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Theory and Key Principles Series

Gas Chromatography (GC)

Session 5 – Alternatives to Liquid Injection

Introduction

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

Presenter

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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

* *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)

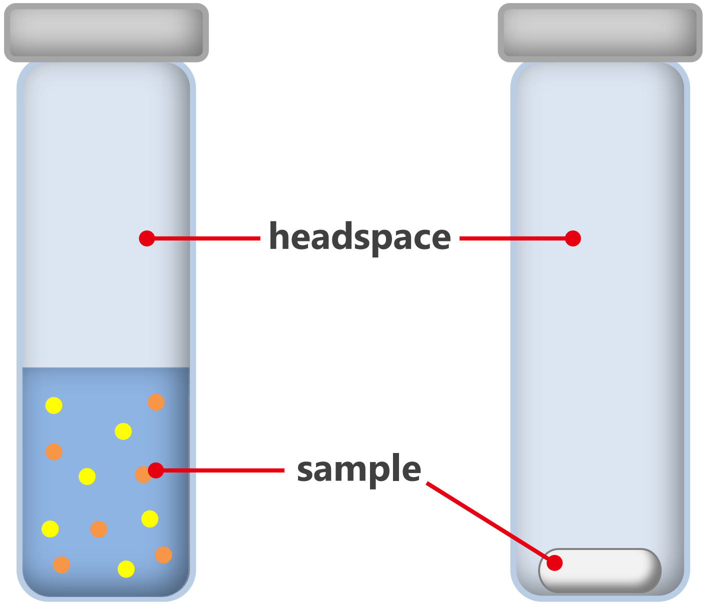
Headspace

'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**.



<u>Common HS-GC applications:</u>

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

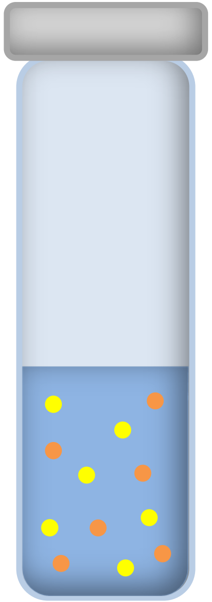
Principles of headspace

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.

There are two benefits to this:

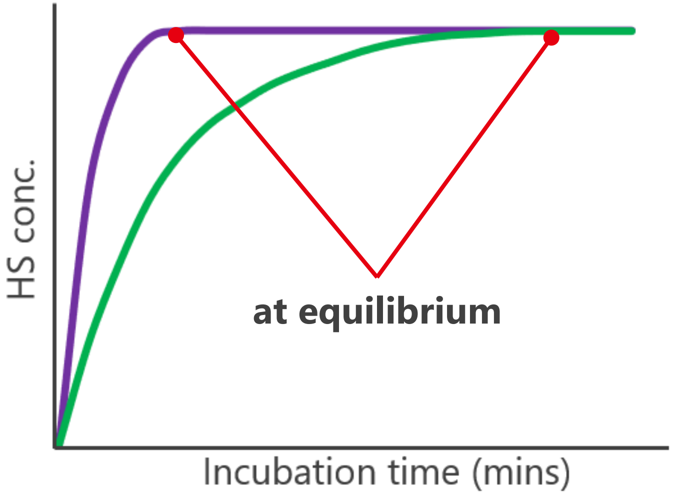
- Ensures constant temperature (stable K)
- Reduces K (higher sensitivity)
    - *Inorganic salts can also be added to liquid samples to reduce K further Known as '**salting out**'*

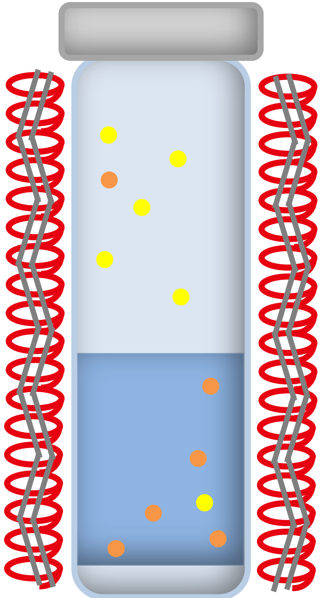
	K Value	
Solvent	**40 °C**	**80 °C**
Ethanol	1355	328

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

With agitation

Without agitation





Headspace autosamplers

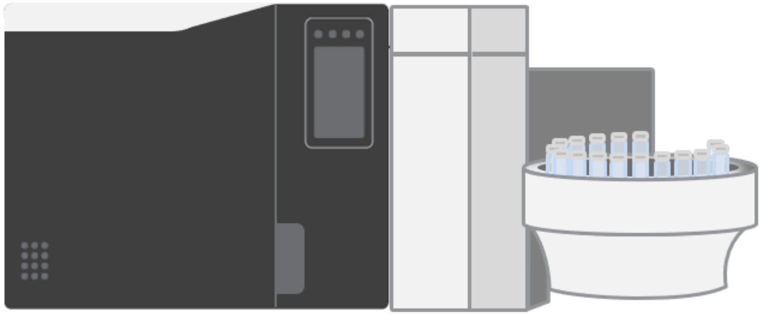
Two main types of autosampler systems:

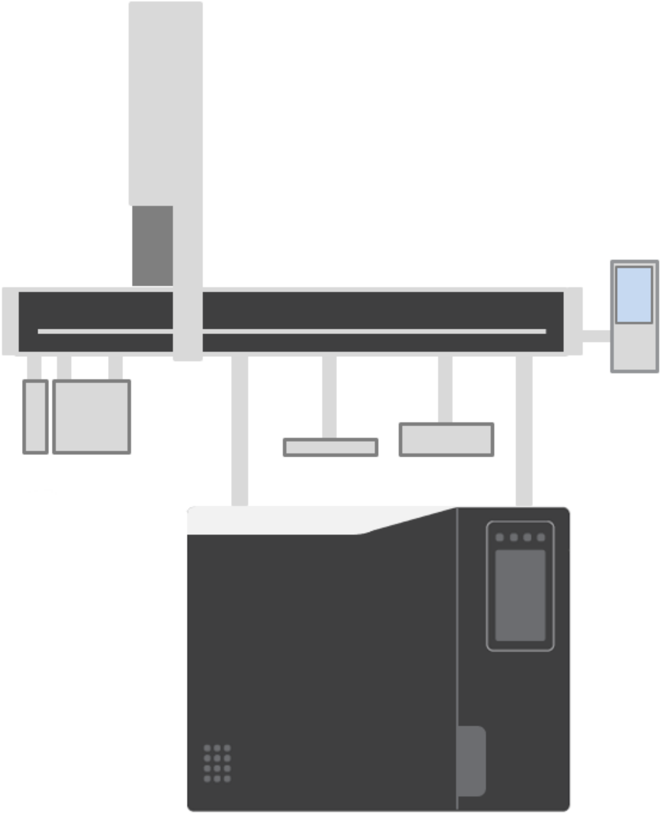
Loop

- 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



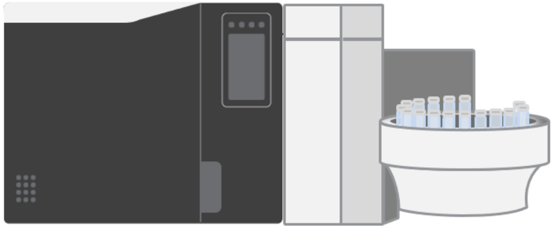


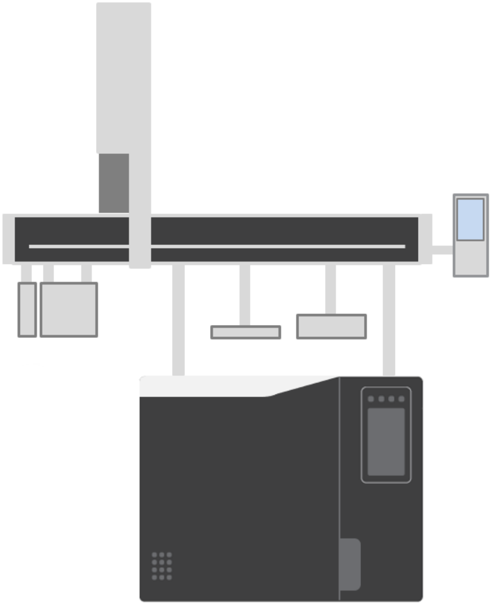
Dynamic headspace

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.





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Solid Phase Micro-Extraction (SPME)

SPME

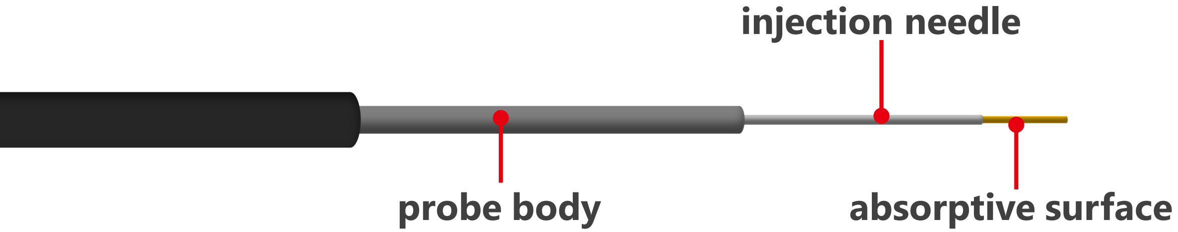
SPME is a **sample concentration** technique for **solids** & **liquids**.

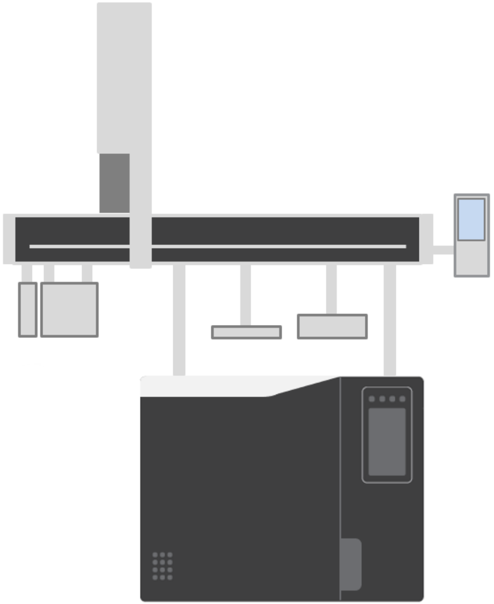
Used for **trace VOC & SVOC analysis**.

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

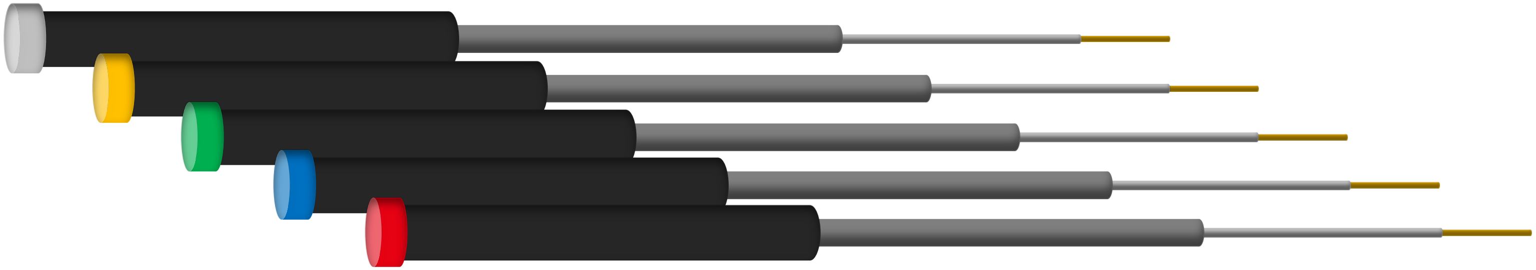
Range of sorbent materials and thicknesses.

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



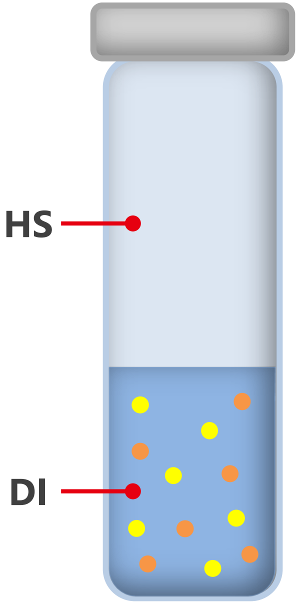
DI-SPME vs. HS-SPME

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

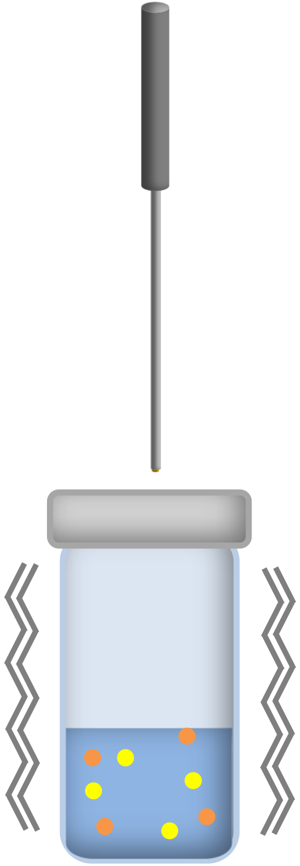
HS-SPME follows the same principles as typical headspace.

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

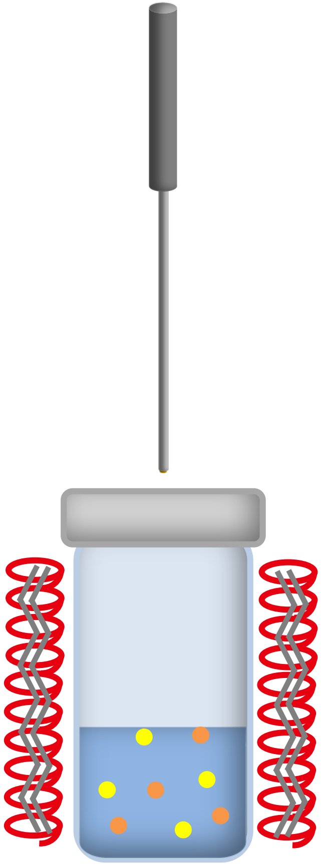
SPME probe inserted into liquid

HS-SPME

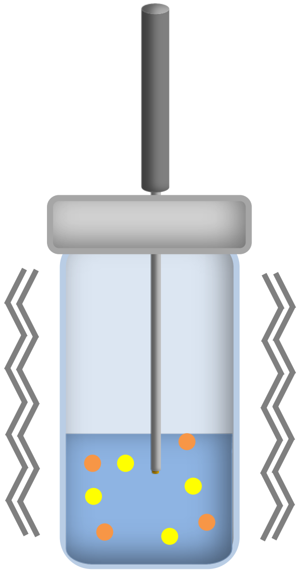
Sample agitation at elevated temperature

Equilibrium achieved

SPME probe inserted into headspace



SPME Sampling



DI-SPME

Sample agitation

SPME probe inserted into liquid

Fiber exposed

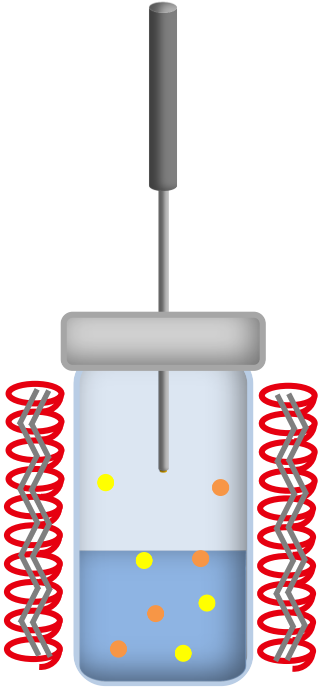
HS-SPME

Sample agitation at elevated temperature

Equilibrium achieved

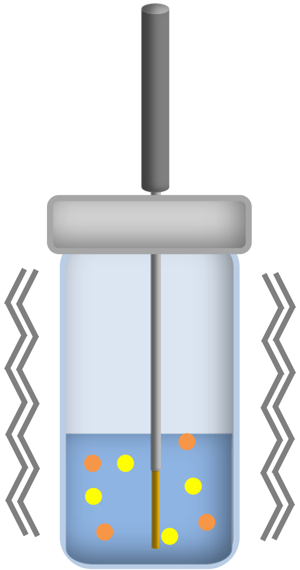
SPME probe inserted into headspace

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

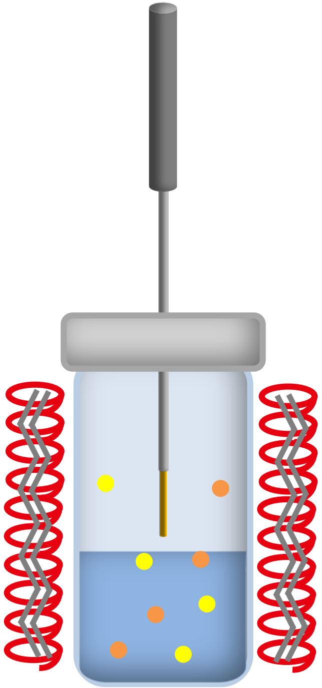
SPME probe inserted into headspace

Fiber exposed

Analytes in HS adsorb to fiber surface

HS concentration reduces

Analytes in sample re-partition to to maintain K value

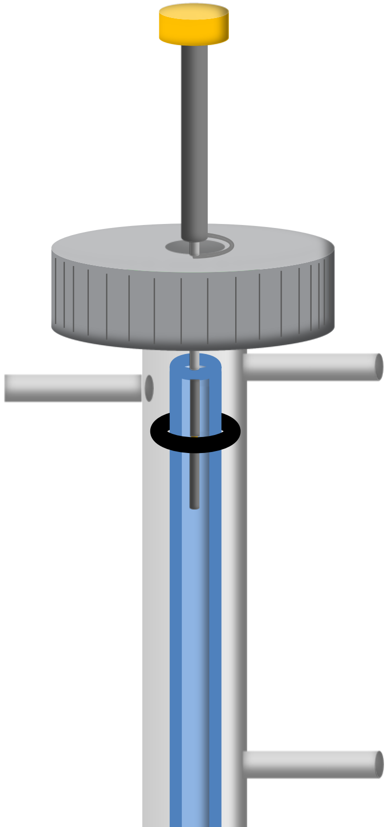


SPME Sampling

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

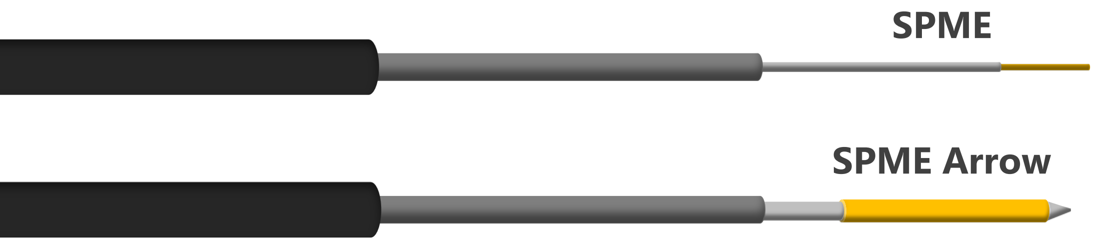
High temperatures desorb analytes from fiber.

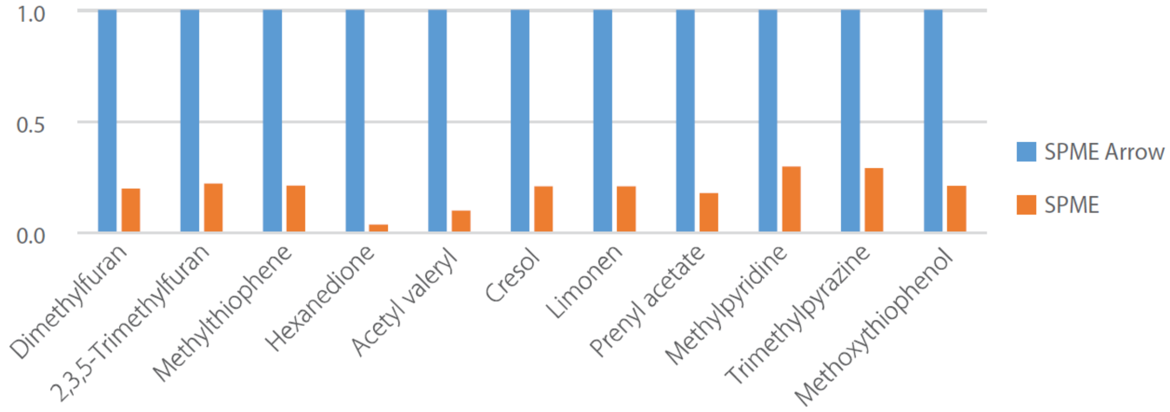
At this point, standard principles of split/splitless inlets apply.

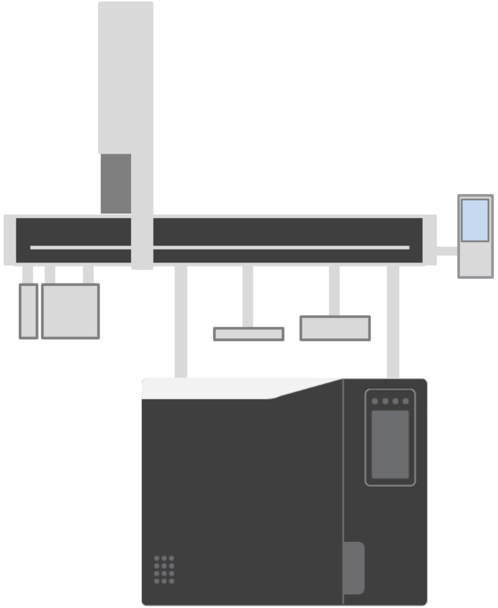


SPME Arrow

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







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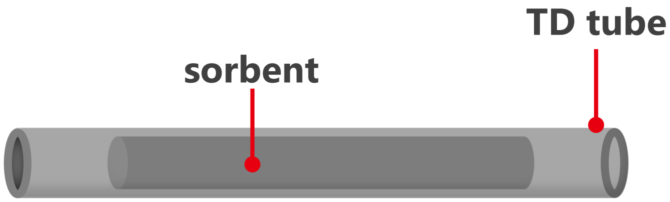
Thermal Desorption (TD)

Thermal desorption

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

Wide range of sampling techniques available:

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

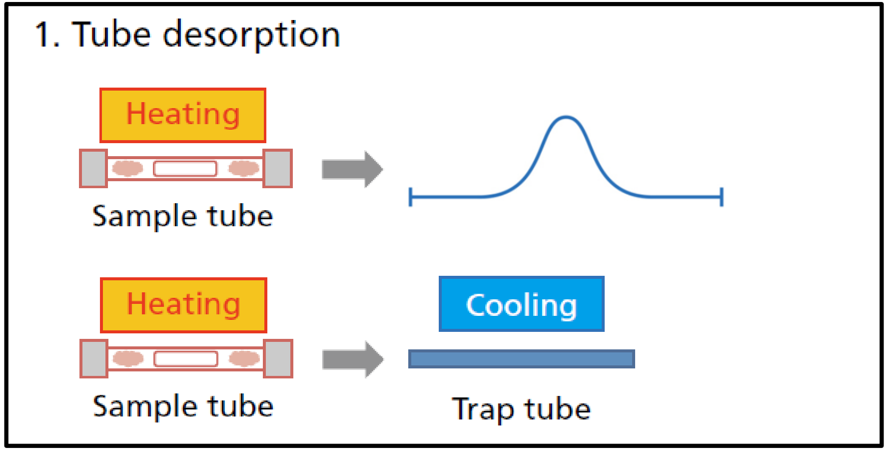


Common applications:

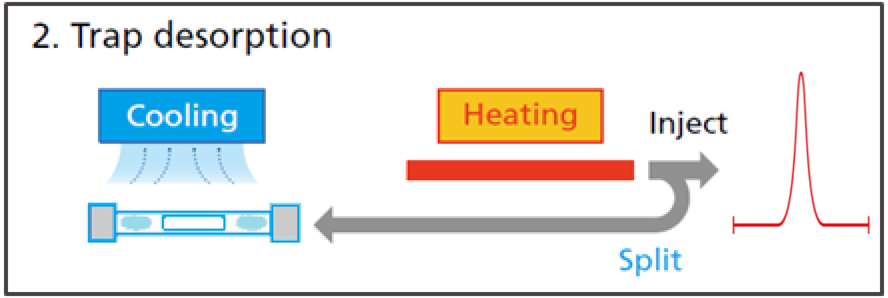
- *Monitoring air for toxic VOCs near landfill sites*
- *Workplace air monitoring*
- *Vehicle emission testing*
- *Aroma profiling in food & beverages*
- *Permeation of VOCs through packaging*
- *Detection of cancer markers in breath*

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.



- 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.



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Pyrolysis (Py)

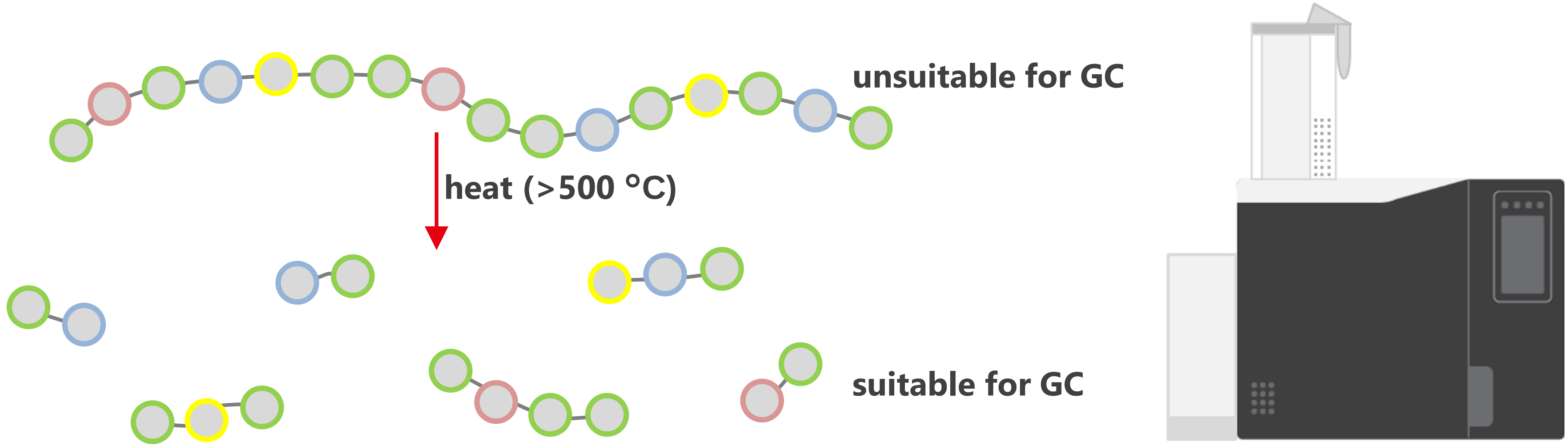
Pyrolysis

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*



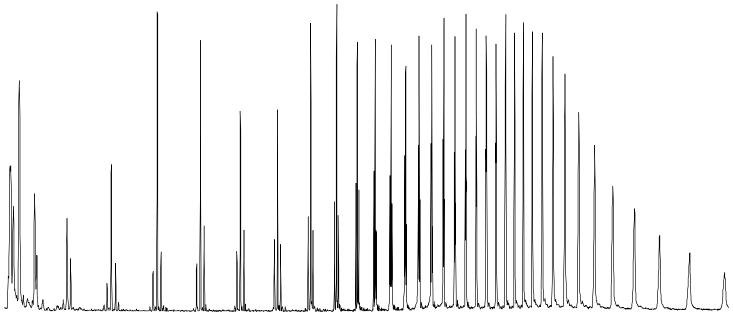
Pyrolysis techniques

Pyrolysers can be used in a variety of ways.

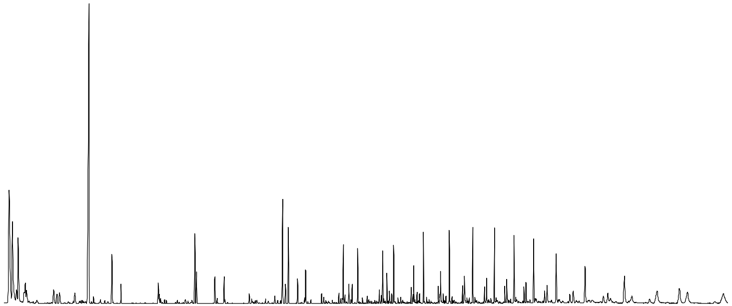
The most common is **single shot** or **flash pyrolysis**.

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

Polyethylene (PE)



Polypropylene (PP)



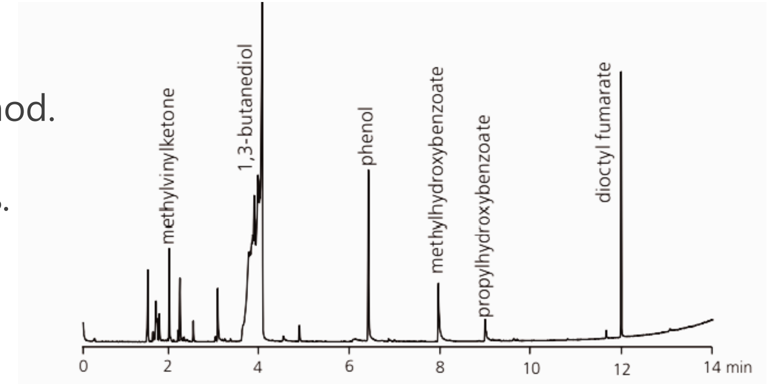
Pyrolysis techniques

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

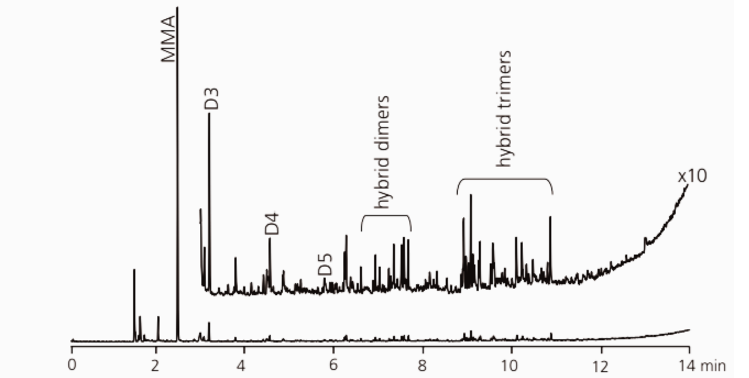
This information is used to create a double-, or multi-shot, method.

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

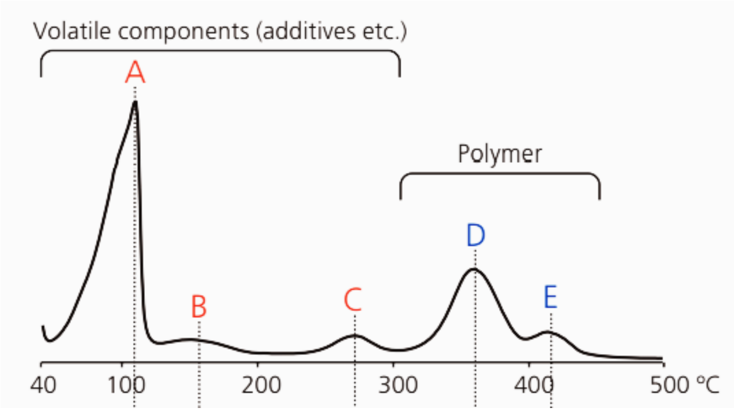
Peaks A+B+C [TD: 100 – 300°C]



Peaks D+E [Py: 600°C]



EGA

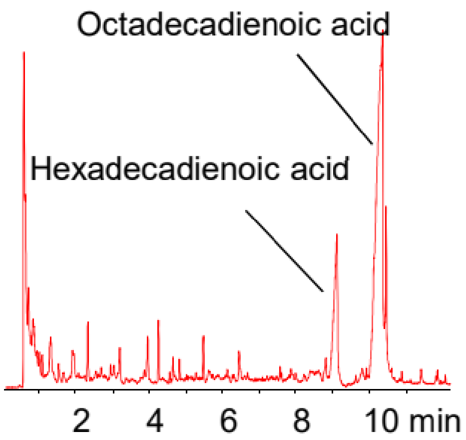


Catalytic pyrolysis (micro-reactors)

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.

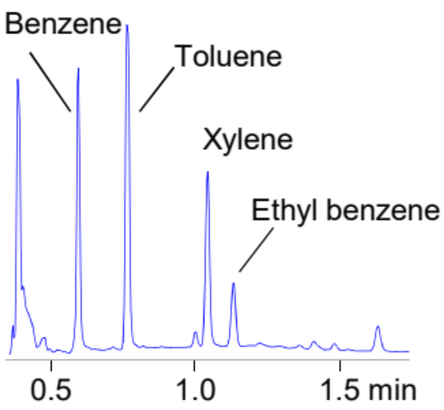
Without catalyst



Analysis of Jatropha (plant).

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

With catalyst



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Gas sampling valves (GSVs)

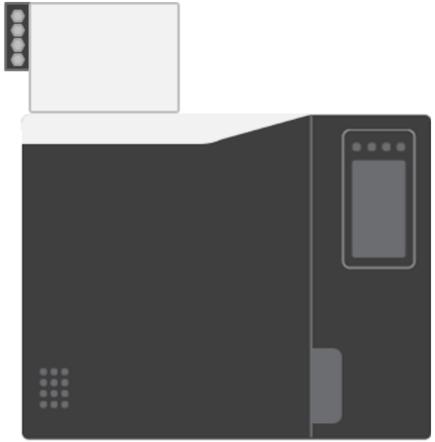
Gas sampling

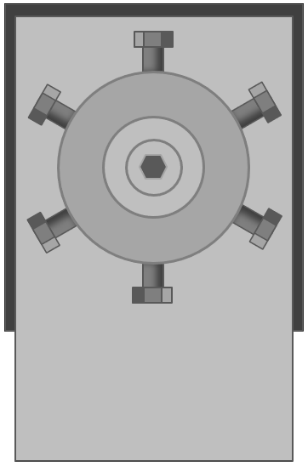
Analysis of **very volatile, gaseous samples**.

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

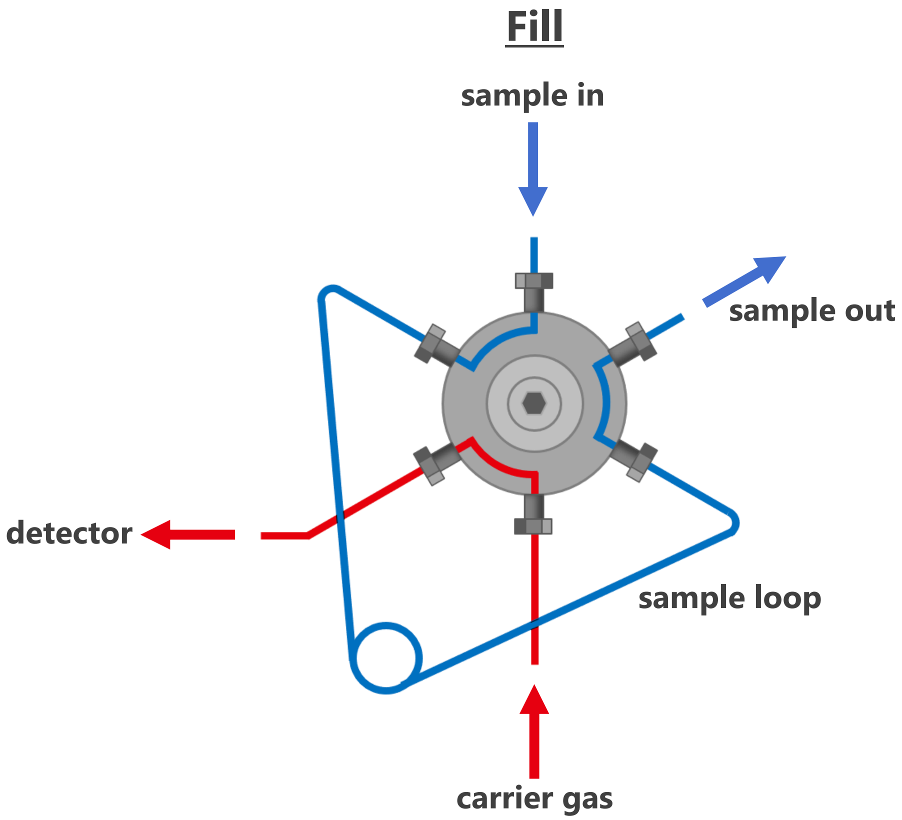
<u>Common applications:</u>

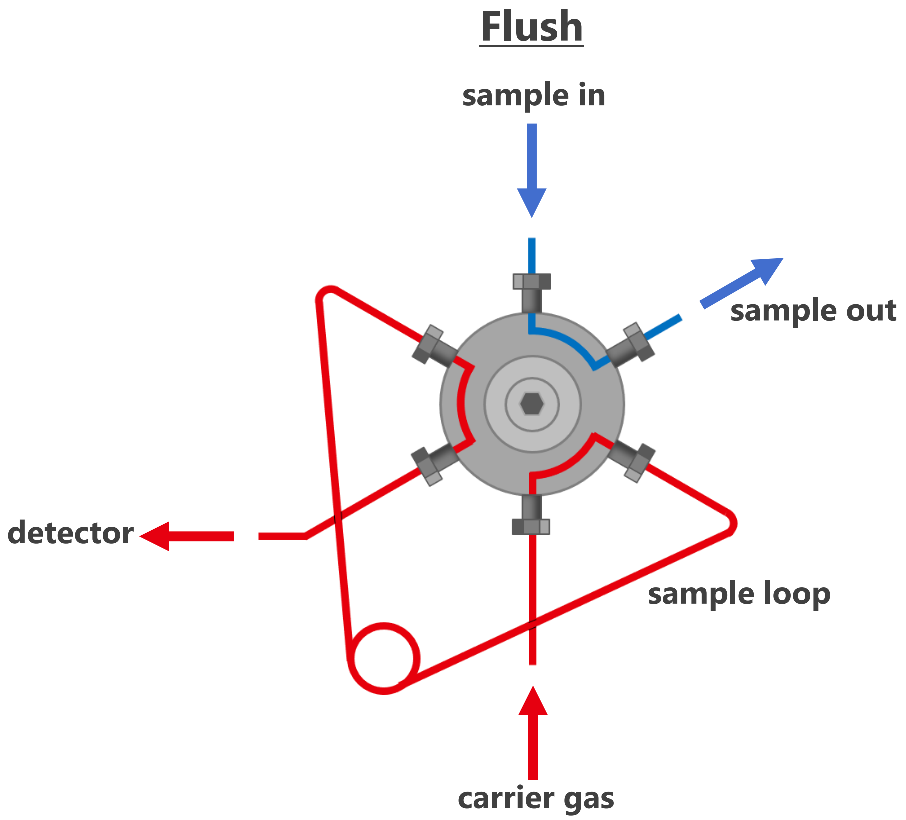
- *Reactor product analysis*
- *Hydrocarbon processing industry*
- *Gas purity analysis*
- *Mask breakthrough testing*





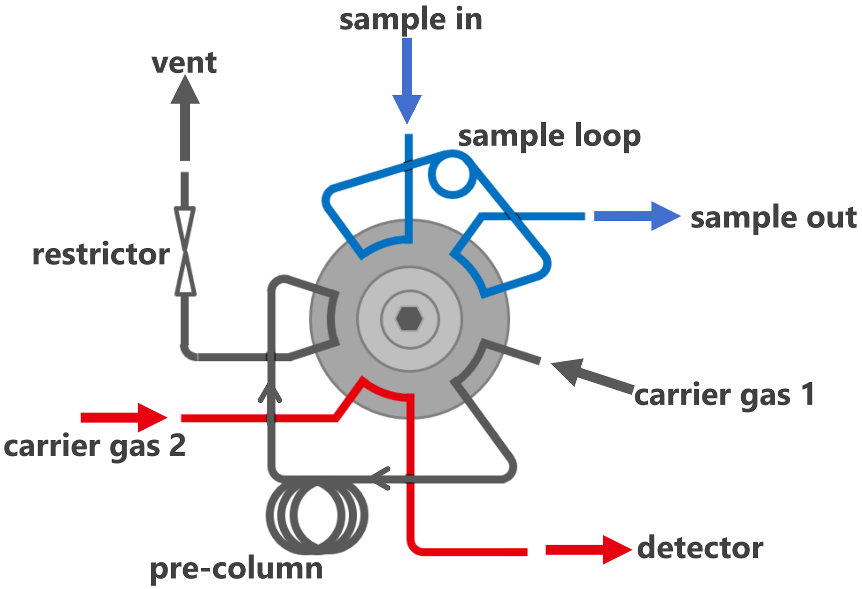
Basic 6-port valve operation



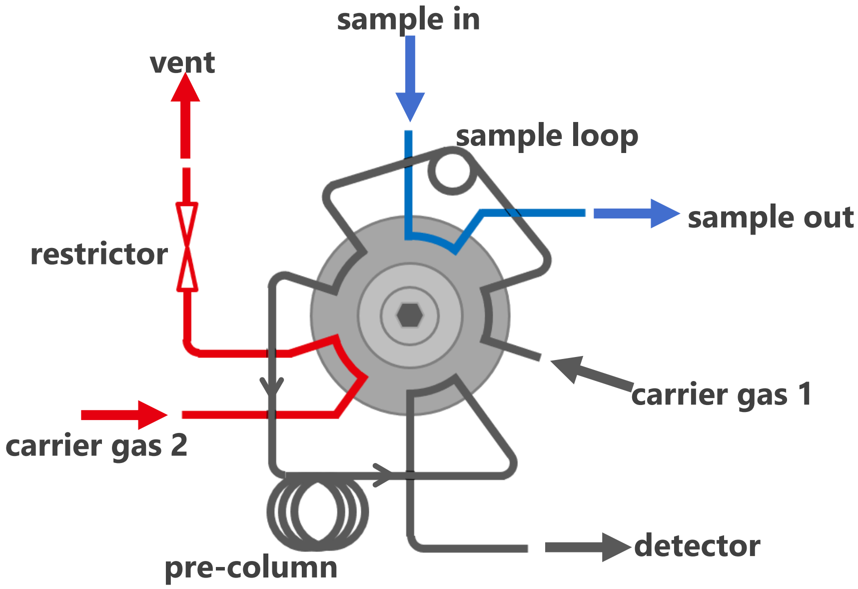


10-port valve operation (with pre-column backflush)

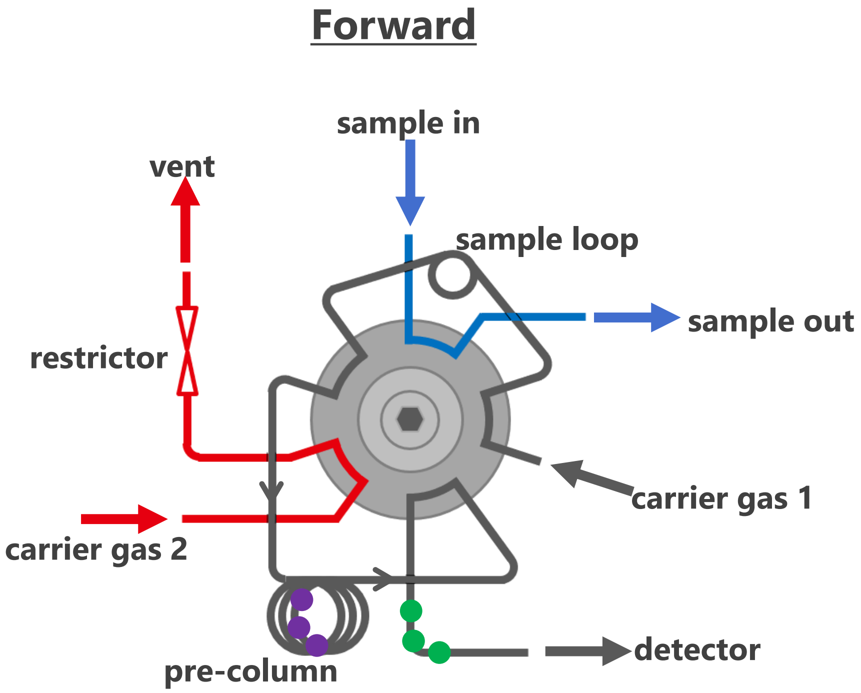
Fill

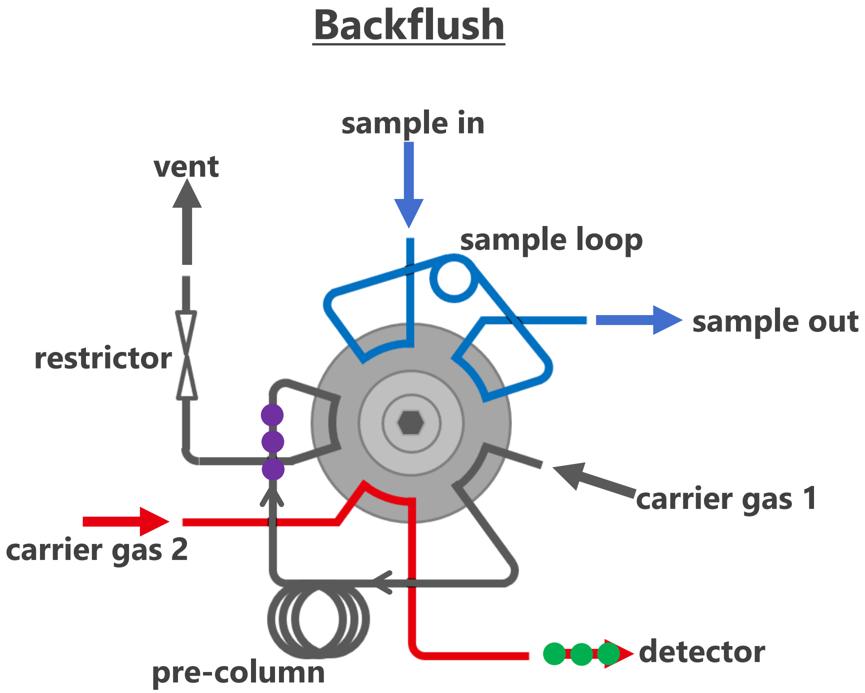


Flush

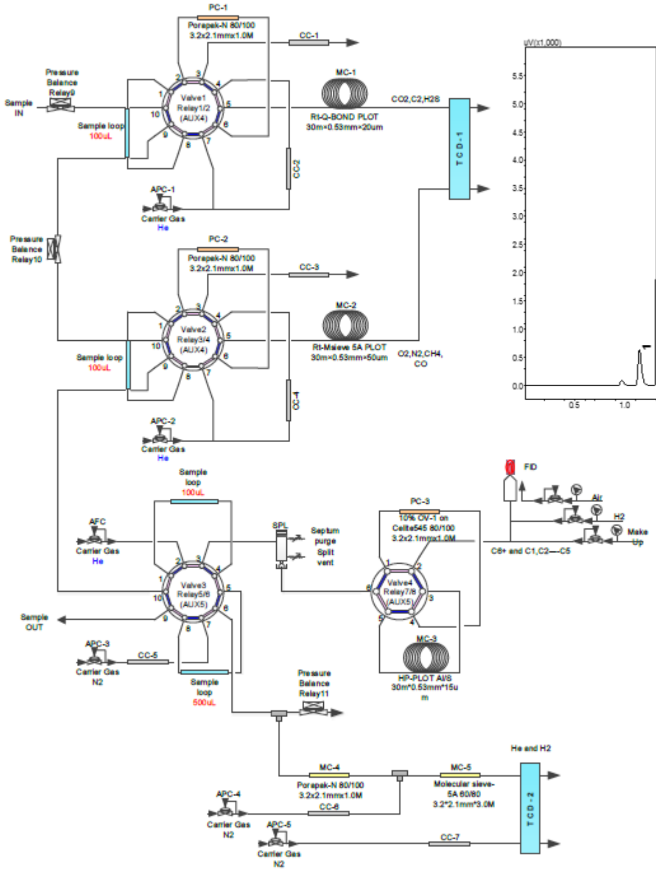


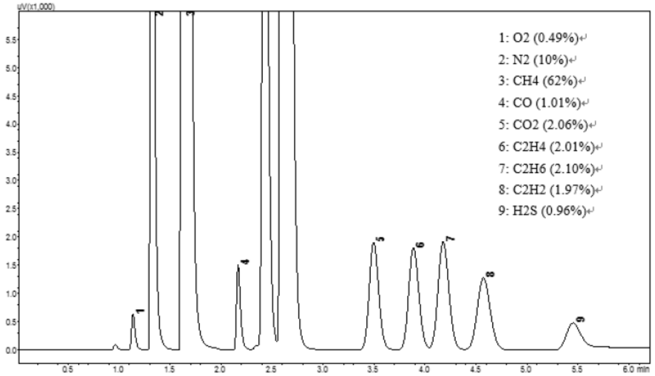
10-port valve operation (with pre-column backflush)

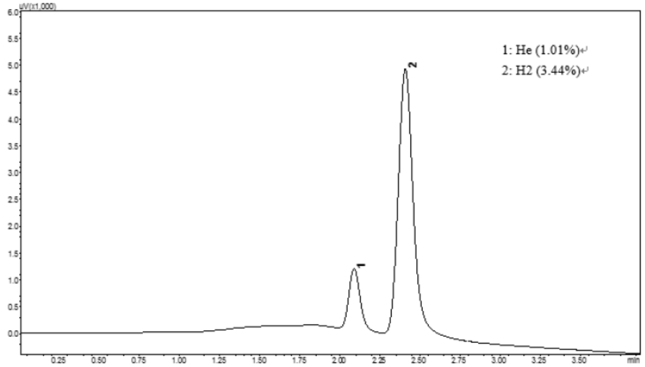


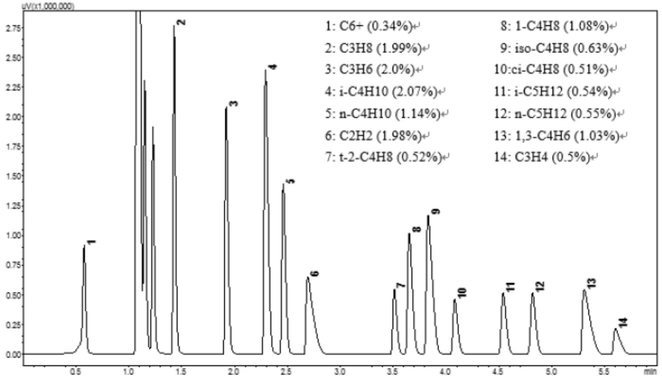


System GC solutions









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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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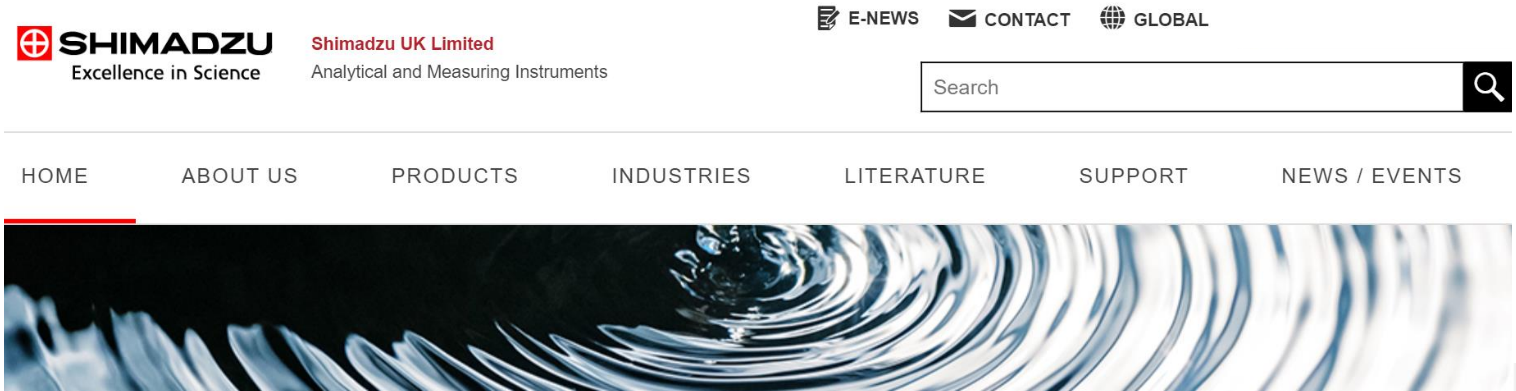

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