MARKES international

Application

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Application Note 061

Diffusion-locking technology

Summary

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).

The principle of diffusion-locking

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.

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).

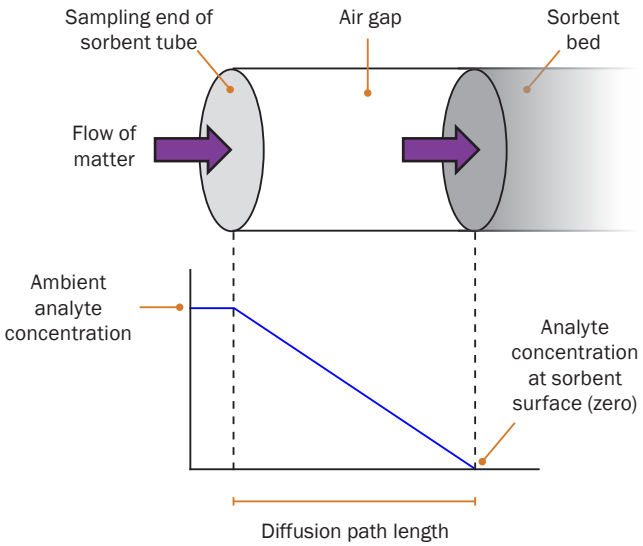

Figure 1: Axial diffusive sampling onto a standard sorbent tube.

If the diffusion path length is extended to 150 mm and the inner diameter reduced to 0.4 mm, the diffusive uptake rate is reduced to ~0.3 µL/min – 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).

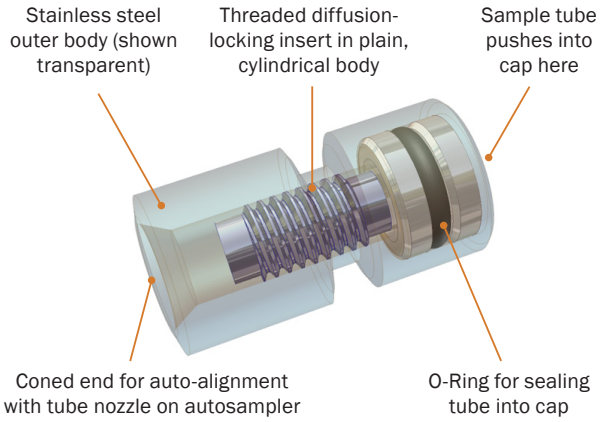

Figure 2: Schematic of a DiffLok cap.

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.

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Cone-shaped tube seals on ULTRA™ and TD100™ autosamplers 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.

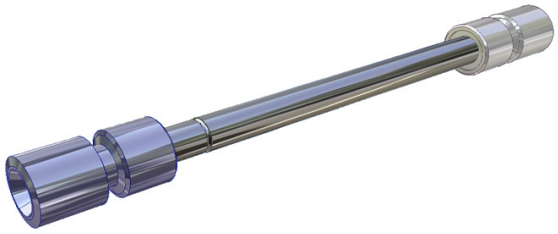

Figure 3: Schematic of sample tube fitted with two DiffLok caps, ready to be placed in an automated thermal desorber. The cap at the sampling end of the tube (on the left) is inert-coated stainless steel, whereas the cap at the non-sampling end (on the right) does not encounter the flow of analytes and so is regular stainless steel.

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.

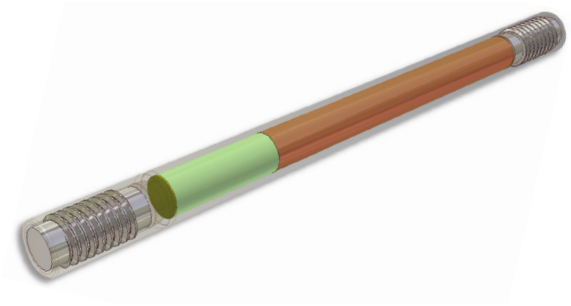

Figure 4: Schematic of SafeLok tube incorporating diffusion-locking inserts at both ends, shown here with two sorbent beds.

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 compared to 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 'over-enthusiastic' tightening of tube seals.
- Protects against contamination due to poorly-fitted storage caps.
- 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.
- Makes it safer to handle tubes 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:

Artefact ingress

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

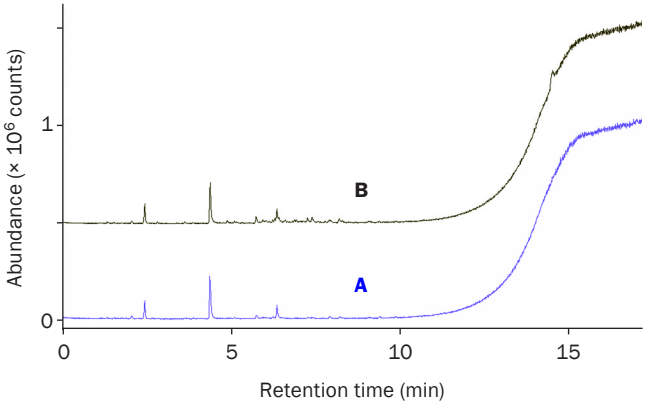

Figure 5: Responses from blank DiffLok-capped tubes packed with Tenax® TA and analysed (**A**) immediately after sampling, and (**B**) after storage for 8 days (top), showing negligible artefact ingress.

Sample stability

No loss of recovery was observed from tubes capped with DiffLok caps and placed on on a TD100™ automated thermal desorber for 44 hours (Figure 6). This compares very well with alternative automated TD seals, which have shown significant losses (~25%), particularly of benzene, after only 14 hours.[2]

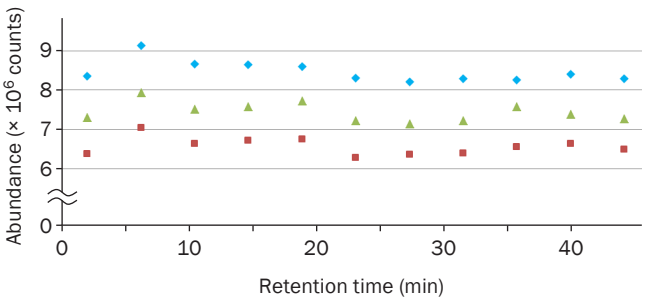

Figure 6: Storage of DiffLok-capped tubes loaded with benzene (■), toluene (▲) and xylene (◆), showing storage stability for over 40 hours (the consistent differences between runs can be ascribed to differences in the volume injected). For clarity, data for benzene and xylene are vertically displaced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

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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.