Application Note 005

Advice on sorbent selection, tube conditioning, tube storage and air sampling

Summary

This Application Note gives advice on which sorbent to use for pumped or diffusive tube monitoring of various vapour-phase organics, and suggests parameters for conditioning and storing packed tubes. See also Application Note 027 for more information.

Note that guidance given for sorbent selection for a given analyte or analytes will typically apply whether that sample tube is to be used in pumped or diffusive mode. (For further information on diffusive sampling, see Application Notes 001, 002 and 010).

Introduction

Selection of the correct sorbent or series of sorbents for sampling and release of the analytes of interest is one of the most important factors when developing a valid and robust thermal desorption method. Tube conditioning and capping are also critical issues.

The choice of sorbent principally depends upon the volatility (specifically the vapour pressure) of the analyte concerned. In short, the sorbent or series of sorbents selected must quantitatively retain the compounds of interest from the volume of air/gas sampled, and must then release those compounds as efficiently as possible during thermal desorption.

As vapour pressure data is not always readily available, a useful rule-of-thumb is to use the boiling point of the component as a guide to its volatility.

In general – the more volatile the analyte to be trapped, the stronger the sorbent must be.

See Figure 1 for an approximate guide to sorbent strength.

The following pages provide summary information on some of the most commonly used sorbents, in order of increasing strength. Note that sorbent tubes should typically be conditioned using higher temperatures and faster gas flows than those selected for analysis, provided the temperature limits of the materials are not exceeded.

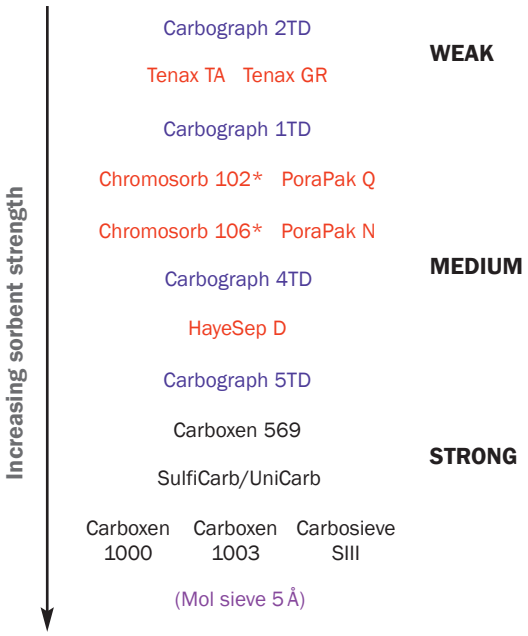

Figure 1: Relative strengths of some commonly used sorbents.
Red = Porous polymers.
Blue = Graphitised carbon blacks.
Black = Carbonised molecular sieves.
Purple = Zeolite molecular sieves.

* Now becoming obsolete.

Types of sorbents

Porous polymers

Most porous polymer sorbents are inert, making them suitable for the analysis of labile and reactive compounds such as thiols, terpenes and CS gas. In addition, their hydrophobic nature allows them to be used for sampling in humid conditions.

However, some porous polymer sorbents (*i.e.* Chromosorb, PoraPak and HayeSep) can exhibit high artefact levels and significant batch-to-batch variation. Aromatic hydrocarbons can also be generated over time, and for these reasons we recommend that these porous polymer sorbents are avoided for monitoring trace-level analytes.

The Chromosorb Century series sorbents have also recently been obsoleted by their manufacturer, and are increasingly difficult to obtain.

Graphitised carbon blacks

These are non-specific carbon sorbents, widely used for trace-level applications due to their minimal artefact levels. They vary from very weak to medium/strong, and are used for a wide range of VOCs and SVOCs. They are fairly hydrophobic and therefore suitable for sampling under humid conditions. They can, however, contain trace levels of metals, which means they are not 100% inert. This makes them less suitable for some labile or highly reactive species, *e.g.* thiols and monoterpenes.

Physically, these sorbents are very friable, *i.e.* they are susceptible to formation of fines, particularly when subjected to mechanical shock. Avoid dropping tubes packed with carbon blacks and ensure they are adequately protected during transportation. Over-compression of these sorbents during packing can also lead to high back-pressure. In extreme circumstances, sorbent tubes may become blocked and will need repacking.

Although generally considered to be non-porous, the strongest graphitised carbon sorbents (*i.e.* Carbograph 5TD) do exhibit microporosity, which improves the ability of these sorbents to trap ultra-volatile compounds. These sorbents therefore provide a 'bridge' between the graphitised carbon blacks and the stronger carbonised molecular sieves.

Carbonised molecular sieves

Carbonised molecular sieves are the strongest sorbents and are used to trap the most volatile compounds. Because they function according to both adsorption and molecular sieve principles, their specific surface area is not the key indicator of their strength. The size and shape of both the analyte molecule and the particle pores determine the analytes that each sorbent is most suited to.

These sorbents are not very hydrophobic and therefore may require dry-purging prior to desorption to remove excess water. Due to their strength, carbonised molecular sieves are easily contaminated by higher-boiling compounds, and should be protected by a front bed of weaker sorbent, except when used for diffusive sampling.

They also require a more extensive purge than normal sorbents to completely remove oxygen prior to desorption – ideally at least 60 mL for standard thermal desorption tubes.

Zeolite molecular sieves

These are very selective hydrophilic sorbents used for specific thermal desorption applications, *e.g.* occupational hygiene monitoring of nitrous oxide (molecular sieve 5 Å).

N.B. In the list of sorbents below, where more than one mesh size is available, an asterisk (*) indicates the recommended mesh size.

Carbograph™ 2TD (20/40, 40/60*, 60/80)

Sorbent type	Graphitised carbon black
Sorbent strength	Very weak
Specific surface area	~10 m^2/g
Approx. analyte volatility range	n-C_8 to n-C_{20}
Example analytes	Alkylbenzenes, hydrocarbons to n-C_{20}, semi-volatiles
Recommended conditioning temp.	Up to 380 °C
Recommended desorption temp.	Up to 360 °C

Notes:
- Hydrophobic
- Minimal (<0.1 ng) artefacts
- Friable and compressible – CARE: Compressing these sorbents leads to high back-pressures and blocked tubes
- 40/60 mesh is recommended for ideal flow characteristics in sorbent tubes and focusing traps
- Repack tubes after 200 thermal cycles.
- Not as efficient as Tenax at releasing high-boiling compounds.

Tenax® TA (35/60*, 60/80)
Tenax® GR (35/60*, 60/80)

Tenax TA is a general-purpose sorbent used in several air monitoring and occupational hygiene applications. It is the most thermally stable of the porous polymers, but still benefits from being used at the lowest possible temperature, to minimise artefacts/degradation.

Tenax GR contains 23% graphitised carbon as an integral part of the material (the graphitised carbon is co-precipitated with the Tenax polymer). For some compounds, Tenax GR offers slightly higher breakthrough volumes. For both Tenax TA and Tenax GR, the 35/60 mesh size is strongly recommended for optimum performance in sorbent tubes.

Sorbent type	Porous polymer
Sorbent strength	Weak
Specific surface area	~35 m^2/g
Approx. analyte volatility range	n-C_7 to n-C_{30} b.p. 100 °C to 450 °C
Example analytes	Aromatics (except benzene), apolar compounds b.p. >100 °C, polar compounds b.p. >150 °C, semi-volatile compounds, including many chemical warfare agents (CWAs)
Recommended conditioning temp.	Up to 330 °C
Recommended desorption temp.	280 °C for trace-level work and up to 320 °C generally

Notes:
- Hydrophobic
- Low inherent artefacts (<1 ng)
- Inert – suitable for labile components
- Do not exceed sorbent maximum temperature – sorbent will break down and may contaminate system flow path
- Repack sorbent tubes after 100 thermal cycles
- Allows efficient desorption, giving sharp GC peaks.

Carbograph™ 1TD (20/40, 40/60*, 60/80)

This is a widely used sorbent that is also often employed in two- or three-bed sorbent tubes.

Sorbent type	Graphitised carbon black
Sorbent strength	Weak/medium
Specific surface area	~100 m^2/g
Approx. analyte volatility range	n-$C_{5/6}$ to n-C_{14}
Example analytes	Ketones, alcohols, aldehydes, apolar components, perfluorocarbon tracer gases; benzene, toluene, xylene (1–4-week diffusive exposure in ambient air)
Recommended conditioning temp.	Up to 380°C
Recommended desorption temp.	Up to 360°C

Notes:
- Hydrophobic
- Minimal (<0.1 ng) artefacts
- Friable and compressible – CARE: Compressing these sorbents leads to high back-pressures and blocked tubes
- 40/60 mesh is recommended for ideal flow characteristics in sorbent tubes and focusing traps
- Repack tubes after 200 thermal cycles.

Chromosorb® 102 (60/80)

The Chromosorb Century series of porous polymers was popular for thermal desorption applications.

Chromosorb 102 was slightly polar, and commonly used for light halogenated hydrocarbons.

Sorbent type	Porous polymer
Sorbent strength	Medium
Specific surface area	~350 m^2/g
Approx. analyte volatility range	b.p. 50°C to 200°C
Example analytes	Volatile halogenated hydrocarbons
Recommended conditioning temp.	Up to 220°C
Recommended desorption temp.	Up to 200°C (see Notes)

Notes:
- Hydrophobic
- High artefacts (~10–50 ng/component)
- Keep the desorption temperature to a minimum to reduce artefact levels
- Conditioned Chromosorb 102 may self-generate aromatic hydrocarbons over time. It is recommended that tubes packed with this sorbent are used as soon as possible after conditioning
- Inert – suitable for labile components
- Repack sorbent tubes after 100 thermal cycles or less
- Not generally suitable for:
  - Multi-bed sorbent tubes
  - Focusing traps (special applications only)
  - Long-term (>8 h) diffusive sampling.

PoraPak™ Q (50/80)

There are several PoraPak porous polymers available that vary in strength (specific surface area) and polarity, and PoraPak Q is one of the most commonly used in thermal desorption applications.

PoraPak Q is weaker than PoraPak N, is only slightly polar, and is a general-purpose PoraPak sorbent.

Sorbent type	Porous polymer
Sorbent strength	Medium
Specific surface area	~500 m^2/g
Approx. analyte volatility range	b.p. 50°C to 200°C
Example analytes	Oxygenated compounds
Recommended conditioning temp.	Up to 220°C
Recommended desorption temp.	Up to 190°C

Notes:
- Hydrophobic
- High artefacts (~10–50 ng/component)
- Keep the desorption temperature to a minimum to reduce artefact levels
- Conditioned PoraPak Q may self-generate aromatic hydrocarbons over time. It is recommended that tubes packed with this sorbent are used as soon as possible after conditioning
- Inert – suitable for labile components
- Repack sorbent tubes after 50 thermal cycles
- Not generally suitable for:
  - Multi-bed sorbent tubes
  - Focusing traps (special applications only)
  - Long-term (>8 h) diffusive sampling.

Chromosorb® 106 (60/80)

The Chromosorb Century series of porous polymers was popular for thermal desorption applications.

Chromosorb 106 was the strongest of the Chromosorb series, and completely non-polar.

Sorbent type	Porous polymer
Sorbent strength	Medium
Specific surface area	~750 m^2/g
Approx. analyte volatility range	b.p. 50°C to 200°C
Example analytes	Benzene, volatile hydrocarbons, oxygenated compounds
Recommended conditioning temp.	Up to 220°C
Recommended desorption temp.	Up to 200°C (see Notes)

Notes:

- Hydrophobic
- High artefacts (~10–50 ng/component)
- Keep the desorption temperature to a minimum to reduce artefact levels
- Conditioned Chromosorb 106 may self-generate aromatic hydrocarbons over time. It is recommended that tubes packed with this sorbent are used as soon as possible after conditioning
- Inert – suitable for labile components
- Repack sorbent tubes after 100 thermal cycles or less
- Not generally suitable for:
  - Multi-bed sorbent tubes
  - Focusing traps (special applications only)
  - Long-term (>8 h) diffusive sampling.

PoraPak™ N (50/80)

There are several PoraPak porous polymers available that vary in strength (specific surface area) and polarity.

PoraPak N is the most polar (and least thermally stable) PoraPak sorbent, and is typically used for monitoring volatile nitriles.

Sorbent type	Porous polymer
Sorbent strength	Medium
Specific surface area	~300 m^2/g
Approx. analyte volatility range	b.p. 50°C to 200°C
Example analytes	Volatile nitriles
Recommended conditioning temp.	Up to 170°C
Recommended desorption temp.	Up to 165°C

Notes:

- Hydrophilic
- High artefacts (~10–50 ng/component)
- Keep the desorption temperature to a minimum to reduce artefact levels
- Conditioned PoraPak N may self-generate aromatic hydrocarbons over time. It is recommended that tubes packed with this sorbent are used as soon as possible after conditioning
- Inert – suitable for labile components
- Repack sorbent tubes after 50 thermal cycles
- Not generally suitable for:
  - Multi-bed sorbent tubes
  - Focusing traps (special applications only)
  - Long-term (>8 h) diffusive sampling.

Carbograph™ 4TD (20/40)

Sorbent type	Graphitised carbon black
Sorbent strength	Medium
Specific surface area	~130 m^2/g
Approx. analyte volatility range	n-$C_{4/5}$ to n-C_{12}
Example analytes	Light hydrocarbons
Recommended conditioning temp.	Up to 380°C
Recommended desorption temp.	Up to 360°C

Notes:

- Hydrophobic
- Minimal (<0.1 ng) artefacts
- Friable and compressible – CARE: Compressing these sorbents leads to high back-pressures and blocked tubes
- Not recommended for focusing traps
- Repack tubes after 200 thermal cycles.

HayeSep® D (60/80)

HayeSep polymers were developed to exhibit less bleed and shrinkage than other porous polymers. HayeSep D is the strongest sorbent in this series. However, its use tends to be restricted to very specialised applications, *e.g.* monitoring of certain chemical warfare agents.

Sorbent type	Porous polymer
Sorbent strength	Medium
Specific surface area	~800 m^2/g
Approx. analyte volatility range	n-C_5 to n-C_{12} b.p. 50°C to 200°C
Example analytes	Specifically used for GB/GE derivatives of VX (chemical warfare agent)
Recommended conditioning temp.	Up to 280°C
Recommended desorption temp.	Up to 260°C (see Notes)

Notes:
- Hydrophobic
- High artefacts (~10–50 ng/component)
- Keep the desorption temperature to a minimum to reduce artefact levels
- Inert – suitable for labile components
- Repack sorbent tubes after 50 thermal cycles, or more frequently if used the the maximum temperature limit
- Not generally suitable for:
  - Multi-bed sorbent tubes
  - Focusing traps (special applications only).

Carbograph™ 5TD (20/40, 40/60*)

Sorbent type	Graphitised carbon black
Sorbent strength	Medium/strong
Specific surface area	~100 m^2/g
Approx. analyte volatility range	n-$C_{3/4}$ to n-C_8 b.p. 50°C to 150°C
Example analytes	Light hydrocarbons; buta-1,3-diene (1-week diffusive exposure)
Recommended conditioning temp.	Up to 380°C
Recommended desorption temp.	Up to 360°C

Notes:
- Hydrophobic
- Minimal (<0.1 ng) artefacts
- Friable and compressible – CARE: Compressing these sorbents leads to high back-pressures and blocked tubes
- 40/60 mesh is recommended for ideal flow characteristics in sorbent tubes and focusing traps
- Repack tubes after 200 thermal cycles.

Carboxen™ 569 (20/45)

Sorbent type	Carbonised molecular sieve
Sorbent strength	Strong
Specific surface area	~485 m^2/g; also functions on molecular sieve principles
Approx. analyte volatility range	C_3 to n-C_8 b.p. –30°C to 150°C
Example analytes	Volatile hydrocarbons
Recommended conditioning temp.	Up to 380°C *N.B.* The temperature should be increased gradually from 100°C, especially during initial conditioning, to remove oxygen and avoid rapid expansion of volatiles, which can crack the sieves
Recommended desorption temp.	Up to 360°C

Notes:
- Less hydrophilic than most carbonised molecular sieves, but may require dry-purging
- Assume safe sampling volumes are reduced by a factor of 10 when sampling in air at >80% relative humidity
- Easily contaminated by higher-boiling compounds; protect by a front bed of weaker sorbent, except when sampling diffusively
- Minimal (<0.1 ng) artefacts
- Repack tubes after 200 thermal cycles.

SulfiCarb™ (40/70)
UniCarb™ (60/80)

Sorbent type	Carbonised molecular sieve
Sorbent strength	Very strong
Specific surface area	~1200 m^2/g; also functions on molecular sieve principles
Approx. analyte volatility range	C_3 to n-C_6 b.p. –30°C to 150°C
Example analytes	Very volatile compounds, *e.g.* vinyl chloride monomer, CS_2, methanol, ethanol, acetone *etc.* Used for very volatile but sterically large molecules, *e.g.* SF_6
Recommended conditioning temp.	Up to 380°C *N.B.* The temperature should be increased gradually from 100°C, especially during initial conditioning, to remove oxygen and avoid rapid expansion of volatiles, which can crack the sieves
Recommended desorption temp.	Up to 360°C

Notes:
- UniCarb is no longer available, but we are able to supply a similarly inert sorbent, SulfiCarb, which has the same physical properties and very similar performance for reactive sulfur species and light VOCs
- Not very hydrophobic; may require dry-purging
- Assume safe sampling volumes are reduced by a factor of 10 when sampling in air at >80% relative humidity
- Easily contaminated by higher-boiling compounds; protect by a front bed of weaker sorbent, except when sampling diffusively
- Minimal (<0.1 ng) artefacts
- Inert – suitable for labile compounds
- Repack tubes after 200 thermal cycles.

Carboxen™ 1000 (60/80)

Sorbent type	Carbonised molecular sieve
Sorbent strength	Very strong for small molecules
Specific surface area	>1200 m^2/g; also functions on molecular sieve principles
Approx. analyte volatility range	Permanent gases and light hydrocarbons b.p. –60°C to 80°C
Example analytes	Ultra-volatile hydrocarbons
Recommended conditioning temp.	Up to 380°C *N.B.* The temperature should be increased gradually from 100°C, especially during initial conditioning, to remove oxygen and avoid rapid expansion of volatiles, which can crack the sieves
Recommended desorption temp.	Up to 360°C

Notes:
- Retains some water – avoid using in humid conditions if possible, and dry-purge extensively
- Assume safe sampling volumes are reduced by a factor of 10 when sampling in air at >80% relative humidity
- Easily contaminated by higher-boiling compounds; protect by a front bed of weaker sorbent, except when sampling diffusively
- Minimal (<0.1 ng) artefacts
- Repack tubes after 200 thermal cycles.

Carboxen™ 1003 (40/60)

Carboxen 1003 offers the best performance of all the carbon molecular sieves (*e.g.* Carbosieve SIII, Carboxen 1000), from the perspective of retention of ultra-light compounds whilst allowing breakthrough of water. Markes recommends using Carboxen 1003 for many air monitoring methods that may previously have specified Carboxen 1000 or Carbosieve SIII.

Sorbent type	Carbonised molecular sieve
Sorbent strength	Very strong for small molecules
Specific surface area	1000 m^2/g; also functions on molecular sieve principles
Approx. analyte volatility range	Ethane to n-$C_{5/6}$
Example analytes	Ultra-light compounds
Recommended conditioning temp.	Up to 380°C *N.B.* The temperature should be increased gradually from 100°C, especially during initial conditioning, to remove oxygen and avoid rapid expansion of volatiles, which can crack the sieves
Recommended desorption temp.	Up to 360°C

Notes:
- Not very hydrophobic; may require dry-purging
- Assume safe sampling volumes are reduced by a factor of 10 when sampling in air at >80% relative humidity
- Easily contaminated by higher-boiling compounds; protect by a front bed of weaker sorbent, except when sampling diffusively
- Minimal (<0.1 ng) artefacts
- Repack tubes after 200 thermal cycles.

Carbosieve™ SIII (60/80)

Sorbent type	Carbonised molecular sieve
Sorbent strength	Very strong
Specific surface area	~800 m^2/g, but primarily functions on molecular sieve principles
Approx. analyte volatility range	Ethane to n-C_5 (also ethylene from small volumes) b.p. –60°C to 80°C
Example analytes	Ultra-volatile hydrocarbons
Sorbent max. temp.	>450°C
Recommended conditioning temp.	Up to 380°C *N.B.* The temperature should be increased gradually from 100°C, especially during initial conditioning, to remove oxygen and avoid rapid expansion of volatiles, which can crack the sieves
Recommended desorption temp.	Up to 360°C

Notes:
- Significantly water-retentive – avoid using in humid conditions if possible.
- Assume safe sampling volumes are reduced by a factor of 10 when sampling in air at >80% relative humidity
- Easily contaminated by higher-boiling compounds; protect by a front bed of weaker sorbent, except when sampling diffusively
- Minimal (<0.1 ng) artefacts
- Repack tubes after 200 thermal cycles.

Molecular sieve 5 Å

Sorbent type	Zeolite molecular sieve
Sorbent strength	Very strong
Pore size	5 Å
Typical application	Nitrous oxide monitoring in occupational hygiene applications
Recommended conditioning temp.	300°C to 350°C *N.B.* The temperature should be increased gradually from 100°C, especially during initial conditioning, to remove oxygen and avoid rapid expansion of volatiles, which can crack the sieve
Recommended desorption temp.	165°C (for N_2O applications)

Notes:
- High (~10 ng) artefacts
- Significantly hydrophilic – do not use in humid conditions
- Repack tubes after 200 thermal cycles
- Molecular sieve tubes used for N_2O monitoring should be desorbed in the sampling direction to allow selective release of N_2O.

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General notes for sorbent tube sampling

Industry-standard sorbent tubes for air monitoring are available in stainless steel,inert-coated stainless steel and glass. They are 3½″ (89 mm) long and ¼″ o.d., with the middle 60 mm packed with sorbent and in direct contact with the tube oven during thermal desorption. Markes International also offers a range of 4½″ glass DAAMS (Depot Area Air Monitoring System) tubes. Markes' series 2 UNITY™ and ULTRA™ instrumentation is available in either 3½″ or 4½″ tube configurations.

The mass of sorbent packed into a single standard 3½″ tube varies with sorbent density and tube type (5 mm metal and 4 mm i.d. glass), and varies from ~200 mg to ~1000 mg.

Gas–solid chromatographic theory dictates that mesh size does not impact upon retention volume as long as there are at least five particles of sorbent across the diameter of the tube. This means that even 20–40 mesh sorbent (mean particle size ~0.9 mm) will not compromise retention volumes in metal tubes.

Tube capacity (breakthrough) is rarely a function of the mass of analyte adsorbed, but depends on sorbent–sorbate affinity. In other words, what happens within the tube is primarily a gas–solid chromatographic process, and the retention time (retention volume) of that tube for a given analyte will be the same whether the mass of analyte introduced is large or small. This is true for the same reason that GC retention time is not usually affected by peak size. The mass of analyte retained by a tube during air sampling can range from sub-ng to tens of milligrams in extreme cases, *e.g.* high-concentration stack-emission sampling.

If the atmospheric concentration is >100 ppm, or if there are high concentrations of other volatiles in the air (*e.g.* >80% relative humidity), this can cause competition within the tube and reduce retention volumes. In the case of carbonised molecular sieves, the impact of high humidity can be very significant, and may reduce retention volumes by as much as a factor of 10.

Optimum pump flow rates for sampling on standard tubes range from 10–200 mL/min, with 50 mL/min being broadly accepted as the best.

Flow rates below 10 mL/min should not be used because diffusive ingress occurs at 0.5–1 mL/min on standard tubes, so this will introduce significant errors if lower flows are used. *N.B.* Markes' SafeLok™ tubes can be used at low pump flow rates (*e.g.* 1 mL/min) for extended pumped monitoring periods if required.

The retention volume will begin to drop significantly at flow rates above 200 mL/min – especially for volatile compounds, *i.e.* those analytes with lowest affinity for the sorbent selected. However, flow rates up to 500 mL/min can be used for collecting vapour-phase VOCs for short-term monitoring (periods up to 15 min), or for sampling semi-volatiles that are very well retained by the sorbent.

The air gap within a metal tube is precisely defined by the groove in the tube and the sorbent retaining gauze which is located in that groove. The air gap between the gauze and the sampling end of the tube is 14 mm, extending to 15 mm when a diffusion cap is fitted. Glass tubes are not generally suited for diffusive monitoring because it is much more difficult to define the air gap sufficiently precisely.

Note that, as a general rule, safe sampling volumes (see below) are quoted at 20°C and (approximately) halve for every 10°C increase in temperature.

Retention volumes/safe sampling volumes

Retention volumes (RVs) can be used to determine whether a particular sorbent tube will quantitatively retain a given analyte. Retention volumes are usually quoted in litres per gram of sorbent, and can be used to estimate the retention volume on the mass of that sorbent in a standard tube. RVs are always quoted at a set temperature – usually 20°C.

A comprehensive list of retention volumes for different analytes on several sorbents packed into industry-standard 3½″ × ¼″ o.d. tubes is provided in Application Note 020. See also EN ISO 16017-1, US EPA Method TO-17, ASTM D6196 and MDHS 72 – Volatile Organic Compounds in Air (listed in Application Note 003).

It is possible to measure retention volumes in the laboratory using a gas chromatograph configured with a ¼″ packed column. The procedure is as follows:

- Pack the chromatographic column with a known weight of the sorbent of interest
- Operate the column at an appropriate temperature, typically between 150°C and 250°C
- Inject the analyte in question, and note the retention time and column flow at each temperature
- Reset the GC oven temperature and repeat the experiment
- From this information, calculate the specific retention volume in litres per gram for each temperature
- Plot the log of the specific retention volume against the reciprocal of the absolute column temperature, to obtain a linear relationship
- Extrapolate the graph to give the log of the retention volume at 20°C.

See EN ISO 16017-1, Annex B, for more details.

In order to minimise the risk of breakthrough during pumped sampling, a safe sampling volume (SSV) is usually quoted as being half the extrapolated retention volume. A sampling strategy that limits the volume of air sampled to the SSV or less is therefore considered to be prudent.

Note also that safe sampling volumes on some sorbents, particularly those with some hydrophillicity, are significantly affected by high atmospheric humidity. For example, SSVs on SulfiCarb, Carbosieve SIII and Carboxen 1000 should typically be reduced by a factor of 10 at relative humidities above 80%.

Breakthrough volumes and safe sampling volumes

Another way of estimating safe sampling volumes is to determine the breakthrough volume. This can be done by passing a moderately high concentration (1–10 ppm) gas standard of the compound of interest through a tube, packed with the sorbent under test, at a controlled temperature and flow rate (20 to 200 mL/min). Gas exiting the end of the tube should be monitored using a suitable detector, and breakthrough is confirmed when the detector signal shows that the concentration of analyte in the exhaust air is 5% of the concentration entering the tube. The volume of gas that has passed through the sorbent tube up to that point is called the breakthrough volume (see EN ISO 16017-1, Annex A, for more details.)

The breakthrough volume can be determined in this way at a range of temperatures and using gas streams of varying relative humidity to evaluate how these factors affect breakthrough.

By convention, and to give a margin of safety during air sampling, the SSV is usually taken to be two-thirds of the breakthrough volume.

Sampling a wide volatility range

It is often the case that the list of analytes to be monitored requires more than one sorbent. For example, if both toluene and methanol are to be monitored simultaneously, two sorbents – a medium/weak one for toluene and a strong one for methanol – should be used. For diffusive monitoring, this can only be achieved by using two or more tubes in parallel and by stringently conditioning the tube packed with the stronger sorbent before re-use. Pumped monitoring requires samples to be drawn through the two or more sorbents in series. Sampling onto sorbents in series can be achieved in one of two ways:

Method 1: Linking together two tubes containing the individual sorbents required.

Method 2: Packing both sorbents as two separate beds in one tube.

In Method 1, tubes are connected together using ¼″–¼″ stainless steel couplings fitted with PTFE ferrules. The tubes must be connected in series such that the tube containing the weakest sorbent is at the front of the sampling train, and both tubes must be oriented such that the sample passes through from the sampling (grooved) end of each tube. This ensures that the higher-boiling components in the mixture are adsorbed by the weaker sorbent and eliminated from the sample stream before reaching the strong sorbent. Note that three or more tubes can be linked together in series as described, provided all the tubes are arranged in order of increasing sorbent strength and that the pump can cope with the total impedance.

In Method 2, small plugs of glass wool or sorbent-retaining gauzes separate the two or three sorbents in the tube. The weaker sorbent is packed at the front (sampling) end of the tube, followed by a plug of glass wool, and then the stronger sorbent. Again, this ensures that when air is drawn through the tube the mixture reaches the weaker sorbent first where the higher-boiling components are trapped.

Note that if two or more sorbents are to be packed into a single tube, all the sorbents must have similar maximum temperatures. If one or more of the sorbents has a significantly lower maximum temperature than the other(s) in the tube, it will not be possible to stringently condition the more stable sorbents without exceeding the temperature limitations of the less stable material. For this reason, Chromosorb and PoraPak sorbents are not recommended to be used in multi-sorbent tubes.

Long-term storage of clean and sampled tubes

Conditioned or sampled sorbent tubes should always be capped using ¼″ brass Swagelok-type screw caps fitted with PTFE ferrules, as recommended by international standard methods for thermal desorption. These should be tightened using Markes' CapLok™ tool or using conventional spanners/wrenches.

The CapLok tool was invented by scientists at the French Environmental Centre (INERIS), and makes it easier to cap tubes in the lab or field. The CapLok tool also prevents over-tightening and distortion of the PTFE ferrules.

Capped, conditioned, or sampled tubes should always be stored in as clean an atmosphere as possible. As an additional precaution, batches of clean or sampled tubes can be wrapped in uncoated aluminium foil and placed in clean, non-emitting, air-tight containers such as unused paint cans, or freezer-grade food storage containers during transportation or extended storage.

It is not necessary to store capped tubes (blanks or sampled) in refrigerated conditions – unless the sampled tubes contain more than one sorbent. In this case, refrigeration is recommended to minimise risk of middle-volatility analytes migrating from weaker to stronger sorbents during storage and thus resulting in incomplete recovery during analysis. If refrigeration is used, the caps must be re-tightened using the CapLok tool once they have reached their storage temperature. Refrigerated tubes must also be removed from the freezer/refrigerator and left to equilibrate at laboratory temperature before the storage caps are removed for analysis. If the tubes are uncapped while they are still cold, water vapour in the air can condense inside the cold tube, causing subsequent analytical difficulties.

N.B. Be aware that that the air within many general-purpose laboratory fridge/freezers is highly contaminated with volatiles from other samples or from the refrigeration system itself.

Note also that if tubes are to be transported in such a way as to be exposed to very low temperatures, *i.e.* in an aircraft hold, or by rail/road overnight during cold weather, it is advisable to follow the above re-tightening procedure by cooling the tubes prior to shipment and retightening the caps.

For further information on minimising artefacts, see Application Note 019.

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