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Theory and Key Principles Series

Gas Chromatography (GC)

Session 1 – Introduction to Gas Chromatography

Theory & Key Principles Series – GC

- **Introduction to Gas Chromatography**
- GC Columns
- The Split/Splitless Inlet
- Advanced Liquid Injection Techniques
- Alternatives to Liquid Injection
- Choices of Detectors for GC
- Processing GC Data
- Maintenance & Troubleshooting

GCMS series to follow!

Introduction to gas chromatography

In this presentation:

- Welcome and introduction
- Principles of gas chromatography
- Uses of gas chromatography
- Hardware overview
- Carrier gas

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Principles of Gas Chromatography

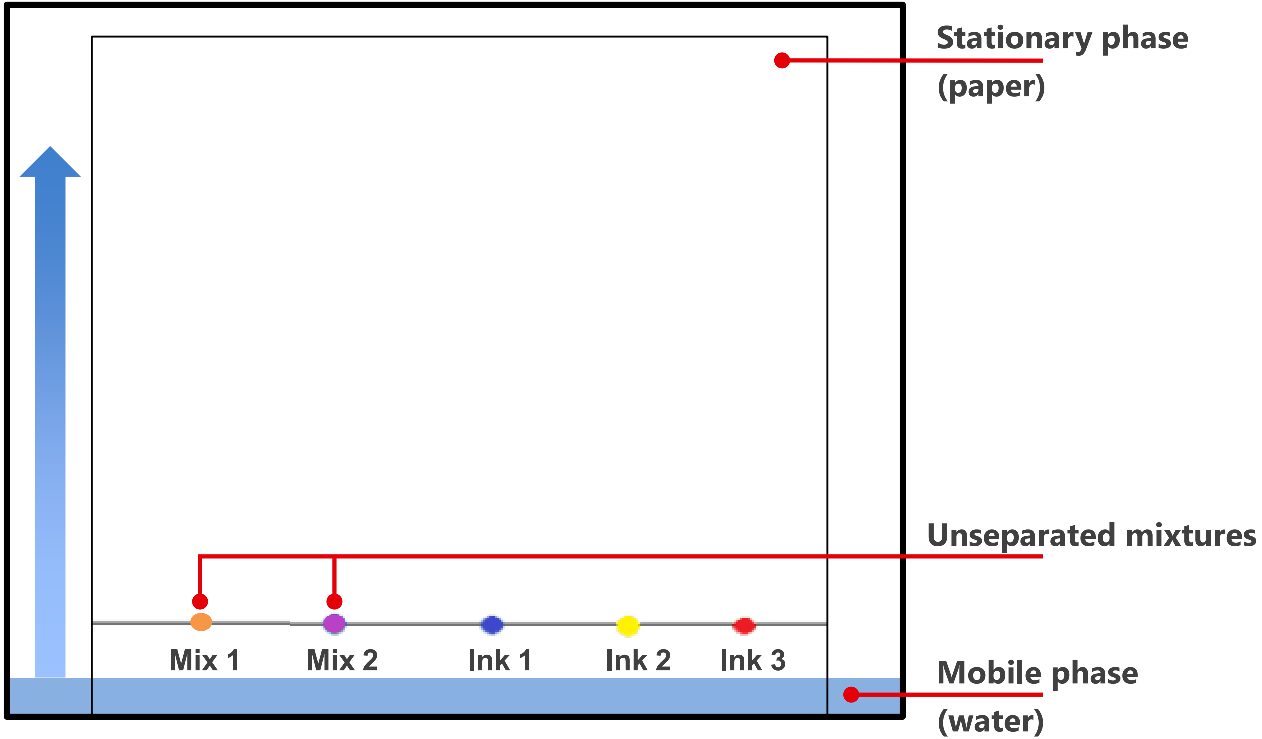
What is chromatography?

Chromatography is a technique for ***separating a mixture of substances****.*

It has a ***mobile phase****, which the sample is dissolved in, or transported with, and a* ***stationary phase*** *that the sample travels on or through.*

The different substances in the mixture have ***different affinities for the stationary phase****, so spend more or less time adsorbed to its surface.*

Paper Chromatography



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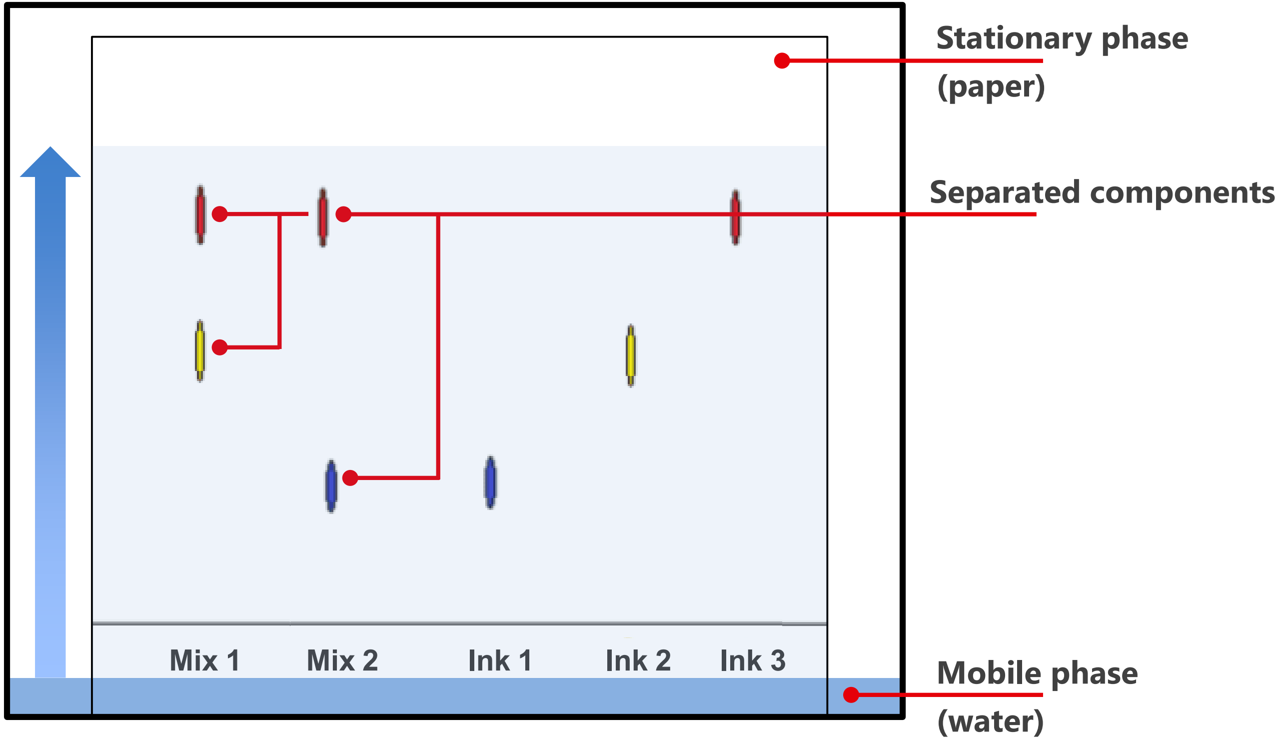


Examples of common chromatographic techniques

- **Paper chromatography (previous slide)**
- **Thin layer chromatography (TLC)**

  Good for simple mixtures

  - A thin film of material (silica) fixed to a surface - STATIONARY PHASE
  - A liquid (solvent) that flows up the dry adsorbent - MOBILE PHASE

  - As the mobile phase rises, it transports the sample. This moves with the mobile phase and separates out, based on the interaction with the silica stationary phase.

  - In optimal chromatography, these fractions would consist of single components from the sample mixture!

- **Liquid chromatography (LC)**
- **Ion chromatography (IC)**
- **Gas chromatography (GC)**

Shimadzu offers equipment for all these techniques

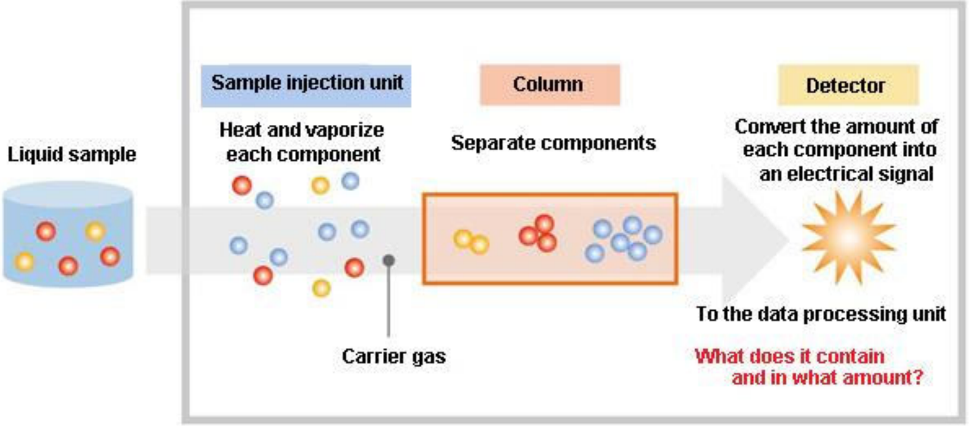
What is gas chromatography (GC)?

Gas chromatography is a technique…
performed using a **Gas Chromatograph**…
by a **Chromatographer**…
to generate a **Chromatogram.**

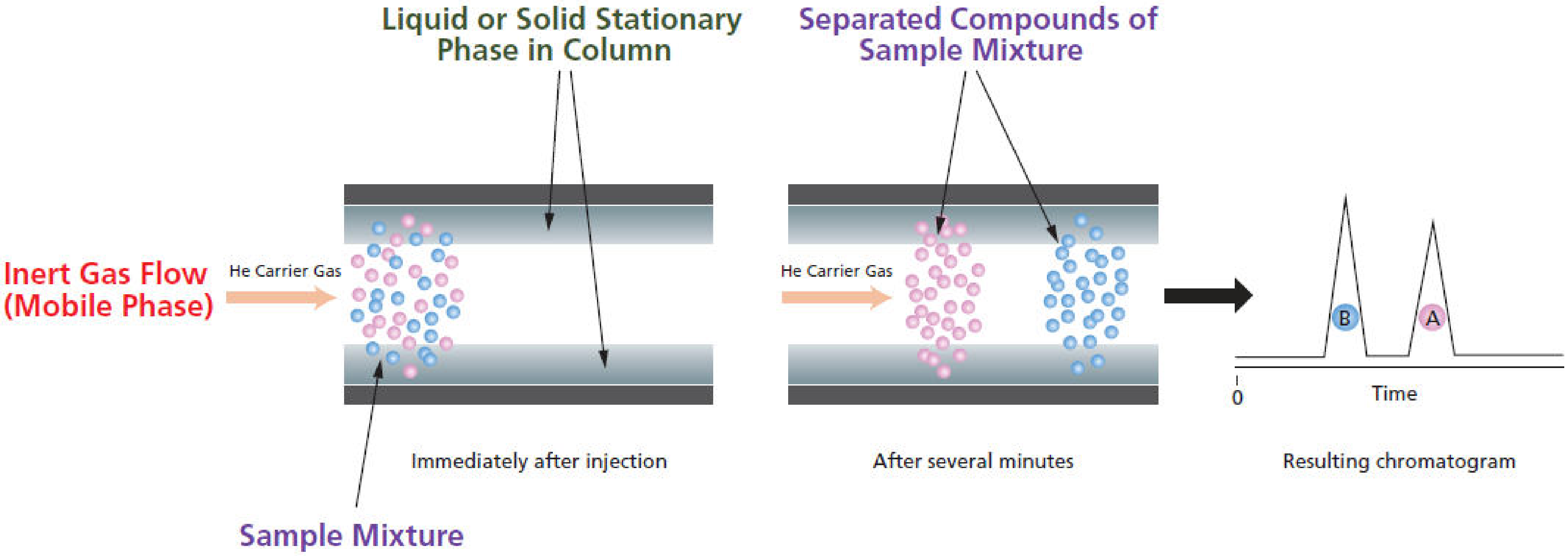
In gas chromatography:

A viscous liquid or solid is fixed to a supporting, hollow tube (column)	- STATIONARY PHASE
A carrier gas flows through the tube, carrying the mixture	- MOBILE PHASE

- In a simple system:



What is gas chromatography?



Liquid or Solid Stationary Phase in Column

Separated Compounds of Sample Mixture

Inert Gas Flow (Mobile Phase)

He Carrier Gas

He Carrier Gas

Immediately after injection

After several minutes

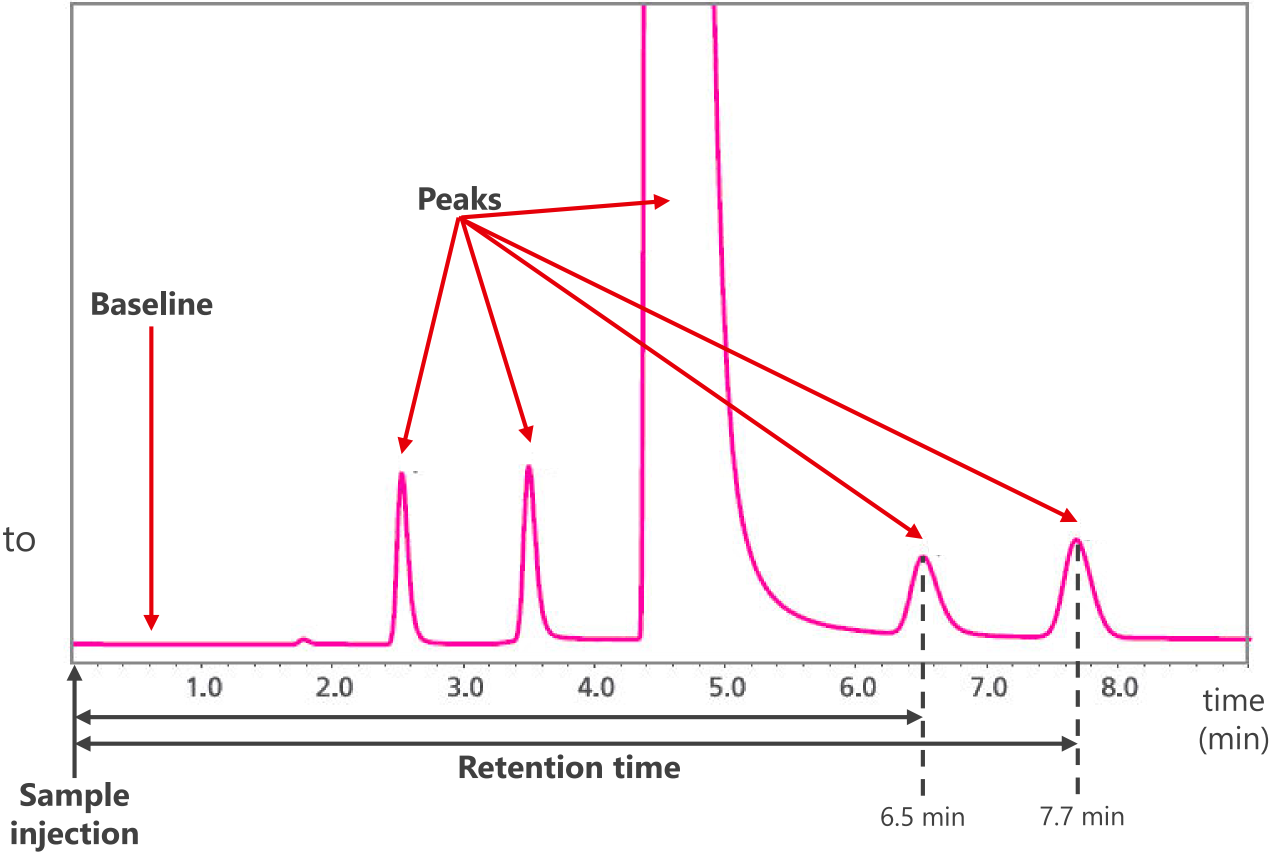
Resulting chromatogram

Sample Mixture

What is gas chromatography?

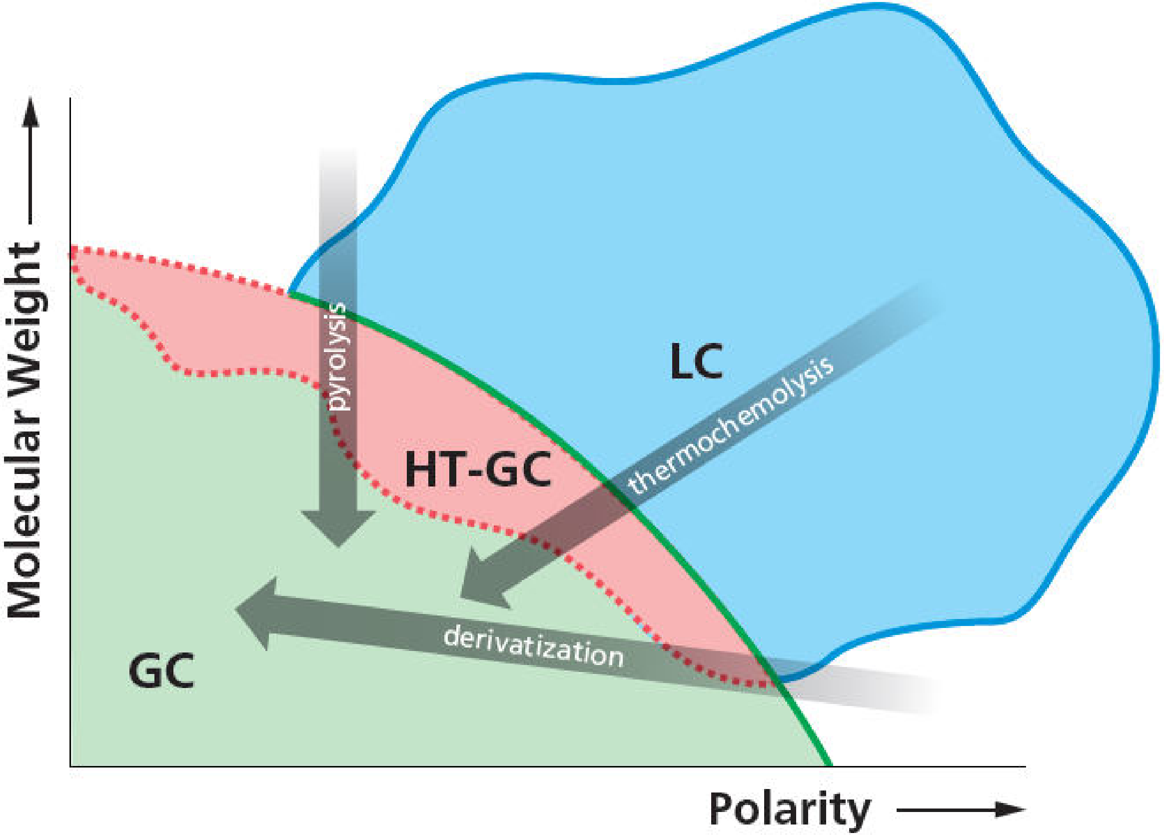
The chromatogram shows signal intensity on the y-axis and **retention time** (mins) on the x-axis.

Retention time is the time between **sample injection** on the front of the column and a **component eluting** into the detector at the other end.



Uses of Gas Chromatography

What can GC be used for?



Typical applications

Flavor & Fragrance

Analysis of aromatics in perfume, wine and coffee

Pharmaceuticals

Impurities & residual solvent analysis

Food & Beverage

Analysis of pesticides, additives & contaminants

Oil, Gas & Chemical

Analysis of sulfur, inorganic gases & light hydrocarbons

Environmental Testing

Analysis of volatile environmental pollutants

Forensic Toxicology

Steroid and drug analysis

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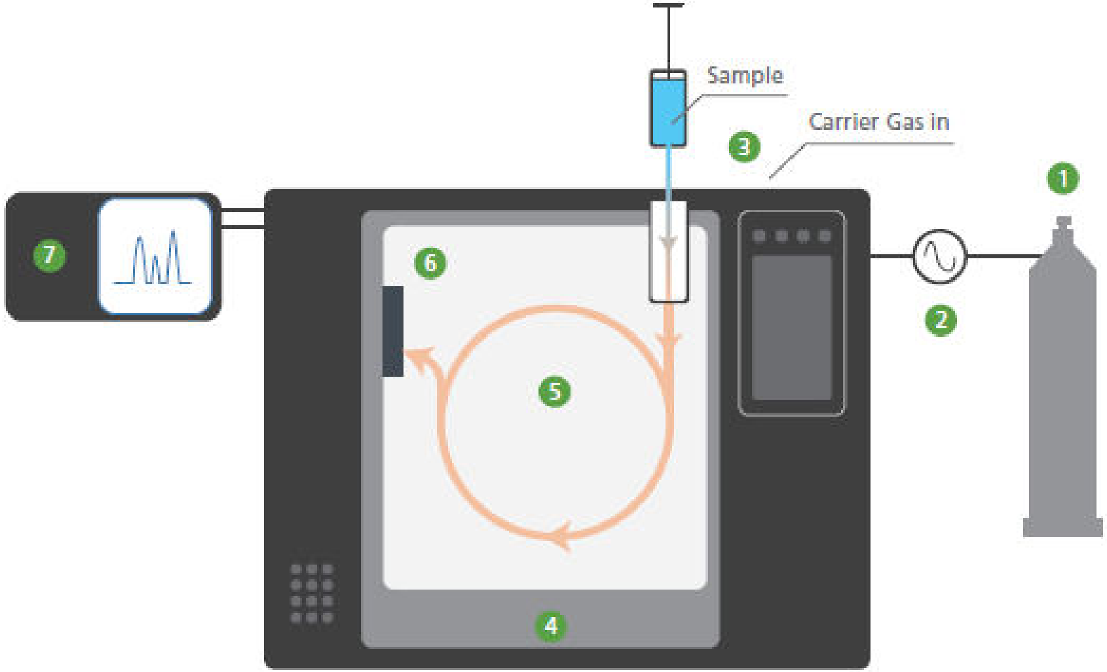
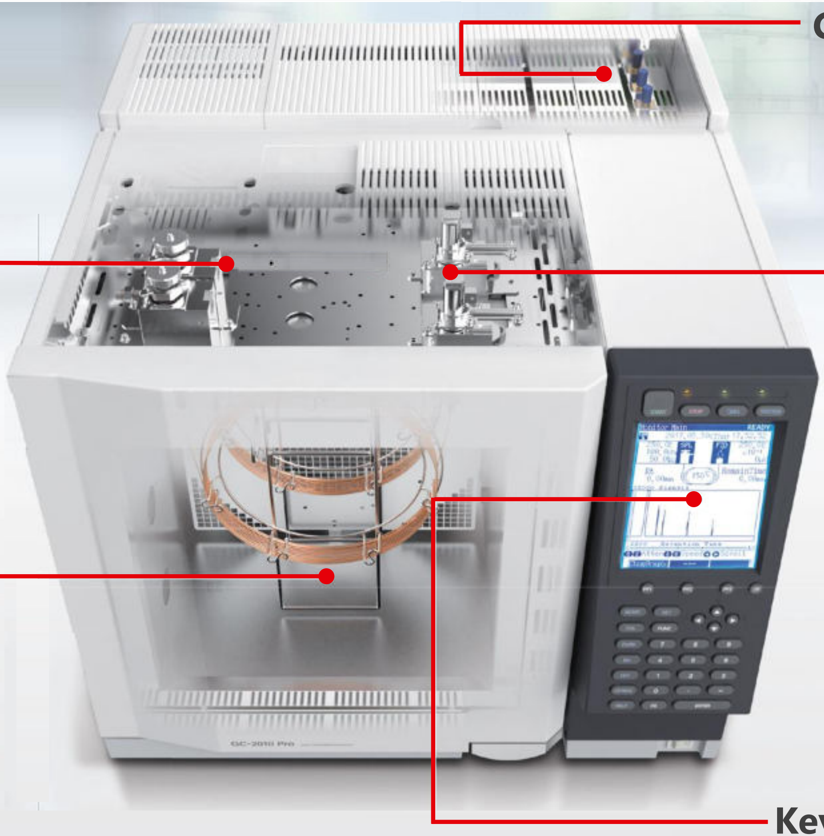
Hardware overview

Typical gas chromatograph



① Carrier Gas (Gas Cylinders)
② Flow Regulator
③ Injection Port
④ Column Oven (thermally-controlled)
⑤ Column
⑥ Detector
⑦ Computer and Output

Modern gas chromatograph



Carrier & Detector Gas Controls

Sample Injection (Inlet)

Detectors

Column and Column Oven

Keypad & Display

Carrier gas

Carrier gas (mobile phase)

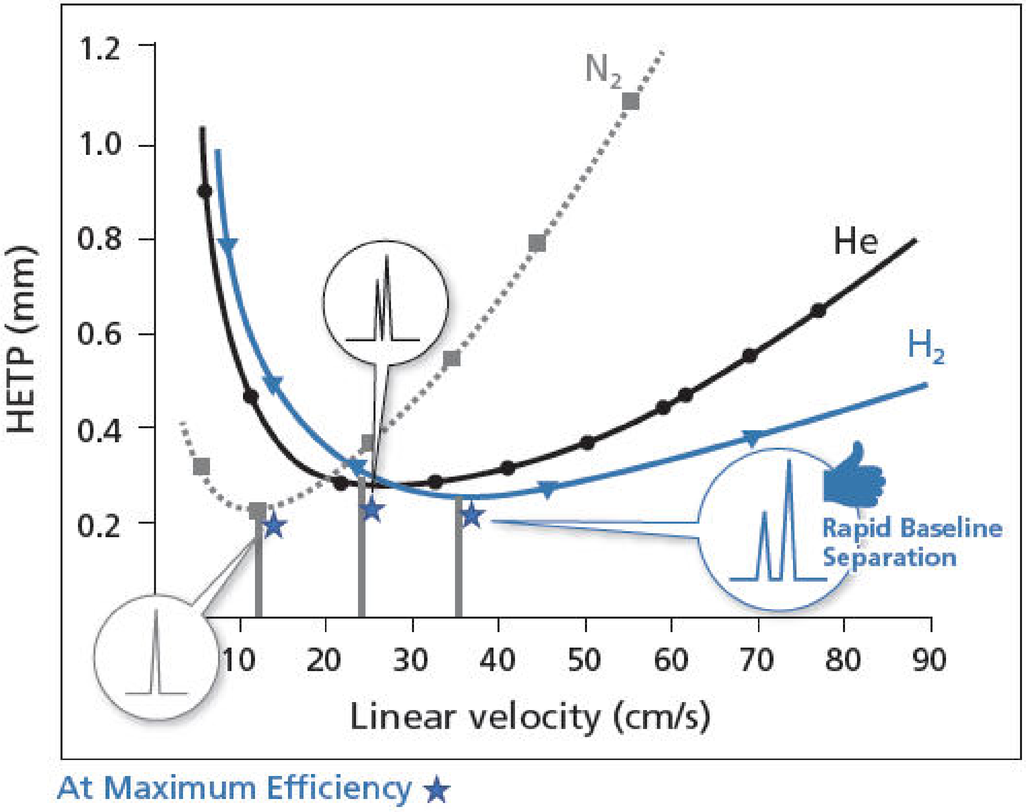
It must be **inert**, **extremely pure** and **completely dry**.

Typically this is helium, although hydrogen and nitrogen can also be used.

For normal GC applications, the required purity is typically 5.0 (99.999%) or above.
For high-sensitivity GCMS, 6.0 (99.9999%) is needed!

The gas must be pressurised with an output pressure typically between 500-900 kPa, using a regulator.

Carrier gas properties


van Deemter plot for GC capillary column

HETP: Height equivalent to a theoretical plate (parameter that indicates the separation efficiency of a column)

Low HETP

⬇

Better resolution

Linear velocity: Average value of the speed of a carrier gas flowing in a column

Carrier gas properties

Carrier Gas	Pros	Cons
Hydrogen (H_2)	• High diffusivity and linear velocities • Gets good separation efficiencies • Short analysis and run time (results in cheap operational cost)	• Flammable • Not completely inert (e.g. reacts with some compounds at high temperature)
Helium (He)	• Inert (safe) and non-flammable • Gives high resolution	• Expensive, not easily available
Nitrogen (N_2)	• Cheap and easily available	• Not suited for use in temperature-programmed GC analysis • Long analysis and run time

Summary

Summary

- **Gas chromatography is a common technique for analysing mixtures of volatile and semi-volatile compounds.**
    - It is suited to analysing light organics, but is not suitable for heavier compounds, metals or salts.

- **It separates using gas as a mobile phase and a column coated with a stationary phase.**

- **A GC system comprises of an:**
    - **High-purity gases** (mobile phase and for detectors to function)
    - **Injector** (to introduce the sample onto the column)
    - **Column** (to perform the separation)
    - **Column oven** (to control the separation and elution of compounds)
    - **Detector** (to detect the eluting components)
    - **Data system** (to process the signal from the detector)

- **The mobile phase is high-purity “carrier” gas** (typically helium, hydrogen or nitrogen)
- **The stationary phase is supported on a column**

Next time

The next session will be on…

GC Columns

This will cover:

- *Different types of GC columns*
- *The different column dimensions and their relevance*
- *Column phases and polarity*
- *Temperature ranges for columns*

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Theory and Key Principles Series

Gas Chromatography (GC)

Session 2 – GC Columns

Theory & Key Principles Series – GC

- *– Introduction to Gas Chromatography **
- **– GC Columns**
- – The Split/Splitless Inlet
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- – Choices of Detectors for GC
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- – Maintenance & Troubleshooting

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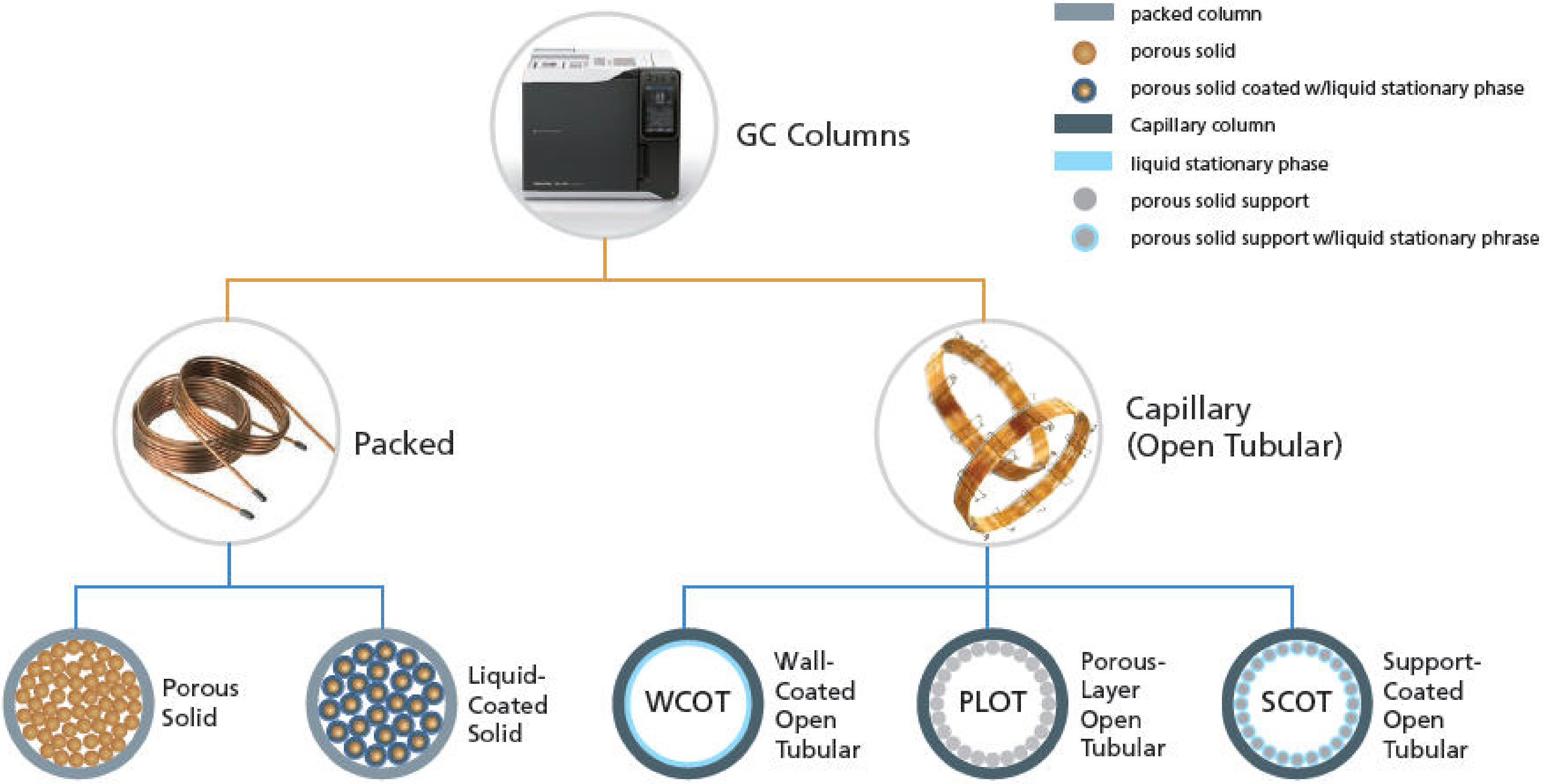
Introduction to gas chromatography

In this presentation:

- Different types of GC columns
  - Packed & capillary
- The different column dimensions and their relevance
  - Length, internal diameter & film thickness
- Column phases and polarity
  - Non-polar, mid-polar & polar
  - Different phase materials
- Temperature ranges

Types of columns

Types of columns

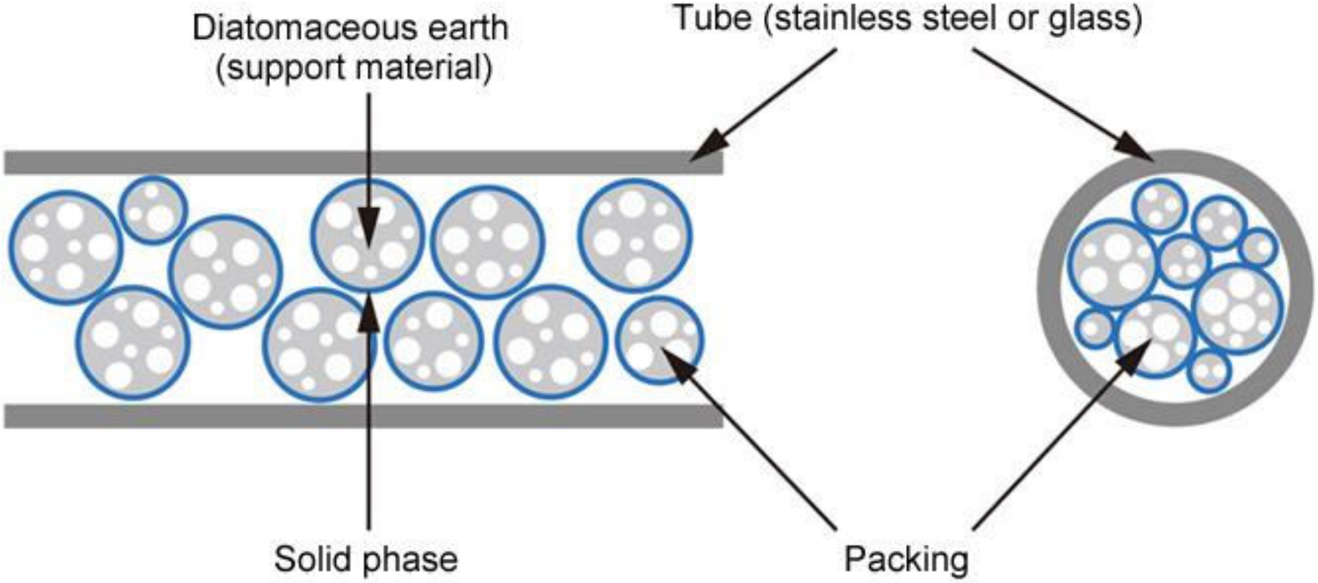


- ▬ packed column
- ● porous solid
- ◉ porous solid coated w/liquid stationary phase
- ▬ Capillary column
- ▬ liquid stationary phase
- ● porous solid support
- ◉ porous solid support w/liquid stationary phrase

GC Columns

- Packed
  - Porous Solid
  - Liquid-Coated Solid
- Capillary (Open Tubular)
  - WCOT: Wall-Coated Open Tubular
  - PLOT: Porous-Layer Open Tubular
  - SCOT: Support-Coated Open Tubular

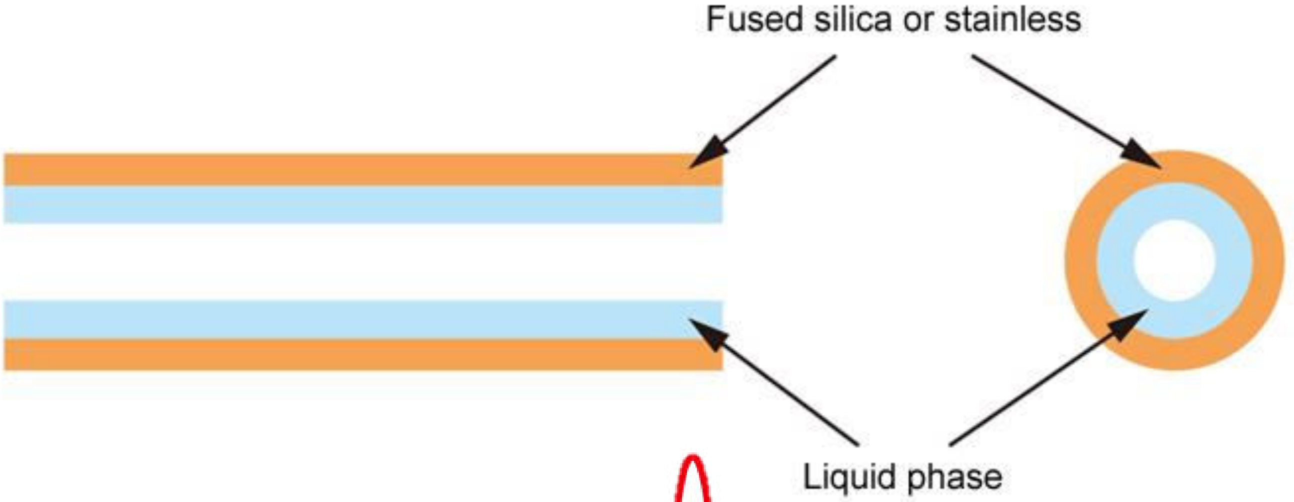
Packed columns



Packed column

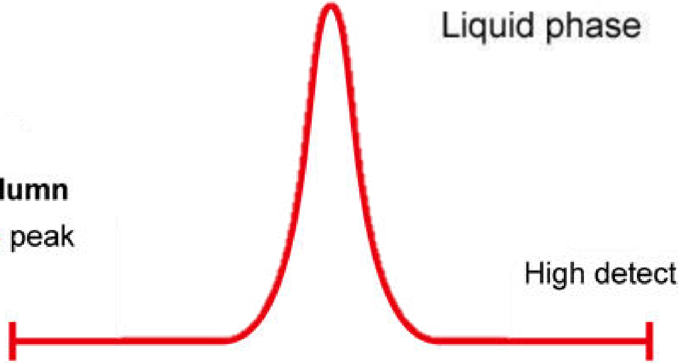
> Broad peak

Capillary columns



Capillary column

> Sharp peak



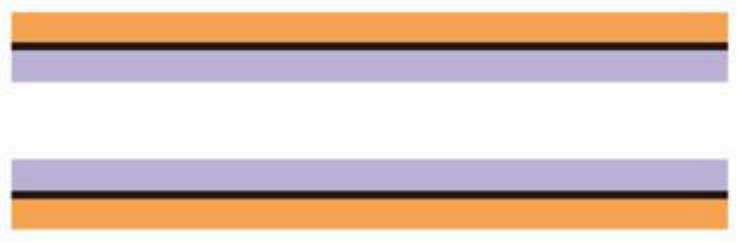
High detection sensitivity

Capillary columns

Wall Coated Open Tubular (WCOT)

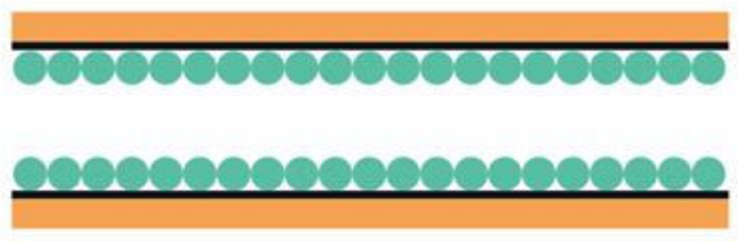
Lined with liquid phase or a chemical bonding layer

Most common in modern GC applications



Porous Layer Open Tubular (PLOT)

Lined with immobilised porous polymer or alumina, etc.

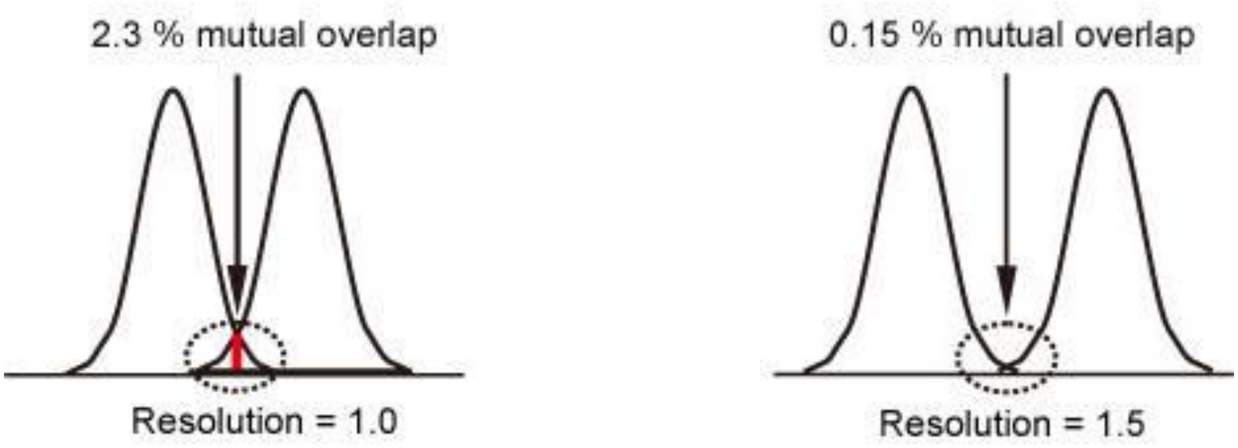


Resolution

The main difference between packed and capillary column chromatography is **resolution**.

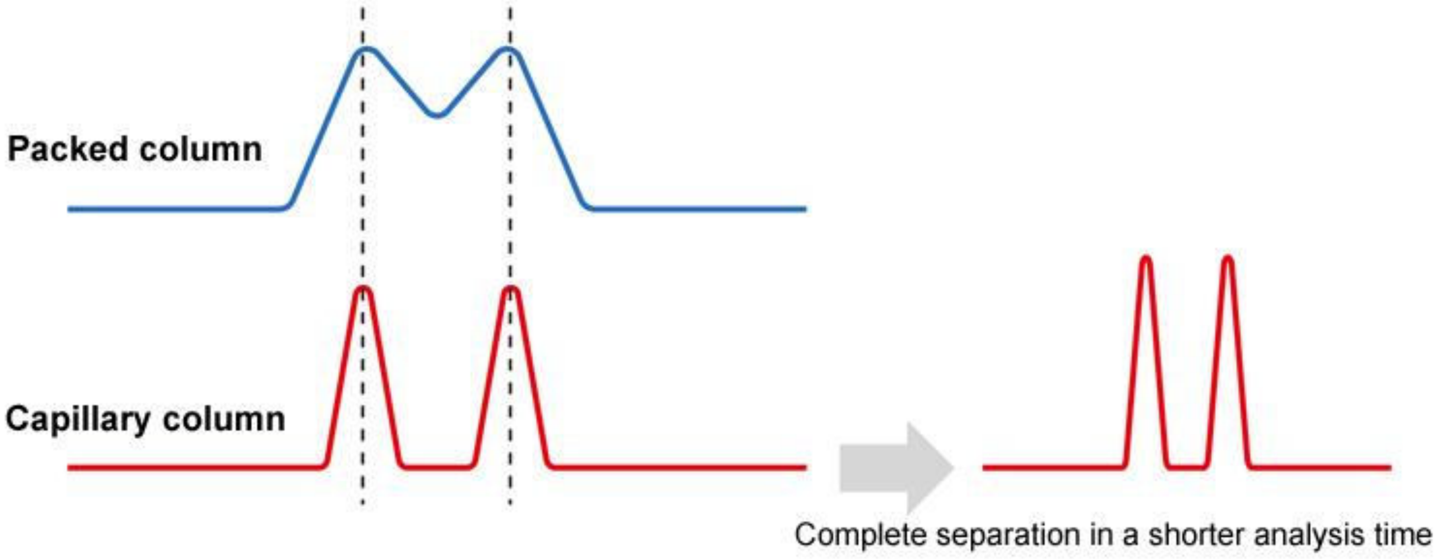
This is a **measure of separation** between two components on a chromatographic system.

The more separated two peaks are, the greater the resolution.



Benefits of capillary columns

Resolution can be >10x higher than packed columns
This means we can separate components on column efficiency rather than selectivity
Fewer stationary phase chemisties are required



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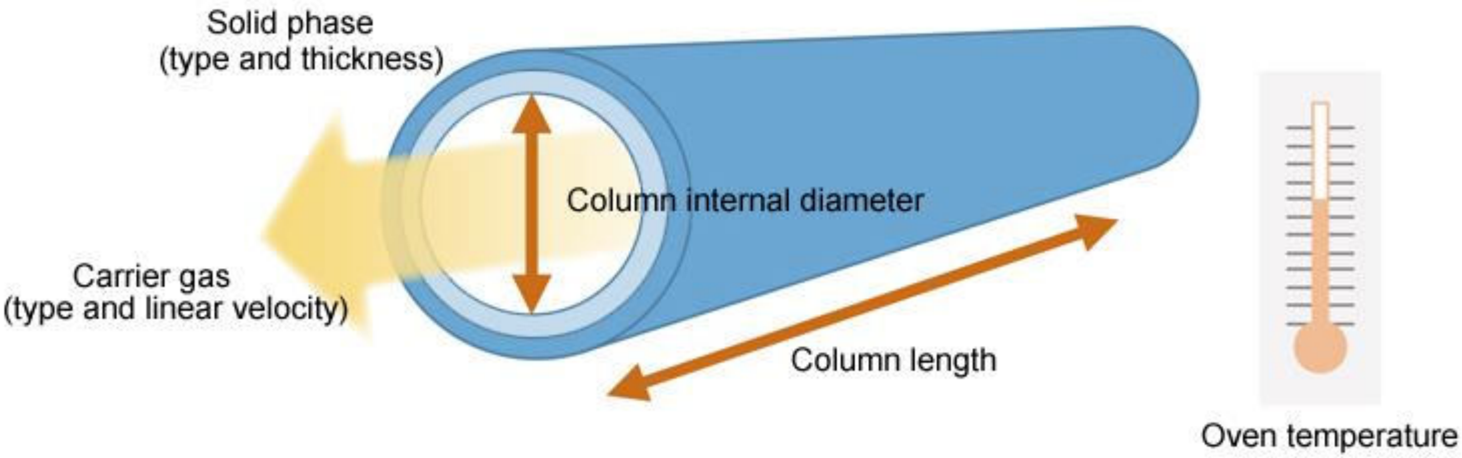
Capillary column properties

Capillary columns

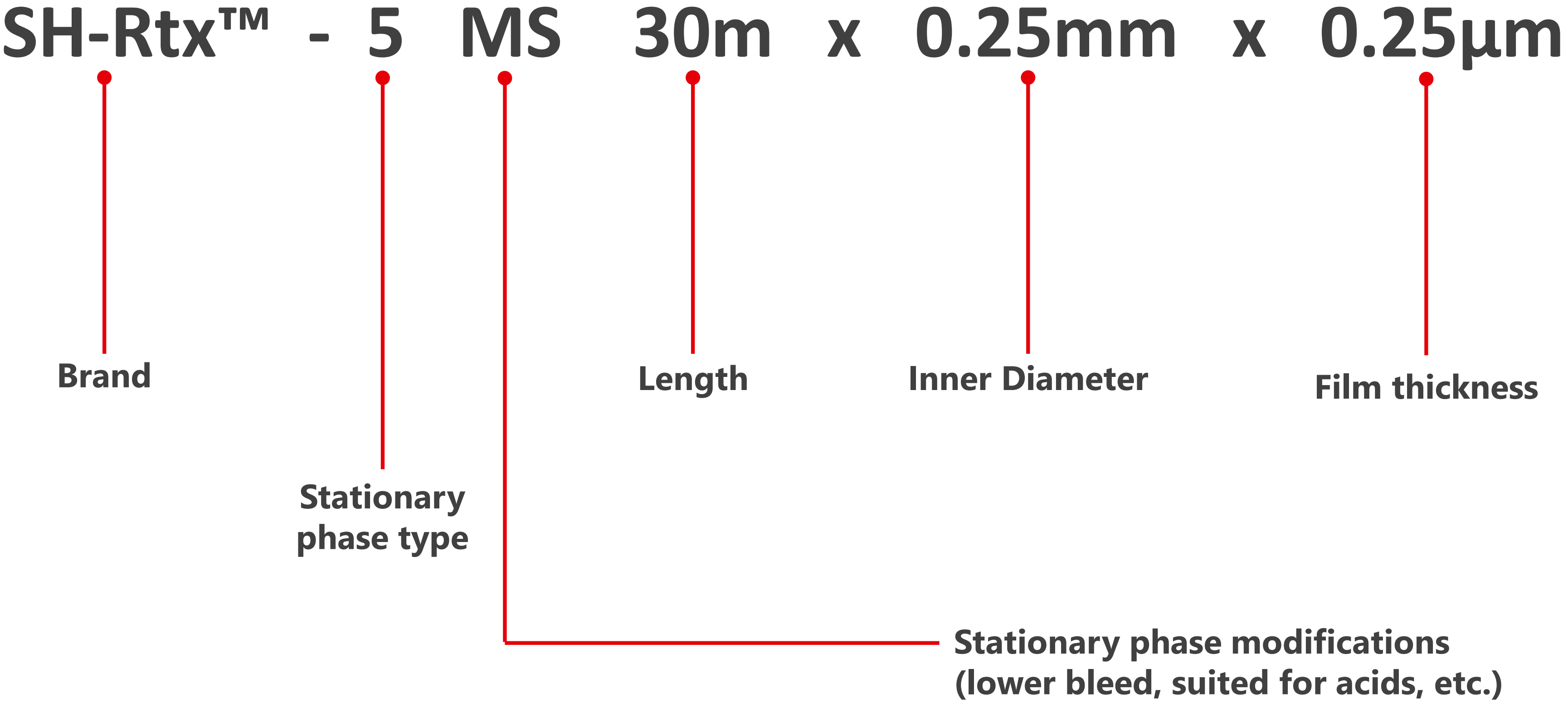
4 Key Properties

Length(m)
Internal diameter (mm)
Film thickness (μm) of stationary phase
Solid phase chemistry

These parameters, combined with **carrier gas** (type and speed) and **oven temperature** determine the separation of components



How to identify capillary columns



SH-Rtx™ - 5 MS 30m x 0.25mm x 0.25µm

Brand

Stationary phase type

Length

Inner Diameter

Film thickness

Stationary phase modifications (lower bleed, suited for acids, etc.)

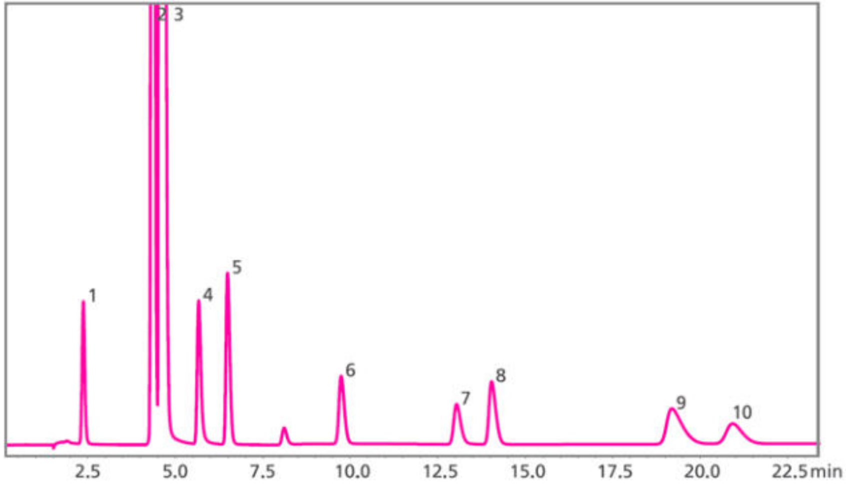
Dimensions

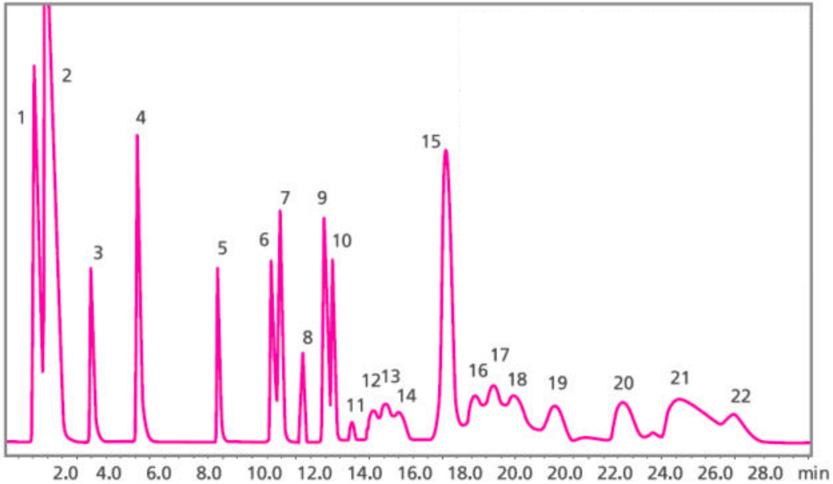
Column dimensions

Length

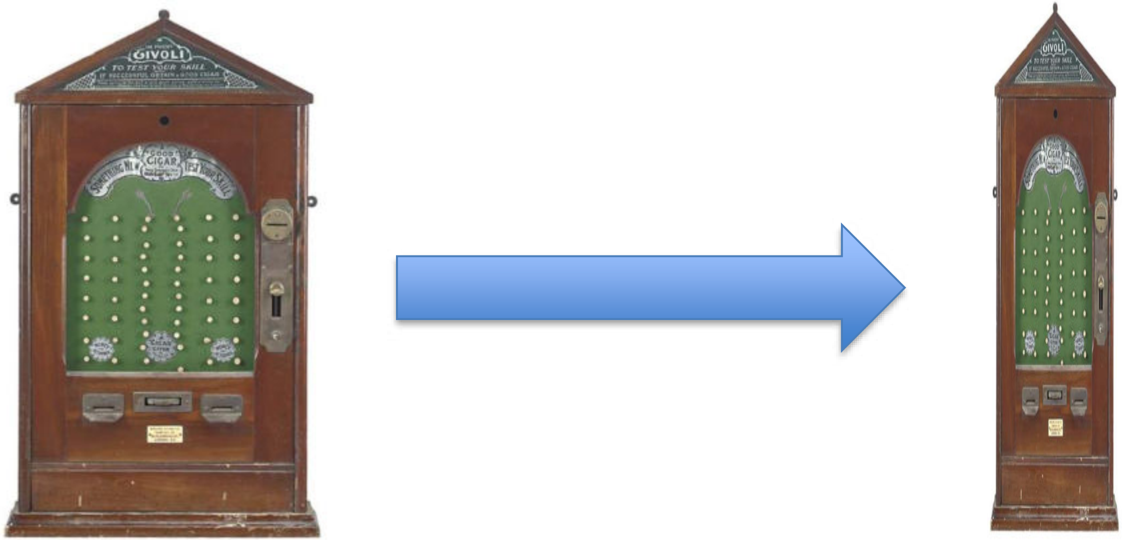
Whilst increasing column length increases separating power (resolution), it is not a linear relationship!
A column that is 2x longer will not have 2x resolution.

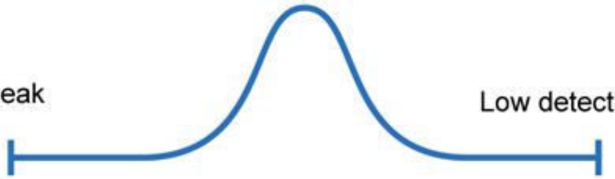
But, the longer a column is, the more time compounds spend inside. Long retention times cause compounds to broaden, reducing sensitivity & peak separation.





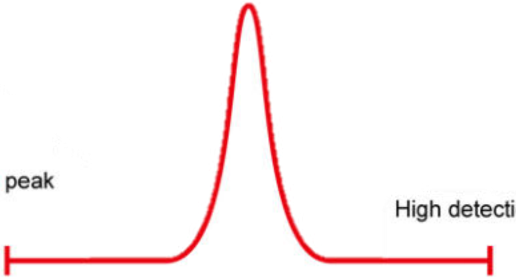
Column dimensions





> Broad peak

Low detection sensitivity



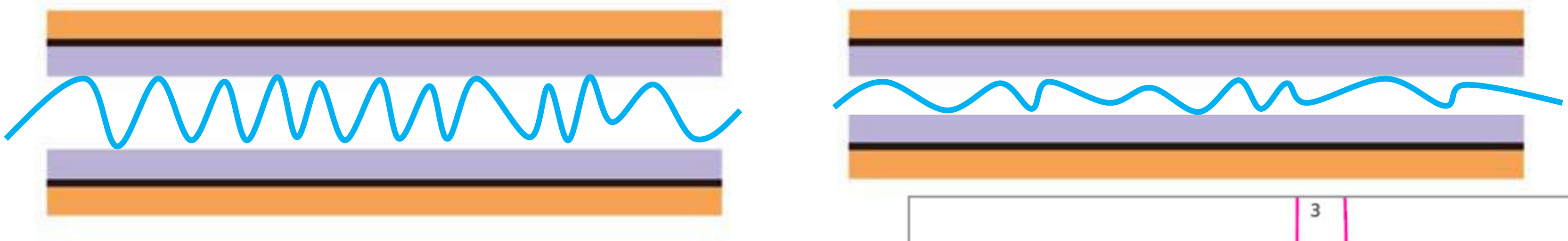
> Sharp peak

High detection sensitivity

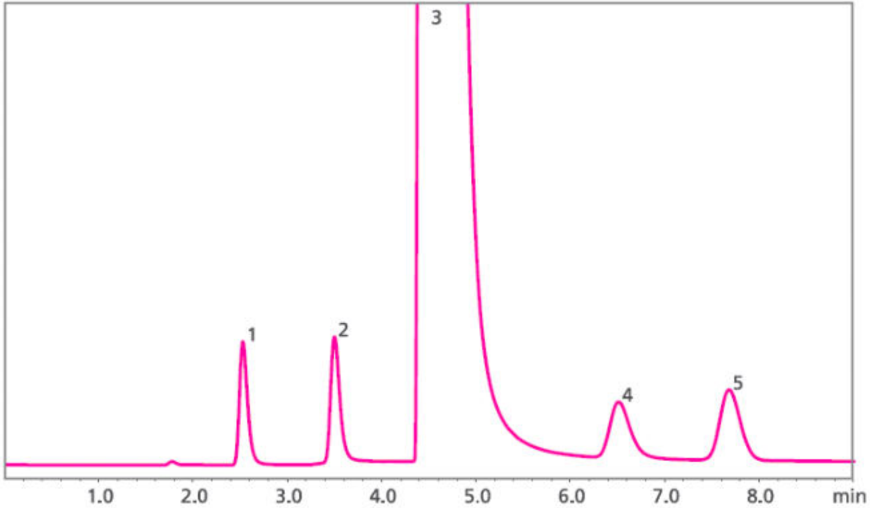
Column dimensions

Internal diameter

A narrower internal diameter gives sharper peaks, therefore better resolution and sensitivity.



But, a narrower column reduces the amount of sample that can be effectively separated! Injecting too much of a single compound causes **column overload**.



Column dimensions

Film thickness

Thicker films will retain compounds longer, so thick films are good for very volatile compounds. Equally, a thin film will have a lower retention, so is ideal for very high-boiling components.

Common dimensions

Length	Internal Diameter	Film Thickness	Application
30m	**0.25mm**	**0.25um**	**Most common dimensions, suitable for 90% of applications.**
30m	0.32mm	1.4um	Analysis of very volatile organics in waste water.
15m	0.25mm	0.1um	Analysis of high-boiling phthalates in electrical components
10m	0.1mm	0.1um	Fast GC applications (for higher sampler throughput)

Stationary phase chemistry

Stationary phase chemistry

Capillary column chemistry is usually measured based on its polarity.

Columns are largely described as being polar, mid-polar or non-polar/a-polar.

Like Dissolves Like

Analysis of non-polar compounds → Non-polar column
Analysis of polar compounds → Strongly polar column

What do the numbers mean?

Roughly speaking, a larger number equates to a higher polarity column

i.e. **Rtx-1** is non-polar **Rtx-5** is largely non-polar **Rtx-35** is mid-polar **Rtx-Wax** is polar

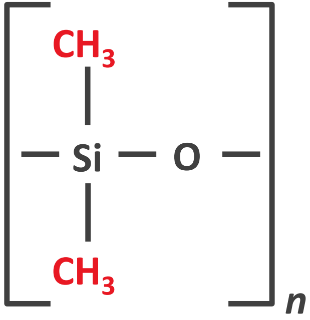
Stationary phases

Type of Solid Phase	Polarity	Separation Characteristics	Application	Temp Ramge (approx.)
Dimethyl polysiloxane	Non-polar	Boiling point order	Petroleum, solvents, high boiling-point compounds	-60 to 360 °C
Phenylmethyl polysiloxane	Non-polar to Mid-polar	Phenyl groups retain aromatic compounds	Perfumes, environmental compounds, aromatic compounds	-60 to 340 °C
Cyanopropyl phenol	Mid-polar to Strongly-polar	Effective separation of oxygenates and isomers	Agricultural chemicals, PCBs, oxygenates *not suited to some detectors (NPDs)	-20 to 280 °C
Trifluoropropyl methyl polysiloxane	Mid-polar to Strongly-polar	Specifically retains halogenated compounds	Halogenated compounds, polar compounds, solvents	-20 to 340 °C
Polyethylene glycol	Strongly polar	Strong retention of polar compounds	Polar compounds, solvents, perfumes, fatty acid methyl esters (FAMEs)	40 to 250 °C

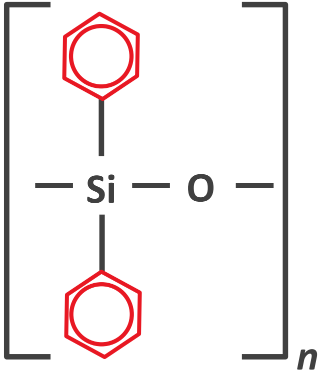
Stationary phases

Polysiloxane phases

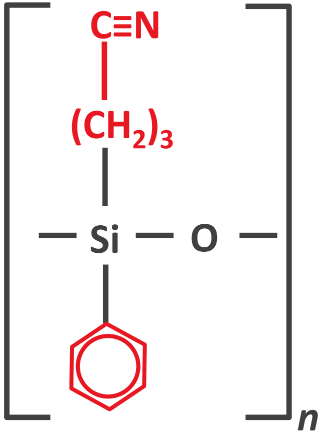
Dimethyl-



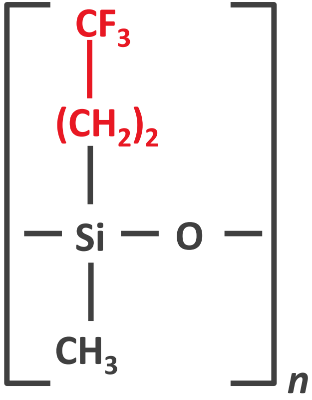
Phenylmethyl-



Cyanopropyl phenyl-

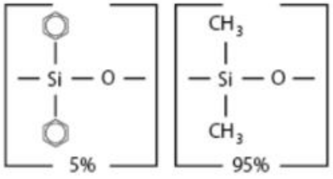


Trifluoropropyl methyl-

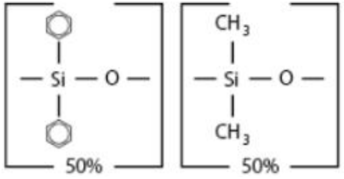


Polysiloxane columns often feature a mixture of the building blocks above:

Rtx-5

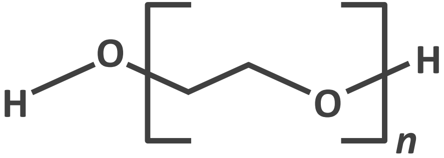


Rtx-17



Special phases

Polyethylene glycol



Temperature considerations

All columns have temperature limits to prevent damage. The details of the limits are on the column box.

Where two temperature limits are stated, these refer to the **isothermal** and **programmed** limits.

Overheating a column causes stationary phase damage, increasing **column bleed** and reducing separation performance.

As columns age, the column bleed starts to increase. **Conditioning** can improve things, but eventually columns have to be replaced.

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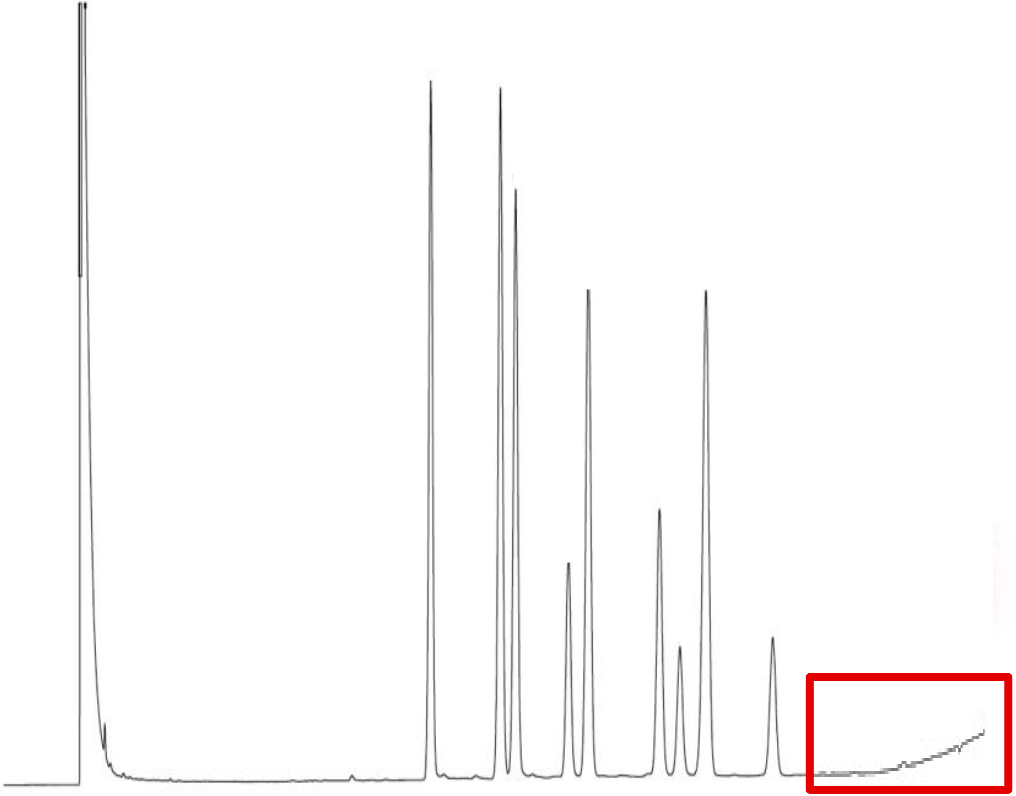

Summary

- **We can categorise GC columns into two types: packed and capillary (or open tubular)**
  - Packed columns contain a packing material made of a porous solid or a liquid-coated solid
  - Capillary columns are hollow tubes with coatings supported on the inside wall of the column

- **Capillary columns, specifically WCOT, are utilised far more in modern systems as they give a higher resolution**

- **Capillary columns have 4 key properties:**
  - Length – *doubling the length gives small improvements in separating power, but increases run-time*
  - Inner diameter – *a narrower i.d. provides a much higher resolution but can hold less sample*
  - Film thickness – *a thicker film retains compounds for longer, so is good for analysis of more volatile compounds*
  - Phase chemistry – *the make-up of the inner-coating defines how compounds will separate*

- **Phases for WCOT columns are described based on their polarity, from non-polar to polar.**
  - A more polar phase often has a lower maximum temperature, so choosing a suitable phase can be tricky
  - These are a wide range of column phases available – use literature examples to help guide your choice!

Next time

The next session will be on…

The Split/Splitless Inlet

This will cover:

- *The difficulties of getting a sample onto the analytical column*
- *The different method parameters and what they all mean*
- *Why using split mode is the easiest & best option*
- *How and when to use splitless mode*

Theory and Key Principles Series

Gas Chromatography (GC)

Session 3 – The Split/Splitless Inlet

Theory & Key Principles Series – GC

- *Introduction to Gas Chromatography **
- *GC Columns **
- **The Split/Splitless Inlet**
- Advanced Liquid Injection Techniques
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The Split/Splitless Inlet

In this presentation:

- The GC Inlet
  - The packed injector – let's start simple!
- The Split/Splitless Inlet
  - Why can't we just use a packed inlet?
- Split Mode
  - The split ratio
- Splitless Mode
  - Why, when & how?
  - High pressure splitless injection
- Carrier Gas Saver

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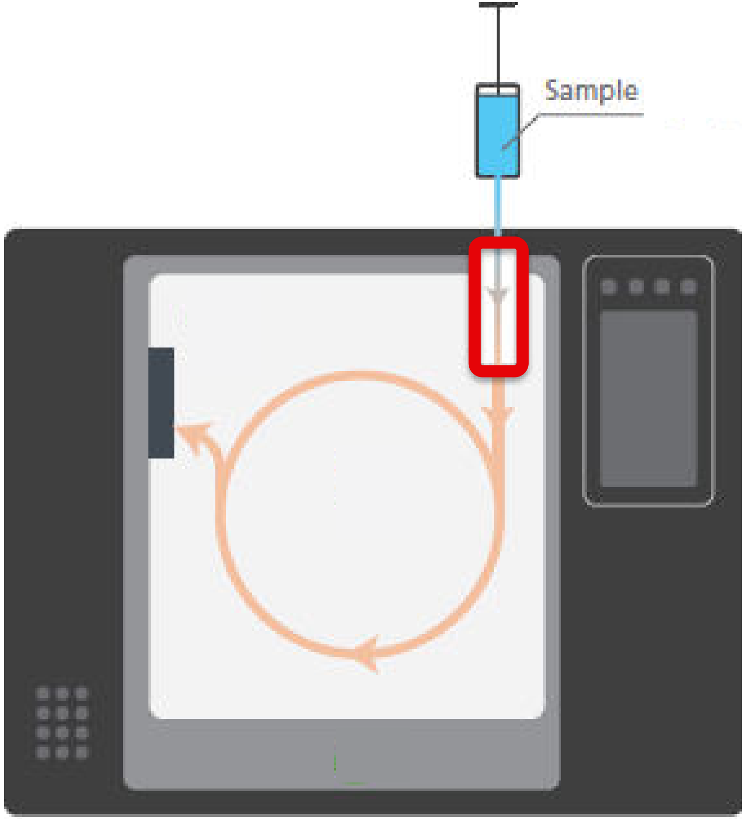
The GC Inlet

The GC inlet

Sometimes called a GC Injector

“Entry system” for sample & carrier gas onto the column.

A **flow controller** manages the pressure/speed/flow of gas down the column.

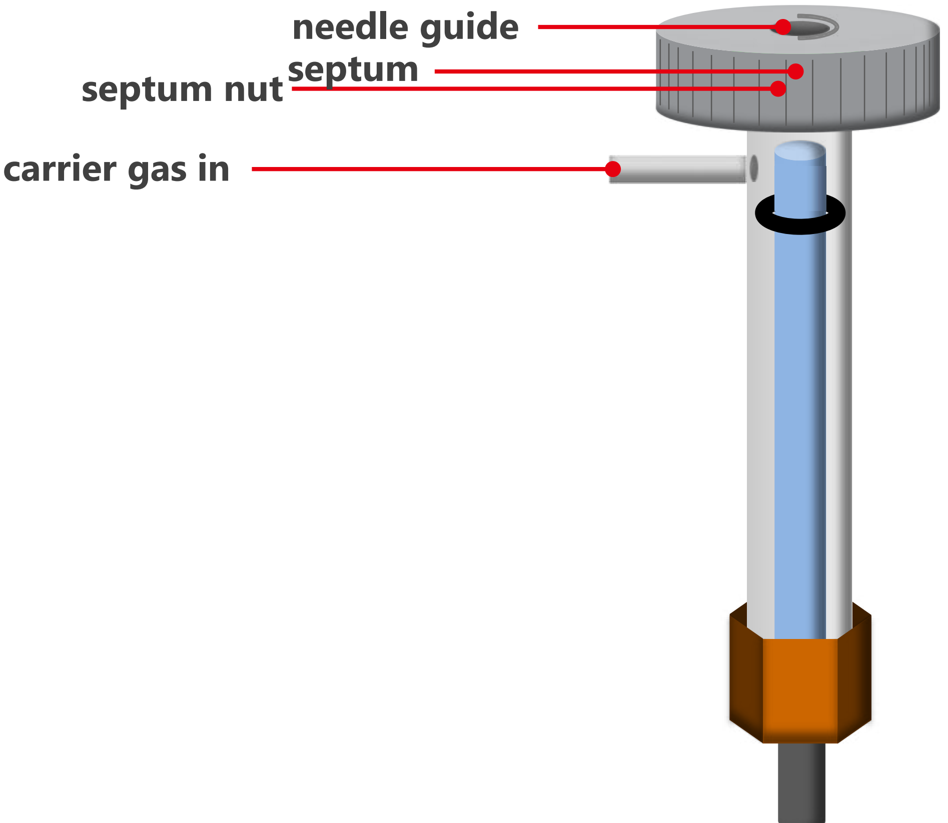


The GC inlet

A metal tube brings the **carrier gas** from the flow controller.

A **septum nut**, with a **needle guide**, is screwed on the top.

A rubber **septum** allows the needle to inject sample inside.



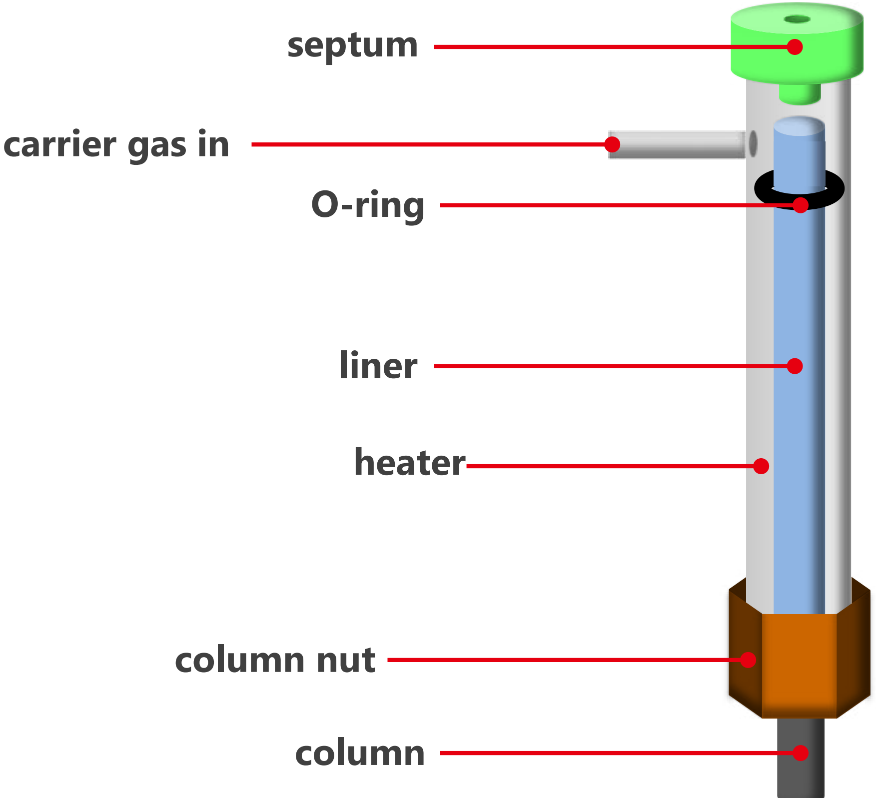
The GC inlet

The **liner** is a hollow, glass tube where a sample mixes with the carrier gas.

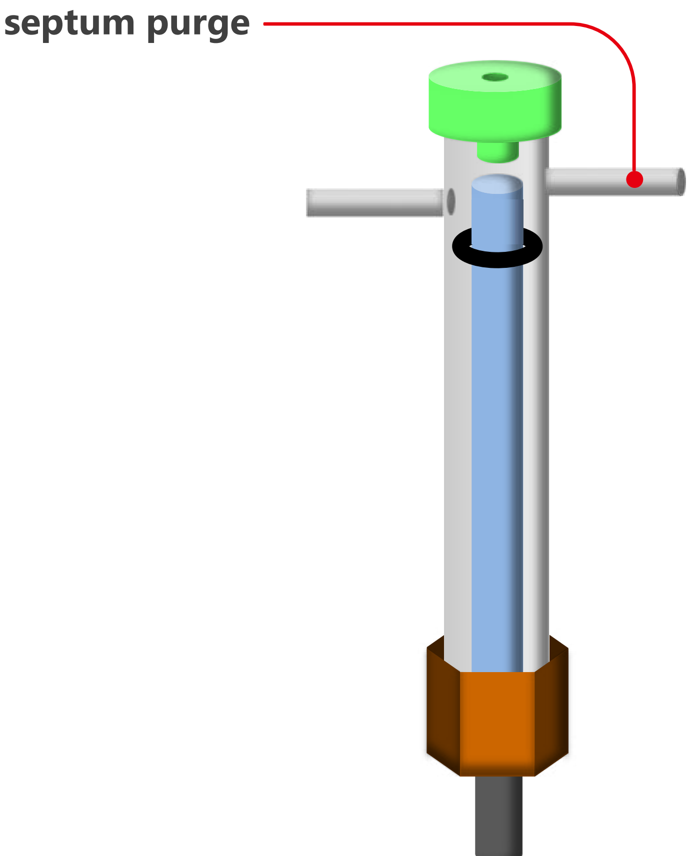
The **O-ring** forces carrier gas to travel through the liner.

The **column** connects to the bottom of the inlet, held in place with a **column nut**.

The inlet is **heated**, to around 250 °C, to vaporise the sample.



Septum purge



At high temperatures, chemicals can be released from the septum and appear as **ghost peaks** on a chromatogram.

To remove this contamination, most inlets are fitted with a **septum purge**.

A small flows prevents the off-gassed chemicals going down the liner.

The septum purge is connected to the **flow controller**, where the flow rate is regulated to around 3 mL/min.

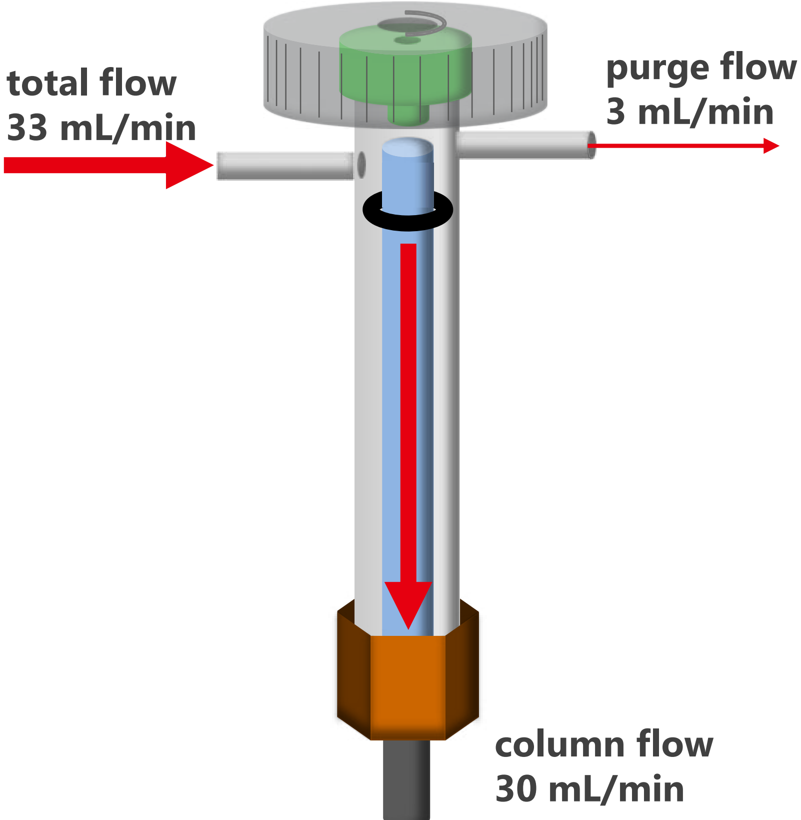
Packed injector

This completes the components of a **packed injector**.

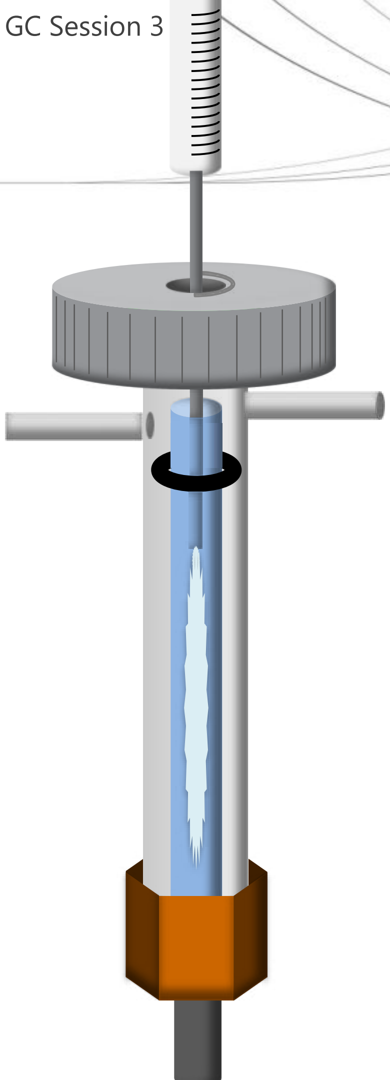
For **packed columns**, or **wide-bore capillary columns** (>0.53 mm i.d.).

For a packed column, a typical **column flow** is 30 mL/min.

With a **purge flow** of 3 mL/min, this gives a **total flow** of 33 mL/min.



Injection process



With a typical liquid injection, 1 µL of a diluted sample is injected.

Under common conditions, 1 µL of liquid expands to about 250 µL of gas!

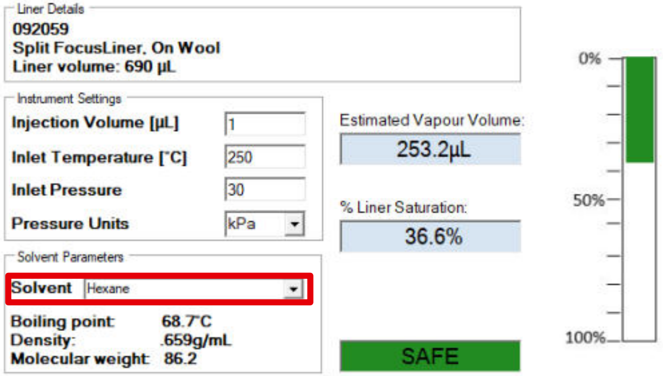
Injection process

1 µL of liquid expands to about 250 µL of gas!

Volume of gas must be less than the volume of the liner. Liner volume is approx. 500uL.

Injecting too much can result in **backflash**.

Highly polar solvents have a much greater expansion volume – the injection volume must be reduced.

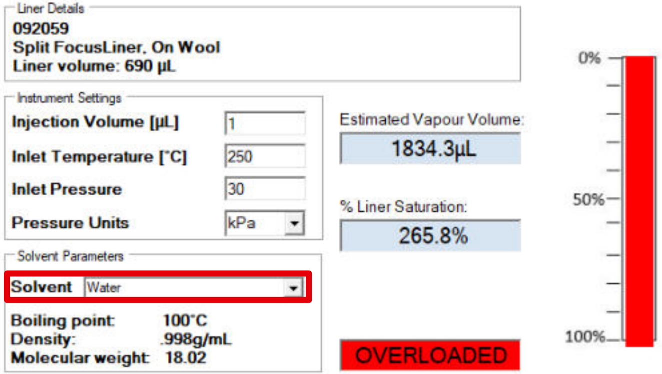


Liner Details
092059
Split FocusLiner, On Wool
Liner volume: 690 µL

Instrument Settings
Injection Volume [µL]: 1
Inlet Temperature [°C]: 250
Inlet Pressure: 30
Pressure Units: kPa

Solvent Parameters
Solvent: Hexane
Boiling point: 68.7°C
Density: .659g/mL
Molecular weight: 86.2

Estimated Vapour Volume: 253.2µL
% Liner Saturation: 36.6%
SAFE



Liner Details
092059
Split FocusLiner, On Wool
Liner volume: 690 µL

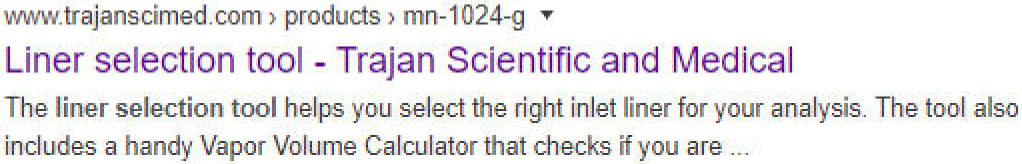
Instrument Settings
Injection Volume [µL]: 1
Inlet Temperature [°C]: 250
Inlet Pressure: 30
Pressure Units: kPa

Solvent Parameters
Solvent: Water
Boiling point: 100°C
Density: .998g/mL
Molecular weight: 18.02

Estimated Vapour Volume: 1834.3µL
% Liner Saturation: 265.8%
OVERLOADED

Solvent expansion calculators

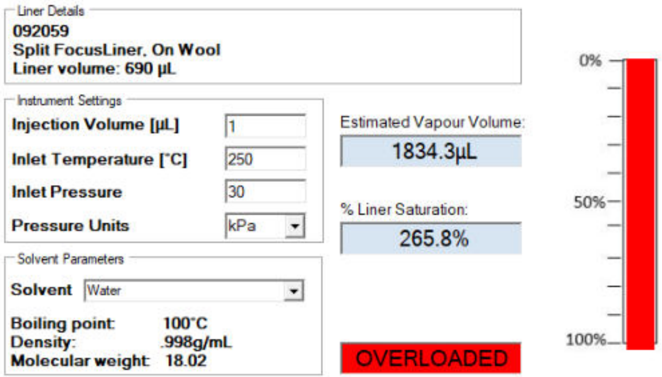
Google ‘**Liner Selection Tool**’:



www.trajanscimed.com › products › mn-1024-g ▾

Liner selection tool - Trajan Scientific and Medical

The liner selection tool helps you select the right inlet liner for your analysis. The tool also includes a handy Vapor Volume Calculator that checks if you are ...



Liner Details

092059
Split FocusLiner, On Wool
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Instrument Settings

Injection Volume [µL]	1
Inlet Temperature [°C]	250
Inlet Pressure	30
Pressure Units	kPa

Solvent Parameters

Solvent Water

Boiling point:	100°C
Density:	.998g/mL
Molecular weight:	18.02

Estimated Vapour Volume: 1834.3µL

% Liner Saturation: 265.8%

OVERLOADED

Liner volume

The liner volume has an important effect on **peak shape**.

At 30 mL/min, the sample is flushed from the 0.5 mL liner in 1 second.

Sample bandwidth is 1 second wide at the head of the column.

Remember: **peaks typically only get wider** over time!

The Split/Splitless Inlet

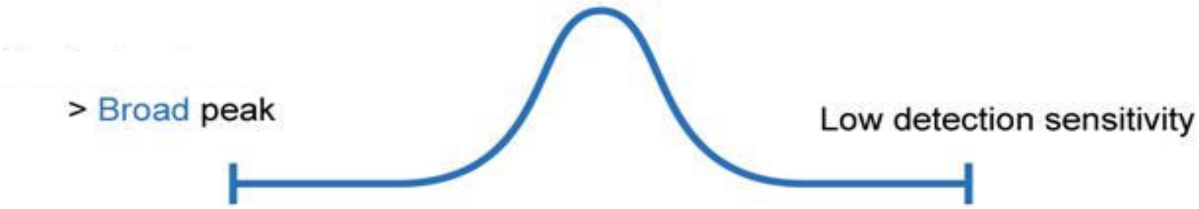
Problems with capillary columns

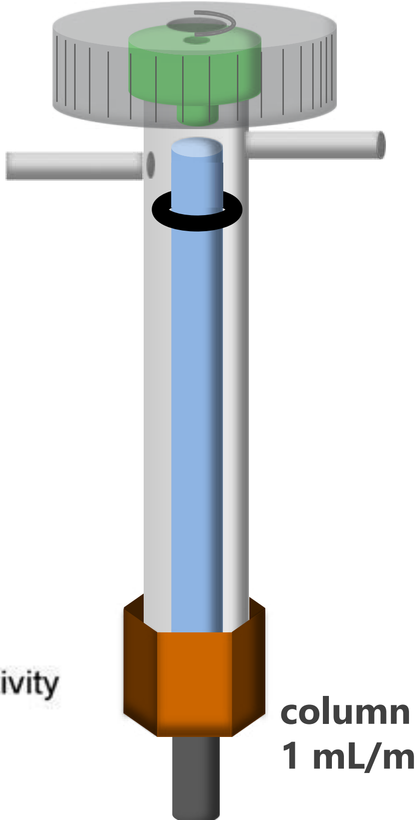
Much narrower inner diameter than packed columns.

To maintain the optimal linear velocity, column flow is very low.

To flush the 0.5 mL liner volume now takes 30 seconds!
This is far too long.

Peak widths need to be approx. 3 seconds.





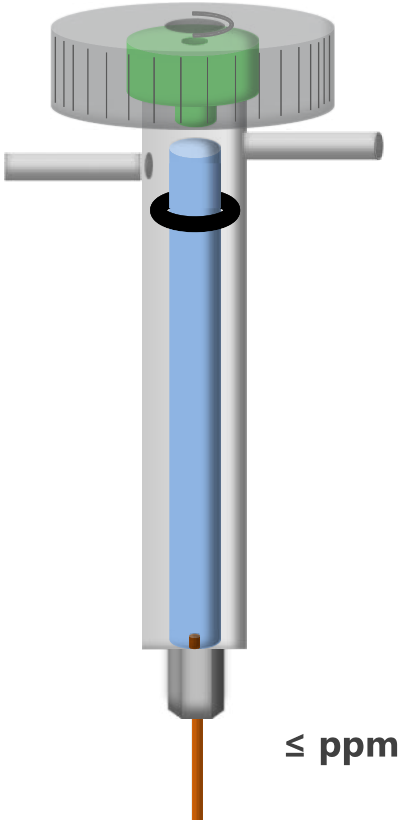
**column flow
1 mL/min**

Problems with capillary columns

Packed columns are 'packed' with stationary phase.

Capillary columns have just **mg amounts of stationary phase**.

Injecting too much sample causes **column overload,** which leads to very poor peak shape.



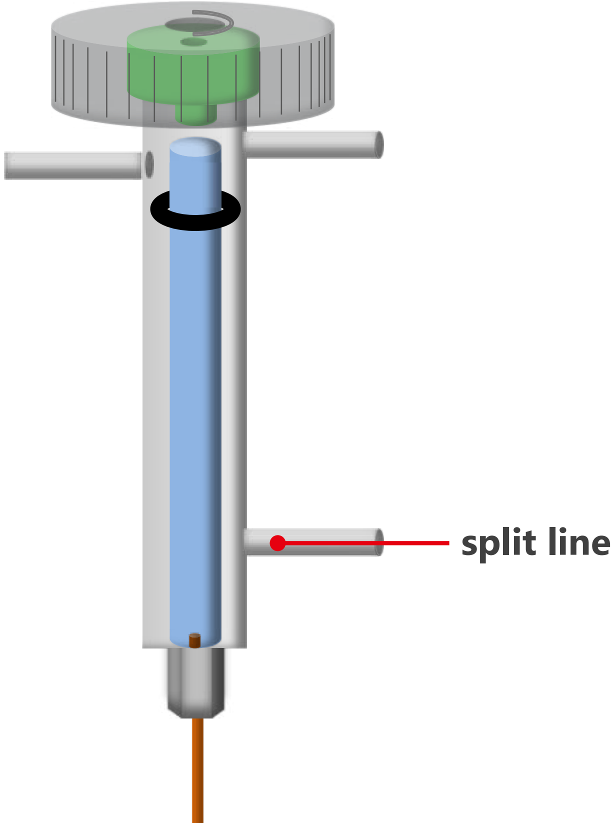
Split flow

The solution – add a **split line!**

This is an ‘escape route’ for the excess flow that can no longer go down the column.

This allows:
- **Optimised column flow**
- **High flow rate through the liner**
- **Sample dilution**

Split line flow is regulated by the flow controller.



Split Mode

Split ratio

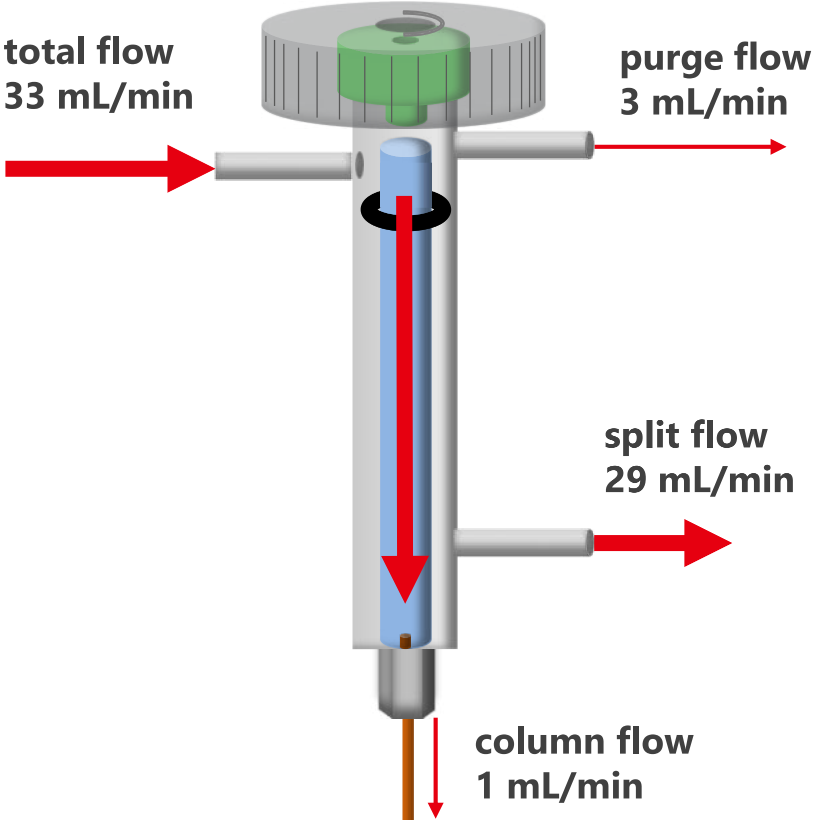
The **split ratio** determines the dilution factor of the sample onto the column.

1 mL/min **column flow**

29 mL/min **split flow**

For every 30 portions of sample, 1 is analysed.

Split ratio = 30:1



Split ratio

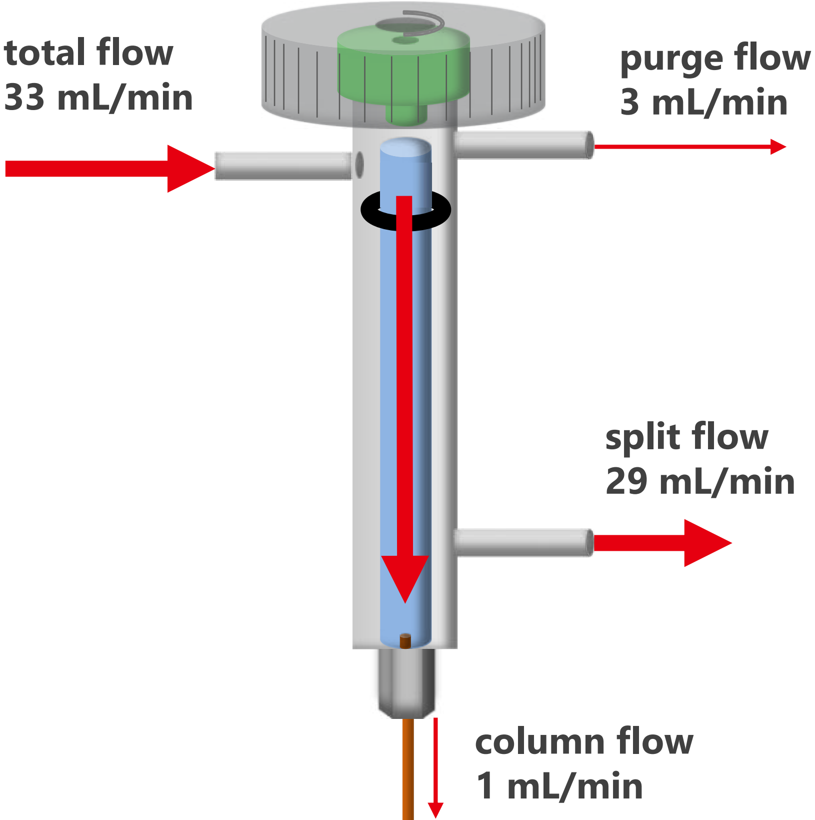
What effect does split ratio have on peak shape and size?

Higher split ratio =

- **Narrower** peaks
- **Smaller** peak area

Lower split ratio =

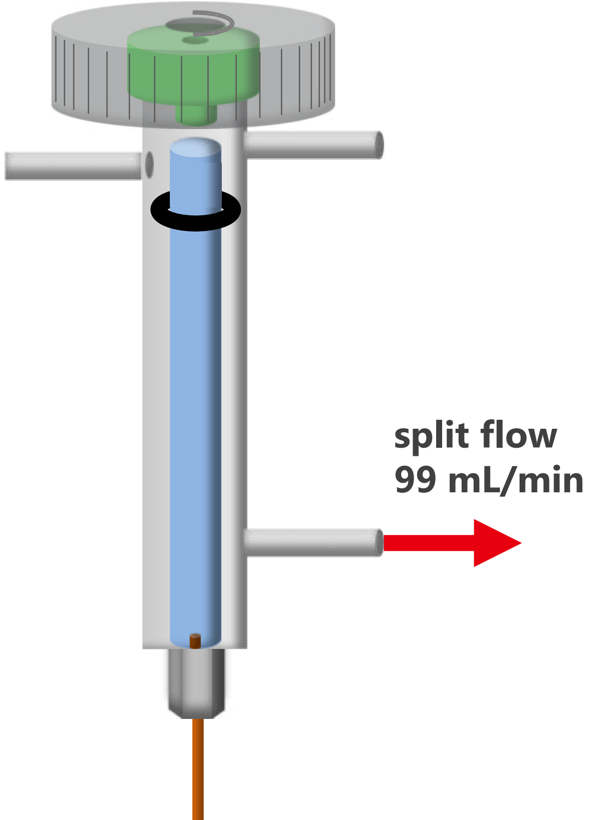
- **Wider** peaks
- **Larger** peak area



Drawbacks of split mode

A high split flow also results in a high carrier gas consumption rate.

Relies on high sample concentrations to enable further dilution.



Splitless Mode

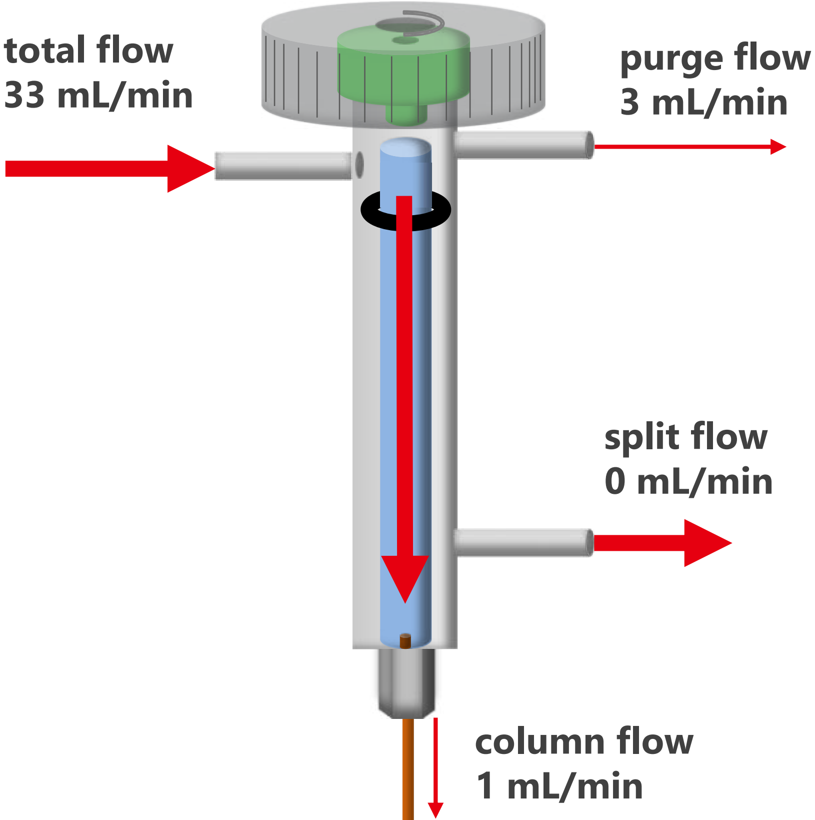
Splitless mode

Used when **sample concentration is too low** for split analysis.

Split flow is off so everything transfers onto the column.

Column flow is still 1 mL/min.

Sample bandwidth is around 1 minute.

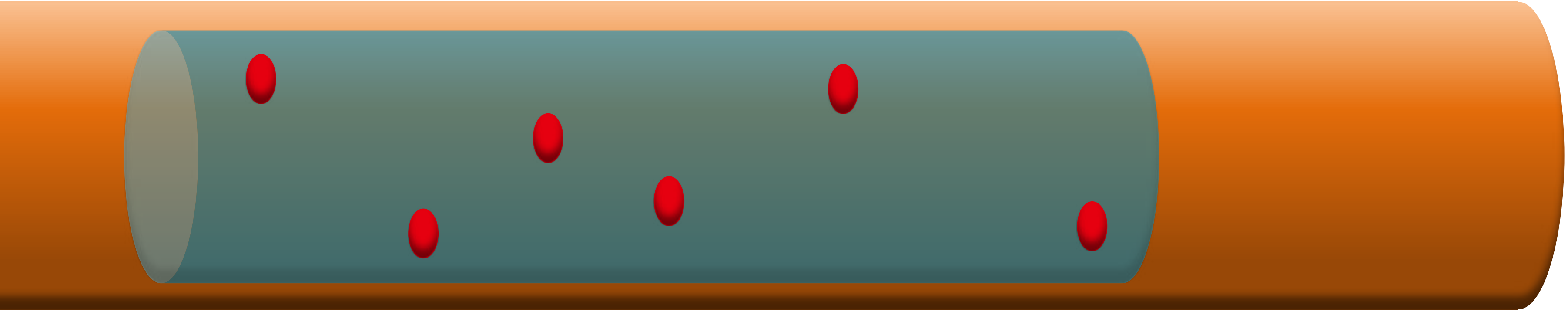


Solvent effect

The vaporised sample transfers from inlet to column.

The column inside the oven is kept at least 20 °C below the solvent boiling point.

Sample condenses on the head of the column.



Solvent effect

The vaporised sample transfers from inlet to column.

The column inside the oven is kept at least 20 °C below the solvent boiling point.

Sample condenses on the head of the column.

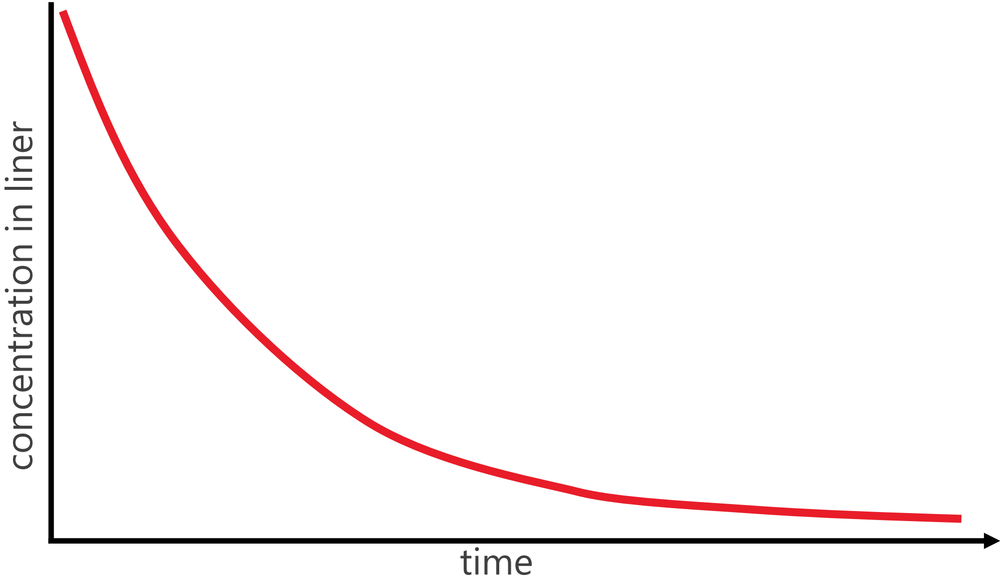
Oven heats, evaporating solvent, which leaves behind a sharp band of analytes.

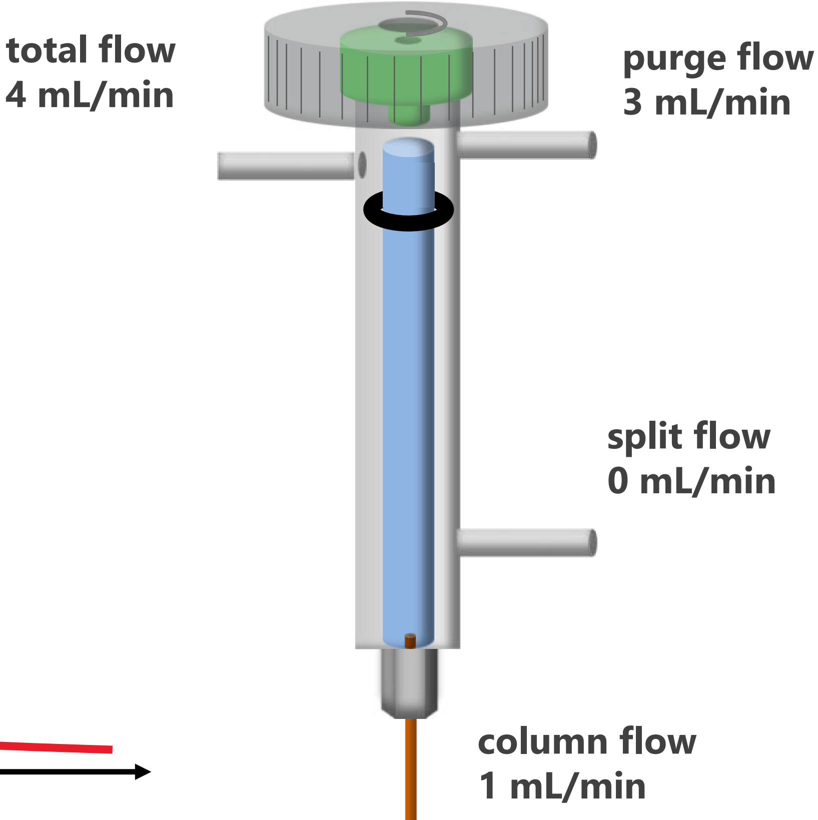
- These analytes must have a **boiling point at least 20 °C above solvent boiling point**, or they'll evaporate with the solvent.

Sampling time

The sampling time is:
time taken to flush the liner 1.5 – 2x

$$\frac{1\ \text{mL/min}}{0.5\ \text{mL volume}} \quad \times 2 \quad = 1\ \text{min}$$





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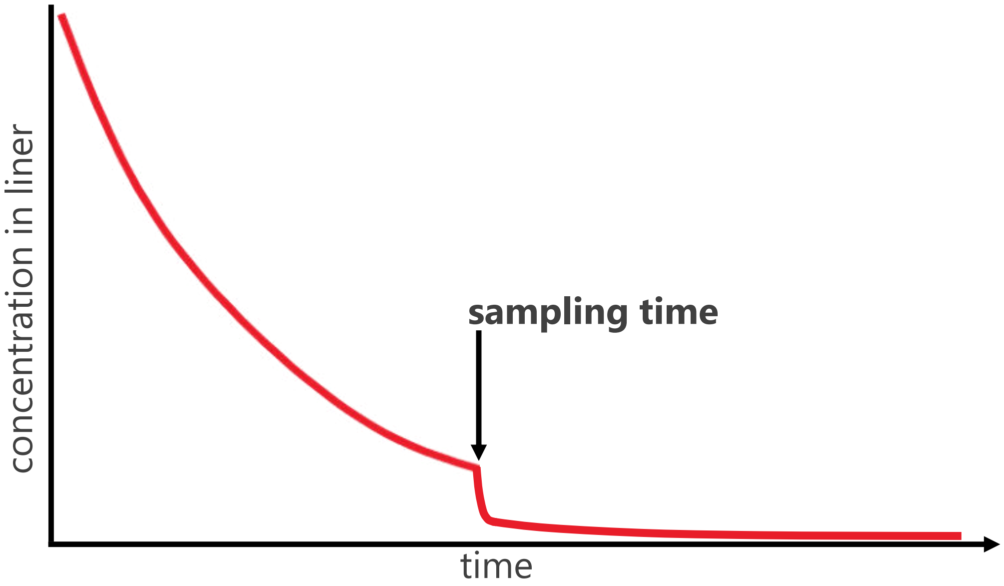

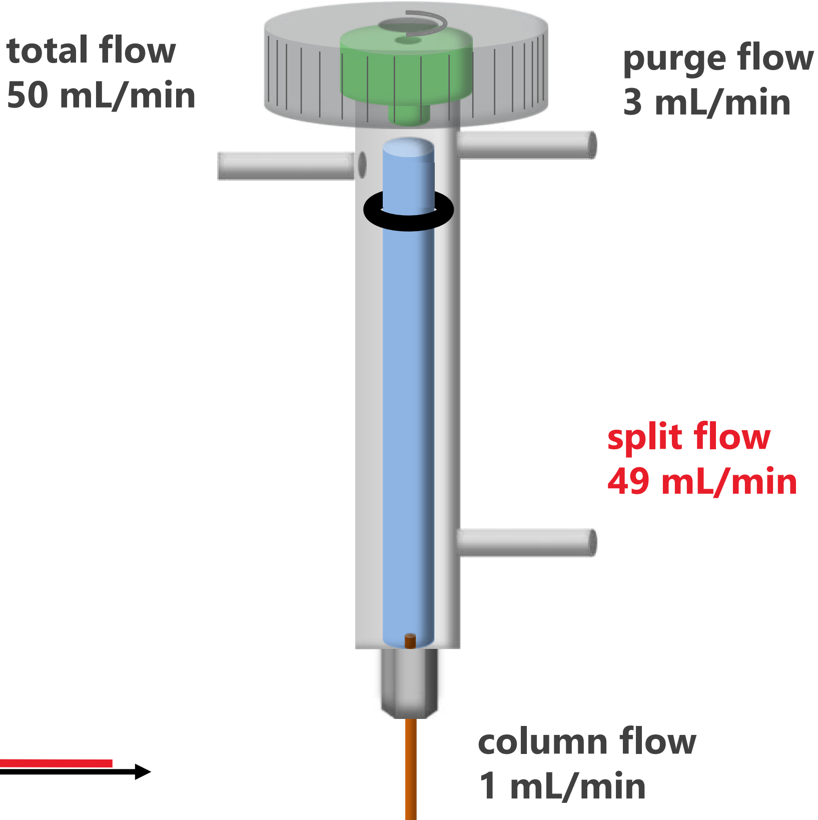

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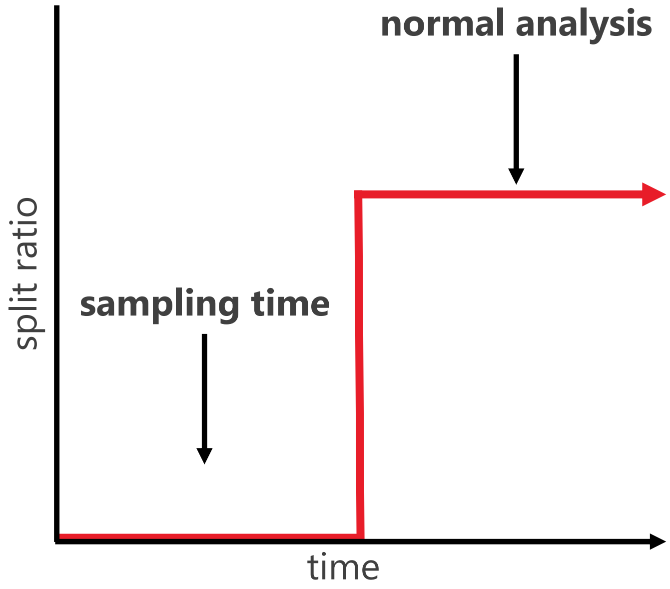
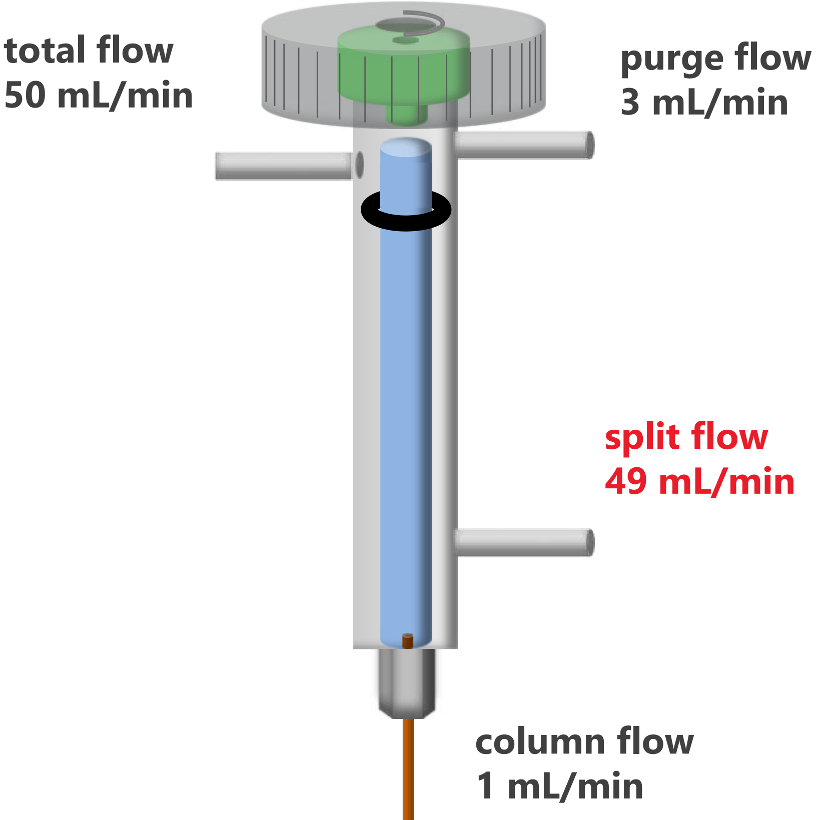
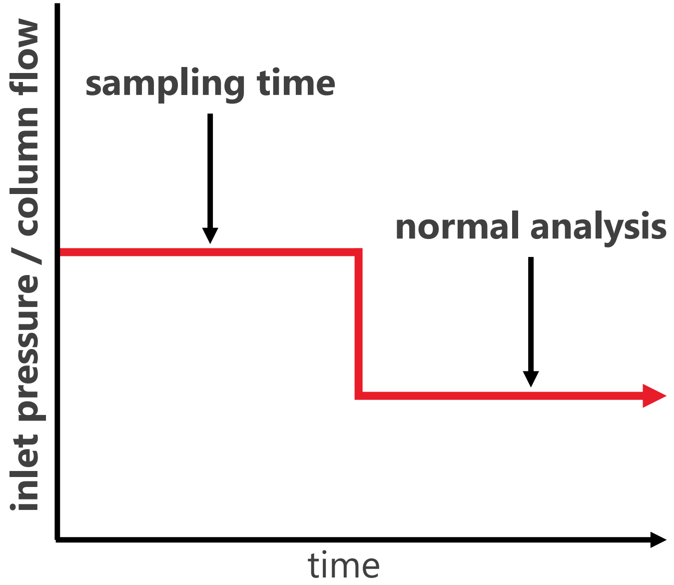


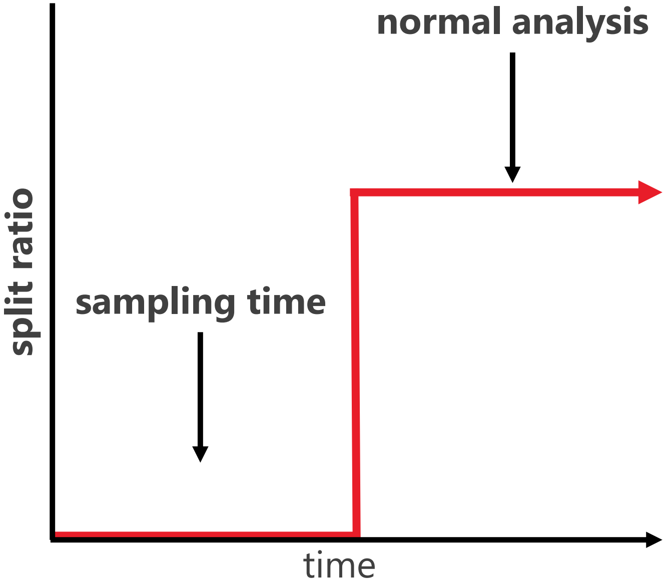


High pressure injection

Sometimes called **pulsed splitless**.

Inlet pressure is increased during sampling time to speed up transfer to column.





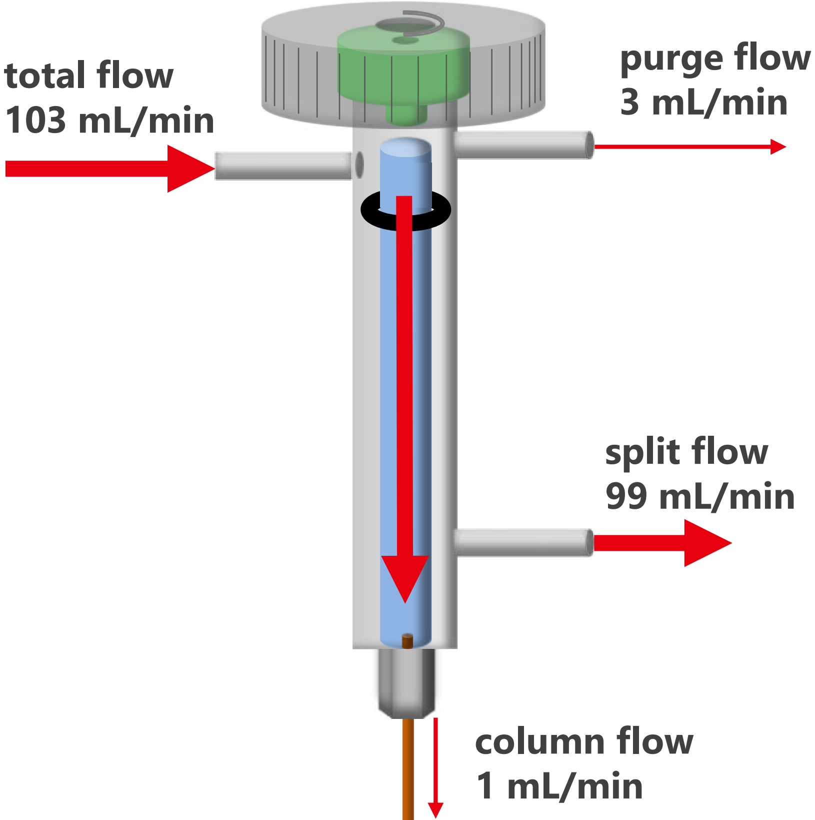
Carrier gas saver mode

High carrier gas flow rates

High gas consumption costs time & money.

Both split & splitless modes can consume very large quantities of gas (>100 mL/min).

Modern GC hardware and software has a built-in **gas saver mode** to minimise consumption.



When to turn down the flow

In **split mode**, a high split dilutes the sample and increases transfer rate.

But what does the high split flow do after all the sample is transferred? **Not much!**

In **splitless mode**, a high split flow helps remove the final traces of the sample from the inlet.

But for how long does the inlet need to be flushed?

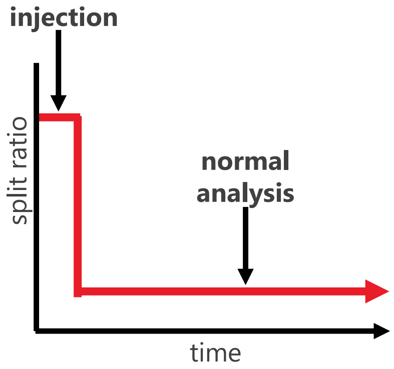
Carrier gas saver mode settings

All of these extra tubes on the inlet make it easy for air to diffuse inside, so always maintain a low flow rate through the split line (except in the sampling time for splitless mode).

A split ratio of 5:1 is usually sufficient.

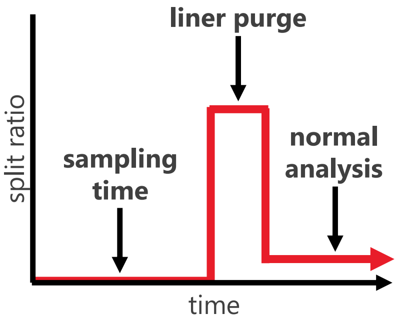
Split mode

Enable carrier gas saver mode after 1 minute.



Splitless mode

Enable carrier gas saver mode 1 minute after the sampling time has finished.



Summary

Summary

- **The split/splitless inlet is optimised for use with capillary columns.**
- It is comprised of:
    - **Septum nut** and **septum**
    - **Liner** with **O-ring** (with a fixed internal volume, making **backflash** possible if the injection volume is too high)
    - A **heated** body
    - **Septum purge** (to remove contaminants caused by a heated septum)
    - **Split line** (to dilute sample flow and increase sample transfer)

- **Split mode** is the most common technique, and is the go-to mode.
    - The split line speeds up transfer of the sample onto the column and dilutes it down prior to column transfer.
    - The **split ratio** defines the sample dilution – the higher the ratio, the less sample is transferred to the column.
    - Higher split ratios give thinner, sharper peaks

- **Splitless mode** is used only when sample concentration is too low to split it.
    - The split line is closed to facilitate full sample transfer to the column.
    - It relies on **solvent focussing**, where the analytes need to be significantly less volatile than the solvent.

- **Carrier gas saver** helps reduce gas consumption by reducing the split ratio after the injection.

Next time

The next session will be on…

Advanced Liquid Injection Techniques

This will cover:

- *When is split/splitless unsuitable*
- *Programmable Temperature Vaporisation (PTV) technique*
- *On-Column Injection (OCI) technique*
- *Large Volume Injection (LVI) using a Multi-Mode Inlet (MMI)*

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- Alternatives to Liquid Injection
- Choices of Detectors for GC
- Processing GC Data
- Maintenance & Troubleshooting

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Advanced Liquid Injection Techniques

In this presentation:

- When is split/splitless not suitable
- Programmable Temperature Vaporisation (PTV)
- On-Column Injection (OCI) or Cool On-Column (COC)
- Multi-Mode Inlets (MMI)
    - Large Volume Injection (LVI)

When is the split/splitless inlet unsuitable?

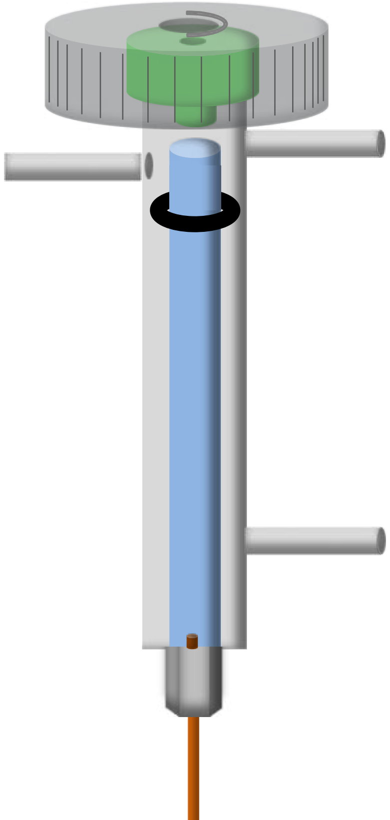
When to look for an alternative inlet

Split/splitless inlets (SPL or S/SL) are useful for about 95% of liquid sampling applications.

But it's not a "one size fits all" solution.

There are five key situations when using an SPL isn't suitable:

- *Thermally labile compounds*
- *Very wide boiling point range*
- *Standard methods (ASTM, DIN, EN, ISO, etc.)*
- *High sample matrix*
- *Non-liquid sample*



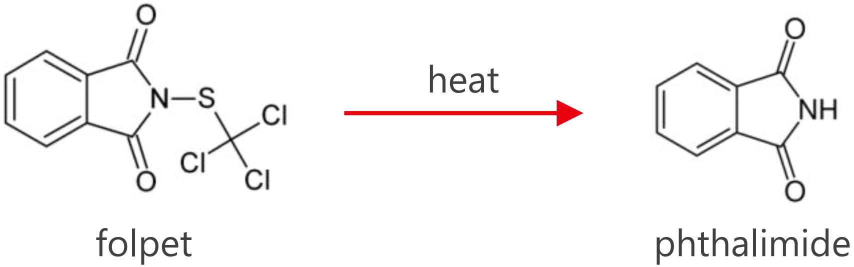
Samples containing thermally labile compounds

Thermally labile compounds

Some compounds are not thermally stable.

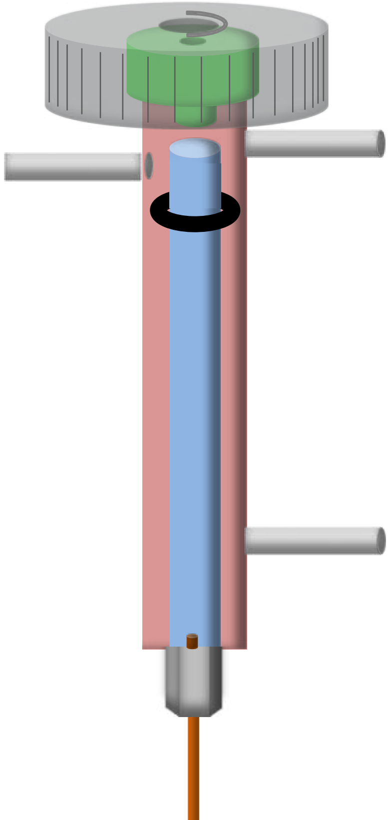
This means they tend to break down inside a hot GC inlet.

Common issue in pesticide screening where many pesticides are unstable at high temperatures.



folpet

phthalimide

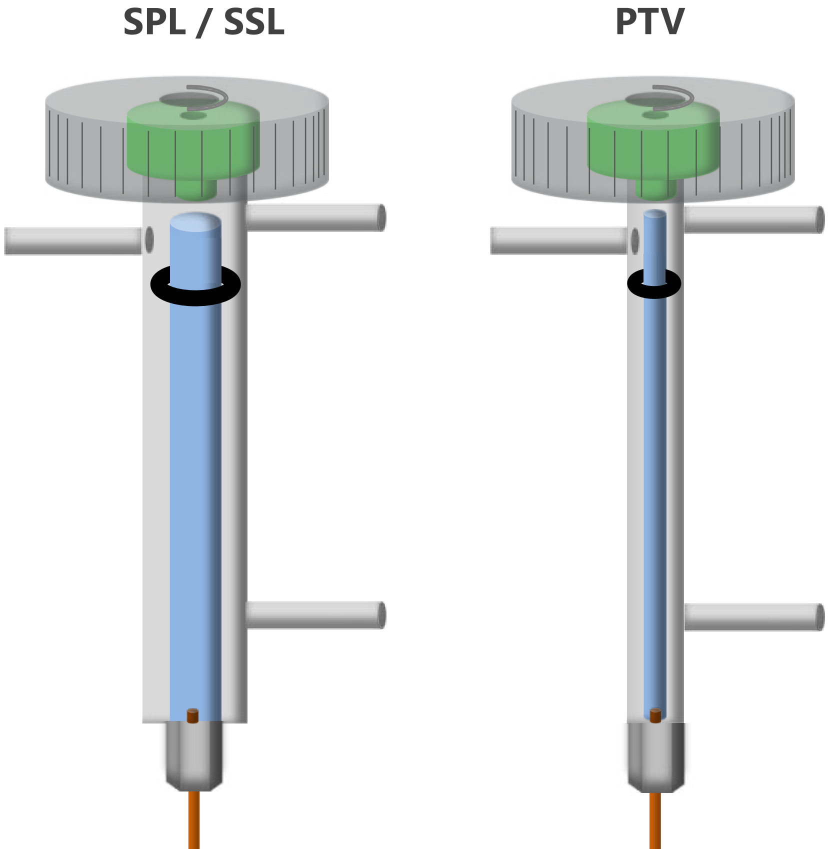


Programmable Temperature Vaporisation (PTV)

SPLs are isothermal inlets.

PTV technique uses a **programmable temperature** on the inlet.

Inlet is significantly narrower than SPL, reducing liner volume to <100 uL.



Programmable Temperature Vaporisation (PTV)

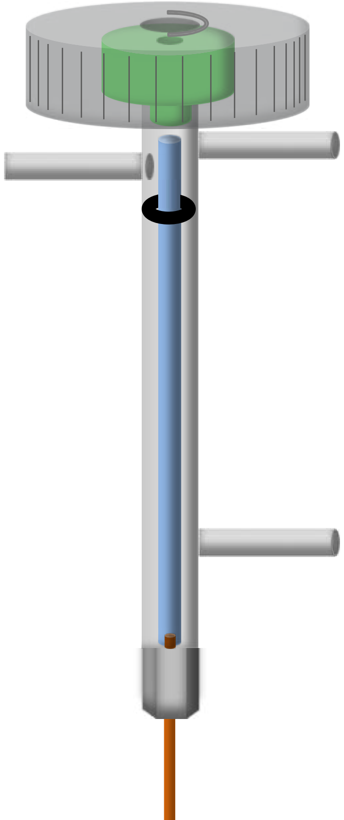
SPLs are isothermal inlets.

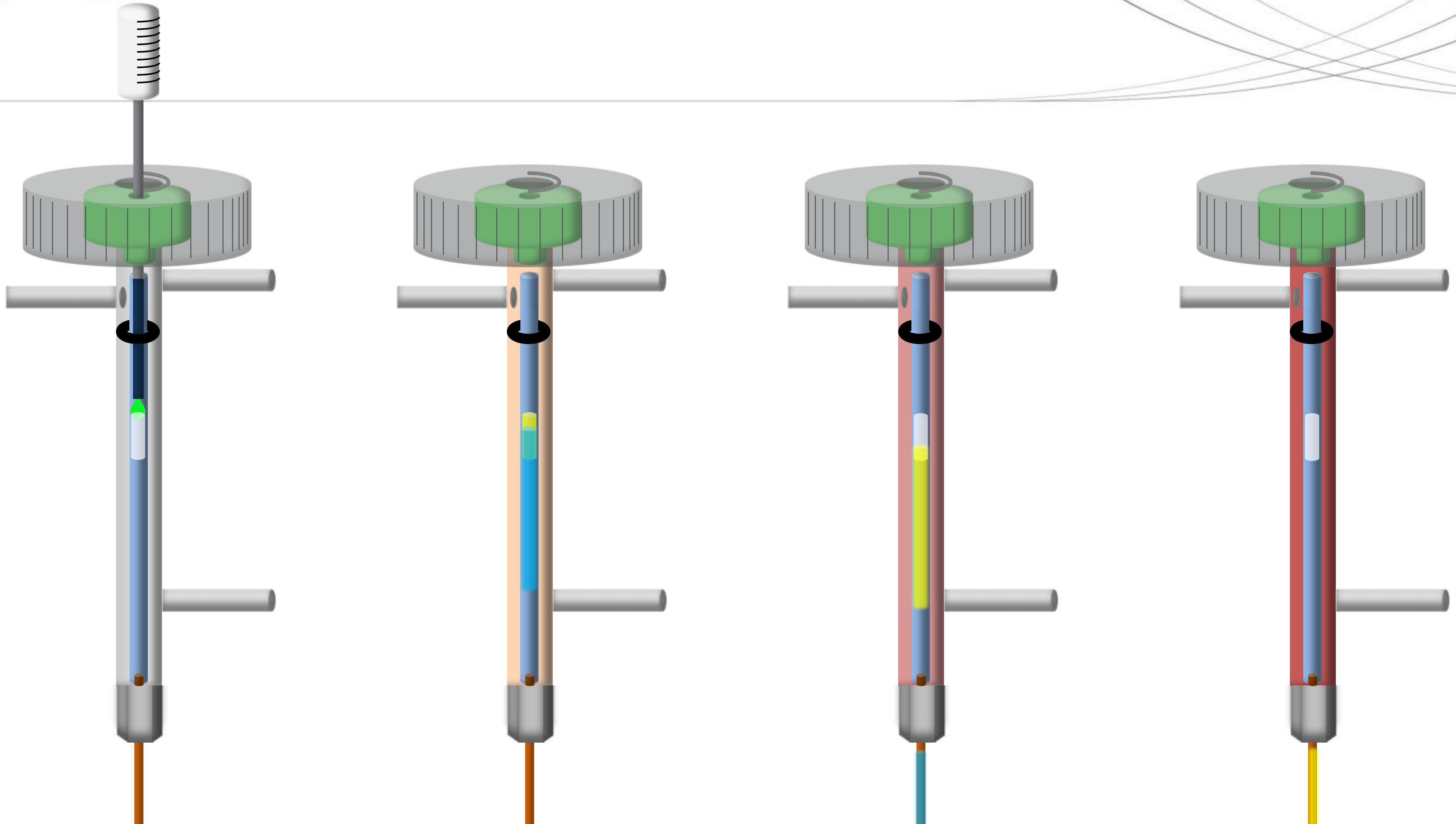
PTV technique uses a **programmable temperature** on the inlet.

Inlet is significantly narrower than SPL, reducing liner volume to <100 uL.

‘Cold’ injection at 40-50 °C before controlled heating.

Heating rate can be up to 250 °C/min.



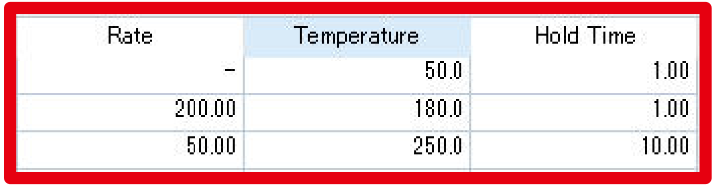


Operation

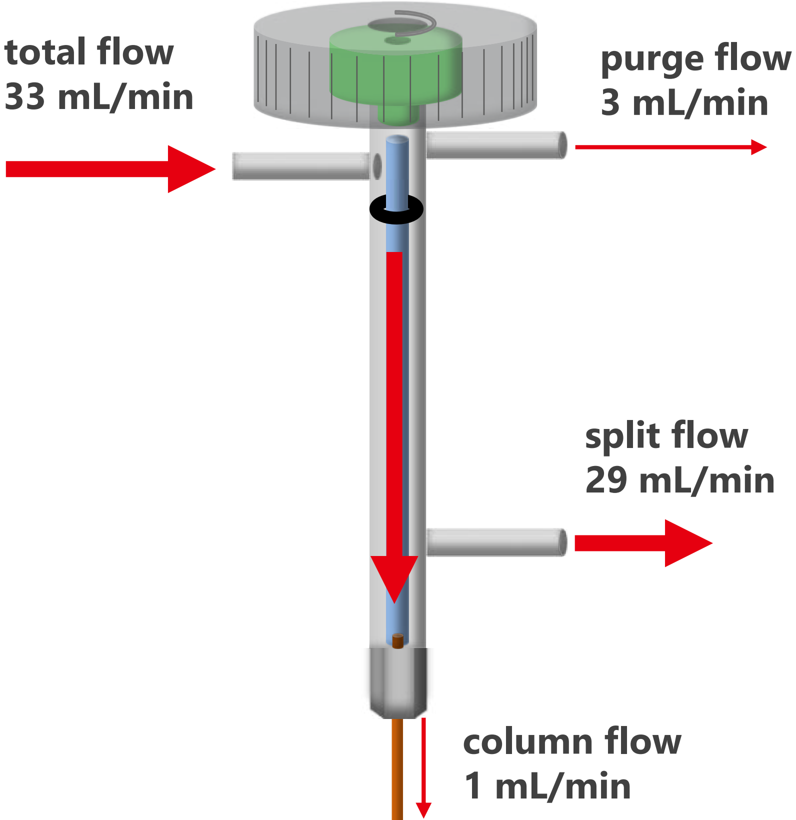
PTV can be operated just like an SPL:

- Split mode
- Splitless mode

Key difference is inlet temperature program:



Rate	Temperature	Hold Time
-	50.0	1.00
200.00	180.0	1.00
50.00	250.0	10.00



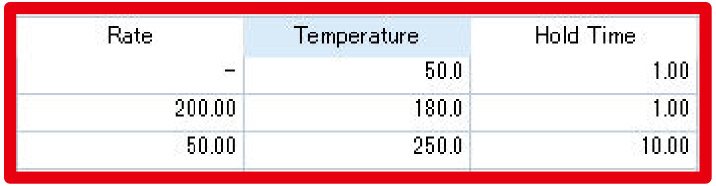
total flow
33 mL/min

purge flow
3 mL/min

split flow
29 mL/min

column flow
1 mL/min

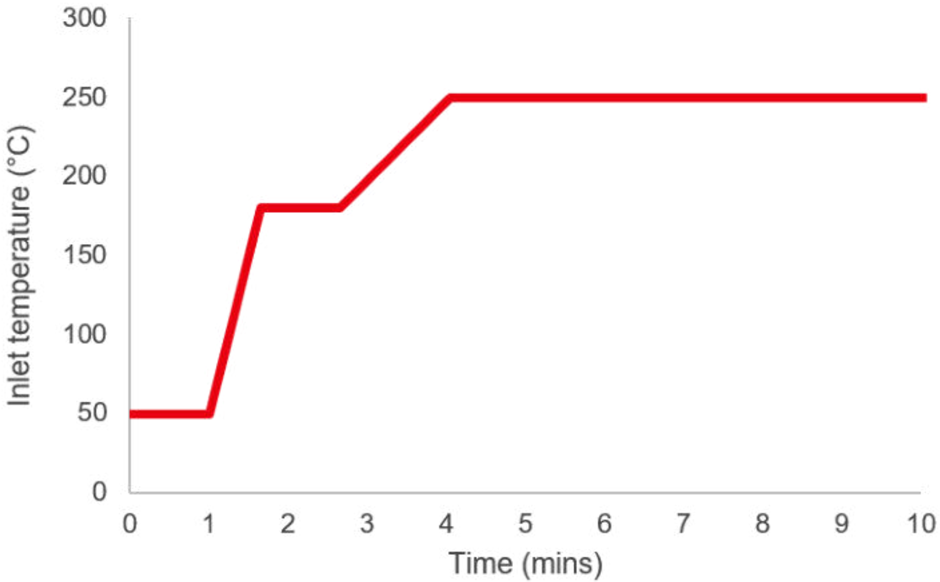
Temperature program



Rate	Temperature	Hold Time
-	50.0	1.00
200.00	180.0	1.00
50.00	250.0	10.00

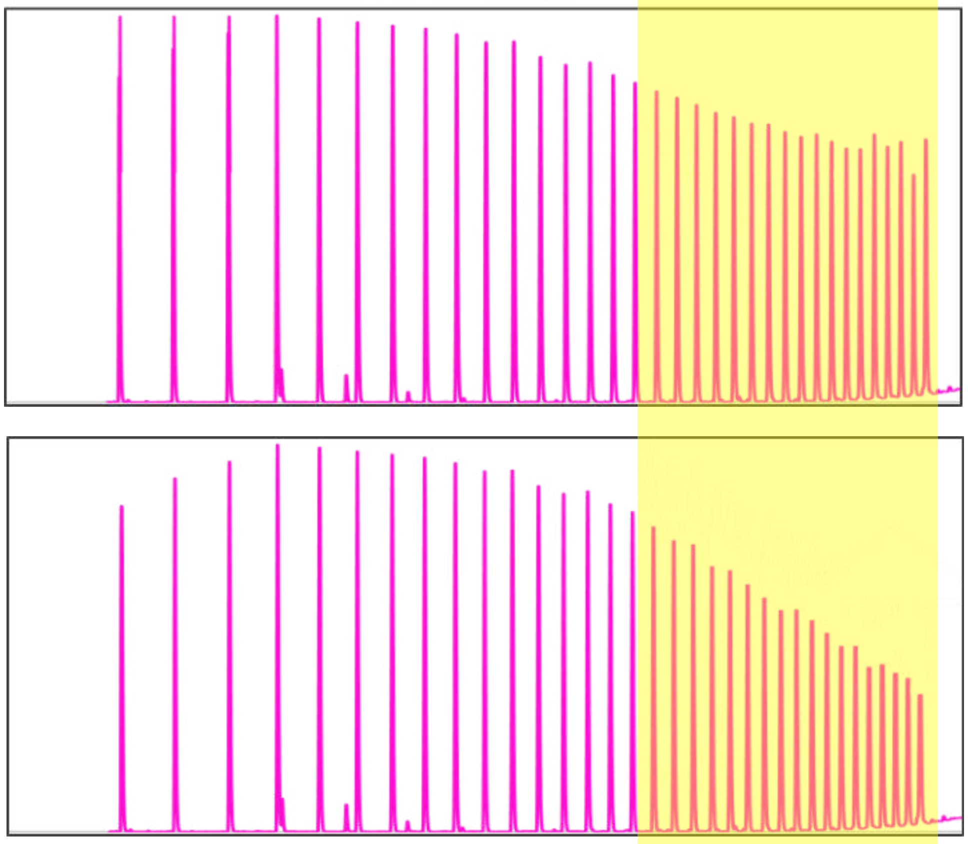
Temperature increase tends to be rapid

Holds can be used to enable complete transfer of labile compounds before further heating



Samples with wide boiling point ranges

Very wide boiling point range



SPL inlets can suffer from **mass discrimination**.

This results in a change in response for the early and late eluting species compared to compounds in the middle.

$$\frac{\textbf{Area (n-C60)}}{\textbf{Area (n-C10)}} = \textbf{mass discrimination}$$

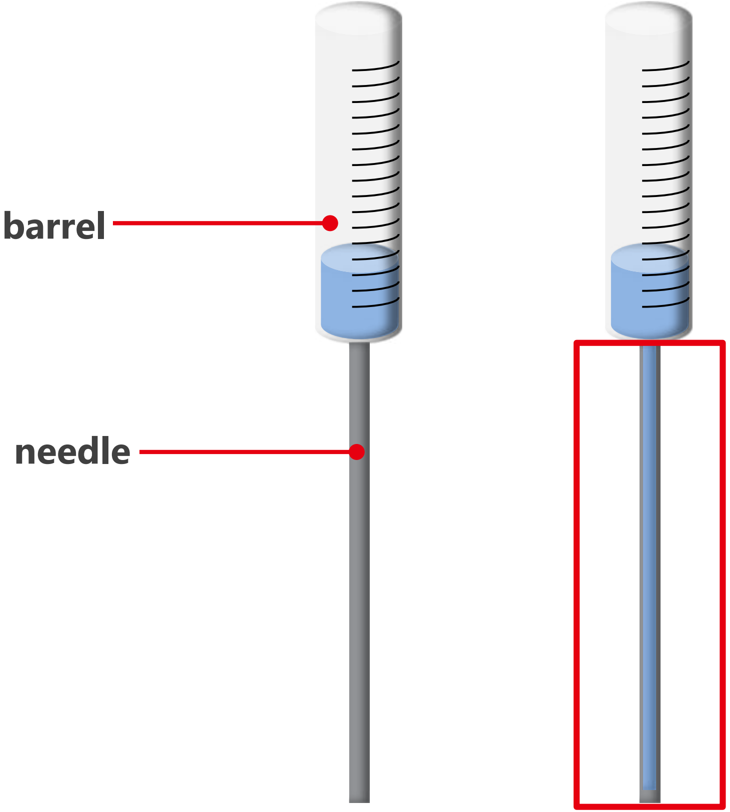
Mass discrimination

Caused by **syringe** (indirectly).

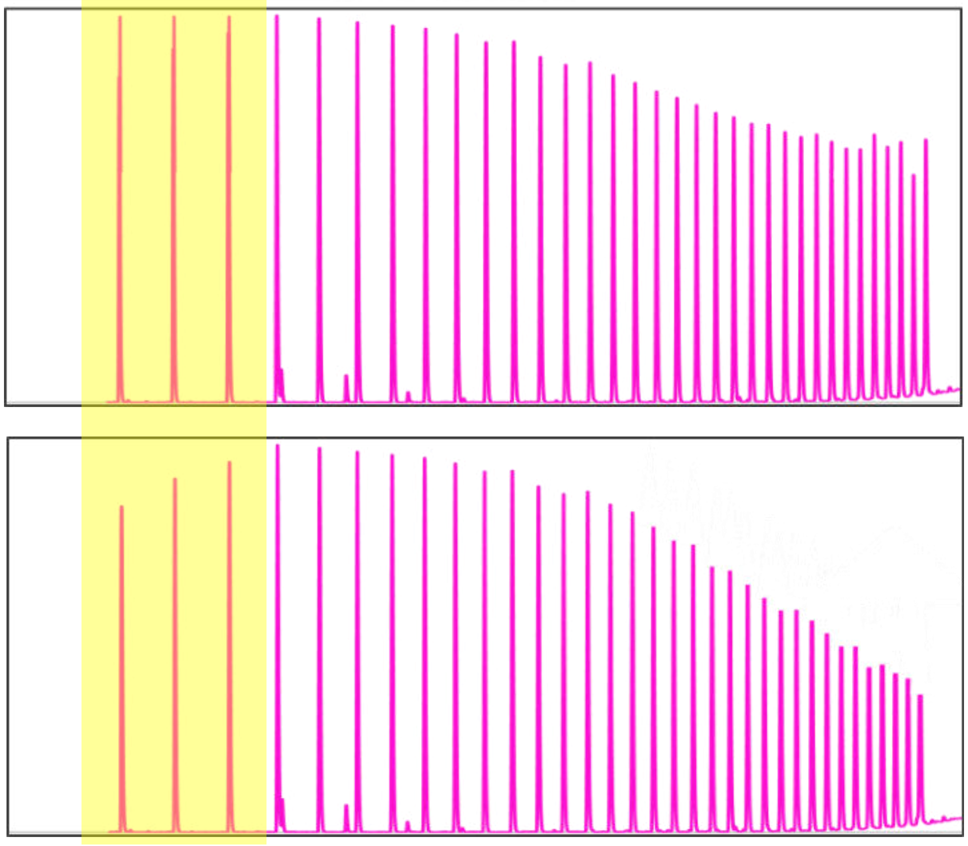
Volatile content in the syringe's needle is vaporised during injection process.

High-boiling content remains within the needle.

Also caused by insufficient inlet temperature.



Very wide boiling point range



Mass discrimination at the **front-end** is also possible.

Usually from evaporation of volatiles during sample preparation or storage.

Front-end discrimination

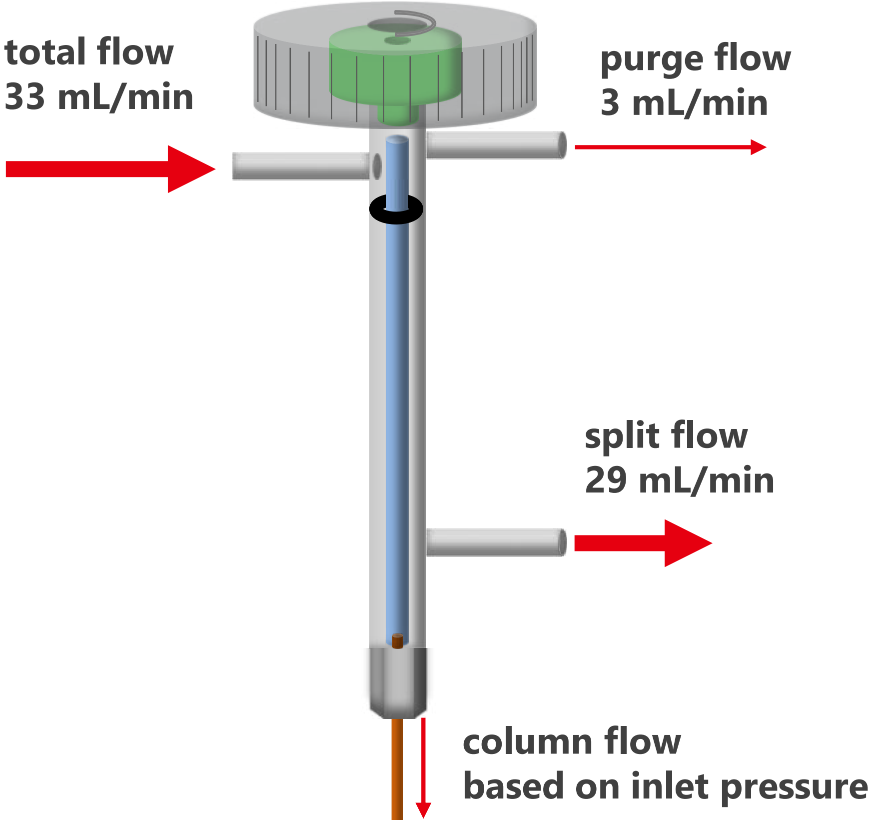
Volatile components diffuse faster.

Diffusion into purge line is possible, resulting in loss of peak area.

Vaporisation creates a pressure spike. This causes spike in column flow:

$$\frac{29 + 1\ \text{mL/min}}{1\ \text{mL/min}} = 30:1$$

$$\frac{29 + 1.5\ \text{mL/min}}{1.5\ \text{mL/min}} = \textbf{approx. 20:1}$$

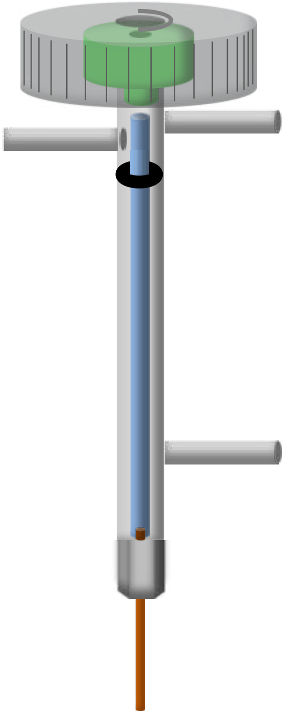


Modern GC systems

Mass discrimination is far less pronounced in modern split/splitless inlet systems:

- Autosamplers can inject in a fraction of a second.
- Flow controllers can monitor and respond to inlet pressure variations extremely quickly.
- Inlet & liner geometries have been optimised.

But they’re still not perfect!



Standard methods (ASTM, DIN, EN, ISO, etc.)

ASTM D7169

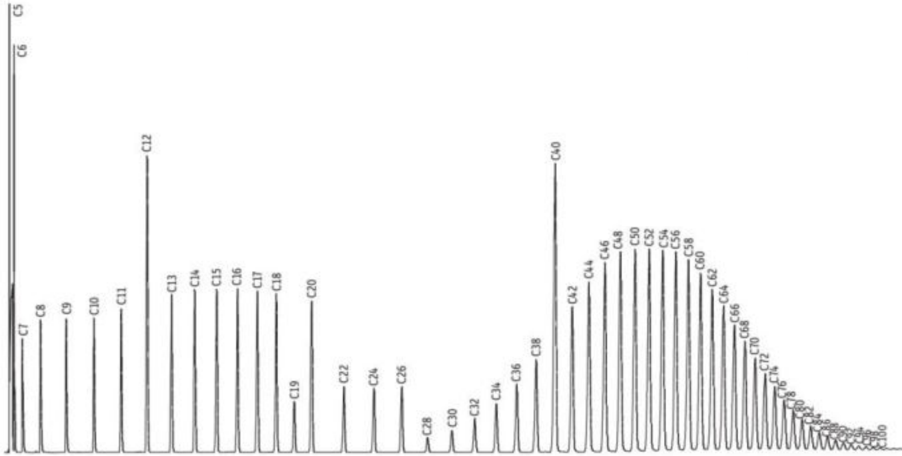
Analysis of boiling point distribution in samples containing crude oil residues.

Technique is known as simulated distillation (or SimDist).

n-C5 – n-C100 range.

Must be performed using inlet with programmable temperature!

Most often used with an **on-column injector**.



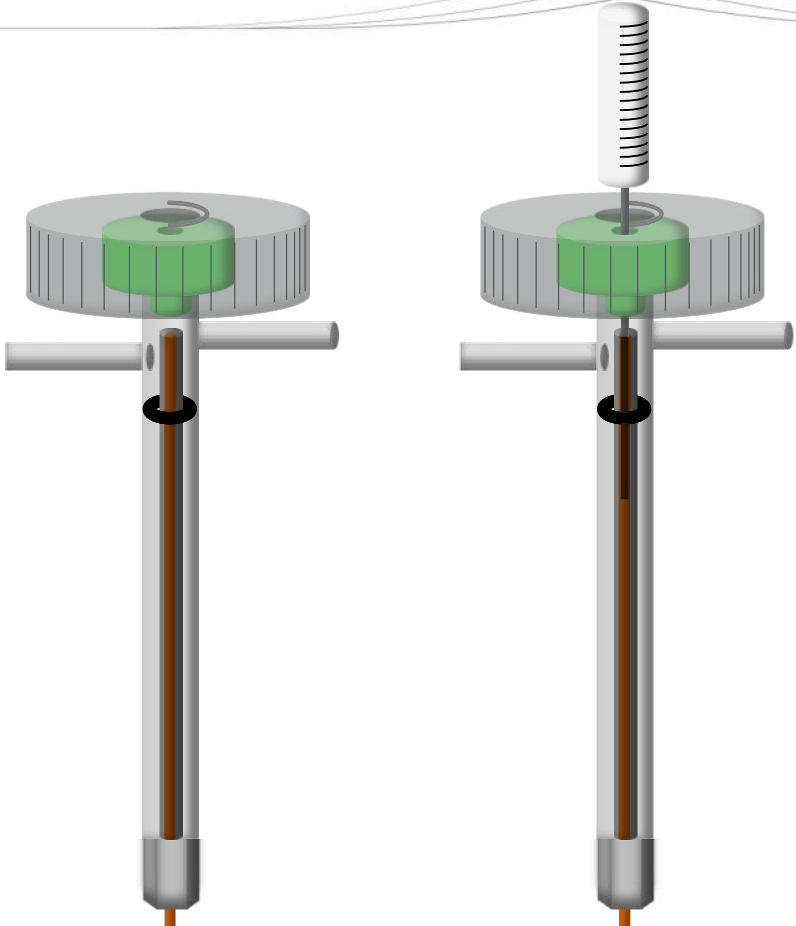
On-column injection

Sometimes called cool-on column (COC)

Almost identical to a PTV inlet, except the sample is **injected directly into the column**!

No ability to 'split' the sample – splitless injection.

Well suited to **chemically labile/active compounds**.



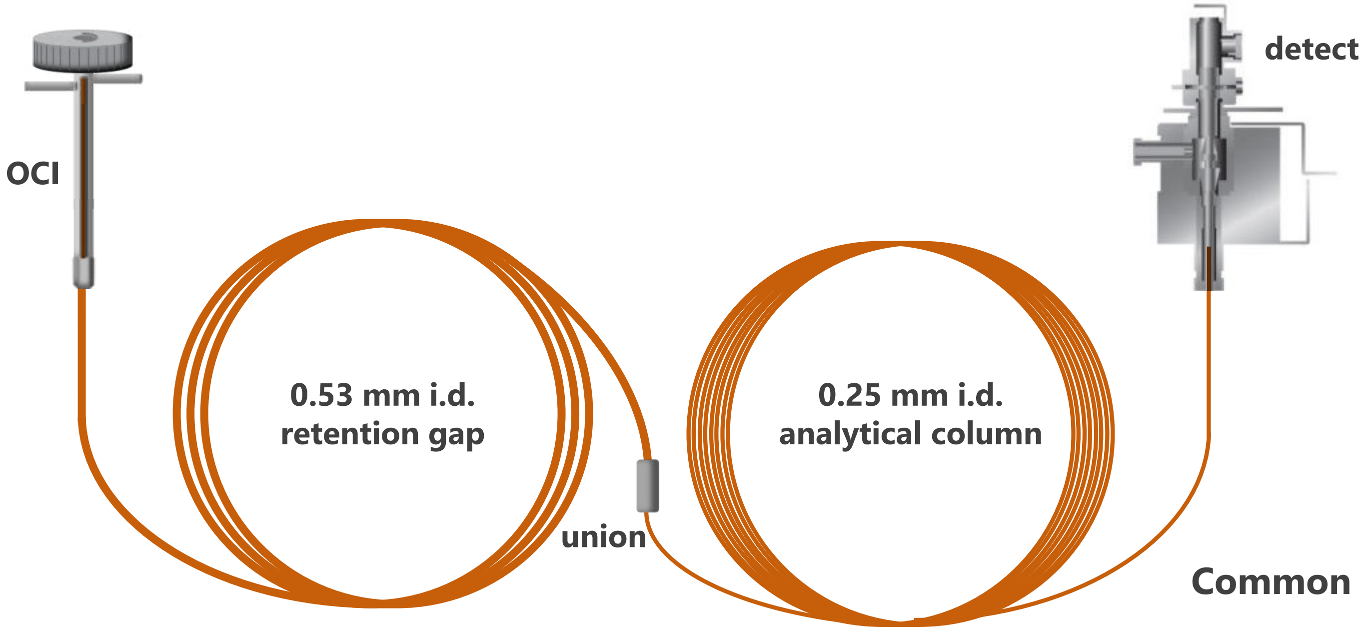
Hardware requirements

OCI has specific hardware requirements:

Column i.d. > Needle o.d.

Column installed into inlet must be **0.53 mm i.d.**

Hardware requirements



Common unions:

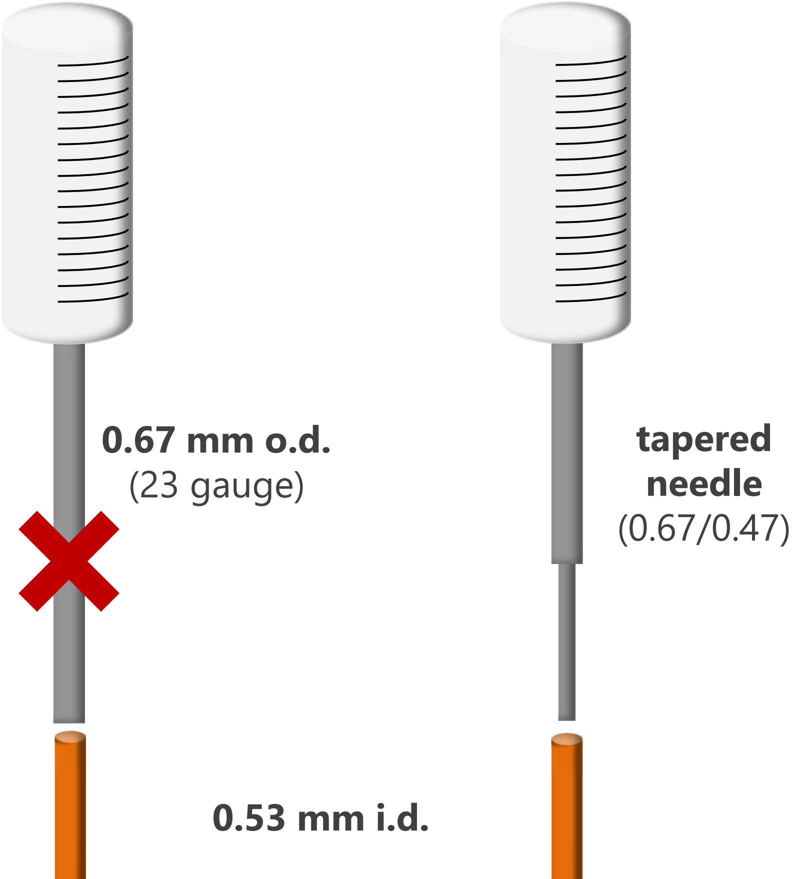
- Press-Tight
- Trajan SilTite Mini Union
- Trajan SilTite µ-Union

Hardware requirements

OCI has specific hardware requirements:

Column installed into inlet must be **0.53 mm i.d.**

Syringe needle must be **0.47 mm o.d.** (26 gauge)
or use a tapered needle



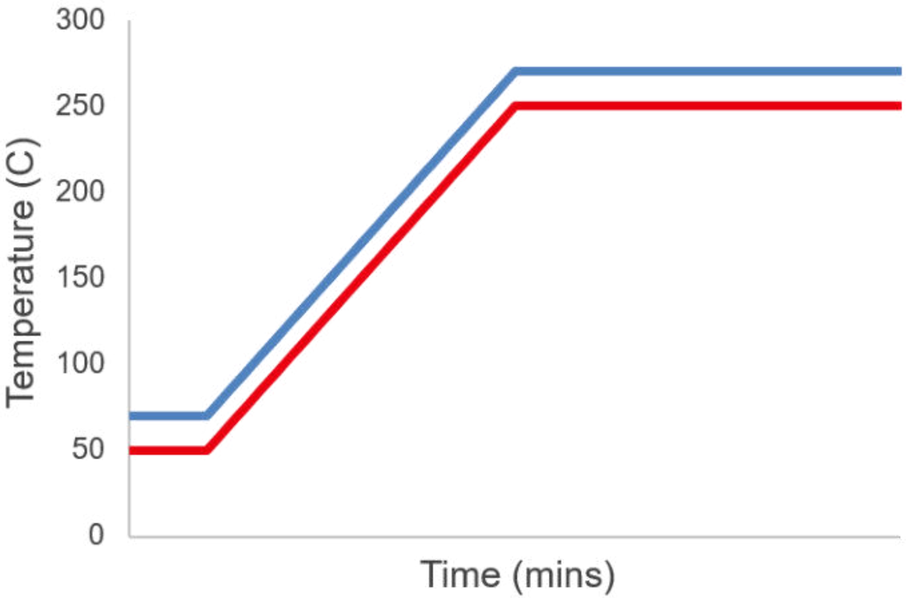
Operation & temperature program

OCI can be operated in the same manner as PTV, but there's no split option.

For OCI, the inlet is an extension of the oven.

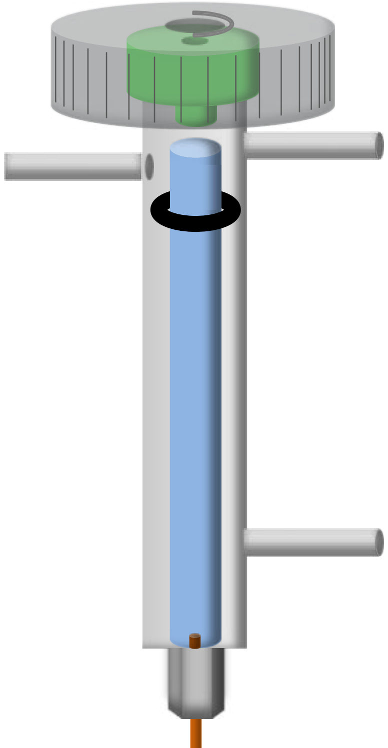
Same temperature program used for the oven and the inlet.

Some methods will use an offset of approx. ±20 °C between oven and inlet.

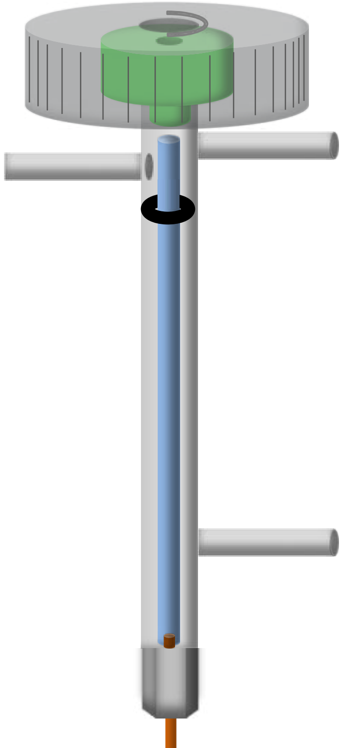


Comparison

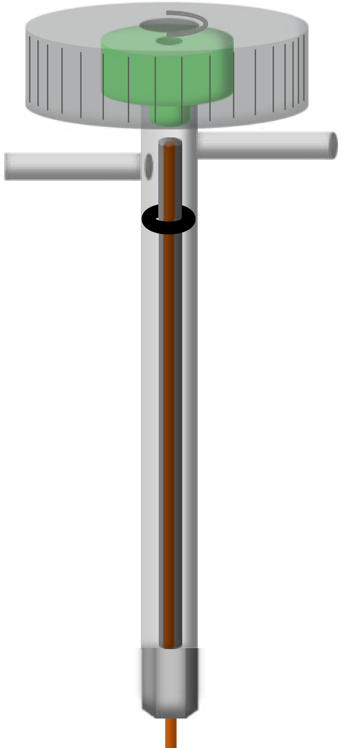
SPL / SSL



PTV



OCI / COC



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Multi-mode inlets

Best of both worlds

Multi-mode inlet must offer the functionality of SPL & PTV:

SPL

Hot split/splitless injections
with high reproducibility & good liner volume

PTV

Cold split/splitless injections
with no mass discrimination

Modern MMIs can offer significantly more than this…

MMIs

The OPTIC-4 can do:

- Hot split/splitless injection (SPL)
- Cold split/splitless injection (PTV)
- Direct on-column injection (OCI)
- Pyrolysis
- Thermal desorption
- In-system derivatisation
- Difficult Matrix Introduction (DMI)
    - For solids & difficult liquids

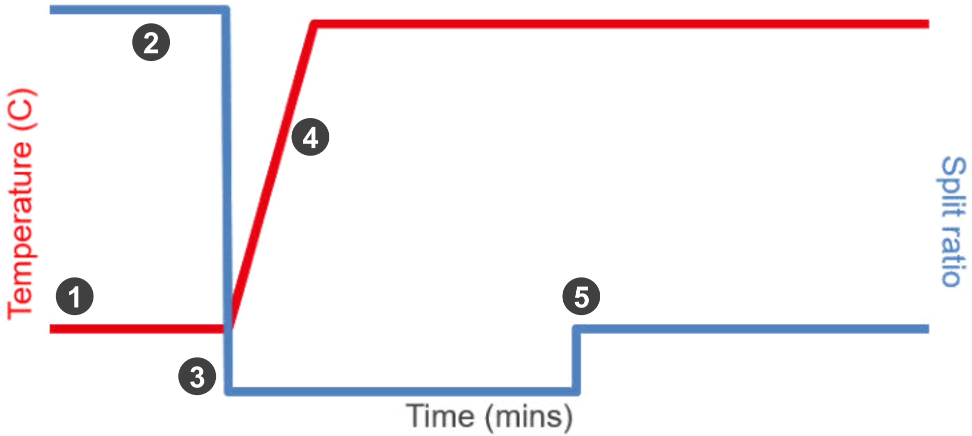
Large Volume Injection (LVI) enables analysis of ultra-trace analytes.

Large Volume Injection (LVI)

Requires high-capacity liner or slow injection speed.

1. Inlet temperature starts just below solvent boiling point.
2. High split ratio (>100:1) means, as solvent evaporates, very little goes on the column.
3. Once solvent evaporation is complete, split ratio drops to 0 for splitless injection of analytes.
4. Inlet heats and sample is transferred to column.
5. Split vent opens after sampling time.

Solvent must be more volatile than analytes!



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Summary

Comparison

	SPL / SSL	PTV	OCI / COC	MMI
Novice user	✓	~	~	✗
Hot split injections	✓	✗	✗	✓
Hot splitless injections	✓	✗	✗	✓
Cold split injections	✗	✓	✗	✓
Cold splitless injections	✗	✓	✓	✓
Thermally labile	✗	✓	✓	✓
Chemically labile	~	✗	✓	✓
Wide boiling point range	~	✓	✓	✓

Summary

- **The split/splitless inlet is best suited to hot split & hot splitless injections**
  - It can cause thermal degradation of labile compounds, such as pesticides
  - It suffers from mass discrimination for samples spanning a wide boiling point range

- **Programmable temperature vaporisation (PTV) is suitable for cold split & cold splitless injections**
  - This is ideal for analysing thermally labile species
  - Does not suffer from mass discrimination
  - Differs from SPL by having a programmable temperature and a smaller liner volume

- **On-column injection (OCI) is suitable for cold splitless, or direct, injections**
  - Alternative to PTV, but offers no split capabilities
  - Suitable for chemical active and labile compounds by bypassing the liner
  - Requires 0.53mm i.d. column, or retention gap, and 26 gauge needle or tapered needle

- **PTV & OCI inlets are not suitable for hot split or splitless injections**
  - Offer poor reproducibility & robustness

- **Multi-mode inlets can combine the functionality of SPL & PTV in a single inlet**
  - They can often perform far more sampling types, too!

Next time

The next session will be on…

Alternative to Liquid Injection

This will cover:

- *Headspace (HS)*
- *Thermal Desorption (TD)*
- *Solid Phase Micro-Extraction (SPME)*
- *Pyrolysis (Py)*
- *Gas Sampling*

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Theory and Key Principles Series
Gas Chromatography (GC)

Session 5 – Alternatives to Liquid Injection

Theory & Key Principles Series – GC

- *Introduction to Gas Chromatography **
- *GC Columns **
- *The Split/Splitless Inlet **
- *Advanced Liquid Injection Techniques **
- **Alternatives to Liquid Injection**
- Choice of Detectors for GC
- Processing GC Data
- Maintenance & Troubleshooting

** Now available on demand at www.shimadzu.co.uk/webinars*

Alternatives to Liquid Injection

In this presentation:

- Headspace (HS)
    - Loop & Syringe systems
- Solid Phase Micro-Extraction (SPME)
- Thermal Desorption (TD)
- Pyrolysis (Py)
- Gas Sampling Valves (GSVs)

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Headspace (HS)

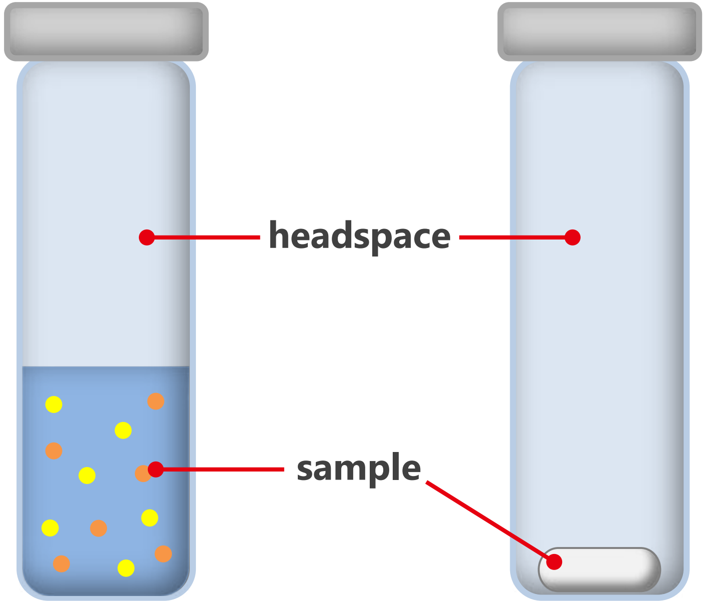
Headspace

‘Headspace’ (HS) is the **gas above a sample**, where the sample can be **liquid** or **solid**.

Headspace is a **sample pre-treatment** technique for the analysis of **VOCs** (volatile organic compounds).

Suitable for **solid** & **liquid** samples.

Enables analysis of samples with a dirty **sample matrix**.



Common HS-GC applications:

- *Blood alcohol content*
- *Testing for residual solvents in pharmaceuticals*
- *Analysing toxic VOCs in waste water (usually HS-GCMS)*

Principles of headspace

In a **sealed vessel**, molecules of analytes exist in the **sample phase** or the **gas phase** (headspace).

A **partition coefficient** (**K**), is the distribution of analytes, at equilibrium, in the sealed vessel.

- K is dependant on the analyte, the sample matrix & temperature.

The **phase ratio** (**β**) relates to the relative volumes of sample and headspace in the vial.

Solvent	K Value
Ethanol	1355
Isopropanol	825
Ethyl acetate	62.4
Dichloromethane	5.65
Toluene	2.82
Cyclohexane	0.077

Air/water system at 40 °C

$$K = \frac{\text{Conc. (sample)}}{\text{Conc. (gas)}}$$

$$\beta = \frac{\text{Volume (gas)}}{\text{Volume (sample)}}$$

$$\text{HS conc.} = \frac{\text{Sample conc.}}{(K + \beta)}$$

Smaller K = Higher sensitivity

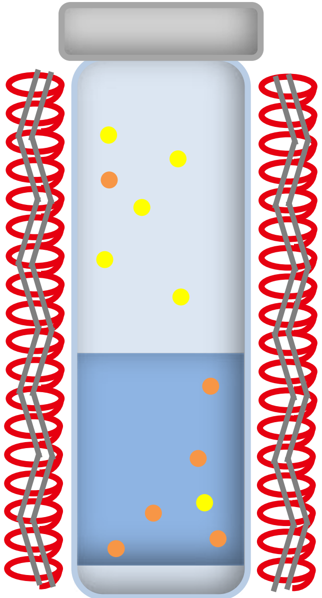
Smaller β = Higher sensitivity

Heating & agitating

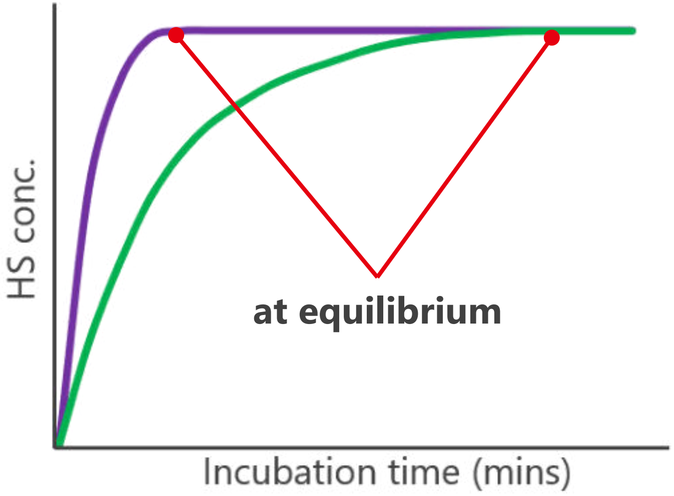
In almost all headspace analysis, the sample is **heated**, or incubated.

	K Value	
Solvent	**40 °C**	**80 °C**
Ethanol	1355	328

There are two benefits to this:
- Ensures constant temperature (stable K)
- Reduces K (higher sensitivity)
  - *Inorganic salts can also be added to liquid samples to reduce K further Known as '**salting out**'*



Samples also tend to be **agitated**.
This reduces the **equilibration time**



With agitation

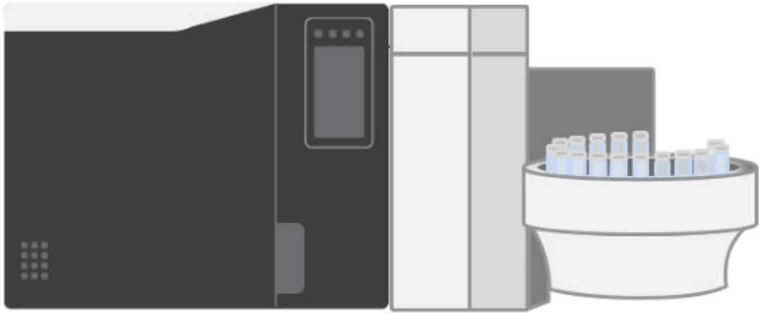
Without agitation

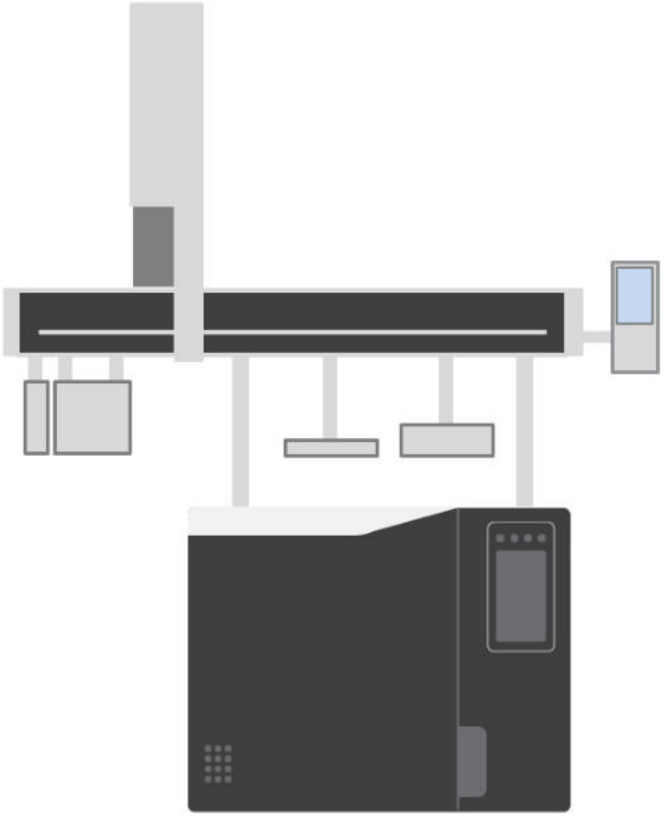
Headspace autosamplers

Two main types of autosampler systems:

Loop
- Sample vial is pressurised
- Pressure is released into fixed-volume loop
- Loop is flushed onto column
- Offers split or splitless operation *via* flow controller (no SPL)

Syringe
- Gas-tight syringe draws sample of gas from above solid/liquid
- Injects into split/splitless inlet



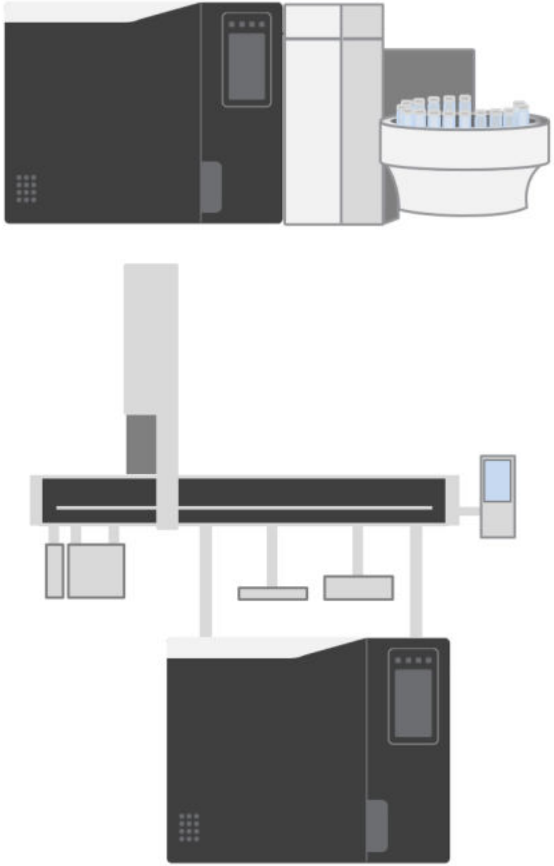


Dynamic headspace

Previous discussion covered **static headspace**.

Dynamic headspace continuously removes analytes from the headspace to reach **lower limits of detection**.

- **Multiple Headspace Extraction** (MHE) is **semi-dynamic** and involves multiple sampling steps on loop-based system, where **loop is flushed onto trap**.
- **Purge & Trap** bubbles carrier gas through sample to purge the analytes into gas.
- **In-Tool Extraction** (ITEX) uses a **syringe with a built-in trap** to draw analytes onto the trap.



Solid Phase Micro-Extraction (SPME)

SPME

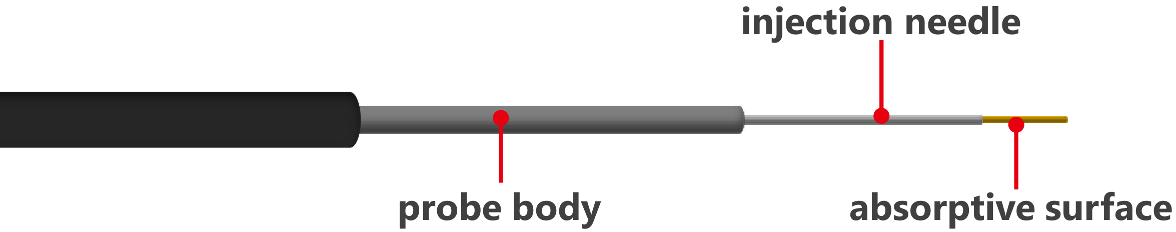
SPME is a **sample concentration** technique for **solids** & **liquids**.

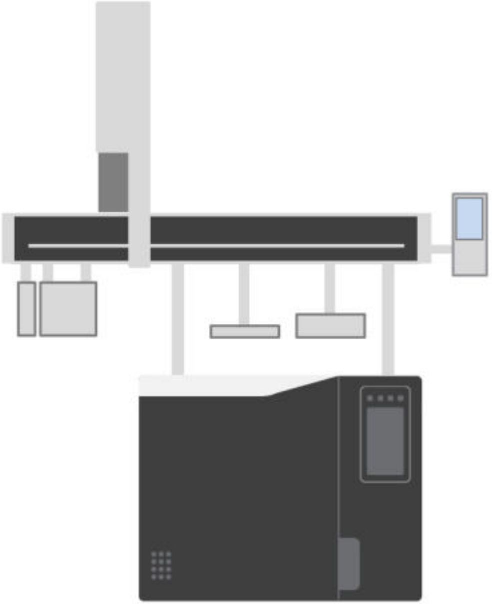
Used for **trace VOC & SVOC analysis**.

It uses a **solid sorbent** or **liquid polymer** to trap volatile analytes on a probe.

Common applications:

- *Food & beverage aroma/flavour profiling*
- *Low-level environmental pollutants*





SPME fiber materials

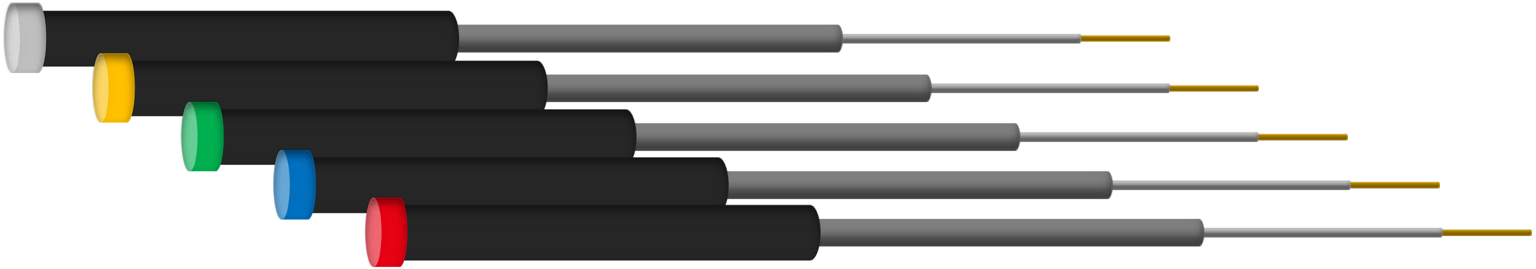
Range of sorbent materials and thicknesses.

Sorbent and analyte chemistries should match.

Common sorbents:
PDMS (polydimethylsiloxane)
Carboxen
DVB (divinylbenzene)
Polyacrylate
PEG (polyethylene glycol)

	Suitability
PDMS	Non-polar
Carboxen	Very volatiles
DVB	Aromatics
PA	Polar
PEG	Polar

Multi-sorbent option can be used for more universal analysis



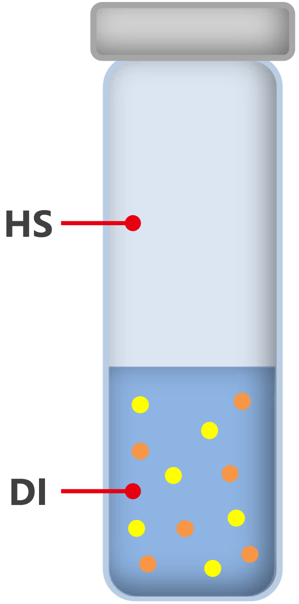
DI-SPME vs. HS-SPME

Liquid samples can be analysed using **Direct Immersion (DI)** or **Headspace (HS) SPME**.

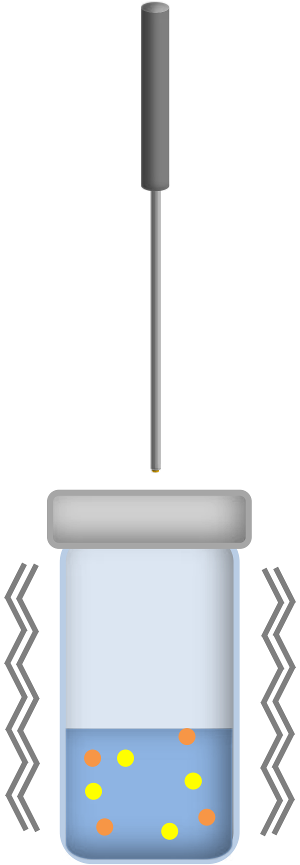
HS-SPME follows the same principles as typical headspace.

DI-SPME involves submerging the fiber into a liquid sample.

	DI-SPME	**HS-SPME**
Analyte volatility	Low to medium	High to medium
Analyte polarity	Medium to high	Low to medium
Matrix	Clean liquids are best	Any liquid or solid
Advantages	Higher-efficiency extraction	Can be used with very dirty matrices
Disadvantages	Shorter fiber lifetime Can require sample pre-treatment	Matrix modification may be required to boost sensitivity



SPME Sampling



DI-SPME

Sample agitation

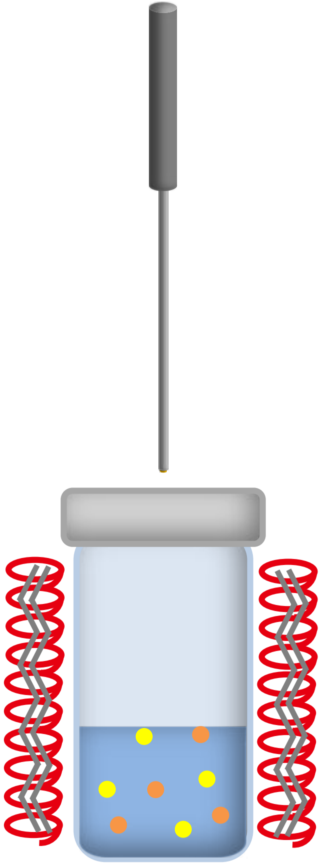
SPME probe inserted into liquid

HS-SPME

Sample agitation at elevated temperature

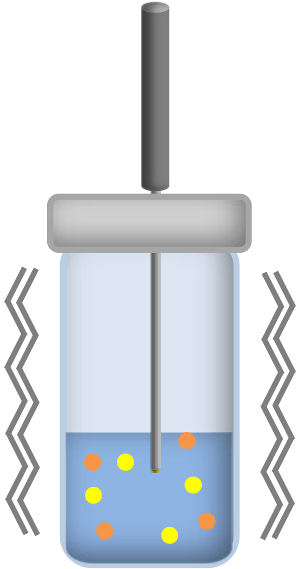
Equilibrium achieved

SPME probe inserted into headspace



SPME Sampling

DI-SPME



Sample agitation

SPME probe inserted into liquid

Fiber exposed

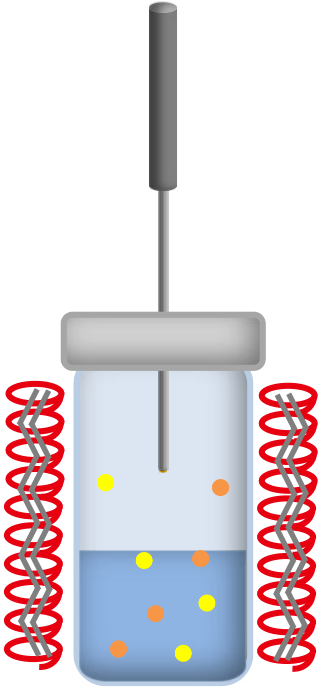
HS-SPME

Sample agitation at elevated temperature

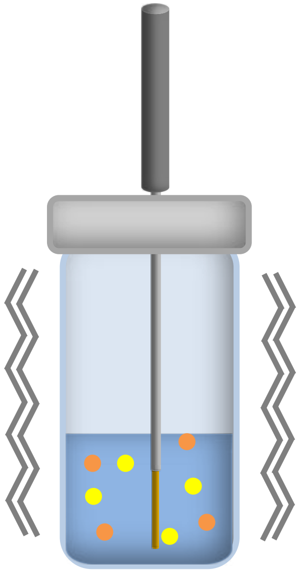
Equilibrium achieved

SPME probe inserted into headspace

Fiber exposed



SPME Sampling



DI-SPME

Sample agitation

SPME probe inserted into liquid

Fiber exposed

Analytes adsorb to fiber surface

Fiber removed and dried before sampling

HS-SPME

Sample agitation at elevated temperature

Equilibrium achieved

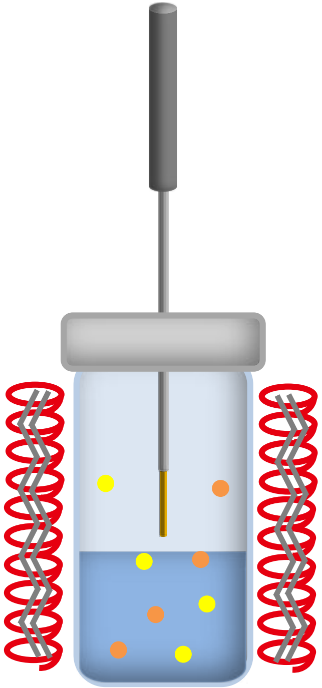
SPME probe inserted into headspace

Fiber exposed

Analytes in HS adsorb to fiber surface

HS concentration reduces

Analytes in sample re-partition to to maintain K value

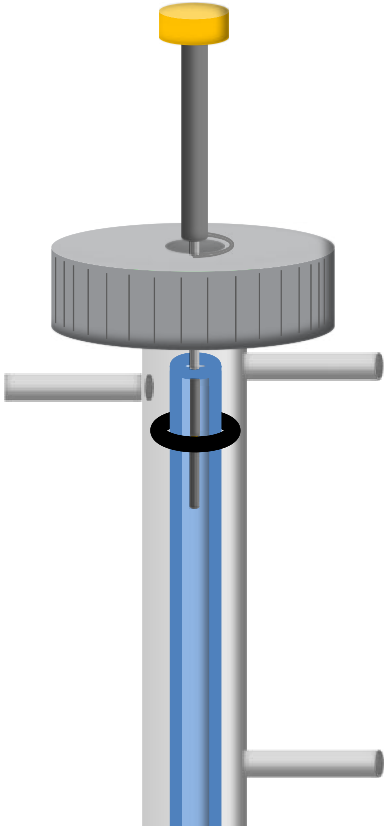


SPME Sampling

Probe is injected into hot split/splitless inlet & fiber exposed.

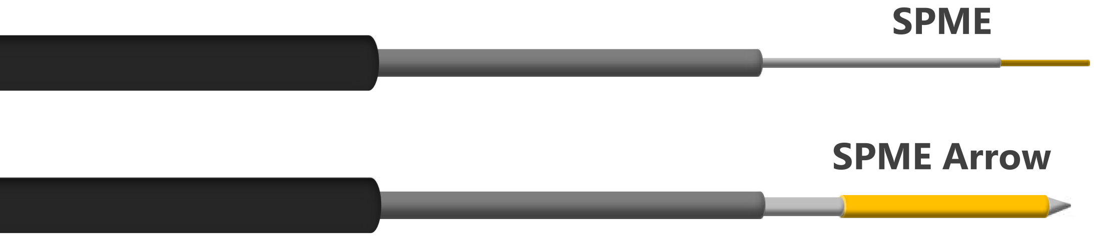
High temperatures desorb analytes from fiber.

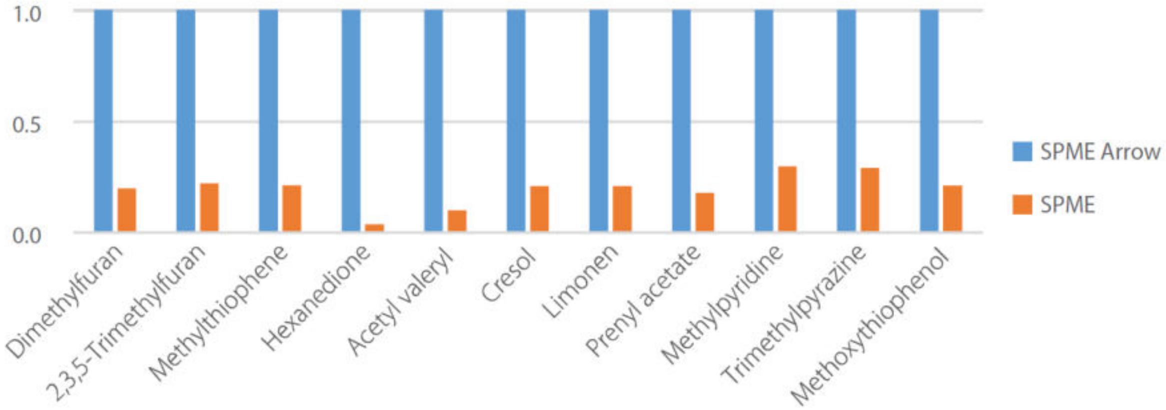
At this point, standard principles of split/splitless inlets apply.

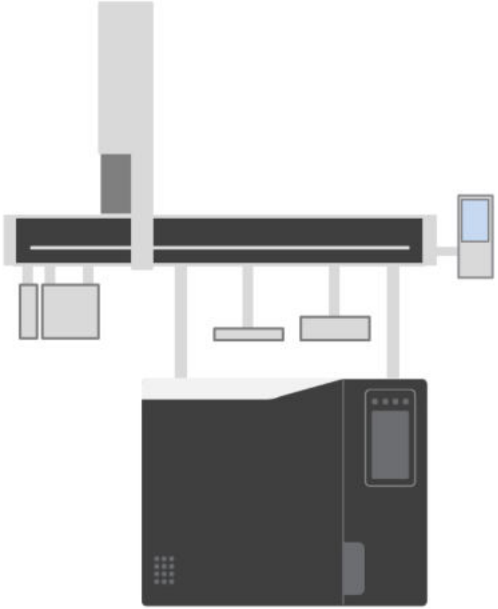


SPME Arrow

SPME Arrow technology offers a more robust & sensitive SPME solution.







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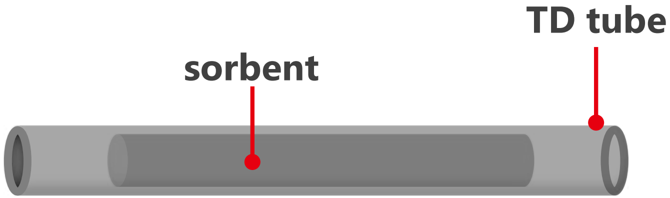
Thermal Desorption (TD)

Thermal desorption

Thermal desorption is a **sample pre-concentration** technique.

Wide range of sampling techniques available:

- Passive
- Active
- Permeation
- Breath
- *Direct*

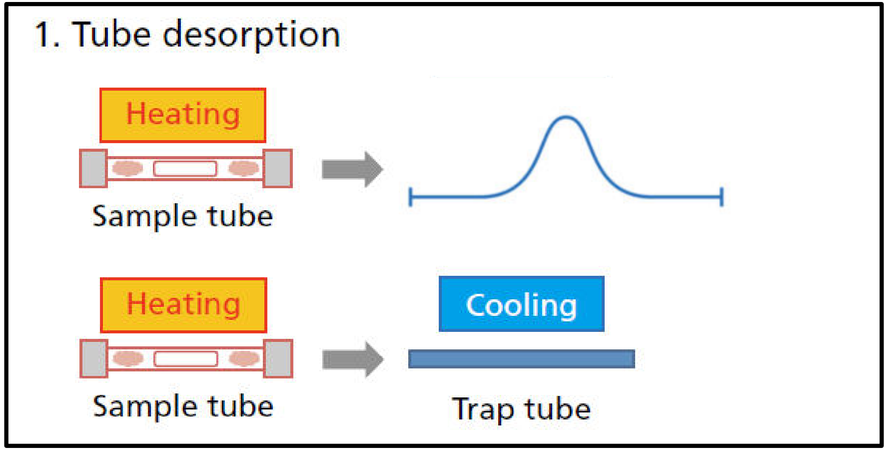


Common applications:

- *Monitoring air for toxic VOCs near landfill sites*
- *Workplace air monitoring*
- *Vehicle emission testing*
- *Aroma profiling in food & beverages*
- *Permeation of VOCs through packaging*
- *Detection of cancer markers in breath*

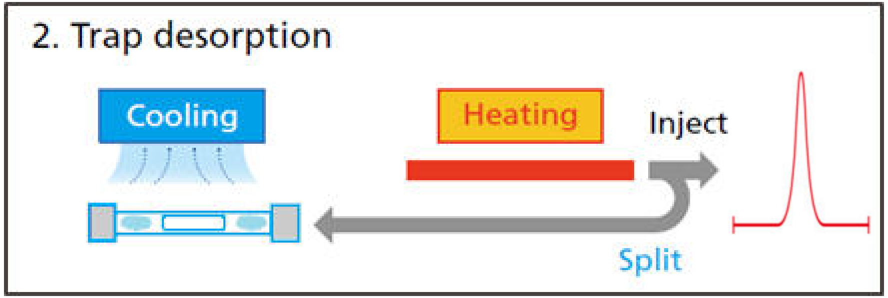
TD operation

- Sample tube is heated to desorb analytes.
- Desorption from sample tube can take several minutes.
- Desorbed onto a smaller 'trap', which is cooled to prevent samples breaking through.



1. Tube desorption

- Trap is rapidly heated to desorb analytes quickly onto the column.
- Sample can be diluted using split flow.
- Split flow can be recovered on second tube.



2. Trap desorption

Pyrolysis (Py)

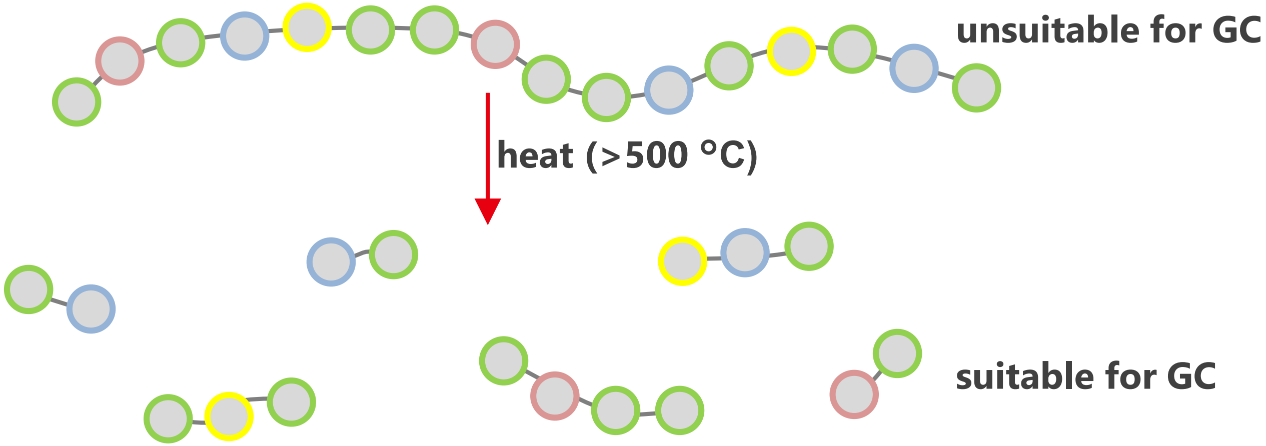
Pyrolysis

Pyrolysis is a technique that splits large molecules into smaller fragments (**pyrolysates**) using heat.

These smaller fragments are volatile enough for GC analysis.

Suitable for analysing a wide range of samples:

- *Plastics*
- *Rubber*
- *Adhesives*
- *Paints*
- *Polymer additives*
- *Wood*



unsuitable for GC

heat (>500 °C)

suitable for GC

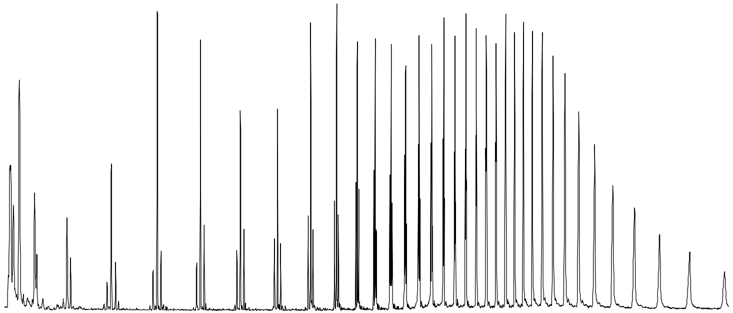
Pyrolysis techniques

Pyrolysers can be used in a variety of ways.

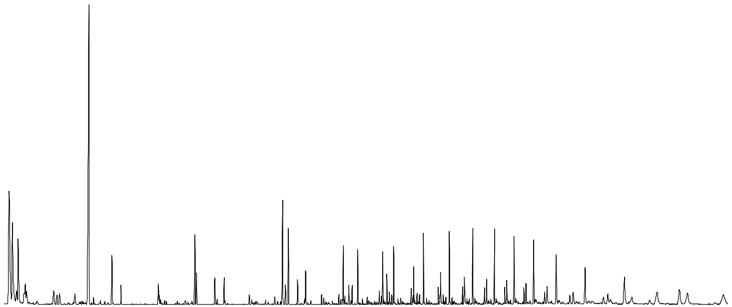
The most common is **single shot** or **flash pyrolysis**.

This can be used to identify polymers using **pyrograms**:

Polyethylene (PE)



Polypropylene (PP)



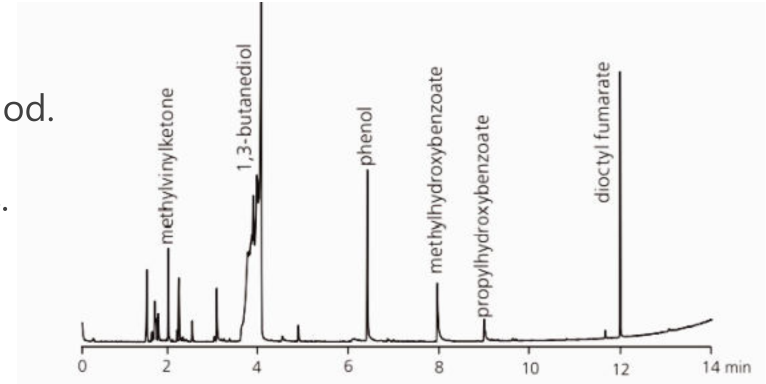
Pyrolysis techniques

Evolved Gas Analysis (EGA) is used for method development.

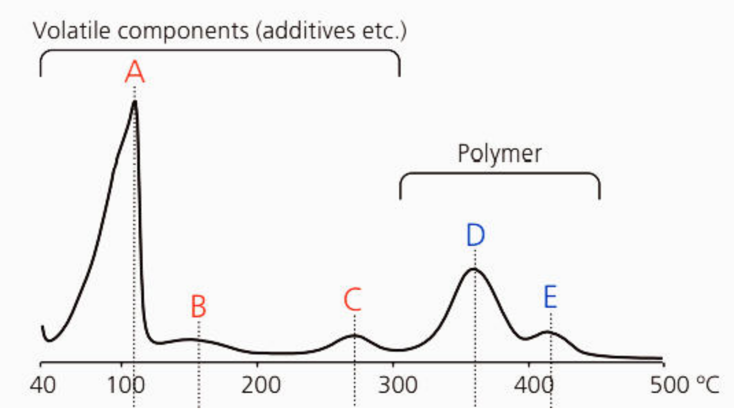
This information is used to create a double-, or multi-shot, method.

Sample is analysed at different temperatures to **simplify results**.

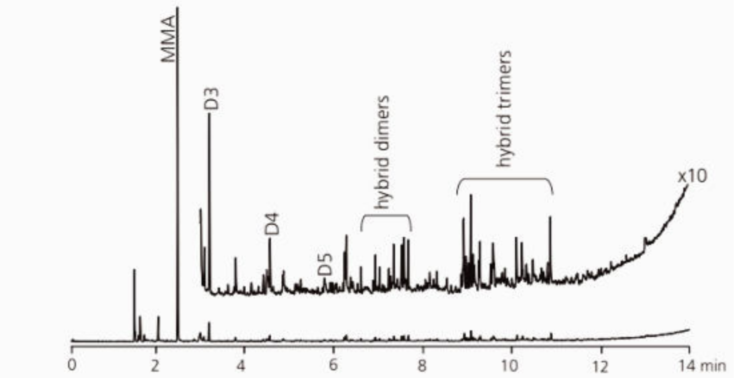
Peaks A+B+C [TD: 100 – 300°C]



EGA



Peaks D+E [Py: 600°C]

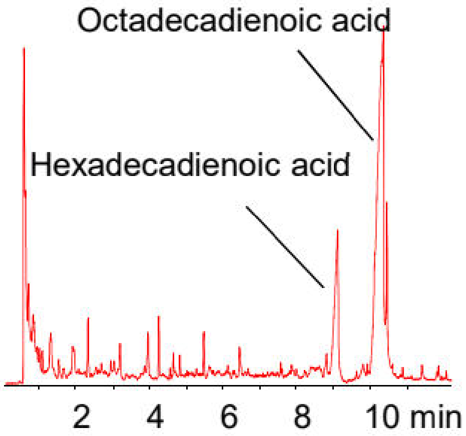


Catalytic pyrolysis (micro-reactors)

Some pyrolyser furnaces can be fitted with a catalyst bed.

Enables analysis of catalytic products of pyrolysates for catalyst development & optimal temperature and pressure settings for reactors.

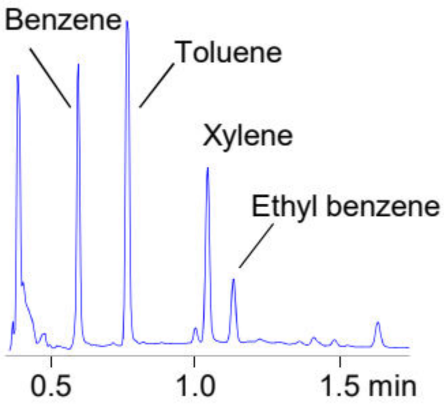
Without catalyst



Analysis of Jatropha (plant).

With zeolite catalyst, useful bio-based chemicals are generated.

With catalyst



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Gas sampling valves (GSVs)

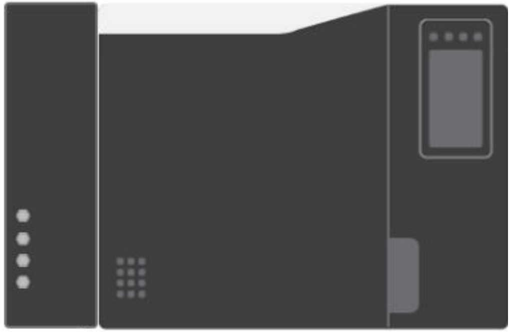
Gas sampling

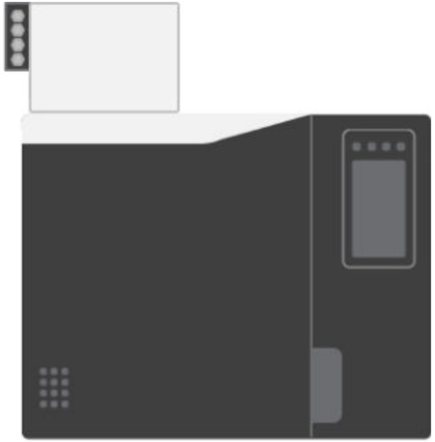
Analysis of **very volatile, gaseous samples**.

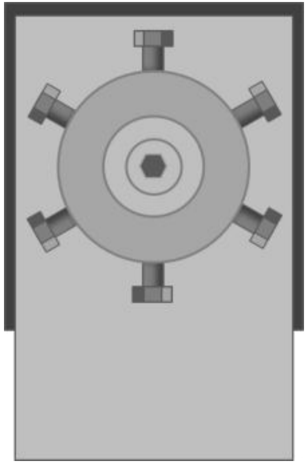
Injection *via* syringe gives poor reproducibility so gas sampling valves (GSVs) are used.

Common applications:

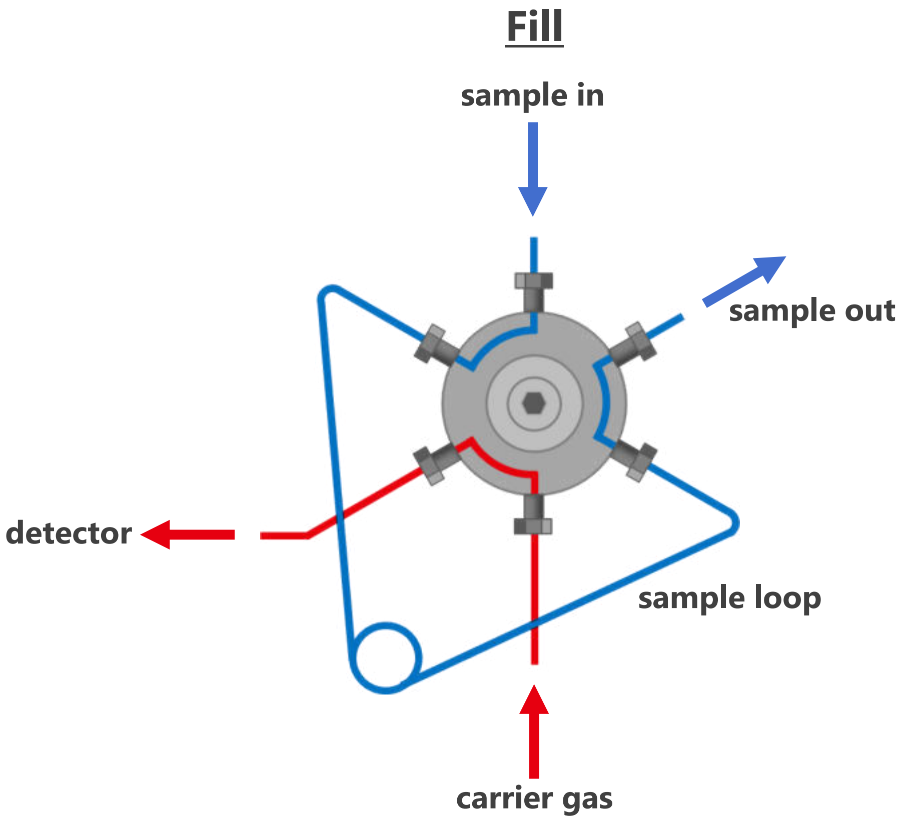
- *Reactor product analysis*
- *Hydrocarbon processing industry*
- *Gas purity analysis*
- *Mask breakthrough testing*

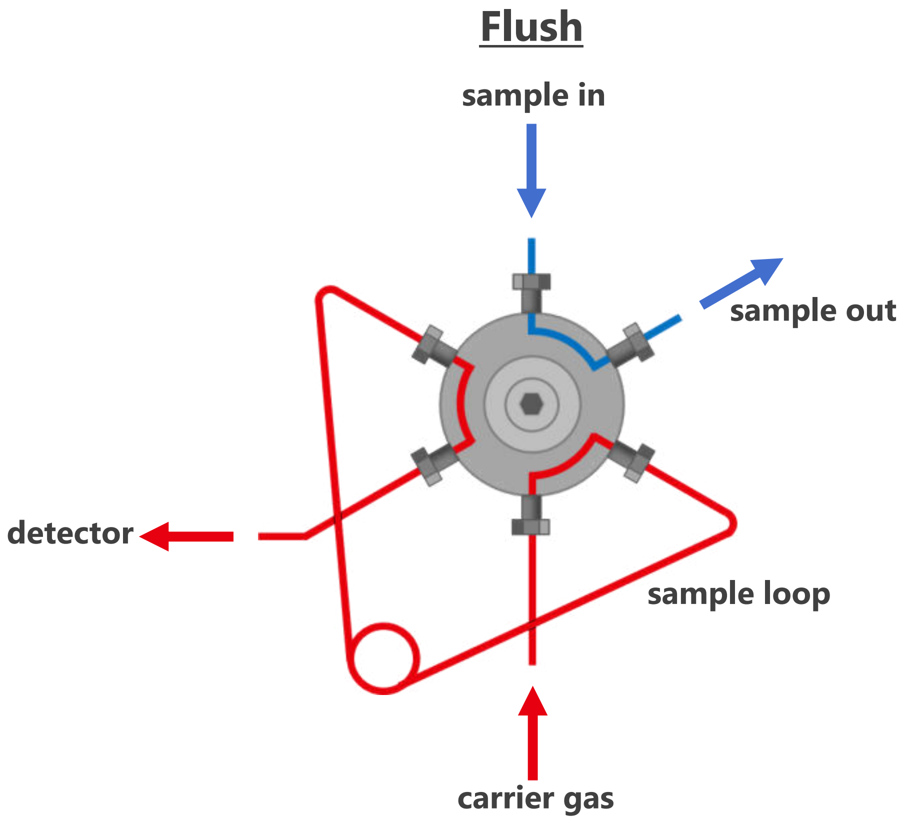






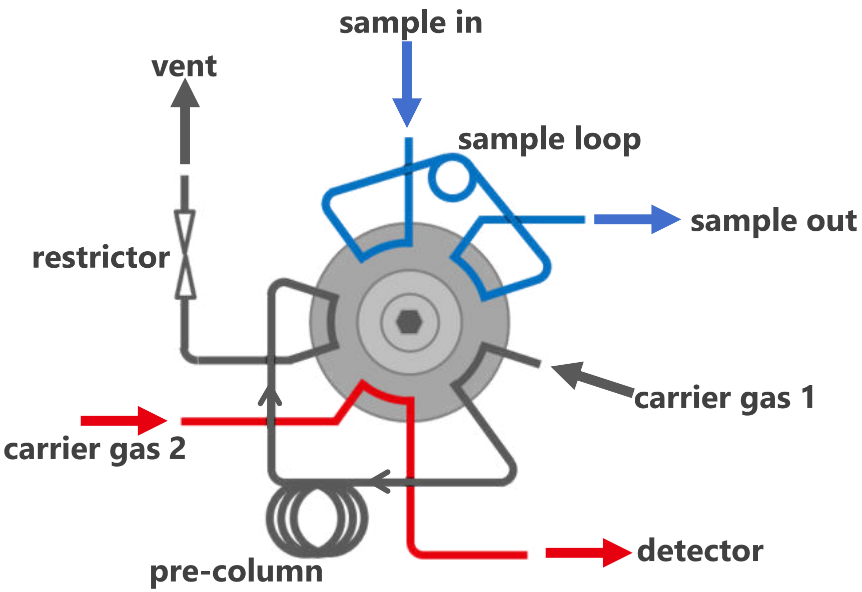
Basic 6-port valve operation



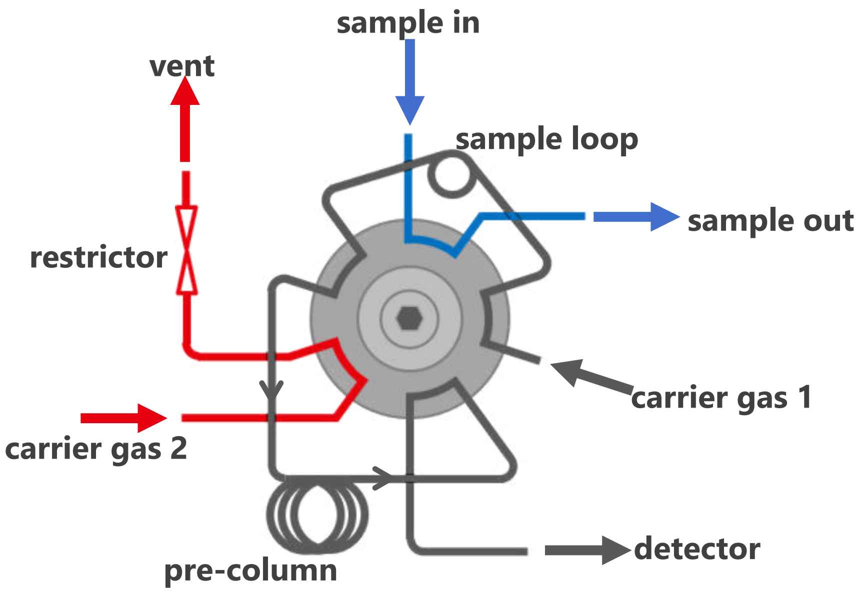


10-port valve operation (with pre-column backflush)

Fill

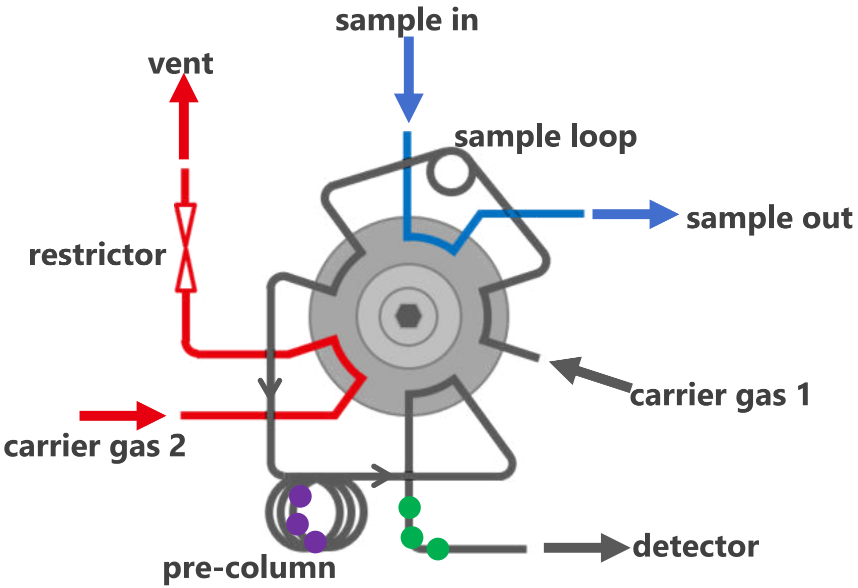


Flush

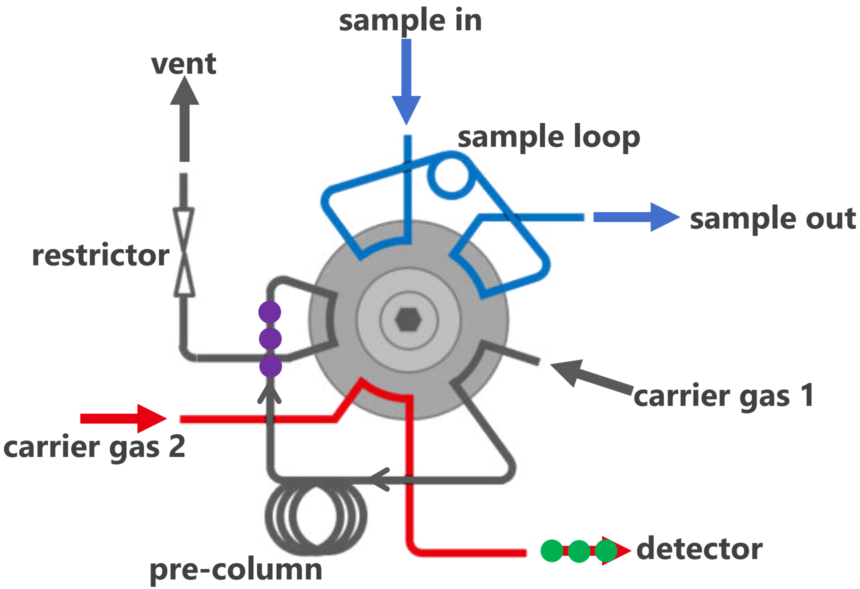


10-port valve operation (with pre-column backflush)

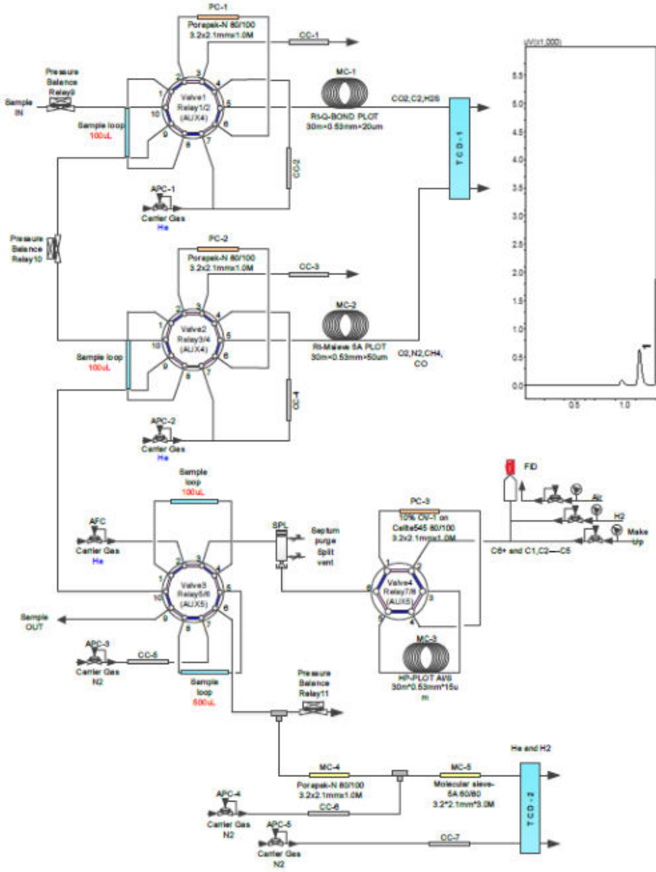
Forward

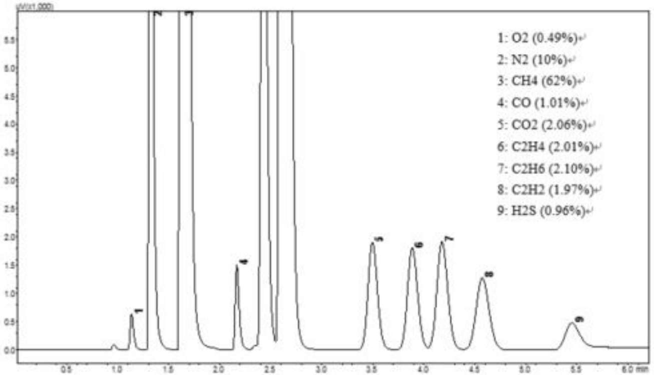


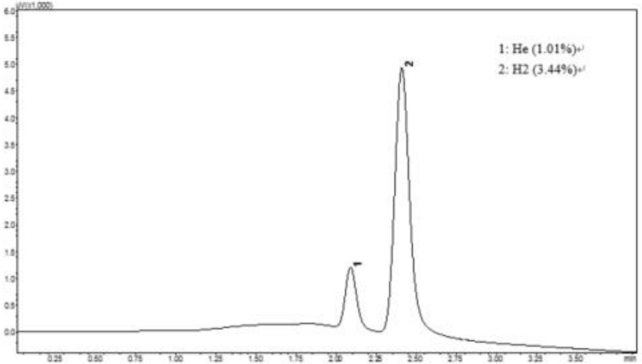
Backflush

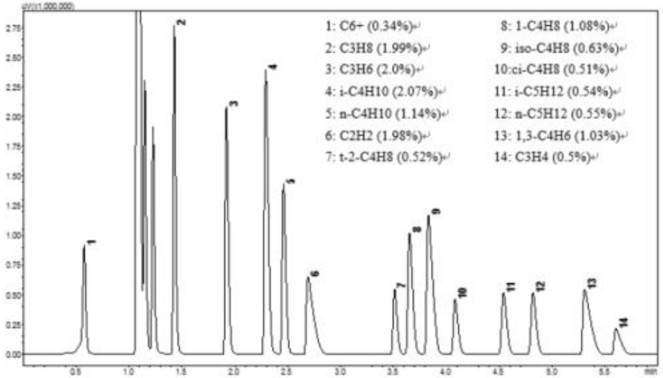


System GC solutions









Summary

Comparison

	Gas	Liquid	Solid
Liquid injection	✗	✓	✗
Headspace	✗	✓	✓
SPME	✗	✓	✓
Thermal Desorption (TD)	✓	✓	✓
Pyrolysis	✗	✓	✓
Gas Sampling Valves	✓	✗	✗

Summary

- **GC is an extremely versatile technique that can be used to analyse gaseous, liquid and solid samples.**

- **Headspace is used to analyse VOCs by extracting them from the gas phase above a sample.**
    - Static headspace can use loop or syringe sampling systems.
    - Dynamic headspace, such as purge & trap offers lower detection limits.

- **SPME uses a fiber to trap VOCs & SVOCs either from the sample or gas phase.**
    - HS-SPME is well suited to non-polar VOCs.
    - DI-SPME offers better extraction and is useful for polar SVOCs.

- **Thermal desorption (TD) uses sorbent-packed tubes to trap VOCs & SVOCs.**
    - Offers pre-concentration of up to 10^6 for gas analysis.
    - Very wide range of sampling options to cover a range of applications.

- **Pyrolysis uses a high-temperature furnace to break down large molecules into VOCs & SVOCs.**
    - Advanced instruments can perform multiple techniques, such as EGA, TD and even catalytic conversion.

- **Gas sampling valves (GSVs) offer a highly reproducible means of analysing gaseous samples.**
    - Use a 2-position valve that has fill and flush modes.
    - Systems range from a 6-port valve with one column, up to systems with multiple valves and as many as 8 columns.

Next time

The next session will be on…

Choice of GC Detectors

This will cover:

- *Considering which detector to use*
- *How the detectors operate*
- *Sensitivity & selectivity*
- *Requirements*
- *Typical applications*

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Theory and Key Principles Series

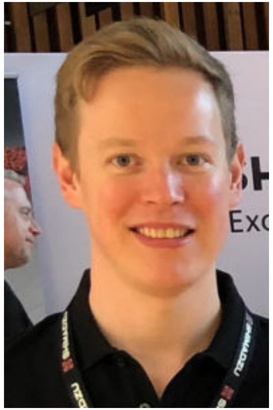
Gas Chromatography (GC)

Session 6 – Choice of Detectors for GC

Introduction

Welcome to Shimadzu's Gas Chromatography Theory and Key Principles Series!

Presenter



Ollie Stacey

GC/GCMS
Technical
Specialist

- Part of Shimadzu team for >2.5 years
- Previous experience with TOF-GCMS
- Expertise in GCxGC and GCxGC-MS

Theory & Key Principles Series – GC

- *Introduction to Gas Chromatography **
- *GC Columns **
- *The Split/Splitless Inlet **
- *Advanced Liquid Injection Techniques **
- *Alternatives to Liquid Injection **
- **Choice of Detectors for GC**
- Processing GC Data
- Maintenance & Troubleshooting
- Method Development

** Now available on demand at www.shimadzu.co.uk/webinars*

Choice of Detectors for GC

In this presentation:

- Factors to consider

- Key principles of operation
- Sensitivity & selectivity
- Requirements
- Considerations

Flame Ionisation Detector	**(FID)**
Thermal Conductivity Detector	**(TCD)**
Electron Capture Detector	**(ECD)**
Barrier Discharge Ionisation Detector	**(BID)**
Sulfur Chemiluminescence Detector	**(SCD)**
Flame Photometric Detector	**(FPD)**
Flame Thermionic Detector	**(FTD)**

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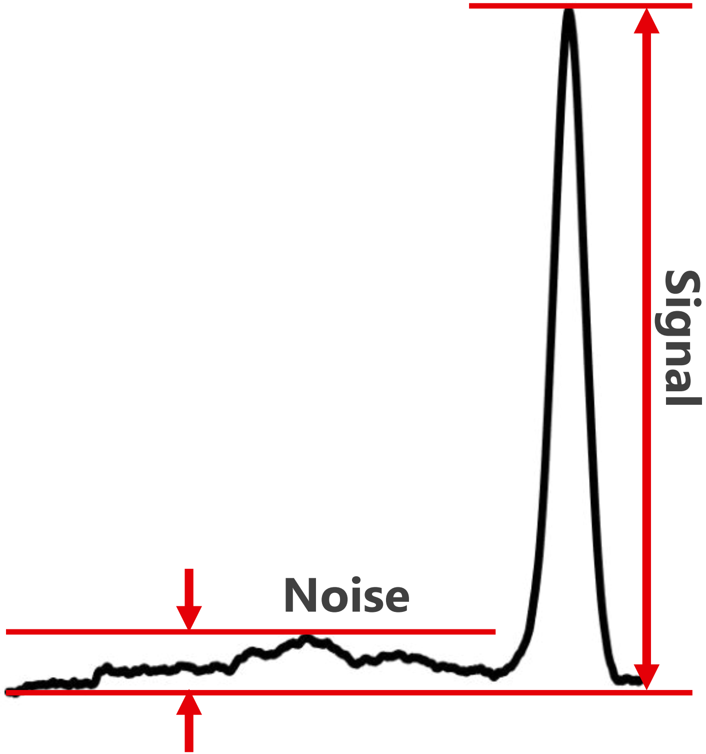
Factors to consider

Sensitivity

The most obvious consideration is sensitivity!

Different detectors offer different sensitivity limits.



How is sensitivity defined?

Most detectors have a Minimal Detectable Quantity (MDQ).

Sensitivity is also method-related – Method Detection Limit (MDL).

Most commonly used for day-to-day analytical work are
Limit Of Detection (LOD) and Limit Of Quantitation (LOQ).

These are usually related to a **signal-to-noise ratio** (S/N or SNR).

Typically: LOD = 3:1 LOQ = 10:1

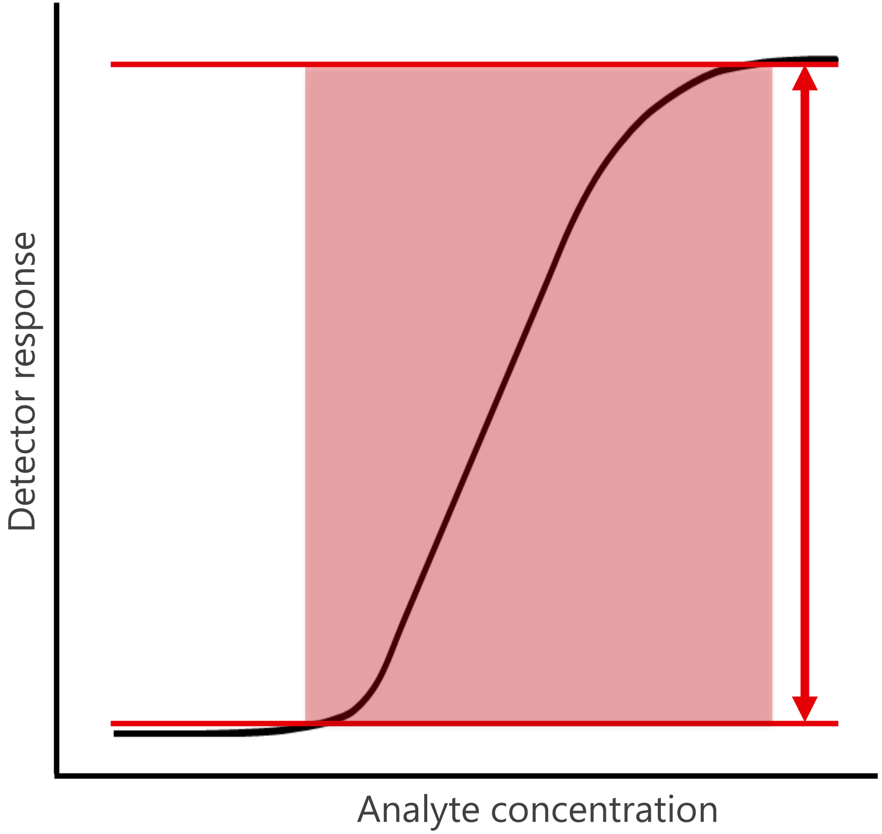
Dynamic range

Dynamic range

Range over which a change in analyte concentration causes a change in detector response.

Lowest point = minimum detectable quantity

Highest point = detector saturation



Dynamic range

Dynamic range

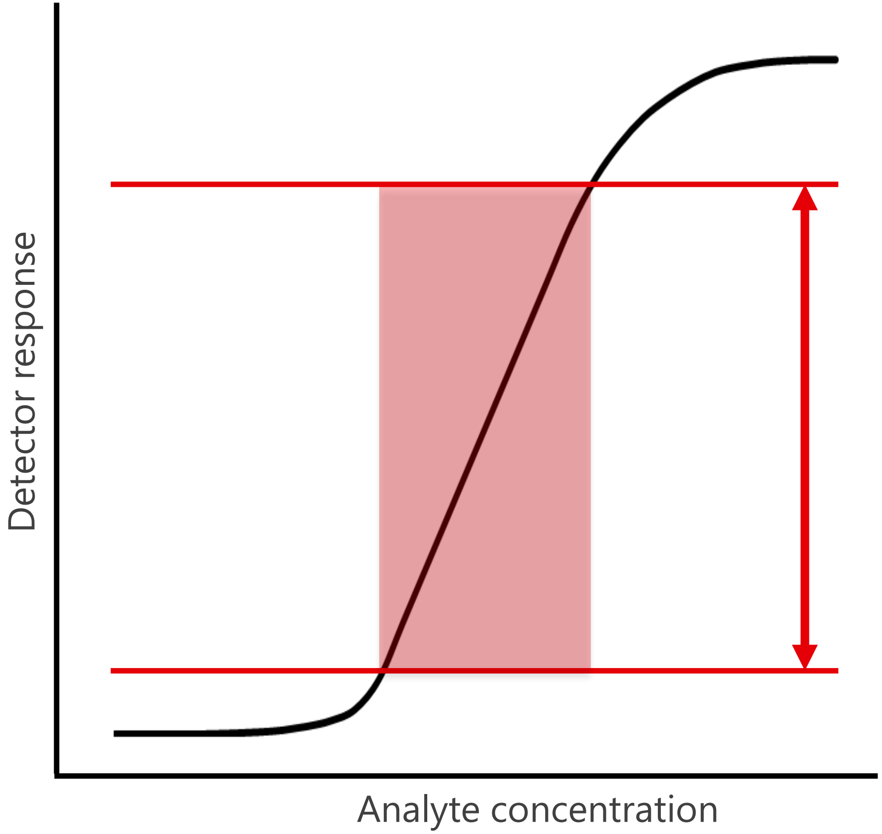
Range over which a change in analyte concentration causes a change in detector response.

Lowest point = minimum detectable quantity

Highest point = detector saturation

Linear dynamic range (LDR)

Range over which a linear change in analyte concentration causes a linear change in detector response.



Universal vs. selective

Not all detectors can detect everything!

Universal	**Selective**
Detects everything, or almost everything	Detects specific elements or chemical properties
General purpose – can be used for a wide range of different applications	Specialised – might only be useful for a single application
Matrix effects might hide compounds of interest	Matrix can become invisible to the detector
e.g. Impurity testing	e.g. Sulfur content in fuel & feedstocks
Tend to be very robust	Less robust

Other properties

Destructive vs. non-destructive

Non-destructive detectors can be coupled to a second detector!

Concentration detector vs. mass detector

Concentration detectors measure the concentration of analytes in the gas flow.
Signal is affected by column flow and make-up gases.

Mass detectors measure the total mass, or mass flow.
Signal is is independent of make-up flows.

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Flame Ionisation Detector (FID)

Flame Ionisation Detector (FID)

Most common detector in gas chromatography!

Can be used for almost all compounds with C-H or C-N bonds.

Used mostly for the analysis of organic compounds in a wide range of applications.

Specificity	Universal (mostly)
Sensitivity	0.1 ppm [0.1 ng]
Dynamic range	10^7
Detector type	Mass detector
Properties	Destructive

Fundamentals

FID uses an air-hydrogen flame to burn analytes.

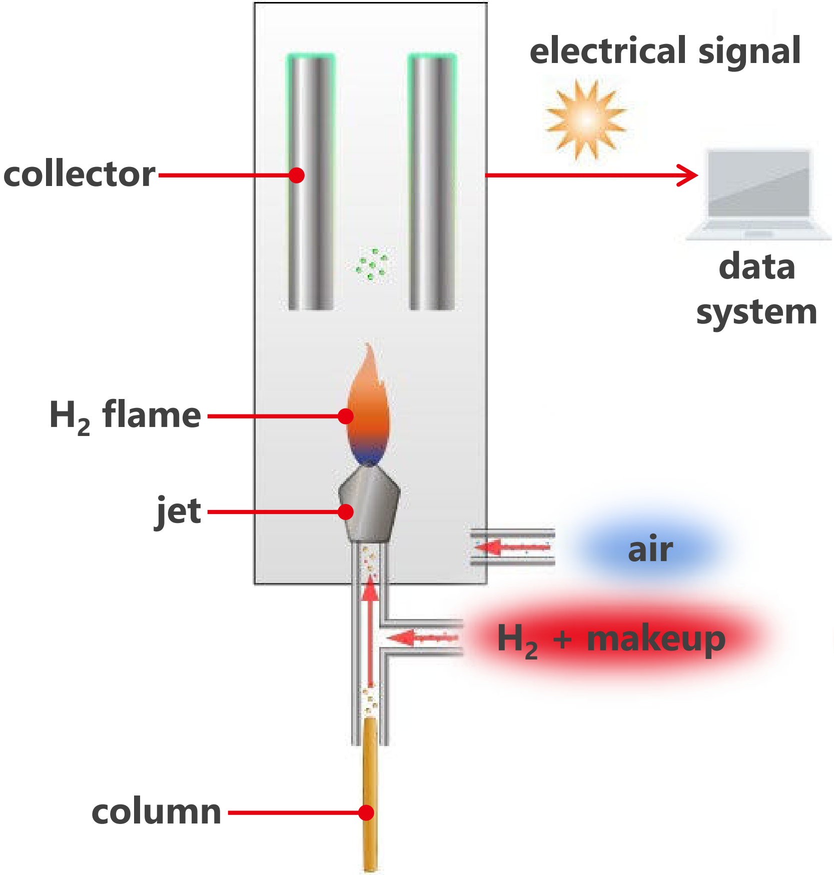
Oxidative process results in electrons being formed, which are picked up on the collector.

$CH \longrightarrow CHO^{+} + e^{-}$

$CN \longrightarrow NO^{+} + CO + e^{-}$

This generates a positive electrical signal response.

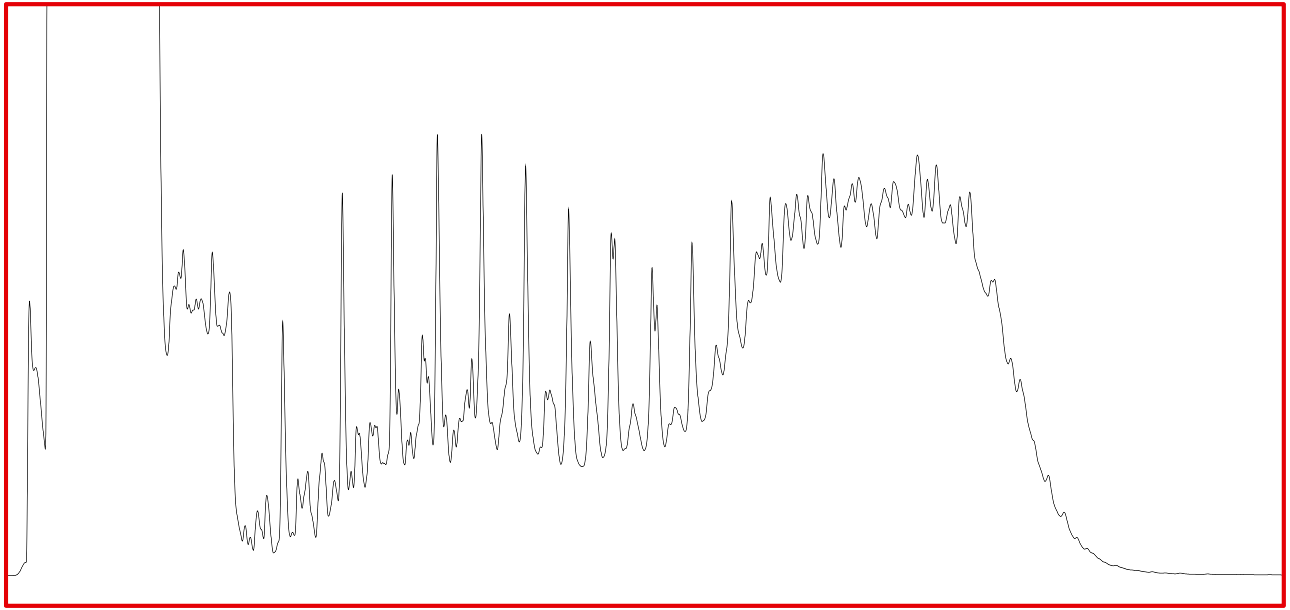
Most FIDs use a make-up gas to optimise sensitivity.



Application

Analysis of water, sediment and soil for hydrocarbon contamination.

Results are usually expressed as a total amount.



Considerations

Requires hydrogen.

Carbonyl groups (C=O) are not detectable.

Does not respond to He, Ar, N_2, O_2, CO, CO_2, CO_2, H_2O, etc.

Can be used with a methaniser for CO & CO2.

Response is proportional to number of C-H or C-N bonds.

10 ppm of $C_{10}H_{22}$ will have a higher response than 10 ppm of C_2H_6

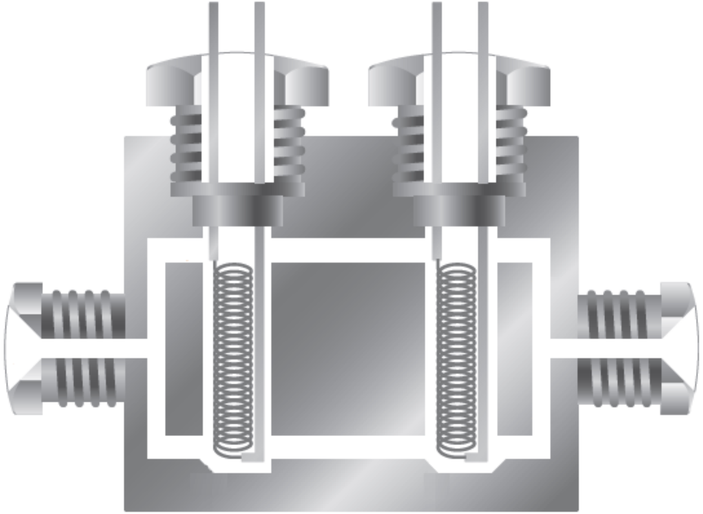
Thermal Conductivity Detector (TCD)

Thermal Conductivity Detector (TCD)

Very common detector in gas chromatography!

Completely universal detector.

Used for gas analysis and where sensitivity is not a priority.



Specificity	Universal
Sensitivity	10 ppm [10 ng]
Dynamic range	10^7
Detector type	Concentration detector
Properties	Non-destructive

Fundamentals

Different compounds have different thermal conductivity constants.

Compound	**Thermal conductivity constant (10^{-6} cal/s·cm·°C)**
Helium	*408*
Hydrogen	*547*
Nitrogen	*73*
Argon	*52*
Oxygen	76
Water	60
Ethane	77
Methane	98
Carbon monoxide	69
Carbon dioxide	49

Fundamentals

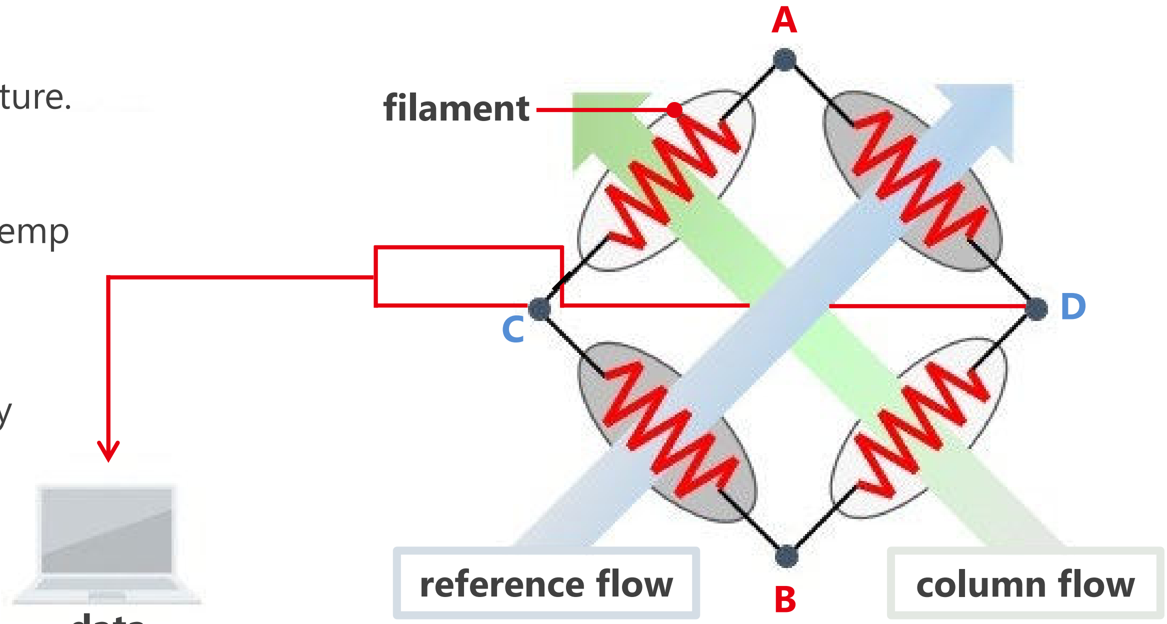
Voltage or direct current applied between A & B.

Filaments are held at a constant temperature.

As analyte passes through cell, filament temp increases/decreases.

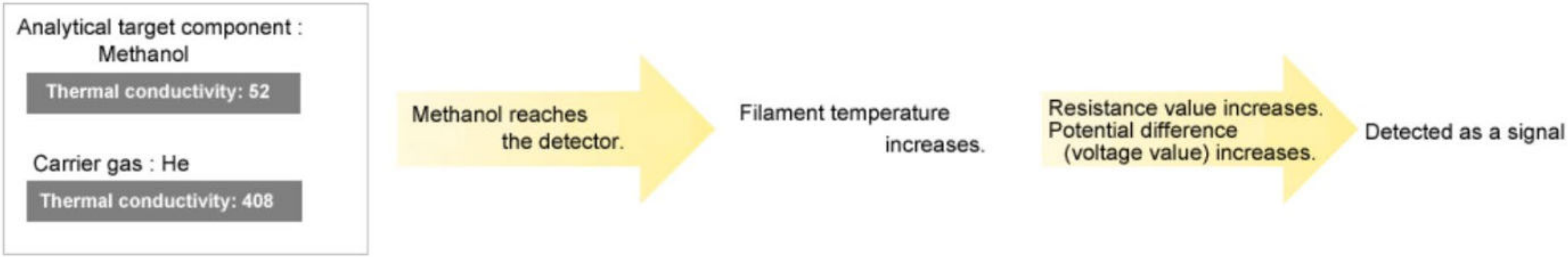
Detects difference in thermal conductivity between analyte and carrier gas.

Signal registers on data system.



Fundamentals

When the Thermal Conductivity of the Analytical Target Component is Lower than the Carrier Gas



Analytical target component : Methanol

Thermal conductivity: 52

Carrier gas : He

Thermal conductivity: 408

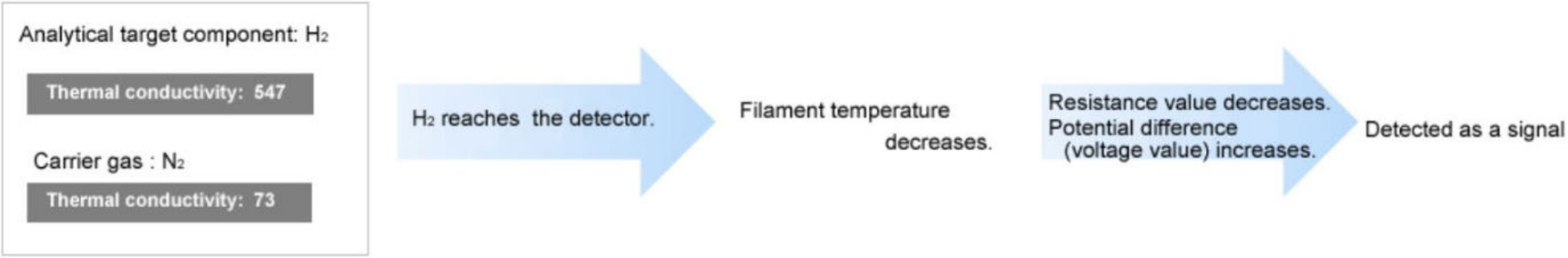
Methanol reaches the detector.

Filament temperature increases.

Resistance value increases.
Potential difference (voltage value) increases.

Detected as a signal

Selection by Analytical Objective



Analytical target component: H_2

Thermal conductivity: 547

Carrier gas : N_2

Thermal conductivity: 73

H_2 reaches the detector.

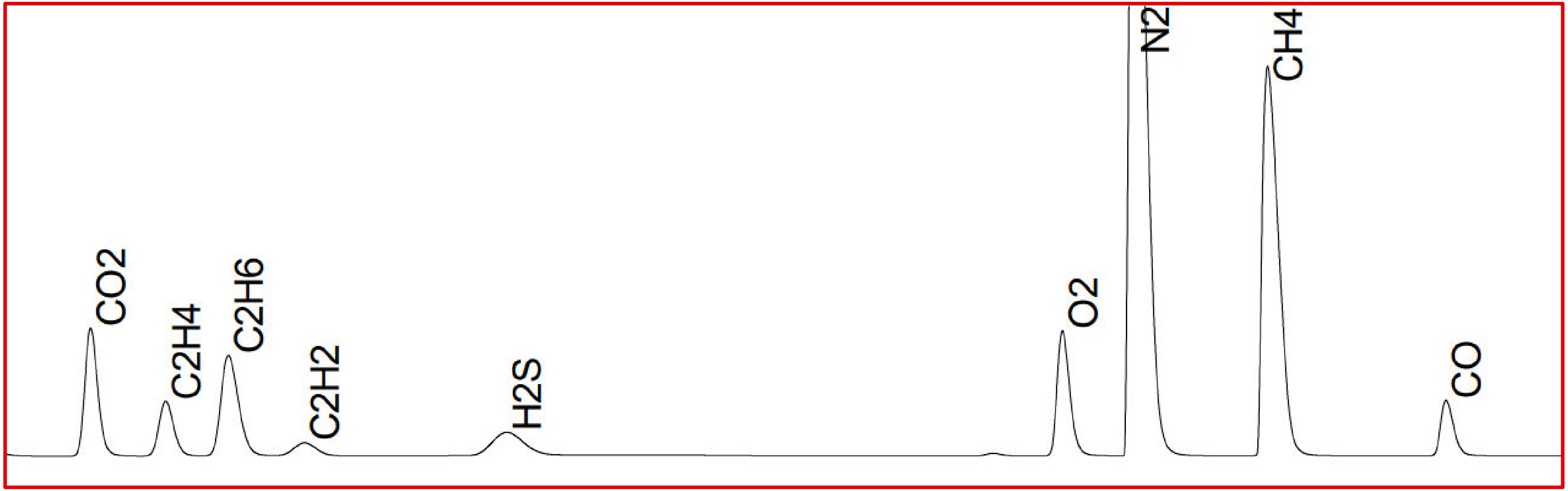
Filament temperature decreases.

Resistance value decreases.
Potential difference (voltage value) increases.

Detected as a signal

Application

Analysis of permanent gases and gas content within natural gas and refinery gas.

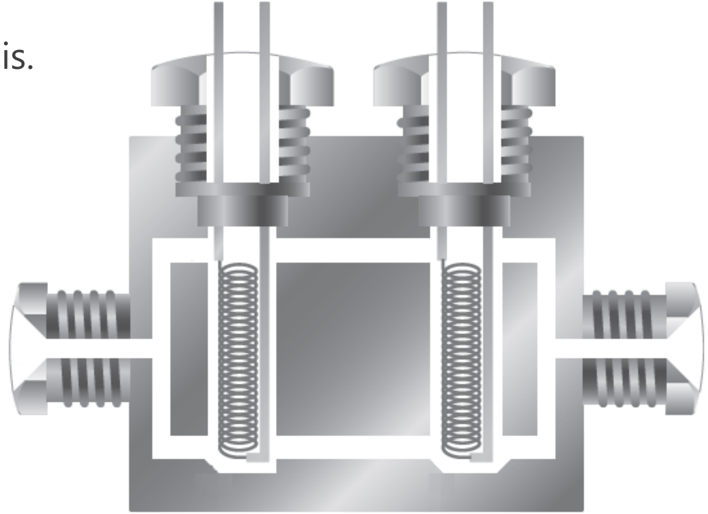


Considerations

Sensitivity is poor.

Thermal Conductivity Constant must be significantly different for a good response.
- Cannot detect carrier gas.
- Cannot detect H2 with He carrier.
- N2 is a poor carrier option for low-level permanent gas analysis.

Response impacted by flow rate.



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Barrier Discharge Ionisation Detector (BID)

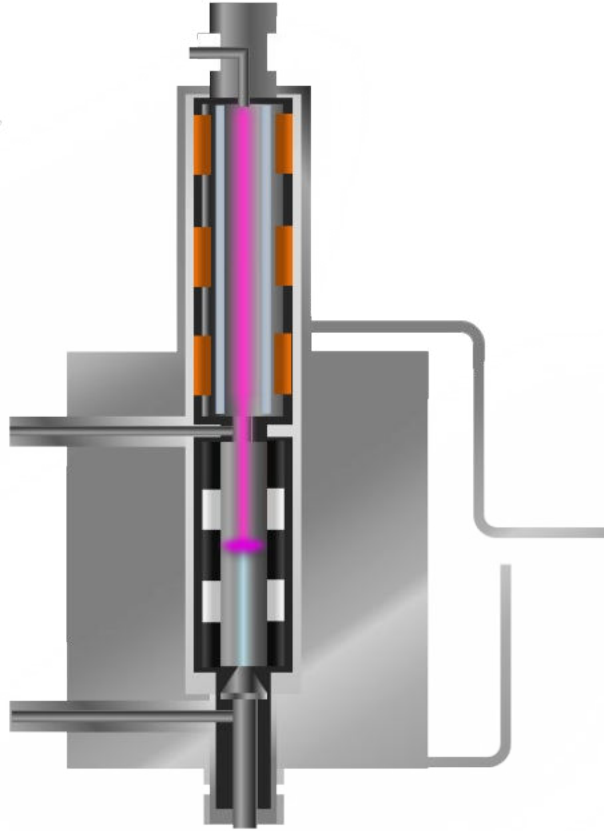
Barrier Discharge Ionisation Detector (BID)

Unique detector for high-sensitivity, universal analysis.

Combines sensitivity of FID* with universal detection of TCD.

** sensitivity is actually around 2x FID.*

Specificity	Universal (except He & Ne)
Sensitivity	0.05 ppm [0.05 ng]
Dynamic range	10^5
Detector type	Mass detector
Properties	Destructive



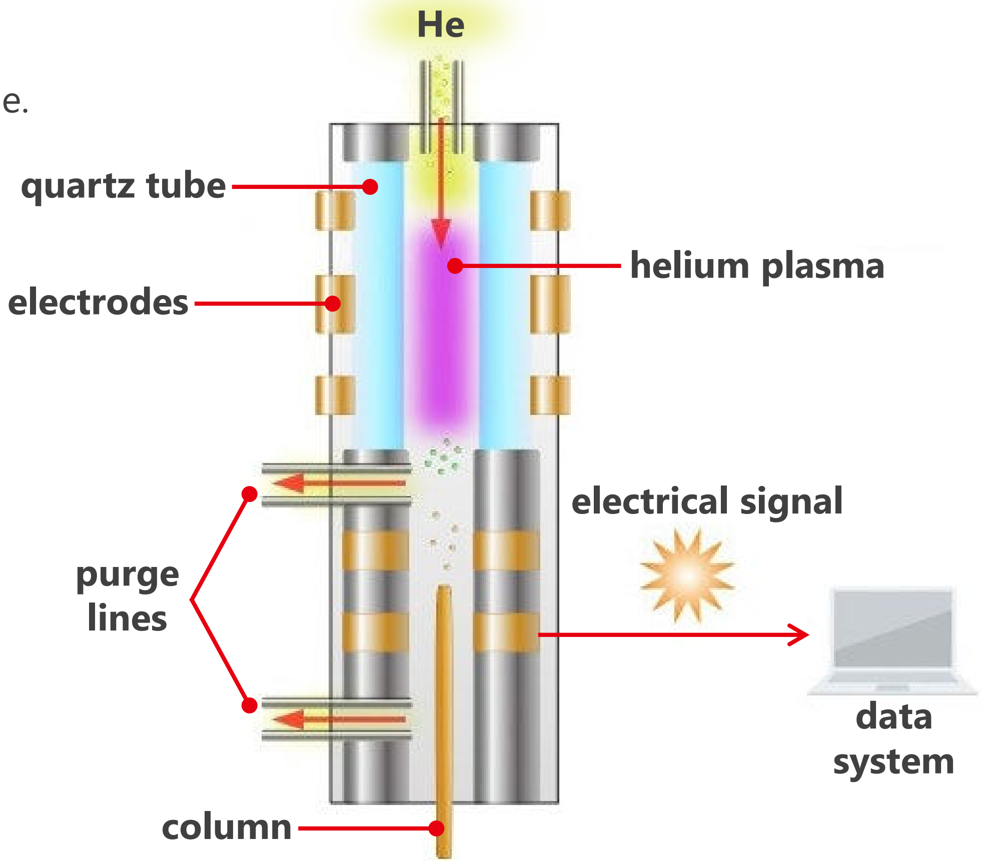
Fundamentals

Helium is used for form a plasma inside a quartz tube.

Plasma transfers energy to analytes, ionising them.

$M \longrightarrow M^{+} + e^{-}$

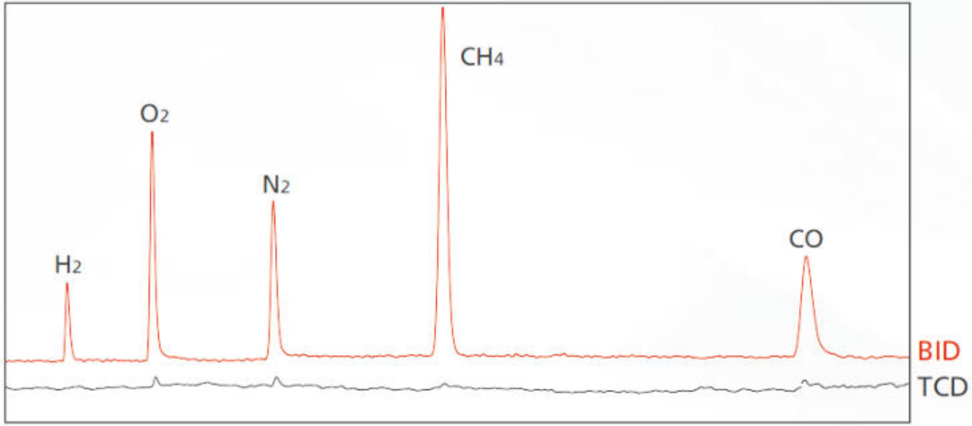
Signal generated by collector electrodes.

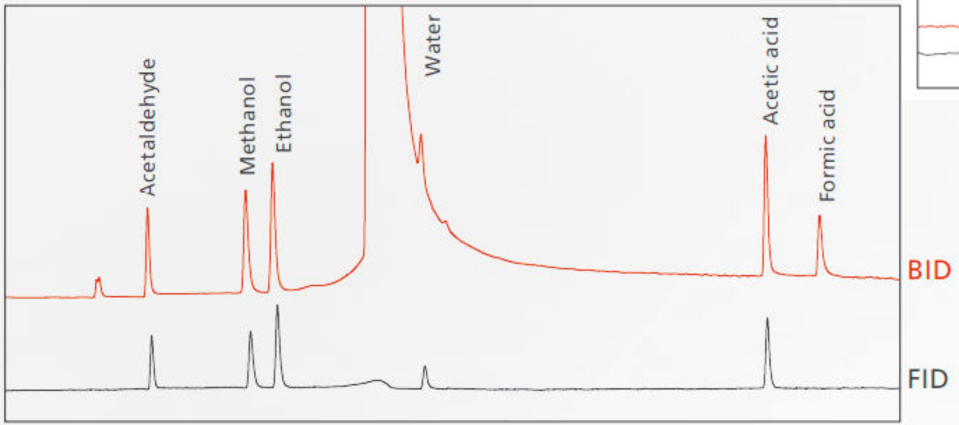


Application

Low-level analysis of analytes incompatible with FID, such as formic acid, acetaldehyde, & water.

Low-level permanent gas analysis.

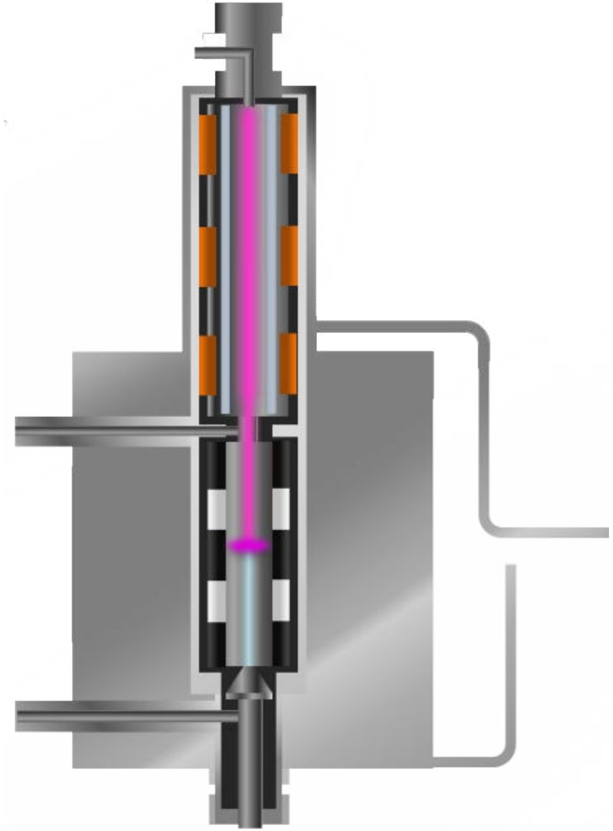




Considerations

Requires high-purity helium for detector gas and carrier gas supply.

Takes time to stabilise on power-up.



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Selective, high-sensitivity detectors

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Flame Photometric Detector (FPD)

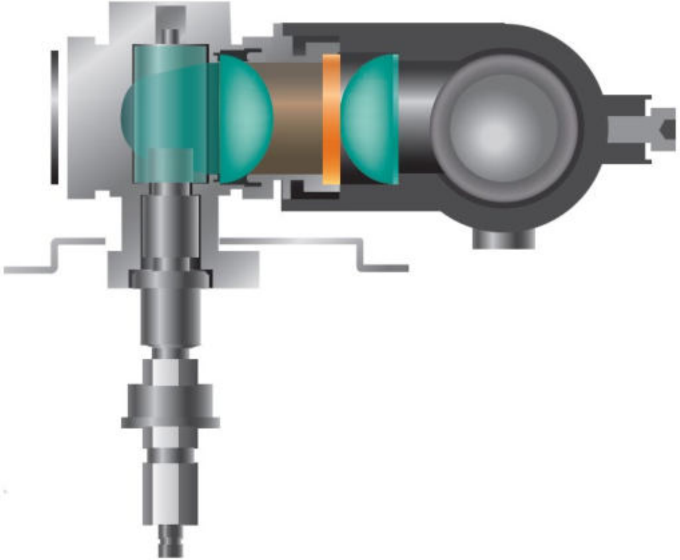
Flame Photometric Detector (FPD)

Used for the analysis of sulfur, phosphorous or tin-containing analytes.

Commonly used for organotin and pesticide analysis.

Some vendors offer a 'pulsed' version (PFPD):

Higher sensitivity & selectivity.



Specificity	Selective (sulfur, phosphorous and tin)
Sensitivity	10 ppb [10 pg]
Dynamic range	10^3
Detector type	Mass detector
Properties	Destructive

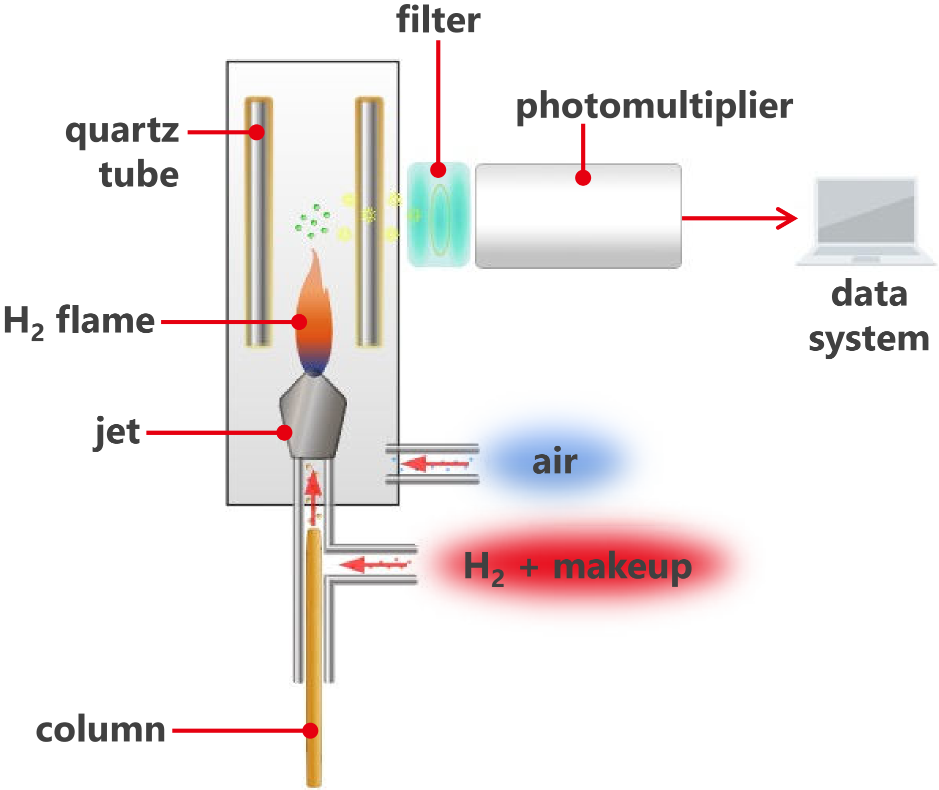
Fundamentals

Analytes are burned in same way as FID.

Those containing S, P & Sb emit light after excitation from burning.

Emitted light is at specific wavelengths for each element.

Emitted light is filtered to enable transmission to photomultiplier, which generates signal.



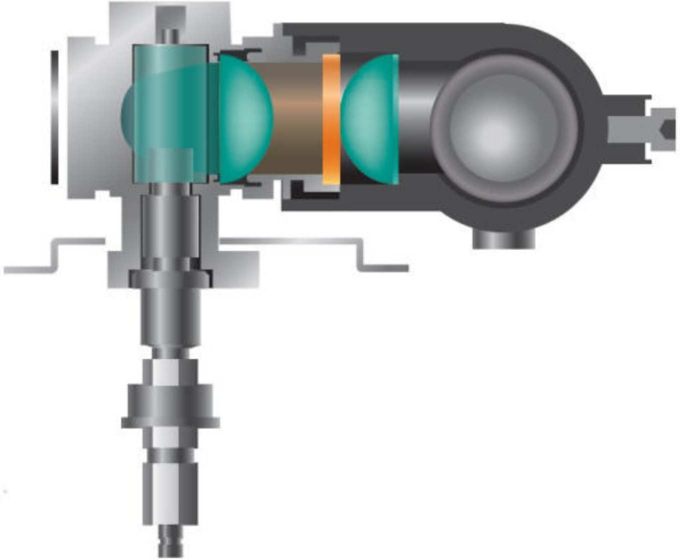
Considerations

Sulfur is in its diatomic state, so the FPD gives a square law response.
If concentration doubles, signal response quadruples.

Carbon quenching can reduce response.

Same gas requirements as FID (hydrogen, air & make-up gas).

Can only detect one element at a time!



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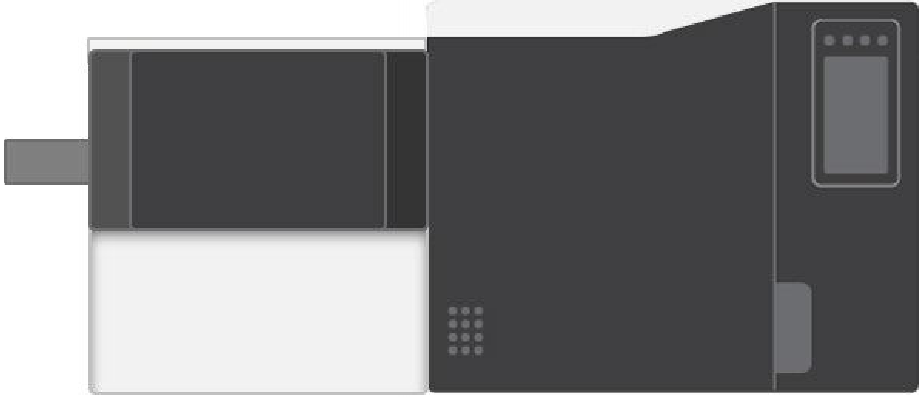
Sulfur Chemiluminescence Detector (SCD)

Sulfur Chemiluminescence Detector (SCD)

Similar to FPD – it detects sulfur.

Different from FPD:

- Higher sulfur selectivity
- Higher sensitivity
- Higher linearity
- Equimolarity



Specificity	Selective (sulfur)
Sensitivity	1 ppb [1 pg]
Dynamic range	10^6
Detector type	Mass detector
Properties	Destructive

Fundamentals

Furnace

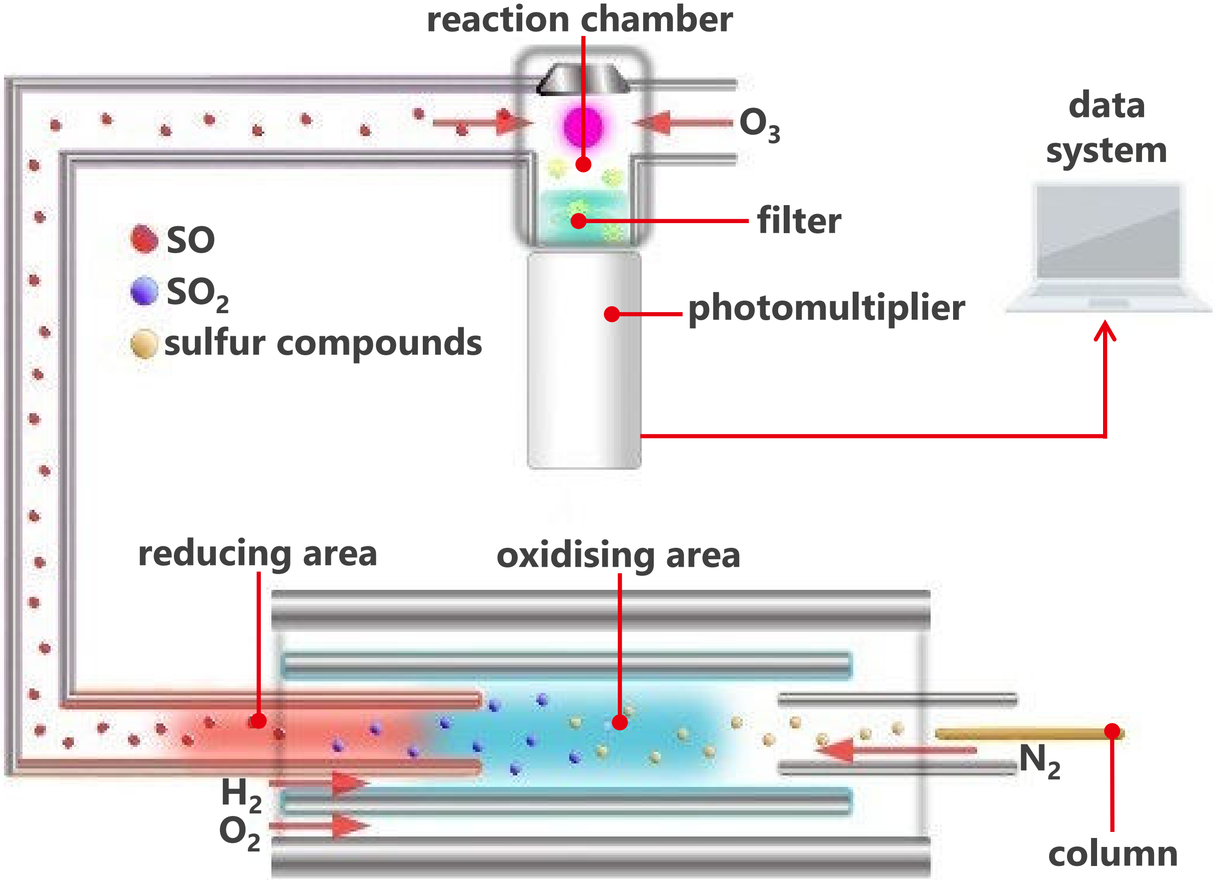
Oxidation to SO_2 (using O_2)
Reduction to SO (using H_2)

Reaction chamber

Oxidation to SO_2^* (using O_3)

Decays to SO_2
Light emitted (300-400 nm)

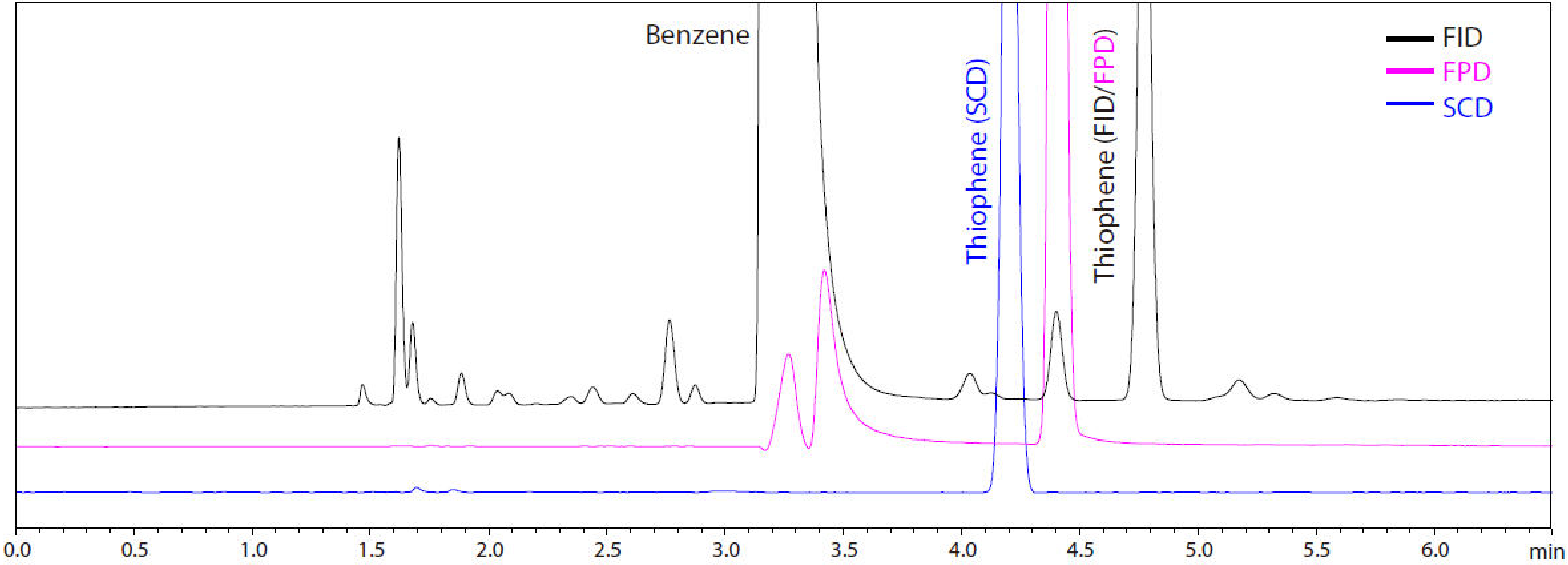
Vacuum system



Applications

Trace sulfur affecting taste and flavour profiles of food & beverage.

Sulfur impurities in feedstocks.



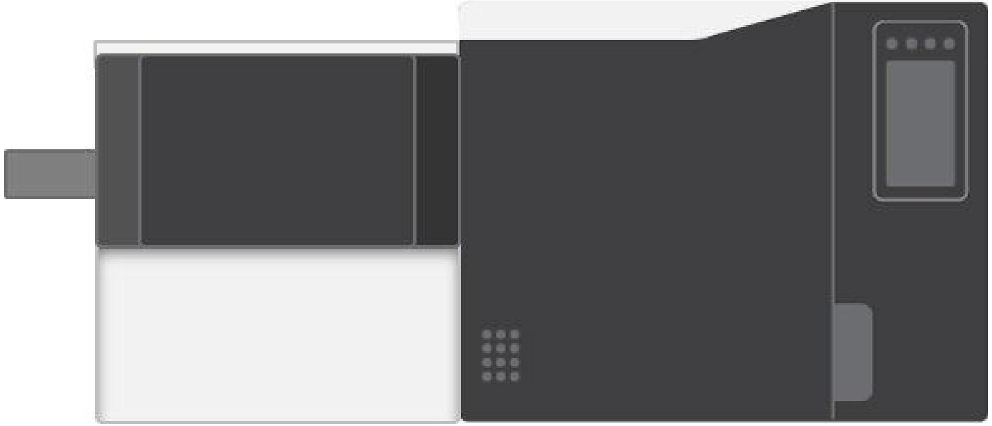
Considerations

Larger instrument footprint than standard GC system.

Higher maintenance requirements.

Long stabilisation times.

Requires hydrogen and oxygen gases.



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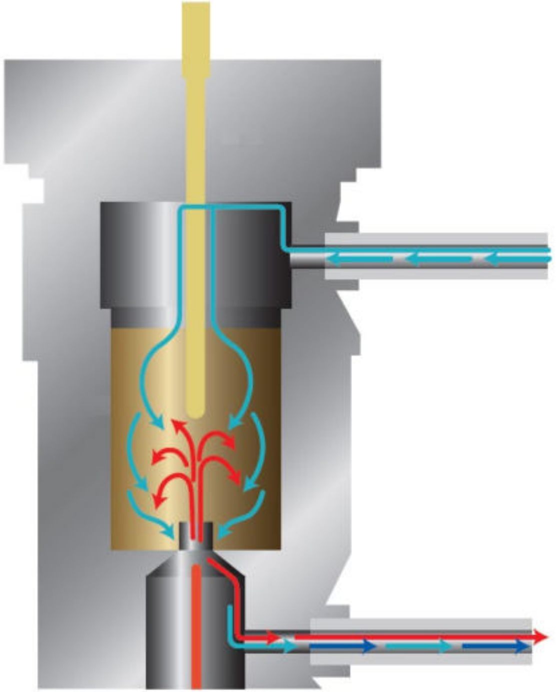
Electron Capture Detector (ECD)

Electron Capture Detector (ECD)

The ECD is used primarily for the analysis of halogenated species.



Specificity	Selective (electrophilic compounds)
Sensitivity	0.01 ppb [0.01 pg]
Dynamic range	10^5
Detector type	Concentration detector
Properties	Non-destructive

Fundamentals

Radioactive detector, emitting beta rays.

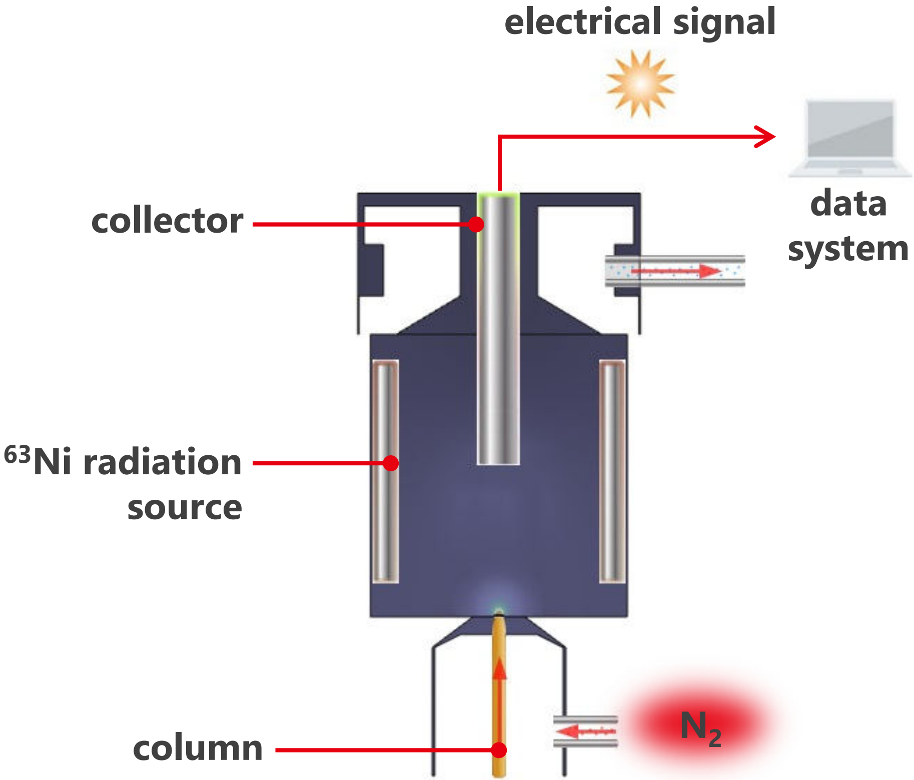
Nitrogen make-up gas is ionised.

$N_2 \xrightarrow{\hspace{3cm}} N_2^+ + e^-$

$PCB + e^- \xrightarrow{\hspace{2cm}} PCB^-$

Electrophilic compounds, like PCBs, pick up e^-.

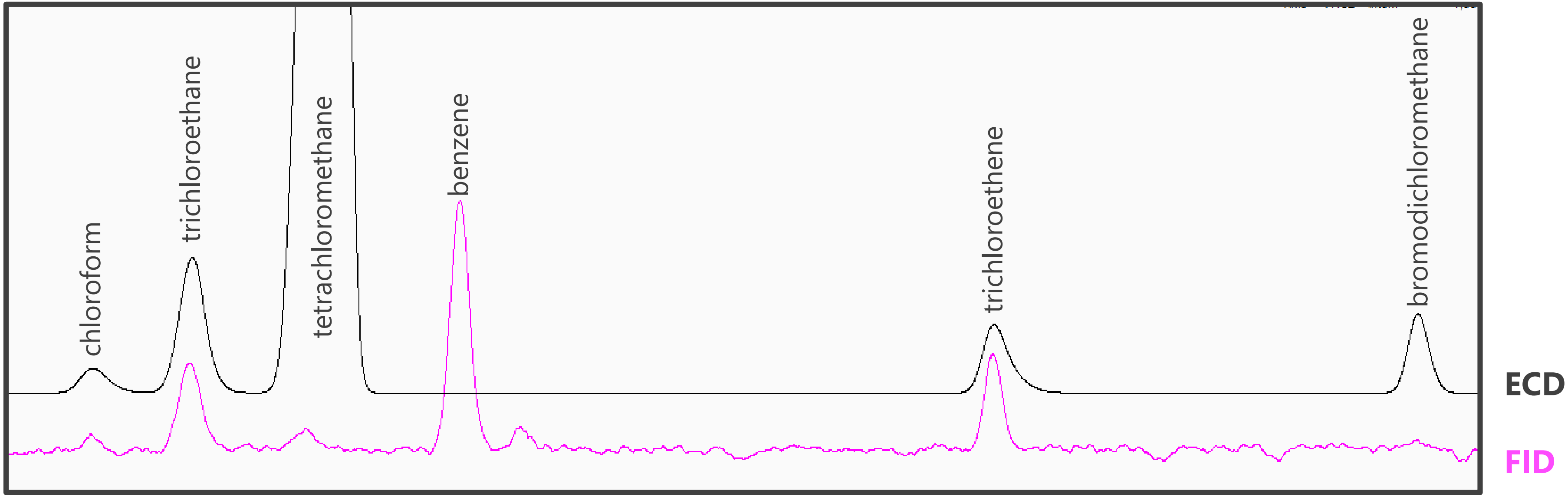
Standing current drops, generating signal.



Applications

PCBs in transformer oil.

Low-level analysis of halogenated VOCs in water.



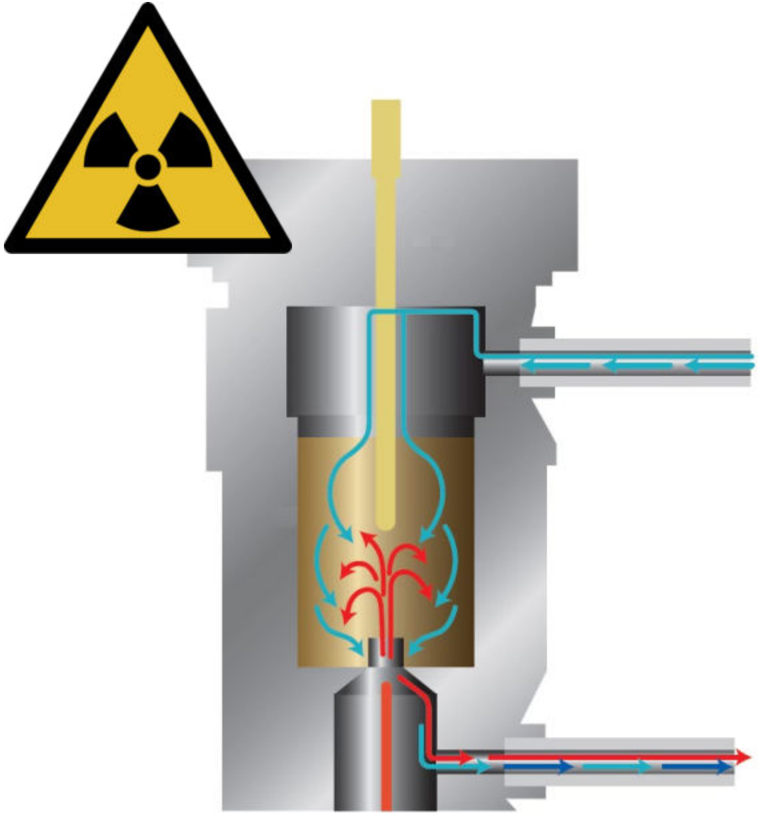
Considerations

Radioactive!!

Saturation can damage detector.

Requires high-purity gases (99.9999%).

Leaks can damage the cell due to oxidation.



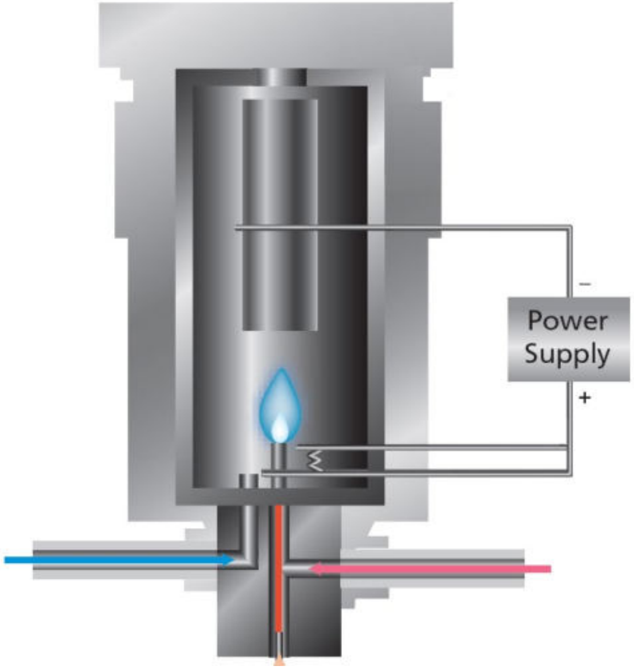
Flame Thermionic Detector (FTD)
Nitrogen Phosphorous Detector (NPD)

Flame Thermionic Detector (FTD)

Used for the analysis of nitrogen- and phosphorous-containing compounds.

Common applications include drug and pesticide analysis.

Specificity	Selective (nitrogen & phosphorous)
Sensitivity	0.1 ppb [0.1 pg] (P) 1 ppb [1 pg] (N)
Dynamic range	10^7
Detector type	Mass detector
Properties	Destructive



Fundamentals

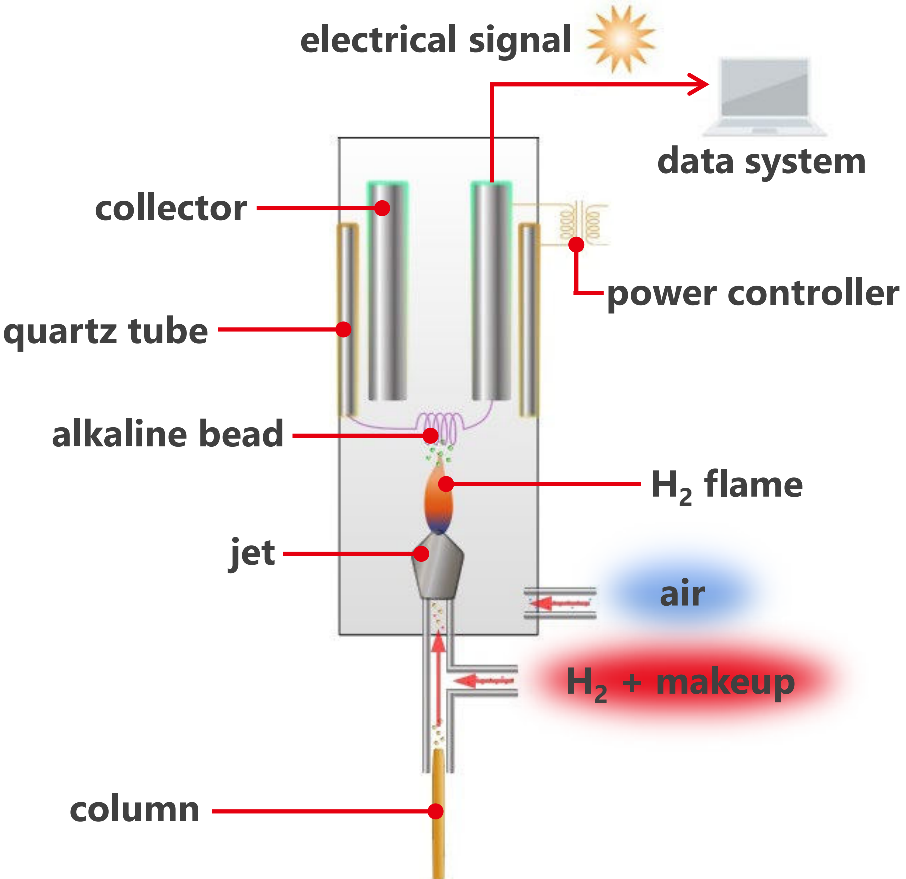
Analytes burnt in hydrogen flame, like FID & FPD.

Electically-heated alkaline bead generates plasma.

$CN + Rb^{*} \longrightarrow Rb^{+} + CN^{-}$

$PO_2 + Rb^{*} \longrightarrow Rb^{+} + PO_2^{-}$

Ions are collected to generate electric current.



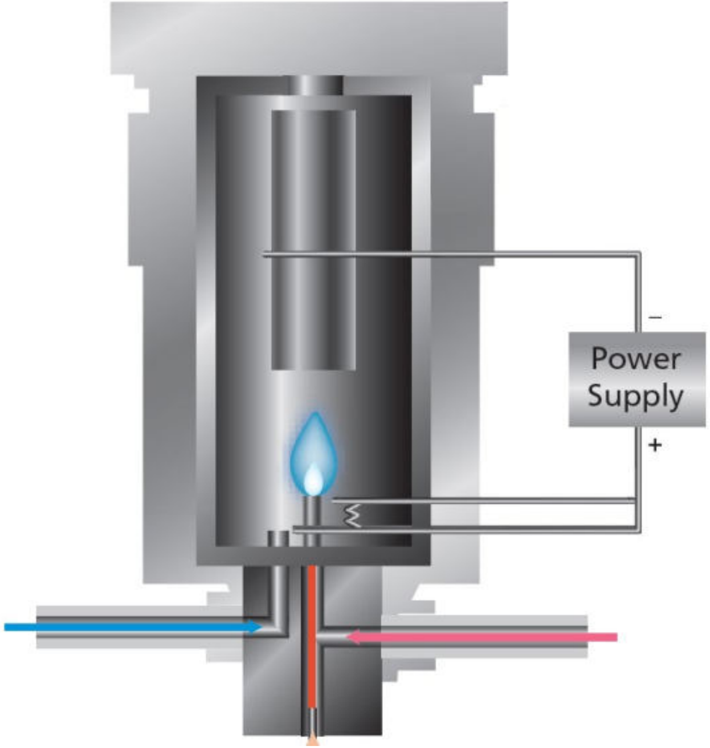
Considerations

Requires hydrogen, air & make-up gases.

Can’t analyse inorganic nitrogen species (incl. ammonia).

Bead requires periodic replacement.

Detector stability is lower than other detectors.
Requires frequent re-calibration.



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Mass Spectrometry (MS)

Mass Spectrometer (MS)

Widely used for high-sensitivity analysis and analysis of unknown compounds.

Specificity	Universal, mostly
Sensitivity	<ppt – ppm (<fg – ng), depending on type
Dynamic range	$10^{2\text{-}6}$, depending on type

Summary

Comparison

	Selectivity	Sensitivity	Dynamic Range
FID	Universal (C-H or C-N)	0.1 ppm	10^7
TCD	Universal (except carrier gas)	10 ppm	10^7
BID	Universal (except He & Ne)	0.05 ppm	10^6
MS	*Universal*	*< ppt - ppm*	10^{2-6}
FPD	S, P & Sb	10 ppb	10^2
SCD	S	1 ppb	10^6
ECD	Electrophilic	0.01 ppb	10^5
FTD	N & P	1 ppb [N] 0.1 ppb [P]	10^6

Universal

Selective

Summary

- **Detector properties (sensitivity, dynamic range & selectivity) vary considerably.**

- **Detector sensitivity is often defined by minimum detectable quantities (MDQ).**
  - Sensitivity can also be expressed as:
    - Method detection limit (MDL)
    - Limit of detection (LOD)
    - Limit of quantitation (LOQ)
    - Signal-to-noise (S/N or SNR)

- **Detectors have a dynamic range, where a change in sample amount/concentration alters signal response.**
  - Beyond the dynamic range, changes in amount/concentration are not seen by the detector.
  - Linear dynamic range (LDR) is the range where a linear increase in amount/concentration, has linear increase in response.

- **Detectors can be universal or selective.**
  - Selective detectors can improve sensitivity by removing matrix interference.
  - Universal detectors are ideal when information about the full content of sample is required (purity analysis).

- **Choosing the right detector is one of the most important aspects when specifying instrument hardware.**

- **Common GC detectors include: FID, TCD, BID, FPD, SCD, ECD, FTD & MS**

Next time

The next session will be on…

Data Processing

This will cover:

- *Qualitative analysis*
- *Quantitative analysis*
- *Sample types (standards, unknowns, etc.)*
- *Compound types (surrogates, internal standards, etc.)*

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Theory and Key Principles Series

Gas Chromatography (GC)

Session 7 – Processing GC Data

Questions, feedback & certificates

Please use the panel on the left-hand side to ask **questions**.

We'll send an email within 48 hours of this session, which will include the link to a **survey**.

As well as giving you the opportunity to provide **feedback**, the survey includes a **quiz**, to test your knowledge, and the ability to request a **certificate**.

Theory & Key Principles Series – GC

- *Introduction to Gas Chromatography **
- *GC Columns **
- *The Split/Splitless Inlet **
- *Advanced Liquid Injection Techniques **
- *Alternatives to Liquid Injection **
- *Choice of Detectors for GC **
- **Processing GC Data**
- Maintenance & Troubleshooting
- Method Development

** Now available on demand at www.shimadzu.co.uk/webinars*

Processing GC Data

In this presentation:

- Sample types
  - Samples, standards, quality controls
- Compound types
  - Targets, standards, internal standards, surrogates
- Qualitative analysis
  - Component identification
- Quantitative analysis
  - Area percent
  - External standards
  - Internal standards
  - Standard addition

Sample types

Sample types

Samples (unknowns)

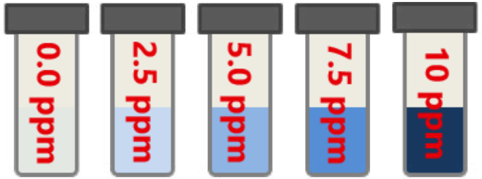
Unknown samples for analysis – containing one compound, or a mixture of compounds, that we'd like to know answers to questions:

- *how pure is my product?*
- *what concentration is target analyte x at?*
- *is target analyte y present?*
- *what is the ratio between analyte x and y?*

Sample types

Standards

A standard contains a known concentration of target analytes.

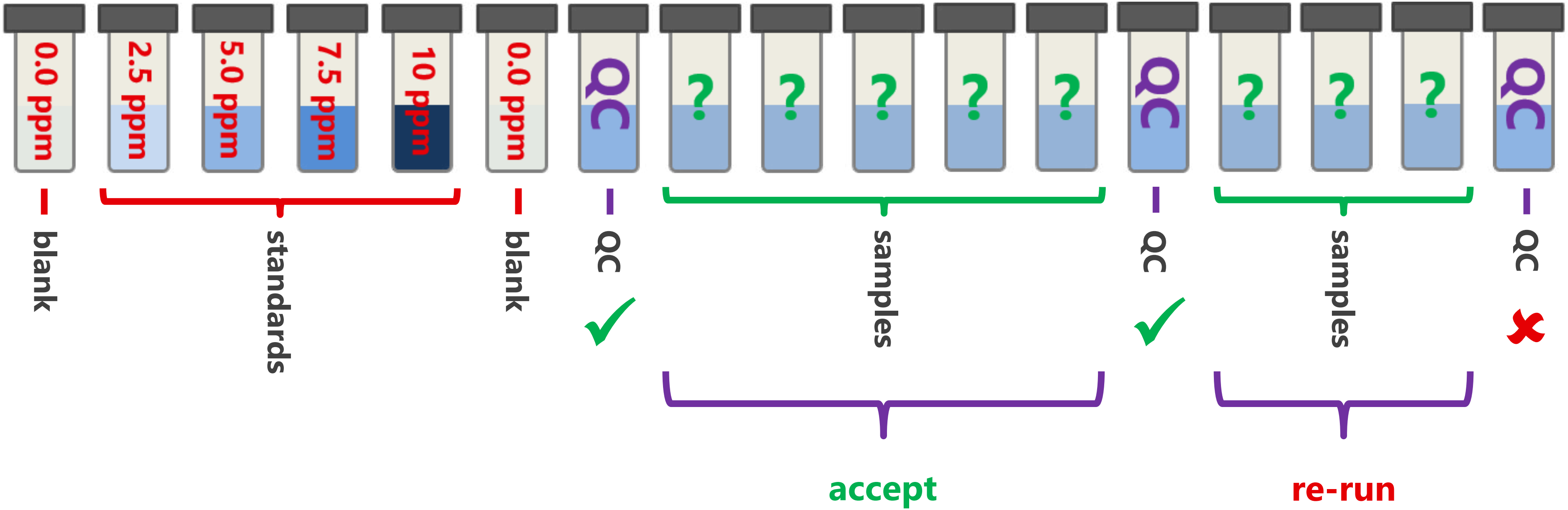


Usually a number of standards are required in order to determine the concentration of analytes in the samples.

Quality Controls (QCs)

Either matrix samples spiked with known concentration of analyte or a standard of a known concentration to confirm the system calibration is still valid.

Typical analysis batch



blank

standards

blank

QC ✓

samples

QC ✓

samples

QC ✗

accept

re-run

Compound types

Compound types

Targets

- Compounds of analytical interest.
- Usually to determine how much is present.

Matrix

- Other compounds in the sample not of analytical interest.
- Matrix can cause increased noise or changes in target response.

Internal Standards (ISTDs)

- Spiked into a prepared sample (and standards & QCs).
- Used to account for instrument variability.
- Usually similar to target (i.e. xylene with benzene target).
- Can’t be present in sample.

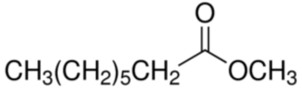
Surrogates

- Spiked into a sample before any preparation is performed.
- Used to determine recovery of targets during sample preparation.
- Must be as chemically-similar to the target as possible (i.e. isotope).

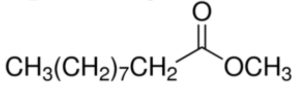
Compound types

Targets

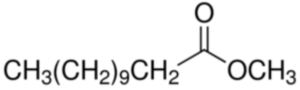
C_8, C_{10} & C_{12} saturated fatty acids. [Require derivatisation to FAMEs].



$CH_3(CH_2)_5CH_2\overset{O}{\overset{\|}{C}}OCH_3$



$CH_3(CH_2)_7CH_2\overset{O}{\overset{\|}{C}}OCH_3$



$CH_3(CH_2)_9CH_2\overset{O}{\overset{\|}{C}}OCH_3$

Matrix

Plant material.

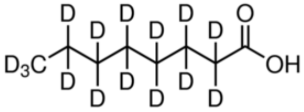
Internal Standards (ISTDs)

Commercially-purchased FAME reference standard i.e. C_{11}.
Potentially need to use a non-FAME compound, so n-C_{12} (dodecane).

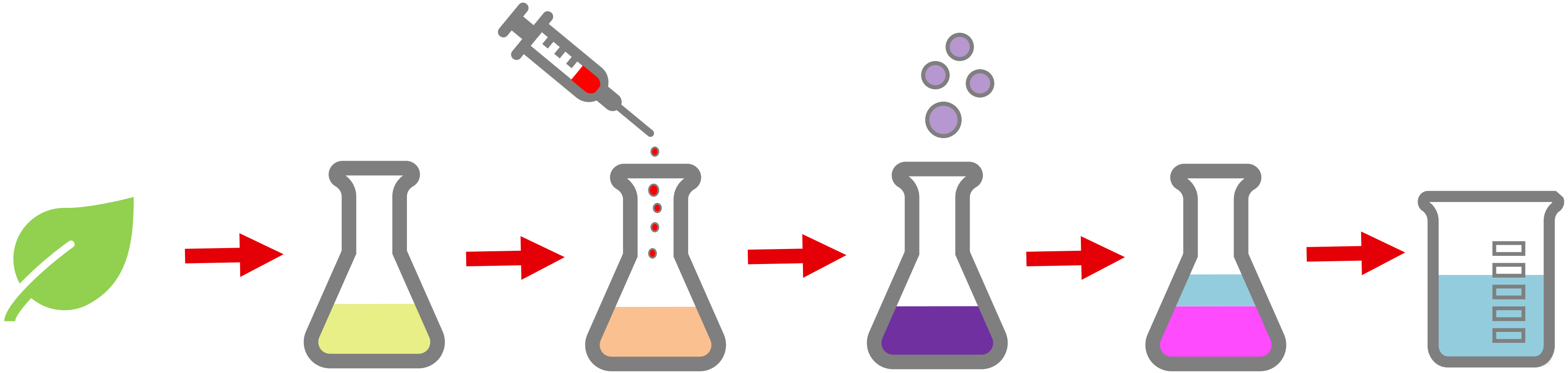
$CH_3(CH_2)_{10}CH_3$

Surrogates

If using GCMS, d_{15}-C8 fatty acid standard.
If using GC-FID, usually another fatty acid.



Sample preparation



Sample

Might be crushed or blended.

Dissolve

Suspended or dissolved in suitable solvent, such as water.

Surrogate Addition

Surrogate usually added at this stage.

Derivatisation

Derivatisation agent(s) added and sample incubated.

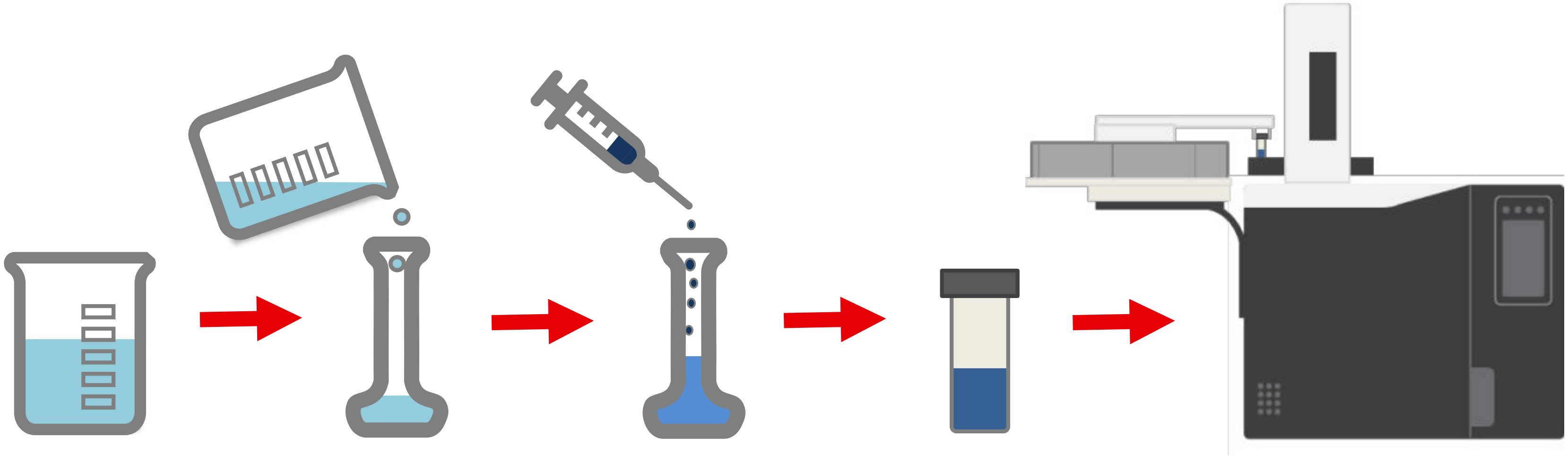
Extraction

Organic solvent, such as hexane added.

Separation

Organic phase collected.

Sample preparation



Derivatised Sample

Dilution

Sample measured into volumetric flask and diluted if required.

ISTD Addition

ISTD added and sample made up to volume of flask.

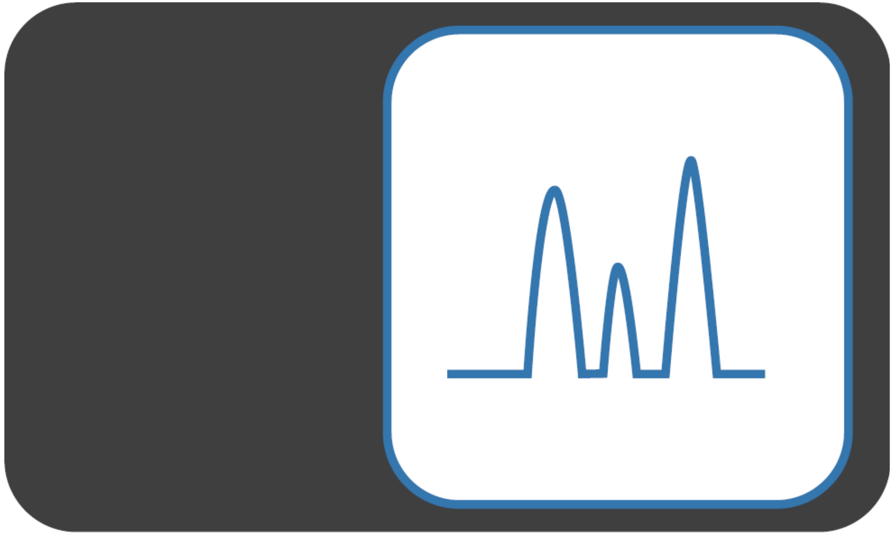
Decant

Sample transferred to vial.

Analyse

Sample analysed on GC.

Data acquisition



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Data processing

Qualitative vs. Quantitative

Qualitative analysis

- What's in my sample?
- Is compound *x* in my sample?

Quantitative analysis

- How pure is my product?
- How much of compound *x* is in my sample?

Qualitative analysis

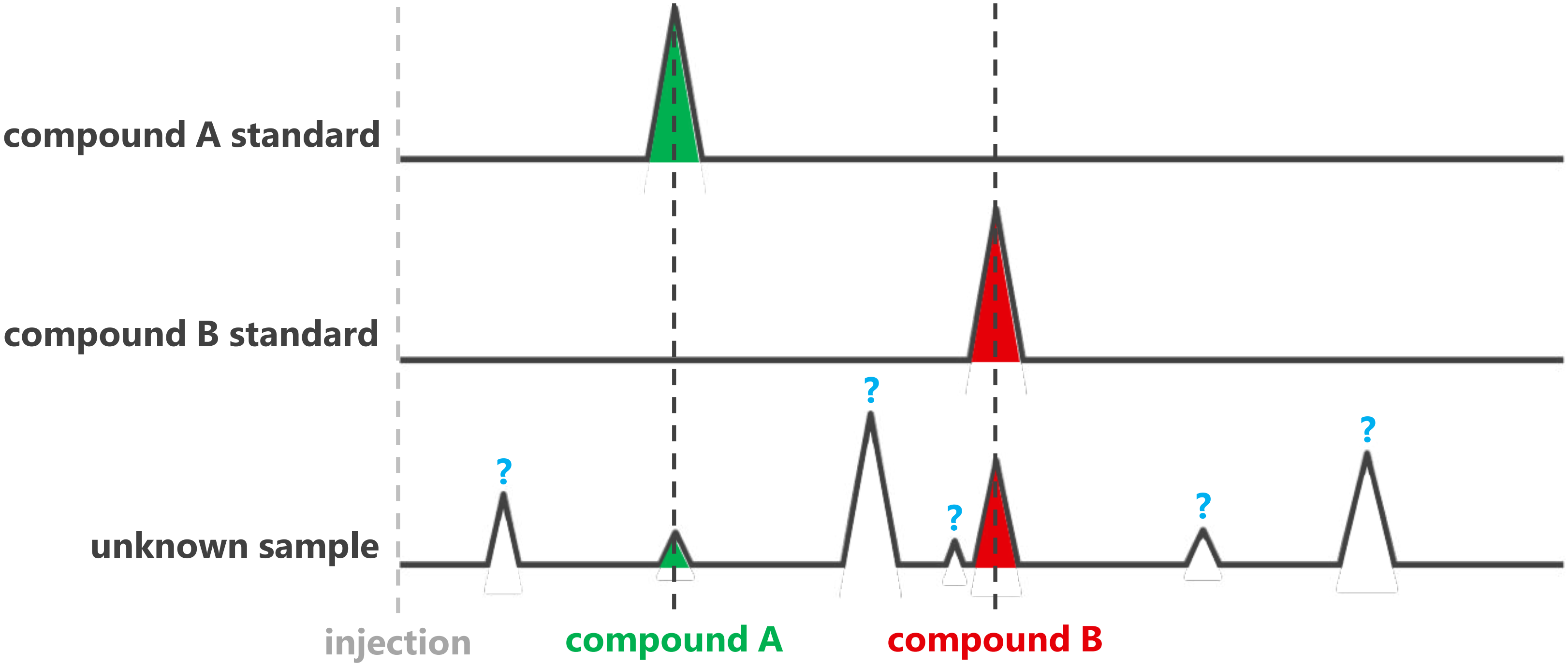
Qualitative analysis

For GC detectors, identity confirmation is based solely on retention time (RT).

To identify compounds within a sample, a standard containing that compound must be analysed.

When analysed under the same conditions, a specific compound always elutes at the same time.

Qualitative analysis

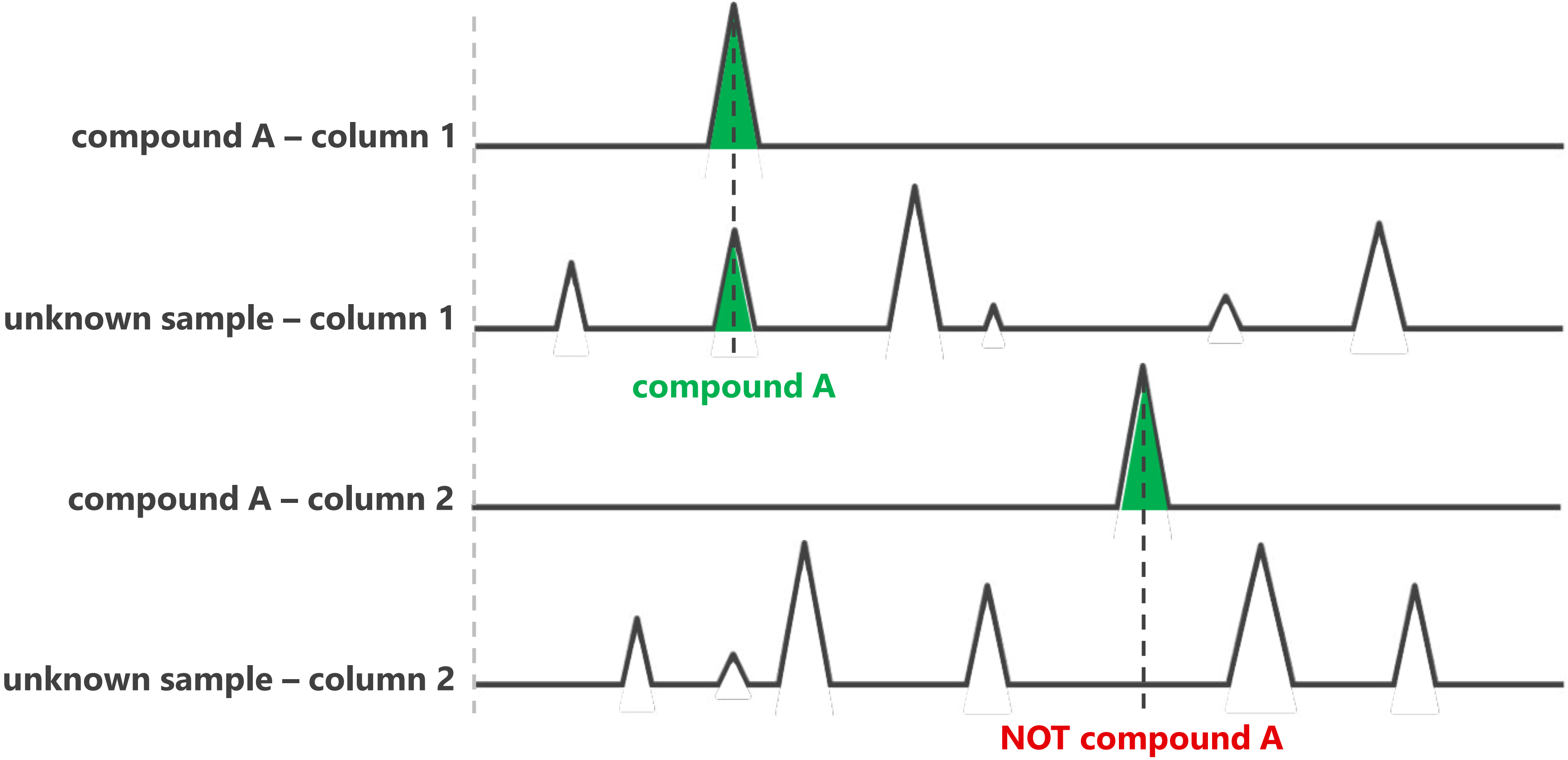


Qualitative analysis

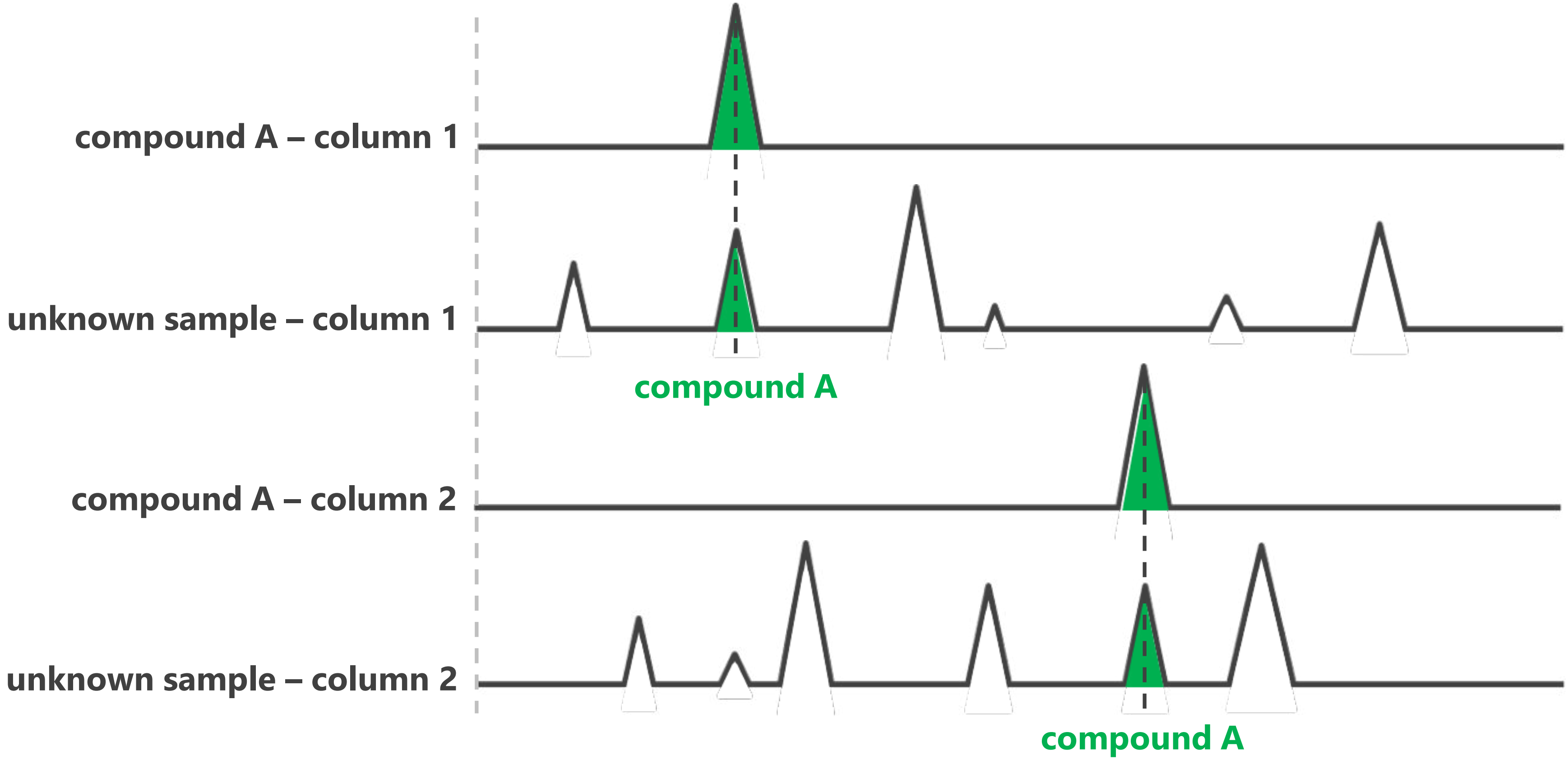
BUT…

Multiple compounds will possess the same retention times as that analyte, so confirmation must be sought.

Qualitative analysis



Qualitative analysis



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Quantitative analysis

Quantitative analysis

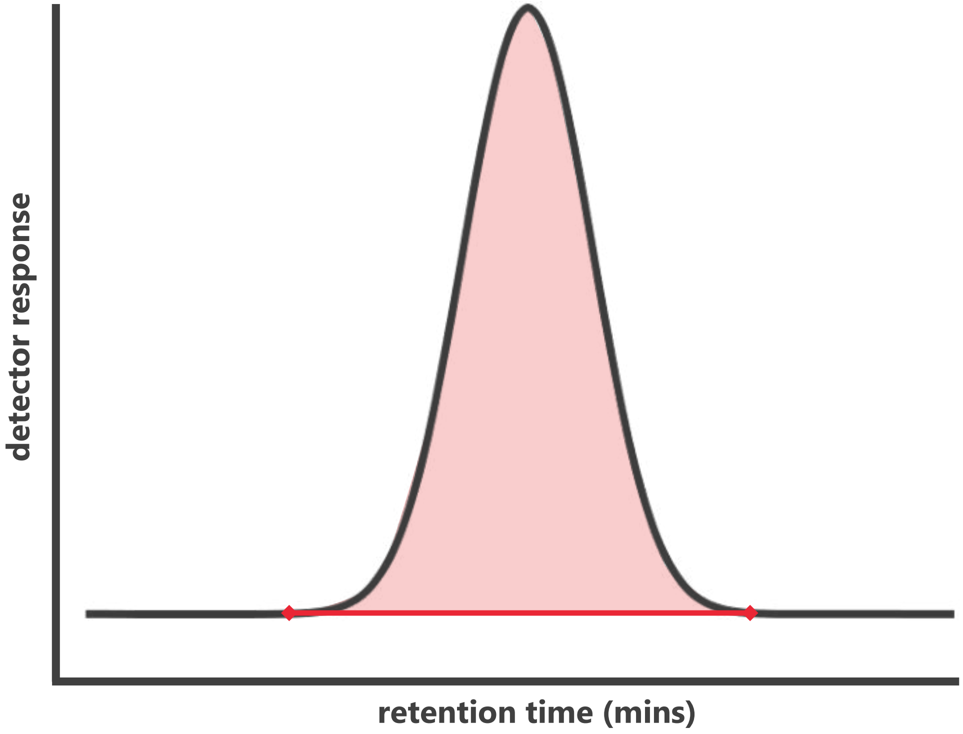
- Area %
- External Standard Calibration
- External Standard Calibration with Internal Standard (ISTD)
- Standard Addition

Integration

Integration determines peak area.

Most software packages use their own algorithm to perform integration.

Refer to your software's manual for details.



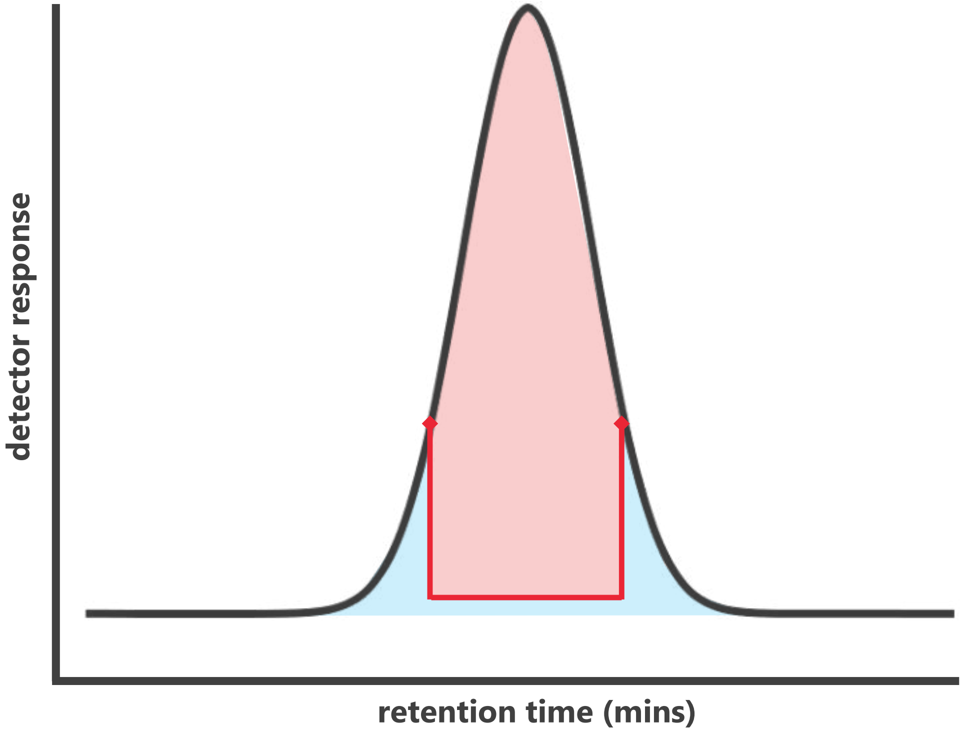
Integration

Integration determines peak area.

Most software packages use their own algorithm to perform integration.

Refer to your software's manual for details.

Incorrect integration = incorrect results



Area %

Area %

peak area 350 450 1100 50 150 900 **total area = 3000**

compound A concentration = 15 %

Area %

Advantages	**Disadvantages**
• Simple analysis method	• Makes assumptions: • All compounds have same response factor • All compounds are detected
• Requires no standard samples	• Doesn’t give definitive amounts

Corrected area %

Corrected area %

peak area	350	450	1100	50	150	900
RRF	1	1	2	2	3	2

corrected area = 1875

compound A concentration = 24 %

RRF = relative response factor

Corrected area %

Advantages	**Disadvantages**
• Simple analysis method • Requires no standard samples	• Makes assumptions: ~~• All compounds have same response factor~~ • All compounds are detected • Doesn’t give definitive amounts

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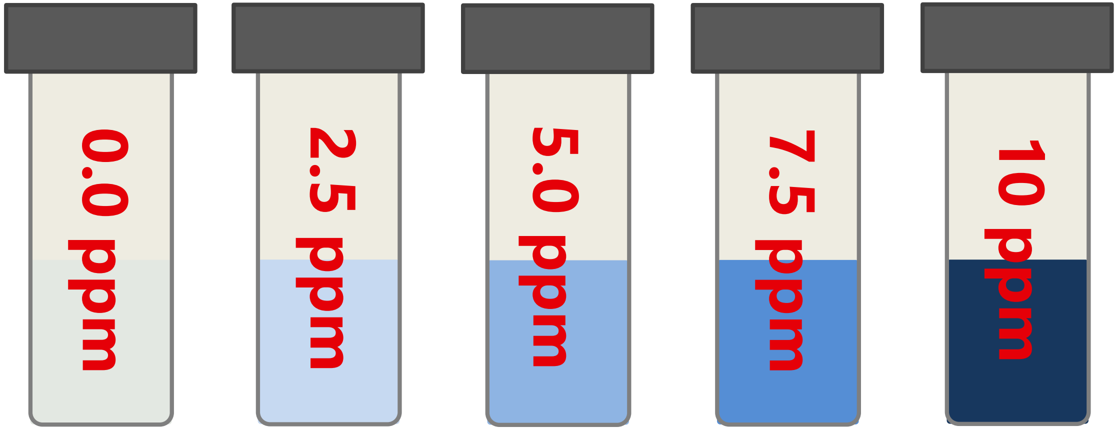
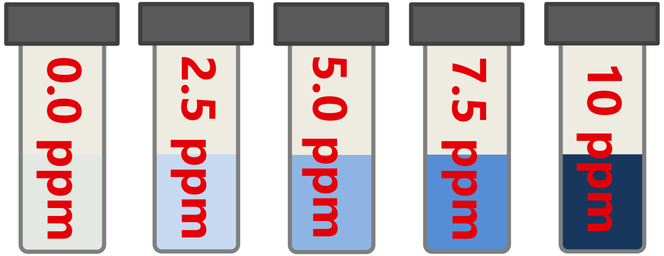
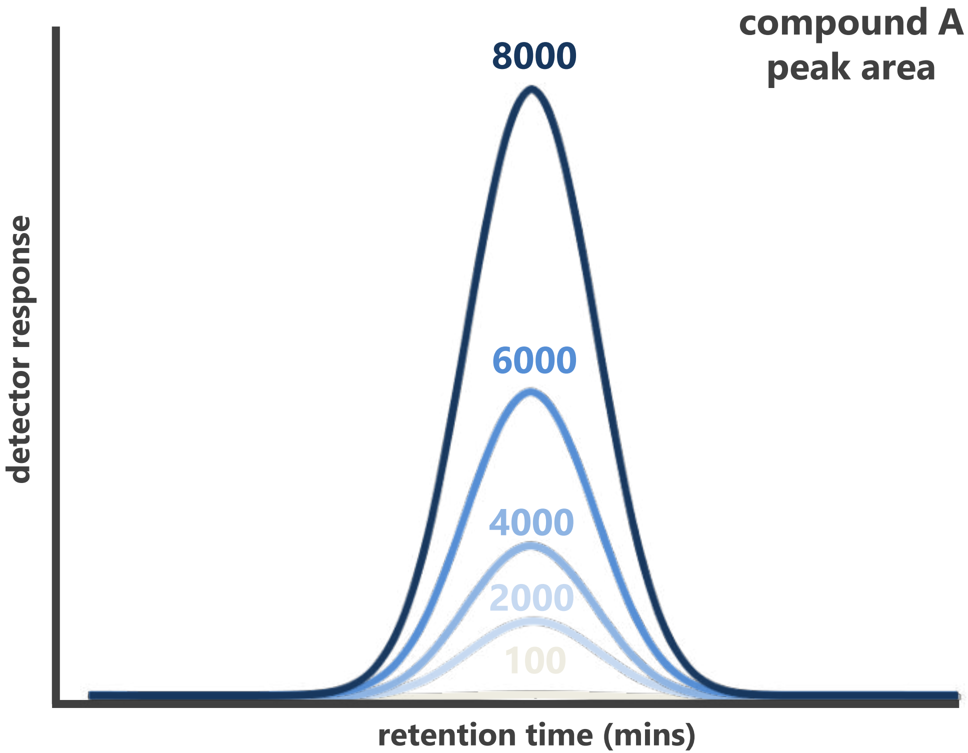
External standard calibration

External standard calibration

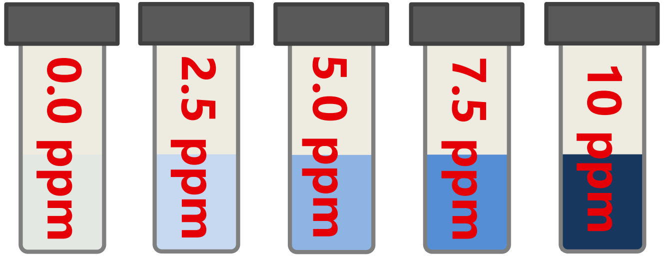


External standard calibration

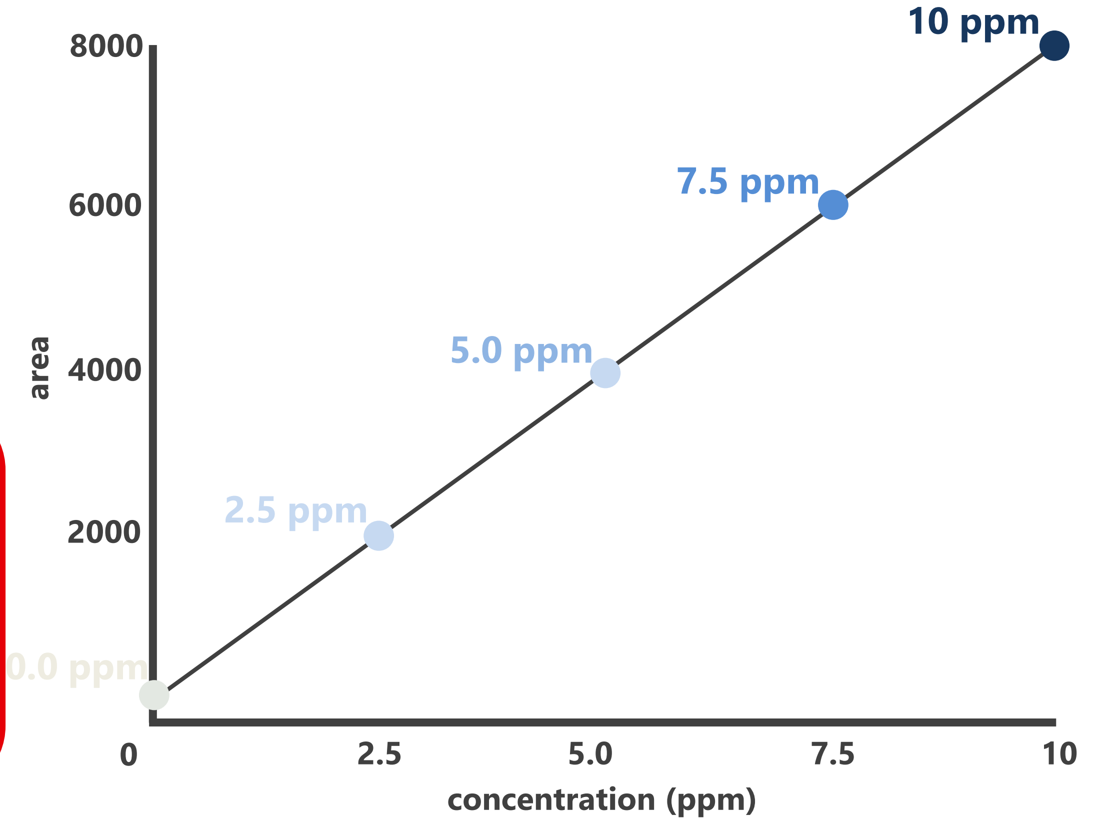




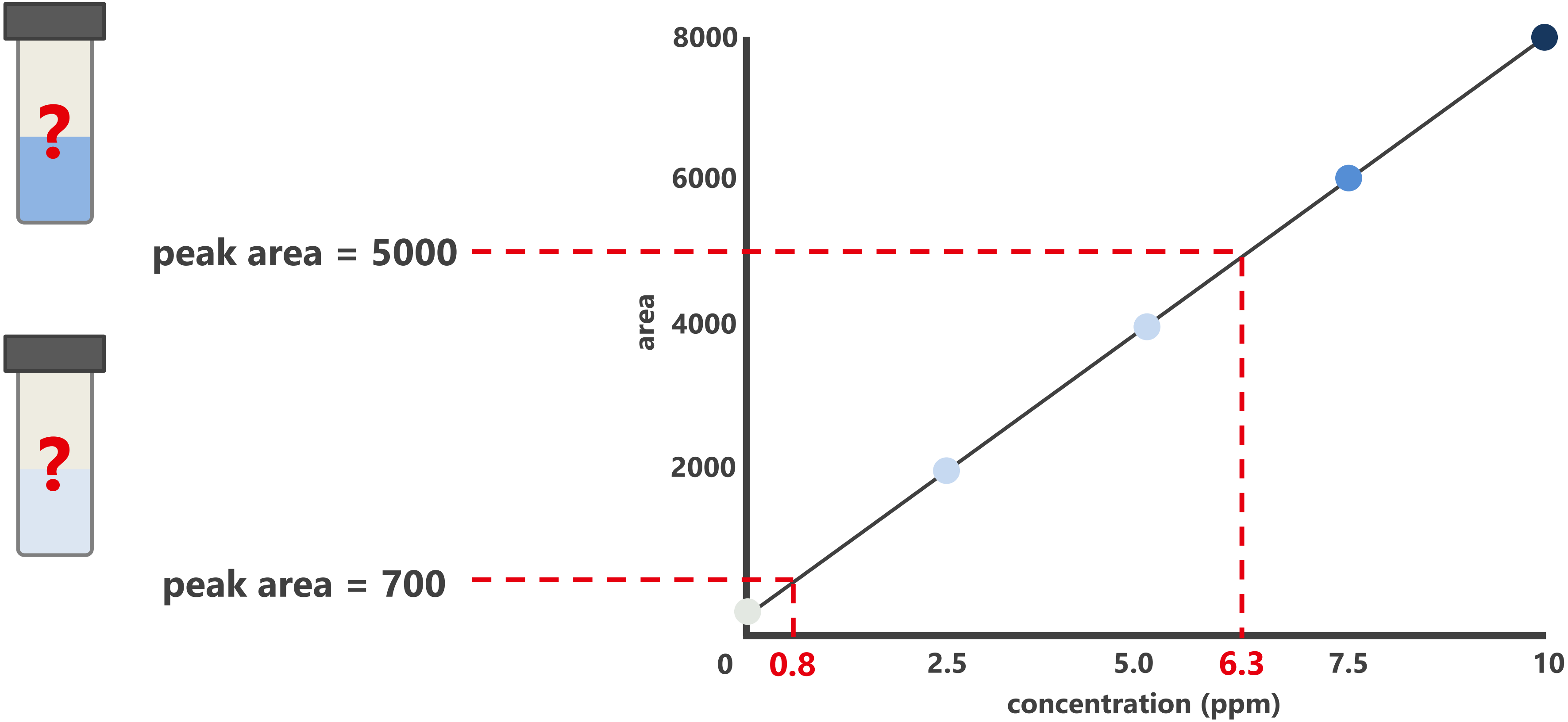
External standard calibration



concentration	peak area
0.0 ppm	100
2.5 ppm	2000
5.0 ppm	4000
7.5 ppm	6000
10 ppm	8000



External standard calibration



peak area = 5000

peak area = 700

External standard calibration

Advantages	**Disadvantages**
• Quantity of compounds can be calculated • Must more robust than area %	• No correction for injection volume variation • Requires preparation of standards

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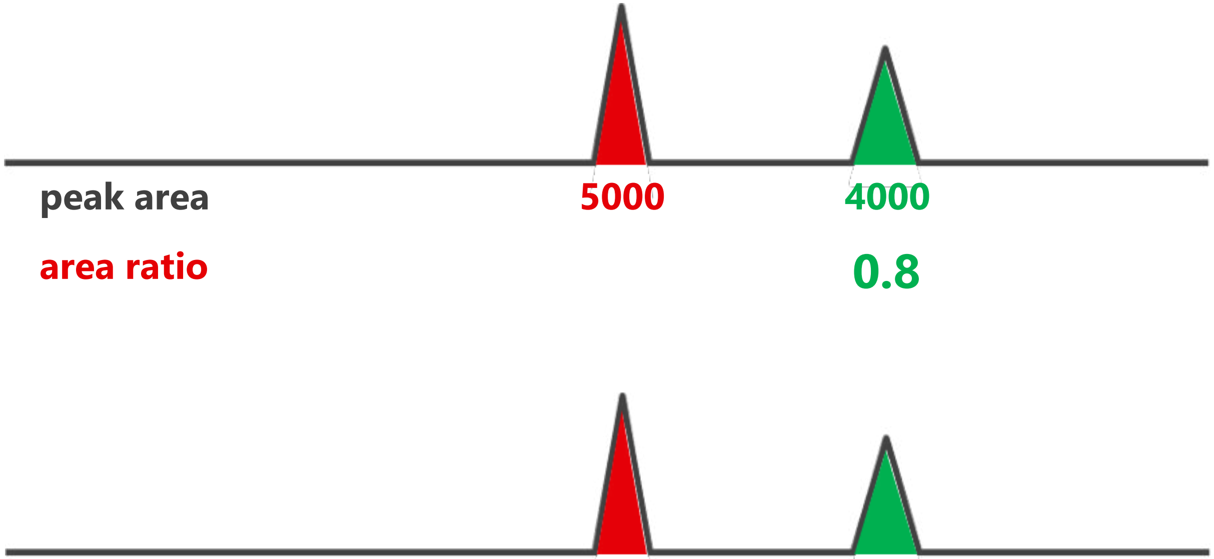
External standard calibration with ISTD

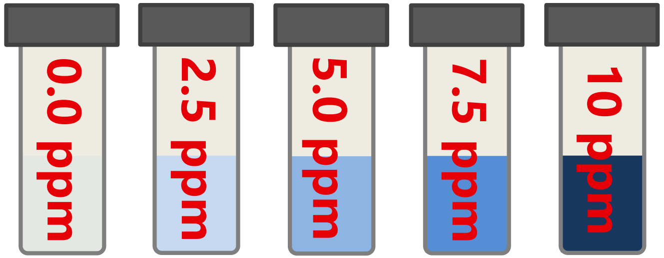
External standard calibration with ISTD

$$\text{area ratio} = \frac{\text{compound area}}{\text{ISTD area}}$$

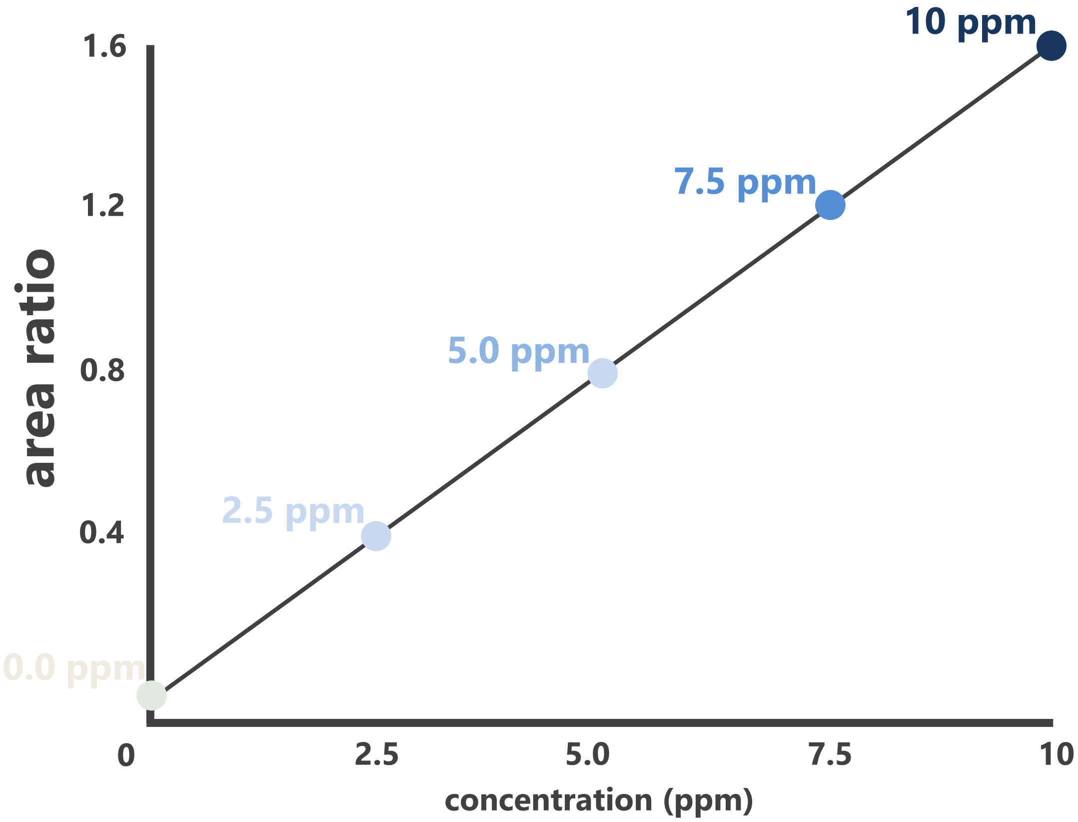


	ISTD	compound A
standard sample injection 1		
peak area	5000	4000
area ratio		0.8
standard sample injection 2		
peak area	4100	3280
area ratio		0.8

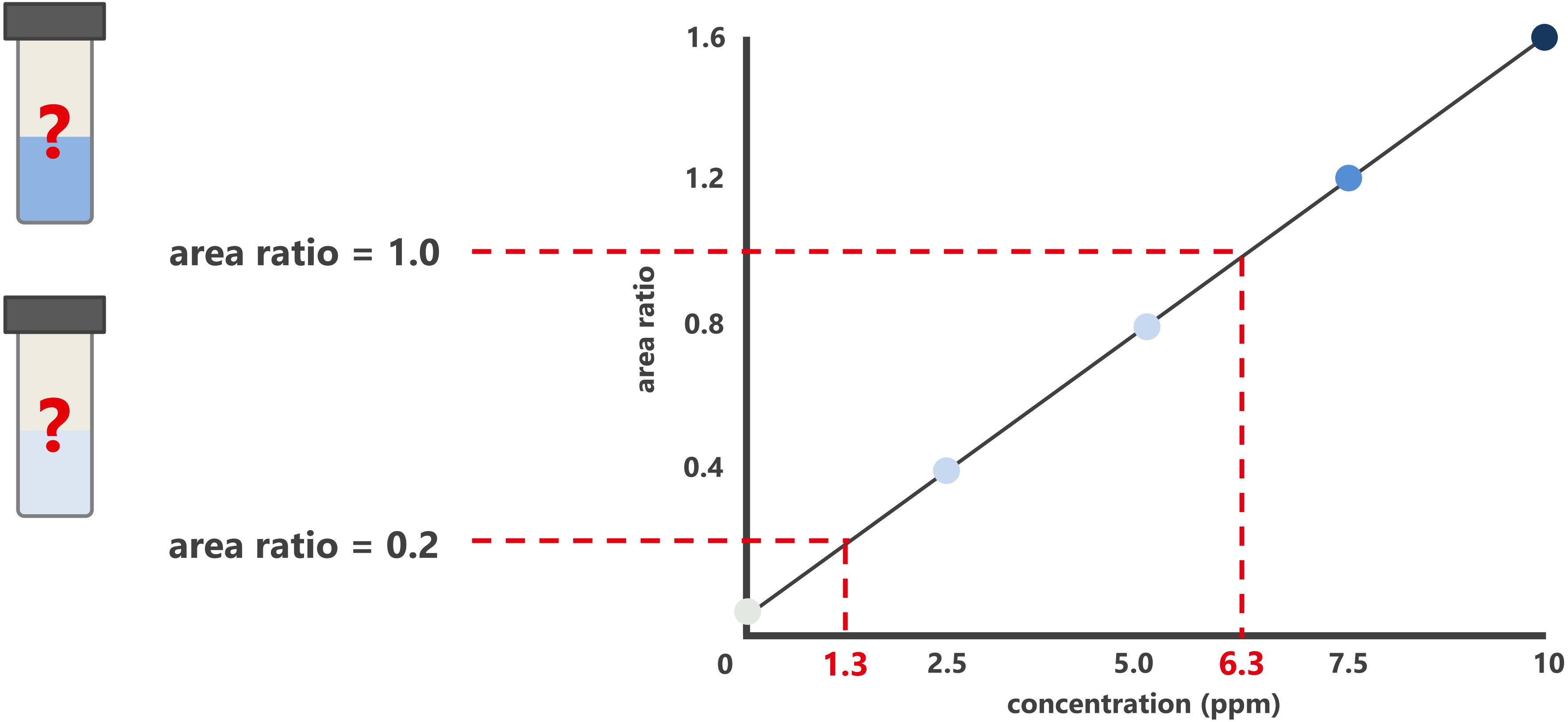
External standard calibration with ISTD



concentration	peak area	area ratio
0.0 ppm	100	**0.02**
2.5 ppm	2000	**0.4**
5.0 ppm	4000	**0.8**
7.5 ppm	6000	**1.2**
10 ppm	8000	**1.6**



External standard calibration with ISTD

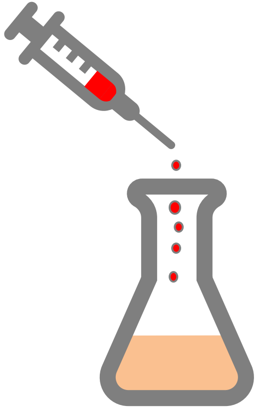


External standard calibration with ISTD

Advantages	**Disadvantages**
• Quantity of compounds can be calculated • More robust method of quantitation	~~• No correction for injection volume variation~~ • Requires preparation of standards • Requires additional preparation

Recovery

Recovery (with surrogate)



Surrogate Addition

after all dilutions:

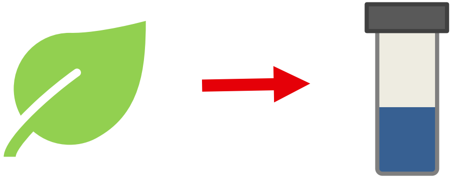
1ppm

Result:

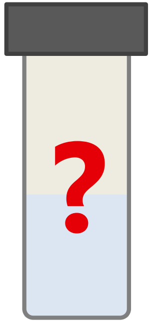
0.7ppm

Recovery:

70%



Recovery (with surrogate)



$$\frac{\text{reported concentration}}{\text{recovery}} = \text{concentration in sample}$$

$$\frac{1.3\ \text{ppm}}{70\ \%} = \textit{1.9 ppm of compound A in}$$ 🍃

Surrogates

Advantages	**Disadvantages**

• Allows tracking of losses during sample preparation
• Can help account for sensitivity changes due to matrix
	• Requires further preparation of standards
	• Requires additional preparation
	• Typically requires ^{13}C, ^{2}D or ^{15}N isotopes
	  • Expensive
	  • Might not be readily available
	  • Requires MS

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Standard addition

Principles of headspace

In a **sealed vessel**, molecules of analytes exist in the **sample phase** or the **gas phase** (headspace).

A **partition coefficient** (K), is the distribution of analytes, at equilibrium, in the sealed vessel.

- **K is dependant on the analyte, the sample matrix & temperature.**

The **phase ratio** (β) relates to the relative volumes of sample and headspace in the vial.

Solvent	K Value
Ethanol	1355
Isopropanol	825
Ethyl acetate	62.4
Dichloromethane	5.65
Toluene	2.82
Cyclohexane	0.077

Air/water system at 40 °C

$$K = \frac{\text{Conc. (sample)}}{\text{Conc. (gas)}}$$

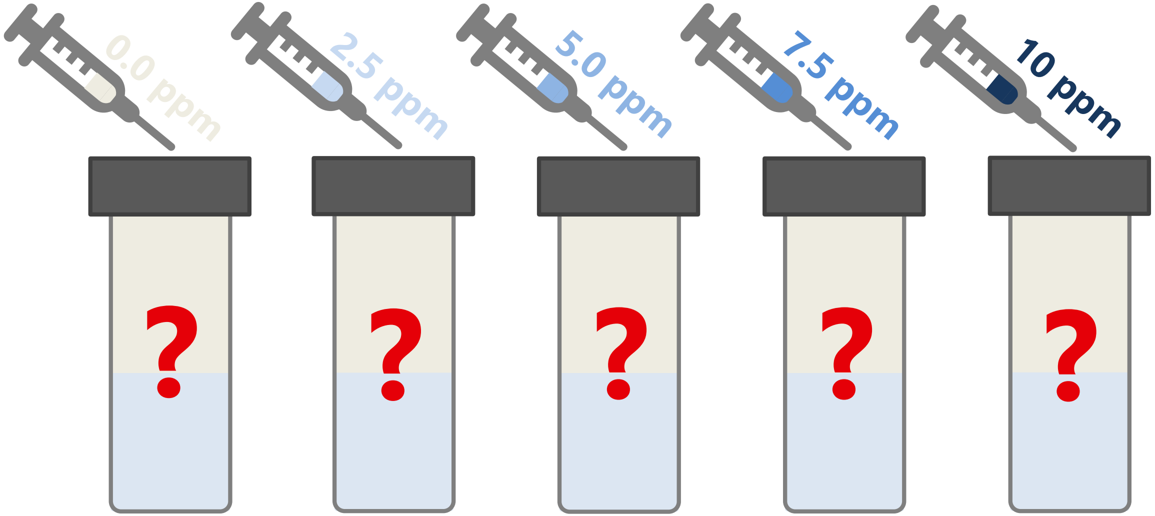
$$\beta = \frac{\text{Volume (gas)}}{\text{Volume (sample)}}$$

$$\text{HS conc.} = \frac{\text{Sample conc.}}{(K + \beta)}$$

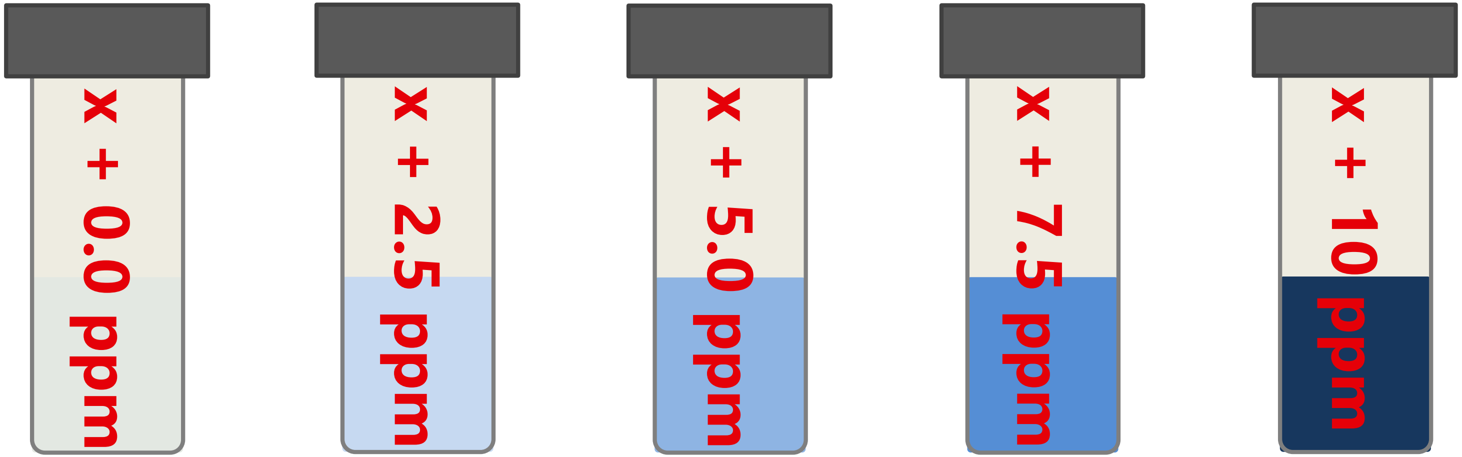
Smaller K = Higher sensitivity

Smaller β = Higher sensitivity

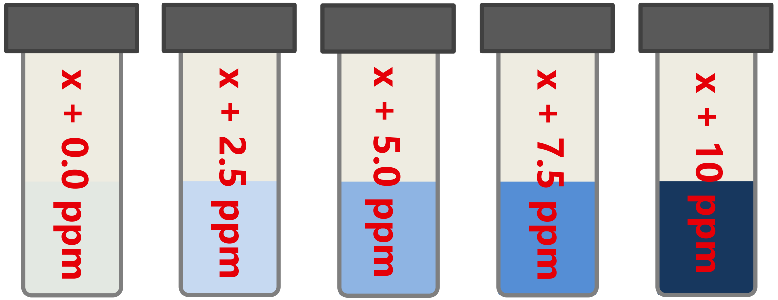
Standard addition



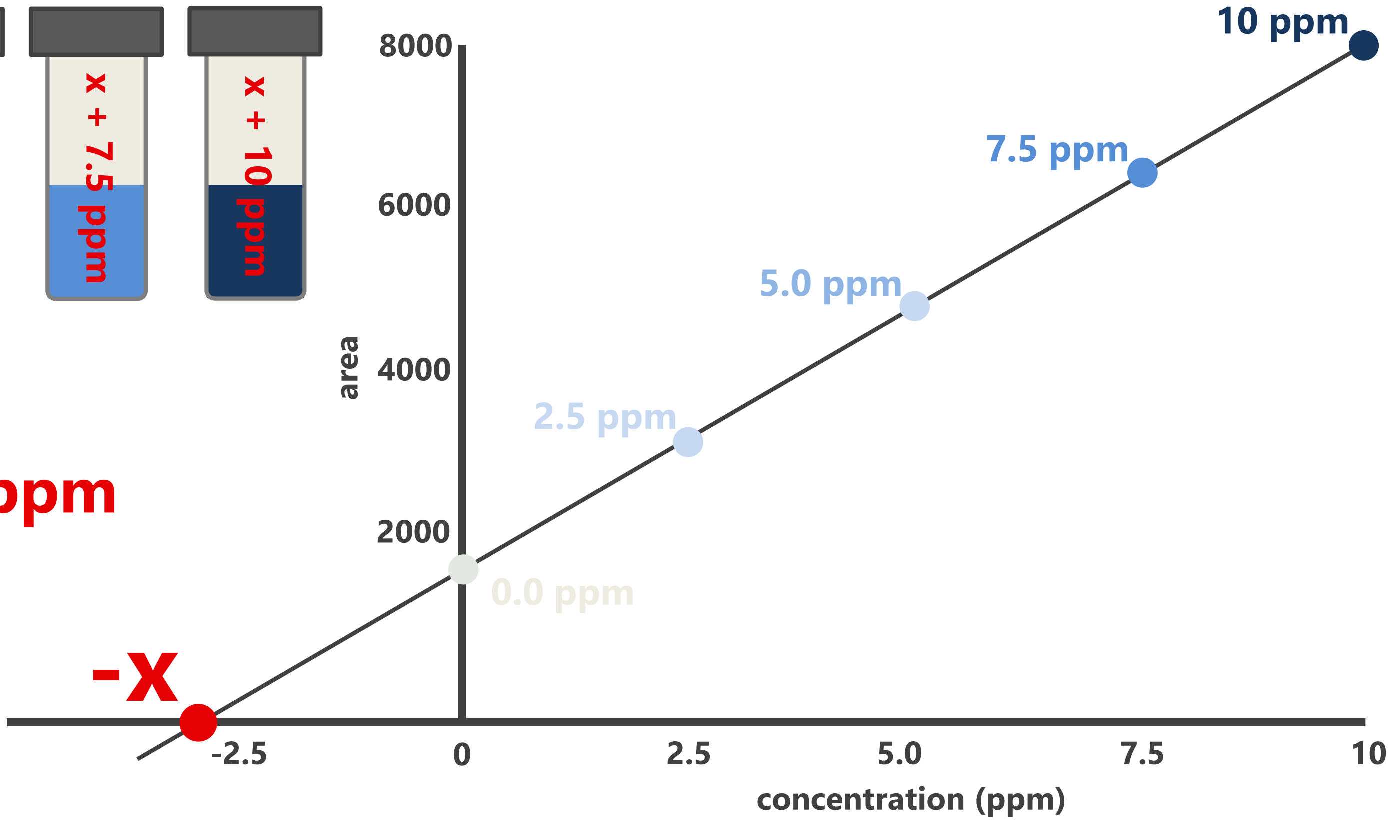
Standard addition



Standard addition



x = 2.6 ppm

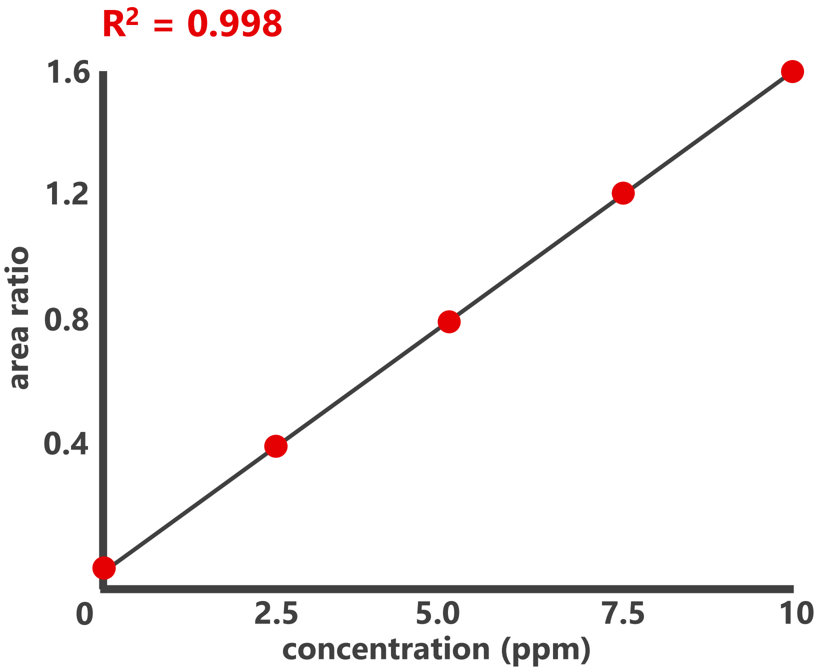


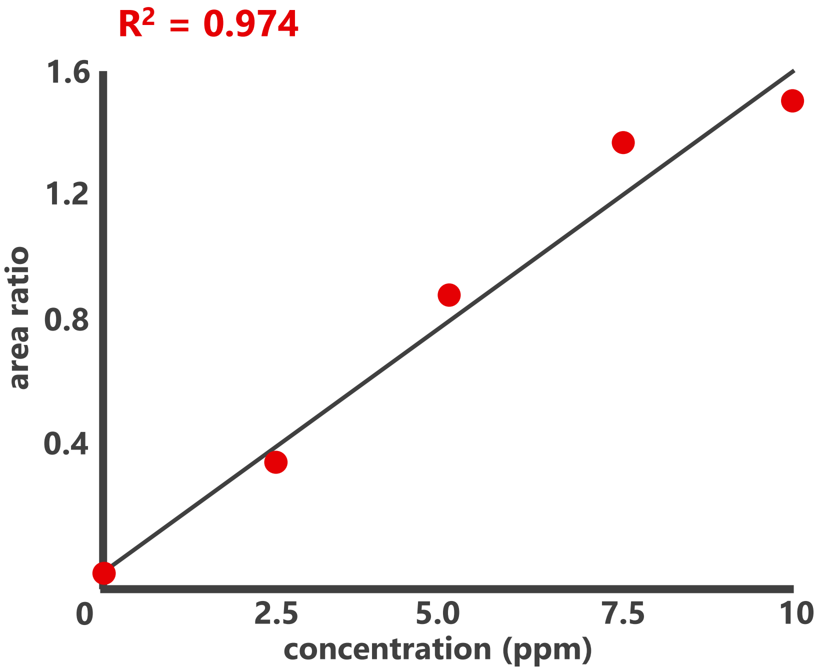
Standard addition

Advantages	Disadvantages
• Accounts for matrix variations • Can be combined with ISTDs	• Very labour and instrument intensive • Requires a separate calibration for every sample!!

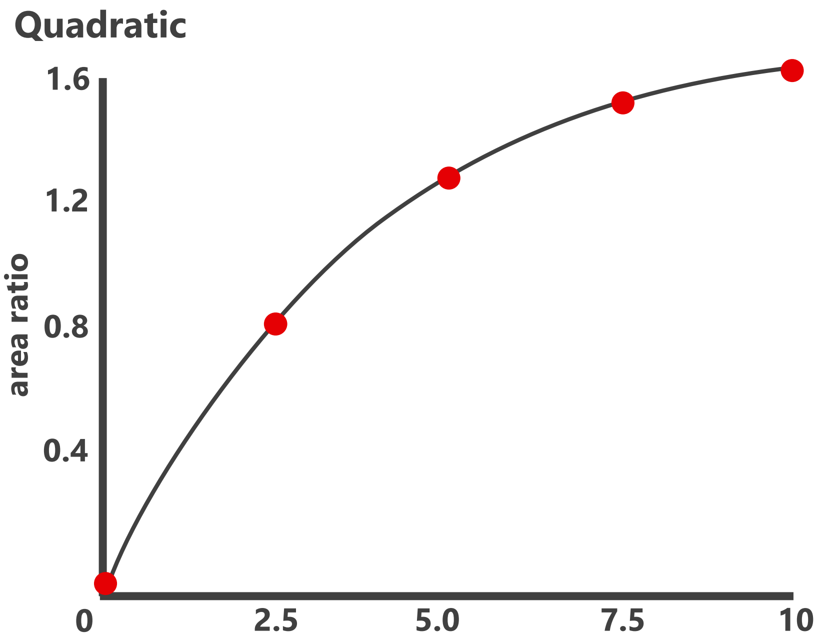
Calibration curve

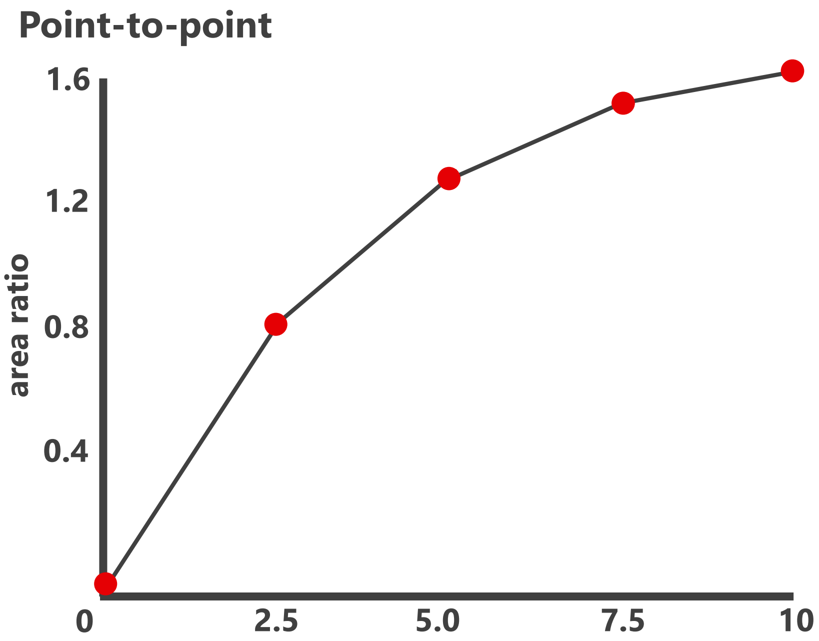
R^2 (coefficient of determination)





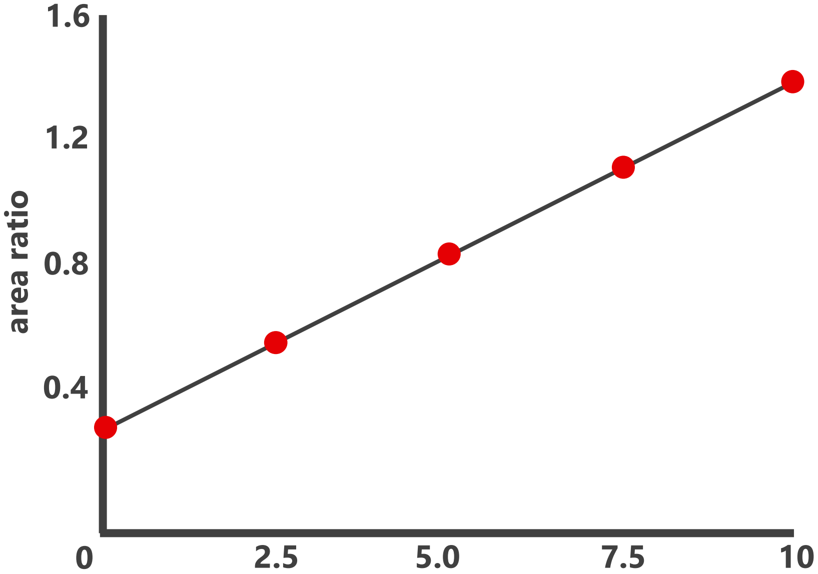
Curve fit


Quadratic
1.6
1.2
0.8
0.4
area ratio
0
2.5
5.0
7.5
10

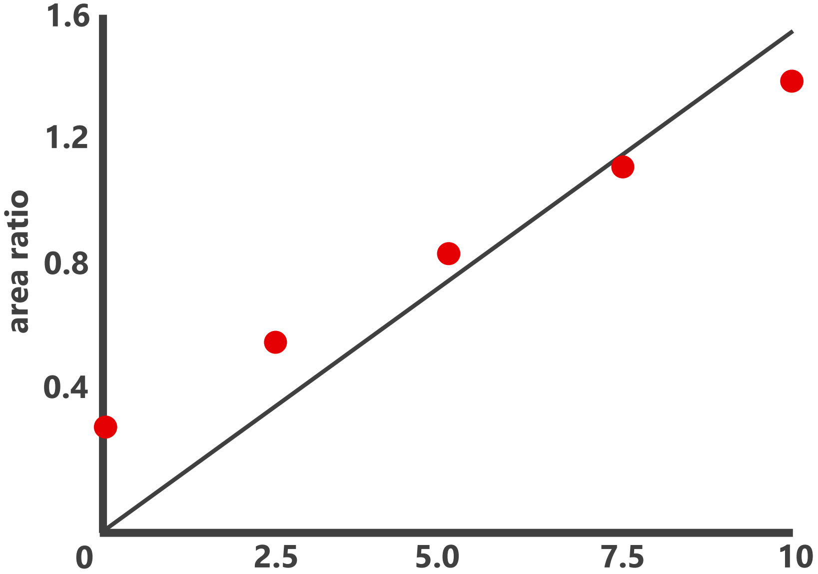

Point-to-point
1.6
1.2
0.8
0.4
area ratio
0
2.5
5.0
7.5
10

Origin

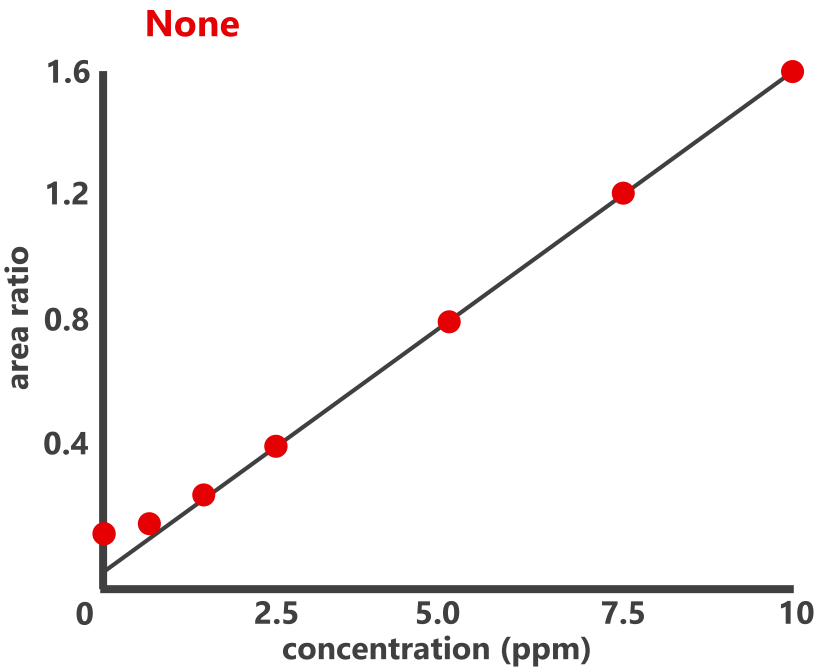
Ignore

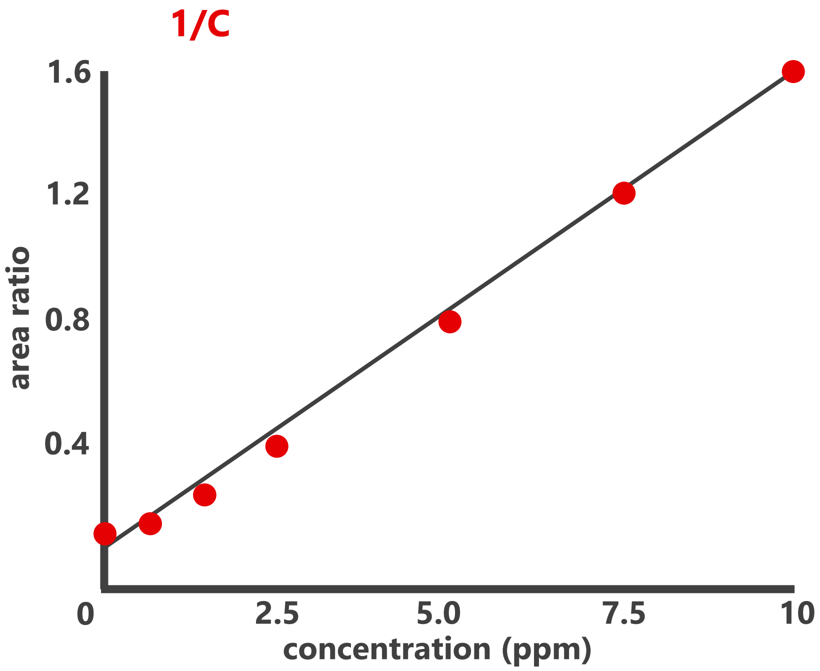


Force through



Weighting


None
1.6
1.2
0.8
0.4
area ratio
0
2.5
5.0
7.5
10
concentration (ppm)


1/C
1.6
1.2
0.8
0.4
area ratio
0
2.5
5.0
7.5
10
concentration (ppm)

Summary

Summary

- **Sample types include samples (unknowns), standards and quality controls (QCs).**

- **Compound types include:**
    - **Targets** - compounds of interest
    - **Matrix** - compounds in sample but not of interest
    - **Internal standard (ISTD)** - added after sample preparation to correct for instrument variability
    - **Surrogates** - added before sample preparation to calculate recovery

- **Qualitative analysis** - what's there?

- **Quantitative analysis** - how much is there?

    - Area % (and corrected area %)
    - External standard
    - External standard with ISTD
    - Standard addition

- **Calibration curves**
    - R^2, origin, curve fit & weighting

Next time

The next session will be on…

Maintenance & Troubleshooting

This will cover:
- *Inlet maintenance*
- *Column installation & maintenance*
- *Detector maintenance*
- *Common troubleshooting*

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Theory and Key Principles Series

Gas Chromatography (GC)

Session 8 – Maintenance & Troubleshooting

Theory & Key Principles Series – GC

- *Introduction to Gas Chromatography **
- *GC Columns **
- *The Split/Splitless Inlet **
- *Advanced Liquid Injection Techniques **
- *Alternatives to Liquid Injection **
- *Choice of Detectors for GC **
- *Processing GC Data **
- **Maintenance & Troubleshooting**
- Method Development

** Now available on demand at www.shimadzu.co.uk/webinars/gc*

Maintenance & Troubleshooting

In this presentation:

- Inlet maintenance
- Column maintenance & installation
- Detector maintenance
- Common troubleshooting

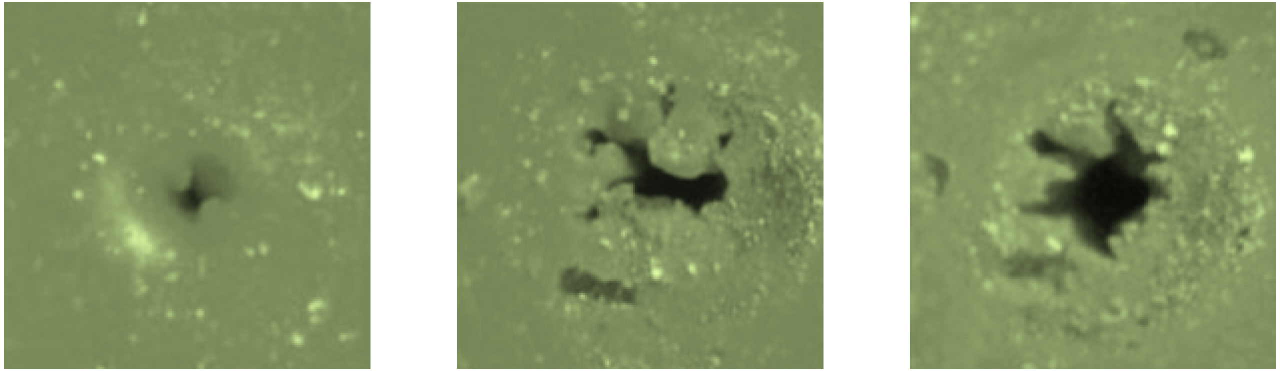
Inlet maintenance

Septum

One of most commonly replaced consumables on liquid GC system.

Repeated piercing can cause septum coring & leaks.

Wide variety of septum types.



Liner & O-ring

Even with clean samples/standards, deposits build up in the liner.

Frequency of replacement is application/sample specific.

The O-ring should be replaced at the same time as the liner!

Liner & O-ring

Split

With wool

Split/splitless

Splitless

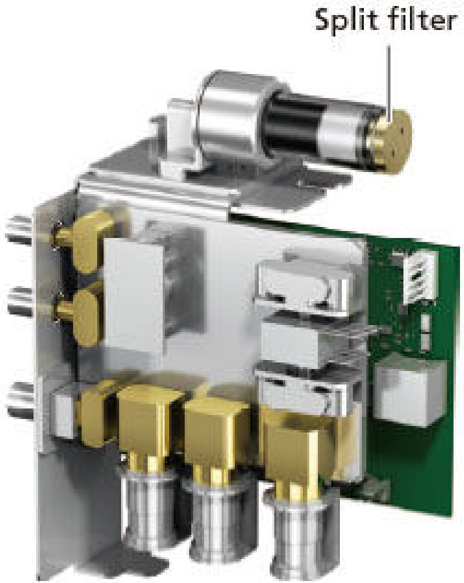
Split filter

Sits in flow path of split line between inlet and flow controller.

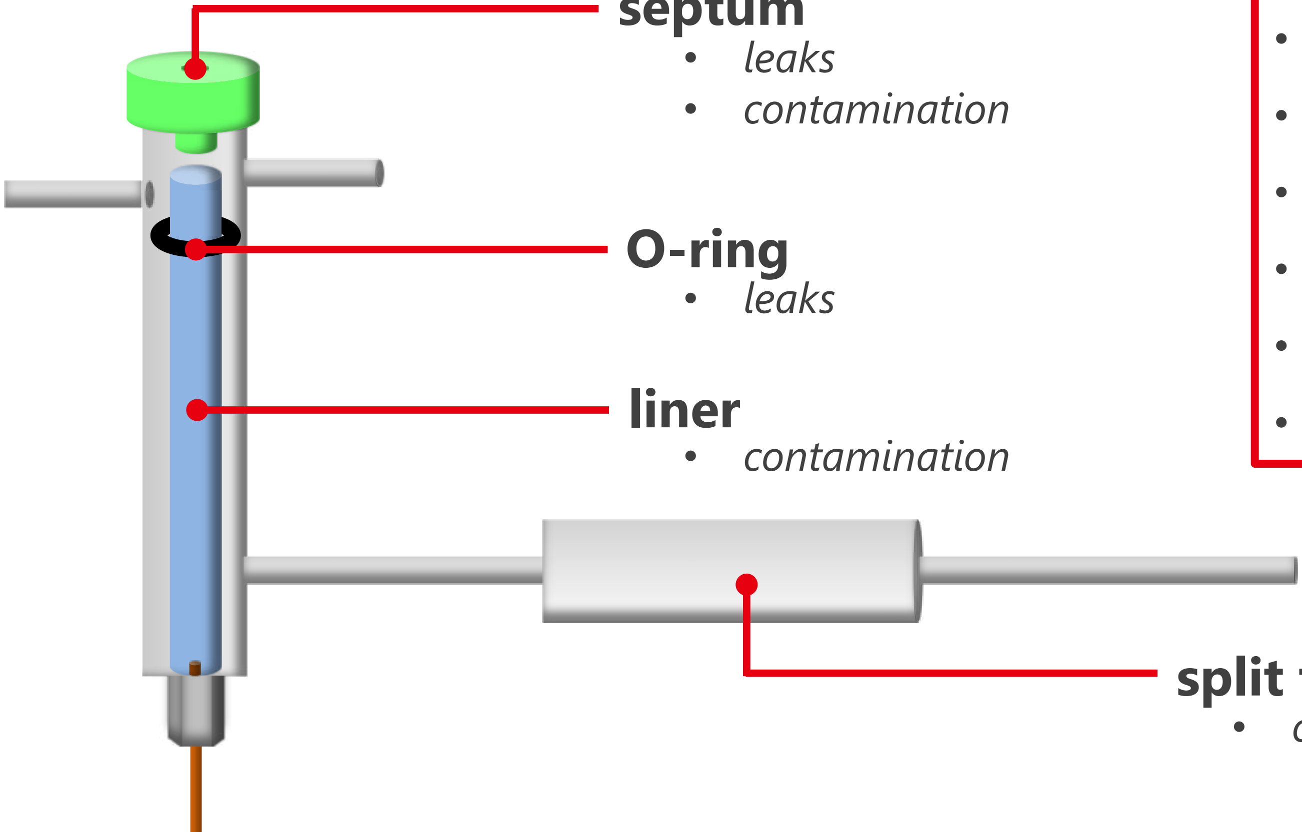
Protects flow controller from contamination.

Needs to be replaced periodically.

Modern GCs have indicators to highlight when to replace.



Inlet maintenance



septum
- *leaks*
- *contamination*

O-ring
- *leaks*

liner
- *contamination*

split filter
- *contamination*

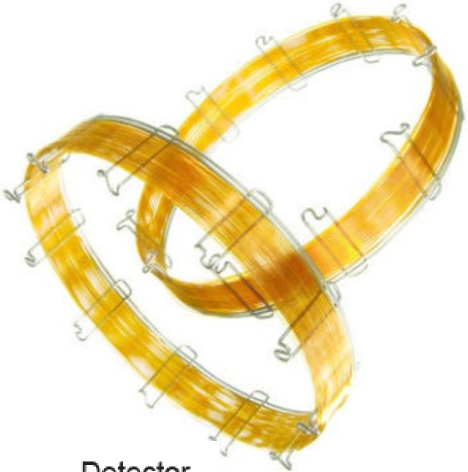
- Turn off heaters
- Let system cool
- Turn off flow
- Perform maintenance
- Purge system
- Heat back up

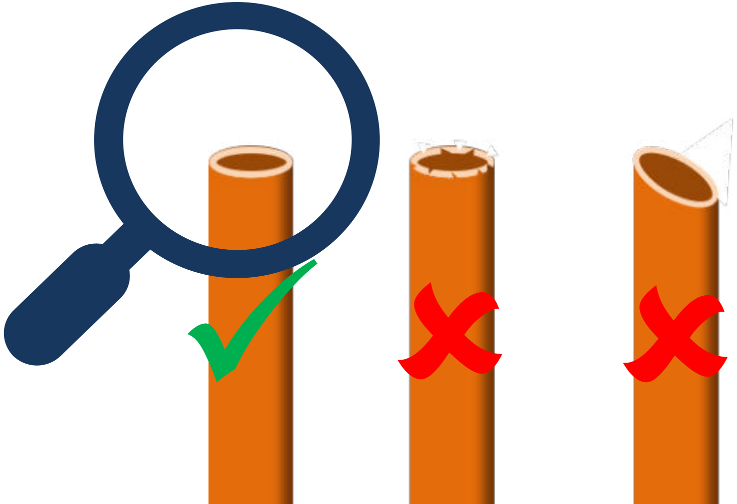
Column maintenance & installation

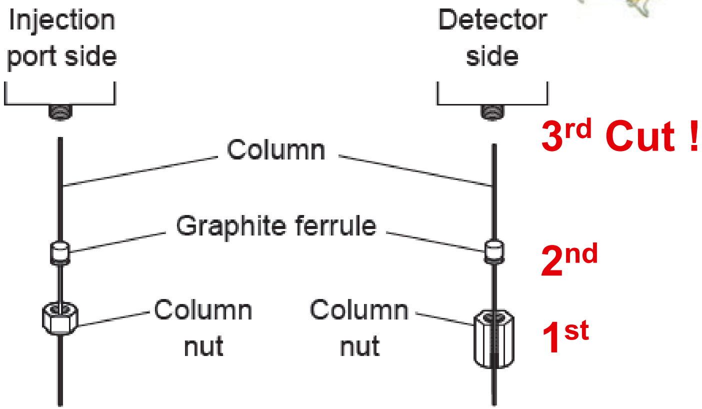
Column (WCOT & PLOT) installation

Requires:

- Trimming column
- Connecting column to inlet & detector
- Purging & conditioning column







Ferrules

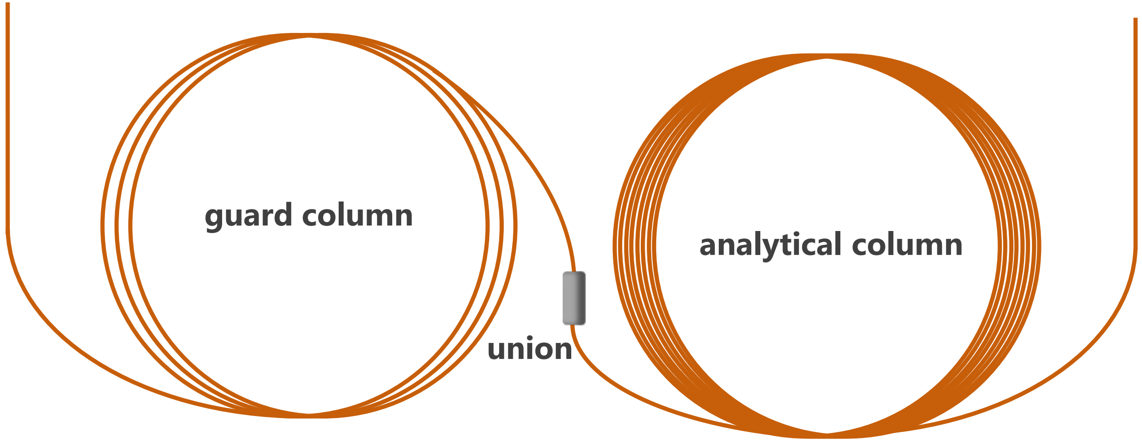
Graphite	Graphetised Vespel (GV)	Metal
Soft material so ferrule can be easily removed	Mixture of soft graphite with harder vespel – ferrules can usually be removed	Makes a permanent seal to the column
Very malleable so makes a very easy seal & difficult to overtighten	Overtightening is possible but often needs to be extreme to cause issues	Overtightening results in column snapping, sometimes after a few heat cycles!
Sometimes requires re-tightening	Requires re-tightening after first few heat cycles	Once it’s on, it’s never coming off!
Air-permeable – not for MS 	Suitable for MS 	Suitable for MS 

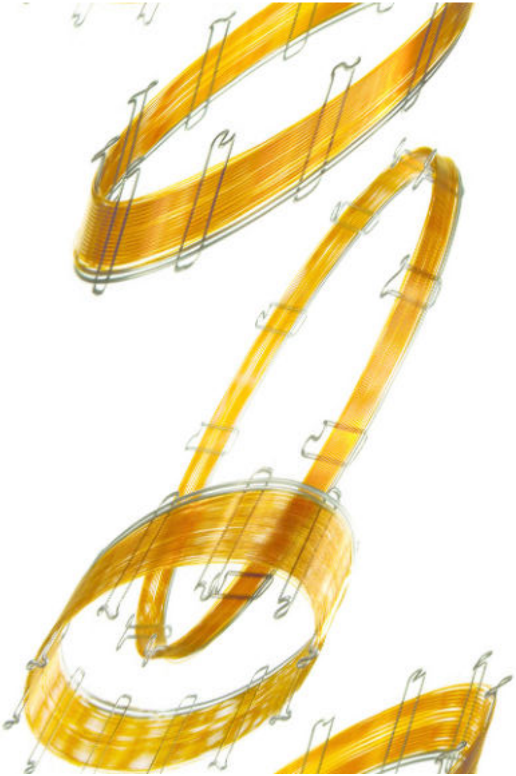
Column (WCOT & PLOT) maintenance

Columns get contaminated, just like liners

Periodic trimming of the front-end is required

Eventually, columns become too short/too old and need replacing





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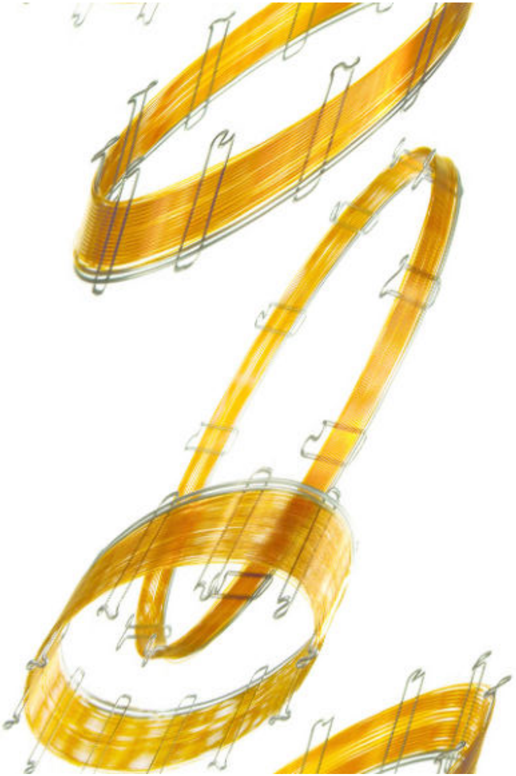

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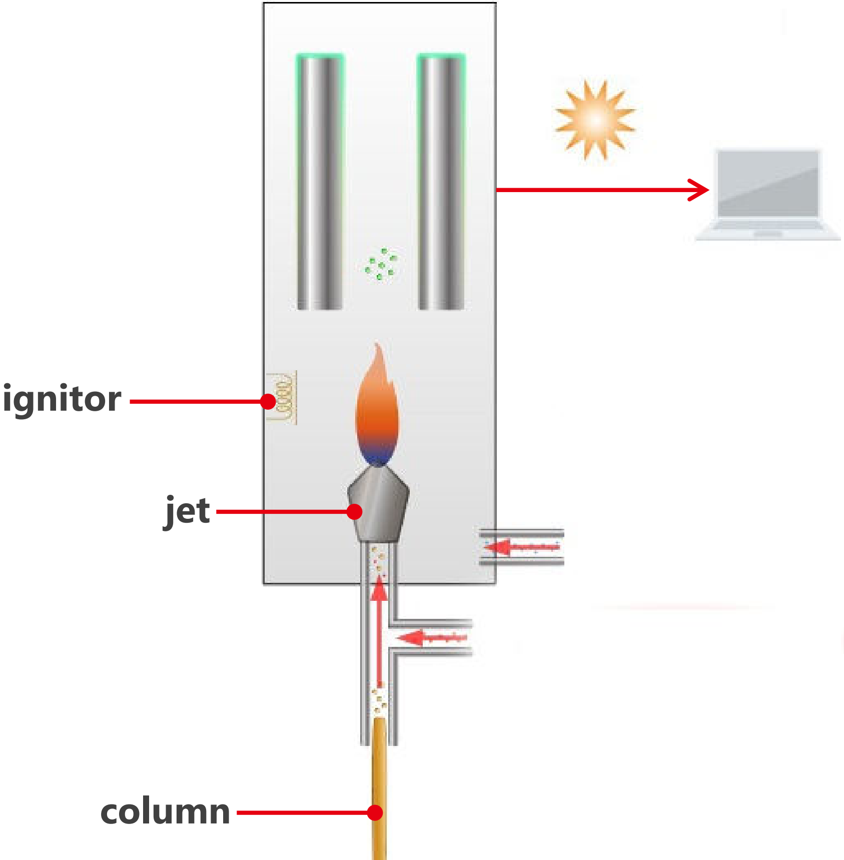
Detector maintenance

Detector maintenance

FID

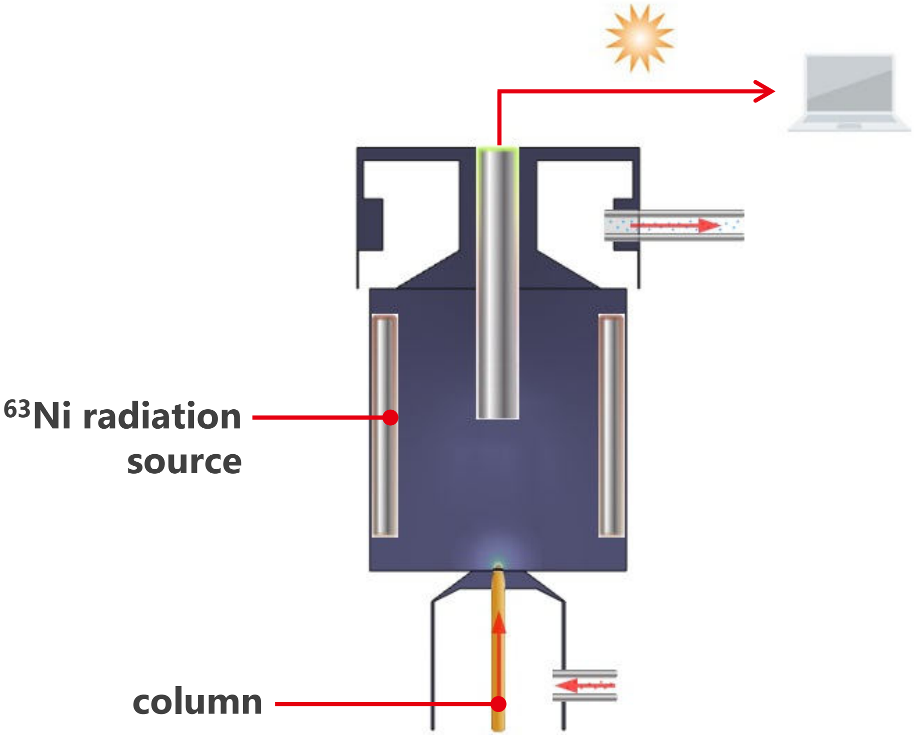
- Column
- Ignitor
- Jet



Detector maintenance

ECD

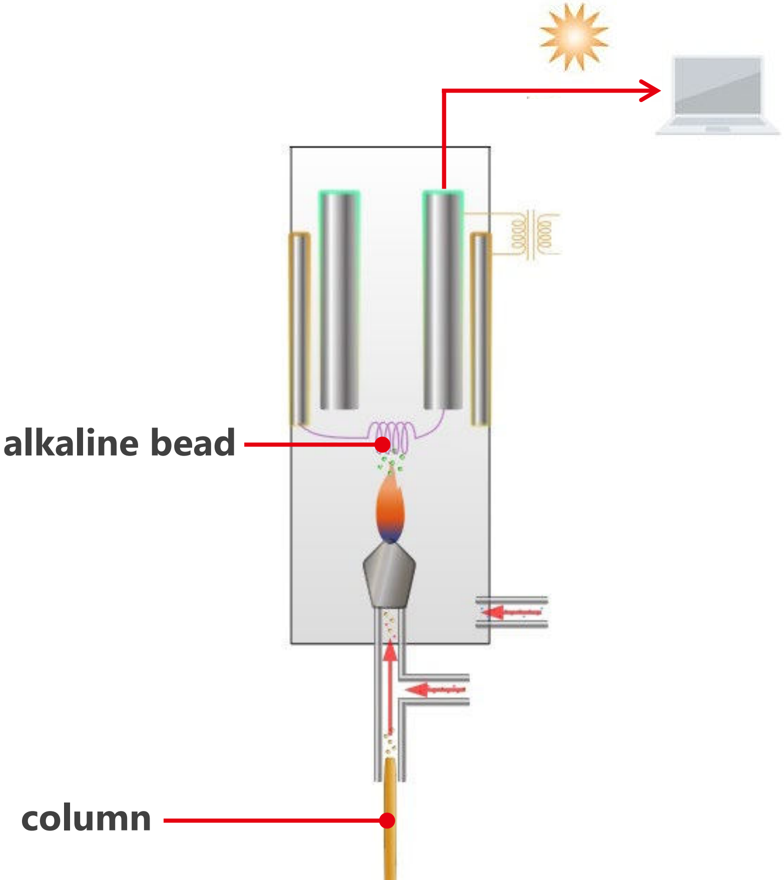
- Cell (bake-out only)
- Column



Detector maintenance

FTD (NPD)

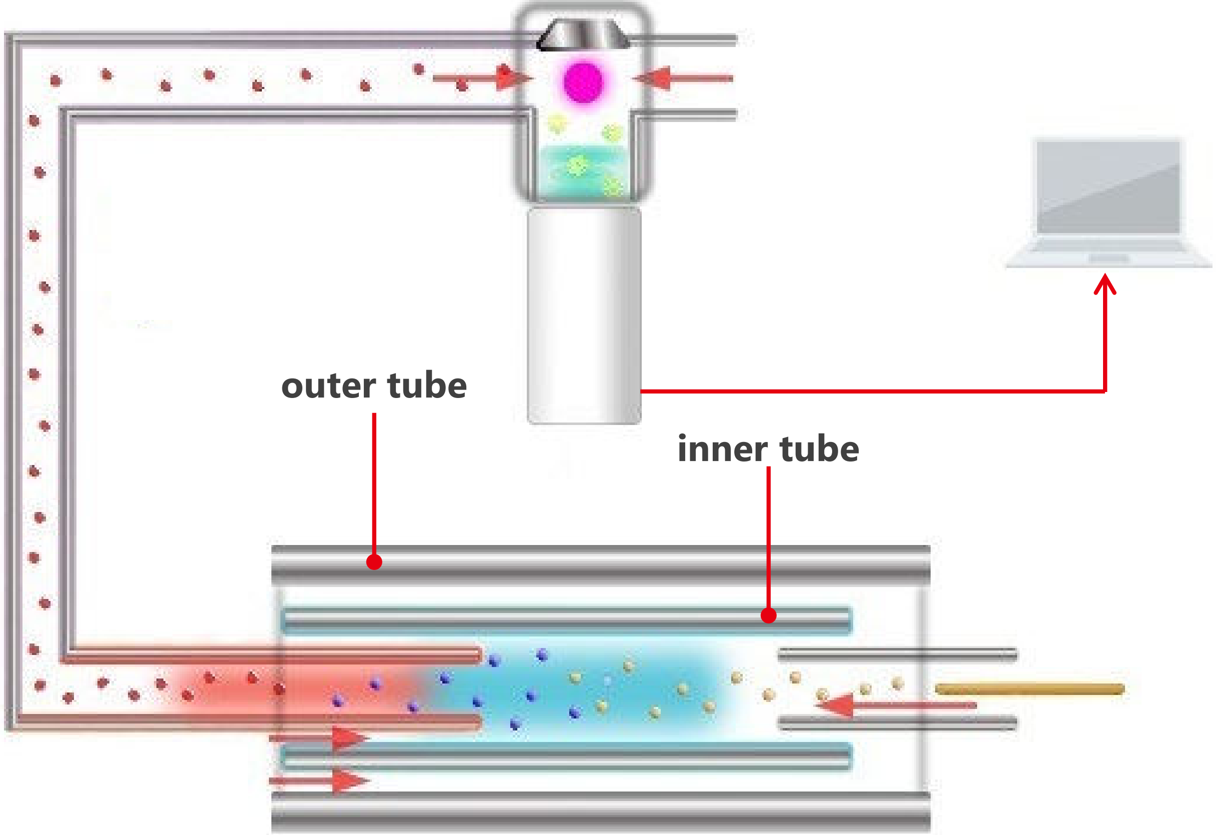
- Alkaline bead
- Column



Detector maintenance

SCD

- Ceramic tubes
- Column



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Other maintenance

Other maintenance

- Gas cylinders (annual inspections, regulator replacement, etc.)
- Gas generators
- Gas filters
- Autosamplers (syringes, tension chords, valves, needles, etc.)
- Flow devices (backflush, detector splitting, etc.)
- PC maintenance (software updates, back-ups, etc.)

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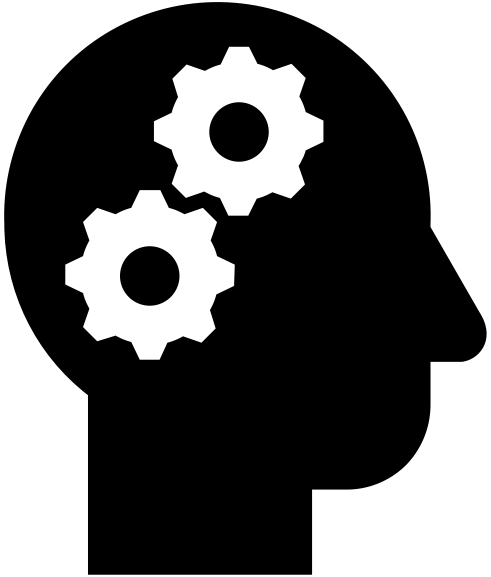
Troubleshooting

Basic steps

Check the obvious!!

- Power
- Comms cables
- Gases
    - Purity
    - Pressure
    - Correct gas
- Typing error
- Vial in right place



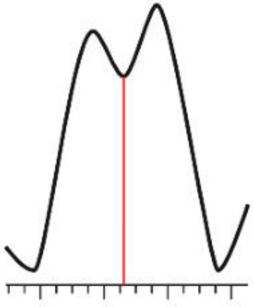
Basic steps

Identify the cause

- Make sure the problem really exists – repeat the test
- Consider what has been changed
- Change **ONE** thing at a time!
- Throw away any old parts

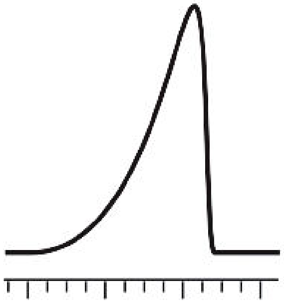
Common issues

Poor resolution



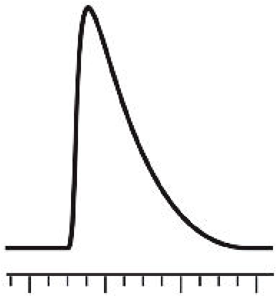
- wrong column
- sample overload
- bad method

Fronting



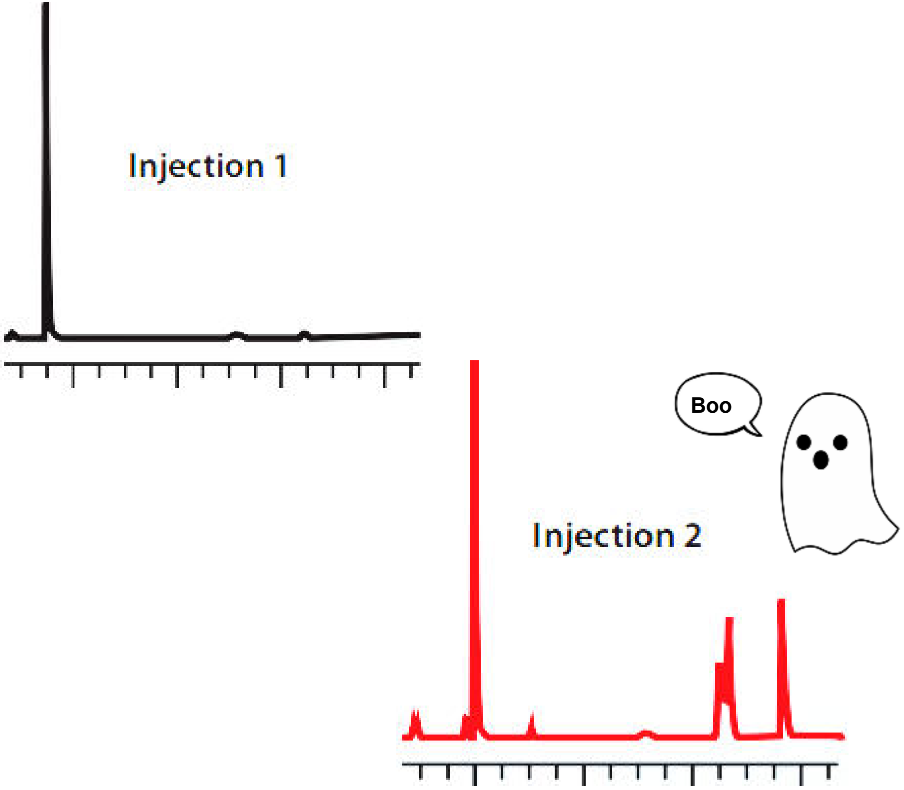
- wrong column
- sample overload

Tailing



- contamination
- active sites
- adsorption
- leak
- install error

Ghost peaks

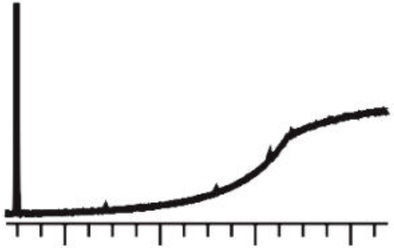


How to ghost hunt

- is it a repeatable event?
- does it appear if you run the GC without performing an injection?
- is the retention time consistent?
- does the liner & septum need replacing?
- are you **SURE** it’s not in the sample?!

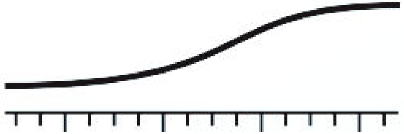
Baseline issues

Bleed



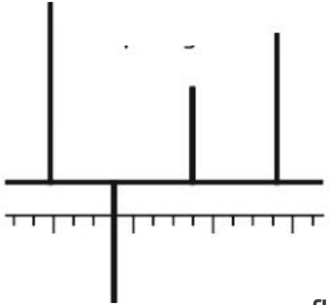
- poor conditioning
- aging column
- excessive temperature

Drift

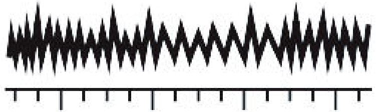


- gas quality
- gas flow

Spiking



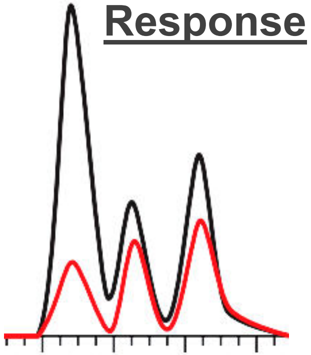
Noise



- gas flow issue
- contamination
- column bleed
- cable/electrical issue

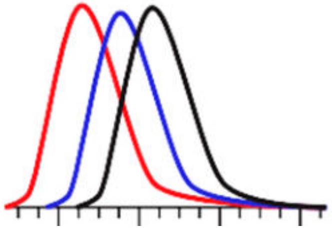
Peak inconsistencies

Response



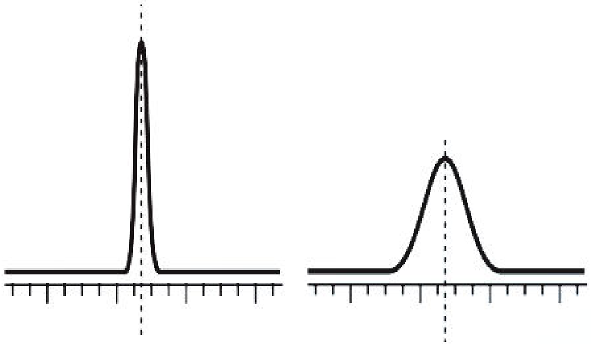
- is there a pattern?
- increase, decrease, neither?
- sample issue
- syringe issue
- detector issue

Shifting RT



- incomplete vaporisation
- leaks
- liner overload

Broad peaks



- low liner flow
- slow analysis
- poor focussing

Summary

- **Maintenance prevents troubleshooting!**
  - Preventative steps are always best

- **Most issues arise from inlet**
  - Replace septum, liner & O-ring frequently
  - Split filter should be changed periodically
  - Column requires occasional trimming

- **Correct column installation is crucial**
  - Use correct ferrules
  - Cut column properly
  - Ensure installation depth is accurate
  - Condition according to instructions

- **Detector maintenance is infrequent for most systems**
  - Usually far less maintenance requirements than inlet (except MS)

- **Troubleshooting is all about approach**
  - Check the obvious first!
  - Think about what might have changed
  - One step at a time
  - Try and isolate where the problem is originating

Next time

The next session will be on…

Method Development

This will cover:

- *Things to consider*
- *Carrier gas selection*
- *Detector selection*
- *Liner choice*
- *Oven program*
- *Derivatisation*

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