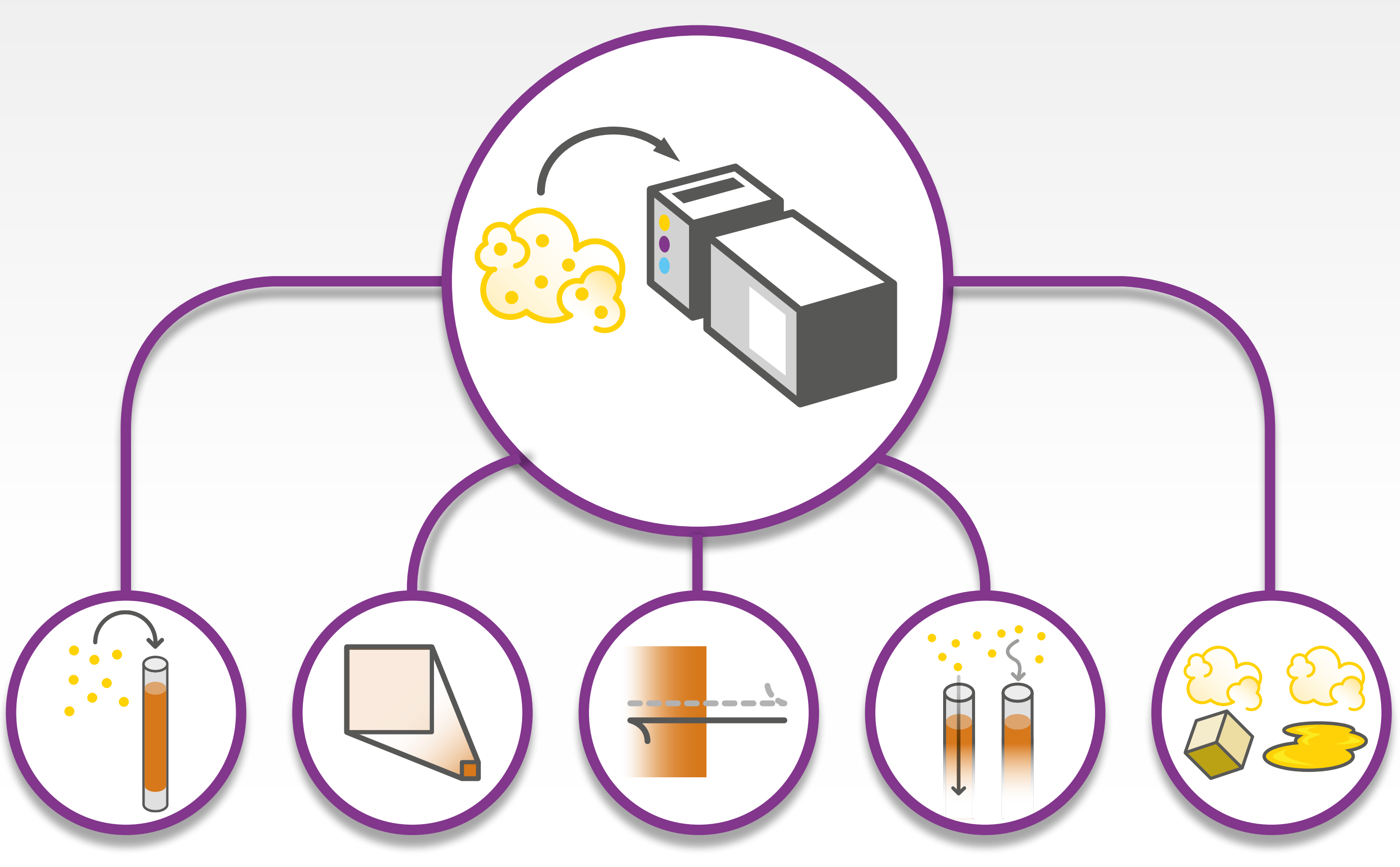
INTRODUCTION TO
TUBE-BASED THERMAL DESORPTION

WHAT IS IT?

Tube-based thermal desorption is a technique for getting VOCs and SVOCs from a sample into a GC–MS.

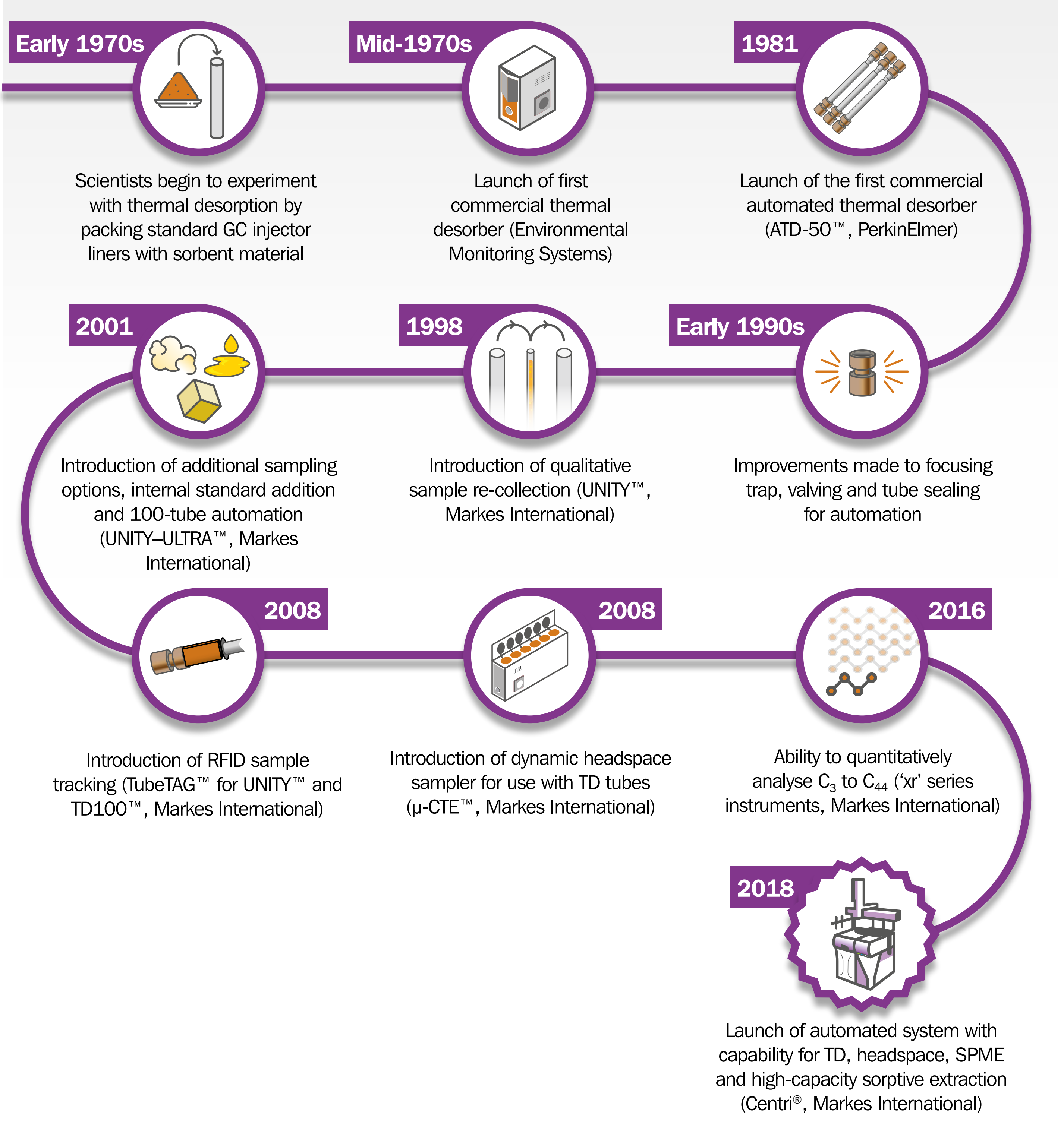


- Samples vapours onto a sorbent-packed TD tube
- Uses a focusing step to enhance sensitivity
- Complete sampling technique (not equilibrium)
- Two main methods: Pumped and passive
- Ideal for air and gas, and headspace of solids and liquids

KEY APPLICATIONS

- Pollutants in ambient air
- Harmful emissions from industry
- Toxins in construction materials
- Flavour compounds in foods and beverages
- Additives and fragrances in consumer products
- Homeland security
- Forensic investigations
- Biomarkers for disease diagnosis
- Metabolites in biological samples

HISTORY



Early 1970s Scientists begin to experiment with thermal desorption by packing standard GC injector liners with sorbent material

Mid-1970s Launch of first commercial thermal desorber (Environmental Monitoring Systems)

1981 Launch of the first commercial automated thermal desorber (ATD-50™, PerkinElmer)

Early 1990s Improvements made to focusing trap, valving and tube sealing for automation

1998 Introduction of qualitative sample re-collection (UNITY™, Markes International)

2001 Introduction of additional sampling options, internal standard addition and 100-tube automation (UNITY–ULTRA™, Markes International)

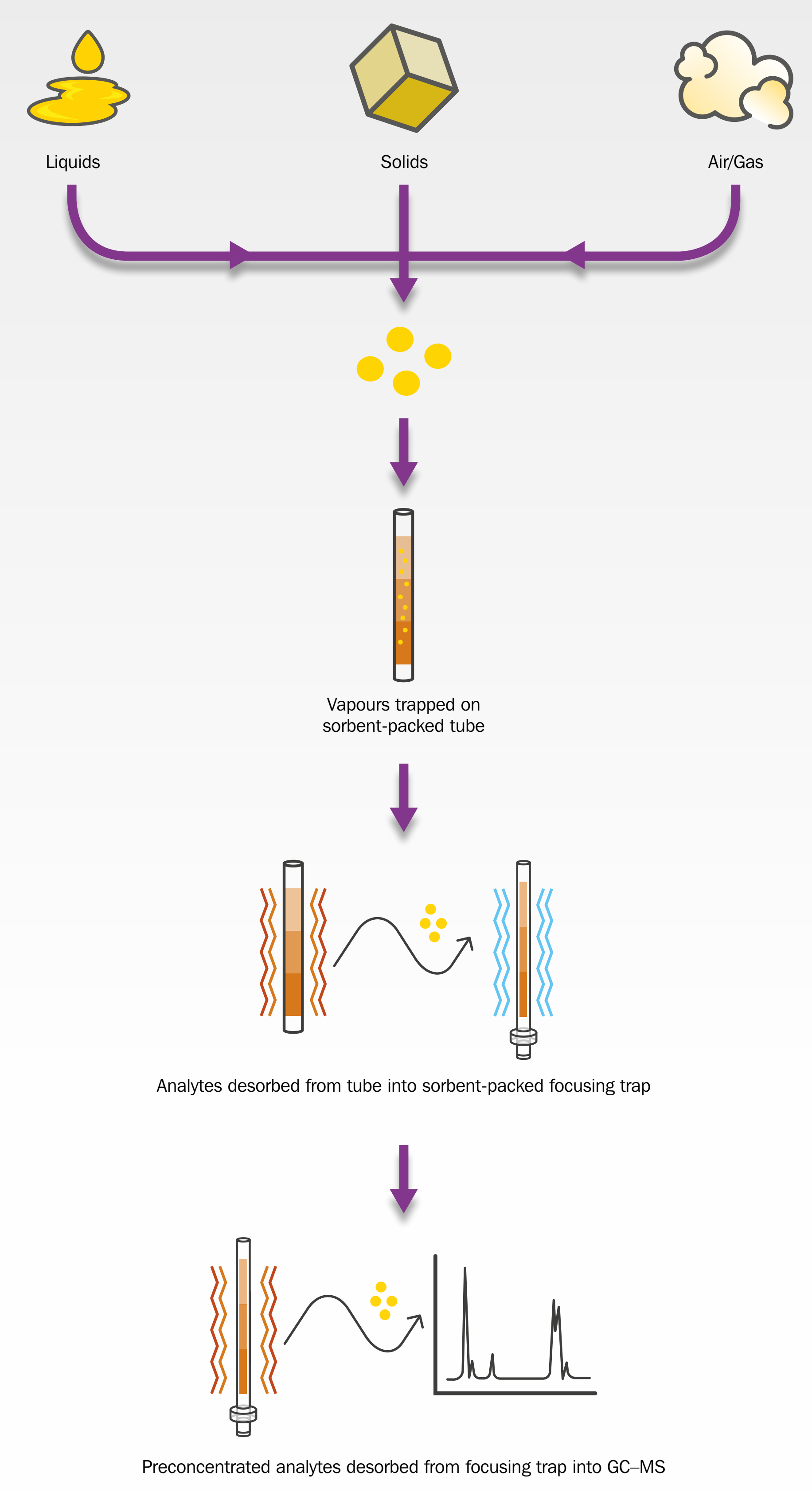
2008 Introduction of RFID sample tracking (TubeTAG™ for UNITY™ and TD100™, Markes International)

2008 Introduction of dynamic headspace sampler for use with TD tubes (μ-CTE™, Markes International)

2016 Ability to quantitatively analyse C_3 to C_{44} ('xr' series instruments, Markes International)

2018 Launch of automated system with capability for TD, headspace, SPME and high-capacity sorptive extraction (Centri®, Markes International)

TYPICAL WORKFLOW

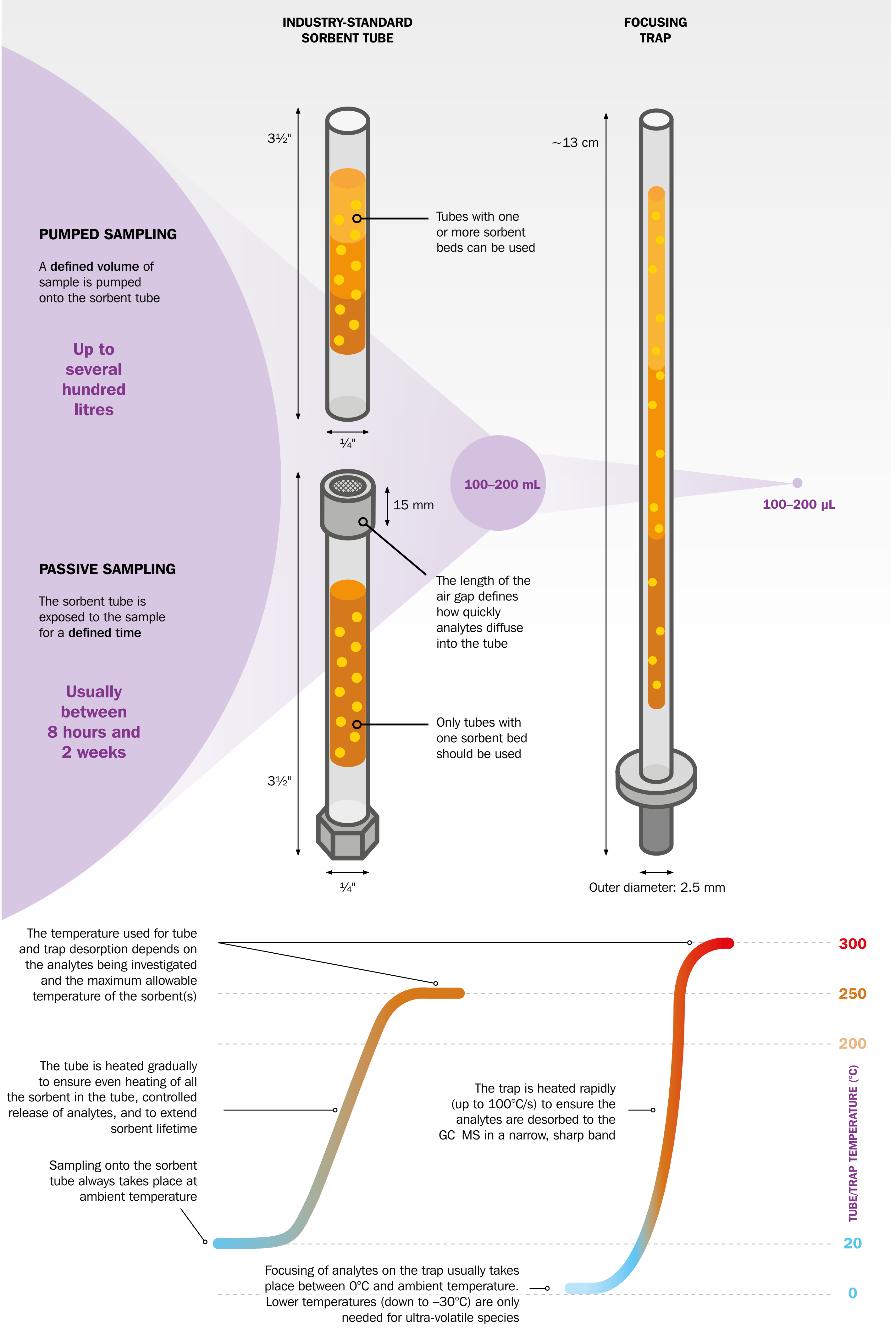


Vapours trapped on sorbent-packed tube

Analytes desorbed from tube into sorbent-packed focusing trap

Preconcentrated analytes desorbed from focusing trap into GC–MS

HOW THERMAL DESORPTION WORKS



PUMPED SAMPLING

A **defined volume** of sample is pumped onto the sorbent tube

Up to several hundred litres

PASSIVE SAMPLING

The sorbent tube is exposed to the sample for a **defined time**

Usually between 8 hours and 2 weeks

Tubes with one or more sorbent beds can be used

The length of the air gap defines how quickly analytes diffuse into the tube

Only tubes with one sorbent bed should be used

The temperature used for tube and trap desorption depends on the analytes being investigated and the maximum allowable temperature of the sorbent(s)

The tube is heated gradually to ensure even heating of all the sorbent in the tube, controlled release of analytes, and to extend sorbent lifetime

Sampling onto the sorbent tube always takes place at ambient temperature

The trap is heated rapidly (up to 100°C/s) to ensure the analytes are desorbed to the GC–MS in a narrow, sharp band

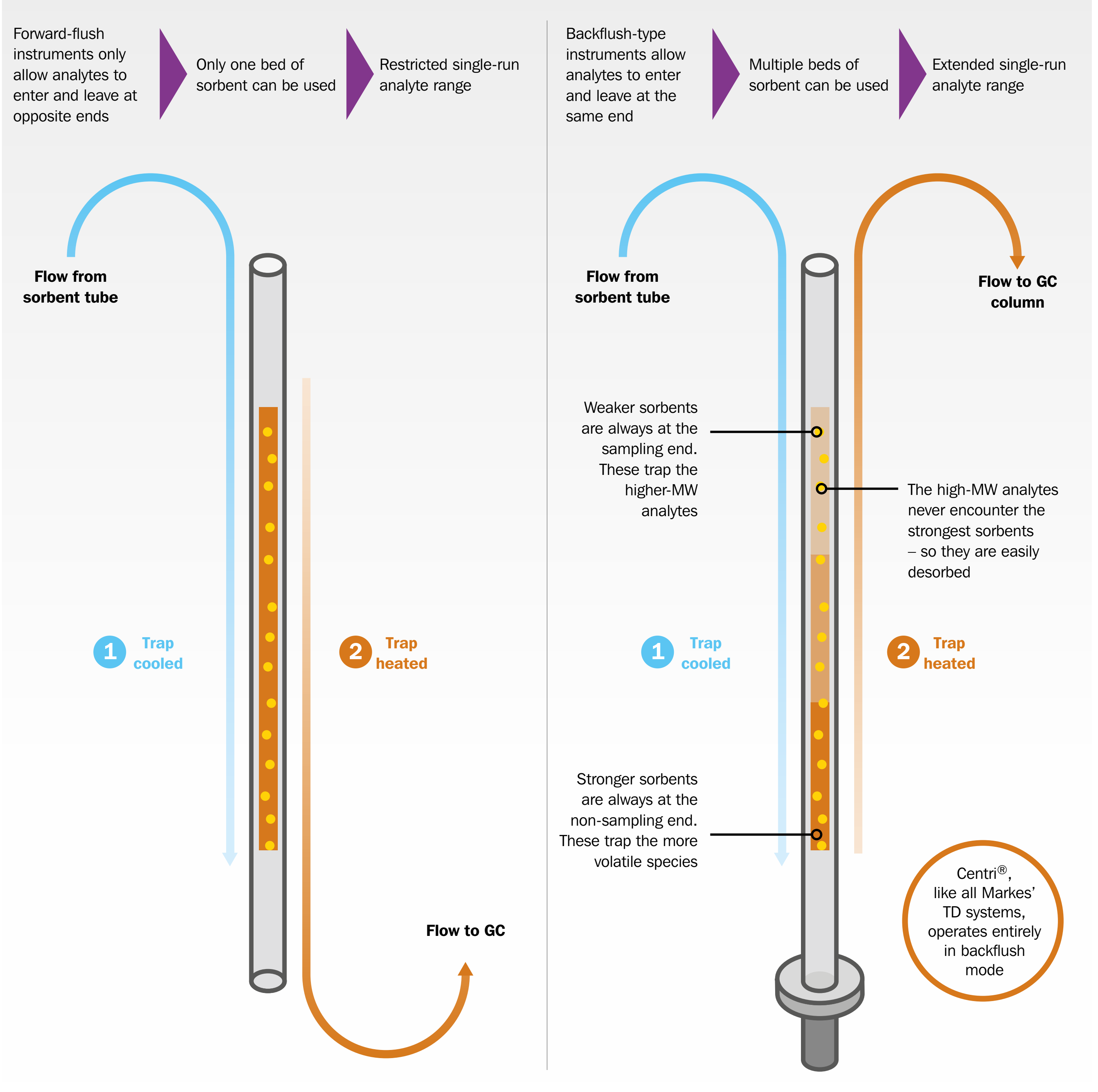
Focusing of analytes on the trap usually takes place between 0°C and ambient temperature. Lower temperatures (down to –30°C) are only needed for ultra-volatile species

FORWARD-FLUSH OR BACKFLUSH TRAPPING?

The choice of forward-flush or backflush operation is a key factor in determining the analyte range and performance that can be achieved.

Forward-flush instruments only allow analytes to enter and leave at opposite ends ▶ Only one bed of sorbent can be used ▶ Restricted single-run analyte range

Backflush-type instruments allow analytes to enter and leave at the same end ▶ Multiple beds of sorbent can be used ▶ Extended single-run analyte range



Weaker sorbents are always at the sampling end. These trap the higher-MW analytes

The high-MW analytes never encounter the strongest sorbents – so they are easily desorbed

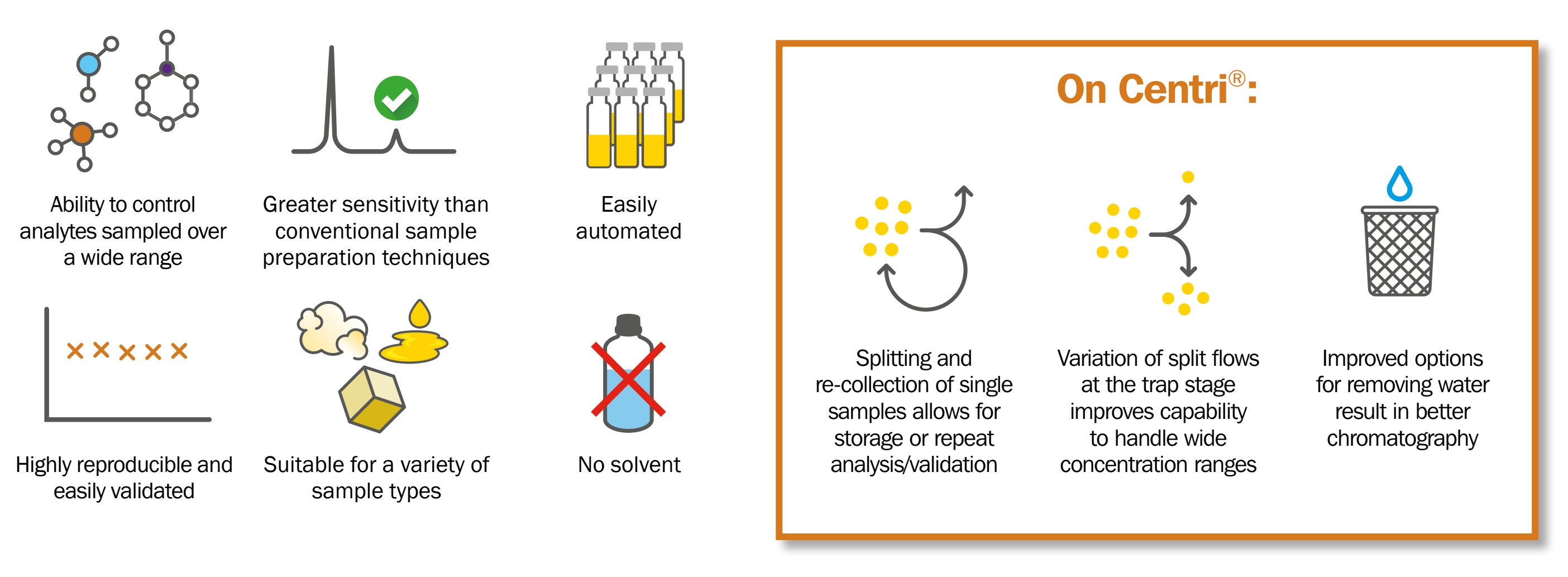
Stronger sorbents are always at the non-sampling end. These trap the more volatile species

Centri®, like all Markes' TD systems, operates entirely in backflush mode

ADVANTAGES & DISADVANTAGES

Thermal desorption is a versatile technique with a range of benefits.

ADVANTAGES

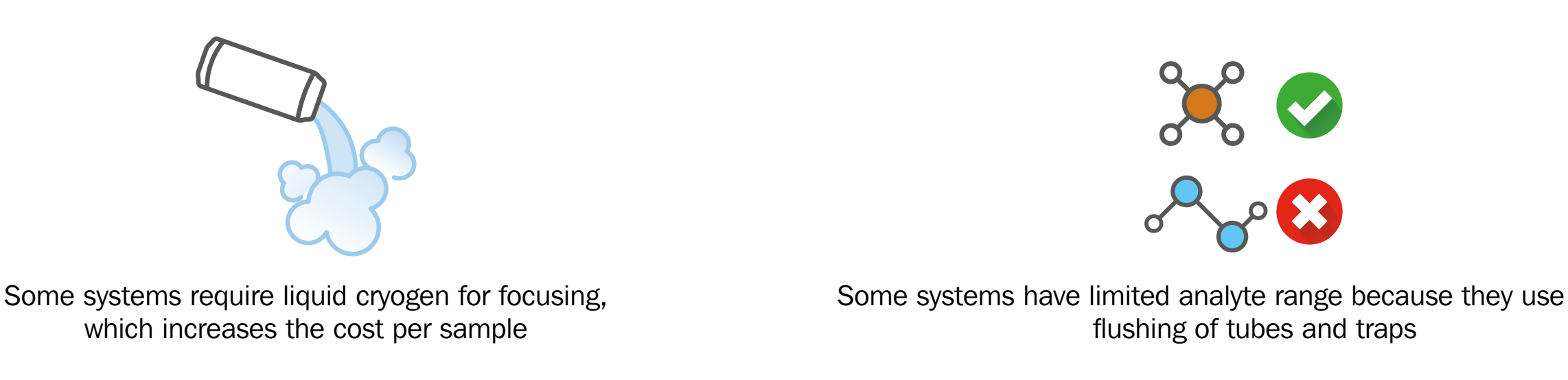


- Ability to control analytes sampled over a wide range
- Greater sensitivity than conventional sample preparation techniques
- Easily automated
- Highly reproducible and easily validated
- Suitable for a variety of sample types
- No solvent

On Centri®:

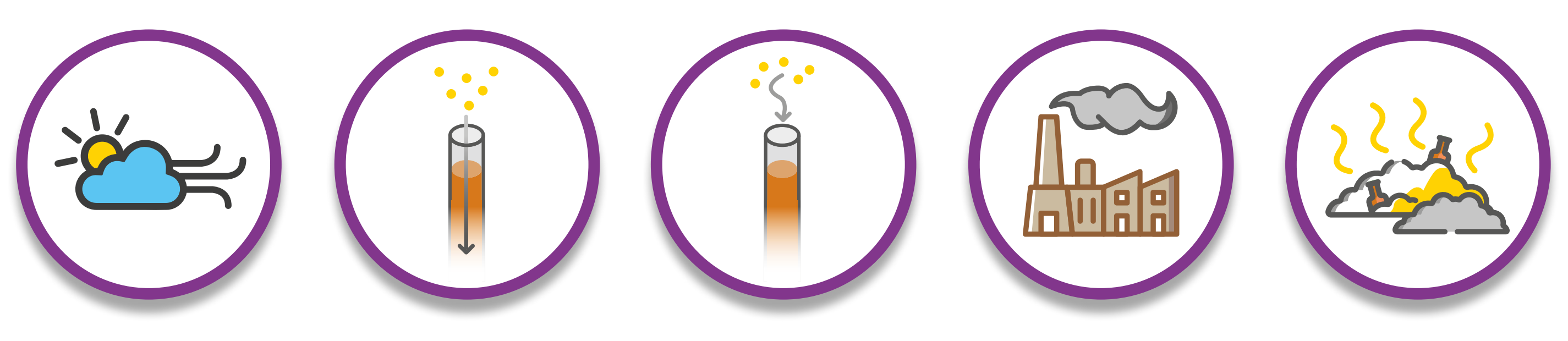
- Splitting and re-collection of single samples allows for storage or repeat analysis/validation
- Variation of split flows at the trap stage improves capability to handle wide concentration ranges
- Improved options for removing water result in better chromatography

DISADVANTAGES



- Some systems require liquid cryogen for focusing, which increases the cost per sample
- Some systems have limited analyte range because they use forward-flushing of tubes and traps

KEY STANDARD METHODS



Air monitoring – General protocols
ASTM 6196
NIOSH Method 2549

Air monitoring – Pumped
US EPA Method TO-17
ISO 16017-1
Chinese EPA Method HJ 644
EN 14662-1 (benzene)

Air monitoring – Passive
EN 14662-4 (benzene)
US EPA Method 325
ISO 16017-2

Stationary source emissions
CEN/TS 13649

Landfill gas
UK Environment Agency Method LFTGN 04

To learn more about automating tube-based thermal desorption using Markes' Centri® multi-mode sampling and preconcentration platform, visit **chem.markes.com/Centri-Platform**

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