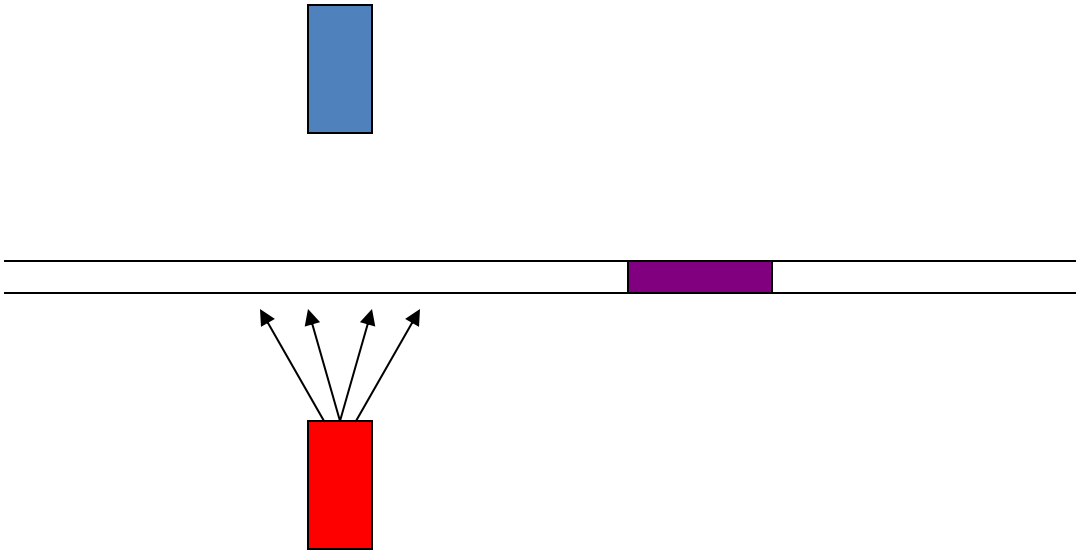
Jet Modulator Principle

- Active cooling and heating stages
- Thermal scanners only have one active stage (either heating or cooling, but not both)

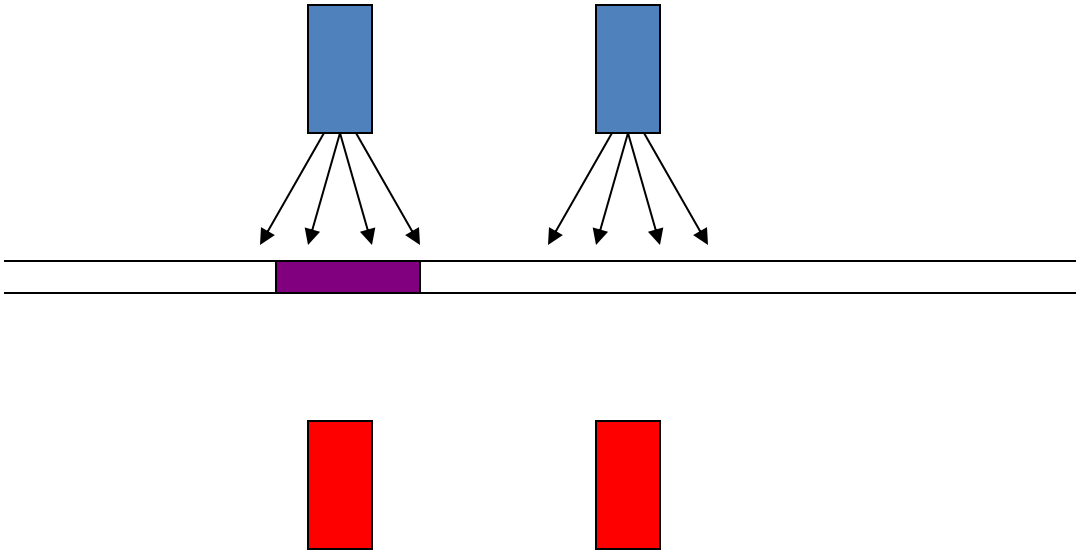
Single-Stage, Dual-Jet (Beens, 2001)



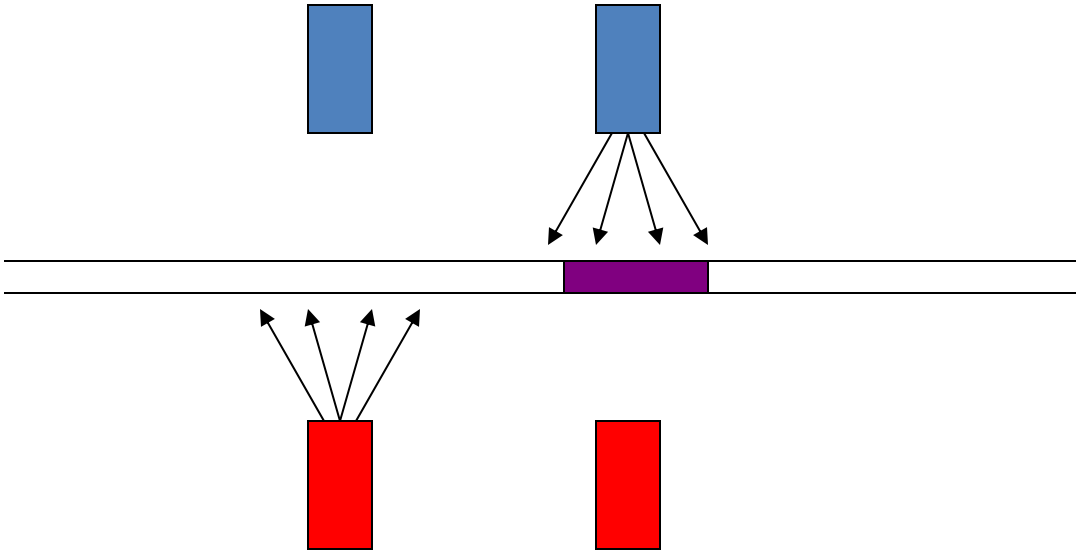
Single-Stage, Dual-Jet



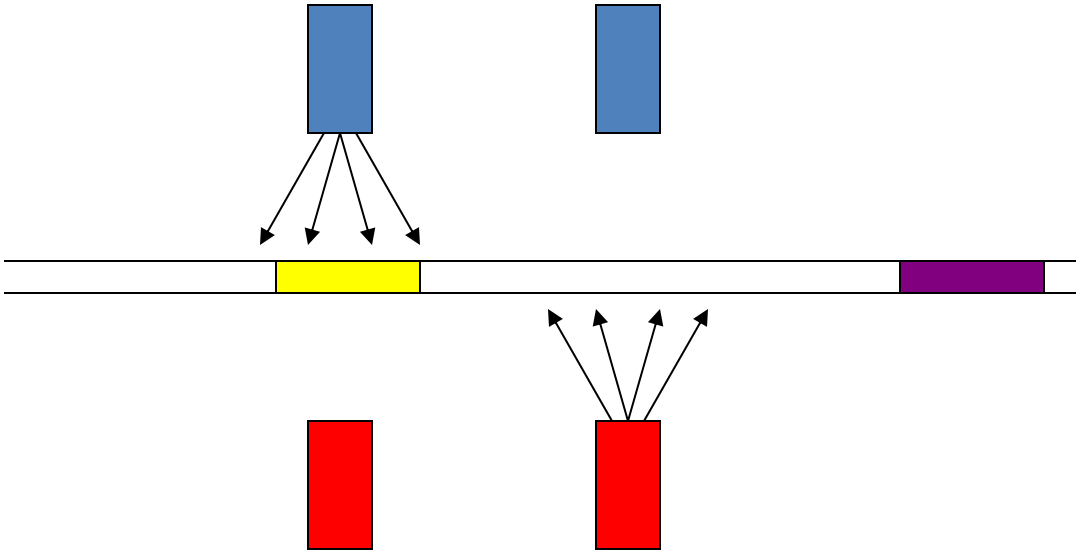
Two-Stage, Quad-Jet Modulation (Ledford, 2001)



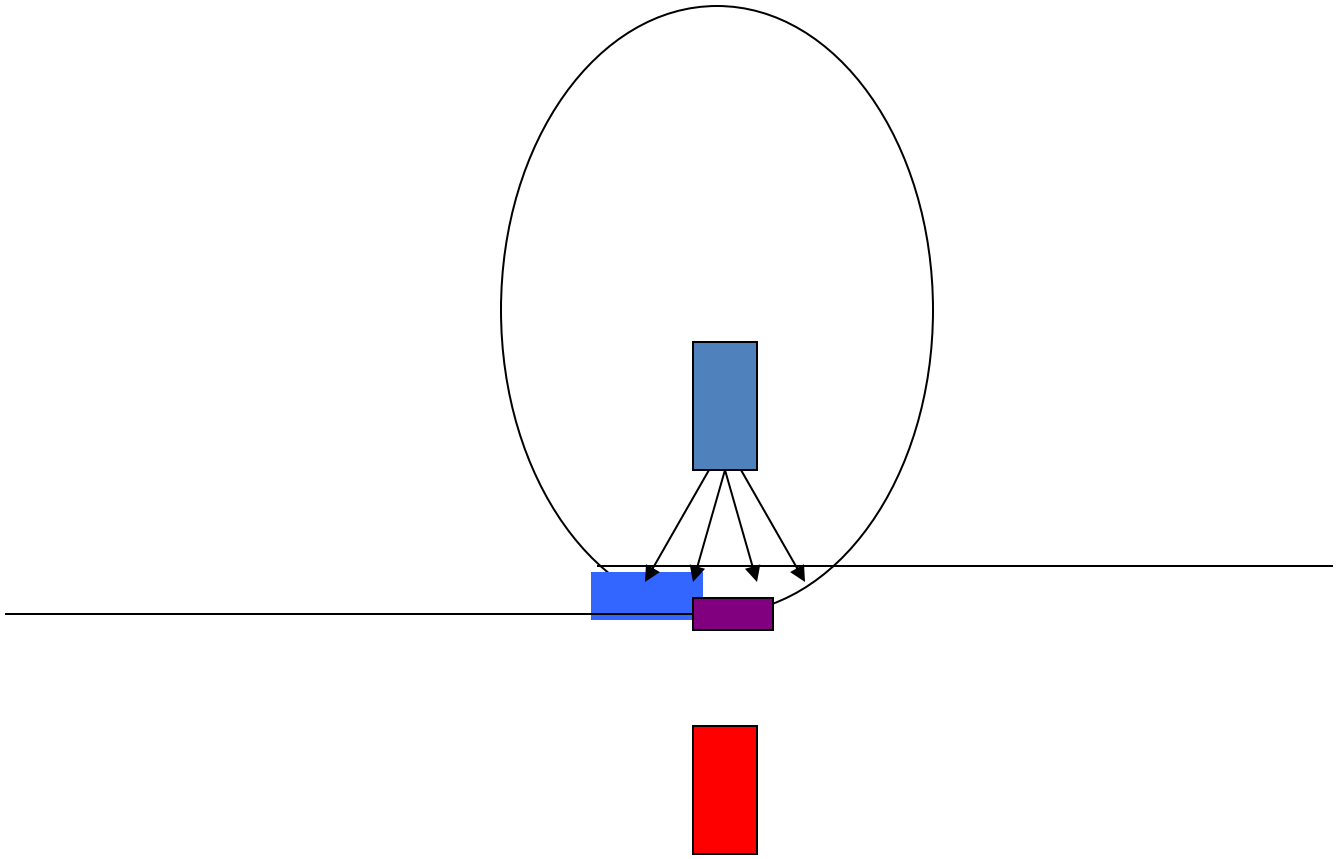
Two-Stage, Quad-Jet Modulation



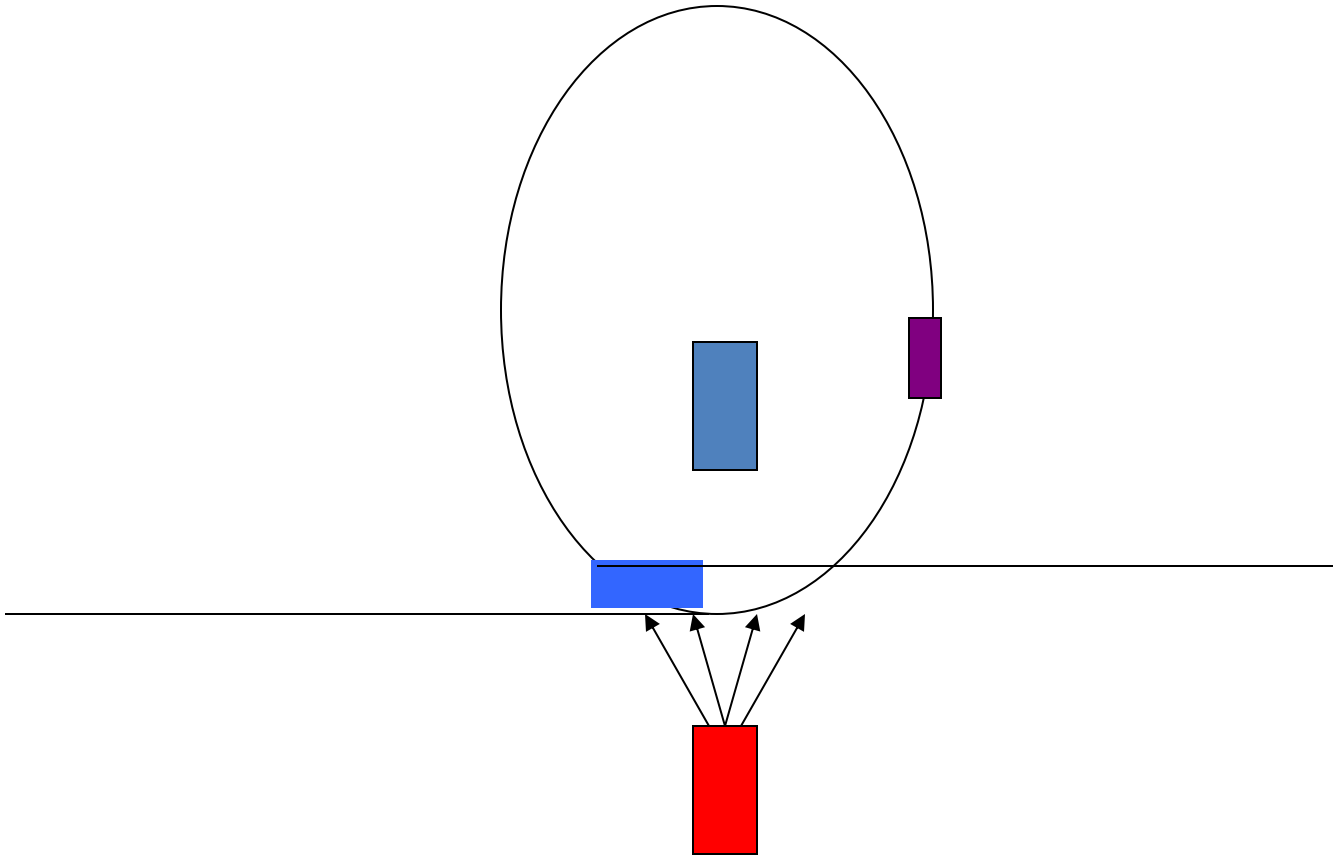
Two-Stage, Quad-Jet Modulation



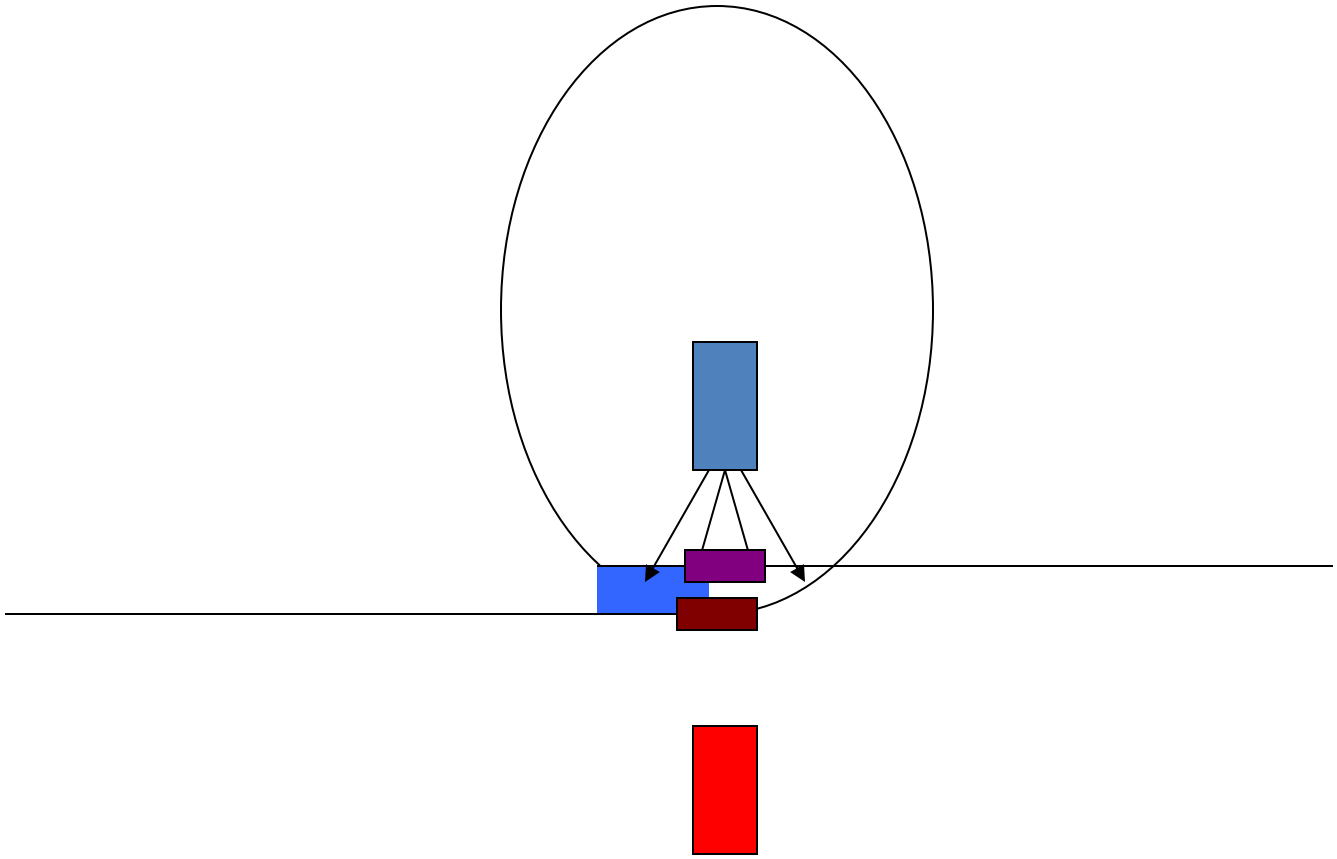
Two-Stage, Dual-Jet Modulation (Ledford, 2002)



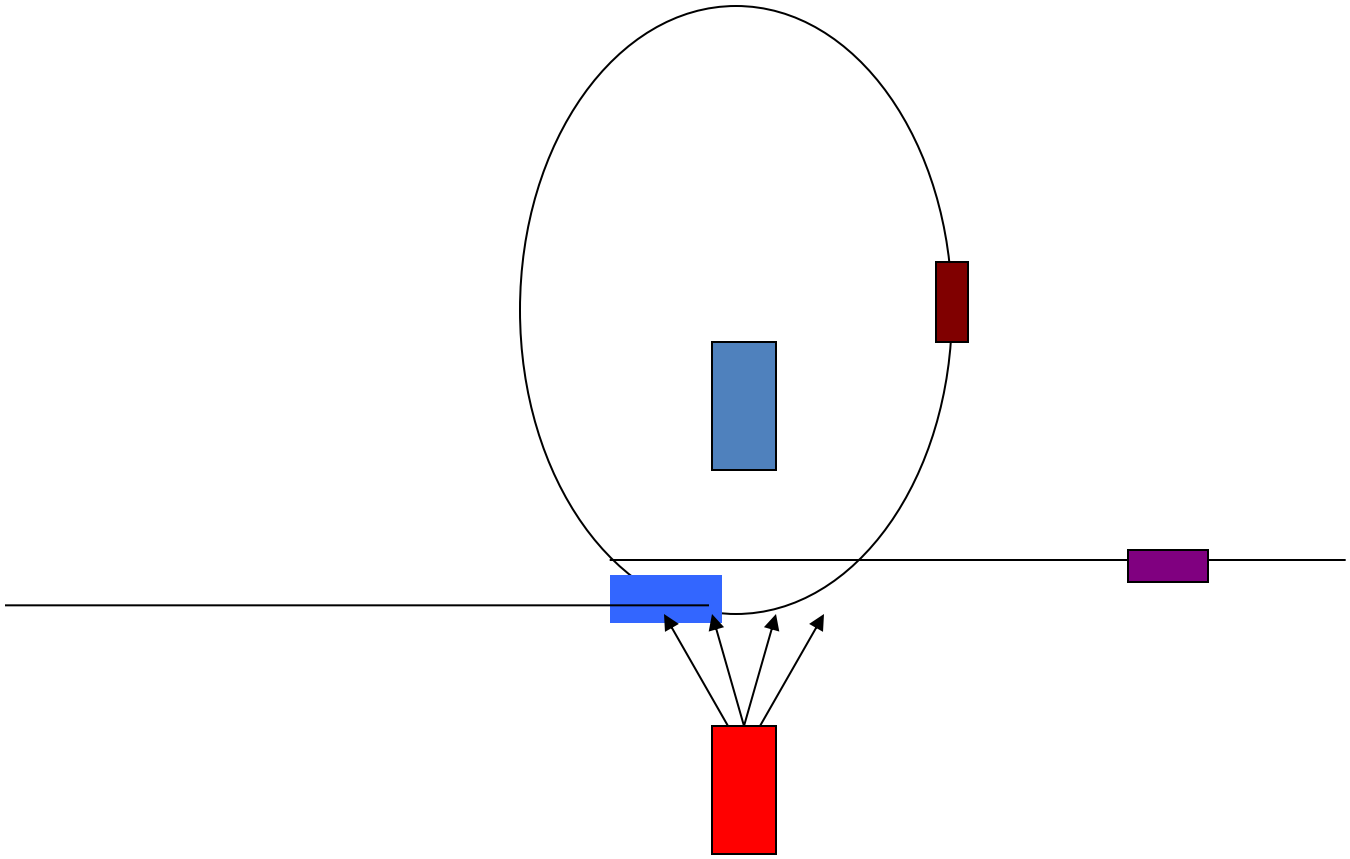
Two-Stage, Dual-Jet Modulation



Two-Stage, Dual-Jet Modulation



Two-Stage, Dual-Jet Modulation



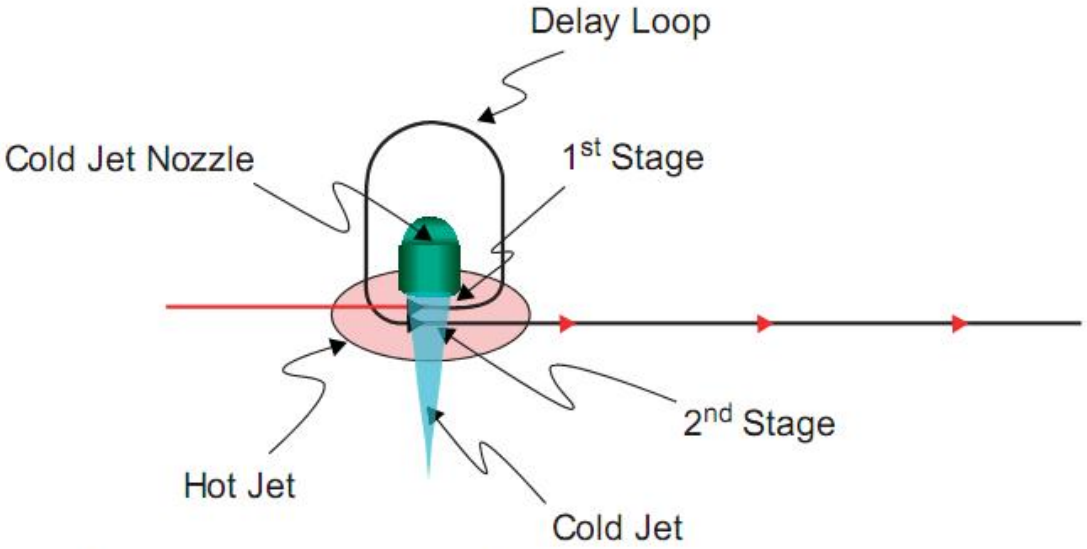


Figure 15 Design of the loop modulator [50].

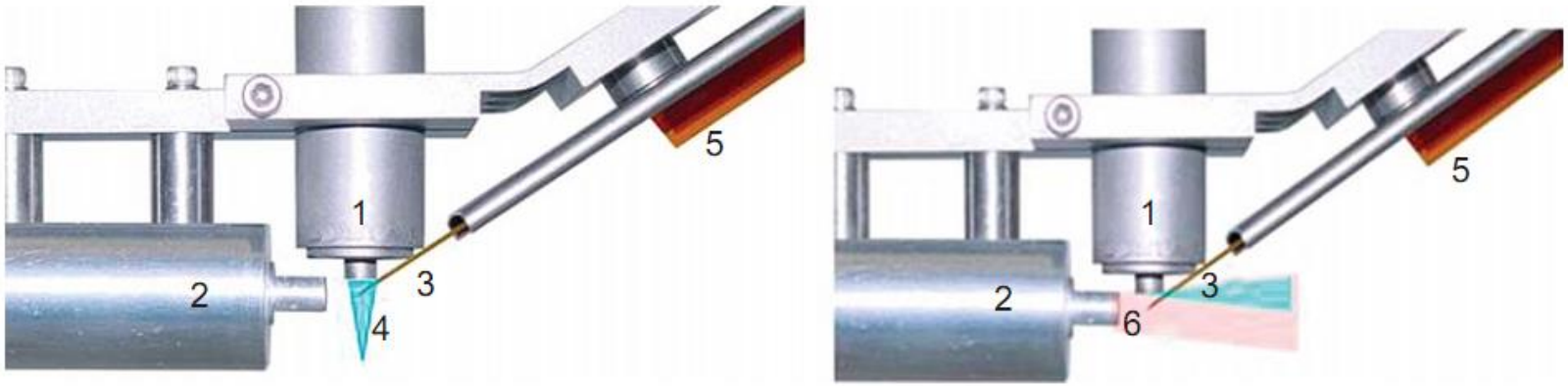
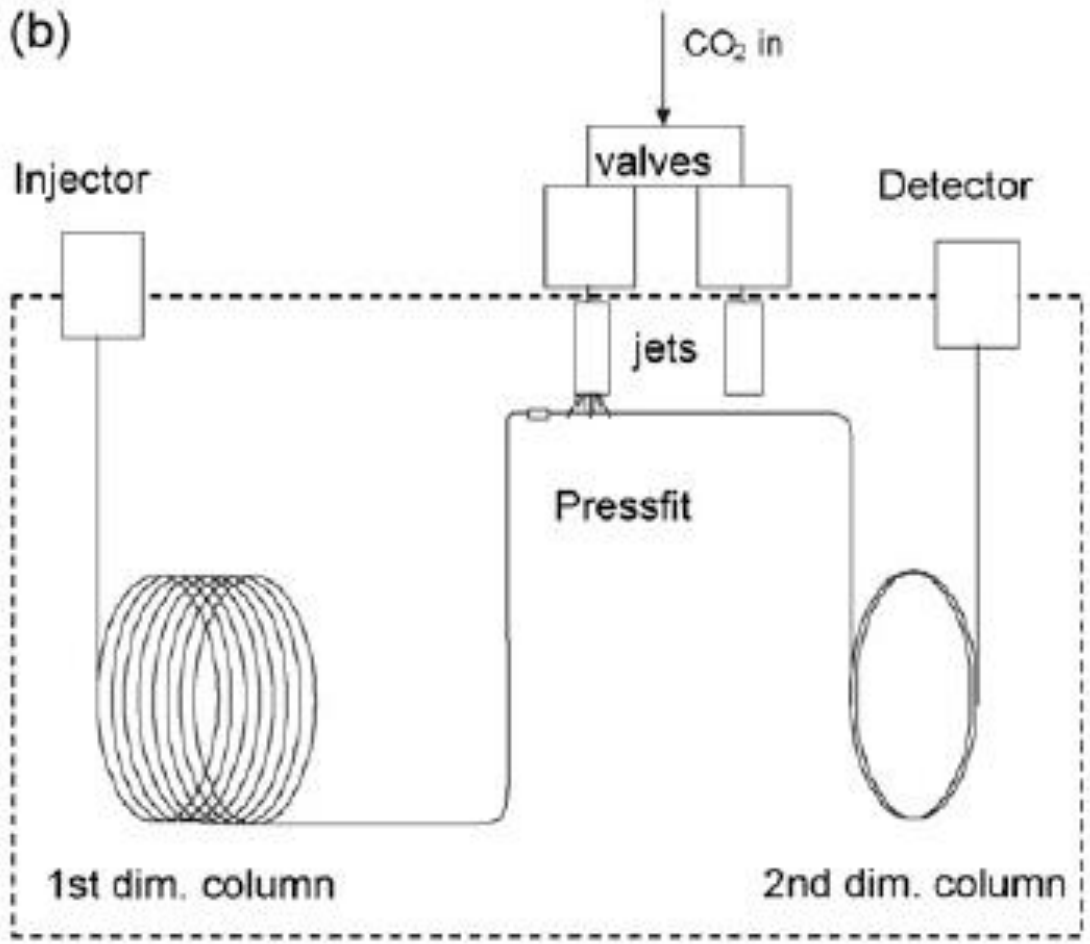


Figure 16 Jet sequence in the loop modulator [50]. 1, cold jet; 2, hot jet; 3, delay loop; 4, trap zone; 5, second column; 6, hot jet in action to release analytes.

Thermal Jet Summary

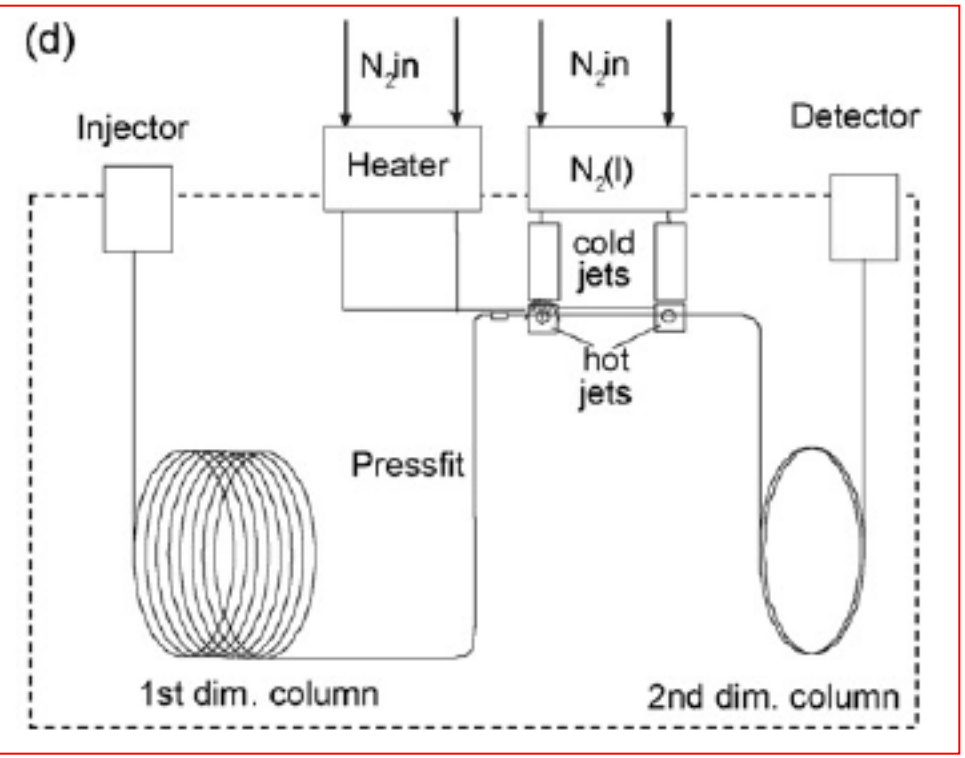
- Curent commercially available state-of-the-art in GCxGC
- Industry, academia, government
- Achilles heel: consumables

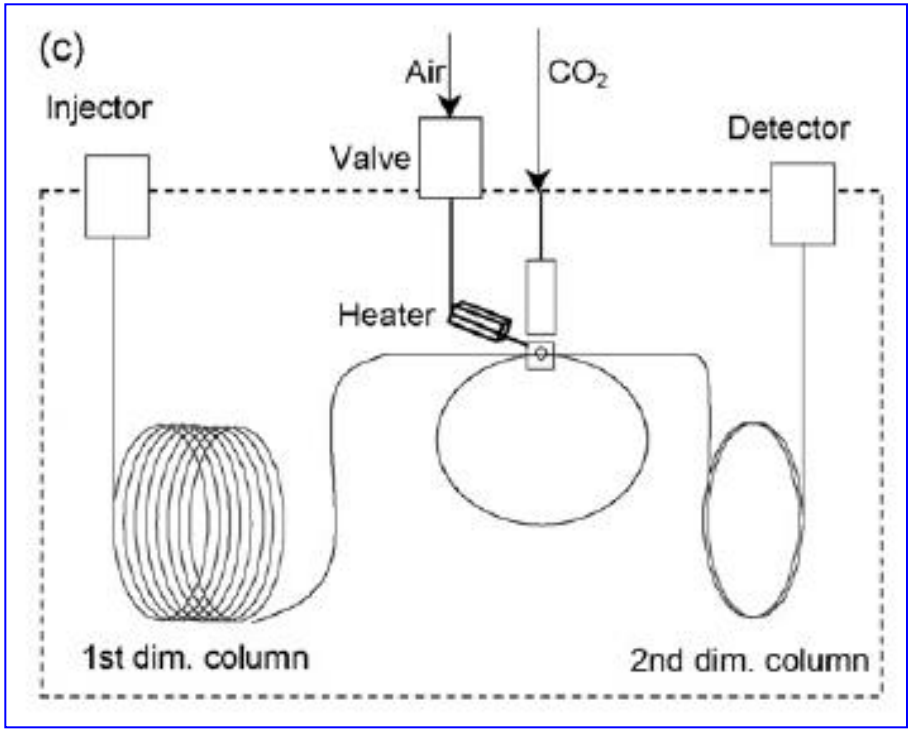
Dual-jet CO2 Modulator



M. Adahchour, J. Beens, U.A.Th. Brinkman *Journal of Chromatography A*, 1186 (2008) 67–108

KT2003, dual-jet N2 cryo

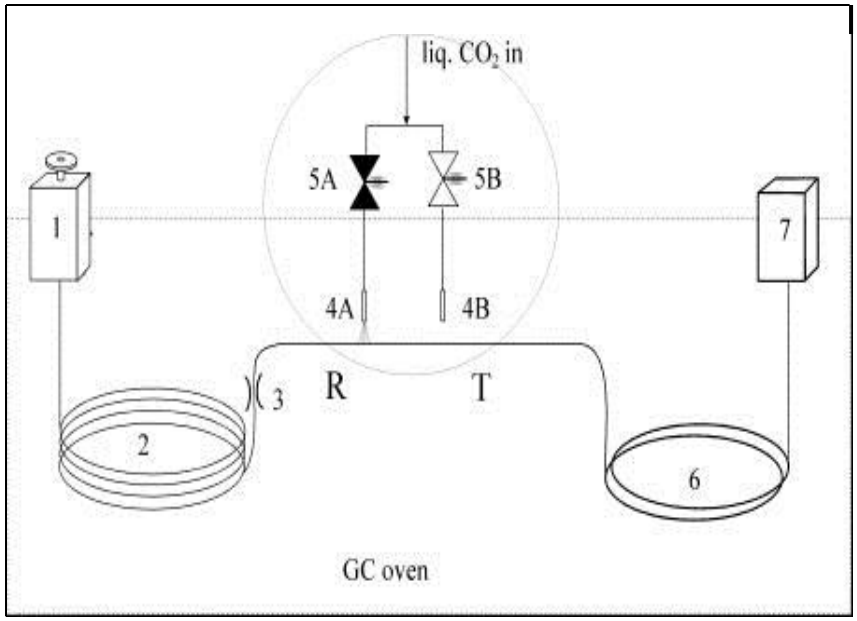




KT2001, four-jet N2 cryo

M. Adahchour, J. Beens, U.A.Th. Brinkman *Journal of Chromatography A*, 1186 (2008) 67–108

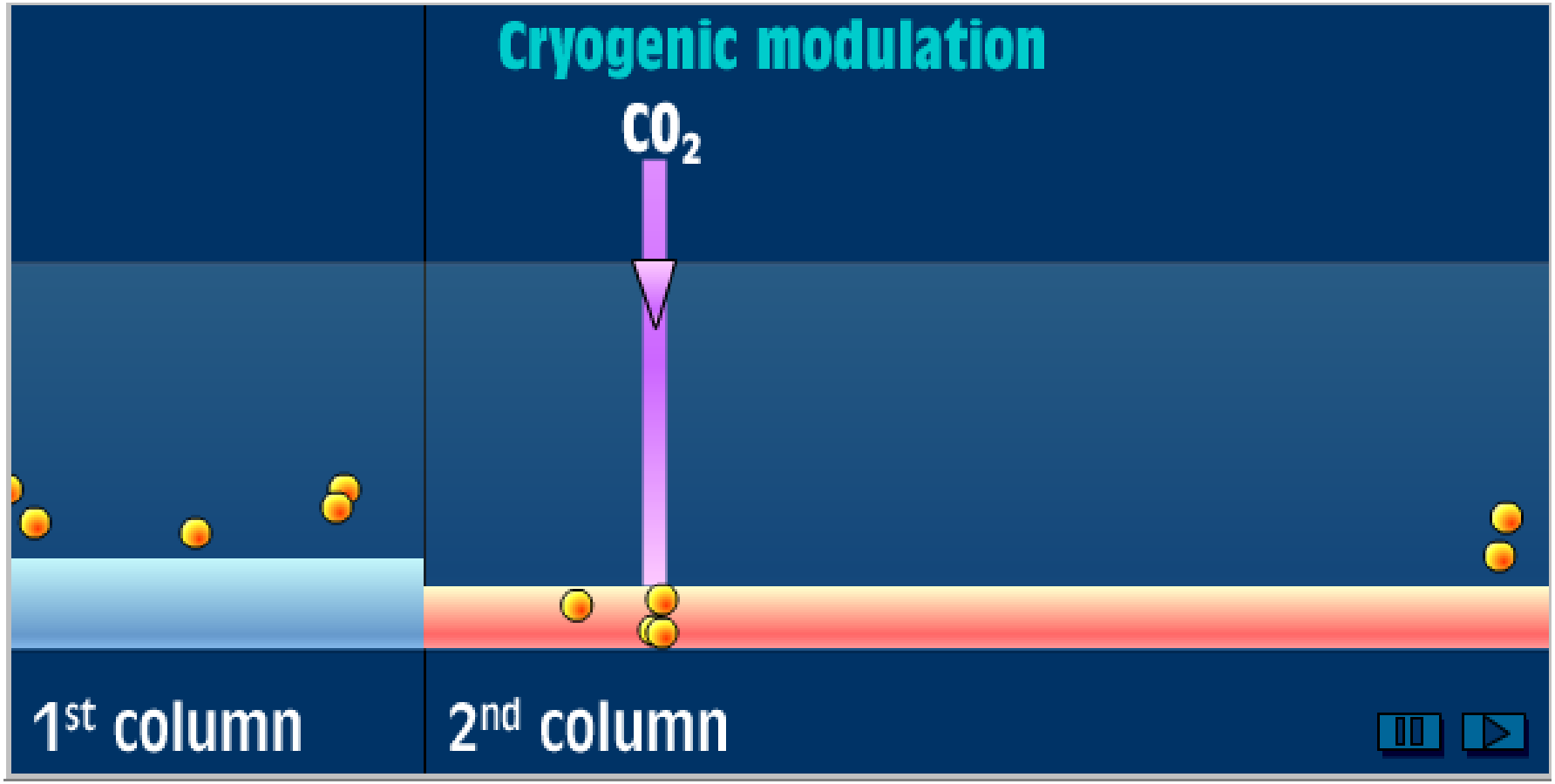
Dual-jet CO_2 modulator



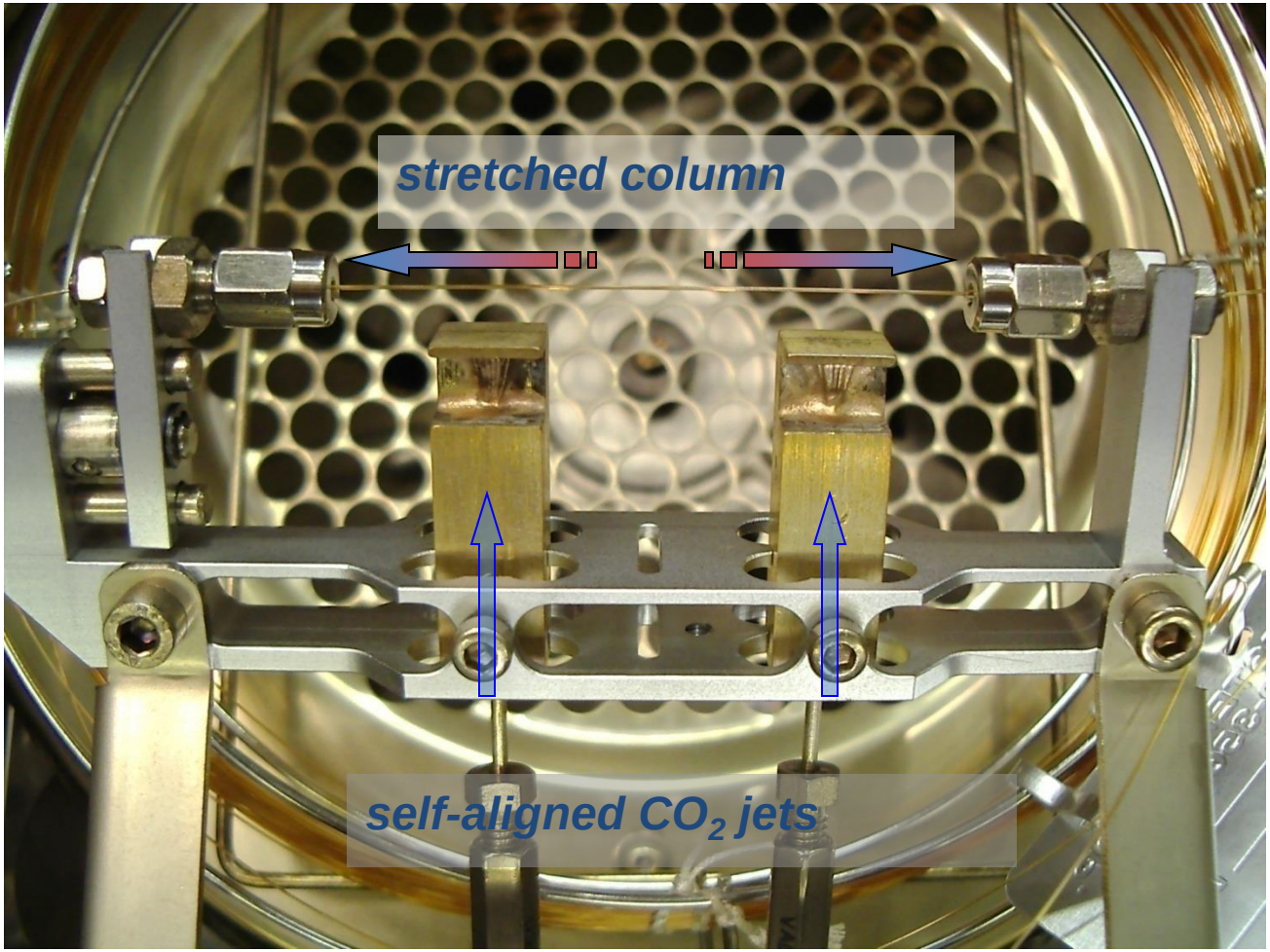
Developed in cooperation with Dr. J.Beens, Amsterdam Free University

- Liquid CO2 as cooling medium
- Completely solid state, no parts in motion
- Simple installation and column alignment
- Valves activation synchronized with data acquisition
- Trapping temperature at about 100°C below the oven T
- Heating step due to the hot circulating air into the GC oven
- Easy modulator control via GC keyboard

Dual-jet CO_2 modulator



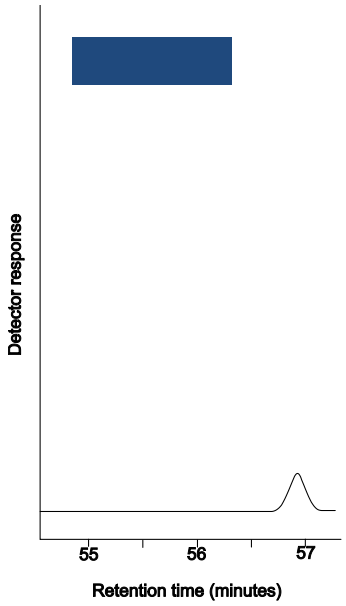
Dual-jet CO_2 modulator

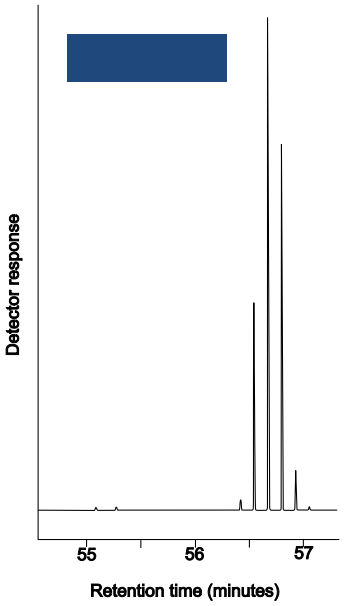


License from Zoex Corporation on patents related with thermal modulation

Dual-jet CO_2 modulator

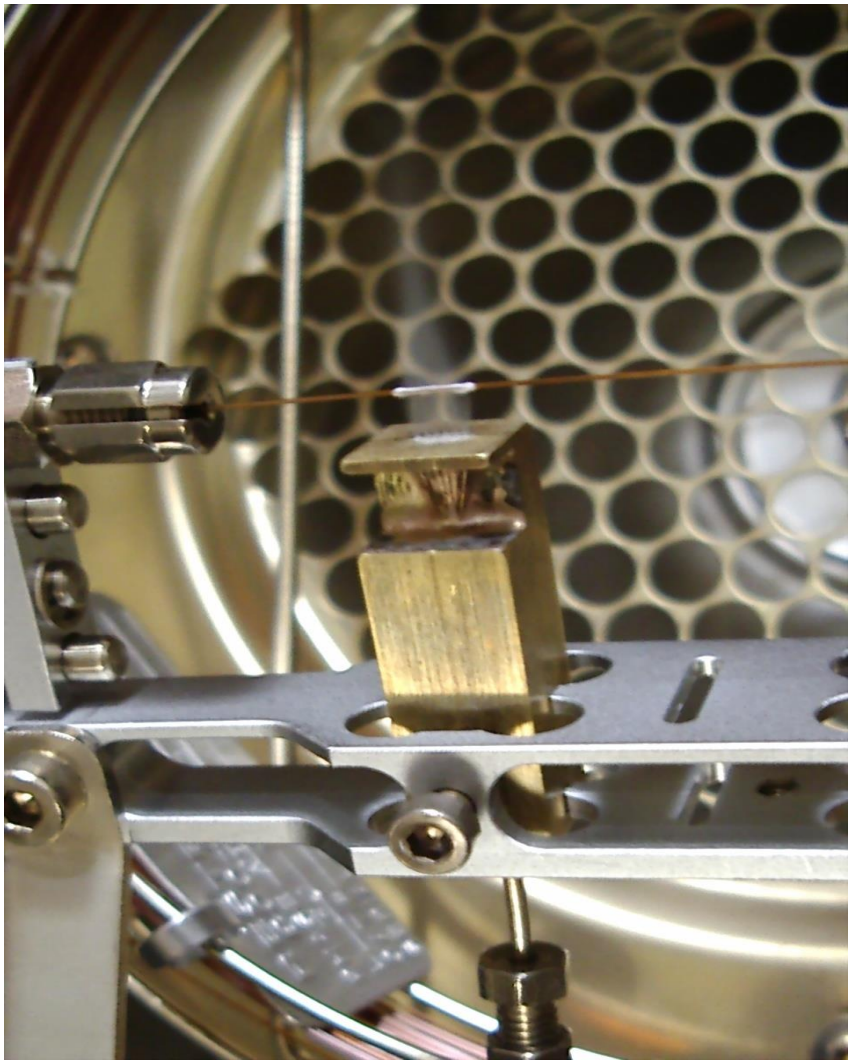
Trapping and release

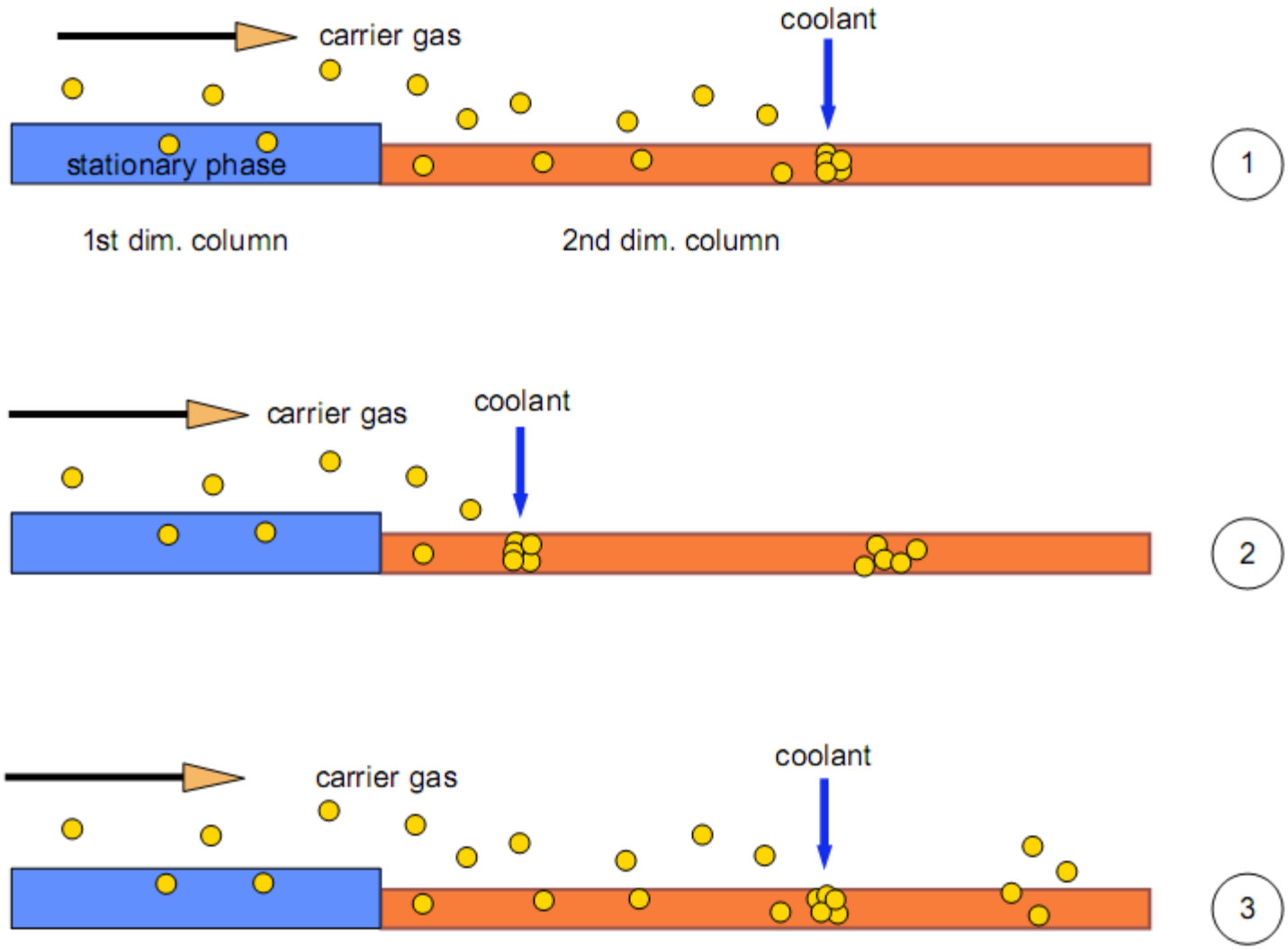




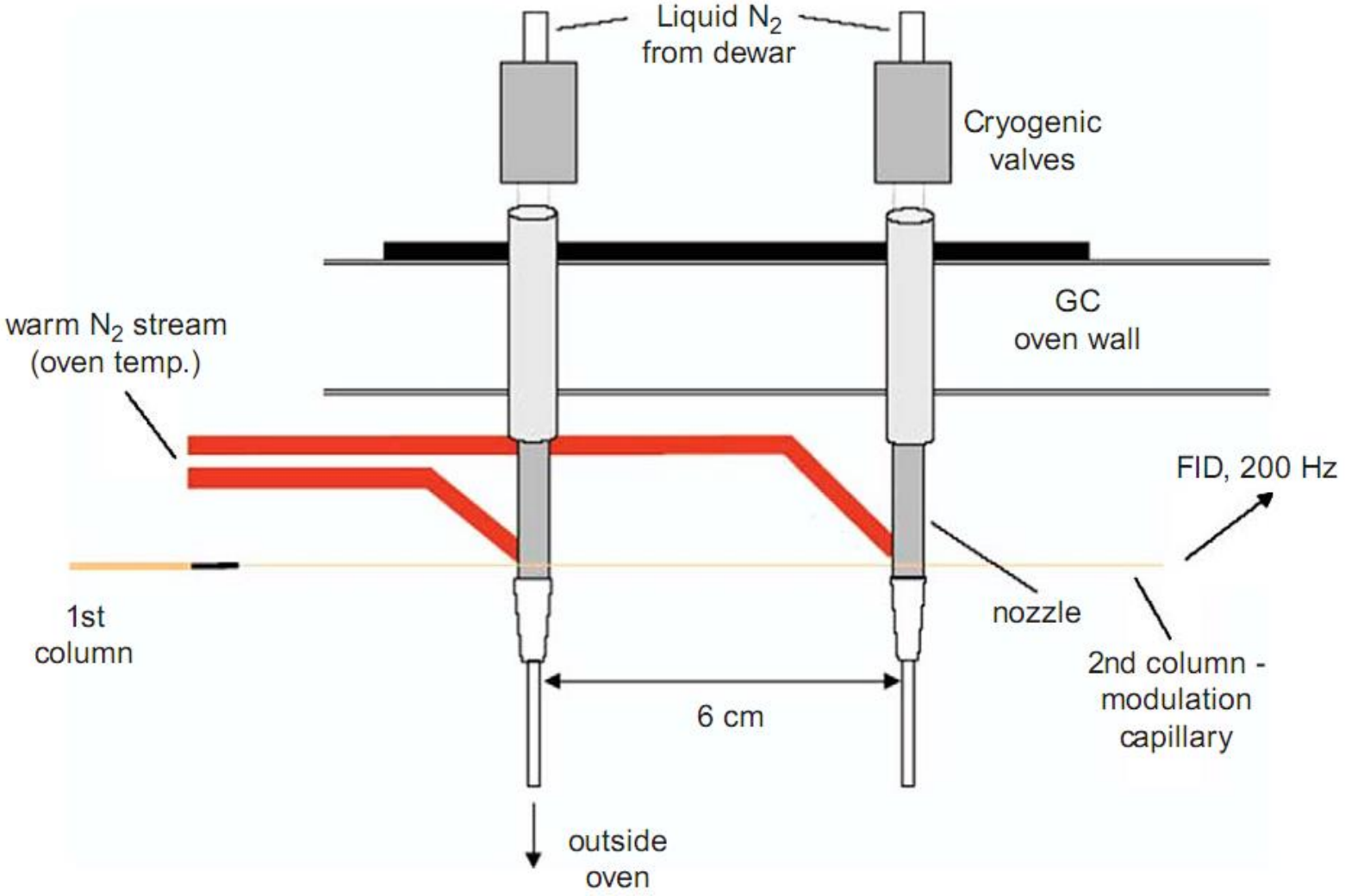
No modulation

Modulated peak



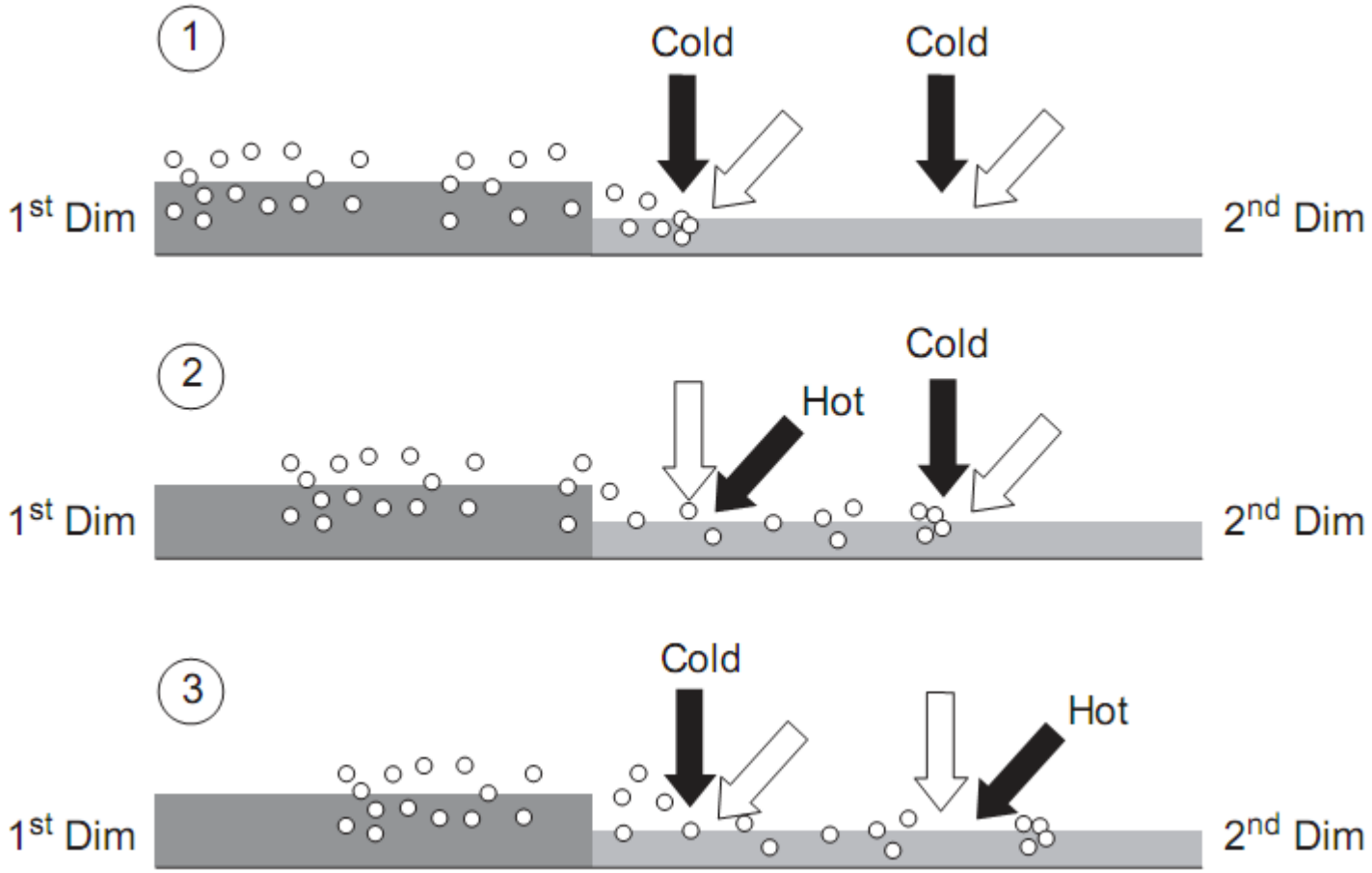


The modulation process in a dual-stage liquid CO2 cryogenic modulator.



Design of the quad-jet N2 modulator

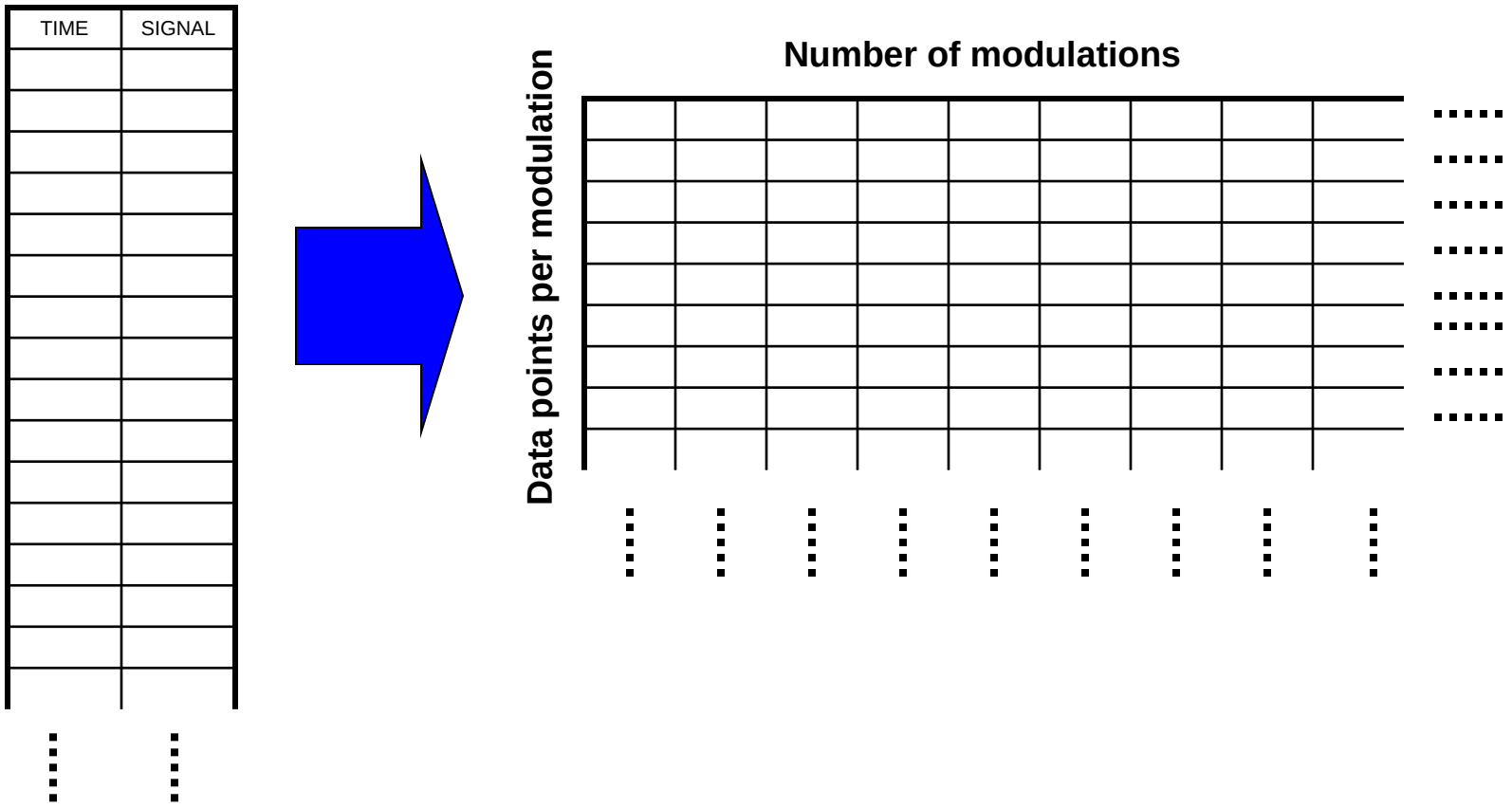
COMPREHENSIVE ANALYTICAL CHEMISTRY, ´ D. BARCELO, 2009 Elsevier



Sequence of events responsible for (1) trapping, (2) releasing and refocusing, and (3) reinjecting into the second column using a quad-jet dual-stage cryo-modulator

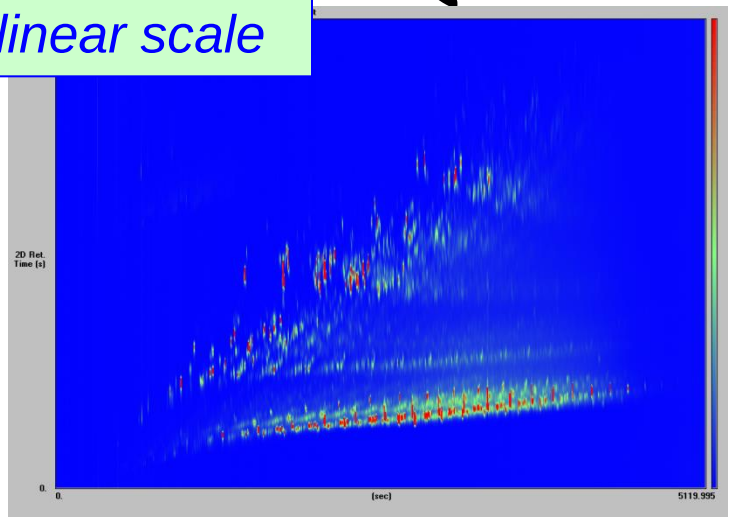
HyperChrom Data System – Data handling

Automatic GCxGC data conversion according to acquisition and modulation frequency

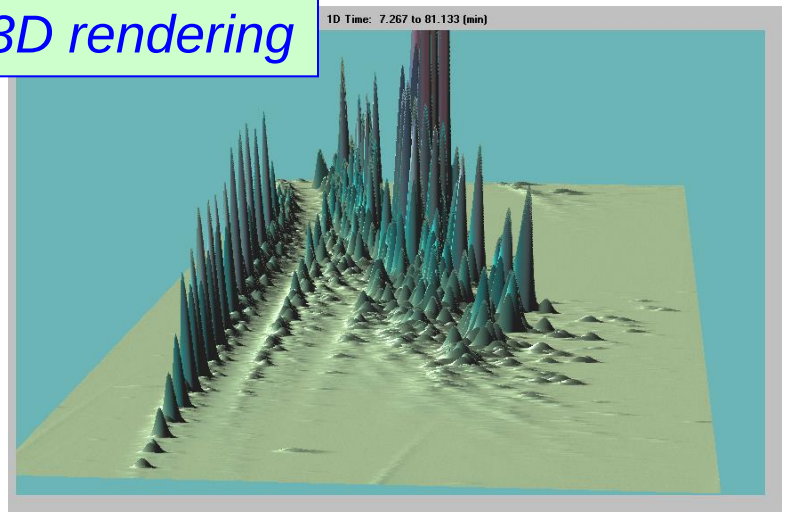


HyperChrom Data System – Qualitative Approach

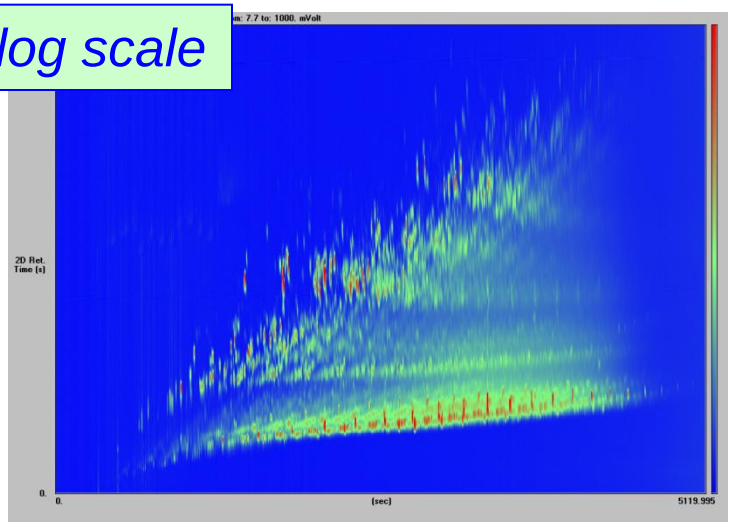
linear scale



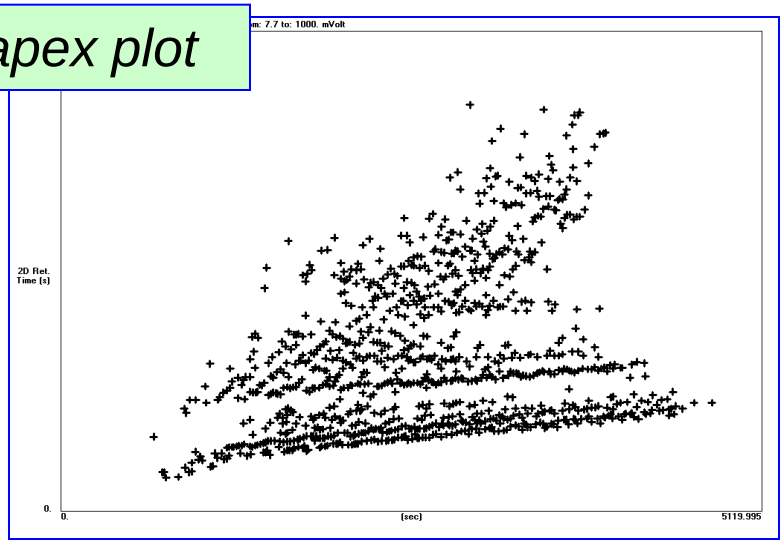
3D rendering



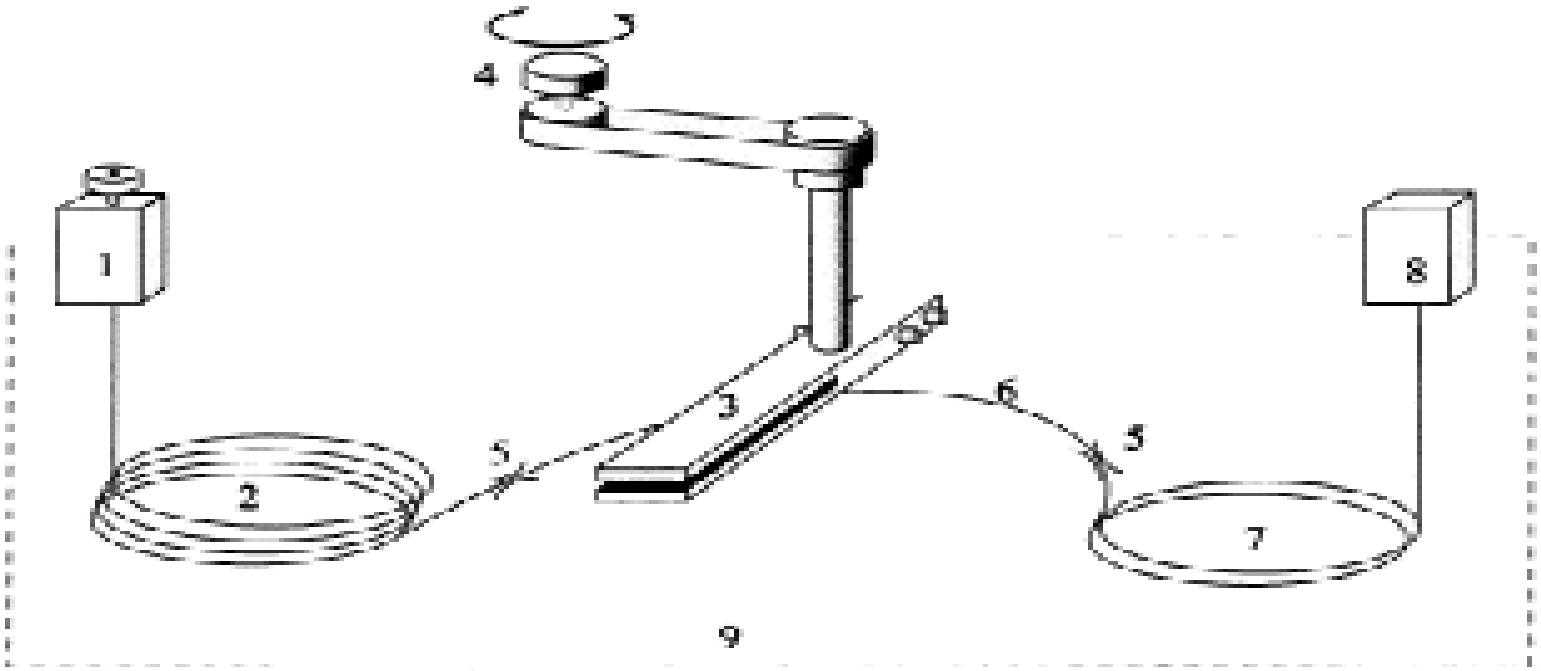
log scale



apex plot



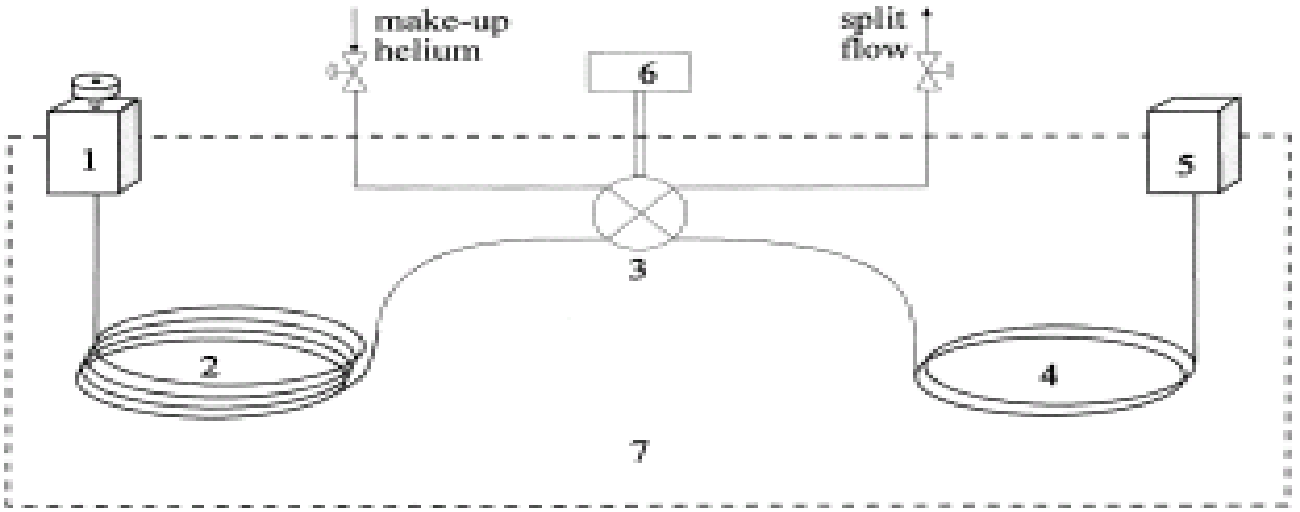
Modulator



Sweeper

Both modulators had significant disadvantages. It was practically impossible to collect volatile compounds with the heating trap. In addition, in order to prevent the thermal degradation of the stationary phase in the capillary used as a trap, the final oven temperature had to be 1001C lower than the upper working temperature of the stationary phase. Consequently, the maximum first-dimension column temperature was 230°C.

Modulator

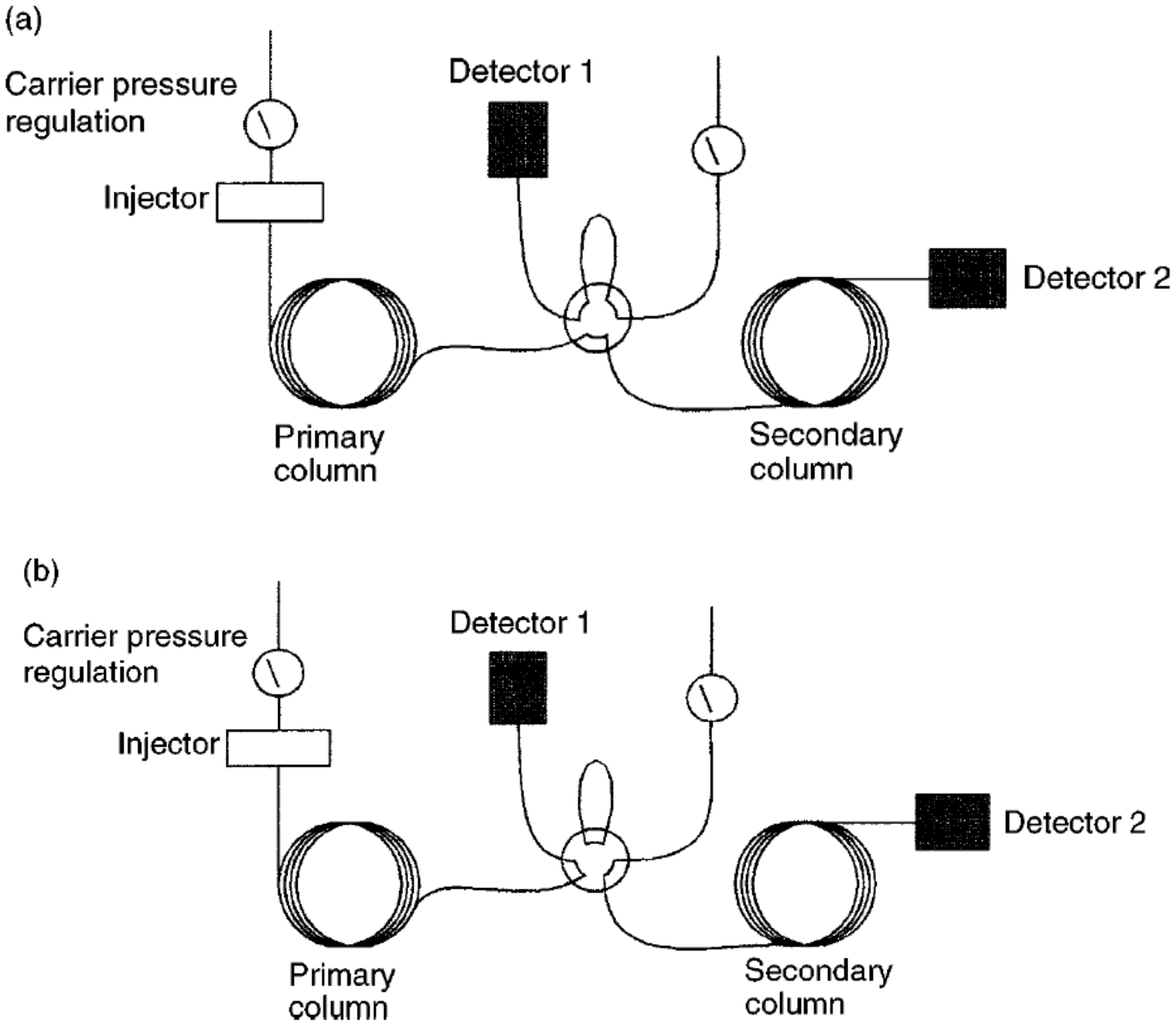


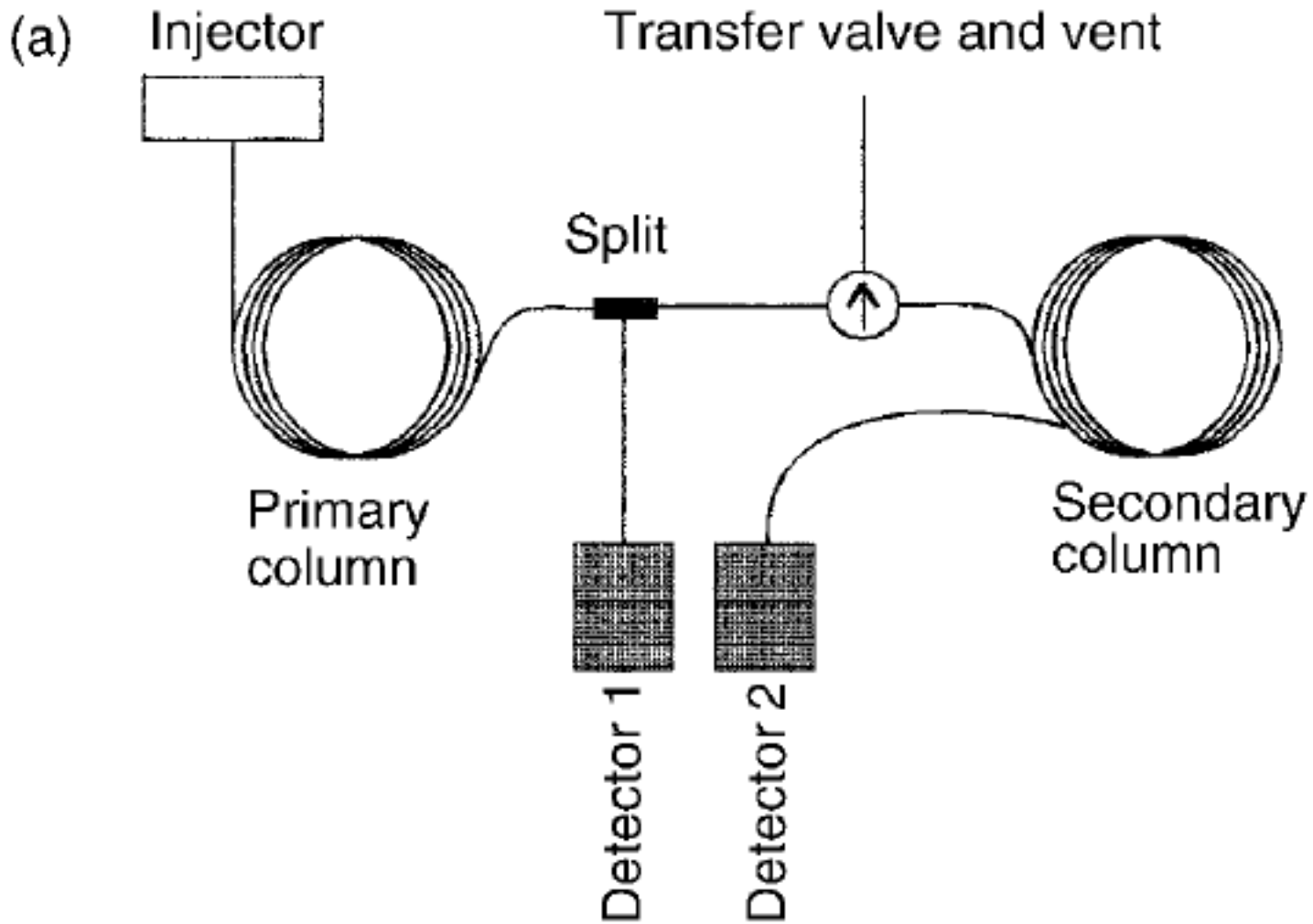
Valve

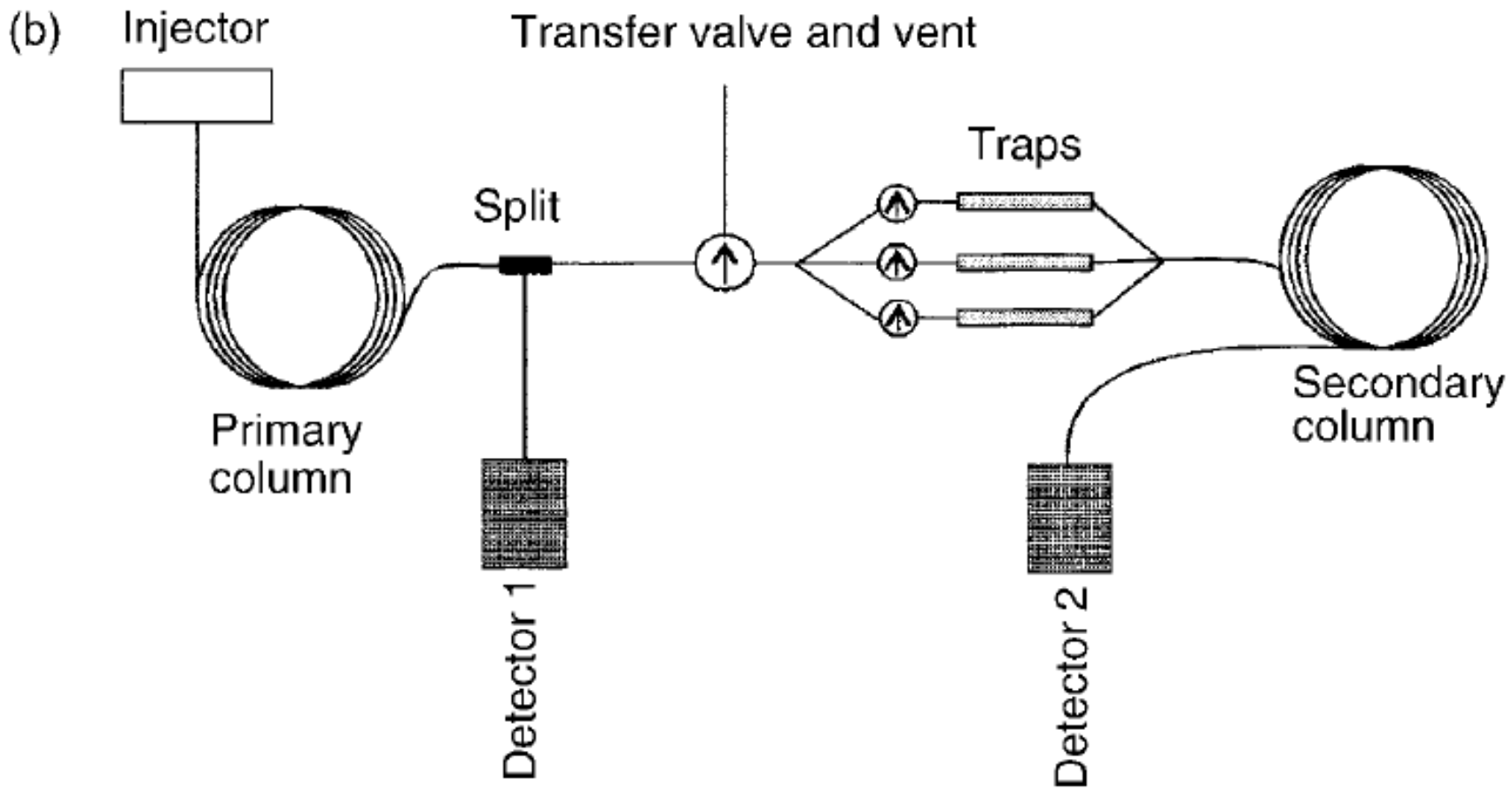
Valve switching interface (modulator)

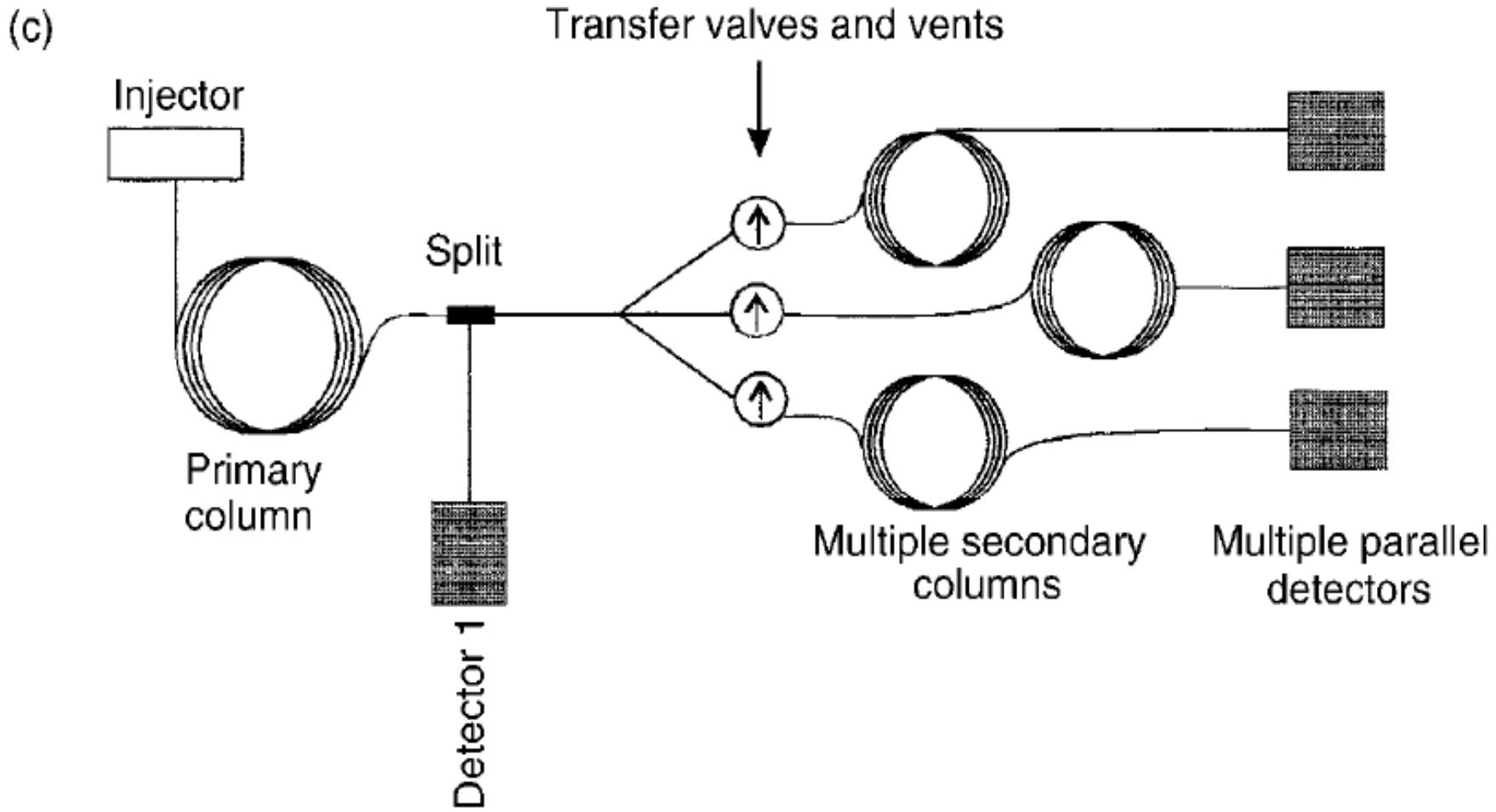
In the literature, some attention has been devoted to valve-based modulation, mainly in order to avoid breakthrough of even the most volatile analytes, or enable a more flexible second dimension column operation.

J. Harynuk, T. Gorecki, J. Chromatogr. A 1105 (2006) 159.
J.V. Seeley, N.J. Micyus, S.V. Bandurski, S.K. Seeley, J.D. McCurry, Anal. Chem. 79 (2007) 1840.


(a)
Carrier pressure regulation
Injector
Detector 1
Detector 2
Primary column
Secondary column
(b)
Carrier pressure regulation
Injector
Detector 1
Detector 2
Primary column
Secondary column


(a)
Injector
Transfer valve and vent
Split
Primary column
Secondary column
Detector 1
Detector 2


(b)
Injector
Transfer valve and vent
Traps
Split
Primary column
Secondary column
Detector 1
Detector 2


(c)
Transfer valves and vents
Injector
Split
Primary column
Detector 1
Multiple secondary columns
Multiple parallel detectors

Valve switching systems: the techniques

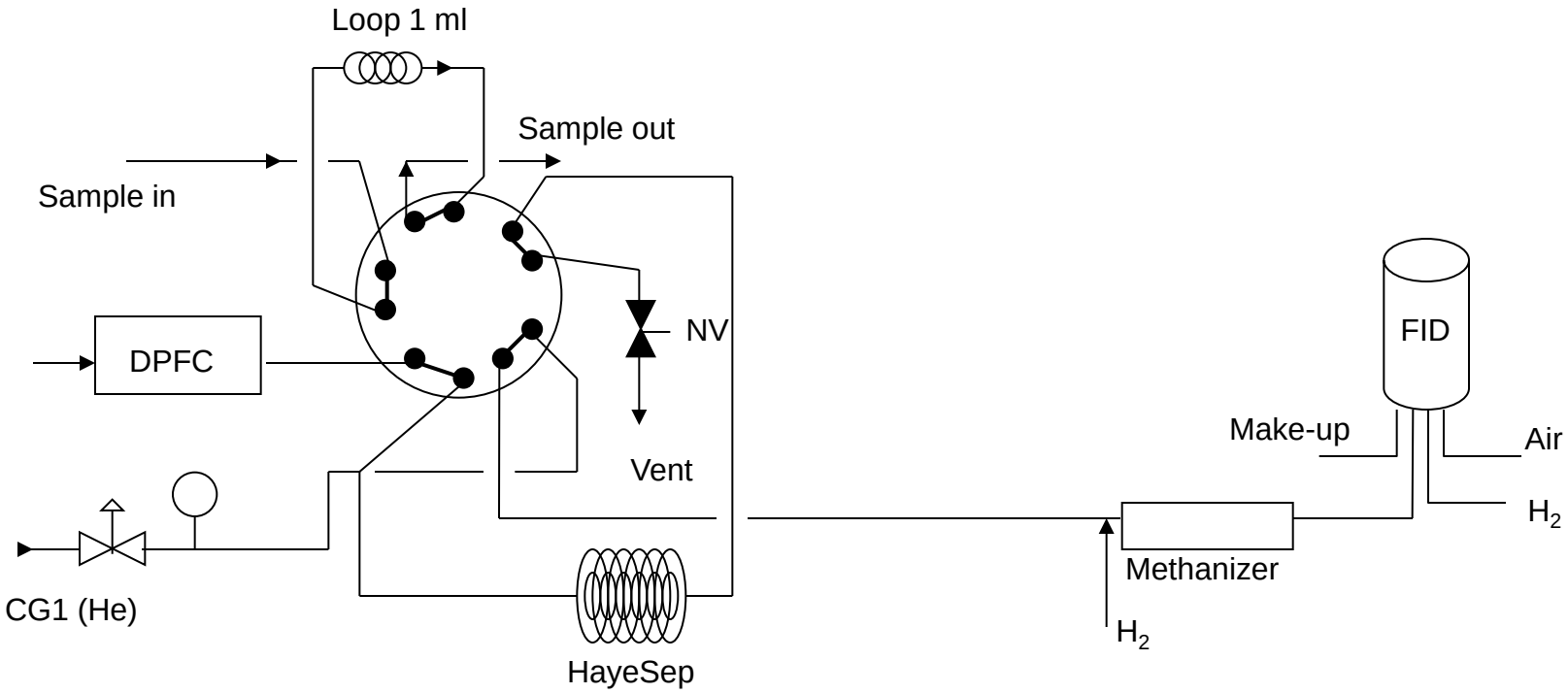
- Backflushing
  - Shortening of analysis time
  - Removal of high boiling compounds, fast reconditioning of the system
  - Reduction of complex samples onto only a few components of interest
- Cutting
  - Reduction of complex samples onto only a few components of interest
  - Protection of columns or detectors from stressing substances
  - Analysis of traces in the tailing of main components (Heart-cutting)

Valve switching systems: the technique

- Backflushing
  - Shortening of analysis time
  - Removal of high boiling compounds, fast reconditioning of the system
  - Reduction of complex samples onto only a few components of interest

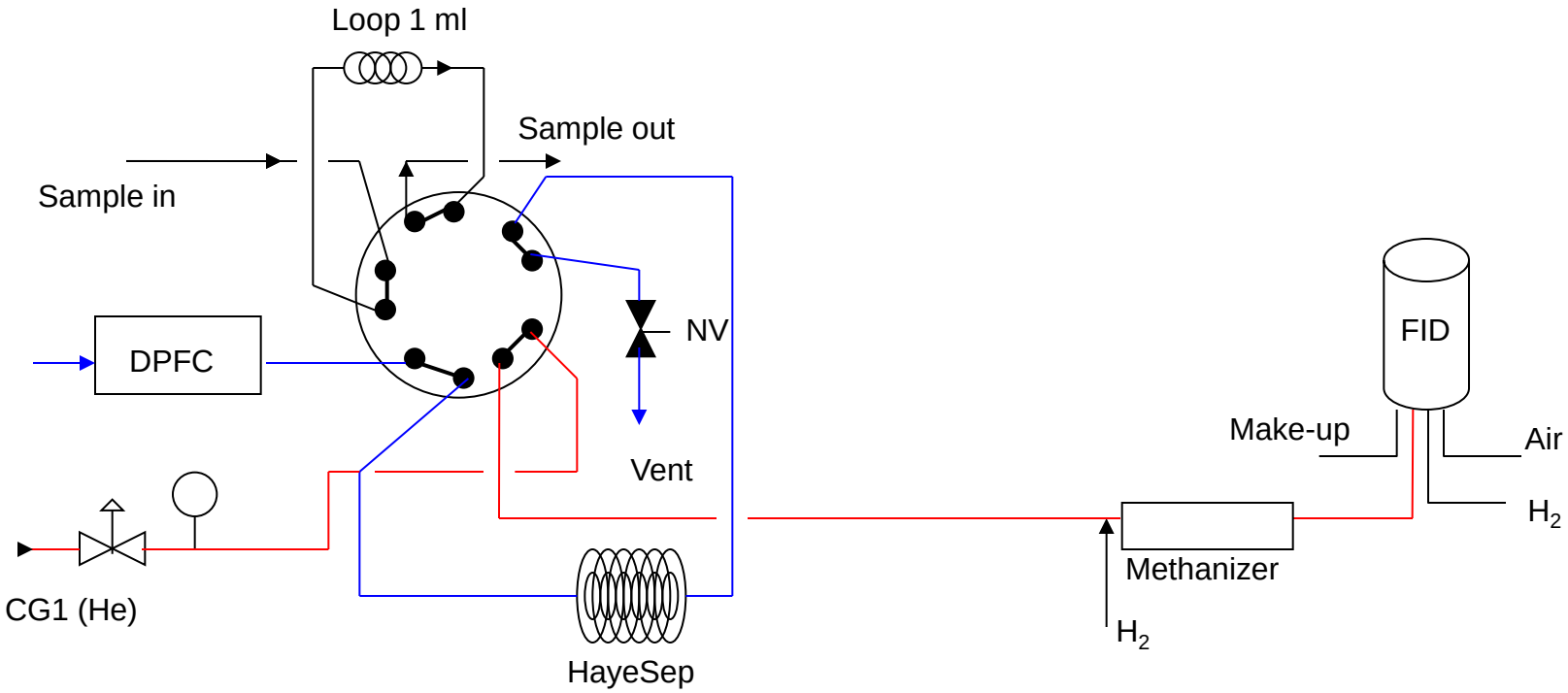
Example of backflush system

Analysis of CO and CO2 in Ethylene or Propylene streams



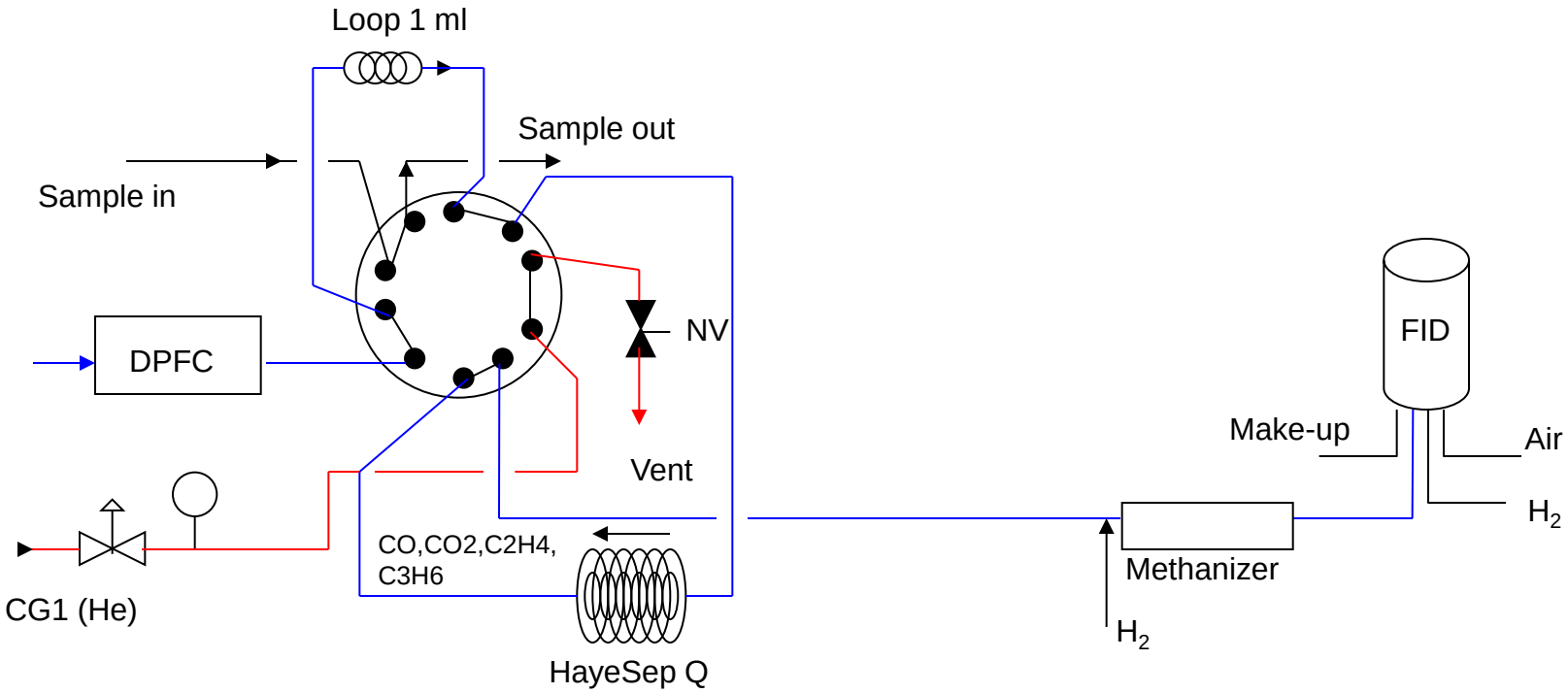
Example of backflush system

Step 1 Sample Loop filling



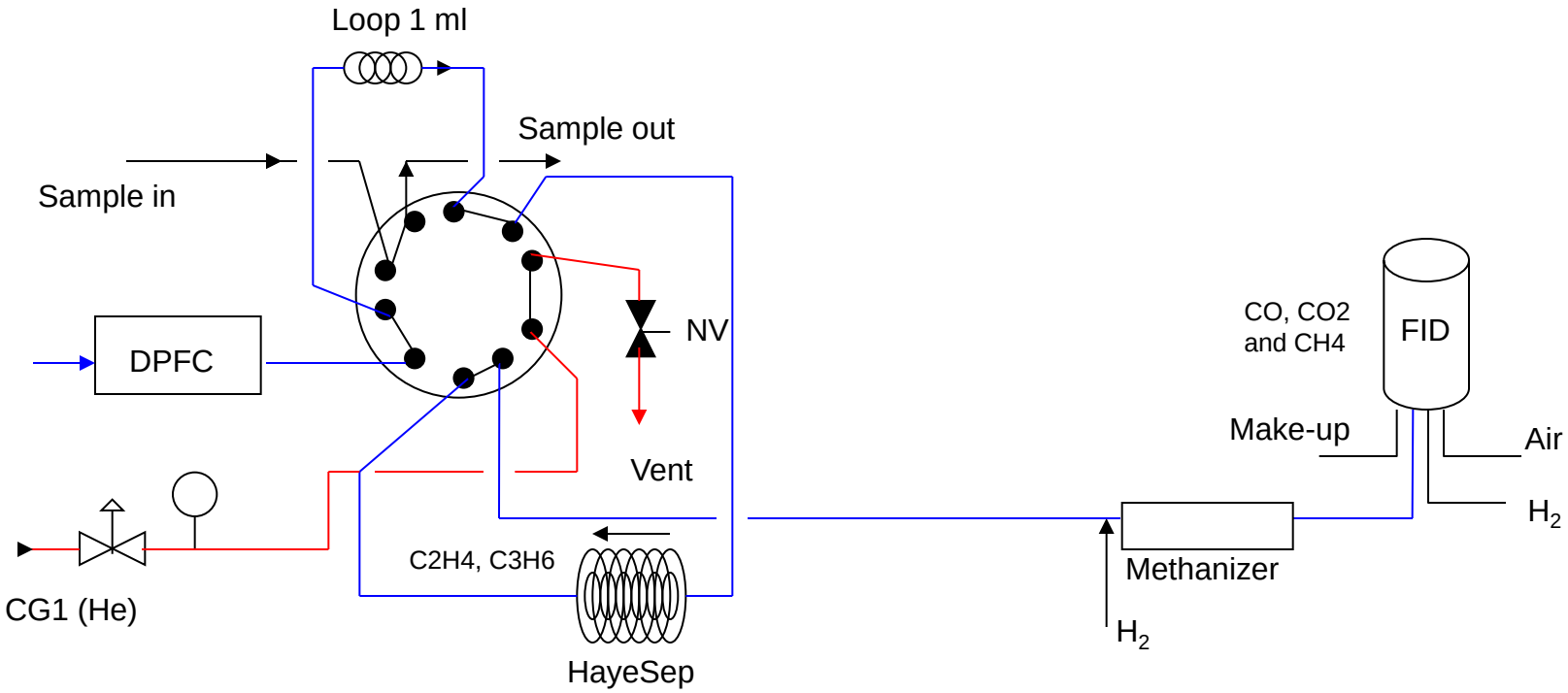
Example of backflush system

Step 2 Injection and gases trapping



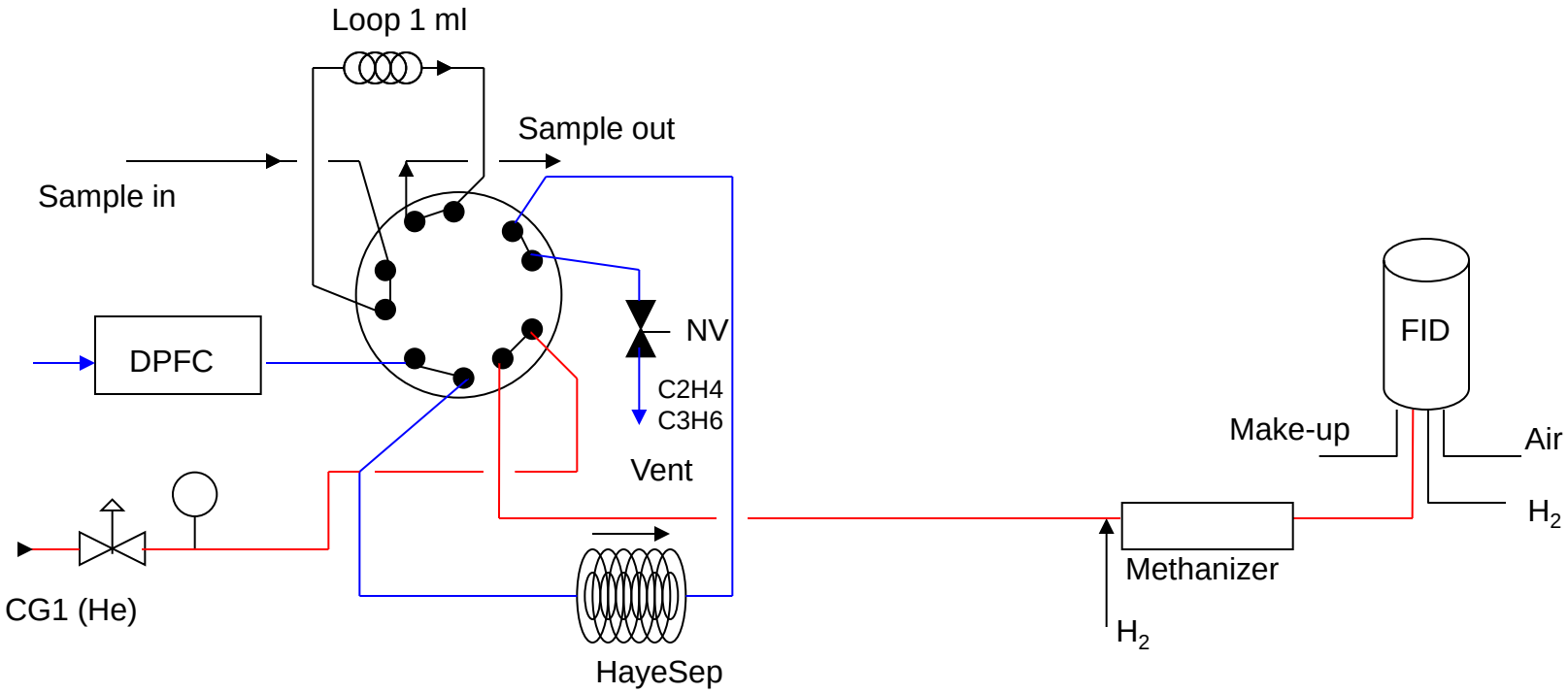
Example of backflush system

Step 3 CO, CO2 elutes from Hayesep, converted and determined as methane

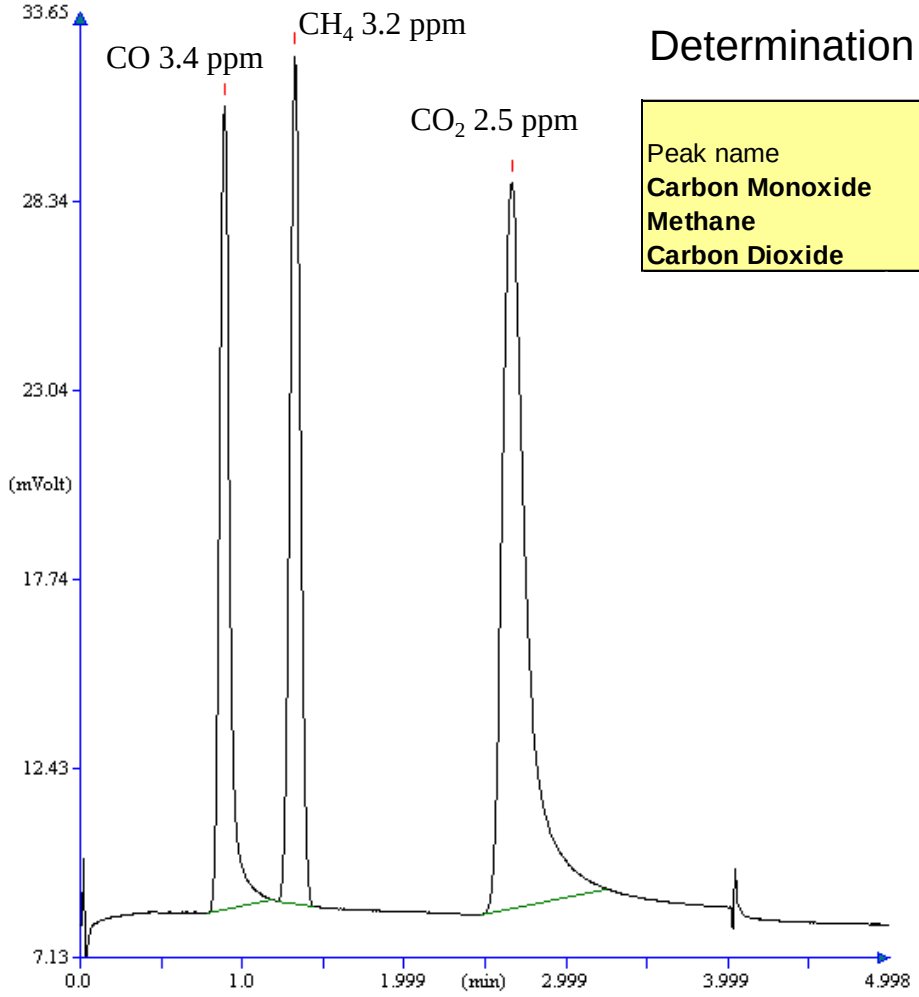


Example of backflush system

Step 4 Ethylene or Propilene are backflushed to vent



Example of backflush system

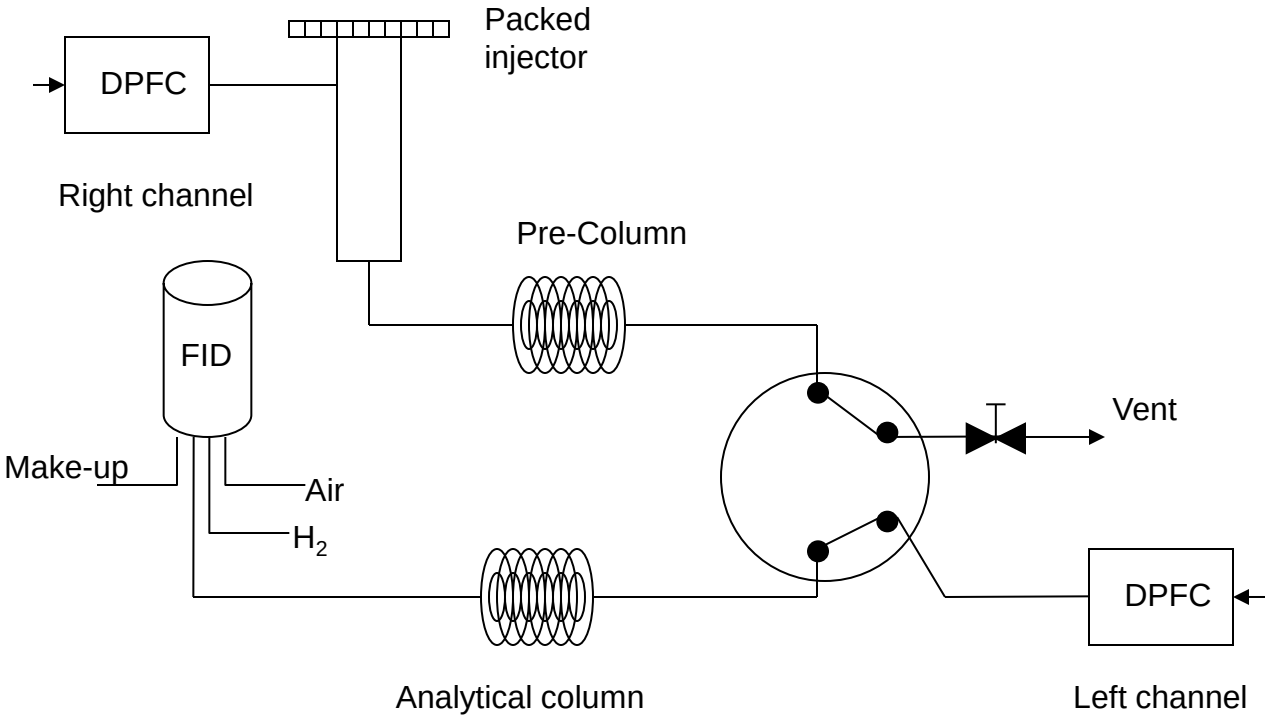


Determination of traces of CO and CO_2

		Repeatability		
Peak name	**RT**	**RSD%**	**Peak area**	**RSD%**
Carbon Monoxide	0.92	0.21	543529	0.60
Methane	1.28	0.18	568752	0.63
Carbon Dioxide	2.76	0.10	672345	0.58

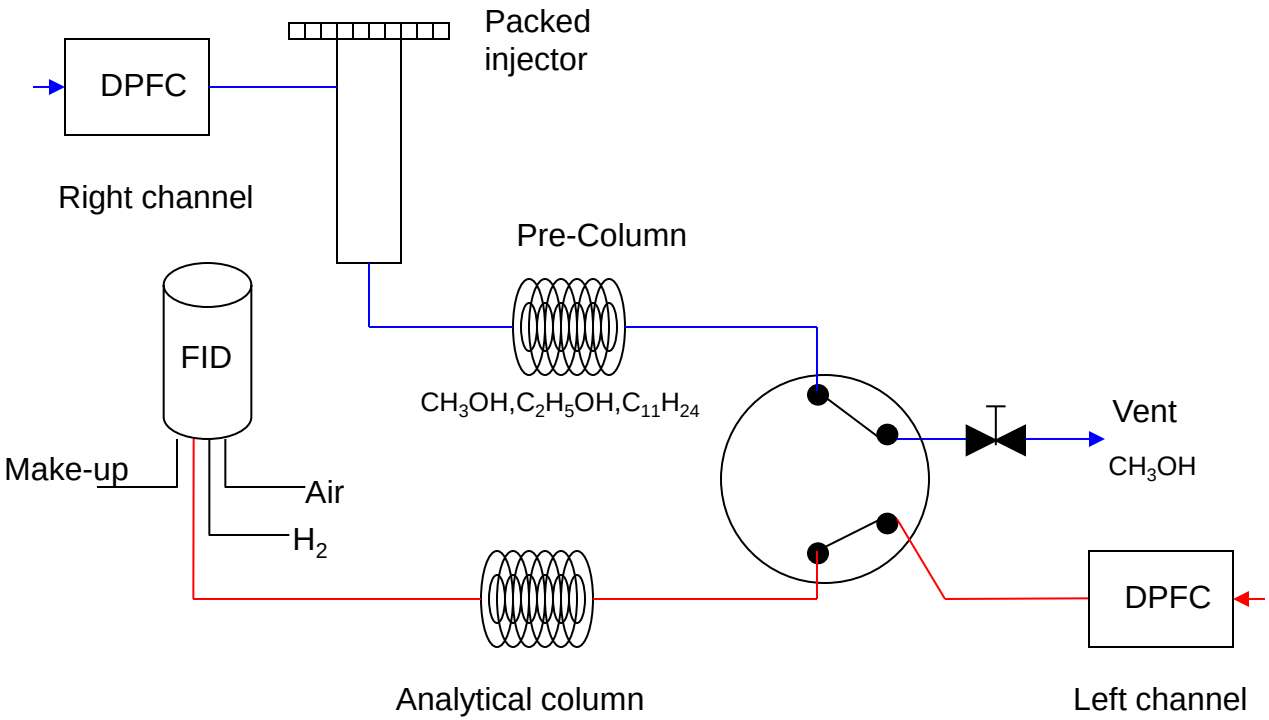
Example of Heart-cutting system

Analysis of Ethanol and Undecane in pure Methanol



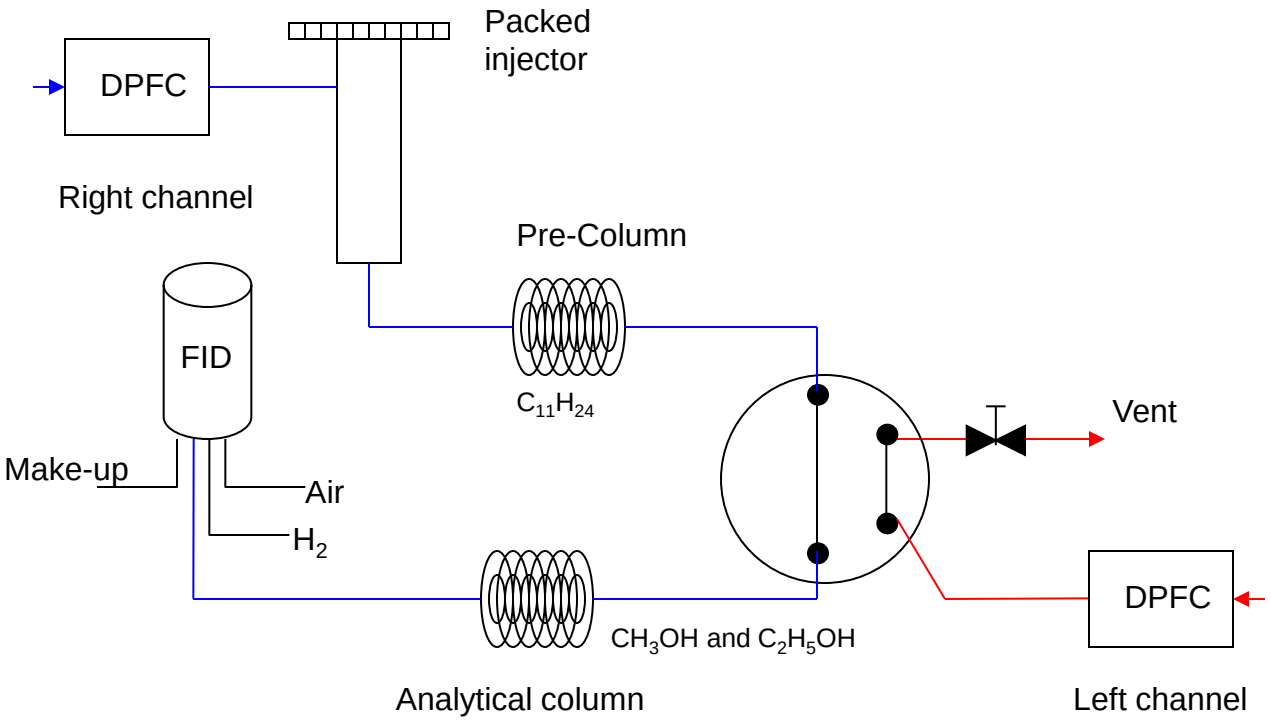
Example of Heart-cutting system

Step 1 Injection of the sample and venting out of methanol excess



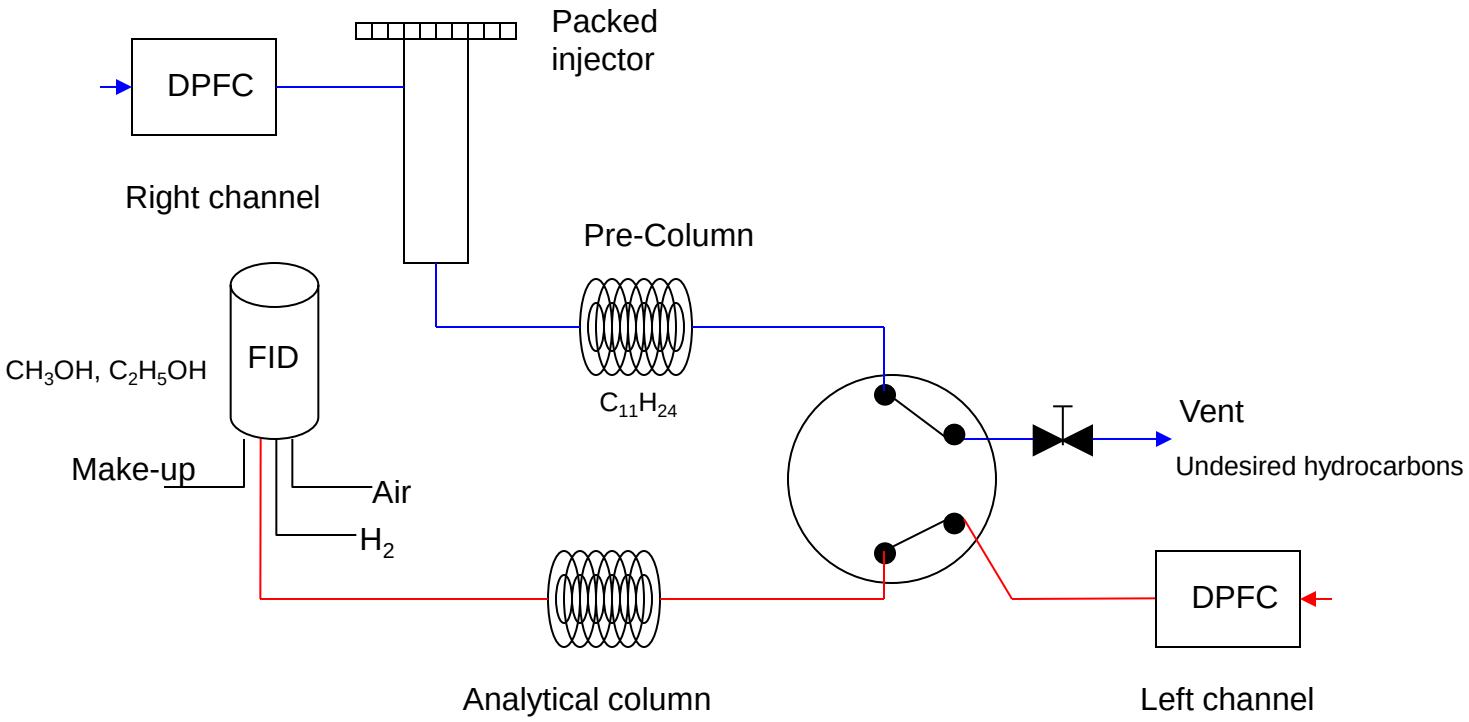
Example of Heart-cutting system

Step 2 Ethanol and methanol elute on to the analytical column
The cutting valve is switched for 50 seconds only



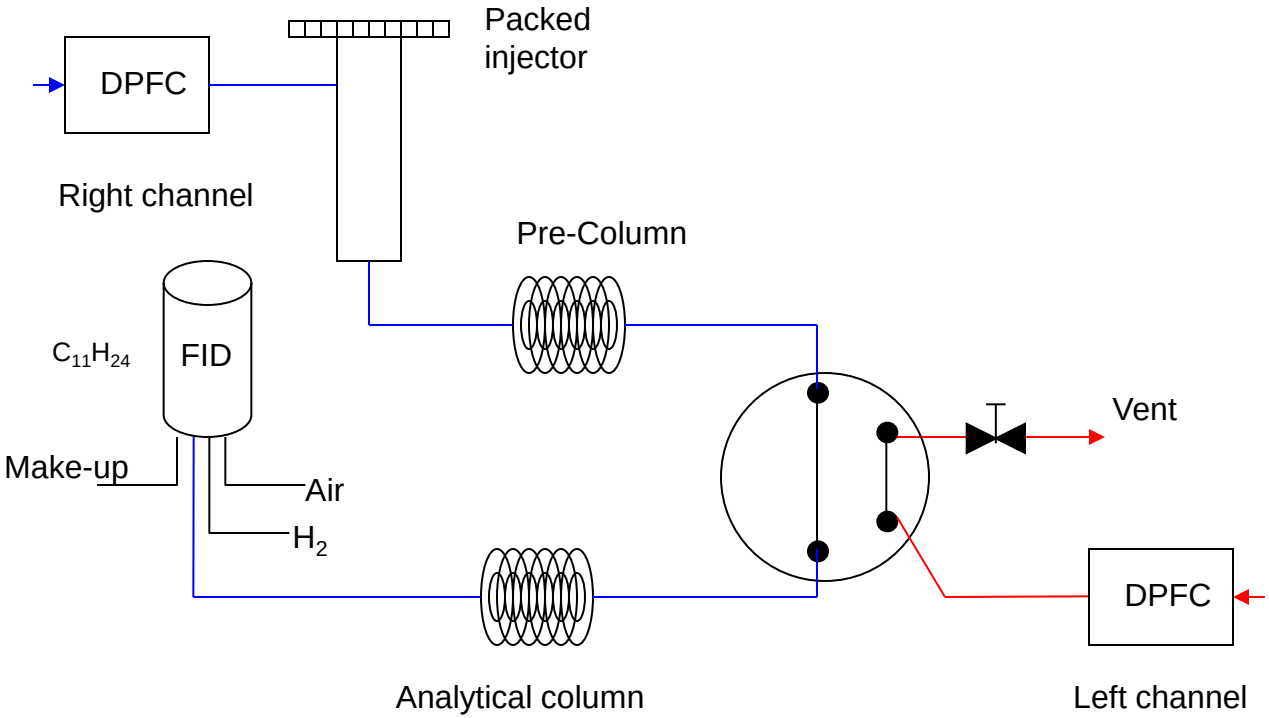
Example of Heart-cutting system

Step 3 Ethanol and methanol to the detector and venting out of hydrocarbons
Temperature programming from 50°C to 200°C

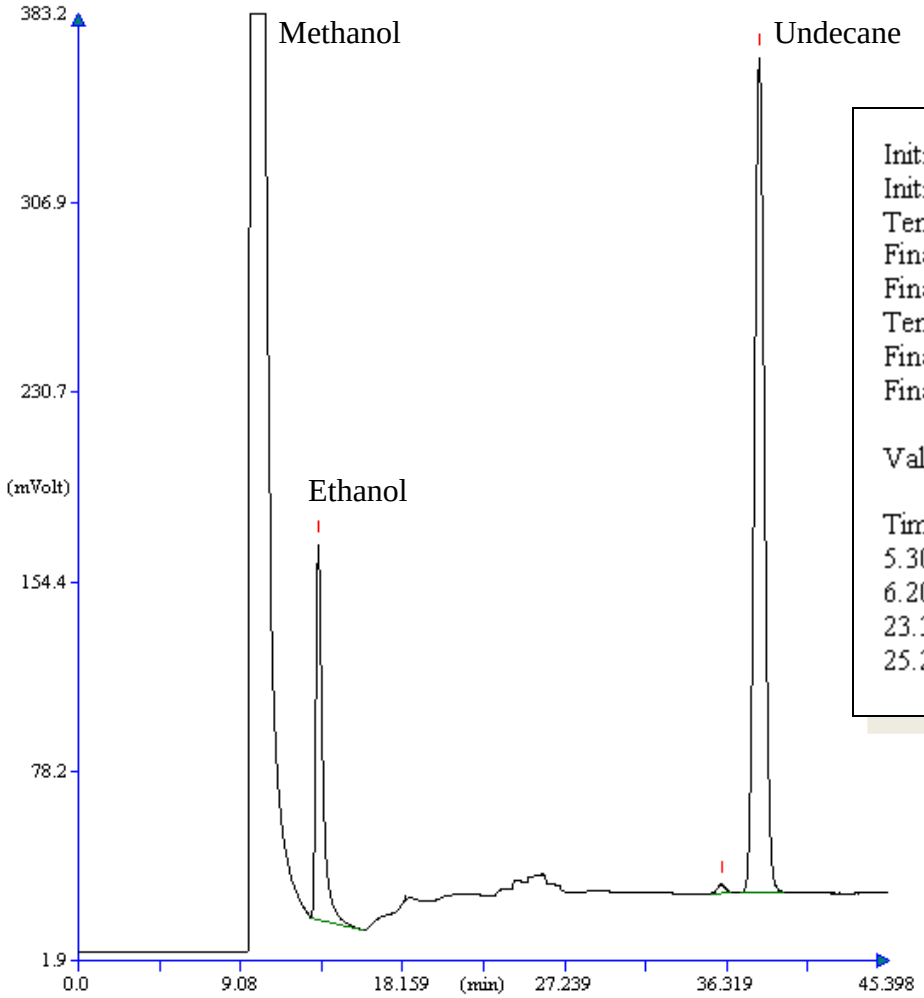


Example of Heart-cutting system

Step 4 Undecane elutes to analytical column and to FID



Example of Heart-cutting system

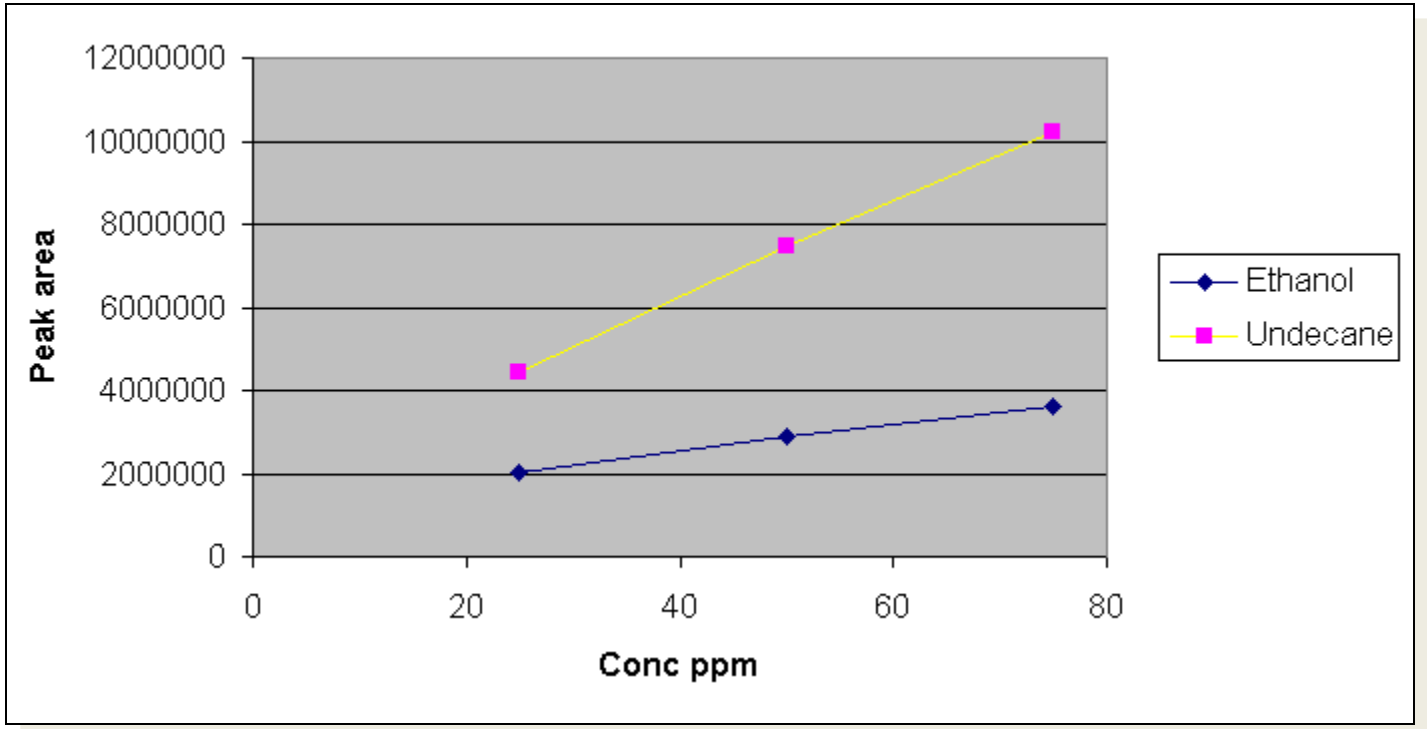


Initial oven temperature	50°C
Initial time	10 min
Temperature Rate # 1	5°C/min
Final temperature # 1	80°C
Final time # 1	0 min
Temperature Rate # 2	50°C/min
Final temperature # 1	200°C
Final time # 2	27 min
Valve oven temperature (Aux 0)	150°C

Time	Item	Setting
5.30	Valve#1	ON
6.20	Valve#1	OFF
23.30	Valve#1	ON
25.20	Valve#1	OFF

Example of Heart-cutting system

Linearity evaluation



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  - Reduction of complex samples onto only a few components of interest
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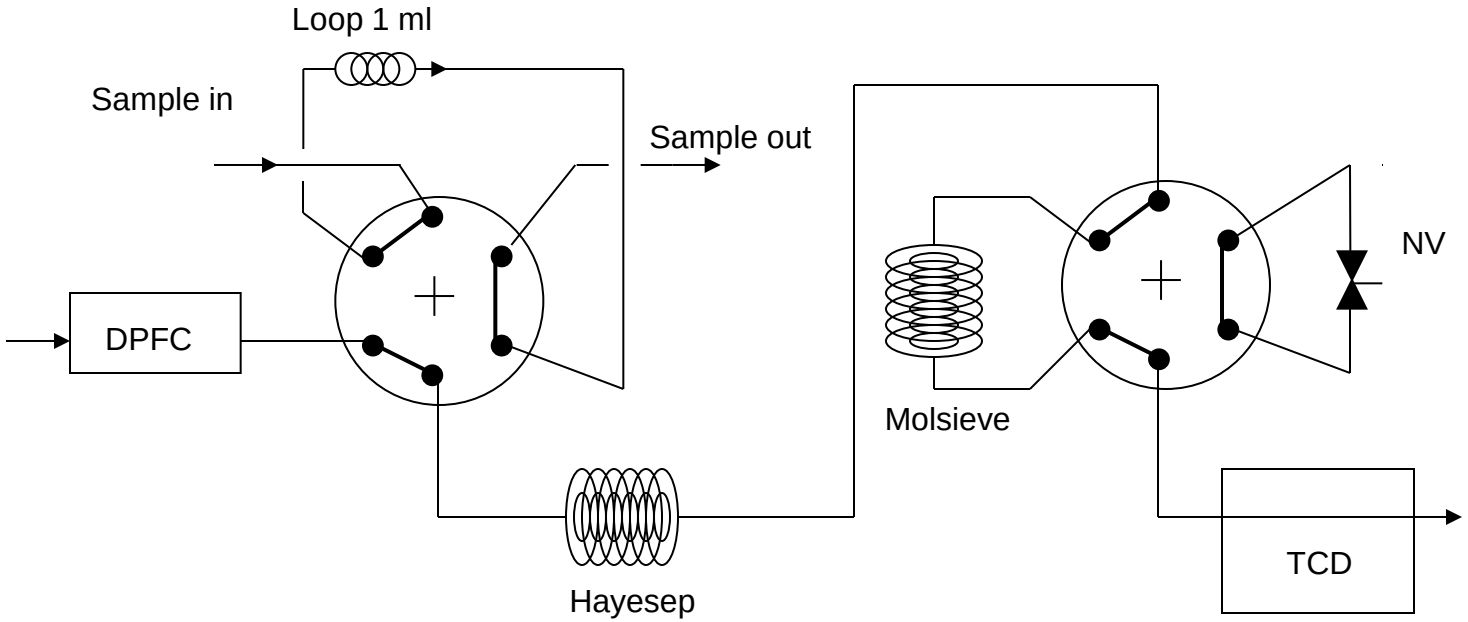
  - Analysis of traces in the tailing of main components (Heart-cutting)
- Stopped Flow mode

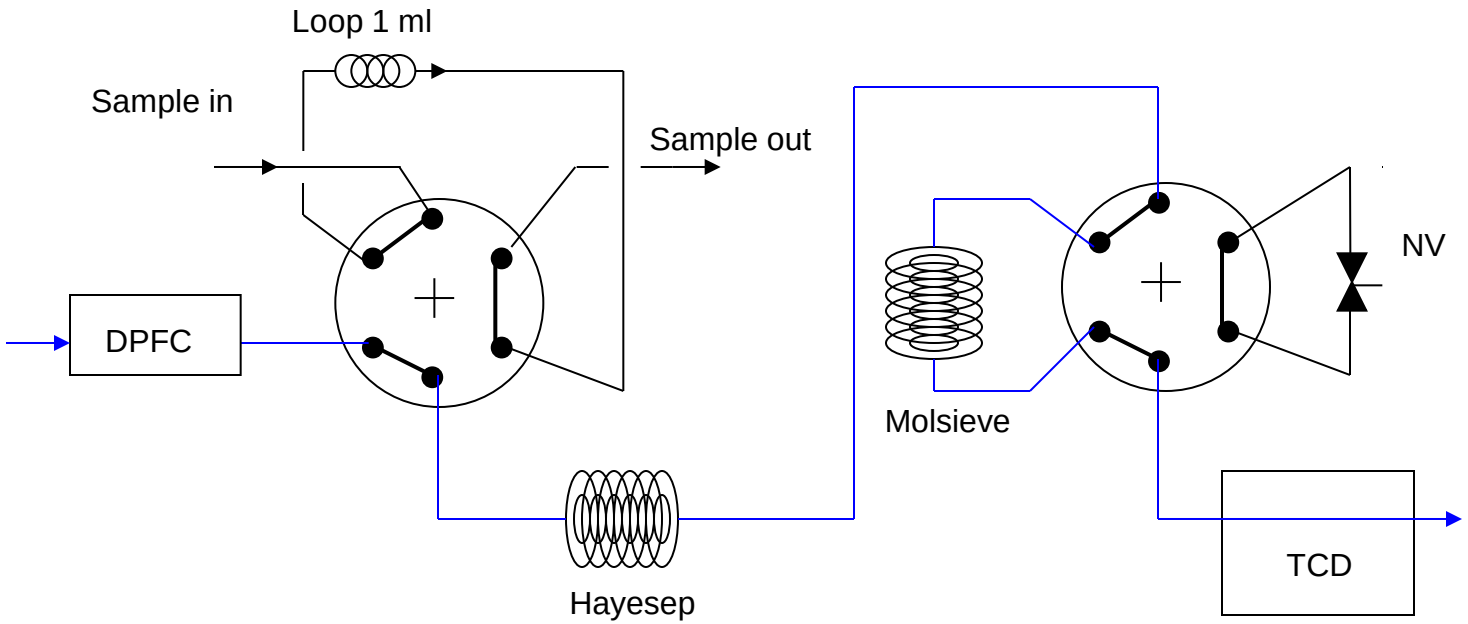
Example of stopped-flow mode

Analysis of flue gases: O_2, N_2, CO, CO_2, CH_4



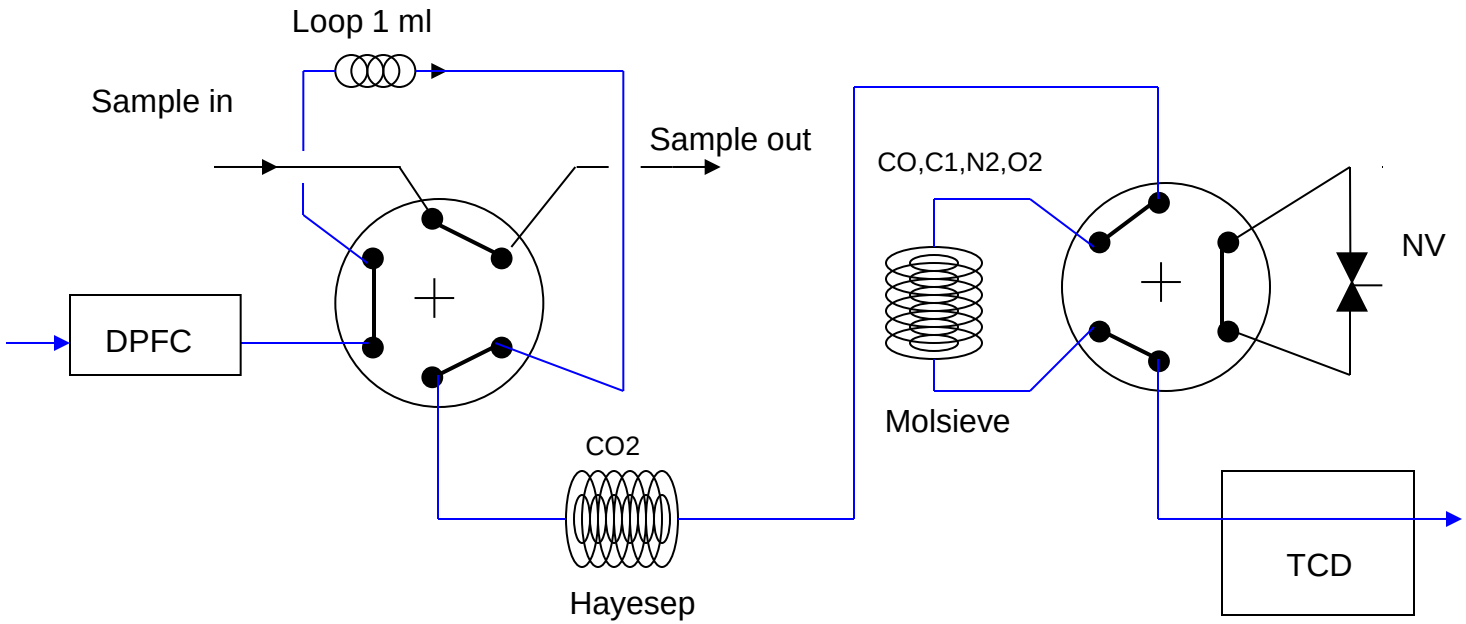
Example of stopped-flow mode

Step 1 Sample Loop filling



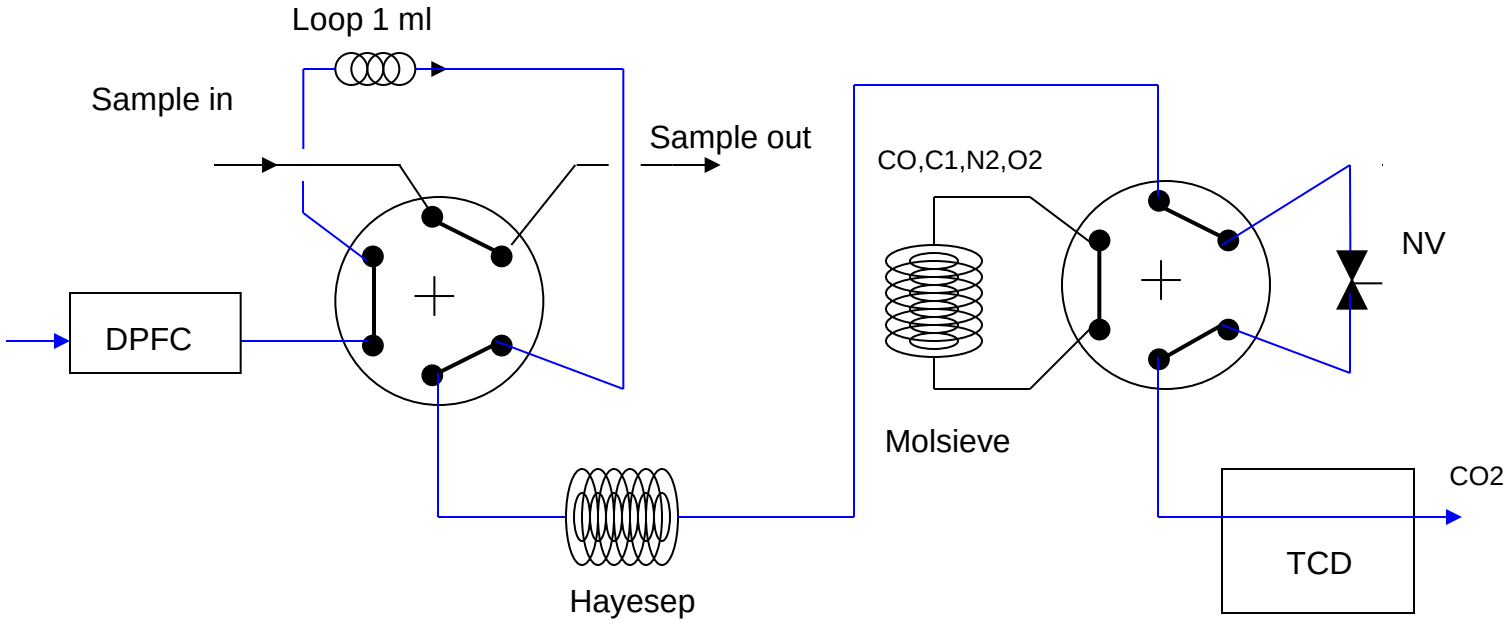
Example of stopped-flow mode

Step 2 Injection and gases trapping



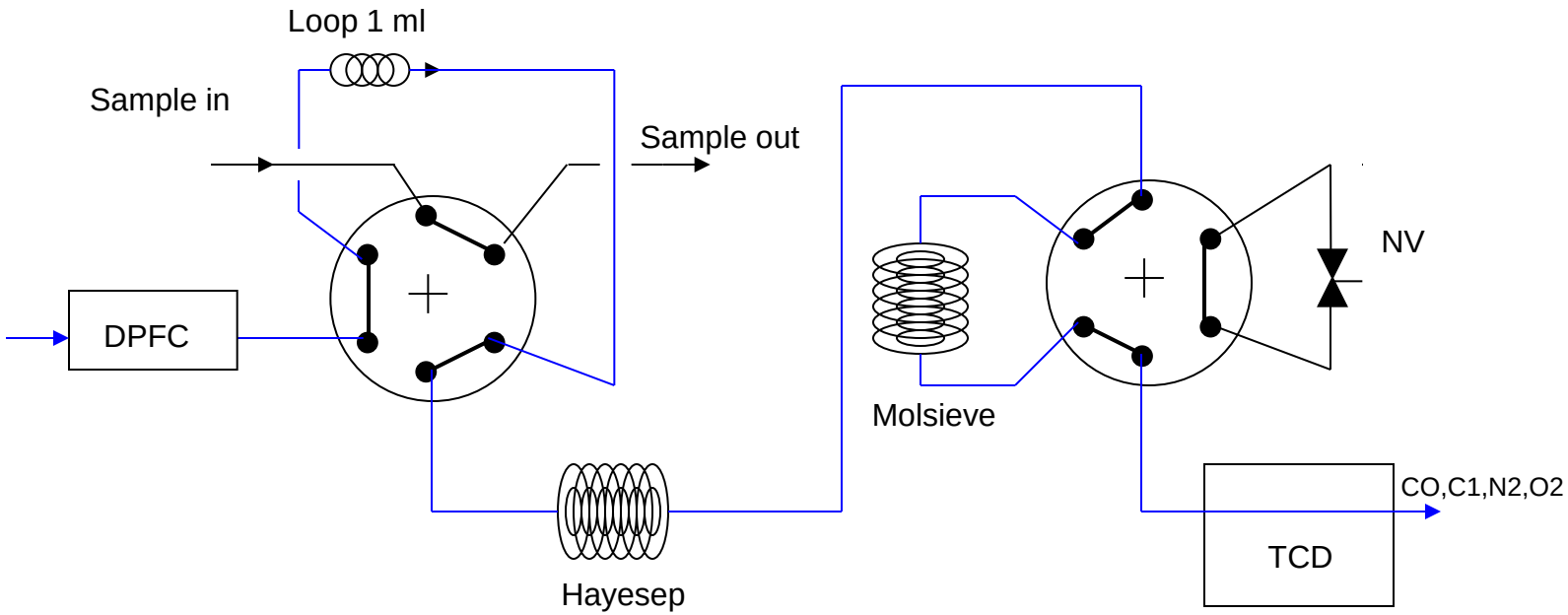
Example of stopped-flow mode

Step 3 Elution of CO_2



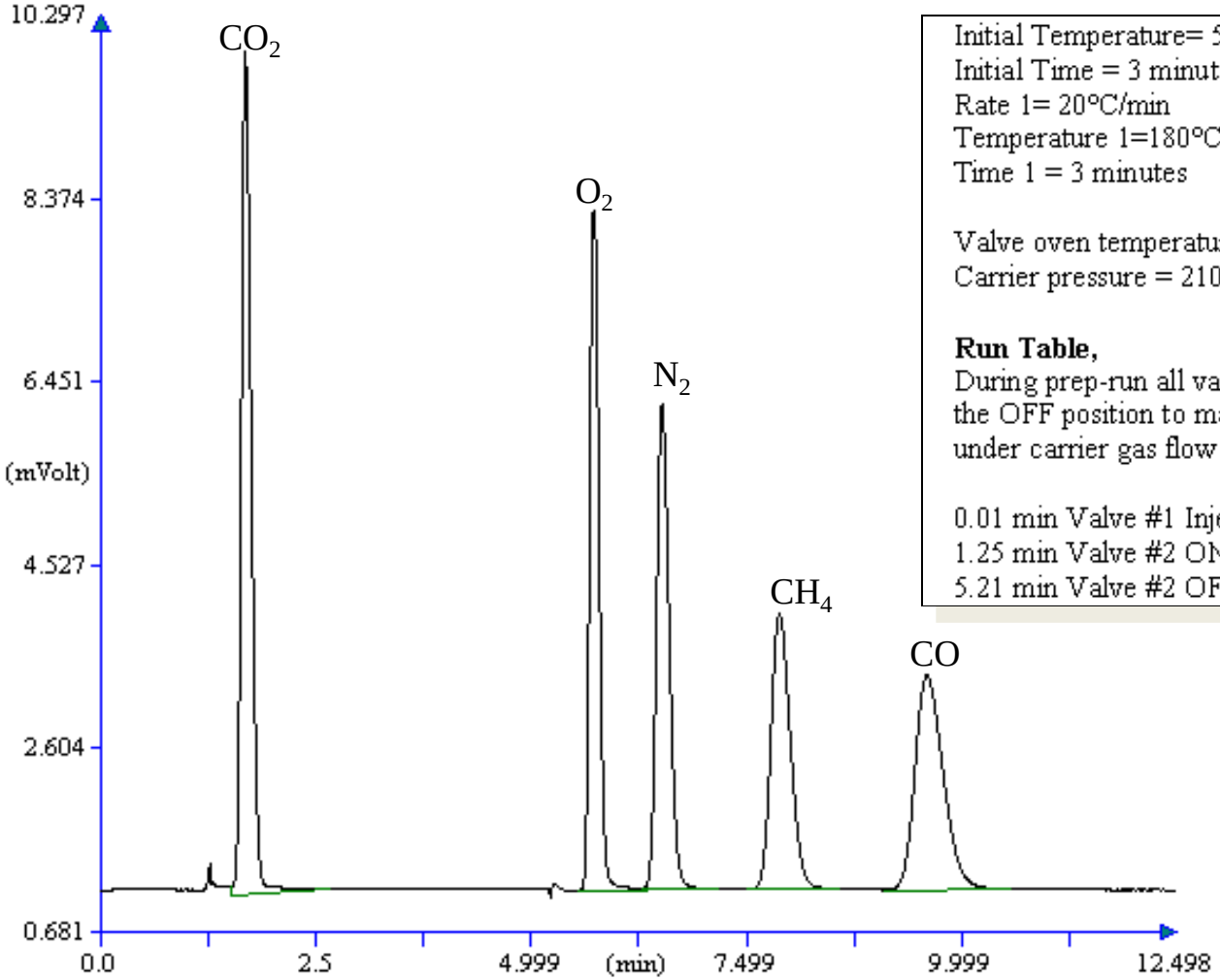
Example of stopped-flow mode

Step 4 O_2, N_2, CO and CH_4 eluted to TCD



Example of stopped-flow mode

Temperatures and other parameters



Initial Temperature= 50°C
Initial Time = 3 minute
Rate 1= 20°C/min
Temperature 1=180°C
Time 1 = 3 minutes

Valve oven temperature = 50°C
Carrier pressure = 210 kPa

Run Table,
During prep-run all valves are kept in the OFF position to maintain all columns under carrier gas flow rate.

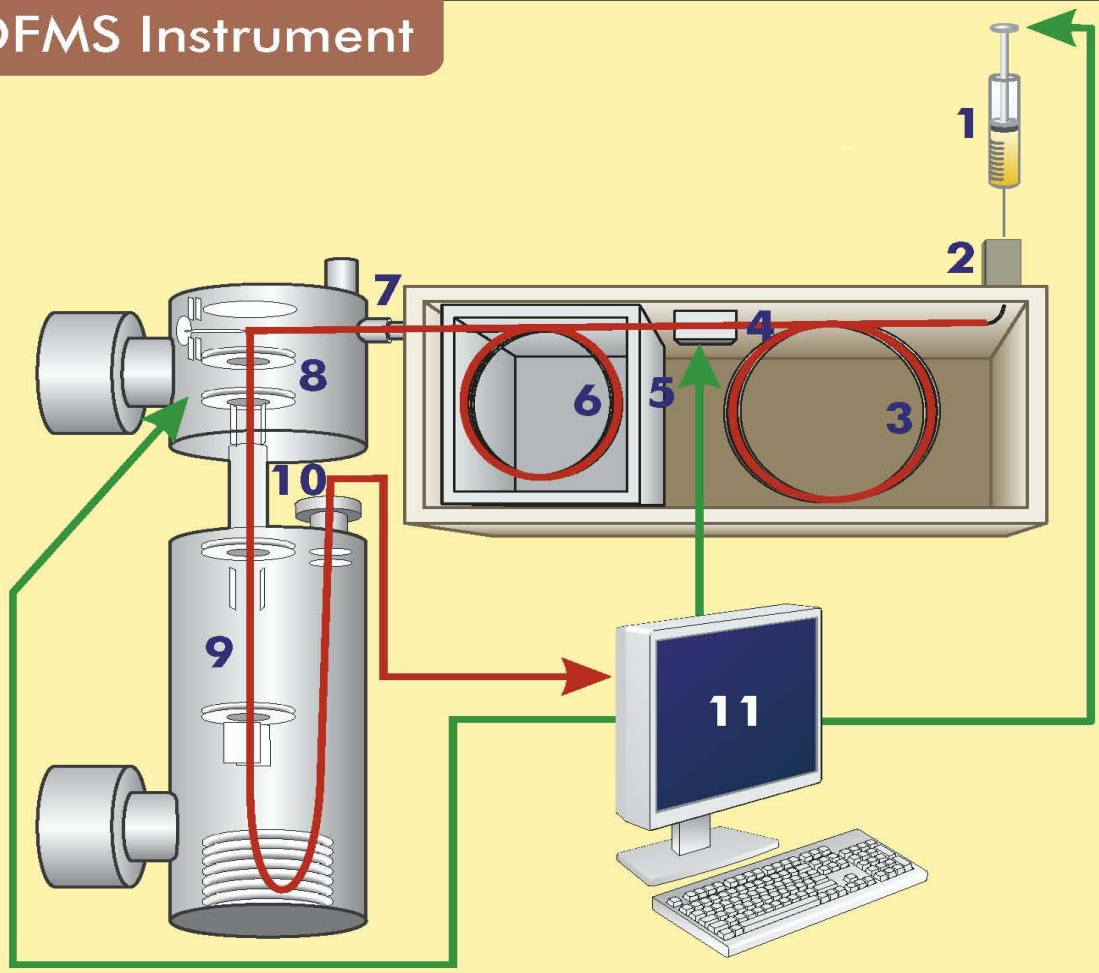
0.01 min Valve #1 Inject for 0.5 minutes
1.25 min Valve #2 ON
5.21 min Valve #2 OFF

Detectors

2D GC-ToFMS

Diagram of GCxGC-TOFMS Instrument

1. Sample
2. Inlet
3. First-dimension column
4. Modulator
5. Secondary oven
6. Second-dimension column
7. Transfer line
8. Ion source
9. Flight tube
10. Time-array detector
11. Instrument control/data processing computer



TRACE GC for Chemical and Petrochemical application

- Hardware available:
  - Valve Oven for Multidimensional GC applications
  - Specific detector (PDD, TCD), accessories (Methanizer, deans switching) and customized software packages (SimDist, Heat value calculation)
  - Special instrument arrangements: three detectors simultaneously installed and operating