

## Application Note 114

# Passive monitoring of benzene and other hazardous air pollutants at refinery perimeters in accordance with US EPA Method 325

### Summary

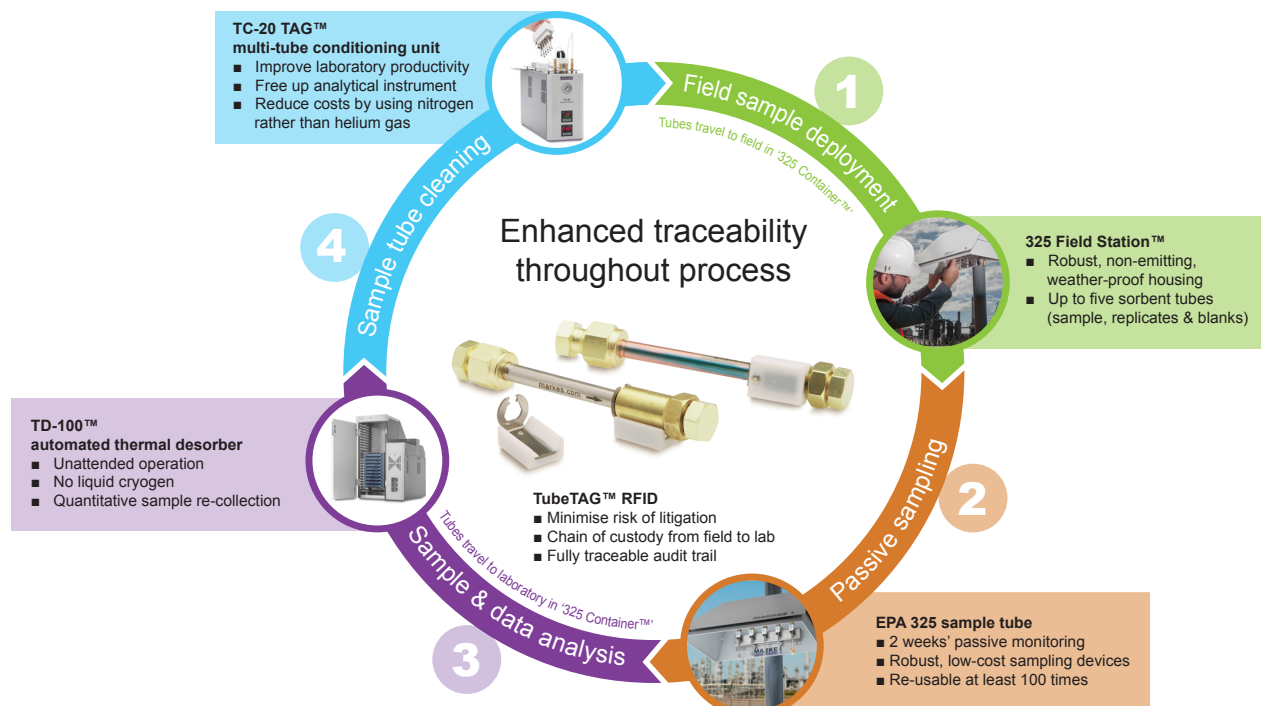
This Application Note describes a stepwise approach to complying with US EPA Method 325 for monitoring volatile organic compounds (VOCs) at refinery perimeters. A range of equipment from Markes International is outlined that allows fully method-compliant deployment of tube-based passive samplers, sample analysis and tube cleaning. All these stages are underpinned by a radio-frequency identification tagging system to ensure a robust chain of custody from field to lab.



### Introduction

US EPA Method 325 has been developed to enable refineries to comply with the updated US federal regulation CFR 40, and requires monitoring of VOCs around the boundary of refineries.<sup>1</sup> This involves two-week passive (diffusive) sampling onto sorbent tubes, followed by analysis by thermal desorption (TD) in conjunction with gas chromatography (GC), with analysis by mass spectrometry (MS) or other detection technique.

While benzene is the primary target compound, the sampling and analysis methodology can also be used to determine other VOCs, including butadiene, toluene, ethylbenzene, xylenes and other hazardous air pollutants (HAPs). This Application Note will explain the stepwise process of the method (Figure 1) and discuss how innovative sampling and analytical instrumentation from Markes International is used to fully comply with Method 325.



**Figure 1:** The stepwise sampling and analytical process using equipment from Markes International, enabling compliance with Method 325. See ref. 2 for a listing of the sections of Method 325 corresponding to each of the stages.

## What do you need to carry out Method 325?

Sampling and analytical equipment available from Markes International to carry out VOC monitoring in accordance with Method 325 is listed in Table 1.

Description	Part number
<b>Sampling accessories</b>	
325 Field Station	C-325FS
EPA 325 tube for BTEX and butadiene, with TubeTAG, pk 10 (inert-coated stainless steel tubes, conditioned & capped)	C1-CCAX-5020
Caps, diffusion, axial, aluminium, pk 100	C-DF100
325 Container (an air-tight, non-emitting container for 15 capped tubes), pk 2	C-325CT
TubeTAG starter kit	C-TAGKT
<b>Thermal desorption system</b>	
TD-100 Advance, electronic re-collection, with internal standard dry-purge, TAG-ready	U-TD100-221-2S
Calibration Solution Loading Rig	C-CSLR
325 trap	U-T18325-2S
Cap, DiffLok (one stainless steel, one inert), ¼", pk 100 pairs	C-DL1P0
TC-20, compatible with TubeTAG	R-TC20-TAG
Pneumatic gas controller	U-GAS03
Internal standard gas	Call Markes for advice

**Table 1:** Method 325 equipment available from Markes International.

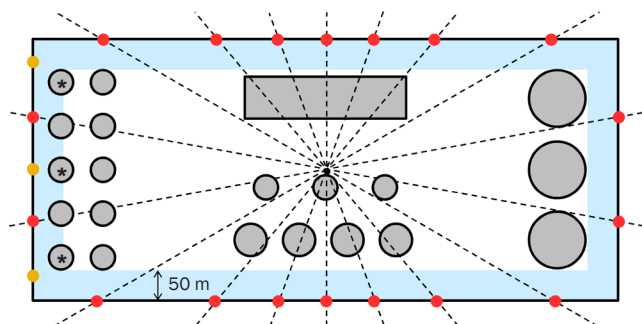
Method 325 requires that the shelters that house the sampling tubes are mounted on 1.5–3 m poles located around the perimeter of the facility. Markes' **325 Field Station™** (Figure 3) is a robust, non-emitting, weather-proof shelter capable of housing five sorbent tubes (suitable for samples, replicates and blanks) for diffusive sampling of ambient air at these locations.



**Figure 3:** Top: Markes' 325 Field Station, pictured with passive sampling tubes equipped with diffusion caps, storage caps and TubeTAG. Bottom: Sampling tubes *in situ* within the shelter.

## 1 Field sample deployment

Method 325 states that up to 24 monitoring locations should be distributed around the perimeter (fenceline) of the refinery, in a pattern that depends upon the size and shape of the site (see Figure 2). Additional monitoring stations may also be required – for example, where the regular distribution of monitoring stations does not adequately cover certain VOC emission sources, or where there are potential interfering sources such as major roads or neighbouring industrial plants.



**Figure 2:** Example of monitoring stations on a rectangular site of 750–1500 acres containing emission sources (grey). Monitoring sites (●) are placed just beyond the boundary at 20° intervals. Sources between two monitoring stations and within 50 m of the boundary (\*) require that additional monitoring stations (●) are installed.<sup>2</sup>

In accordance with standard practice in diffusive monitoring, the 325 Field Station should be positioned away from trees, walls, buildings and other large obstructions, which may cause wind funnelling or other effects that could cause local deviations in ambient air concentration. Note that during the sampling process meteorological data from the nearest available centre must also be collected.

The samplers themselves, which should be thoroughly conditioned before use (see Section 4), are simply pushed into clips within the shelter, without the use of any tools. Each tube is fitted with a downward-pointing diffusive cap at the sampling end, which minimises particulate ingress and eliminates any turbulence in the air gap – a strategy that maintains constant uptake rates even at high wind speeds.

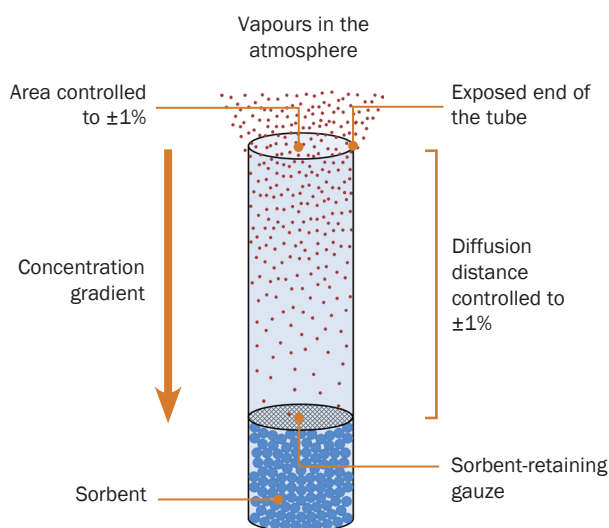
When transporting sampling tubes from the lab to the field and vice versa, caution must be used to avoid mixing the sample tubes and clean tubes, ready for the next round of sampling. To avoid this the capped, sampled tubes must be placed in an inert, sealable container for transport and storage under normal ambient conditions (~20°C/68°F). Markes' 325 Containers fulfil these requirements and are clearly labelled to avoid mixing of sample tubes and clean conditioned tubes.

## 2 Passive sampling

Markes' specially developed **325 tube** is packed with the most popular 325 sorbent (see below), and can trap a range of compounds, including butadiene, benzene, toluene, ethylbenzene and xylenes (the latter four usually being referred to as BTEX).

Clean, conditioned and capped sorbent tubes are sent to the field in Markes' customer-labelled **325 Containers™**, and allowed to equilibrate at ambient temperature before removal from the storage container to minimise risk of condensation. At the start of sampling, the storage cap at the sampling end of the tube is removed and replaced with a diffusion cap.

If more than one sampler is being used at a given monitoring station, they should all be deployed in quick succession, so they effectively have the same start time. Sampling is carried out for a minimum of 14 days, during which time gaseous VOCs migrate into the air gap inside the tube, and adsorb onto the sorbent (Figure 4). At the end of the sampling period, the diffusion caps are removed from the sample tubes and replaced with the long-term storage caps, ready for transport to the analytical laboratory.



**Figure 4:** Schematic showing axial diffusive sampling on sorbent tubes.

The rate at which a specific analyte is adsorbed onto a particular sorbent depends on the strength of the analyte-sorbent interaction and is known as the uptake rate. Widespread use of diffusive sampling over many years has resulted in a large number of published uptake rates, meaning that new users do not need to determine them experimentally.

Method 325 states the use of sorbent tubes packed with Carbograph™ 1TD, Carbpac™ B, or Carbpac X† (or equivalent, *i.e.* Carbograph 5TD). Two-week uptake rates of benzene onto these sorbents are provided in Table 2 (see Appendix for other relevant HAPs).

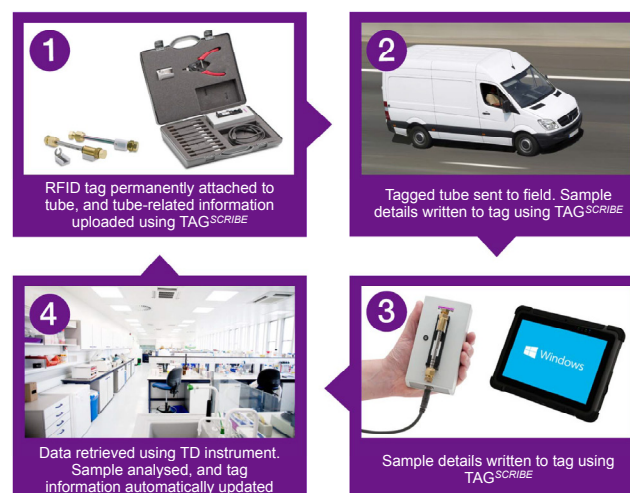
† Note that Markes' 325 tube are specially packed with the recommended mass of this sorbent unless specified otherwise.

Field blank tubes must be deployed at the same time as the sampling tubes and must be housed in the shelter – on these tubes the long-term storage caps stay fitted to both ends. Sampling end time and date information is usually logged at this stage, either manually or electronically.

Sorbent	Uptake rate (mL/min)	Uptake rate (ng ppm <sup>-1</sup> min <sup>-1</sup> )	Ref.
Carbograph 1TD or Carbpac B	0.64	2.03	3
	0.63	2.00	4
Carbpac X or Carbograph 5TD	0.61	1.93	5

**Table 2:** Two-week diffusive sampling uptake rates for benzene on Markes' passive sampling tubes.

Markes' tubes are all etched with a unique ID number in barcode and numerical format for tracking of sample information. However, when handling the large number of tubes required by Method 325, Markes' patented **TubeTAG™** system is recommended (Figure 5). This prevents manual transcription errors, optimising the audit trail and eliminating any risk of litigation.



**Figure 5:** The simple stepwise process involved in using Markes' TubeTAG system to log tube- and sample-related information electronically both in the field and during laboratory analysis.

Robust radio-frequency identification (RFID) tags are fitted to the tubes, and a portable **TAGSCRIBE™** unit is used to enter information such as sampling location, sampling start and finish times, sorbent type, date of packing, and number of analytical cycles. This information is then logged by the thermal desorption system and the information added to the reports. By doing this, TubeTAG allows the development of a robust 'chain of custody' from field to lab, ensures a verifiable method for audit trails, and enhances the general QC of sorbent tubes.

### 3 Sample & data analysis

When the sampled tubes reach the laboratory, they are analysed using thermal desorption–gas chromatography (TD–GC), typically with detection by mass spectrometry (MS).

Markes' thermal desorption instruments operate by desorbing the sample from the tube and transferring it to the focusing (cold) trap, before desorbing it from the trap and injecting it onto the GC column. This efficient two-stage desorption process results in a narrow band of vapour, optimising concentration enhancement and analytical sensitivity.

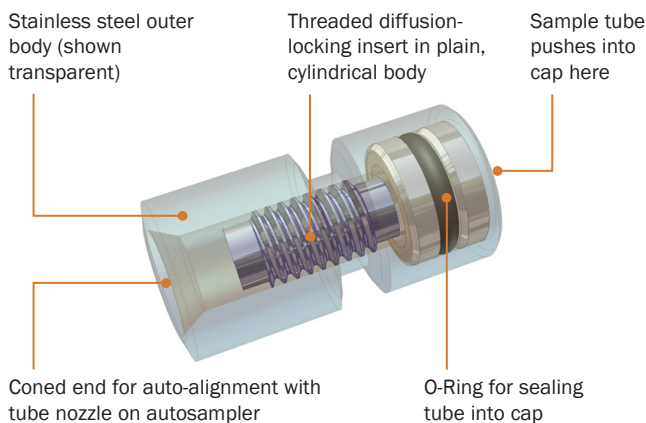
Markes' **TD-100™** thermal desorber (Figure 6) has the capacity to run 100 sample tubes automatically without the need for liquid cryogen, reducing running costs and allowing unattended operation over entire weekends.



**Figure 6:** Markes' TD-100 automated thermal desorber.

Stringent leak-testing and automatic addition of internal standards onto each sample tube on the TD-100 ensures sample and analytical integrity. In addition, the (patented) ability of the TD-100 to quantitatively re-collect the split portion of samples onto a fresh sorbent tube enables repeat analysis of thermal desorption samples, facilitating simple and reliable repeat analysis and validation of analyte recovery.<sup>6</sup>

Method 325 states that tubes must remain sealed at all times after sampling, to avoid contamination and/or analyte loss. Long-term storage caps are used to seal blank and sampled tubes throughout transport and storage. However, immediately before analysis they are replaced with Markes' push-on **DiffLok™** caps, which protect the tubes while they are on the TD autosampler. The patented<sup>7</sup> diffusion-locking technology in DiffLok caps eliminates the need for uncapping within the instrument, by allowing gas to flow through the tube when pressure is applied, while also minimising the risk of sample loss or contaminant ingress (Figure 7).

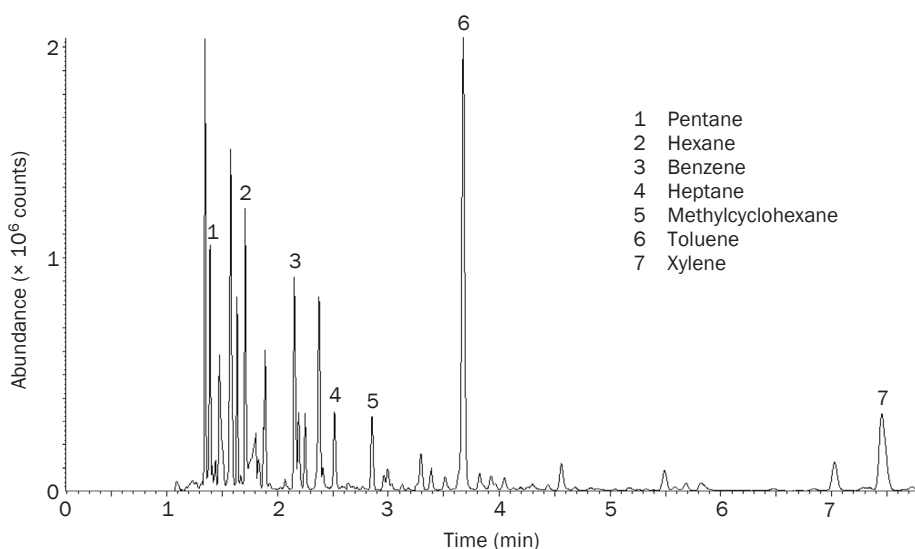


**Figure 7:** Schematic of a DiffLok cap.

#### Data interpretation

While the primary objective of Method 325 is to quantify the level of benzene, the sampling and analytical techniques described above also allow the simultaneous analysis of a wide range of compounds using the same workflow, without additional effort or cost.

A representative TD–GC–MS analysis of contaminated refinery fenceline air, using two-week passive sampling, is shown in Figure 8. Note in particular the detection of benzene, toluene and xylene.



#### Typical analytical conditions

Sampling: Diffusive (passive) sampling onto 325 tubes  
 TD system: TD-100  
 Desorption: 5 min at 320 °C  
 Trap: 325 trap  
 Split: Low split during trap desorption only  
 Analysis: GC–MS (scan) or GC–FID  
 Column: 30 m × 0.25 mm × 0.25 μm, 5% diphenylsiloxane, 95% dimethylsiloxane phase (low-bleed)  
 Oven: 40 °C (5 min) then 15 °C/min to 300 °C (2 min); 24.3 min total  
 Column flow: 1.5 mL/min  
 Source temp: 230 °C  
 Quad temp: 150 °C  
 Transfer line temp: 310 °C

**Figure 8:** The results of two-week diffusive sampling of contaminated air around a refinery perimeter, with analysis by TD–GC–MS, showing the detection of a number of hazardous VOCs.



To determine the concentration of benzene, five-point calibration curves are used to calculate the mass on tube from the peak abundance. The following equation is then used to determine the airborne concentration:

$$\text{Concentration (ppm)} = \frac{\text{Mass of sample on tube (ng)}}{\text{Uptake rate (ng ppm}^{-1} \text{ min}^{-1}) \times \text{Sampling time (min)}}$$

## 4 Sample tube cleaning

Method 325 states that sorbent tubes must be cleaned ('conditioned'), and demonstrate  $\leq 0.2$  ppbv of any contaminants or interferences before use. Markes' **TC-20 TAG™** (Figure 9) streamlines this process and reduces costs, by allowing up to 20 tagged, industry-standard sorbent tubes to be simultaneously conditioned at elevated temperatures.<sup>8</sup> Using the TC-20 frees up instrument time to run samples rather than condition tubes, providing a rapid return on investment. In addition, it allows tubes to be conditioned using high-purity nitrogen, rather than the more expensive helium carrier gas.



Figure 9: Markes' TC-20 TAG tube conditioner.

## Conclusions

This Application Note has described the various steps required to achieve full compliance with US EPA Method 325. Markes International is the only company that can provide the full range of tubes, accessories and instrumentation to comply with the method, as well as complete solution packages, all fully compliant with Method 325. In addition, we have extensive experience of consulting on standard/ regulatory methodology in the USA and worldwide, and are renowned experts in both sampling and analysis of VOCs.

## References

1. US federal regulation CFR 40, Annex A of Part 63: Petroleum refinery sector risk and technology review and new source performance standards. Implementation of CFR 40 is currently expected by early 2016.
2. Federal Register Vol. 79, No. 125, Appendix A to Part 63 [AMENDED], pages 37046–37074, <https://www.federalregister.gov/articles/2014/06/30/2014-12167/petroleum-refinery-sector-risk-and-technology-review-and-new-source-performance-standards>  
**Field sample deployment:** See Part A, section 6.3 (page 37048).  
**Passive sampling:** See Part A, section 8.5 (page 37052).  
**Sample & data analysis:** See Part B, section 4 (page 37056).  
**Sample tube cleaning:** See Part B, section 6.2 (page 37057) and section 9.2 (page 37059).  
**Tube transport (to field or laboratory):** See Part B, section 6.4.2 (page 37057).
3. R.H. Brown, Environmental use of diffusive samplers: Evaluation of reliable diffusive uptake rates for benzene, toluene and xylene, *Journal of Environmental Monitoring*, 1999, 1: 115–116, <http://dx.doi.org/10.1039/A807686C>.
4. N.T. Plant, M.D. Wright and R.H. Brown, European diffusive sampling initiative: Final project report, 1999, Health & Safety Laboratory.
5. N.A. Martin *et al.*, Measurements of environmental 1,3-butadiene with pumped and diffusive samplers using the sorbent Carbopack X, *Atmospheric Environment*, 2005, 39: 1069–1077, <http://dx.doi.org/10.1016/j.atmosenv.2004.09.078>.
6. For information on quantitative re-collection, see Section 13.4.2 of ASTM D6196: Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air.
7. UK Patent No. GB 2,337,513; US Patent No. US 6,564,656.
8. For more information on improving productivity and reducing costs by off-line sorbent tube conditioning, see [Application Note 109](#).
9. EN 14662-4: Ambient air quality – standard method for the measurement of benzene concentrations. Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.
10. EN ISO 16017: Air quality – Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/capillary gas chromatography. Part 2: Diffusive sampling.
11. C. Walgraave, K. Demeestere, J. Dewulf, K. Van Huffel and H. Van Langenhove, Diffusive sampling of 25 volatile organic compounds in indoor air: Uptake rate determination and application in Flemish homes for the elderly, *Atmospheric Environment*, 2011, 45: 5828–5836, <http://dx.doi.org/10.1016/j.atmosenv.2011.07.007>.

## Trademarks

DiffLok™, 325 Container™, 325 Field Station™, TAG<sup>SCRIBE</sup>™, TC-20 TAG™, TD-100™ and TubeTAG™ are trademarks of Markes International.

Carbograph™ is a trademark of LARA s.r.l., Italy.

Carbopack™ is a trademark of Supelco Inc., USA.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.

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

## Appendix

Compound	Exposure time	Sorbent	Uptake rate (mL min <sup>-1</sup> )	Ref.
Benzene	1 week	Carbograph 1TD or Carbopack B	0.67	9
	2 weeks	Carbograph 1TD or Carbopack B	0.63	9
		Carbopack X	0.62	9
	4 weeks	Carbograph 1TD or Carbopack B	0.58	9
Toluene	1 week	Carbograph 1TD or Carbopack B	0.57	10
	2 weeks	Carbograph 1TD or Carbopack B	0.56	10
	4 weeks	Carbograph 1TD or Carbopack B	0.55	10
All xylenes	1 week	Carbograph 1TD or Carbopack B	0.54	10
	2 weeks	Carbograph 1TD or Carbopack B	0.47	10
	4 weeks	Carbograph 1TD or Carbopack B	0.44	10
Ethylbenzene	4 weeks	Carbopack B	0.52	10
Styrene	1 week	Tenax TA	0.36	11
Trimethylbenzene	2 weeks	Carbopack B	0.44	10
	4 weeks	Carbopack B	0.47	10
		Tenax TA	0.54	10
Propylbenzene	1 week	Tenax TA	0.36	11
n-Octane	1 week	Tenax TA	0.27	11
n-Nonane	1 week	Tenax TA	0.34	11
n-Decane	4 weeks	Tenax TA	0.51	10
n-Undecane	4 weeks	Tenax TA	0.53	10

**Table A1:** Validated sorbents and uptake rates from national and international standard methods for selected Clean Air Act components. An extensive listing of uptake rates can be found in Markes' [Application Note 001](#).