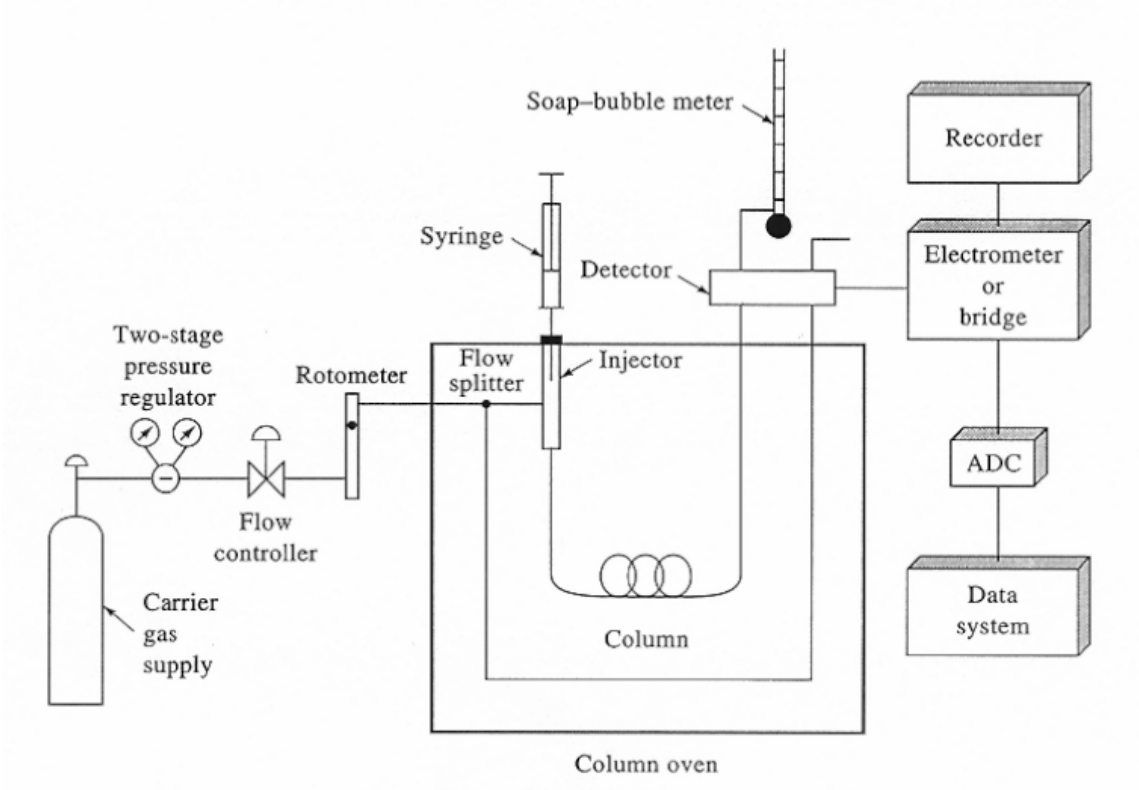
GAS CHROMATOGRAPHY and GC x GC

Overview

- GC involves injection of a volatile sample into an inert stream of flowing gas
- Separation is based on partitioning of analyte between the mobile gas phase and the stationary phase
- Two main types are gas-liquid chromatography (GLC or GC) and gas-solid chromatography (adsorption chromatography); only the former will be discussed

Instrumentation for 1D GC

Basic components are shown below. Note that the flow splitter before the column is used only in cases where the detector measures a change in the gas properties such as thermal conductivity



Carrier gas

- Must be chemically inert to avoid any reactions with analyte, column or detector
- Typical gases include hydrogen, nitrogen or helium, and are delivered using standard pressure regulators with flow rate typically monitored using a soap bubble meter or, more commonly, a digital flow meter
- Typical flow rates are 25 – 150 $mL.min^{-1}$ (packed), 1 – 25 $mL.min^{-1}$ (capillary)
- Choice of gas is often dependent on the type of detector used

Columns Configurations

- Main types of columns are packed and open tubular (capillary)
- Capillary columns are generally more efficient and offer faster separations, and thus are replacing packed columns for most modern applications
- Typical lengths of columns are anywhere from 2 – 50 m (usually coiled), and are generally made from temperature stable materials such as steel, glass or teflon

Detectors

- Many types exist with varying selectivity, sensitivity and versatility
- Most detectors simply report the presence of the analyte in a concentration dependent manner but do not provide sufficient information to positively identify the species
- In some cases, separate instruments (MS or FTIR) can be used to provide structural information on analyte leading to identification in-line with separation

Columns and Stationary Phases for GC

Open Tubular (Capillary) Columns

- These are formed from thin capillaries (75 – 300 μm i.d.) that contain a liquid film or a chemically bonded phase which acts as the stationary phase. Two types are:
    - *Wall-coated open tubular (WCOT)* ⇒ fused silica capillary is directly coated with film leading to very fast and efficient separations (up to 300,000 plates)
    - *Support-coated open tubular (SCOT)* ⇒ capillary is coated with ~30 μm of a porous support material to allow a higher loading of stationary phase and thus higher column capacity
- In each case, narrower columns lead to higher resolution but increase the need for very accurate and reproducible injection (generally use a sample splitter), and require better detector sensitivity owing to the smaller amounts of analyte used
- Recently, megabore columns (530 μm i.d.) have appeared, which allow sample volumes similar to those of packed columns but better performance

TABLE 27-1 Properties and Characteristics of Typical Gas-Chromatographic Columns

	Type of Column*			
	FSOT	WCOT	SCOT	Packed
Length, m	10–100	10–100	10–100	1–6
Inside diameter, mm	0.1–0.53	0.25–0.75	0.5	2–4
Efficiency, plates/m	2000–4000	1000–4000	600–1200	500–1000
Total plates	$(20–400) \times 10^3$	$(10–400) \times 10^3$	$(6–120) \times 10^3$	$(1–10) \times 10^3$
Sample size, ng	10–75	10–1000	10–1000	$10–10^6$
Relative back pressure	Low	Low	Low	High
Relative speed	Fast	Fast	Fast	Slow
Chemical inertness	Best →			Poorest
Flexible?	Yes	No	No	No

*FSOT: Fused-silica, open tubular column.
WCOT: Wall-coated, open tubular column.
SCOT: Support-coated open tubular column.

The Stationary Phase

Stationary phases should show all of the following properties

- Low volatility (bp of liquid should be 100 °C greater than operating temperature of column
- Thermal stability (i.e., no pyrolysis at high temperatures)
- Chemical inertness
- Solvent characteristics that allow k' and α to fall into useful ranges

Ideal stationary phases will show a range of different distribution constants for different analytes, but will not display very high or very low values for K as these will lead to long separation times or poor separation efficiency, respectively

Primary rule of thumb is "like dissolved like" $\Rightarrow$ non-polar analytes will partition strongly into non-polar stationary phases, polar analytes partition into polar phases

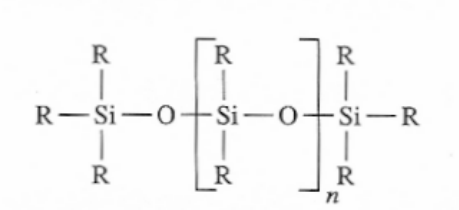
Typical stationary phases are shown below:

TABLE 27-2 Some Common Stationary Phases for Gas-Liquid Chromatography

Stationary Phase	Common Trade Name	Maximum Temperature, °C	Common Applications
Polydimethyl siloxane	OV-1, SE-30	350	General-purpose nonpolar phase; hydrocarbons; polynuclear aromatics; drugs; steroids; PCBs
Poly(phenylmethyldimethyl) siloxane (10% phenyl)	OV-3, SE-52	350	Fatty acid methyl esters; alkaloids; drugs; halogenated compounds
Poly(phenylmethyl) siloxane (50% phenyl)	OV-17	250	Drugs; steroids; pesticides; glycols
Poly(trifluoropropyldimethyl) siloxane	OV-210	200	Chlorinated aromatics; nitroaromatics; alkyl-substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acids; alcohols; ethers; essential oils; glycols
Poly(dicyanoallyldimethyl) siloxane	OV-275	240	Polyunsaturated fatty acids; rosin acids; free acids; alcohols

Typical Stationary Phases

- From above table, polarity of stationary phase increases moving down the table
- Most of the stationary phases are polydimetysiloxanes with the general structure:



First entry in table has R = CH_3 ⇒ very hydrophobic

Other entries in table have some R groups replaced with phenyl (C_6H_5, 10-50%), cyanopropyl (C_3H_6CN) or trifluoropropyl ($C_3H_6CF_3$) to increase the polarity of the coating

The fifth entry is polyethylene glycol, which is used primarily for separating polar compounds ⇒ $HO—CH_2—CH_2—(O—CH_2—CH_2)_n—OH$

Typical separations are shown in the Figure on the right ⇒

Panels (a) – (f) correspond to the stationary phases shown in the previous table

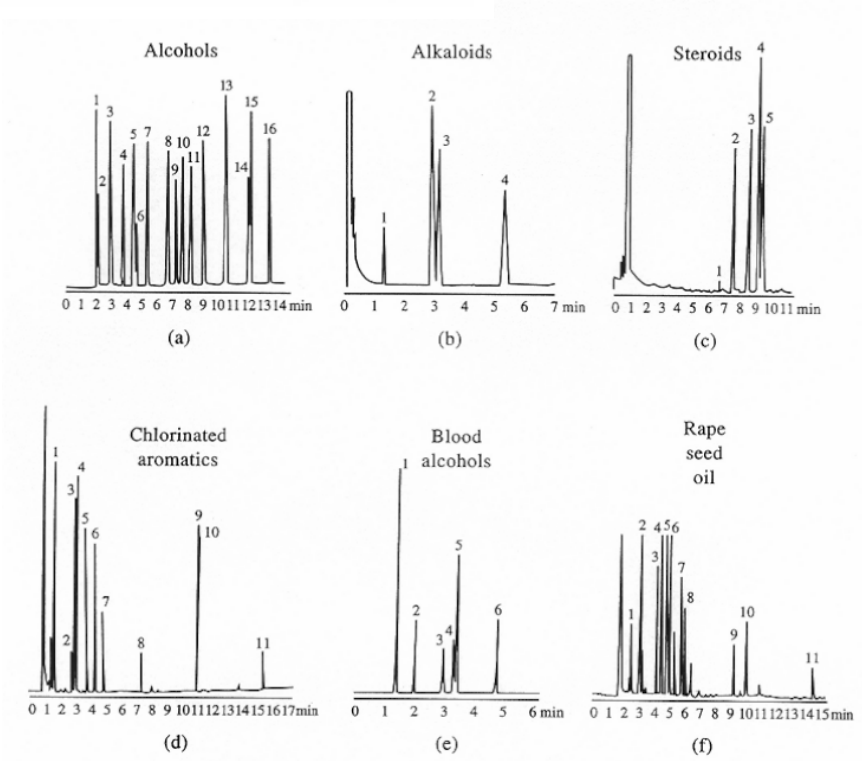


Figure 27-11 Typical chromatograms from open tubular columns coated with (a) polydimethyl siloxane; (b) 5 (phenylmethyldimethyl) siloxane; (c) 50 (phenylmethyldimethyl) siloxane; (d) 50% poly(trifluoropropyl-dimethyl) siloxane; (e) polyethylene glycol; (f) 50% poly(cyanopropyl-dimethyl) siloxane. *(Courtesy of J & W Scientific.)*

Applications of 1D GC

- Mainly used for Volatile Organic Compounds (VOCs)
- Typical samples include:
    - Petrochemical samples (heavy and light oils
    - Biological Oil samples (fish oils, vegetable oils)
    - Essential Oils (flavor and fragrance volatiles)
    - Pesticides
    - Surface-water contaminants
    - Air contaminants

Notes: In many cases, 1D GC is not sufficiently powerful to separate all of the components in these complex samples, even with the higher resolution of the typical GC column – need comprehensive GCxGC for these tasks.

Table 1. Comparison of the relative speed of analysis of GC, fast-GC, and GC × GC in terms of resolvable peak capacity/unit time

Example	Technique	Peak capacity	Analysis time (s)	Analysis speed
1	Conventional GC	350	3000	0.12 peaks/s
2	Fast-GC	350	300	1.2 peaks/s
3	GC × GC	3500	3000	1.2 peaks/s

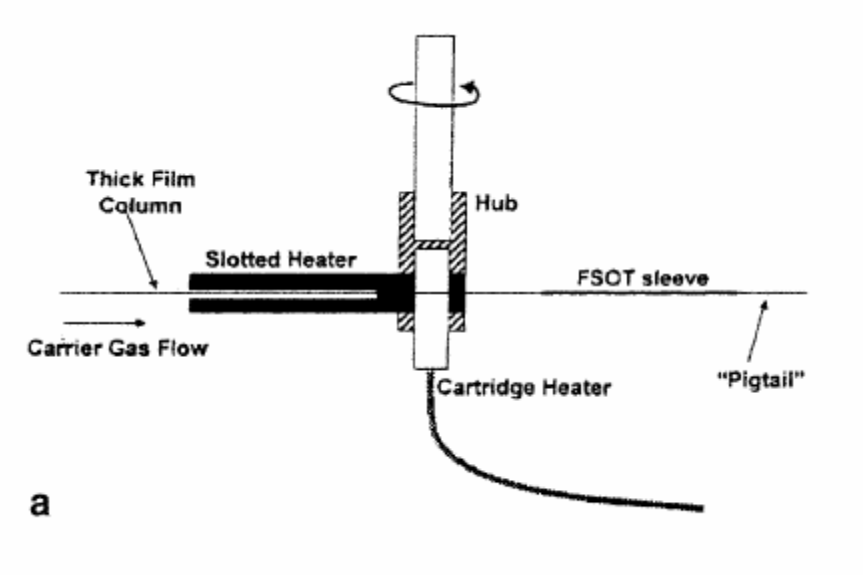
GCxGC Analysis

- As with 2D LC, the goal is to couple 2 orthogonal columns together to effect a much higher peak capacity – better separation power
- Similar to 2D LC, typically use a long first dimension column with relatively slow flowrates coupled to a short second dimension column with fast flow rates
- ***Unlike*** LC, it is not common to use multiport valves to switch analyte from the first to the second column – need alternative coupling methods

GCxGC Modulation Methods

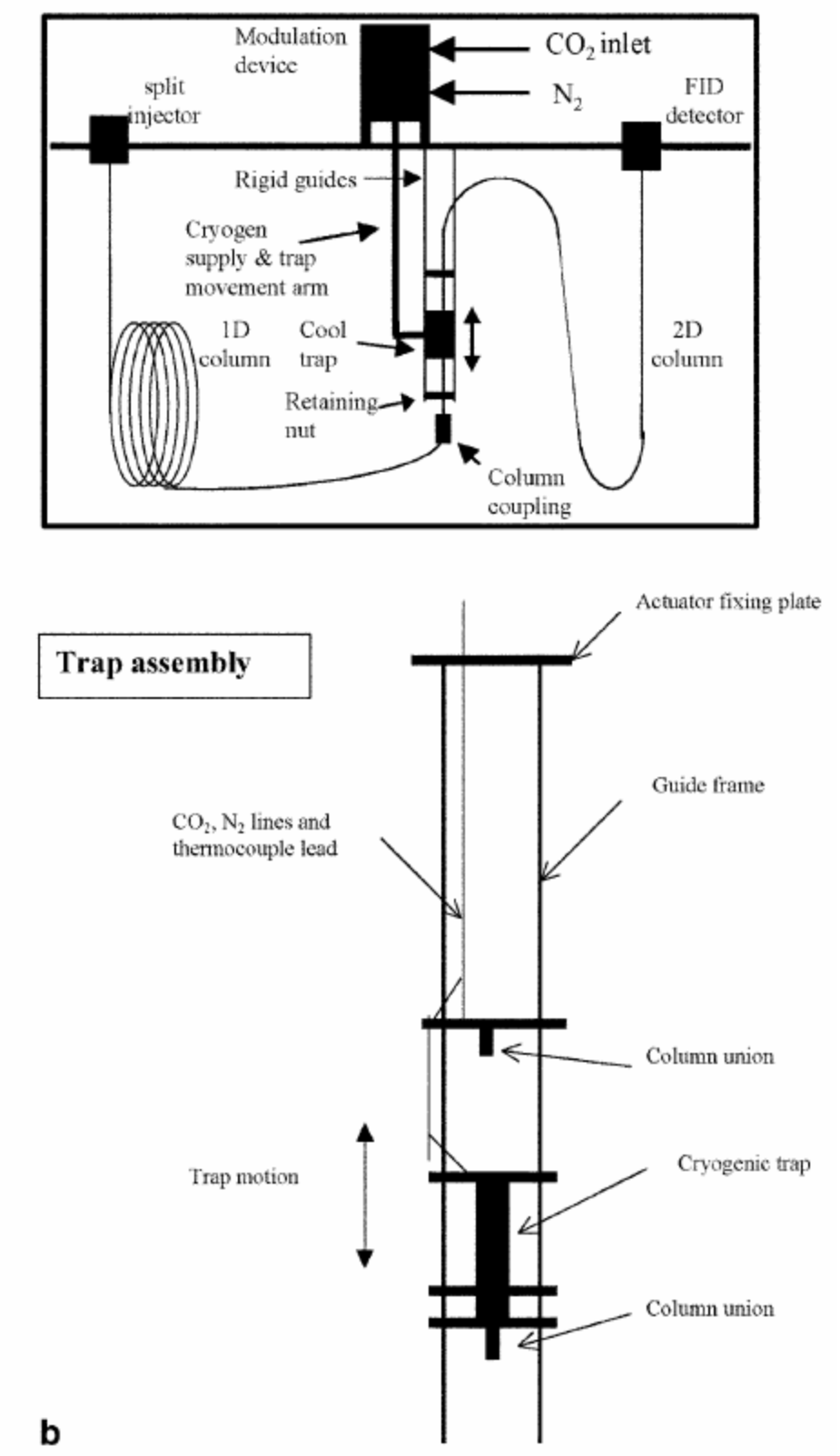
- Most methods involve a thermal modulation step to trap and release volatile compounds, often in conjunction with a short, thick film coated capillary to enhance capture capacity
- Typical examples include:
    - Slotted heater-thermal sweeper modulation
    - Longitudinal Modulation Cryofocussing System (LMCS)
    - Jet-cooled thermal modulation
    - Diaphragm Valve modulation
    - Differential Flow modulation

Slotted Heater – Thermal Sweeper



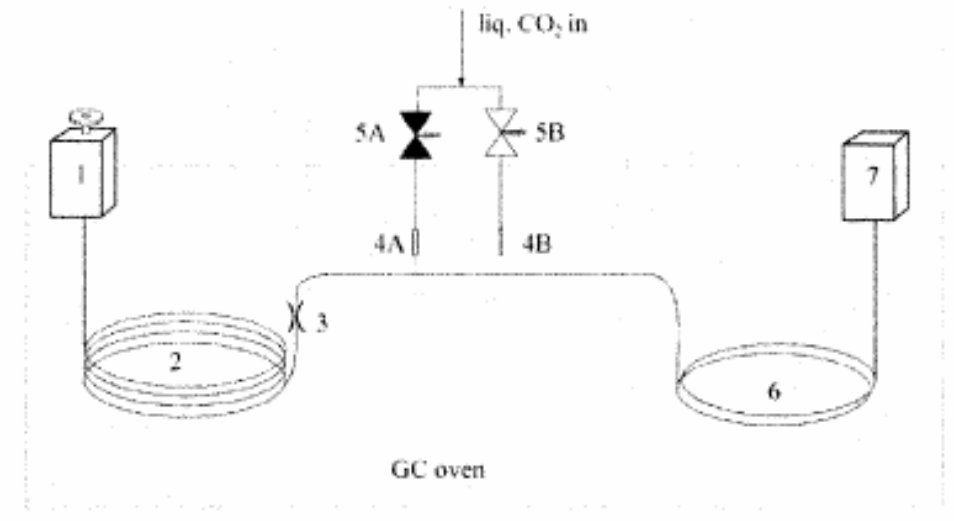
- Trap output of column 1 on a thick film column
- Resistively heat trap to release volatile compounds into column 2
- Collect for ~5s on trap and then rapidly re-inject onto second column (100 ms)
- Can be problematic for low boiling point compounds
- Not possible to modulate very rapidly due to need for sufficient collection time on trap to generate good sensitivity
- Some issues with reliability

Longitudinal Modulation Cryofocussing System (LMCS)



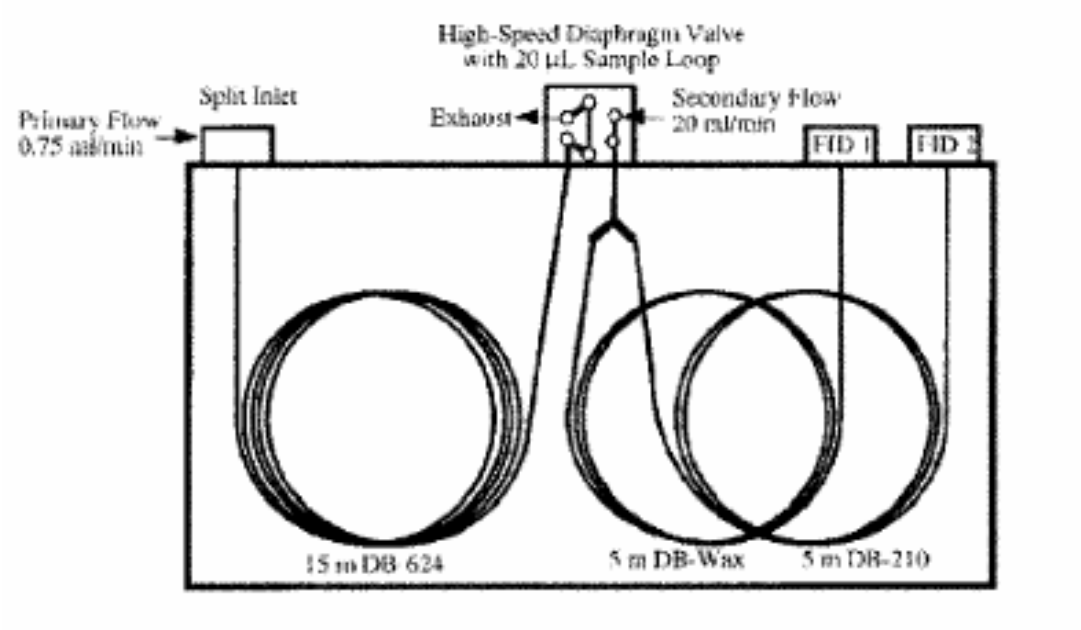
- Use a trap that has a stream of CO_2 impinging on it to cool the output of the first column via the Joule Thompson effect.
- Mechanically modulate the trap between two column connectors to transport output from column 1 onto column 2.
- When trap reaches column 2, it is now away from the cooling gas and will heat up due to the high temperature of the GC oven – releases contents to column 2
- Modulation frequency can be adjusted from 2 – 9 sec
- Enables all solutes from first column to reach second column
- Can be operated at high oven temperatures
- Good for high boiling analytes, but can have trouble with more volatile analytes

Pulsed Jet Modulator



- Modulation now used pulse of cooled gas rather than mechanical switching
- Very fast method – can get 2D GC peak widths of 30 ms

Diaphragm Valve Modulation

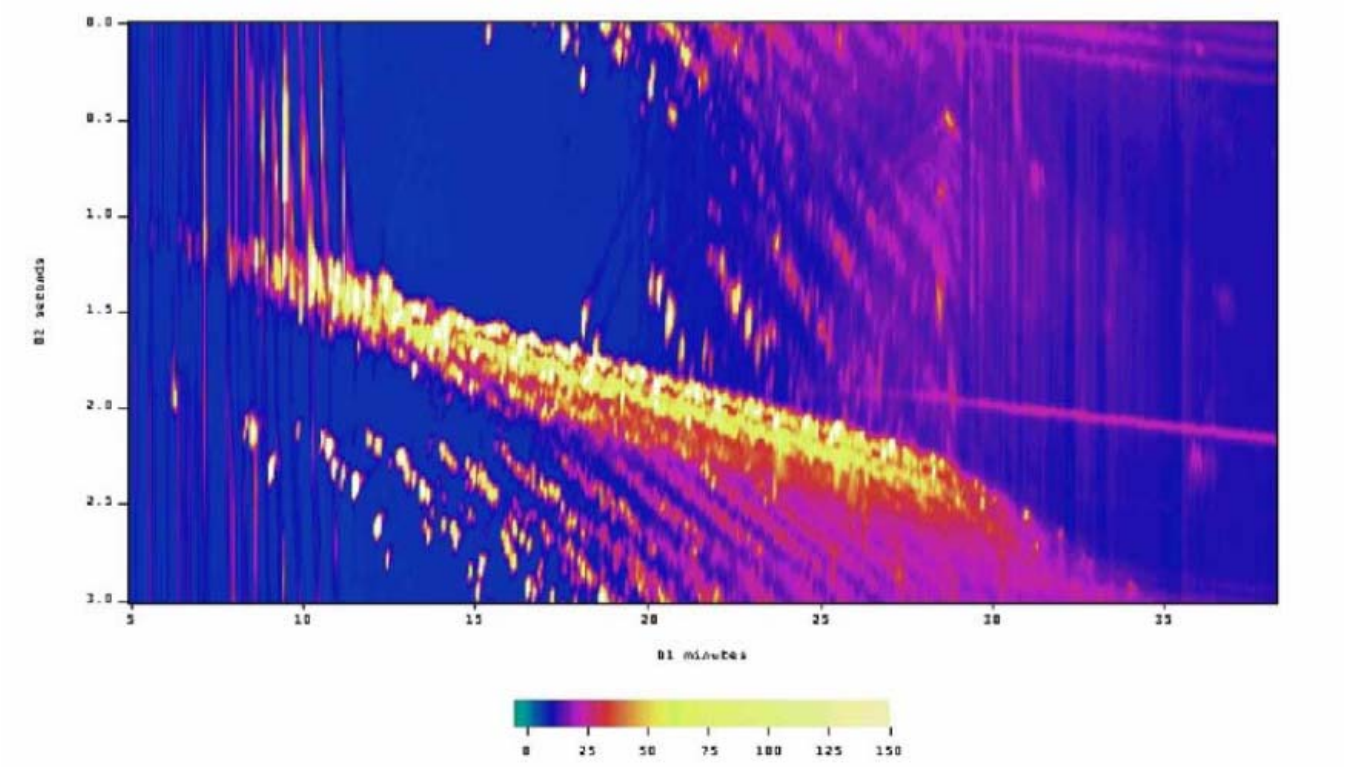


- Based on mechanical switching between two columns using a valve rather than thermal regulation
- Collect for 80% of the time, reinject for 20% of the time
- Use column flow 20x higher in second dimension to allow time to recondition column
- Can also couple to two second dimension columns to obtain greater orthogonality
- Can be operated very rapidly (<1 s per switch), thus possible to get better resolution on first dimension
- Issue with temperature – can't operate above 200 °C, thus limited to fairly volatile compounds

Applications

1) Petroleomics

- LMCS was used to examine “wash oil”, which is similar to the diesel fraction of petroleum
- Note that the separation in the second dimension is not perfectly orthoganol, giving the “diagonal” stripe. Normally, first column separates on basis of boiling point, second on basis of polarity or H-bonding. However, since boiling point has some dependence on H-bonding, can lose orthoganality
- Note “wraparound” effect beyond about 10 min – this indicates that second dimension separation is too slow relative to modulation cycle time.



2) Separation of Essential Oils

- Figure below shows power of GC x GC analysis compared to 1 D GC.
- Chromatograph on top is the 1D GC trace of Vetiver essential oil – note that in may cases the peaks are poorly resolved
- Contour plot shows the much better resolving power obtained when using comprehensive GC analysis