# TDTS 61

## Diffusion-locking technology

### Abstract

This Application Note provides a detailed description of the principles of diffusion-locking, and how it can be applied to enhance both sorbent tube sampling and the automation of analytical thermal desorption (TD).

### Introduction

Diffusion-locking is a patented[1] technology for thermal desorption developed by Markes International. It keeps sample tubes sealed at ambient pressures, but allows gas to flow through the tubes whenever pressure is applied. Diffusion-locking does not involve any kind of valve or other moving parts, and is thus inherently simple and robust.

#### The principles of diffusion-locking

If the inlet/outlet tube of a sampler is sufficiently narrow and long, the process of diffusion of vapours into or out of an attached sorbent tube can be reduced almost to zero.

During conventional (axial) diffusive sampling onto an industry-standard (3½″ long × ¼″ o.d.) sorbent tube, the depth of the diffusion gap (between the sorbent and the sampling surface of the cap) is 15 mm and the inner diameter of the tube is 4.9 mm. Under these conditions, typical VOC uptake rates vary from 0.5 to 1.0 mL/min, depending on the diffusion coefficient (Figure 1).

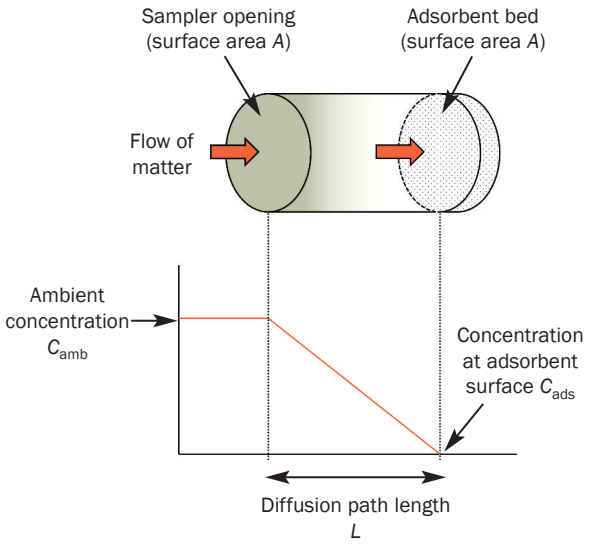


**Figure 1: Axial diffusive sampling onto a standard sorbent tube (uptake rate, *U* = 0.5–1.0 mL/min).**

If the diffusion path length is extended to 150 mm and the inner diameter reduced to 0.4 mm, the rate of diffusive uptake rate is reduced to ~0.3 µL/min – which is equivalent to only 0.4 mL/day.

The diffusion-locking insert, invented by Markes, uses this fact to effectively eliminate diffusion into or out of the tube, but at the same time allow pumped sampling. It consists of a stainless steel threaded insert pushed into a smooth stainless steel cylinder to create a helical path >150 mm long but <0.4 mm wide, in a minimal space.

The diffusion-locking insert is incorporated into DiffLok™ analytical caps (Figure 2) and at both ends of SafeLok™ sampling tubes (Figure 4). The helical gas flow path through the diffusion-locking insert can be made inert by giving the entire assembly a silica-based coating.

### DiffLok analytical end caps for TD automation

DiffLok caps (Figure 2), incorporating diffusion-locking inserts, are fitted onto the end of every sample tube analysed on Markes' automated thermal desorption systems. They are available in both stainless steel and inert-coated stainless steel (the latter suitable for reactive compounds).

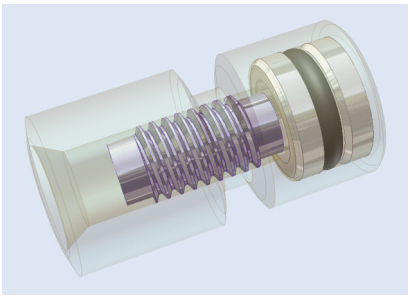

**Figure 2: Schematic of a DiffLok analytical end-cap for sample tubes, showing the threaded insert.**

DiffLok caps protect sampled tubes from both ingress of laboratory air contaminants and the loss of retained volatiles. They also prevent contamination of desorbed/analysed tubes, which thus remain clean and ready for immediate re-use. However, when a tube is selected for desorption and is sealed into the carrier gas flow path of the analytical system, pressure is applied and carrier gas can flow through the caps and tube unimpeded. This greatly simplifies automation, because no uncapping or re-capping is required during tube desorption.

Cone-shaped tube seals on the UltrA™ autosampler simply push into the cone-shaped receivers on the DiffLok caps, creating a low-maintenance, self-aligning tube seal. A sample tube fitted with two DiffLok caps, as it would be placed into an autosampler, is shown in Figure 3.

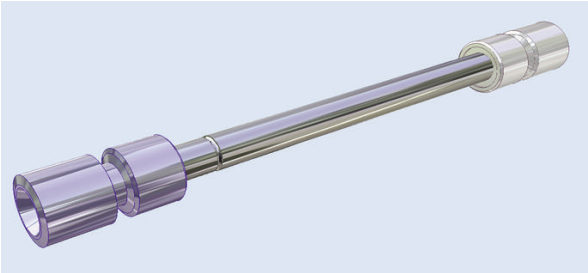

**Figure 3: Schematic of sample tube fitted with two DiffLok caps (the right-hand one stainless steel, the left-hand one inert-coated stainless steel), ready to be placed in an UltrA-UNITY automated thermal desorber.**

## SafeLok tubes for enhanced air sampling

SafeLok tubes incorporate diffusion-locking inserts in the air gap at both ends of the tube (Figure 4). The external dimensions of the tube and the sorbent bed itself (mass, bed length and number of sorbents) are the same as for standard tubes, *i.e.* neither the external dimensions nor the sorbent bed are affected by the presence of the diffusion-locking inserts. This means that all retention-volume data published for industry-standard (3½″ long × ¼″ o.d.) tubes still applies.

**Figure 4: Schematic of SafeLok tube incorporating diffusion-locking inserts at both ends, shown here with two sorbent beds.**

SafeLok tubes are compatible with any TD apparatus designed for standard tubes. Available in stainless steel or inert-coated stainless steel, SafeLok tubes provide enhanced pumped sampling technology. Specific advantages *versus* conventional, open-ended, tubes include:

- Prevents artefact ingress throughout sample storage, transport and analysis, thus enabling monitoring of ultra-trace level vapours in pure atmospheres (*e.g.* for stratospheric or oceanic studies)
- Prevents necking or other damage to tube ends caused by 'overenthusiastic' tightening of tube seals
- Protects against contamination if storage caps are poorly fitted
- Facilitates pumped sampling over extended periods of time at low flow rates (<1 mL/min) – useful when using pumped tubes to validate short- or long-term diffusion (diffusive uptake rates on standard axial tubes are typically in the order of 0.5–1.0 mL/min)
- Makes it safer to handle tubes that have been used for very toxic compounds
- Protects the integrity of blank and sampled tubes during sequential sampling.

## Performance of diffusion-locking technology

The performance of diffusion-locking technology has been tested with respect to two key criteria – prevention of artefact ingress (Figure 5) and sample stability (Figure 6).

This data illustrates the performance of Markes' diffusion-locking technology for protecting both blank and sampled tubes. After 8 days, the level of artefact ingress detected on blank tubes capped with DiffLok caps was indistinguishable from those analysed immediately (Figure 5).

Similarly, no loss of recovery of any of the analytes was observed from tubes capped with DiffLok caps and placed on on a TD-100™ autosampler for 44 hours. This data compares very positively with that from alternative automated TD seals, which have shown significant losses (~25%), particularly of benzene, over only 14 hours[2].

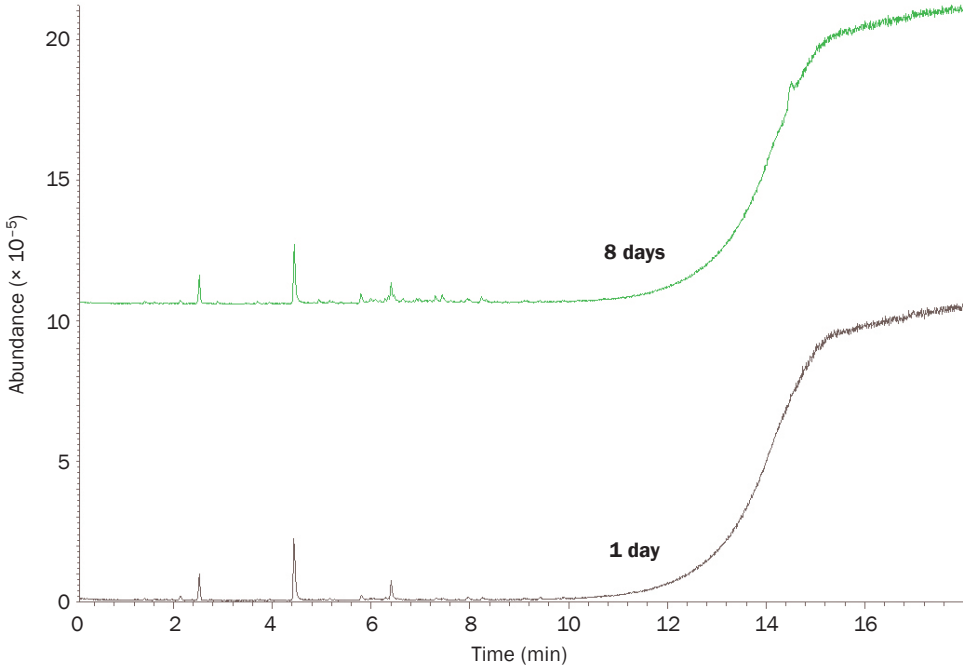


**Figure 5: Storage of blank DiffLok-capped tubes packed with Tenax®, showing negligible artefact ingress over 8 days.**

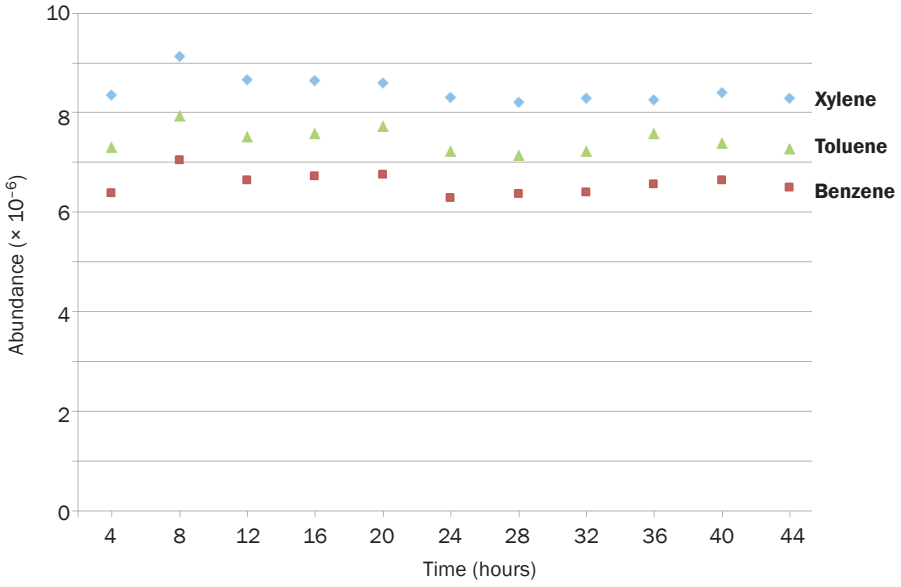


**Figure 6: Storage of DiffLok-capped tubes loaded with a benzene–toluene–xylene standard, showing storage stability for over 40 hours (the consistent differences between runs can be ascribed to differences in the volume injected). For ease of comparison, data for benzene and xylene are vertically displaced by $-1 \times 10^6$ and $+1 \times 10^6$, respectively.**

## References

1. UK Patent No. GB 2,337,513; US Patent No. US 6,564,656.
2. P. Perez-Ballesta, Losses from ATD-400, *The Diffusive Monitor*, 1997, 9: 11–13.

## Trademarks



*Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.*

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