SHIMADZU
Excellence in science

Theory and Key Principles Series

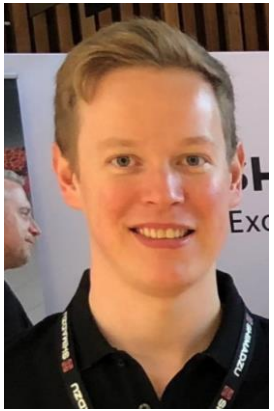
Gas Chromatography (GC)

Session 4 – Advanced Liquid Injection Techniques

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

– Choices of Detectors for GC

– Processing GC Data

– Maintenance & Troubleshooting

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

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)

SHIMADZU
Excellence in science

When is the split/splitless inlet unsuitable?

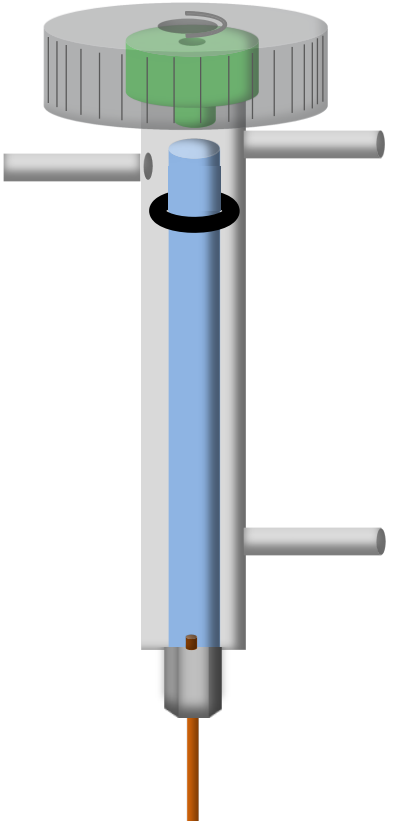
When to look for an alternative inlet

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*



SHIMADZU
Excellence in science

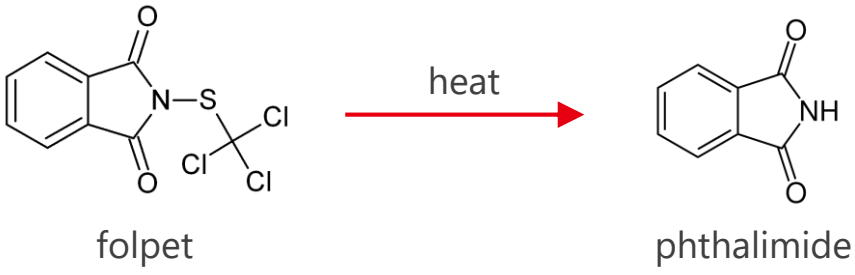
Samples containing thermally labile compounds

Thermally labile compounds

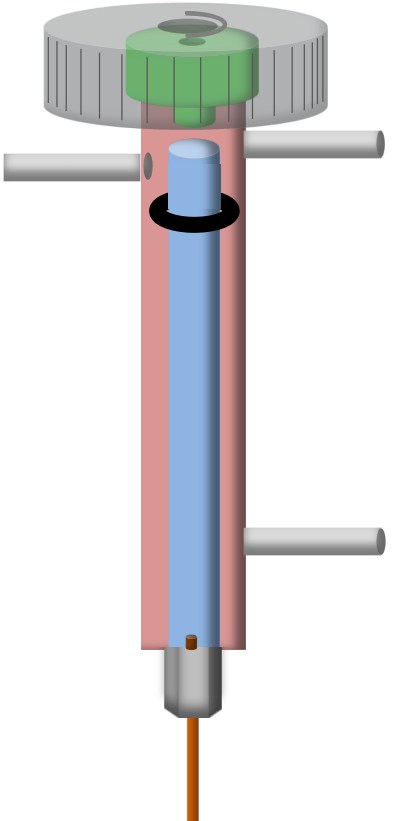
Some compounds are not thermally stable.

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

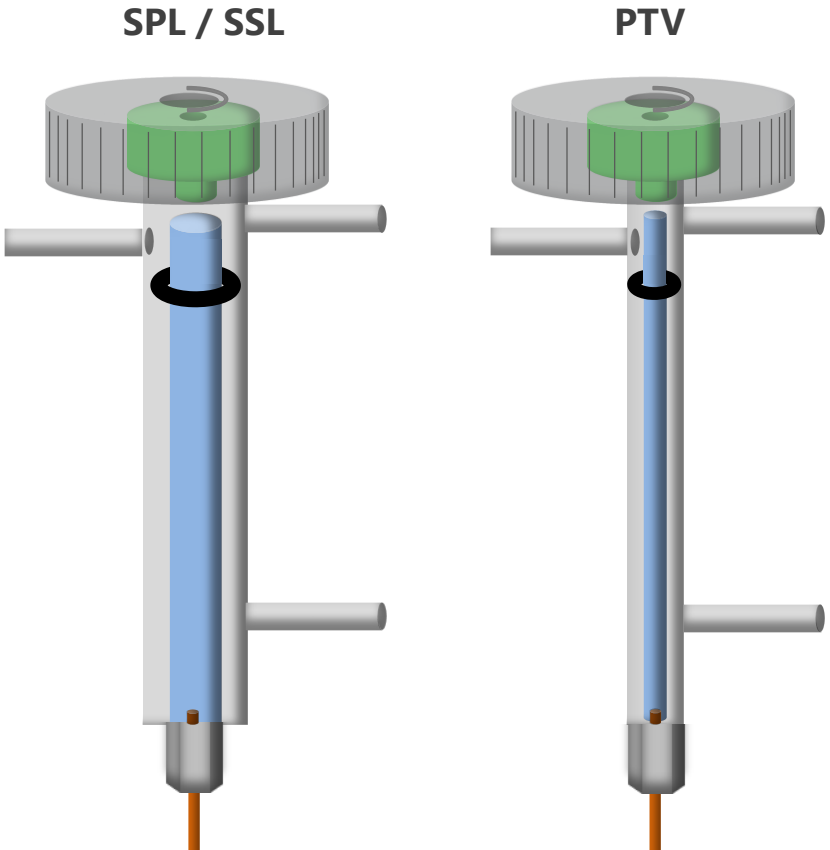


Programmable Temperature Vaporisation (PTV)

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)

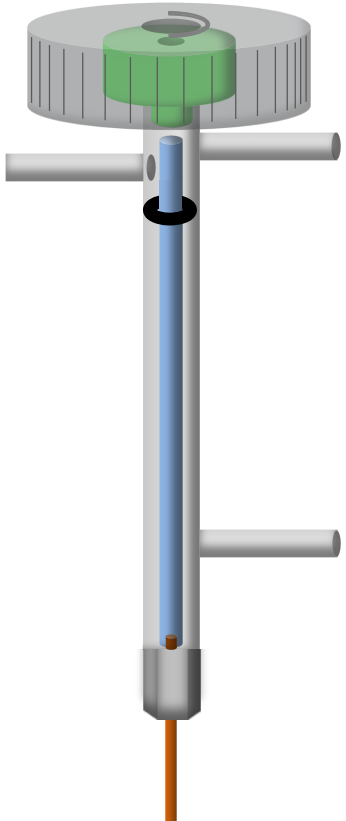
SPLs are isothermal inlets.

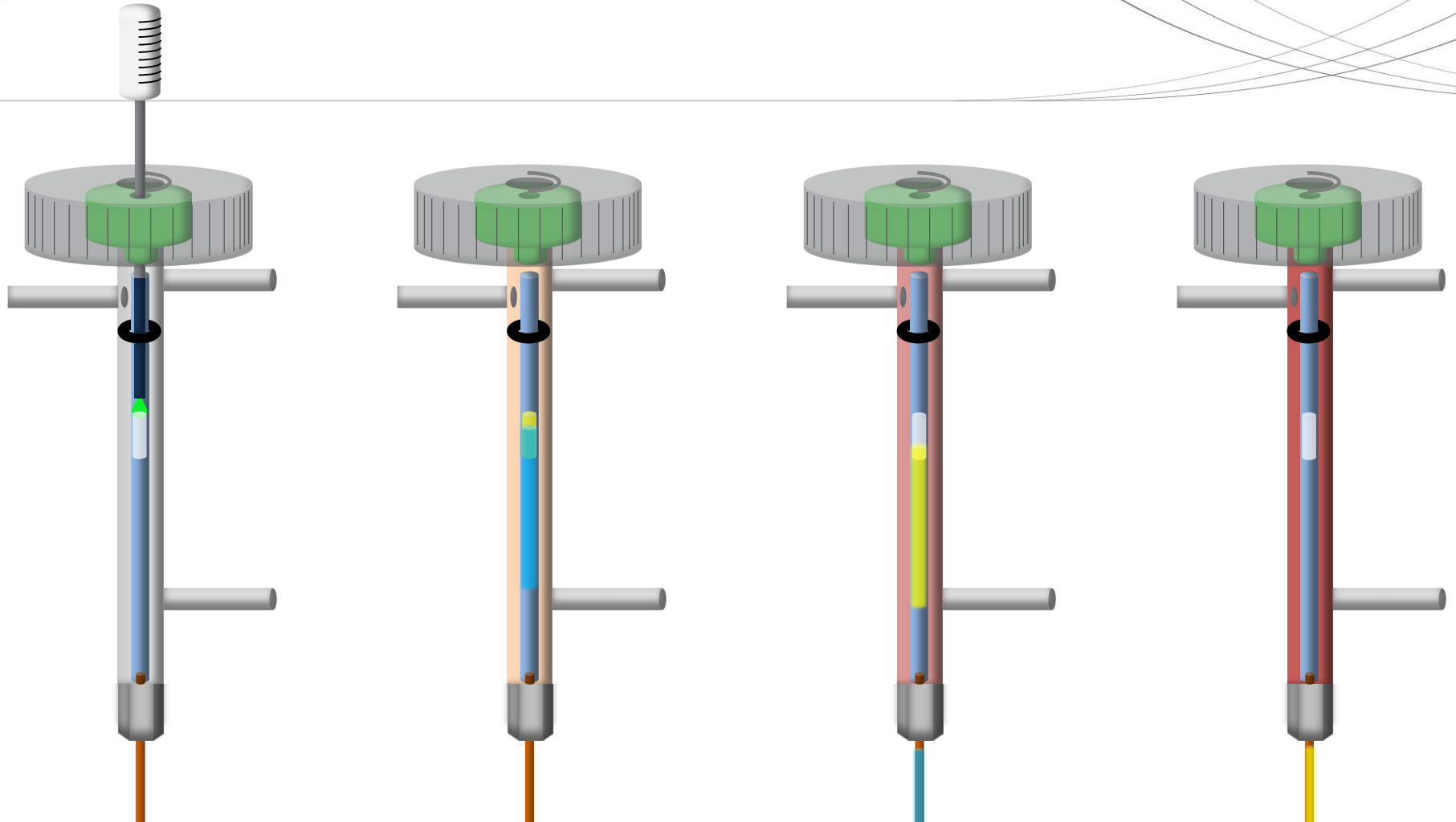
PTV technique uses a **programmable temperature** on the inlet.

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.





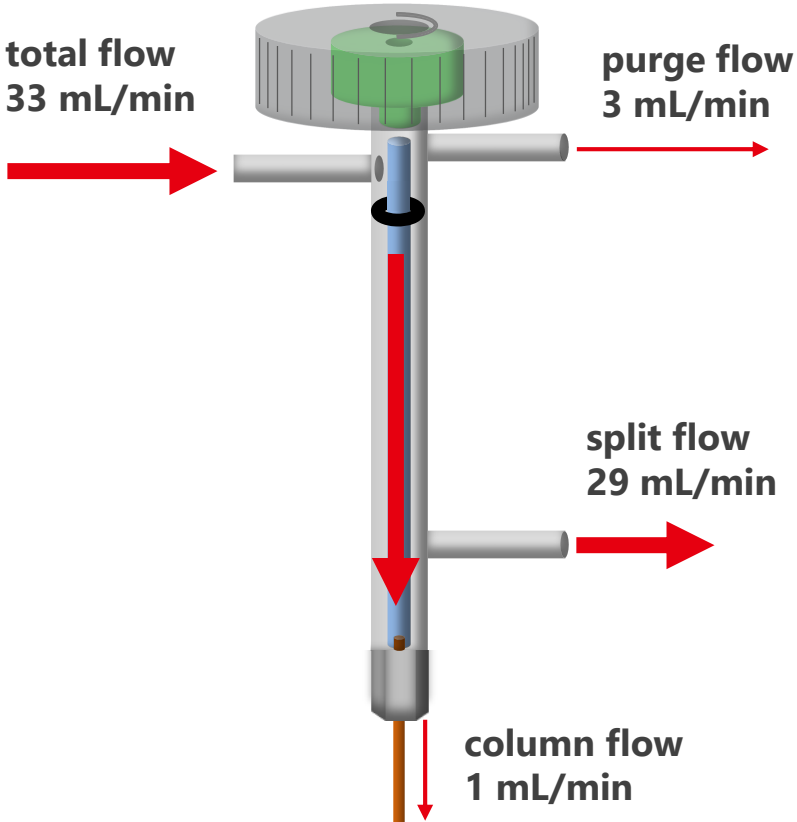
Operation

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

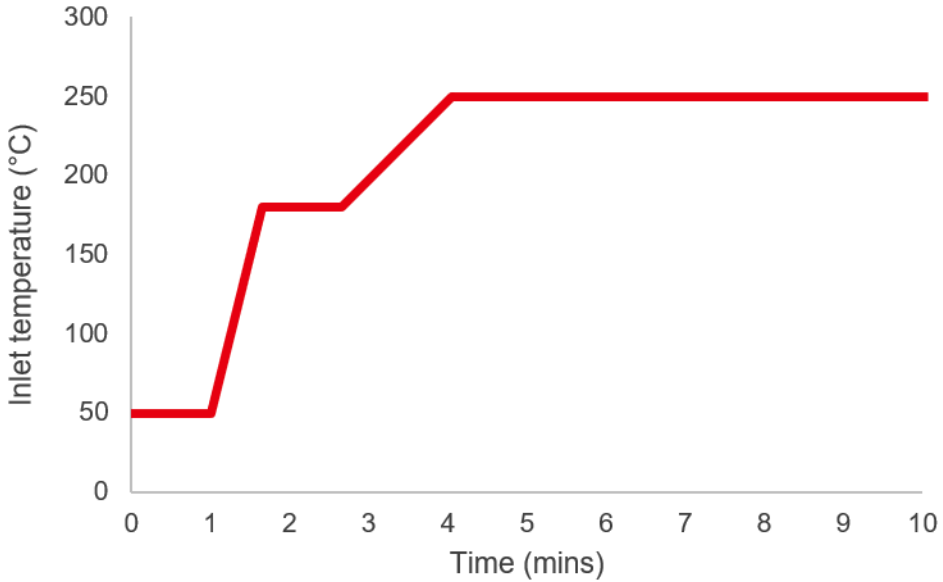


Temperature program

Temperature increase tends to be rapid

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

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



SHIMADZU
Excellence in science

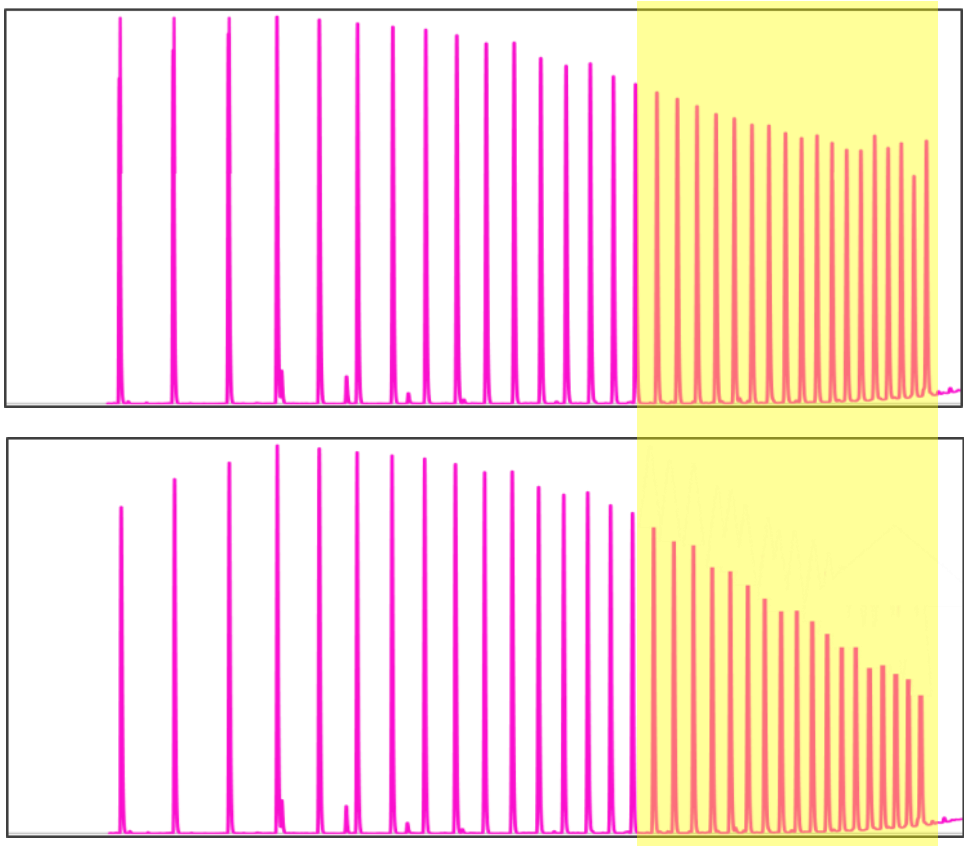
Samples with wide boiling point ranges

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.

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



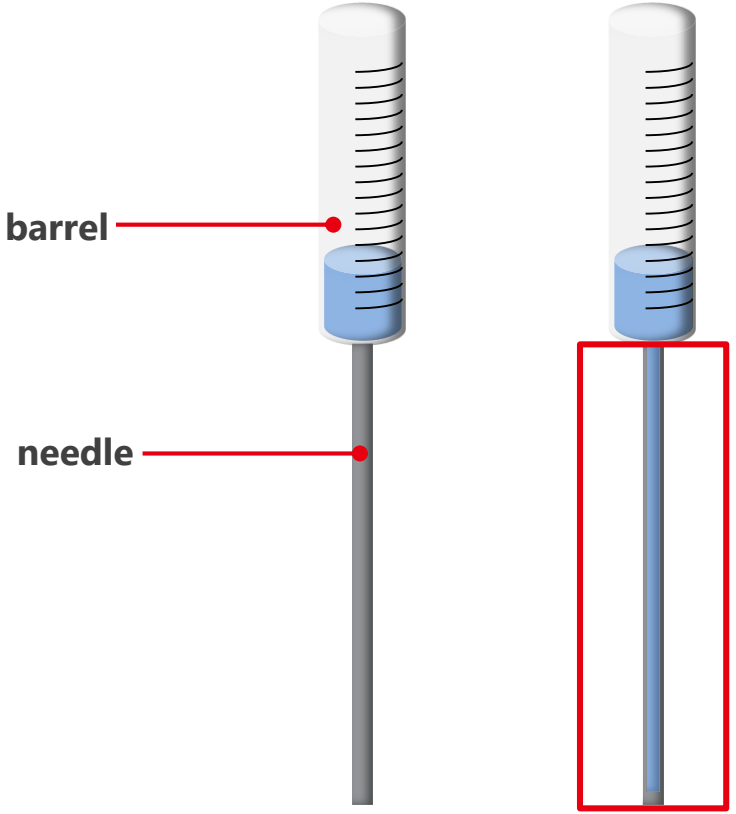
Mass discrimination

Caused by **syringe** (indirectly).

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

High-boiling content remains within the needle.

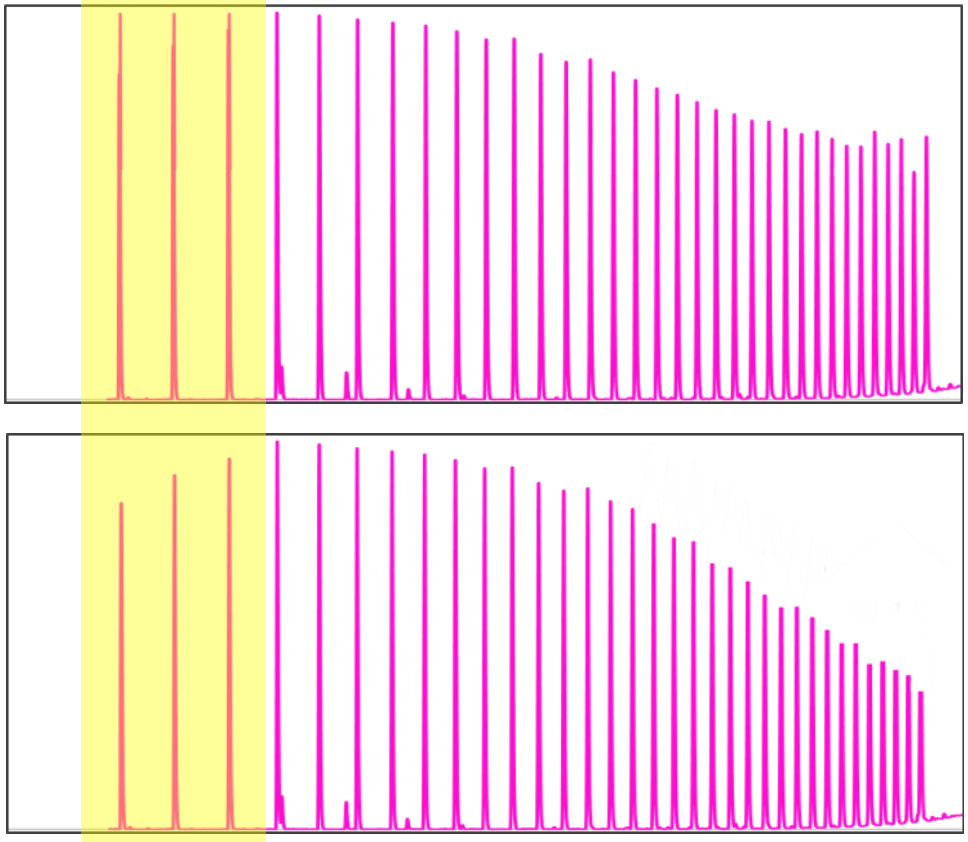
Also caused by insufficient inlet temperature.



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

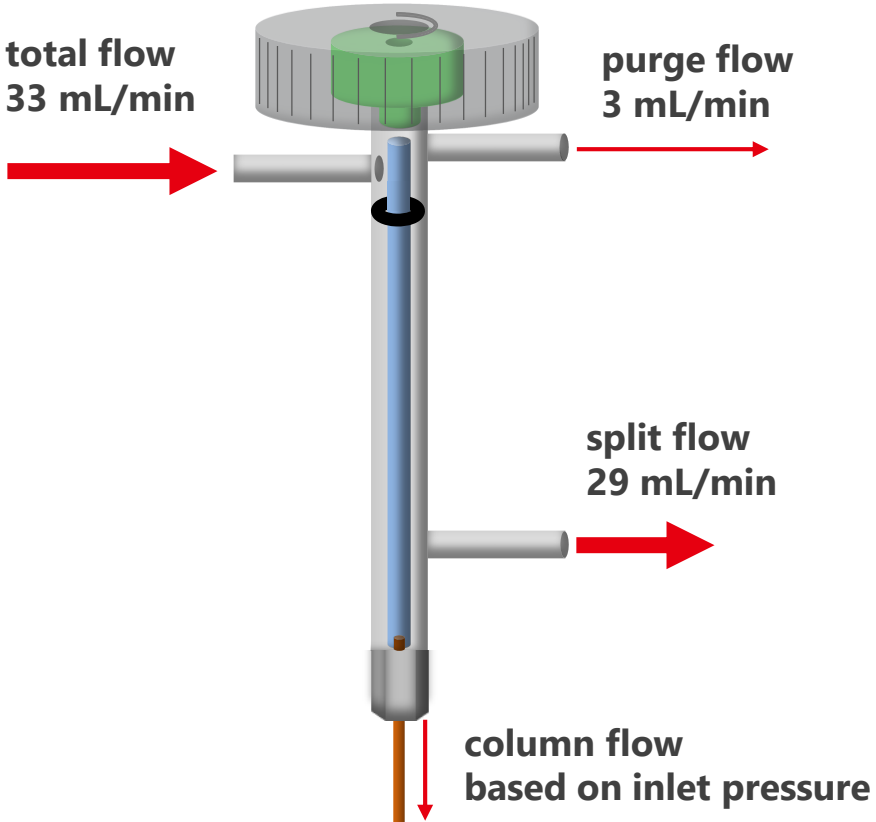
Volatile components diffuse faster.

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

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

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

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

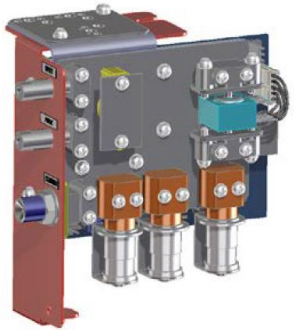


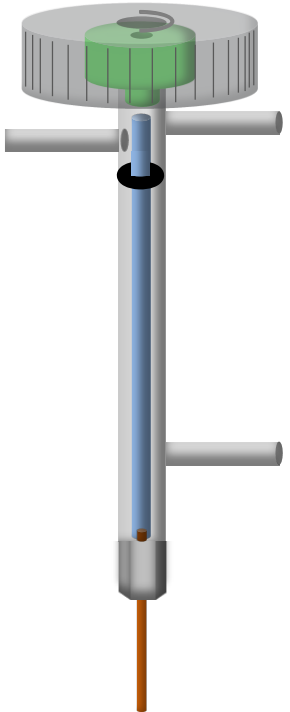
Modern GC systems

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.

<u>But they're still not perfect!</u>





SHIMADZU
Excellence in science

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

ASTM D7169

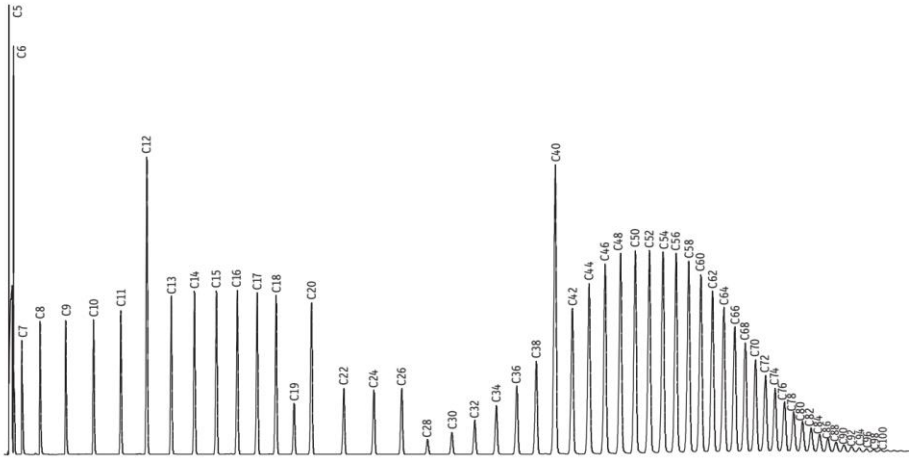
Analysis of boiling point distribution in samples containing crude oil residues.

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**.



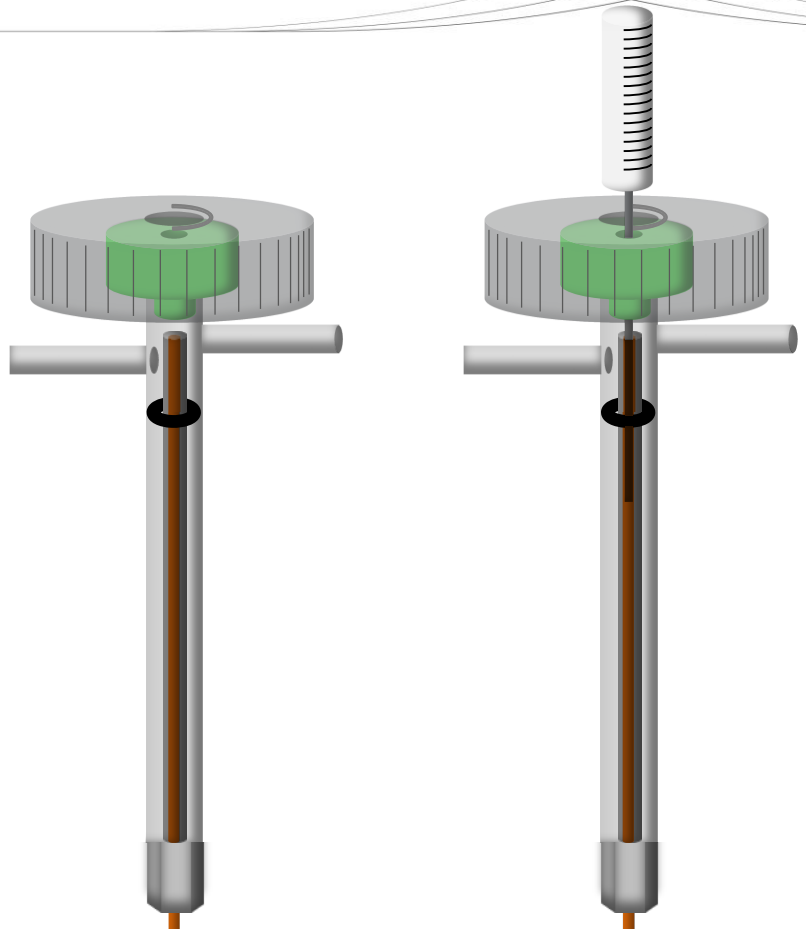
On-column injection

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:

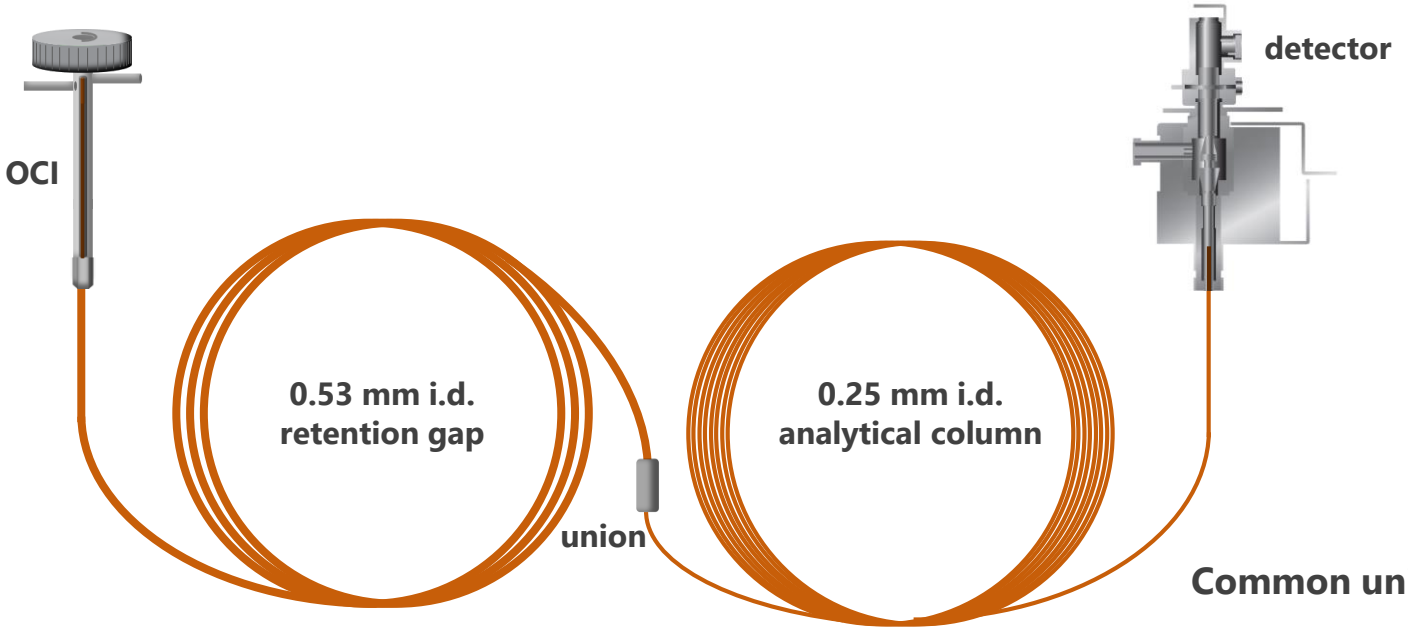
Column i.d. > Needle o.d.

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

0.53 mm i.d.

0.25 mm i.d.

Hardware requirements



Common unions:

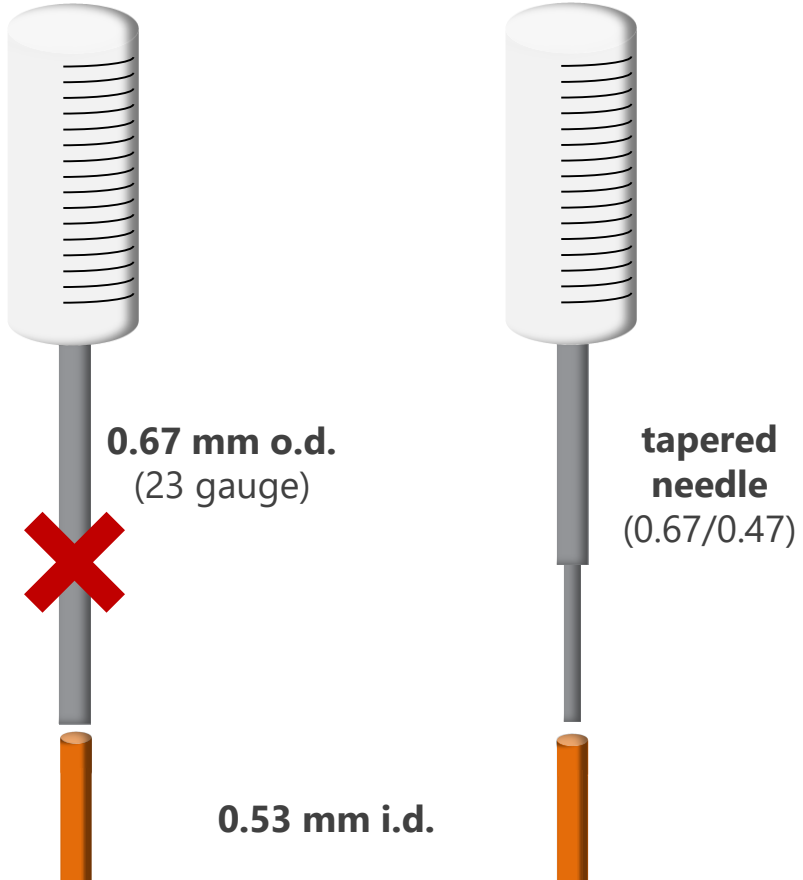
- Press-Tight
- Trajan SilTite Mini Union
- Trajan SilTite µ-Union

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



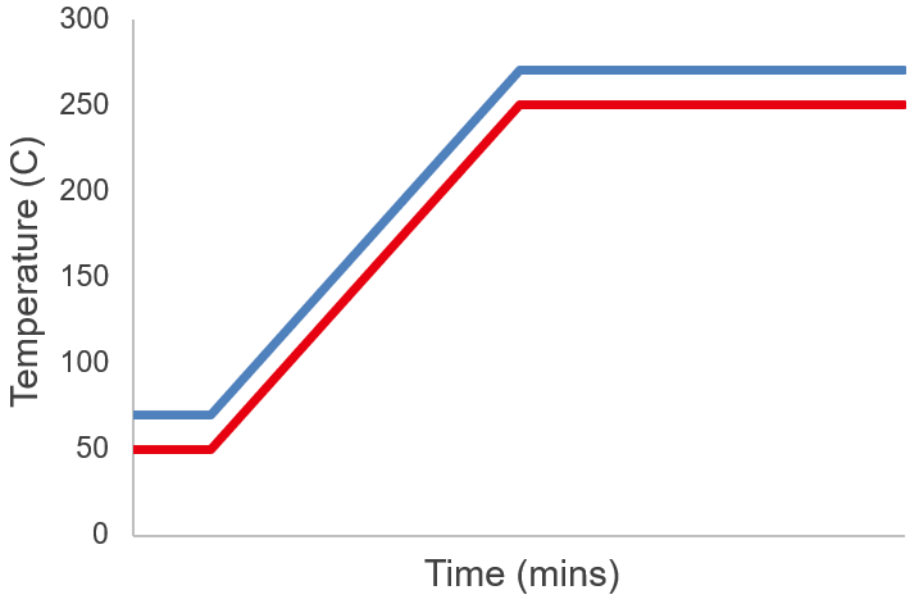
Operation & temperature program

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.

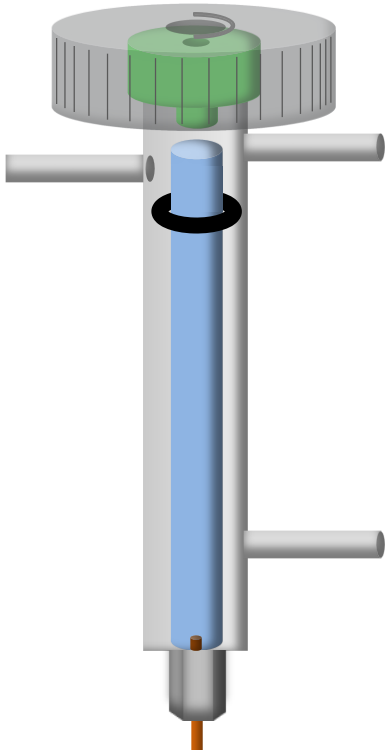
Same temperature program used for the oven and the inlet.

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

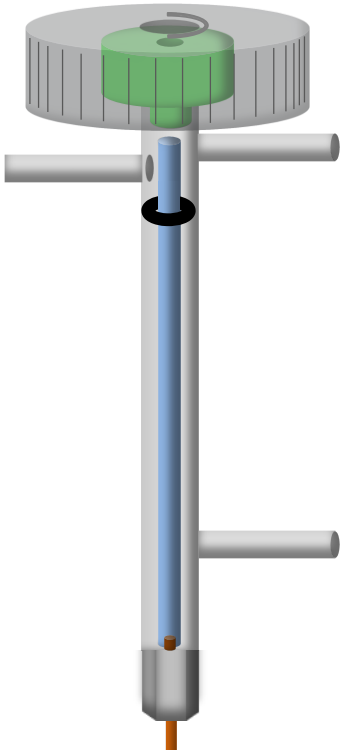


Comparison

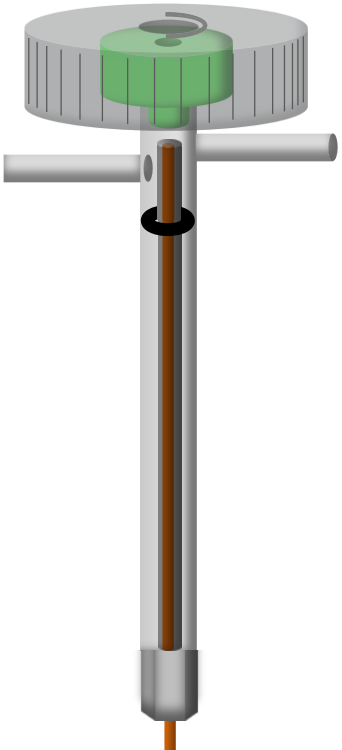
SPL / SSL



PTV



OCI / COC



SHIMADZU
Excellence in science

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

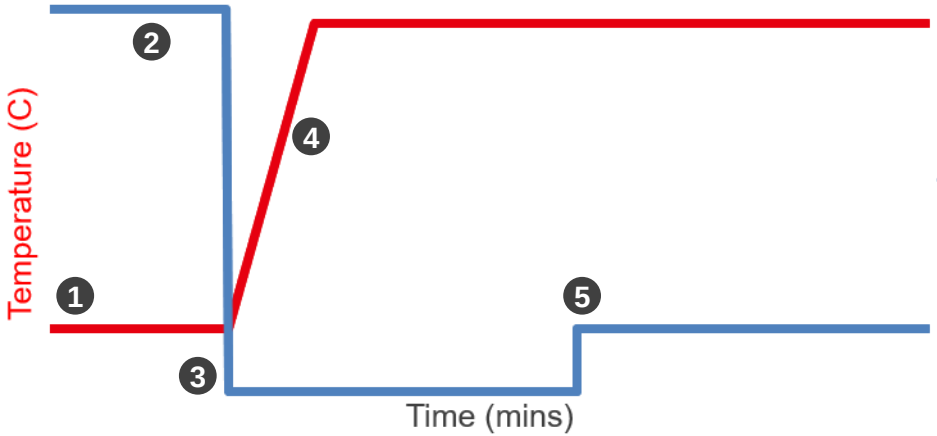
Large Volume Injection (LVI) enables analysis of ultra-trace analytes.

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!



SHIMADZU
Excellence in science

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*

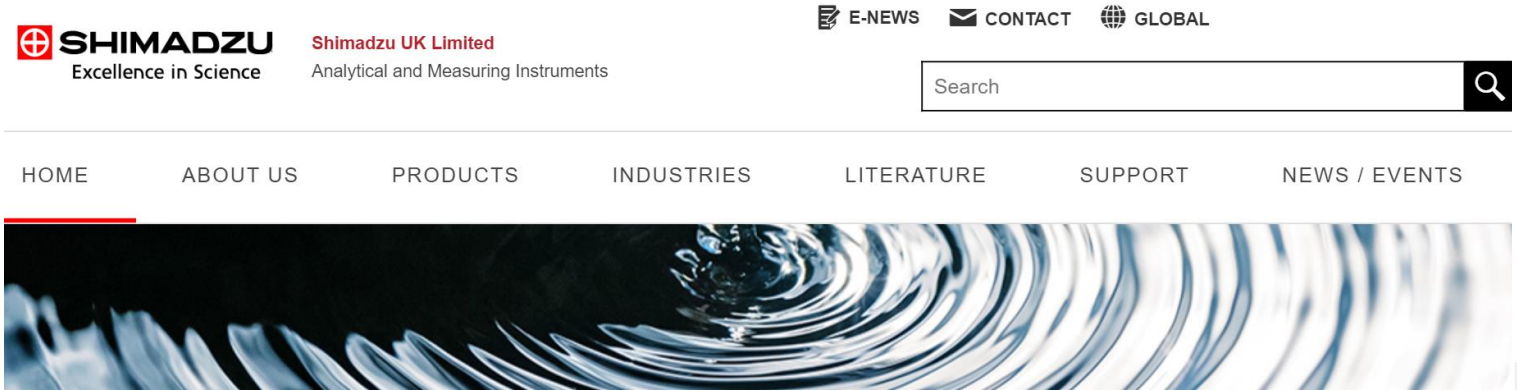
Shimadzu UK e-News

Join our e-News mailing list today!

Benefits of joining:

- Be entered into our prize draws & competitions
- Find out about our latest webinars, workshops & events
- Receive exciting information about the latest analytical technology & application notes

Look for the link in our follow-up email or go to www.shimadzu.co.uk and click on e-News



Shimadzu UK webinars

Please visit our website to check out our other webinar sessions that are open for registration or are available on demand:

www.shimadzu.co.uk/webinars

SHIMADZU

Excellence in Science

UK Contact Details

www.shimadzu.co.uk *info@shimadzu.co.uk* *01908 552209*

@ShimadzuUK *Shimadzu UK Limited*

Thank you for your attention!

SHIMADZU

Excellence in Science

Global Contact Details

www.shimadzu.com/an/