Thermal Desorption Technical Support

Note 27: A review of sorbent-based sampling methods for volatile and semi-volatile organic compounds in air

Keywords

Air monitoring, sorbent tubes, sorbent traps, (S)VOCs, (semi-)volatile organic chemicals, thermal desorption

Abstract

Sorbent tubes/traps are widely used in combination with gas chromatographic (GC) analytical methods to monitor the vapour-phase fraction of organic compounds in air. Target compounds range in volatility from acetylene & freons to phthalates & PCBs, and include apolar, polar and reactive species. Airborne vapour concentrations will vary depending on the nature of the location, nearby pollution sources, weather conditions, *etc.* Levels can range from low percent concentrations in stack and vent emissions to low ppt in ultra-clean outdoor locations. Hundreds, even thousands, of different compounds may be present in any given atmosphere. GC is commonly used in combination with mass spectrometry (MS) detection especially for environmental monitoring or for screening uncharacterized workplace atmospheres.

Given the complexity and variability of organic vapours in air, no one sampling approach suits every monitoring scenario. A variety of different sampling strategies and sorbent media have been developed to address specific applications. Key sorbent-based examples include: active (pumped) sampling onto tubes packed with one or more sorbents held at ambient temperature; diffusive (passive) sampling onto sorbent tubes/cartridges; online sampling of air/gas streams into cooled sorbent traps and transfer of air samples from containers (canisters, Tedlar® bags, *etc.*) into cooled sorbent focusing traps.

Whichever sampling approach is selected, subsequent analysis almost always involves either solvent extraction or thermal desorption (TD) prior to GC(MS) analysis. The overall performance of the air monitoring method will depend heavily on appropriate selection of key sampling and analytical parameters.

This comprehensive review of air monitoring using sorbent tubes/traps is divided into 2 parts:

1. Sorbent-based air sampling methods
2. Sorbent selection and other aspects of optimizing sorbent-based air monitoring methods

The paper presents current state-of-the-art and recent developments in relevant areas such as sorbent research, sampler design, enhanced approaches to analytical quality assurance and on-tube derivatisation.

Part 1: Sorbent-based air monitoring options

Introduction

Airborne organic vapours range in volatility from methane to n-C_{20} & above and include most chemical groups - alcohols, ketones, aldehydes, esters, glycol ethers, chlorofluorocarbons, hydrogenated chlorofluorocarbons, other halogenated organics hydrocarbons, amines, sulphides, volatile fatty acids, mercaptans *etc.* The concentration of these vapours in air will vary depending on the source, ambient temperature, wind/air speed and type of location (indoor, outdoor, *etc.*). Levels can range from low percent in stack and fugitive emissions to low ppt in ultra-clean ambient locations such as the mid-Pacific or Arctic.

Moreover, as there is little toxicological data for many of the VOCs found in air and as the toxicity of compounds for which data does exist varies over 6 orders of magnitude, it is usually necessary to measure the concentration of each individual chemical. Overall or total VOC (TVOC) data – such as that generated by direct read-out detectors – does not give sufficient information to allow an accurate assessment of the potential health risks associated with a given atmosphere. In the case of individual organic components, only methane is quantitatively and routinely monitored using direct read-out detectors.

Given the complexity and variability of organic vapours in air, no one sampling approach suits every monitoring scenario. A variety of different sampling strategies have been developed to address specific applications with most options being based on some form of sorbent tube/trap. Key examples include pumped or diffusive (passive) sampling onto sorbent tubes and using sorbent focusing traps to selectively concentrate vapours from online air streams or whole-air containers (canisters/bags).

Once sampled, the best analytical technology for identifying and measuring individual compounds in the complex 'cocktail' of hundreds, even thousands, of organic chemicals present in air is gas chromatography (GC) combined with mass spectrometry (MS). There are two main options for extracting retained organics from sorbent tubes/traps and transferring them into the GC(MS) – namely thermal desorption (TD) and solvent extraction. Thermal desorption is a gas extraction process offering significant concentration enhancement and 100% transfer of desorbed analytes into the GC column if required. The TD process also lends itself to automation – be it online, or for the sequential analysis of canisters/bags *via* sorbent traps or the automated desorption of sorbent tubes. In contrast, solvent extraction methods are inherently more manual. They typically involve extraction/dilution of compounds in a few milliliters of solvent before 1 or 2 microlitres are injected into the GC/MS. Generally speaking, this translates to a 1000-fold reduction in sensitivity relative to TD.

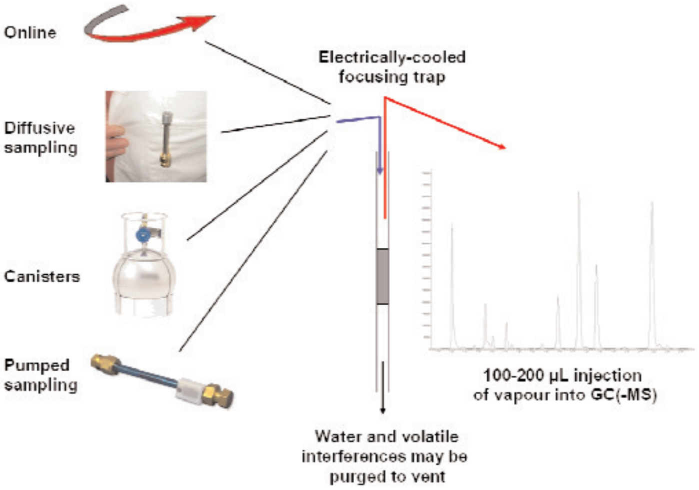


Figure 1: Schematic overview of the two-stage thermal desorption process for sorbent-based air sampling

The first stage of the thermal desorption process normally involves heating sampled sorbent tubes (or solid phase (micro-) extraction [SP(M)E] devices) in a reverse stream of carrier gas (That is, the flow of carrier gas through the tubes during desorption is in the opposite direction to the air flow during sampling.) Alternatively, a metered flow of whole air/gas can be drawn from a container or online manifold. In either case organic vapours are transferred from the primary sampling device (sorbent tube, air sample container or online manifold) and into a sorbent focusing trap maintained at near ambient or sub-ambient temperatures, typically using electrical (Peltier) cooling. Once all the compounds of interest have been transferred to the focusing device, and all unwanted volatiles (*e.g.* water) have been swept to vent, the focusing device is itself thermally desorbed in a reverse flow of inert 'carrier' gas. This final stage of thermal desorption is extremely fast (heating rates up to 100ºC/s are reported) causing target compounds to be transferred (injected) into the analyser in a tiny, concentrated 'slug' of vapour. Modern TD technology allows analytes to be transferred in as little as 100-300 µl total volume of carrier gas. It is this injection volume that ultimately determines the concentration enhancement factor and method sensitivity. An overview of the multi-stage 'thermal desorption' process is illustrated in figure 1 and comparative illustrations of sorbent tubes and focusing traps are shown in figure 2.

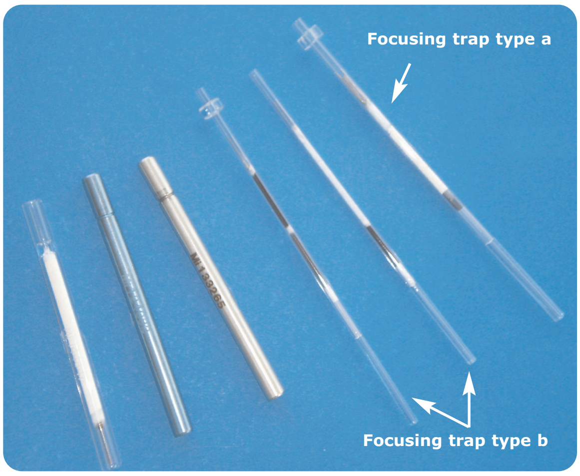


Figure 2: Sorbent tubes and quartz (electrically-cooled) focusing traps commonly used for TD. The tubes shown are of 'standard' dimensions: 89 mm (3.5 inch) long with 6.4 mm (¼ inch) or 6 mm O.D. constructed of glass, stainless steel and Silcosteel®. The larger 'type a' focusing trap has an I.D. of 2.8 mm and the smaller 'type b' focusing traps have a 2 mm I.D.

Note that none of the technologies described above can generally be applied to permanent gases such as the primary constituents of air, or species such as ozone and carbon monoxide (CO). Many such compounds require very specialist GC technology and it is difficult to envisage a selective adsorbent for inorganic gases that didn't get instantly saturated/ overwhelmed with air or carrier gas during the sampling or analytical process. The only inorganic gases that are known to be compatible with TD include N_2O, H_2S and SF_6, which can all be sampled onto sorbent tubes or traps under challenging, but nevertheless achievable, sampling and analytical conditions. See section on whole air sampling below.

Some other challenging components (*e.g.* ammonia) and species that are difficult to analyse by GC, such as formaldehyde and the chemical warfare (CW) agent Lewisite, are the subject of ongoing research into on-tube or pre-tube derivatisation. More information is given below.

Summary of sorbent-based air sampling options

The process of sampling airborne organic vapours using sorbent tubes/traps requires complete retention during sampling (no breakthrough or back-diffusion) and complete extraction/recovery during analysis. [Note: The term 'breakthrough' refers to an analyte passing completely through the sorbent bed and escaping from the far end of the tube during sampling. Back-diffusion refers to sorbed analytes going back into the vapour phase and creating a finite concentration of that analyte in the gas-phase near the surface of the sorbent.] Key examples of sorbent tube/trap based procedures include:

- Pumped (active) sampling onto tubes packed with one or more sorbents held at ambient temperature
- Diffusive (passive) sampling onto sorbent tubes/cartridges
- Whole air sampling methods
    - online sampling of air/gas streams into cooled sorbent traps *and*
    - transfer of air samples from containers (canisters, Tedlar® bags, *etc.*) into cooled sorbent focusing traps.

Each of these is described in more detail below.

Other sorbent-related air sampling technologies are available which rely on a partition or equilibrium system *e.g.* SP(M)E and/or some variations of conventional static headspace methods. Such procedures tend to be very limited in scope and are much less common. They are included in the discussion of alternative air monitoring methods at the end of this part of the paper.

Pumped (active) sampling onto sorbent tubes

While no single sampling method suits all air monitoring applications, pumped (actively sampled) sorbent tubes, as illustrated in Figure 3, perhaps provide the most versatile option.

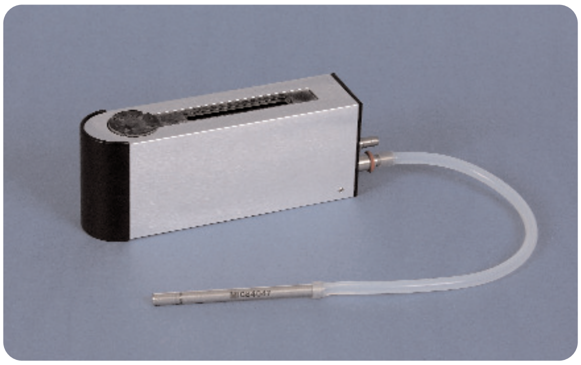


Figure 3: Pump attached to sorbent tube as used for air monitoring

Drawn glass tubes containing activated charcoal have been used for decades for monitoring relatively high concentration (ppm to low percent level) organic vapours in workplace atmospheres and industrial emissions. They are limited to solvent extraction, typically using CS_2, and are best suited to monitoring apolar compounds which transfer efficiently from the charcoal during desorption/extraction. Concerns relate to variable extraction efficiency [1], poor sensitivity (typically 0.1 ppm to 1 ppm detection limits), analytical interference (particularly when using MS detection) and, more latterly, environmental health and safety issues (the toxicity of CS_2, solvent disposal costs, *etc*.). Charcoal/solvent extraction tubes can be analysed using simpler systems (*e.g.* GC-FID with liquid injection) but are relatively labour intensive and are one-use only. Overall, these considerations are leading to a steady transfer of air monitoring methodologies from solvent extraction to thermal desorption.

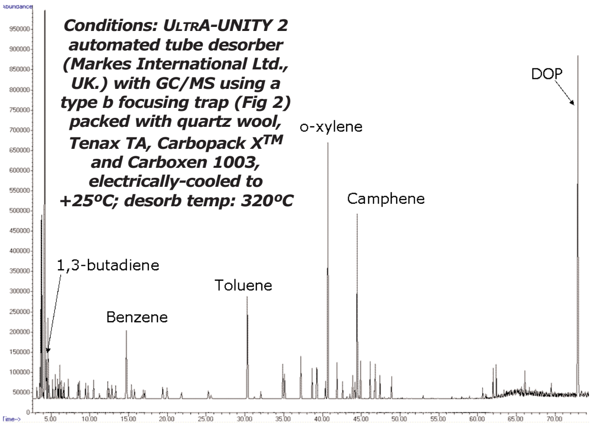
In response to this trend, the number of international standard methods specifying or including thermal desorption procedures has expanded rapidly over recent years. TD standards are now available to cover all relevant applications including monitoring ambient, indoor or workplace atmospheres plus industrial emissions (stack testing) [2-4].

The TD tubes described in most current standard methods are 3.5-inches (89 mm) long with an O.D. of ¼-inch (6.4 mm) **or** 6 mm with an I.D. of either 5 mm (stainless or inert-coated steel) or 4 mm (glass)*. They are re-usable at least 100 times. Most commercial analytical TD systems are compatible with tubes of these dimensions. The central 6 cm length of the tube may be packed with up to 3 (occasionally 4) discrete sorbent beds, arranged in order of increasing sorbent strength from the sampling end. The total sorbent mass typically ranges from 100 to 600 mg depending on sorbent type (density), tube ID and application (target analyte volatility range).

Note that some early air monitoring methods specified large, wide-bore tubes (*e.g.* 6 to 10 mm I.D.) and contained several grams of sorbent [5-7]. These methods were limited by high artifact levels and were also prone to significant error due to diffusive ingress. They have now largely been superseded. Appropriate sorbent selection (see part 2) allows tube sizes to be constrained within the range described in standard methods, while still offering complete retention of all but the most volatile organic compounds *e.g.* methane, C_2 hydrocarbons and the lightest freons. They also offer quantitative recovery of semi-volatiles such as phthalates, PCBs and semivolatiles up to n-C_{32+}. Use of multiple sorbents, in combination with backflush desorption, also facilitates simultaneous desorption/recovery of analytes over a wide range (Figure 4). (*N.B.* 'Backflush' desorption refers to the direction of carrier gas flow during desorption being the reverse of the air flow during sampling.)

More information on sorbent-sorbate interactions and what can effect them, is included in the detailed description of sorbents (see part 2), but retention volume, and the associated parameters of 'breakthrough volume' or 'safe-sampling volume', are most commonly used as measures of the affinity or strength of the interaction between an analyte and a given sorbent tube. The retention volumes of many organic compounds have been determined on various sorbent tubes over the years, typically at 20ºC, and much of this data are included in relevant standard methods

*Referred to as DAAMS tubes



Conditions: ULTRA-UNITY 2 automated tube desorber (Markes International Ltd., UK.) with GC/MS using a type b focusing trap (Fig 2) packed with quartz wool, Tenax TA, Carbopack X^{TM} and Carboxen 1003, electrically-cooled to +25ºC; desorb temp: 320ºC

Figure 4: Use of multiple sorbents coupled with backflush desorption of sample tube and focusing trap allows simultaneous analysis of components over a wide volatility range

[2, 3]. Usable values range from as little as 0.5 or 1 L for very volatile compounds such as n-propane, methylchloride or VCM up to several cubic meters at the other extreme. The ratio of the volume of air sampled to the volume of the band of vapour injected from the focusing trap into the GC column determines the concentration factor. For example, if the vapours from a 1 L sample of air were injected/transferred (splitless) to the head of the GC column in 100 µl of carrier gas, this would represent a concentration factor of 10^4. Similarly a 100 L volume air sample transferred in a 200 µl band of carrier gas would represent a concentration factor of 5×10^5.

If the ambient temperature retention volume of a given vapour is lower than 1 (or 0.5 L), even on sorbent tubes packed with the strongest carbonized molecular sieve sorbents, this would be a good indication that alternative whole air sampling methods should be used with sub-ambient sorbent focusing (see below). Examples of such compounds include C_2 hydrocarbons, H_2S and the most volatile freons and perfluorinated hydrocarbons.

Typically, active (pumped) sampling involves pulling a known volume of air through a sorbent tube at a constant 20-200 ml/min flow rate (optimum is 50 ml/min [8]). Lower flow rate limits are determined by the inherent rate of diffusive ingress (see below) and are typically around 10 ml/min. Upper limits are determined by gas-solid chromatographic principles *i.e.* the flow rate above which retention volumes begin to be compromised. For the standard 5 mm bore stainless or inert-coated stainless steel tubes described above, this typically means 200 ml/min although both short term monitoring (up to 15 minutes) and sampling of higher boiling compounds can be carried out at higher flows (*e.g.* 500 ml/min) without significantly affecting sorptive performance.

Simpler active sampling options are also available, *e.g.* for grab sampling of air/gas volumes up to a few hundred milliliters. Key applications for grab sampling include some industrial emissions (flue gas) measurements, landfill gases [9] and exhaled breath (*e.g.* for biological exposure monitoring [10]). Appropriate devices include bellows-type pumps or even large gas syringes, which can be coupled to the non-sampling end of tubes, allowing air to be pulled through the sorbent tube as the plunger is withdrawn.

In a recent innovation, pumped samplers have been developed to accommodate low flow pumped monitoring (0.5 to 1 ml/min) without interference from diffusive ingress. Such samplers incorporate diffusion limiting technology at each end reducing uptake rates to negligible levels, but without impacting sorbent masses or adding significantly to tube impedance. (See figure 5). Typical applications are reported to include validation of axial diffusive uptake rates (see below), monitoring very low level pollutants and active monitoring of time weighted average vapour concentrations using low flow pumps for extended periods (*e.g.* 7-14 days) [11, 12].

Many of the factors limiting the performance of TD-compatible pumped tube methods are related to sorbent selection and preparation. These aspects are covered in more detail in

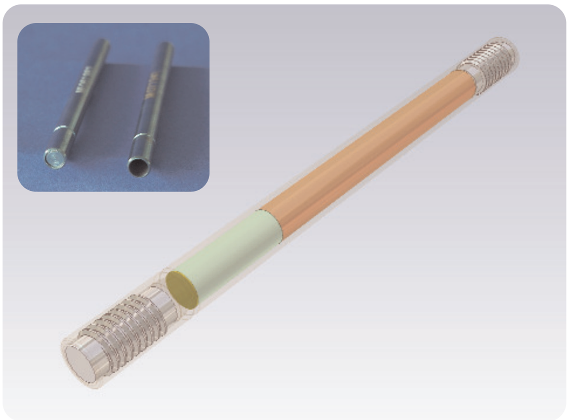


Figure 5: Schematic of stainless steel (or inert-coated stainless steel) 'SafeLok' tube with conventional external dimensions but incorporating diffusion locking technology at both ends to minimize artefact ingress and allow low flow sampling. Insert shows comparison with standard tube

part 2 of this paper. However, provided appropriate sorbent(s) are selected and other common-sense practical aspects are considered (*e.g.* maintenance of sample integrity during transport/storage and selective elimination of water, if required), pumped sorbent tubes can be used for quantitative monitoring of almost every GC-compatible organic vapour in air including very volatile, volatile and semi-volatile components and polar plus apolar species [13-15]. They are also uniquely suited to simultaneous monitoring of compounds covering a wide volatility range, *e.g.* vinyl chloride and naphthalene or 1,3-butadiene and phthalates. (See example in Figure 4.)

Note that standard stainless steel or inert-coated steel TD-tubes, which have a well-defined, fixed air gap between the end of the tube and the sorbent sampling surface, can also be used as axial diffusive (passive) samplers (see below).

Diffusive (passive) sampling

Historically, diffusive (passive) samplers comprised open-faced 'badges' or cartridges containing sorbents such as charcoal. The limitations of these devices in terms of surface air velocity (depletion and turbulence) and back-diffusion were quickly found to compromise and constrain their application [16]. More recently, diffusive sampling has evolved in two directions, i) radial samplers offering options for thermal desorption or solvent extraction or ii) axial diffusive samplers based on standard TD tubes and typically limited to TD-GC/MS analysis. Both of these options have overcome the limitations of earlier designs and now offer quantitative and repeatable air monitoring if used appropriately.

Diffusive sampling (axial and/or radial) is specified or included in a number of international standard methods for air monitoring [3, 17, 18].

Axial diffusive samplers: Developed in the late 1970s [19] axial diffusive samplers typically comprise ¼ inch O.D., 5 mm I.D. stainless steel or inert-coated steel TD tubes packed with a single sorbent and fitted with a cap containing a fine-mesh gauze which defines the sampling surface. The tubes have a fixed 15 mm air gap between the surface of the sorbent and the gauze in the cap at the sampling end of the tube. The other end of the tube is kept capped and sealed. Note that the tubes used for axial diffusive sampling are as used for conventional pumped (active) monitoring.

The mechanism of diffusive (passive) sampling is governed by Fick's law and the concentration gradient across some sort of barrier – in this case the 15 mm air gap. The diffusive (passive sampling) uptake rate is proportional to the sampling surface area (A) and inversely proportional to the length of the air gap (L) (see Figure 6). Once these dimensions have been fixed and provided the vapour concentration at the sorbent surface remains at or near zero, the diffusive (passive) sampling rate will be a constant function of atmospheric concentration. Typical 'uptake rates' are quoted at around 2 ng/ppm/min (or 2 pg/ppb/min) for standard axial diffusive tubes - which is equivalent to a pumped (active sampling) flow of between 0.5 and 1 ml/min. Standard sorbent tubes may be used in diffusive (passive) mode for both short term monitoring (1-8 hours) of ppm-level workplace atmospheres and for long term environmental monitoring (3 days to 4 weeks) of indoor or outdoor air [18, 20, 21].

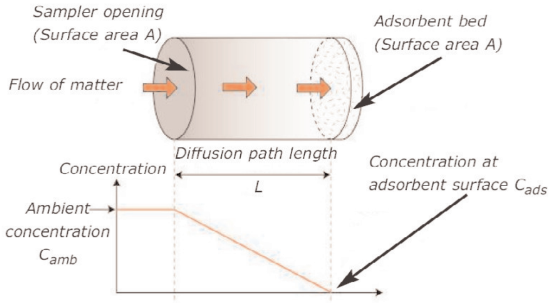


Figure 6: Schematic illustrating the principles of axial diffusive sampling according to Fick's law

As described in the original papers, axial diffusive tubes were designed with a relatively long, precisely-defined 15 mm diffusion (air) gap and narrow (5 mm) I.D. This minimised turbulence along the critical sampling 'gradient'. It also reduced uptake rates thus preventing vapour depletion at the sampling surface. These steps overcame the minimum/maximum air velocity considerations which had hampered earlier badge-type sampler designs and extended the time over which the uptake rate remained constant - *i.e.* delayed the onset of back diffusion. The uptake rates for many common solvents have already been well validated using these tubes [3, 17, 18] and many are relatively stable for 2 weeks or more. The stability of uptake rates on standard sorbent tubes is related to the strength of the sorbent-sorbate interaction and is a function of retention volume (see above) [22, 23]. An ideal sorbent, *i.e.* one that exhibits almost indefinite uptake rate stability, is typically found to exist for analytes having a retention volume in excess of 100 L on the given sorbent in a standard tube. Generally speaking, compounds compatible with axial diffusive (passive) sampling range in volatility from vinyl chloride (using a strong carbonised molecular sieve sorbent such as Unicarb™) to semi-volatiles such as n-C_{16} and above (using a weak sorbent such as Tenax® TA).

Diffusive sampling eliminates the expense and relative complexity of sampling pumps and facilitates large-scale air monitoring campaigns at affordable cost. It also provides a convenient and unobtrusive sampler for personal exposure monitoring *e.g.* for occupational hygiene or for human environmental exposure studies.

Radial diffusive samplers: Commercial radial diffusive samplers typically comprise a sorbent sampling cartridge housed in a porous polymer body which allows sampling along and around the whole cylindrical surface of the sampler (Figure 7). The porous polymer body is designed to slow/control uptake and minimize air velocity effects but radial samplers still sample the air at a rate equivalent to 30-50 ml/min pump flow, resulting in relatively rapid 'saturation' of the sorbent surface and early onset of back-diffusion. Radial samplers are therefore most suitable for short term, 0.5 to 6-hour, air monitoring at ambient/indoor (low ppb) levels and thus provide a useful complement to axial diffusive tubes. Back-diffusion effects are most pronounced for compounds more volatile than benzene. The porous polymer body can also become a sink for higher boiling species such as phthalates. Radial diffusive samplers are thus best suited to compounds ranging in volatility from benzene/n-C_6 to naphthalene/n-C_{10}.

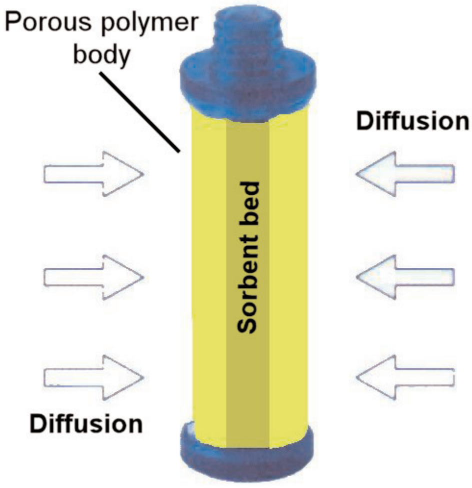


Figure 7: The Radiello® tube - an example of a radial diffusive sampler

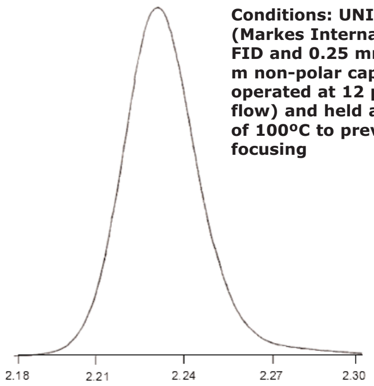
After sampling, the sorbent cartridge at the centre of the radial sampler is analysed using solvent extraction (charcoal versions). Alternative TD-compatible versions, typically packed with a graphitized carbon black sorbent, are transferred from their porous polymer housings into empty 'carrier' TD tubes for analysis by thermal desorption-GC(MS). The sampling cartridge is designed to be an impedance-fit within the carrier tube to ensure gas passes through the sorbent cartridge during desorption. TD-compatible sorbent cartridges may be reused for radial diffusive sampling as many times as a standard, sorbent-packed TD tube.

Whole-air sampling into sorbent focusing traps

Whole air monitoring methods provide a useful alternative to sorbent tubes particularly for ultra-volatile compounds such as acetylene, the lightest perfluorinated compounds and a few TD/GC-compatible permanent gases such as N_2O, H_2S and SF_6. Options include:

- continuous or discontinuous air/gas sampling into a cooled sorbent focusing trap with online analysis *or*
- preliminary sample collection in a suitable container (*e.g.* canister, Tedlar bag or glass sampling 'bomb'), with subsequent offline analysis *via* a cooled sorbent focusing trap and TD-GC(MS).

A fundamental limitation of whole air monitoring methods (on- or offline) is best explained with reference to figure 2. One of the primary functions of a focusing trap is to desorb quickly and release retained analytes as efficiently as possible and in as small as possible a volume of carrier gas. The analyte elution volume has a direct impact on concentration factor, peak shape & analytical sensitivity and, from this perspective, the smaller the trap the better. At the same time, the trap needs to have sufficient sorbent capacity to quantitatively retain even the most volatile components of interest without liquid cryogen coolant and be large enough to prevent ice completely blocking the flow path during the focusing of humid samples. The latest focusing trap technology (Figure 2) is typically packed with a total of 10 to 50 mg of sorbent and represents a compromise between these two requirements. Such traps are electrically-cooled and offer quantitative retention of acetylene from several hundred ml of air without liquid cryogen in combination with minimum desorption volumes; *e.g.* ~1 ml (minimum desorption flow: 5 ml/min) for trap 2a (2.8 mm I.D.) and ~100 µl (minimum desorption flow: 1.5 ml/min) for trap 2b (2 mm/1 mm I.D.) (figure 8).



Conditions: UNITY thermal desorber (Markes International Ltd) with GC-FID and 0.25 mm x 0.25 µm film x 30 m non-polar capillary column, operated at 12 psig (~1.5 ml/min flow) and held at an isothermal temp. of 100ºC to prevent on-column focusing

Figure 8: Unfocused benzene peak desorbed from focusing trap type b (Fig 2); 1.6 secs at half height

Practical sampling flow rates for these focusing traps range from 2 to 50 ml min or up to 100 ml/min for very short term sampling (<5 minutes). Methods involving direct transfer of on- or offline whole air samples to such focusing traps typically operate at 10 to 30 ml/min sampling flow rates with sampled volumes ranging from 100 ml to 1 L. These smaller sample volumes limit sensitivity relative to pumped (actively sampled) tube methods which allow tens or hundreds of litres of air to be sampled in some cases.

Generally speaking, focusing trap flow rate limitations don't constrain canister methods because they are already limited to 1 to 3 L usable air sample volume. However, they can impact online air monitoring and bag sampling. Theoretically it should be possible to employ multi-stage trapping for both online air monitoring or the analysis of large bag samples of air – In other words, to pass the air through a series of sub-ambient, sorbent traps of decreasing size – to concentrate ultra-volatile compounds from larger volumes (*e.g.* tens of litres) of air. However, this is rarely reported in practice. One difficulty is the need to efficiently and selectively remove water from high air flows *en route* to the larger sub-ambient trap(s) – a particular challenge if target analytes include ultra-volatile species such as those described above. If this issue is not adequately addressed in the initial focusing stage, any atmospheric humidity results in an increasingly concentrated band of water passing through the system as the multi-stage trap-adsorption/trap-desorption sequence proceeds. Inevitably, this results in the condensation of liquid water and/or catastrophic ice plug formation in one of the smaller sub-ambient traps – either of which can significantly compromise results. Water management is discussed in more detail in part 2 of this paper.

Online operation

Online air monitoring is primarily limited by the requirement for a complete analytical system at each monitoring location. It is useful for kinetic studies (monitoring changes in air pollution or odour profiles over time) and for near real time monitoring of dangerous chemical processes such as the destruction of chemical weapons or reactions involving dangerous intermediates like bischloromethyl ether.

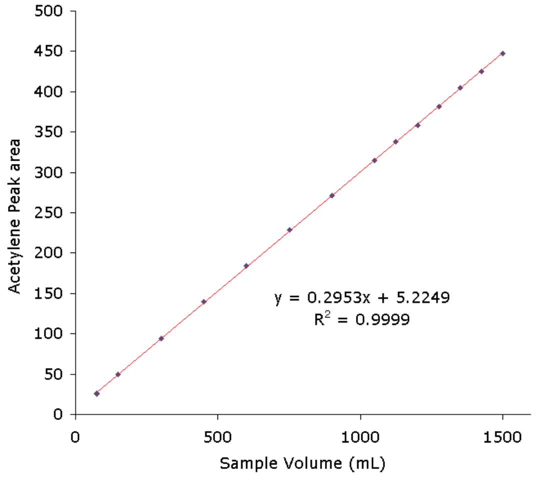
Key environmental applications for online air monitoring include measuring C_2 to C_{10} hydrocarbon 'ozone precursors' in urban air [24], continuous monitoring of landfill odour [25, 26] and tracking the concentration of trace perfluorinated hydrocarbons, which are potent greenhouse gases [27].

Generally speaking, online environmental air samples are drawn from an ambient temperature manifold directly into the sorbent focusing trap of the thermal desorber. Many different types of focusing trap are used. Some are fan-cooled, relying almost entirely on sorbent strength, but this precludes retention of the most volatile species such as acetylene and leaves trapping temperatures subject to variations in laboratory temperature. The continuous operation and field location of many online ambient air monitoring systems also normally precludes the use liquid cryogen - Refilling large dewars of liquid nitrogen every couple of days is not a practical option for most field stations. Moreover, even at liquid nitrogen temperatures, care still has to be taken and appropriate sorbents used to ensure against breakthrough of the lightest compounds and to prevent the heaviest components being lost through aerosol formation [28].

Alternatives, such as moderate electrical (Peltier) cooling of small focusing traps packed with a series of sorbents of increasing strength and desorbed in back flush mode are most commonly deployed nowadays and are described in relevant standard methods (see figure 2) [3, 29]. Such systems offer quantitative retention of ultra volatiles such as acetylene & CF_4 (figures 9 and 10) together with efficient/quantitative release of the least volatile components of interest such as hexachlorobutadiene and trimethyl benzene (figure 11). Continuous monitoring of higher boiling compounds, *e.g.* for industrial or 'demil' applications, requires uniformly heated manifolds and interface-tubing in order to minimize risk of condensation *en route* to the focusing trap.

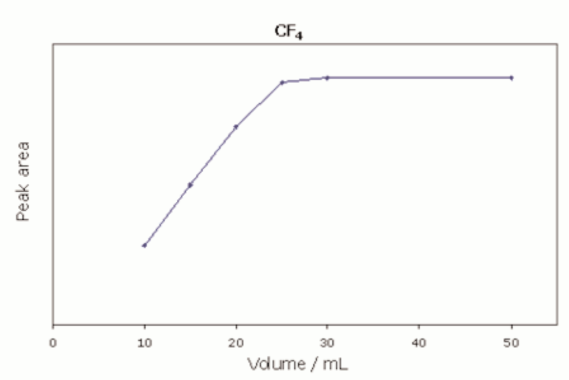
Sampling flows, volumes and times are typically controlled using appropriate electronic mass flow control hardware, pumps and system control software. At the end of the sampling time, the focusing trap heats rapidly to 'inject' the retained analytes into the analytical column. As soon as it re-cools, collection of the next air sample can begin. It is typically possible to sample for 45 to 50 minutes out of every hour depending on the efficiency of the Peltier cooling. Commercial systems normally allow automatic sequencing between a minimum of three channels (*i.e.* standard gas, zero air and one or more channels of sample air) at user defined intervals.

Systems incorporating twin, reciprocally-operated, electrically-cooled sorbent focusing traps have also been developed recently [30]. In this case, sampling is continuous – air is first sampled into trap A while trap B is desorbed and analysed. The sample stream is then redirected into trap B while trap A is desorbed and analysed. Typical applications include near real-time monitoring of very dangerous chemical processes. Counter-terrorism applications also include deployment in first responder vehicles and continuous monitoring of key government buildings.



Conditions: UNITY 2 - Air Server system for online air monitoring (Markes International Ltd, UK) with GC-FID and Gas-Pro column (Agilent Technologies); Focusing trap packed with: quartz wool, Carbograph 1 TD, Carboxen 1003 and Carbosieve SIII; Trapping temp.: -30ºC; Desorb temp.: 250ºC

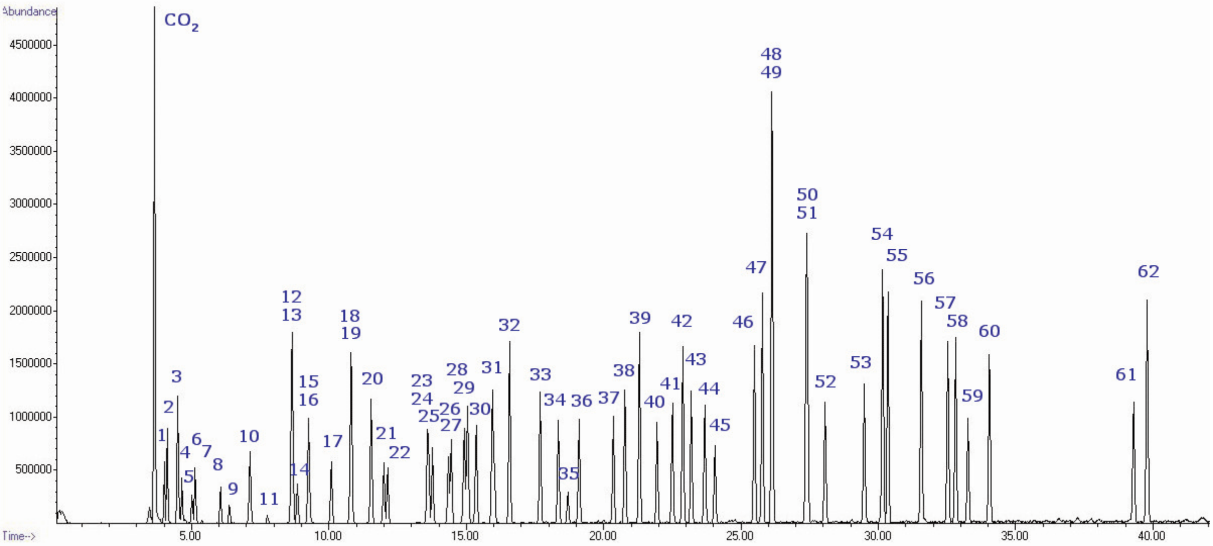
Figure 9: Quantitative retention of acetylene from up to 1.5 L of air without liquid cryogen



Conditions: UNITY 2–CIA 8 TD system for canisters (Markes International Ltd, UK) with GC/MS and Gas-Pro column (Agilent Technologies); Focusing trap packed with: Carbograph 1 TD and Carboxen 1003; Trapping temp.: -30ºC; Desorb temp.: 300ºC

Figure 10: Quantitative retention of CF_4 from up to 25 ml of air without liquid cryogen

Water management can be a major issue for online air monitoring and there are several options to consider. These are discussed in more detail in part 2 of this paper.



Conditions: UNITY 2–CIA 8 TD system for canisters (Markes International Ltd, UK) with GC/MS; Focusing trap packed with:Carbograph 1 TD and Carboxen 1003; Trapping temp.: +25ºC; Desorb temp.: 320ºC

Figure 11: 62 component 'air toxics' standard (1 L, 10 ppb) analysed splitless using the same thermal desorption and focusing trap technology as used for figure 10.

Offline air sampling using containers (canisters, Tedlar bags, etc.)

Unheated containers, such as passivated canisters or Tedlar bags, are appropriate for ultra-volatile chemicals such as C_2 hydrocarbons which are difficult to retain at ambient temperatures using sorbent tubes. Key applications for containers include trace-level, non-polar compounds such as freons and very volatile hydrocarbons - acetylene to toluene. Relevant standard methods include US EPA TO-14, US EPA TO-15 and ASTM D-5466 [31-33].

Evacuated canisters also provide one of the simplest of all air sampling options with 'grab' sample collection *via* release of a single valve. Alternatively, time weighted average (TWA) samples can be collected into clean, evacuated containers (canisters or bags) by sampling at a constant, controlled flow rate over time. This requires relatively complex apparatus, as specified in relevant international standards. (See Figure 12 based on recommendations in US EPA Method TO-14).

Simpler TWA sampling options for evacuated canisters include restricted orifices, which use pressure differential to drive the sampling flow. However, these are of limited utility for monitoring normal variable atmospheric concentrations because the sampling rate decreases over time as the canister fills and the pressure differential is reduced. This means that if the vapour concentrations vary significantly with time (*e.g.* by a factor of 2 or more), the levels in the collected air sample will depend on when the peak concentration occurred in relation to the sampling cycle. In other words, when sampling into canisters using a critical orifice, it is possible for two atmospheres with identical TWA concentrations

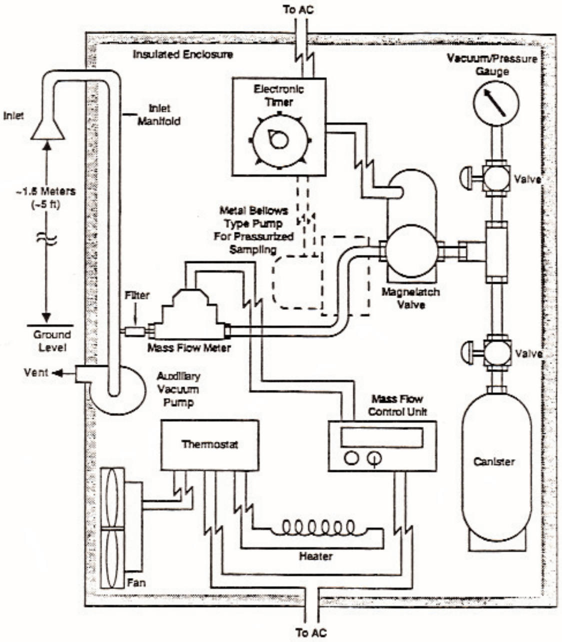


Figure 12: Sampler configuration for time weighted average canister sampling (Ref. 32)

to give completely different results. A higher result would be obtained if the concentration peaked early in the monitoring cycle when the sampling rate was fastest and a lower result would be obtained if the concentration peaked later, when the sampling rate was significantly slower. Unless there is an independent means of assessing how the various chemical concentrations vary with time (*i.e.* when the peaks and troughs occur) it isn't always possible to deduce whether samples collected in canisters using critical orifice/pressure differential are representative of actual time weighted average concentrations.

Once an air sample has been collected in a canister, bag or any other suitable container, it must be relied upon to be stable in the same way as a gas standard. That said, it is notoriously difficult to obtain stable static atmospheres, especially at low pressures/low concentrations, because of sink effects *i.e.* analyte interactions with the inner walls of the container including; adsorption, condensation, dissolution in condensed humidity, *etc*.

Tedlar bags are particularly prone to adsorption and absorption of compounds into the bag material and offer limited storage stability (<24 hours) for all but the most stable and volatile organic vapours [34, 35]. They are also prone to emission of volatile artifacts which may contaminate low level samples and compromise blank levels. Canisters are similarly prone to poor recovery of less volatile or more polar species [36, 37]. For example, compounds less volatile than n-$C_{9/10}$. This is illustrated in Figure 13. Furthermore, if significant concentrations of non-target higher boiling species are present, they can form a film covering the inner walls of the container. This can then act in the same way as stationary phase in a GC column and compromise the recovery of other more volatile target species. Similar issues can be caused by high humidity, particularly if significant condensation results in inner surfaces being coated with a film of liquid water or, worst case, if water is allowed to pool inside the canister. When this happens, organic compounds, particularly the more polar species, will partition between the aqueous and vapour phases, resulting in significant losses.

Tedlar bags are typically but not invariably one-use only. Canisters can be reused indefinitely but require stringent cleaning, involving repeated evacuation and purging, between uses. Cleaning is a major practical consideration for routine air sampling using canisters or other containers. Other practical aspects include the cost and size of canisters and the impact this can have on storage and transportation costs.

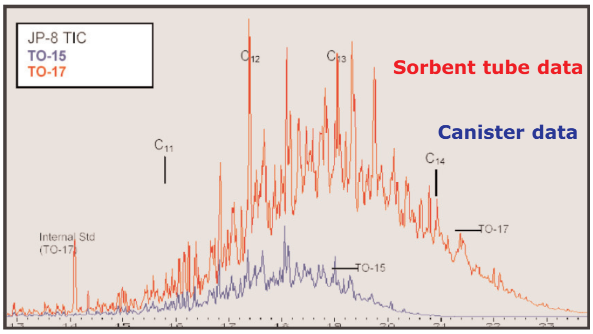


Figure 13: Sampling and analysis of soil gas contaminated with a jet fuel (JP-8). Comparison of data using canisters (TO-15) versus sorbent tubes. Reproduced from ref. 36 as an example

Some older canister methods (*e.g.* US EPA TO-14 [31]) described cryofocusing in capillary tubing or on glass wool/beads prior to GC/MS analysis. However, limitations with respect to water management and ease of use have led to these being largely superceded by methods specifying the type of small sorbent focusing trap described above (*e.g.* US EPA TO-15 [32]).

The use of whole air containers such as canisters, in combination with sorbent trapping/focusing is thus an extremely useful offline option for monitoring very volatile compounds which are difficult to retain quantitatively using sorbent tubes at ambient temperature. However, the limitations described above restrict their performance for polar compounds and species less volatile than n-C_8. Typical total canister volumes are in the range 0.4 to 6 L meaning 0.2 to 3 L usable air sample volume if the samples are unpressurised. The volume of air transferred from the canister to the focusing device is usually in the order of 100-600 ml allowing repeat analysis in most cases. However, as *per* discussion above, the relatively small volumes of sample air introduced to the sorbent trap ultimately limit potential concentration enhancement factors to around 10^3 or 10^4 best case.

A quick review of some alternative air sampling approaches

Solid phase (micro-)extraction (SP(M)E)

SP(M)E is normally used for screening lower volatility organics in aqueous samples but is also occasionally applied to qualitative screening of organic vapours [38].

SP(M)E is fundamentally different to sorbent trapping. Whereas the aim of solid sorbent sampling is complete selective retention of organic vapours from a flow of air gas, SP(M)E relies instead on organic components partitioning between a liquid- or gas-phase sample matrix and a thin layer of solid or liquid sorbent (stationary phase). Typically, the SP(M)E device comprises a fibre or small cylinder covered in a thin coating of sorbent and introduced directly into the liquid or gas phase sample. Analytes partition between the sample and sorbent coating until an equilibrium is reached. Provided analyte concentrations remain stable throughout sampling, then the analyte concentrations in the sorbent coating after equilibrium is reached will be constant and representative of the concentration of that compound in the sample. At the end of the sampling period, the SP(M)E device is removed from the sample, washed & dried (if necessary) and analysed using liquid extraction or thermal desorption in combination with GC(MS). (The relative advantages and limitations of thermal desorption and solvent extraction are described above.)

SP(M)E cannot be used for grab-sampling because the various equilibria take time to establish. It is also unsuitable for TWA monitoring of the variable vapour concentrations observed in most real atmospheres. Results might indicate much lower or higher levels than the true average due to the timing of significant concentration fluctuations during the monitoring period. Quantification can also be compromised by unpredictable competitive effects *e.g.* unusually high humidity or the presence of high transient concentrations of non-target organic analytes – solvents, *etc.* In short, SP(M)E should be regarded as a qualitative tool for all but the most stable atmospheres or for short term monitoring of higher boiling compounds in air.

The low quantities of solid or liquid sorbent (stationary phase) applied to most SP(M)E devices also significantly constrains sensitivity – particularly for compounds more volatile than naphthalene.

Equilibrium/static headspace

Equilibrium or static headspace (HS) is based on similar 'partitioning' principles to SP(M)E and is generally applied, with GC(MS), to measure volatile analytes in liquid or solid phase samples. Air monitoring applications for HS are limited to:

- screening materials for potential chemical emissions to air [39, 40]
- HS-GC(MS) analysis of sorbent transferred from air sampling tubes into HS vials.

Both of these approaches are fundamentally limited by the equilibrium/partitioning nature of static HS. In the former case, headspace concentrations at equilibrium do not correlate well with the range and rates of chemicals emitted from materials under dynamic real world conditions. In the latter case, multiple manual steps are generally required (including transfer of the sorbent from tube to vial and addition of displacement solvents) resulting in a complex, multi-phase sample with analytes partitioning between 3 phases; sorbent, solvent and headspace. Any significant sample-to-sample variation (sorbent batch, atmospheric humidity, organic profile/composition, *etc.*) can impact the partition coefficients unpredictably and thus introduce high measurement uncertainty. Equilibrium headspace also offers limited sensitivity for components higher boiling than n-$C_7/_8$ and limited compatibility with analytes covering a wide polarity range.

In summary it is very difficult to see how any sorbent tube or trap-based air monitoring application would be better served by manually transferring the sampled sorbent to a vial for analysis by static headspace, rather than automatically thermally desorbing the sorbent tube as normal.

Chemi-sorption and on-tube derivatisation

The process of chemi-sorption implies that the target analyte reacts when it comes into contact with the substrate forming a specific derivative that facilitates or enhances measurement. Common examples include colour indicator tubes (used extensively for workplace air quality screening) and the various monitors which use silica-gel substrates, impregnated with dinitrophenyl hydrazine to derivitise formaldehyde prior to analysis with HPLC and UV [41].

Other similar samplers deploy a pad or cartridge, impregnated with reagent, immediately upstream of the sorbent sampler. One example is the use of silver fluoride pads to convert the nerve agent VX to its more stable G analogue. Similar approaches are under development for the chemical warfare agent Lewisite and to convert formaldehyde into a GC(MS) compatible derivative [42]. This area of research has real potential and may extend to other difficult species over time *e.g.* ammonia.

Cryofocusing

Cryofocusing, in its broadest sense, covers many forms of cooled preconcentration device, including the types of sorbent trap described above. However, the term is most commonly applied to narrow open tubular devices (typically 0.3 to 2 mm I.D.), used empty or packed with a simple inert substrate (glass beads or quartz wool) and cooled using a liquid cryogen such as CO_2 or N_2.

Many early TD methods and systems incorporated this type of cryofocusing technology but the limitations described above (running costs, ice blockage, poor retention of ultra-volatiles and loss of higher boilers through aerosol formation) make it an impractical option, particularly for automated work.

Another practical limitation is that for historical reasons cryofocusing is conventionally configured with forward flow rather than backflush thermal desorption which generally limits the analyte volatility range that can be trapped and recovered quantitatively in a single run.

Concluding remarks

As a final note on this section of the paper, whole air monitoring methods (online or offline *via* canisters, bags, *etc.*) are often perceived as alternatives to sorbent-based air monitoring methods, but this is not usually the case. Given the inherent limitations of cryofocusing, most recent standards and regulatory guidance relating to whole air monitoring methods favour the use of one or more sorbent focusing traps held at ambient or moderately-cooled temperatures for subsequent analysis [24, 32]. Sorbent trapping has thus tended to become an integral part of both tube-based and whole air sampling methods, confirming the near universality of modern sorbent trapping technology for monitoring organic vapours in air.

Part 2 of this review will continue with a summary of sorbents and other practical considerations for optimizing air monitoring methods using sorbent tubes/traps. Technical developments and sampling accessories which have extended the application range of sorbent sampling, are also discussed.

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Part 2: Sorbent selection and other aspects of optimizing air monitoring methods

Part 1 of this paper reviewed the main sorbent-based air sampling strategies including active (pumped) tube monitoring, diffusive (passive) sampling onto sorbent tubes/cartridges plus sorbent trapping/focusing of whole-air samples that are either collected in containers (such as canisters or bags) or monitored online. Options for subsequent extraction and transfer to GC(MS) analysis were also summarised and the trend to thermal desorption (TD)-based methods and away from solvent extraction was explained

As a result of this trend, demand for TD-compatible sorbents (alternatives to traditional charcoal) is growing. Part 2 of this paper therefore continues with a summary of TD-compatible sorbents, their respective advantages and limitations and considerations for sorbent selection.

Other analytical considerations for optimizing sorbent-based air monitoring methods are also discussed together with recent technical developments and sampling accessories which have extended the application range of sorbent trapping technology generally

Introduction

For reasons explained in part 1 of this paper (sensitivity, automation, repeatability, *etc*.), thermal desorption (TD) methods are gradually superseding solvent extraction procedures for analysis of air samples collected on sorbent tubes/traps. Whole air monitoring (online or using containers) is already almost exclusively carried out using thermal desorption to extract the target organics from the sorbent focusing traps and transfer them to the GC(MS) analytical system. TD is also the method of choice for most ambient air monitoring and atmospheric research studies because of the 1000-fold sensitivity enhancement it offers when compared with solvent extraction. However, even higher level air monitoring applications such as routine industrial hygiene or fugitive emissions testing, are beginning to transfer to TD methods. The driver in this case isn't usually sensitivity but rather automation and the elimination of solvents such as CS_2 which present both a health & safety hazard to operators and interfere with the subsequent GC(MS) analysis.

It is important to point out that solvent extraction can be carried out using standard GC(MS) instrumentation and that it offers some advantages versus basic TD technology in that it allows repeat analysis – *e.g.* for confirmation of results or repeat analysis under different conditions. However, suitable manual and automated thermal desorbers are now available from multiple commercial sources and are usually compatible with any make of GC(MS). The latest TD technology also allows repeat analysis, overcoming the one-shot limitation of older systems (see below). Moreover, lower running costs versus solvent extraction usually mean that the additional capital investment required for TD is recovered relatively quickly.

One consequence of the trend away from charcoal/CS_2 and towards thermal desorption is the demand for TD-compatible alternative sorbents – Charcoal is too 'strong' and too active to allow reliable thermal desorption of all but the most volatile and stable organic compounds. A summary of the most common sorbents used for thermal desorption and the factors to consider when selecting which sorbent to use for a particular application, are reviewed below.

Selection of TD-compatible sorbents – Factors to consider

Sorbent-packed tubes and focusing traps that are compatible with thermal desorption, typically contain between 1 and 4 sorbents arranged in order of increasing sorbent strength from the sampling end. There are a range of factors to consider when selecting suitable sorbents or sorbent combinations including – the strength of the sorbent-sorbate interaction, artefacts, hydrophobicity, inertness and mechanical strength (friability) [43].

Sorbent 'strength' - Analytical sensitivity and precision are largely determined by sampling efficiency, desorption efficiency and the level of interferences (see section on artefacts below). The sorbent or sorbents selected must be sufficiently 'strong' to retain target analytes during sampling/concentration, but weak enough to release them efficiently during the thermal desorption phase. As described in part 1, sorbent strength is usually measured in terms of retention or breakthrough volumes. Standard air monitoring methods [2, 3] are a good source of validated retention and breakthrough volume information for a wide range of common sorbent/sorbate combinations and describe how these values can be determined experimentally. Such standards may also list 'Safe Sampling Volumes' (SSVs) – derived either by halving the chromatographically determined retention volume or by reducing the experimentally determined breakthrough volume by a factor of 2/3.

Reported retention volumes are susceptible to temperature and are typically quoted at 20ºC. As a (very) approximate rule, retention volumes halve for every 10ºC rise in temperature. The performance (retention characteristics) of strong sorbents such as carbonized molecular sieves are adversely affected by high relative humidity (>80%) as recorded in standard methods. The retention volumes of hydrophobic sorbents such as carbon blacks, Tenax® TA and other porous polymers are much less sensitive to atmospheric humidity with negligible impact reported even up to 90% RH. The competitive effect of other organic vapours is also reported as negligible at levels up to 100 ppm [8].

Flow rate has been shown to have a negligible impact on sorbent strength (*i.e.* analyte retention volumes) provided minimum and maximum rates are observed e.g. 10 to 200 ml/min for std 6.4 mm (¼-inch) O.D. stainless steel tubes with 5 mm I.D. (See part 1 of this paper for more information.)

It is important to select the appropriate sorbent or series of sorbents for the target analytes in question. If the selected sorbent is too weak (for example Tenax TA for n-pentane or acetone) there will be a temptation to use bigger tubes/traps and larger quantities of sorbent. Oversized tubes or traps can significantly compromise air monitoring methods. In the case of whole air sampling (*e.g.* online or canister/bag methods) the larger the cooled focusing trap, the longer it takes to desorb resulting in slower, less efficient transfer to the analytical system. This leads to broader peaks and a consequent reduction in sensitivity and resolution. Using larger masses of sorbent for pumped or diffusive air sampling tubes makes it difficult to get good blanks – Wide bore tubes (*e.g.* 6 to 10 mm I.D.) are notoriously difficult to condition stringently and are also more difficult to purge leading to increased risk of analyte and/or sorbent oxidation. If such tubes are packed with sorbent close to the sampling end, they are also prone to error due to high diffusive uptake.

Selection of sorbents of appropriate strength allows quantitative retention and release of compounds ranging from C_2 hydrocarbons and freons to semi-volatiles such as PCBs, phthalates and PAHs without exceeding optimized tube/trap dimensions and without requiring liquid cryogen coolant (see part 1 of this paper).

A wide range of weak, medium and strong commercial sorbents are now available for air monitoring (Table 1). Generally speaking, vapour-phase organics should be sampled using the weakest compatible sorbent, *i.e.* one that offers a practical/useful retention volume and quick, quantitative recovery during desorption and analysis.

Inertness - Some sorbents contain chemically active materials. This is especially true of carbon blacks, many of which derive originally from natural charcoals and contain trace metals. These sorbents are therefore generally unsuitable for labile (reactive) species - sulphur compounds, terpenes, amines, *etc.*

Hydrophobicity - Most common weak and medium strength sorbents are very hydrophobic, thus their sorbent strength is not compromised even when sampling at high (>80%) relative humidity. However, most strong sorbents comprise some form of carbonised molecular sieve and, in this case, sorbent strength can be reduced by as much as a factor of 10 at 90% RH [8]. If a large amount of water is retained on the tube and not selectively eliminated prior to analysis, this too can adversely affect results. Water management options for sorbent based air monitoring are discussed in more detail below.

Artefacts - Sorbents vary significantly with respect to inherent artefact levels. Some porous polymers such as the Chromosorb® Century series, PoraPak™ and HayeSep™ series sorbents have relatively high artefacts with

Sorbent	Strength	Max. temp.	Features
Quartz wool	Very weak	>450°C	Very inert, non-water retentive
Carbograph 2TD Carbopack C Carbotrap C	Weak	>450°C	Hydrophobic Minimal (<0.1 ng) artefacts Friable. 40/60 mesh recommended to minimise back pressure
Tenax TA	Weak	350°C	Hydrophobic Low inherent artefacts (<1 ng). Inert - suitable for labile components
Carbograph 1TD Carbograph B Carbotrap	Weak/Medium	>450°C	Hydrophobic Minimal (<0.1 ng) artefacts Friable. 40/60 mesh recommended to minimise back pressure
Chromosorb 102	Medium	225°C	Hydrophobic High inherent artefact levels (~10-50 ng/component) Inert - suitable for labile components
PoraPak Q	Medium	250°C	Hydrophobic High inherent artefact levels (~10-50 ng/component) Inert - suitable for labile components
Chromosorb 106	Medium	225°C	Hydrophobic High inherent artefact levels (~10-50 ng/component) Inert - suitable for labile components
PoraPak N	Medium	180°C	Hydrophobic High inherent artefact levels (~10-50 ng/component) Inert - suitable for labile components
HayeSep D	Medium	290°C	Hydrophobic High inherent artefact levels (~10-50 ng/component) Inert - suitable for labile components
Carbograph 5TD	Medium/Strong	>450°C	Hydrophobic Minimal (<0.1 ng) artefacts Friable. 40/60 mesh recommended to minimise back pressure
Carbopack X	Medium/Strong	>450°C	Hydrophobic Minimal (<0.1 ng) artefacts Friable. 40/60 mesh recommended to minimise back pressure
Carboxen 569	Strong	>450°C	Minimal (< 0.1 ng) artefacts Inert - suitable for labile compounds. Less hydrophilic than most carbonised molecular sieves
UniCarb	Strong	>450°C	Inert; not hydrophobic Individual artefacts below 0.1 ng Must be conditioned slowly Requires extensive purge to remove permanent gases
Carboxen 1003	Very strong	>450°C	Inert; not hydrophobic; Individual artefacts below 0.1 ng; Must be conditioned slowly Requires extensive purge to remove permanent gases
Carbosieve SIII	Very strong	>450°C	Minimal (<0.1 ng) artefacts Inert - suitable for labile compounds. Significantly water retentive – don't use in humid conditions
Molecular Sieve 5Å	Very strong	>400°C	High (~10 ng) artefacts Significantly hydrophilic - do not use in humid conditions
Molecular Sieve 13X	Very strong	>400°C	High (~10 ng) artefacts Significantly hydrophilic - do not use in humid conditions

Table 1: Commonly used TD-compatible sorbents and their main features

several peaks at 5-10 ng levels per tube. The porous polymer Tenax TA is better with minimum tube artefact levels between 0.1 and 1 ng for well conditioned materials. Both carbon blacks and carbonised molecular sieves, are excellent with respect to inherent artefacts - with individual artefact levels between 0.01 and 0.1 ng if the tube is well conditioned. However, carbonised molecular sieves require extended conditioning at steadily increasing temperatures and can continue to show a high background of inorganic gases for several days when new. They may also become irreversibly contaminated if allowed to come into contact with compounds higher boiling than xylenes (C_8).
Porous polymeric sorbents may form trace artefacts when sampling air containing significant concentrations of reactive gases such as ozone. This effect has been reported for Tenax TA which generates trace artifacts including benzaldehyde and acetophenone if ozone concentrations exceed 100 ppb [44].

Temperature stability - Most sorbents, including the porous polymer Tenax TA, are stable up to 350°C and many of the carbon sorbents can be taken to temperatures above 400ºC. However, care must be taken with other porous polymer sorbents – Chromosorbs, HayeSeps and PoraPaks - which typically have temperature limits at or below 225°C

Mechanical strength – Graphitised carbon blacks are extremely friable and prone to the formation of fines. Care should be taken not to over compress these sorbents during tube packing and to avoid sharp knocks once the tubes are packed. As the carbon packing ages, the formation of fines may increase tube impedance (back pressure) beyond the limit of some pumps. Most other sorbents are mechanically strong, although Tenax TA can have a high percentage of fines when new and may require sieving before use. Generally speaking, recommended mesh sizes for sorbents in standard 4-5 mm bore sampling tubes range from 30 to 80 mesh (approximately 0.6 to 0.2 mm particle diameter).

Mesh size – Within the 30 to 80 mesh range specified above, sorbent particle size does not play a critical role in sorbent selection because analyte retention volumes will remain constant as the particle size increases up to a limit of 5 particles across the diameter of the sorbent tube/trap. [45]

Sorbent developments

The earliest sorbent-based air monitoring studies were carried out using charcoal with subsequent solvent (CS_2) extraction (see Part 1 of this paper). However, as the advantages of thermal desorption became more widely understood, use of charcoal declined. The strength, hydrophilicity and reactivity of natural charcoal simply make it incompatible with thermal desorption for all but the most volatile and stable organic components. Early TD-based air monitoring methods instead relied heavily on the porous polymers – Tenax TA and other common gas-solid chromatographic media such as the Chromosorb Century series and PoraPak Q, N, *etc.* Over time, it became clear that additional sorbent options were required because Tenax was too weak to be ideal for polar solvents and species more volatile than n-hexane. The inherently high artefact levels and temperature limitations of the other porous polymers also restricted their application e.g. for trace level monitoring and/or for use in combination with other sorbents.

Graphitised carbon blacks were developed by Italian scientists in the late 1970s [46] and were introduced commercially at roughly the same time as the first carbonized molecular sieves (CMSs). CMS-type sorbents were introduced as highly sorptive (retentive) alternatives to charcoal for trapping very volatile compounds but with reduced hydrophilicity. Both these new sorbent groups were compatible with high temperatures and had low inherent artifact levels. Their introduction enabled multi-sorbent tube combinations to be used widely and effectively for the first time allowing compounds ranging in volatility from vinyl chloride to n-hexadecane to be monitored simultaneously [29, 36, 47, 48].

Work on improving sorbent strength for organic vapours while at the same time minimizing water retention continues in both the US and Europe and has led to the introduction of new stronger carbon blacks (*e.g.* Carbopack™ X and Carbograph™ 5 TD) over recent years. This new generation of sorbent materials offers quantitative retention of compounds as volatile as 1,3-butadiene while still remaining largely hydrophobic [49].

A summary of the sorbents most commonly used for air monitoring today is listed in Table 1.

Ongoing sorbent research revolves around different technologies such as nano-particles [50], molecularly imprinted polymers (which can be used to selectively trap large molecules according to their shape [51]) and sorbents impregnated with derivatising agents [42] to selectively retain or stabilise very specific analytes. However, none of these new types of material have yet been demonstrated to offer sufficiently robust and repeatable performance characteristics for widespread application. More research is required in each case.

Multi sorbent tubes

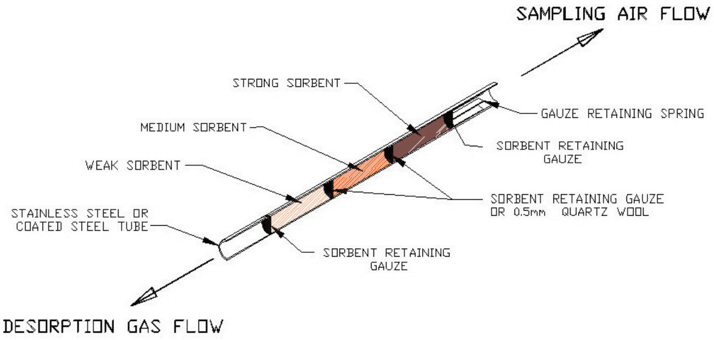

Figure 14. A multi-sorbent tube

If a wide volatility range of compounds is to be monitored, it is often necessary to pack a tube with more than one sorbent material, arranged in order of increasing strength from the sampling end (Figure 14; see also Part 1 of this paper.) Note that in the case of multi-sorbent tubes and traps, it is even more critical than normal to use backflush desorption, *i.e.* the flow of gas through the tube/trap during desorption must be the reverse of the air/gas flow during sampling. Higher boiling analytes are thus retained by and desorbed from the weaker front sorbent(s) without coming into contact with the stronger sorbents behind.

Key issues to consider in relation to sorbent selection for multi-sorbent tubes include:

- The volatility range of target compounds and quantitative retention and efficient desorption of each
- Sorbent compatibility – The temperature required for conditioning the most thermally stable sorbent must not exceed the maximum temperature limit of any other sorbent in the tube.
- Stability during storage. Loosely bound analytes can migrate from weak to strong sorbents within a multi-sorbent tube during storage. In severe cases this can lead to irreversible adsorption and incomplete recovery during subsequent analysis. Some specific sorbent combinations are more prone to this – for example; a short bed of weak sorbent (*e.g.* Carbopack™ C or Tenax TA), backed up directly by a very strong sorbent such as a carbon molecular sieve. Migration can be reduced by extending the bed length of weaker sorbents or inserting a medium strength sorbent between the weak and strong sorbents. Sampled multi-sorbent tubes should also be stored under refrigerated conditions and analyzed quickly – Most standard methods recommend a maximum storage time of 30 days. Furthermore, care must be taken, particularly with multi-sorbent tubes, to make sure the rear sorbent does not extend beyond the heated zone of the thermal desorption oven or this too could compromise recovery.
- Minimising water retention by avoiding water retentive sorbents wherever practicable (see below)

Provided these issues are taken into consideration when selecting the sorbents, active sampling onto multi-sorbent tubes is a relatively straightforward procedure and offers quantitative retention and recovery of analytes over a uniquely wide volatility range [52]. Common sorbent combinations for sampling tubes are as follows:

'Universal' tubes - There is, of course, no such thing as a universal tube. However, perhaps the most broadly applicable combination of sorbents that can be packed into a single tube for pumped monitoring of uncharacterised atmospheres is Tenax TA backed up by a medium strength graphitized carbon black (*e.g.* Carbopack B or Carbograph™ 1 TD) backed up in turn by a carbonized molecular sieve (*e.g.* UniCarb™ or Carboxen™ 1003) (Figure 14). Standard-sized tubes packed with equal bed lengths of each of these sorbents offer quantitative retention and release of compounds ranging in volatility from C_3 hydrocarbons to n-C_{26}.

One limitation of this sorbent combination is that the middle strength carbon black sorbent is not completely inert and may cause degradation of labile analytes such as nitrogen- or sulphur-containing compounds and monoterpenes. The rear, 'strong' sorbent is also a carbon molecular sieve and prone to water retention requiring a dry purge or some other water management step if used to monitor humid atmospheres (see below).

Hydrophobic tubes – Another useful combination of sorbents is a short (~5 mm) bed of clean quartz wool, backed up by Tenax TA, backed up again by Carbopack X or Carbograph 5 TD with the bed lengths of Tenax : carbon being roughly in the proportion 3 or 3.5 : 2. This combination of sorbents is hydrophobic and offers quantitative retention and release of analytes ranging in volatility from 1,3-butadiene to n-C_{32} and above. Relevant application examples include soil gas monitoring (*e.g.* for studies of vapour intrusion into buildings) and monitoring wide boiling range emissions from construction products and other materials.

Tubes used for US EPA-defined 'air toxics' [29] are typically packed with a medium strength carbon black such as Carbopack B or Carbograph 1 TD backed up by a carbon molecular sieve such as Carboxen 1003 in the bed length proportion 2 : 1 or 1 : 1. Such 'air toxics' tubes offer quantitative retention of ethane from small volumes of air combined with efficient release of compounds up to n-$C_{12/14}$.

If odorous and/or reactive compounds are of interest the ideal starting point for monitoring uncharacterized atmospheres is to sample using several replicates of two slightly different sampling trains in parallel. The two types of sampling train should each comprise three inert-coated steel tubes packed with single sorbents, connected together in series using inert, non-emitting fittings. The first would use a totally inert combination of sorbents for example; the front tube packed with Tenax TA, the middle one packed with a stronger porous polymer such as Chromosorb 106 and the third tube packed with UniCarb or Carboxen 1003. The second sampling train would be similar but with an alternative carbon black, medium-strength sorbent used in the middle tube. Subsequent analysis of each of the separate sorbent tubes used in both types of sampling train would highlight any analyte losses caused by use of a carbon rather than porous polymer medium-strength sorbent and would also help identify the optimum combination of sorbents for subsequent monitoring of the same area using single tubes packed with multiple sorbents.

Note that multi-sorbent tubes/traps are only really applicable to active sampling, *i.e.* pumped tubes, canister sampling or online air monitoring. In diffusive sampling, only the sorbent at the front (sampling) surface is significant. Other sorbents may be present further back in the tube, but they generally play little or no role in the sampling process.

Note also that the guidance given in Table 1 relates to sorbent air sampling tubes, pumped or diffusive (see Part 1 of this paper). However, similar considerations impact sorbent selection for the cooled sorbent focusing traps, both as deployed for whole air samples (online monitoring or canister/bag analysis) and as required for refocusing analytes during tube desorption.

Other practical factors to consider for sorbent-based air sampling

Trap/tube materials – Sorbent tubes/traps should be constructed of inert, non-outgassing and thermally-stable materials.

Focusing traps are typically constructed of quartz because it is almost perfectly inert and is a good thermal conductor thus facilitating rapid heating and cooling.

Glass or quartz materials can also be used for sorbent air monitoring tubes, however, they are prone to breakage and aren't generally suitable for diffusive (passive) monitoring (See Part 1 of this paper.) Stainless steel-based tubes are a more robust and versatile option for most field monitoring exercises and inert coated versions (*e.g.* Silcosteel®) provide an inert and robust option for reactive compounds.

Sorbent retaining materials – Sorbents are typically held in place using fine mesh stainless steel or Silcosteel gauzes (stainless steel tubes) or glass restrictions and/or plugs of inert quartz or glass wool (glass tubes.) The steel sorbent retaining gauzes can be very precisely and reproducibly located in metal tubes (see Figure 14) facilitating the required level of precision for diffusive (passive) sampling and the interchange of uptake rate information *e.g.* in standard methods [3, 17, 18].

Preparation of sorbent tubes/traps - Sorbents invariably require stringent conditioning at high temperatures in a flow of inert gas to clean them before use. Some of the older porous polymer-type sorbents also require preconditioning, before being used to pack tubes, because as much as 10-15% of sorbent mass may be lost during the first conditioning cycle. It is rare for any form of solvent washing to be required, but temperature and flow conditions used for tube cleaning should invariably be more stringent than those to be used subsequently for analytical thermal desorption. More information on this important issue is given in the literature [53].

Storage of conditioned and sampled sorbent tubes - Conditioned and sampled tubes should be stored using long-term ¼-inch screw caps fitted with combined PTFE ferrules as described in standard methods [2, 3, 13]. Sampled, single sorbent tubes capped and stored in this way are reported to be stable for up to 27 months [54] at room temperature provided the compounds concerned are not chemically active. Multi-sorbent tubes should be analysed more quickly (within 30 days) to minimize risk of analyte migration within the tube (see above.)

Water management

GC(MS) technology is notoriously sensitive to water interference. Adverse effects include baseline anomalies and unpredictable quenching of the detector response (signal) for compounds which co-elute with the water. High water levels can also reduce the working life of key system components such as capillary columns and MS detectors.

Sorbent tubes (pumped or diffusive) offer many water management options. Wherever possible, the most effective of these is to avoid collecting water in the first place by using hydrophobic sorbents in the sampling tube. (Note that sorbent tubes must never be colder than the sampled air/gas to prevent water condensation within the tube.) The vast majority of vapour phase organics can be quantitatively retained from reasonable volumes of air without resorting to the less-hydrophobic CMS type materials. Compounds as volatile as 1,3-butadiene (boiling point: -4.4ºC) can be quantitatively retained using Carbograph 5 TD or Carbopack X [49, 55].

However, if the compounds of interest include even more volatiles species, such as vinyl chloride or Freon® 113, it will be necessary to include at least a short bed of strong carbon molecular sieve at the rear (non-sampling) end of the tube. Such sorbents are prone to some water retention and water management measures will be required particularly when such tubes are used to sample humid atmospheres. The main options in this case are use of sample splitting (convenient when monitoring high level air contaminants such as work place atmospheres or stack or landfill emissions) or dry purging.

With respect to sample splitting: If the mass of target analytes collected is such that a split ratio of 50:1 or more can be set without compromising detection limits for the lowest concentration of interest, then it is unlikely that any additional water management step will be required. The sample split should be used in two stages for optimum effect *i.e.* during both primary (tube) desorption and secondary (trap) desorption.

Dry purging involves passing a flow of pure dry air or nitrogen through the tube and/or focusing trap in the sampling direction prior to desorption. CMS sorbents have more affinity for organic molecules (even highly polar compounds like light alcohols) than water. This allows dry purge conditions (temperature, dry gas flow and time) to be set such that water is selectively purged to vent without loss of the most volatile/polar compounds of interest [56, 57]. It is most effective to implement dry purging in 2 steps *i.e.* for both the sample tube and focusing trap. Both steps can be automated on most modern commercial TD systems.

It is also important to selectively eliminate water from whole air samples (online or containers) before they are transferred from the focusing device to the analytical system. This is carried out in one of two ways depending on the nature of the application. In the first option, very volatile, non-polar compounds are compatible with in-line permeable membrane dryers such as the Nafion® dryer. Such dryers eliminate water and polar organic compounds from the air or gas sample stream before it reaches the focusing trap. This elimination of polar VOCs can simplify online air monitoring applications which rely on conventional FID detection instead of MS. A key example is monitoring ppb level 'ozone precursors' (C_2 to C_{10} hydrocarbons) in urban air.

If the lightest compounds such as C_2 hydrocarbons or the most volatile freons are not of interest, it is alternatively possible to selectively dry purge water from the focusing device, as described above, whilst retaining the compounds of interest. In this case trapping temperature, sorbents and sampling flow are all selected to minimize water retention while still ensuring quantitative recovery of the compounds of interest. A focusing-trap dry purge step (see above) is also implemented between sampling and trap desorption/analysis. In this case, no inline dryer is required and polar compounds can be measured.

Optimisation of desorption and other analytical parameters

As discussed above, thermal desorption is rapidly displacing solvent extraction as the method of choice for air monitoring generally. Relevant TD applications include ambient air monitoring, indoor (and in-vehicle) air quality assessment, monitoring personal exposure at work (occupational/industrial hygiene), industrial emissions (stack, vent, fugitive emissions), factory fence-line monitoring, landfill gases, odour monitoring and atmospheric/pollution research.

Advice on optimising and validating the thermal desorption and GC(MS) analysis process has been presented in the literature [43] and is outlined in many of the international standard methods cited in this paper. As specified in these standards; key requirements for successful TD-GC(MS) analysis of the organic vapours retained on sorbent tubes and traps include:

- Reliable sealing of tubes before and after analysis (automated systems)
- Automated and stringent leak testing
- Pre-purge of oxygen to vent (in desorption direction) to prevent sorbent or analyte oxidation
- Optional internal standard addition (in sampling direction)
- Optional dry purge (in sampling direction)
- Complete primary (tube) desorption (if applicable) *i.e.* >99% extraction efficiency
- Quantitative (re)focusing of analytes using a cryogen-free sorbent trap
- Fast secondary (trap) desorption with >99% extraction efficiency and rapid transfer/injection of desorbed analytes into the GC(MS) analyser

The linearity of thermal desorption - GC(MS) methods should be the same as can be achieved using GC(MS) systems configured with conventional liquid inlets. The precision of TD methods is typically limited to 1-2% by the manual introduction of external gas or liquid phase standards to sorbent tubes during calibration. However, this is insignificant relative to the overall variability air monitoring methods, typically quoted at 15-30%.

Uncertainty and analytical quality assurance

All air monitoring methods are multi-step processes resulting in relatively high uncertainty. Variability can creep in at every stage – during sample collection, during transport/storage, *via* contamination, because of sorptive losses (sink effects) in the sampler (particularly in canisters or bags), during the TD-GC/MS calibration process and during desorption & analysis.

Solvent extraction based air monitoring methods are also prone to specific and significant additional limitations. These include variable recovery, low sensitivity, analytical interference by the solvent and the number of manual steps required (see Part 1 of this paper).

Thermal desorption-based air monitoring methods were also historically prone to some limitations including limited facilities for internal standard introduction and the inherent 'one shot' nature of the technique which could make it difficult to repeat and confirm results. As early as 1981 tube desorption (TD) systems began to be introduced which addressed the 'one-shot' limitation to some extent by stringently leak testing every sample prior to analysis to minimize risk of error. Essentially TD requires the carrier gas flow path to be broken into each time a new tube is analysed and desorbed. Risk of undetected leaks would bring all TD-GC/MS data into question especially if sample analyses could not be repeated. This is why leak testing is specified as a mandatory requirement in standard TD methods.

As TD technology improved over the years, facilities for automatic introduction of gas-phase internal standards (IS), first onto the rear of sorbent tubes and then onto the sampling end became widely available. Some systems now even offer the ability to load internal standard onto blank as well as sampled tubes allowing pre-spiked sorbent tubes to be used for field monitoring exercises as a check on the entire process - tube transport, storage, field sampling and TD-GC/MS analysis. IS addition is also a standard feature of most automated thermal desorption systems for canisters, bags or online air/gas streams.

Another more recent innovation was the ability to quantitatively re-collect any primary (tube) or secondary (trap) desorption split flow into a single conditioned sorbent tube for repeat analysis. This overcomes the one shot limitation of traditional TD systems, but more importantly provides a convenient means of validating analyte recovery through the thermal desorber. Whereas the earliest standard methods for TD specified validation of recovery by comparing the TD calibration curve with that for a conventional liquid injection under the same conditions, re-collection allows a sequence of repeat analyses to be carried out on a single sample (see Figures 15a and b). Any loss of one or more analytes can be readily identified from the relative responses to other compounds in the mix or by a deviation in the result from that predicted from the split ratio.

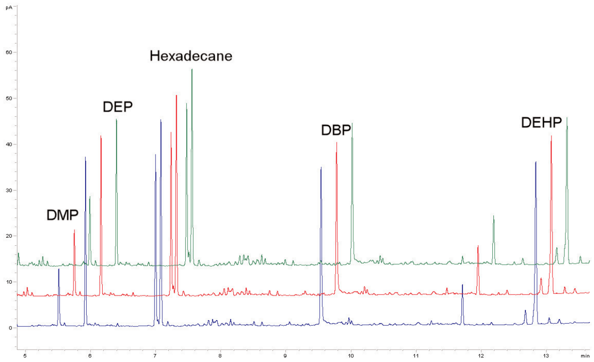

Figure 15a: Sequence of chromatograms showing re-analysis of re-collected phthalate mixture using an automated ULTRA 50:50™ thermal desorber from Markes International Ltd, UK

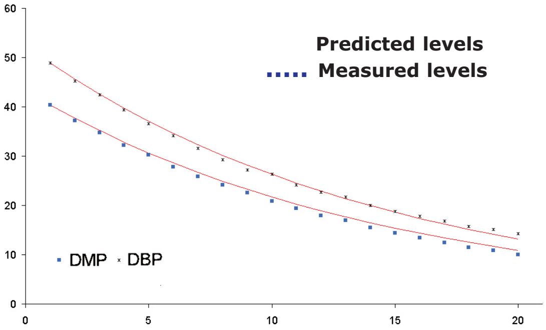

Figure 15b: Plot showing the theoretical and measured peak areas for repeated re-collection and re-desorption of the sample shown in Figure 15a

This approach has now been adopted into some of the most recent thermal desorption standards [3].

Electronic labeling has recently been introduced for sorbent tubes (Figure 16) and other air samplers (canisters, bags, *etc*.), which make it much easier to track the history and performance of individual samplers. The development is based on RFID technology encapsulated in TD-compatible tags which can be attached to the tubes (or canisters). The tags can be used to record field/sample data (dates, sampling start/end times, sampled volumes, pressures, flows, *etc.*), project information and, most importantly, information on the history of the sampler itself – sorbents, packing dates, number of thermal cycles, *etc.* The tags can be used for specific projects – only remaining attached to a given sampler throughout a field monitoring exercise before being removed and redeployed elsewhere. Alternatively (and more commonly) tags are attached to a particular sorbent tube

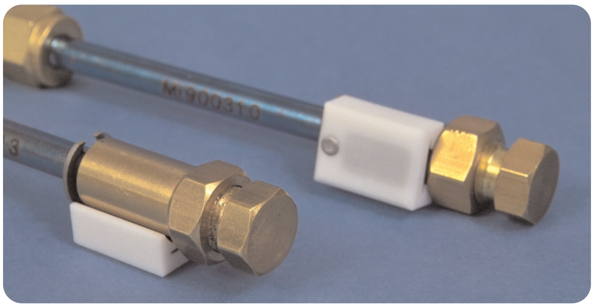

Figure 16: RFID tags attached to thermal desorption sorbent tubes

throughout its life offering users ready confirmation of the sorbents inside and a much improved means of monitoring the performance and validity of that sampler as it ages. Depending on how the technology is implemented on the TD-GC(MS) system key details such as back pressure, number of leak test failures, number of thermal cycles and even artefact levels can be stored and tracked on the tag itself and/or in an associated database thus greatly improving quality assurance [58].

Extending the application range for sorbent based 'air' monitoring technology

A number of specialist sampling accessories have been introduced in recent years to interface difficult or unusual sample matrices to standard air monitoring technology. Three key examples - for materials emissions testing, human breath and soil - are described briefly below. All may be interfaced to sorbent tubes or alternative online air monitoring technology incorporating one or two sorbent focusing traps.

Rapid assessment of chemical emissions from products and materials – Recent legislative activity – e.g. under REACH [59], the California 'formaldehyde rule' [60] plus the European Construction Products Directive (CPD) [61] & its successor the Construction Products Regulation (CPR) [62] – is driving increased evaluation of vapour-phase chemical emissions from products and materials [63, 64]. Many of the new regulations demand both third-party certification of chemical emission levels by accredited laboratories using reference methods plus ongoing demonstration of product conformity *via* 'factory production control'.

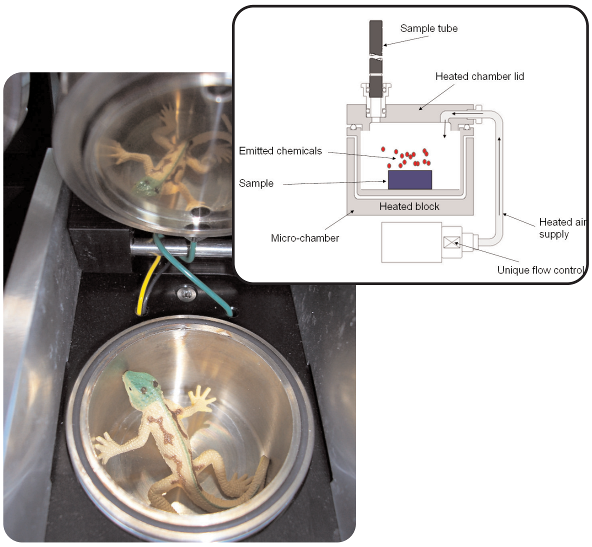

Figure 17: Child's plastic toy inside a microchamber prior to analysis. Inset: schematic of a single micro-chamber as used for bulk emission testing

Reference procedures for product emission testing require sample materials to be placed in test chambers or cells to simulate the indoor environment followed by sample collection on sorbent tubes and subsequent TD-GCMS analysis [13, 14, 65, 66]. These procedures are effective and increasingly well validated [67] but time consuming and expensive. Each test takes between 3 and 28 days. While feasible for certification, faster and simpler tools & procedures are required for in-house emissions screening as part of routine quality control.

Microchamber technology (figure 17) has recently been developed to address this need and allow chemical emissions (bulk or surface-only) to be screened in minutes or hours rather than days. This new approach has been shown to correlate with reference methods [68, 69] and is undergoing rapid standardisation [70, 71]. Most commercial systems can be heated to moderate temperatures and are configured with multiple (typically 4 or 6) micro-chambers allowing multiple samples to be tested in parallel. Both sorbent tubes and DNPH cartridges (for monitoring formaldehyde) are usually accommodated.

In the future microchambers could provide a versatile interface for many natural and man-made materials allowing the power of sorbent tubes/traps and TD-GC/MS air monitoring technology to be applied to vapour profiling an almost universal range of real world solid or liquid samples.

Figure 18: Bio-VOC™ Breath sampler (Markes International Ltd., UK) developed by UK HSL

Breath sampling - A number of breath samplers have been developed over recent years to interface to sorbent tubes [72, 73]. The example shown in figure 18 is a disposable device developed by the UK Health and Safety Laboratory (HSL) for non-invasive studies of biological exposure to chemicals at work, i.e. as a means of assessing the total body burden from all routes of exposure – ingestion and skin absorption as well as inhalation [74]. It collects ~100 ml samples of end-tidal air which are subsequently transferred to sorbent tubes and analysed by conventional thermal desorption – GC/MS.

Other applications for breath testing include monitoring long term environmental exposure - particularly for individuals living near local emission sources (*e.g.* above a dry cleaning shop) or for those living in areas with highly chlorinated water. Breath sampling is also under extensive research as a potential clinical diagnostic tool. [75]

In situ sampling of VOCs in soil - Soil probes fitted with sorbent tubes were initially developed in the petrochemical industry [76] for rapid screening of large industrial sites. Figure 19 shows the type of concentration map obtained from a large scale screening operation of a brownfield site and the inset shows an example soil probe. Diffusive samplers are most commonly used in soil probes [76, 77] because they are easy and cost-effective to deploy in large numbers. *In situ* monitoring of soil contamination involves minimal disturbance of the land allowing a true picture of the level and spread of underground contamination to be built up.

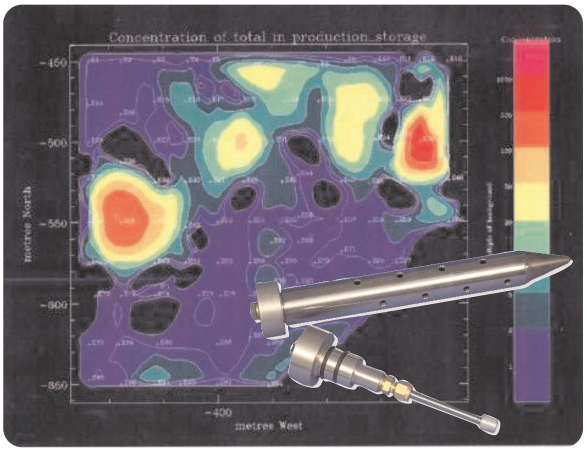

Figure 19: Soil probes arranged in a grid pattern around an industrial site allow low-cost mapping of underground contamination. Inset shows example VOC-Mole™ soil probe

Summary

Sorbent tubes/traps form the basis of most monitoring technology for organic vapours in air and a wealth of supporting information is now available in the literature and in the form of standard methods to those who are new to the field.

New developments, primarily in associated sampling technology, are also extending the application range away from conventional air monitoring and into more exotic fields such as odour & emission profiling and disease diagnosis *via* volatiles in exhaled breath.

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Relevant TDTS notes: parts 1 & 2

1. Uptake rates on axial tube diffusive samplers
2. Prediction of uptake rates for diffusive tubes
3. Relevant national and international standard methods
5. Advice on sorbent selection, tube conditioning tube storage and air sampling
7. Calibration: preparing and introducing standards using sorbent tubes
8. Principles of diffusive monitoring
10. Use of diffusive samplers with thermal desorption – capillary GC analysis for monitoring VOCs in ambient air
13. Evaluation of a new device for non–invasive biological monitoring of VOCs
16. Round the clock, online and cryogen-free monitoring of hydrocarbons from acetylene to trimethyl benzene in ambient air
18. Development in the determination of nitrous oxide using thermal desorption–GC
19. Minimising artefacts – considerations for storage & transportation of sorbent tubes
20. Confirming sorbent tube retention volumes and checking for analyte breakthrough
21. Analytical thermal desorption: developing and optimising methods
22. Selection of gas flows and split ratios during thermal desorption
24. Using UNITY to recollect desorbed samples for repeat analysis
25. Calculating atmospheric concentrations from analyte masses retained on sorbent tubes
26. Minimising analytical interference from water during the analysis of sorbent tubes
28. Optimising analytical performance and extending the application range of thermal desorption for indoor/cabin/vehicle air monitoring
29. VOC air monitoring technology and its application to contaminated land
32. Analysis of sulphur compounds using TD-GC(MS)
33. Analysis of the interior atmosphere of a saloon car using thermal desorption and GC/MS
34. Monitoring trace-level high boiling compounds (triethylphosphate and methyl salicylate) in air
37. Industrial air monitoring using pumped sampling onto sorbent tubes and the UNITY thermal desorber
38. Low Occupational Exposure Limit Levels Favouring Analysis by Thermal Desorption–GC(MS)
39. Analysis of semi-volatile phosphorus pesticides using Mi™ thermal desorption systems – demonstration of method validation using Secure-TD™
42. Uptake rates for Radial Diffusive Samplers
43. Large-scale monitoring of mono ethylene glycol (MEG) vapour in natural gas using pumped sampling onto Tenax tubes followed by thermal desorption - capillary GC analysis
46. Comparing Thermal Desorption with Carbon Disulphide (CS_2) Extraction of Charcoal for Air Monitoring Methods
47. The Analysis of Landfill Gas Compounds using Thermal Desorption GC/MS and a Retention Time Locked Database
49. Fence-line and Ambient Monitoring of Benzene and Other Hydrocarbons using Diffusive Sampling and Thermal Desorption Analysis
53. Quantitative Recovery of high boiling point (>450°C) semi-Volatiles (sVOCs) using Thermal Desorption - GC/MS
56. TD-GC/MS analysis of VOCs for materials emissions testing
62. Materials emissions testing in the semiconductor and associated industries
63. Using the TT24-7 with Twin Electrically-Cooled Focusing Traps for Continuous Monitoring of Trace Level Toxic Chemicals (*e.g.* Chemical Warfare Agents) in Air

67. Using the Micro-Chamber/Thermal Extractor (μ-CTE) to automate materials emissions testing for industrial quality control
75. Tube Impedance and other factors which may cause discrimination during the calibration of Thermal Desorption Methods
77. Using Thermal Desorption for Industrial (Stack) Emission Testing
79. Air monitoring - the respective advantages and applications of canisters and tubes
80. Evaluation of a ‘Soil Gas’ sorbent tube for improving the measurement of volatile and semi-volatile fuel vapors in soil contaminated land
81. Analysis of canister air samples using cryogen-free thermal desorption in compliance with US EPA method TO-15
82. TubeTAG™ - Enhanced tracking of sample- and tube-related information for thermal desorption
86. EPA Method TO-17 for monitoring ‘air toxics’ in ambient air using sorbent tubes and automated, cryogen-free thermal desorption
87. A cryogen-free method for monitoring trace greenhouse gases in air

MiTT017

Technical support document for pumped air monitoring of ambient air using US EPA Method TO-17

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