



Review

Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air

Part 1: Sorbent-based air monitoring options

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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 and freons to phthalates and 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 part per trillion (ppt) levels 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 uncharacterised 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; on-line 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 option. (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.

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1. Introduction

Airborne organic vapours range in volatility from methane to $n\text{-C}_{20}$ and 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 millilitres of solvent before 1 or 2 μl are injected into the GC/MS. Generally speaking, this translates to a 1000-fold reduction in sensitivity relative to TD.

The first stage of the thermal desorption process normally involves heating sampled sorbent tubes (or 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

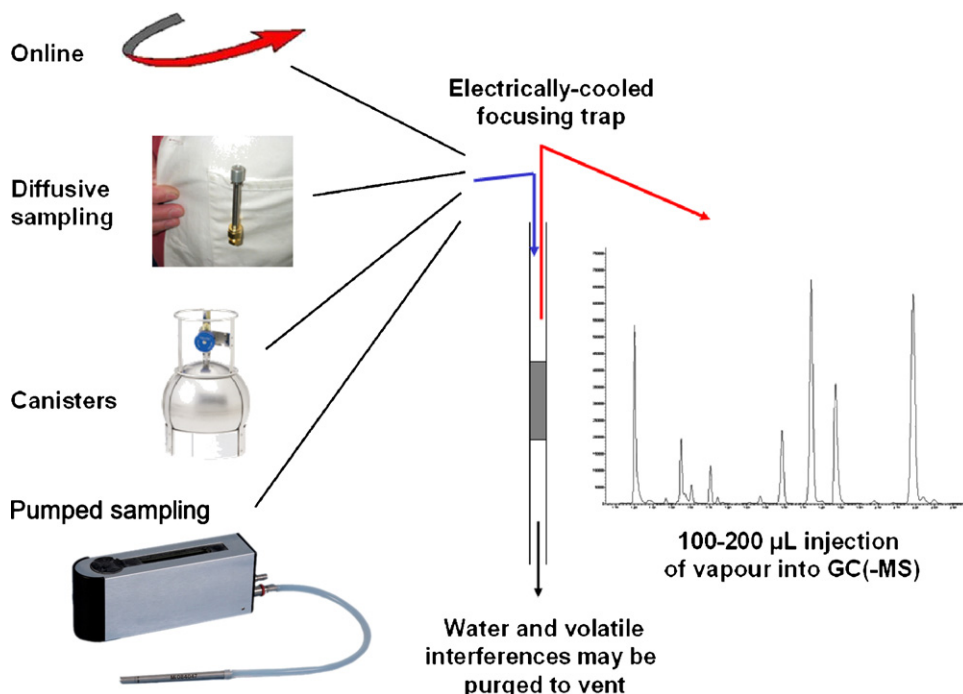


Fig. 1. Schematic overview of the two-stage thermal desorption process for sorbent-based air sampling.

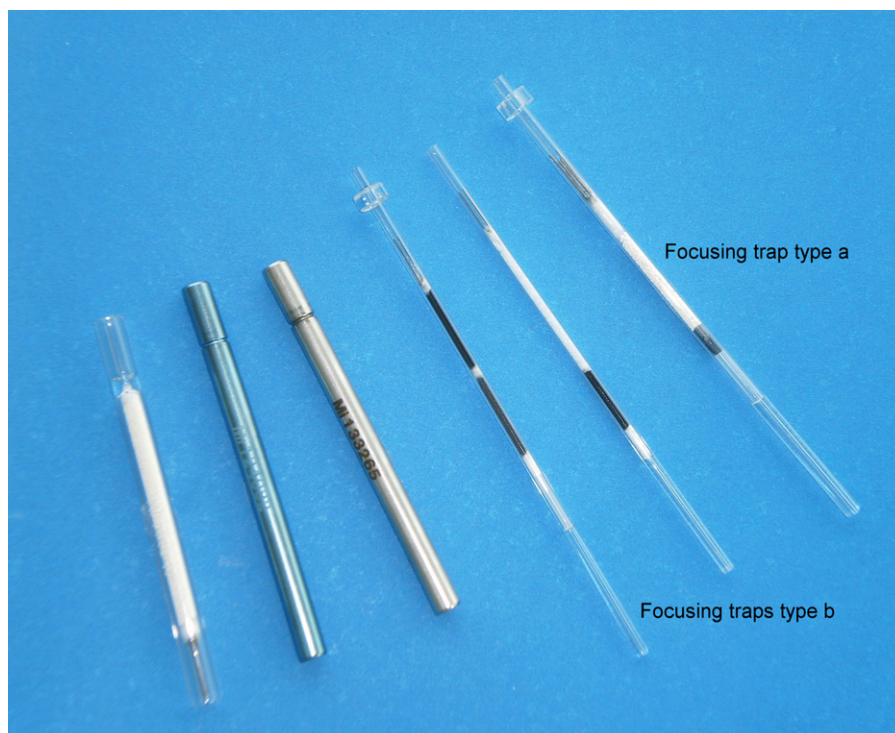


Fig. 2. Sorbent tubes and quartz (electrically cooled) focusing traps commonly used for TD. The tubes shown are of 'standard' dimensions: 89 mm (3.5-in.) long with 6.4 mm (1/4-in.) or 6 mm O.D.—constructed of glass, stainless steel and Silcosteel™. The larger 'type a' focusing trap has an I.D. of 2.8 mm and the smaller 'type b' focusing traps have an I.D. of 2 mm.

a reverse flow of inert 'carrier' gas. This final stage of thermal desorption is extremely fast (heating rates up to 100 °C/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 μ l 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 Fig. 1 and comparative illustrations of sorbent tubes and focusing traps are shown in Fig. 2.

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 a very specialised GC technology and it is difficult to envisage a selective adsorbent for inorganic gases that did not 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 N₂O, H₂S and SF₆ 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 on-going research into on-tube or pre-tube derivitisation. More information is given below.

2. 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.
 - on-line 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 that rely on a partition or equilibrium system, e.g. solid phase (micro-)extraction (SP(M)E) and/or some variations of conventional static headspace methods are available. 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.

3. Pumped (active) sampling onto sorbent tubes

While no single sampling method suits all air monitoring applications, pumped (actively sampled) sorbent tubes, as illustrated in Fig. 1, perhaps provide the most versatile option.

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, industrial emissions and in some high level indoor air monitoring/vapour intrusion studies. They are limited to solvent extraction, typically using CS₂, and are best suited for monitoring apolar compounds that transfer efficiently from the charcoal during des-

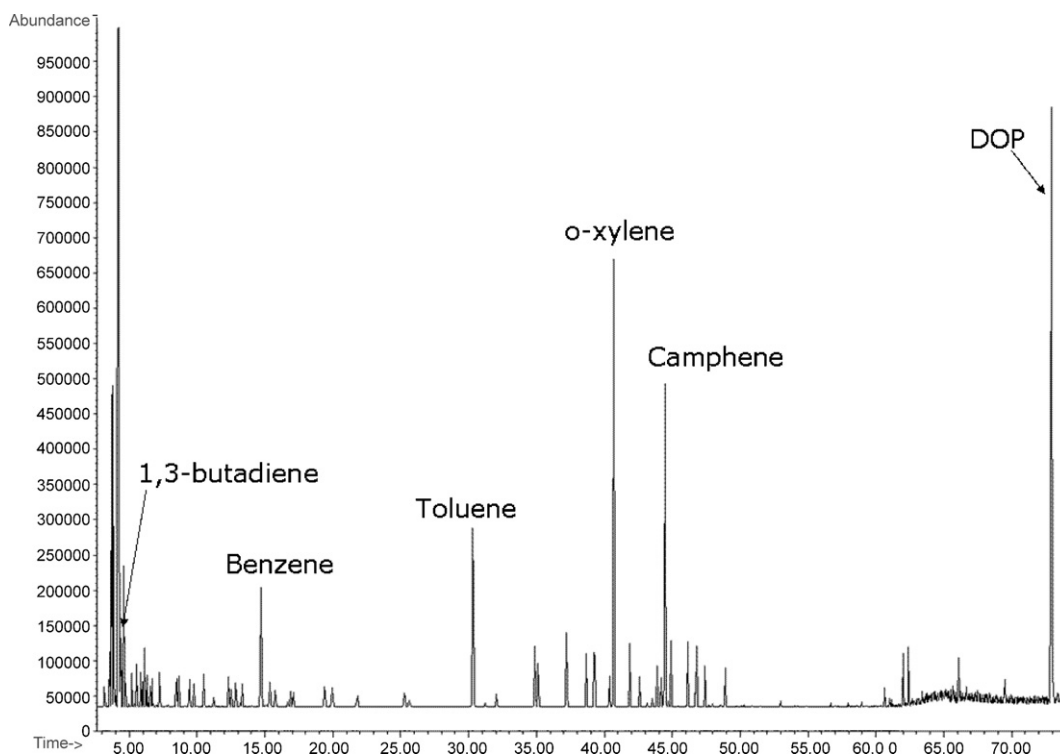


Fig. 3. Use of multiple sorbents coupled with backflush desorption of sample tube and focusing trap allows simultaneous analysis of components over a wide volatility range. Conditions: ULTRA-UNITY 2 automated tube desorber (Markes International Ltd., UK) with GC/MS and a DB1 (60 m × 1 μm) column using a type b focusing trap (Fig. 2) packed with quartz wool, Tenax TA, Carboxen X™ and Carboxen 1003™, electrically cooled to +25 °C. Desorb temperature: 320 °C. GC oven: 35–325 °C.

orption/extraction. Concerns relate to variable extraction efficiency [1], poor sensitivity (typically 0.1–1 ppm detection limits), analytical interference (particularly when using MS detection), and more lately, environmental health and safety issues (the toxicity of CS₂, 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-in. (89 mm) long with an O.D. of 1/4-in. (6.4 mm) or 6 mm and 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) discreet 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 I.D. and application (target analyte volatility range).

Note that some early air monitoring methods specified large, wide-bore tubes (e.g. 6–10 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 [8] 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, C₂ hydrocarbons and the lightest freons. They also offer quantitative recovery of semi-volatiles such as phthalates, PCBs and semi-volatiles up to n-C₃₂₊. Use of multiple sorbents in combination with backflush desorption also facilitates simultaneous desorption/recovery of analytes over a wide range (Fig. 3). (NB ‘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 affect 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 20 °C, and much of this data is included in relevant standard methods [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 10⁴. Similarly a 100 l volume air sample transferred in a 200 μl band of carrier gas would represent a concentration factor of 5 × 10⁵.

If the ambient temperature retention volume of a given vapour is lower than 1 (or 0.51), even on sorbent tubes packed with the strongest carbonised 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 C₂ hydrocarbons, H₂S and the most volatile freons and perfluorinated hydrocarbons.

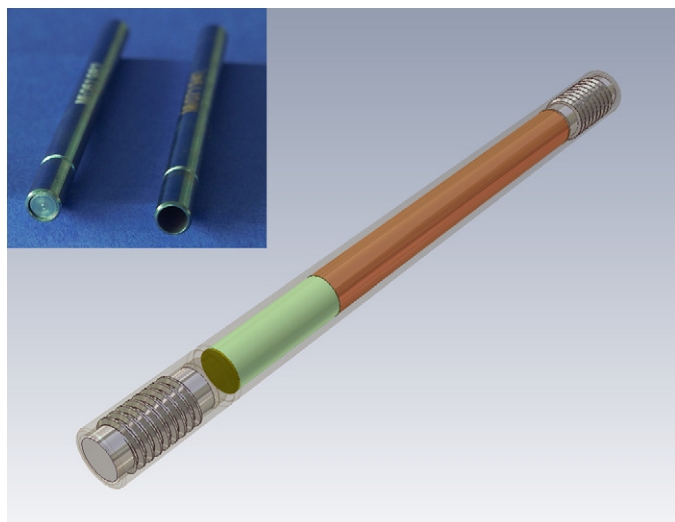


Fig. 4. Schematic of stainless steel (or inert-coated stainless steel) 'SafeLok' tube with conventional external dimensions but incorporating diffusion locking technology at both ends to minimize artifact ingress and allow low flow sampling. Figure (a) shows comparison with standard tube.

Typically, pumped (active) 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 [9]). 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 min) 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 millilitres. Key applications for grab sampling include some industrial emissions (flue gas) measurements, landfill gases [10] and exhaled breath (e.g. for biological exposure monitoring [11]). 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 (active) samplers have been developed to accommodate low flow pumped monitoring (0.5–1 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 Fig. 4). Typical applications are reported to include validation of axial diffusive (passive sampling) 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) [12,13].

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

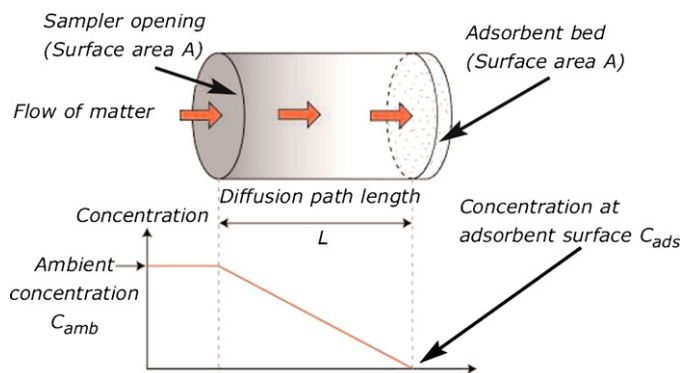


Fig. 5. Schematic illustrating the principles of axial diffusive sampling according to Fick's law.

lar species [14–16]. 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 Fig. 3).

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).

4. 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 [17]. More recently diffusive (passive) 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 (passive) sampling (axial and/or radial) is specified or included in a number of international standard methods for air monitoring [3,18,19].

4.1. Axial diffusive samplers

Developed in the late 70s [20] axial diffusive (passive) samplers typically comprise 1/4-in. 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 Fig. 5). 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

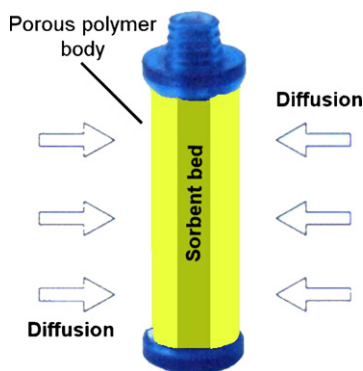


Fig. 6. The Radiello® tube. An example of a radial diffusive sampler.

in diffusive (passive) mode for both short term monitoring (1–8 h) of ppm-level workplace atmospheres and for long term environmental monitoring (3 days to 4 weeks) of indoor or outdoor air [19–22].

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 [3,18,19] 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) [23,24]. 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*-C₁₆ and above (using a weak sorbent such as Tenax TA™).

Diffusive (passive) 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.

4.2. Radial diffusive samplers

Commercial radial diffusive samplers typically comprise a sorbent sampling cartridge housed in a porous polymer body that allows sampling along and around the whole cylindrical surface of the sampler (Fig. 6). 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-h, 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 (passive) samplers are thus best suited to mon-

itoring compounds ranging in volatility from benzene/*n*-C₆ to naphthalene/*n*-C₁₀.

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 (passive) sampling as many times as a standard, sorbent-packed TD tube.

5. 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 N₂O, H₂S and SF₆. Options include:

- continuous or dis-continuous 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 Fig. 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 and 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 (Fig. 2) is typically packed with a total of 10–50 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 I.D.) (Fig. 7).

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 min). Methods involving direct transfer of on- or offline whole air samples to such focusing traps typically operate at 10–30 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 that allow tens or hundreds of litres of air to be sampled in some cases.

Generally speaking, focusing trap flow rate limitations do not constrain canister methods because they are already limited to 1–3 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

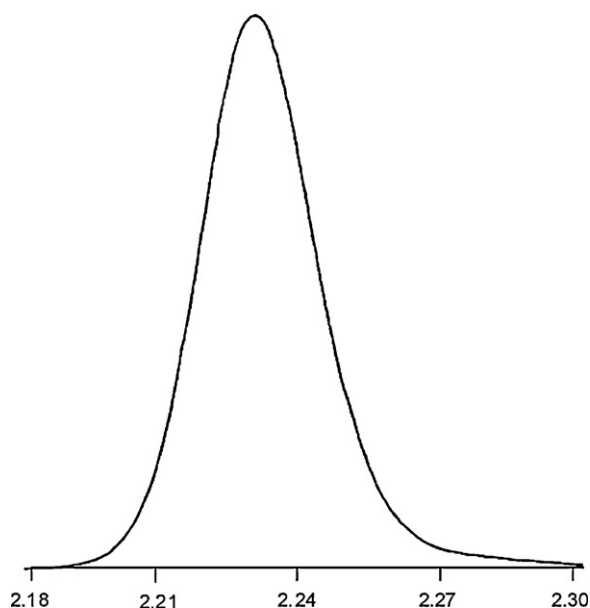


Fig. 7. Unfocused benzene peak desorbed from focusing trap type b (Fig. 2). 1.6 seconds wide at half height. Conditions: UNITY thermal desorber (Markes International Ltd.) with GC-FID and 0.25 mm \times 0.25 μ m film \times 30 m non-polar capillary column, operated at 12 psig (\sim 1.5 ml/min flow) and held at an isothermal temperature of 100 °C to prevent on-column focusing.

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.

5.1. 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 C₂ to C₁₀ hydrocarbon 'ozone precursors' in urban air [25], continuous monitoring of landfill odour [26,27] and tracking the concentration of trace perfluorinated hydrocarbons that are potent 'green house' gases [28].

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 traps 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

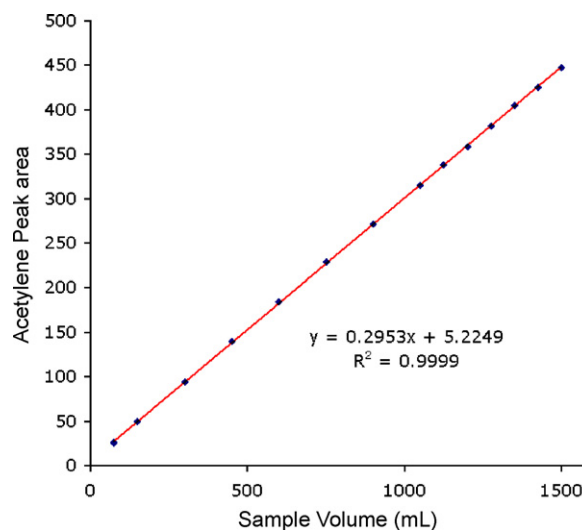


Fig. 8. Quantitative retention of acetylene from up to 1.5l of air without liquid cryogen. Conditions: UNITY2—Air Server system for on-line air monitoring (Markes International Ltd., UK) with GC-FID and Gas-Pro column (Agilent Technologies). Focusing trap packed with: quartz wool, Carbograph 1 TD™, Carboxen 1003 and Carbosieve SIII™. Trapping temperature: -30 °C. Desorb temperature: 250 °C. GC oven: 40–260 °C.

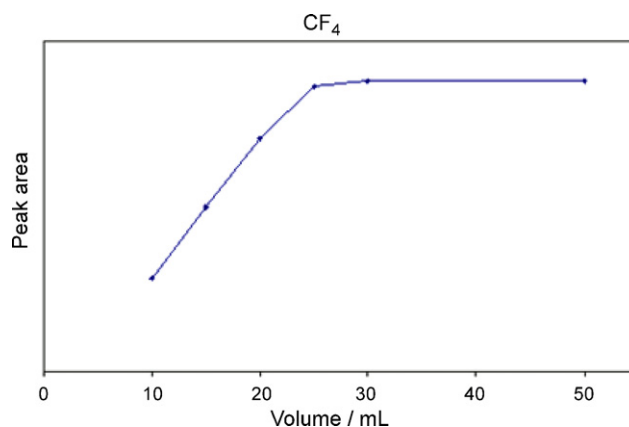


Fig. 9. Quantitative retention of CF₄ from up to 25 ml of air without liquid cryogen. Conditions: UNITY2—CIA 8 TD system for canisters (Markes International Ltd., UK) with GC/MS and Gas-Pro column (Agilent Technologies.). Focusing trap packed with: Carbograph 1 TD and Carboxen 1003. Trapping temperature: -30 °C. Desorb temperature: 300 °C. GC oven: 60–150 °C.

lightest compounds and to prevent the heaviest components being lost through aerosol formation [29].

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 Fig. 2) [3,30]. Such systems offer quantitative retention of ultra volatiles such as acetylene and CF₄ (Figs. 8 and 9) together with efficient/quantitative release of the least volatile components of interest such as hexachlorobutadiene and trimethyl benzene (Fig. 10). 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

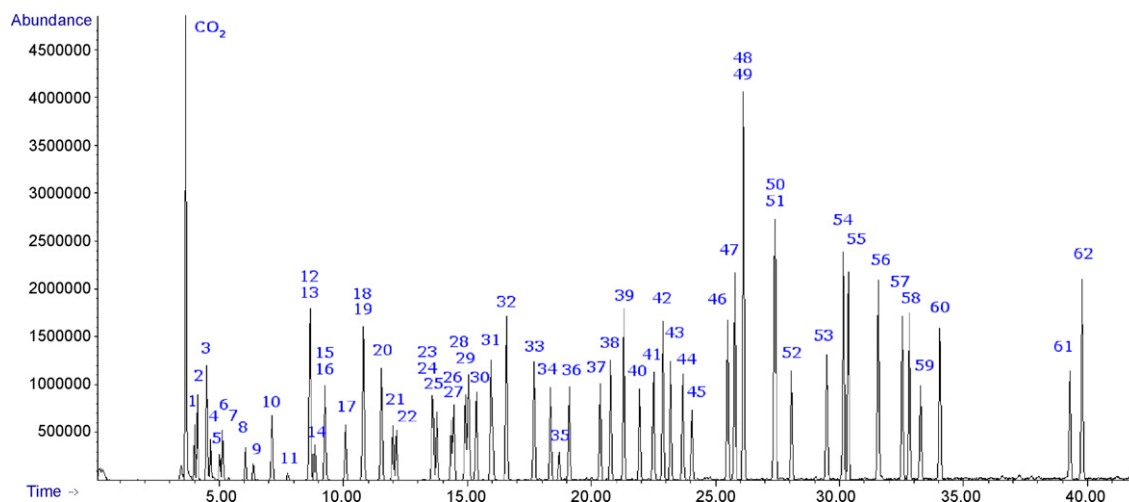


Fig. 10. 62 Component 'air toxics' standard (11, 10 ppb) analysed splitless using the same thermal desorption and focusing trap technology as used for figure. Conditions: UNITY 2—CIA 8 TD system for canisters (Markes International Ltd., UK) with GC/MS and DB-624 column (Agilent Technologies). Focusing trap packed with: Carbograph 1 TD and Carboxen 1003. Trapping temperature: +25 °C. Desorb temperature: 320 °C. GC oven: 35–230 °C.

sample can begin. It is typically possible to sample for 45–50 min 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 [31]. 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.

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.

5.2. 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 C₂ 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 [32–34].

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 Fig. 11 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 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 is not 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 h) for all but the most stable and volatile organic vapours [35,36]. They are also prone to emission of volatile artifacts that may contaminate low level samples and compromise blank levels. Canisters are similarly prone to poor recovery of less volatile or more polar species [37,38], for example, compounds less volatile than n-C_{9/10}. This is illustrated in Fig. 12. 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.

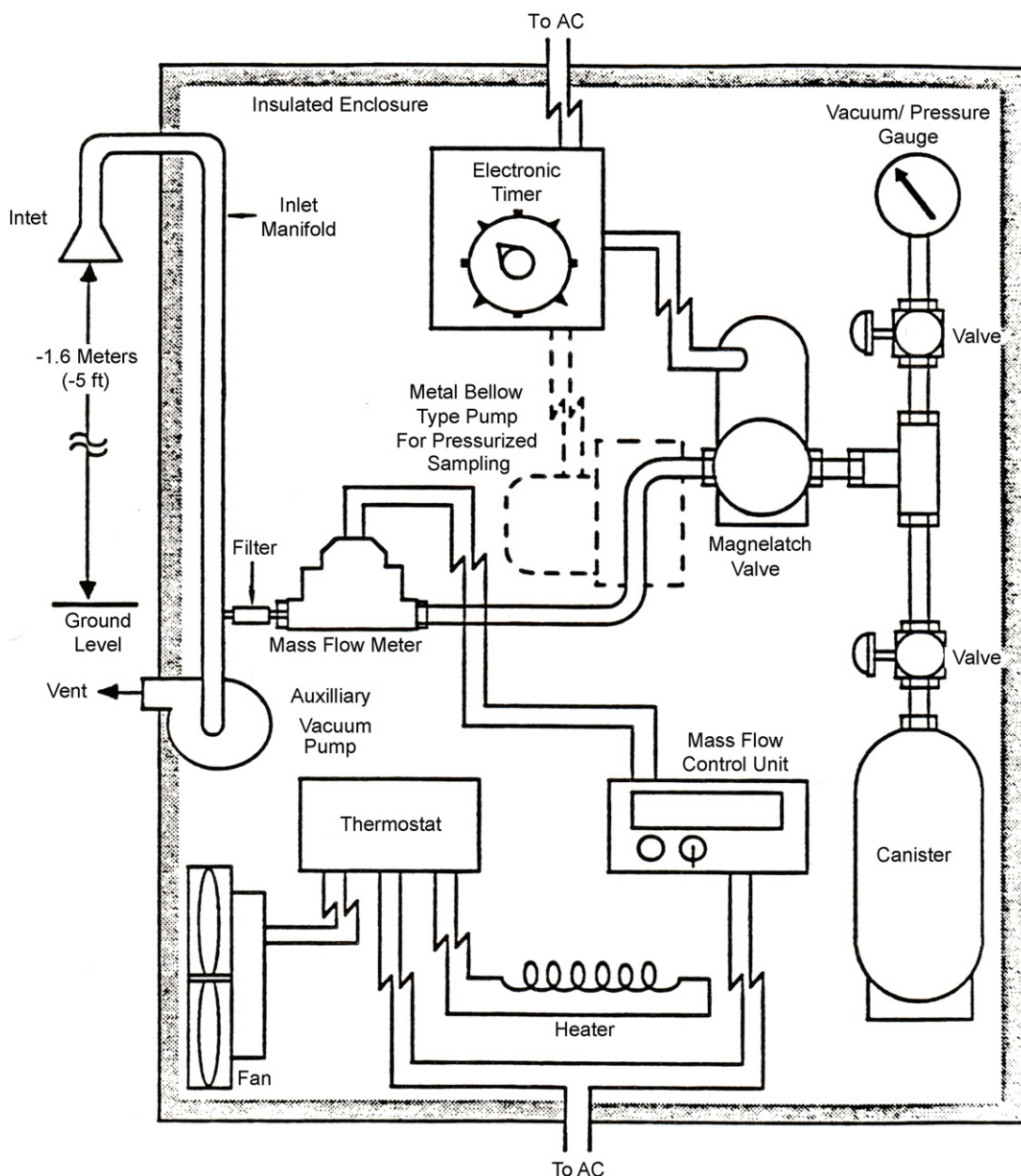


Fig. 11. Sampler configuration for time weighted average canister sampling (Ref. [33]).

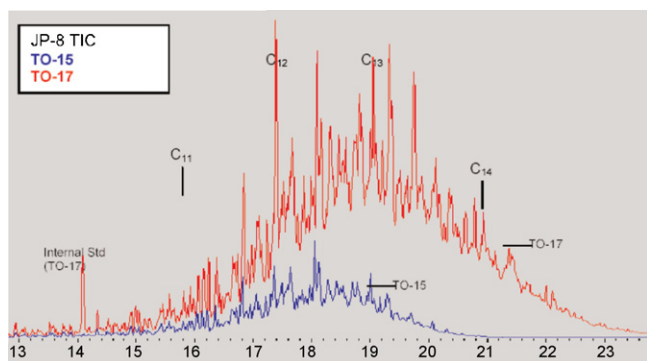


Fig. 12. Sampling and analysis of soil gas contaminated with a jet fuel (JP-8). Comparison of data using canisters (TO-15) versus sorbent tubes. Reproduced from Ref. [37] as an example.

Some older canister methods (e.g. US EPA TO-14 [32]) 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 superseded by methods specifying the type of small sorbent focusing trap described above (e.g. US EPA TO-15 [33]). 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 that 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 $n\text{-C}_8$. Typically total canister volumes are in the range 0.4–6 l meaning 0.2–3 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 poten-

tial concentration enhancement factors to around 10^3 or 10^4 best case.

6. A quick review of some alternative air sampling approaches

6.1. 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 [39].

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 non-polar sorbent which is introduced directly into the liquid or gas phase sample. Analytes partition between the sample and sorbent coating until equilibrium is reached. Generally speaking, the lower the analyte volatility, the higher the partition coefficient, meaning higher boiling compounds are retained more effectively. Provided analyte concentrations remain stable throughout sampling, 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 and 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.

6.2. 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 [40,41].
- 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 man-

ual 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 any sorbent tube or trap-based air monitoring application which 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.

6.3. 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 that use silica-gel substrates, impregnated with dinitrophenyl hydrazine to derivitise formaldehyde prior to analysis with HPLC and UV [42].

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 [43]. This area of research has real potential and may extend to other difficult species over time, for example ammonia.

6.4. 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 0.3–2 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 CO₂ or N₂.

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.

7. 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 [25,33]. Sorbent trapping has thus tended to become an integral part of both these approaches, 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 (their respective advantages and limitations) 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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