Review

Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods

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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. Applications range from atmospheric research and ambient air monitoring (indoor and outdoor) to occupational hygiene (personal exposure assessment) and measuring chemical emission levels. 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.

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1. 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 is not 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.

2. 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) [1].

2.1. Sorbent 'strength'

Analytical sensitivity and precision are largely determined by sampling efficiency, desorption efficiency and the level of interferences (see Section 2.4). 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 20 °C. As a (very) approximate rule, retention volumes halve for every 10 °C 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 [36].

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. 10–200 ml/min for std 6.4 mm (1/4-in.) 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. 6–10 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.

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

Sorbent	Strength	Max. Temp.	Features
Quartz wool	Very weak	>450 °C	Very inert, non-water retentive
Carbograph™ 2TD	Weak	>450 °C	Hydrophobic
Carbopack™ C			Minimal (<0.1 ng) artefacts
Carbotrap C			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	Weak/medium	>450 °C	Hydrophobic
Carbograph™ B			Minimal (<0.1 ng) artefacts
Carbotrap			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 – do not in humid conditions
Molecular sieve 5 Å	Very strong	>400 °C	High (∼10 ng) artefacts
			Significantly hydrophillic – do not use in humid conditions
Molecular sieve 13×	Very strong	>400 °C	High (∼10 ng) artefacts
			Significantly hydrophillic – do not use in humid conditions

2.2. 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.

2.3. 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 [36]. 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.

2.4. Artefacts

Sorbents vary significantly with respect to inherent artefact levels. Some porous polymers such as the Chromosorb® Century series, PoraPak™ and HayeSep™ series have relatively high artefacts with several peaks at 5–10 ng levels. The porous polymer Tenax® TA is

better with minimum 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 – between 0.01 and 0.1 ng if 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 artefacts including benzaldehyde and acetophenone if ozone concentrations exceed 100 ppb [2].

2.5. 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 400 °C. However, care must be taken with most other porous polymer sorbents–chromosorbs, HayeSeps and PoraPaks – which typically have temperature limits at or below 225 °C.

2.6. 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 0.6–0.2 mm particle diameter).

2.7. Mesh size

Within the 30–80 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 internal diameter of the sorbent tube/trap [3].

3. 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 70 s [4] 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 artefact 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 and above to be monitored simultaneously [36,5,6].

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 [7].

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 [8], molecularly imprinted polymers (which can be used to selectively trap large molecules according to their shape [9]) and sorbents impregnated with derivatising agents [36] 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.

4. Multi-sorbent tubes

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. (Fig. 1, 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 sorbent 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 sor-
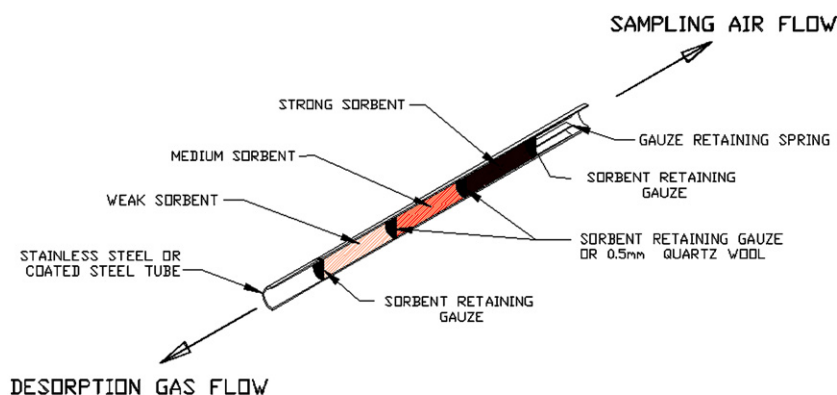
Fig. 1. A multi-sorbent tube.

bent 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 [10] (see Fig. 3 in part 1 of this paper). Research into multi-sorbent tube combinations is ongoing in order to extend the application range even further and better define the working limits – storage times, safe sampling volume, etc.

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) (Fig. 1). 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 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*' [36] 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.

5. Other practical factors to consider for sorbent-based air sampling

5.1. 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 are not 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.

5.2. Sorbent retaining materials

Sorbents are typically held in place using fine mesh stainless steel or Silcosteel gauzes (stainless steel tubes) or glass frits 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 Fig. 1) facilitating the required level of precision for diffusive (passive) sampling and the interchange of uptake rate information e.g. in standard methods [36].

5.3. 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 they are 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 [11].

5.4. Storage of conditioned and sampled sorbent tubes

Conditioned and sampled tubes should be stored using long-term 1/4-in. screw caps fitted with combined PTFE ferrules as described in standard methods [36]. Sampled, single sorbent tubes capped and stored in this way are reported to be stable for up to 27 months [12] at room temperature provided the compounds concerned are not chemically active. Multi-sorbent tubes should be analysed more quickly to minimize risk of analyte migration within the tube (see above).

6. 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: −4.4 °C) can be quantitatively retained using Carbograph™ 5 TD or Carbopack™ X [7,13].

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 [14,15]. It is most effective to implement dry purging in two 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 be a real benefit by simplifying some 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 from the whole air sample. A focusing trap dry purge step (see above) is also implemented between sampling and trap desorption/analysis. In this case, no in-line dryer is required and polar compounds can be measured.

7. 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) analytical process has been presented in the literature [1] 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%.

8. 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 and 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 restricted 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 explains 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 including 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.
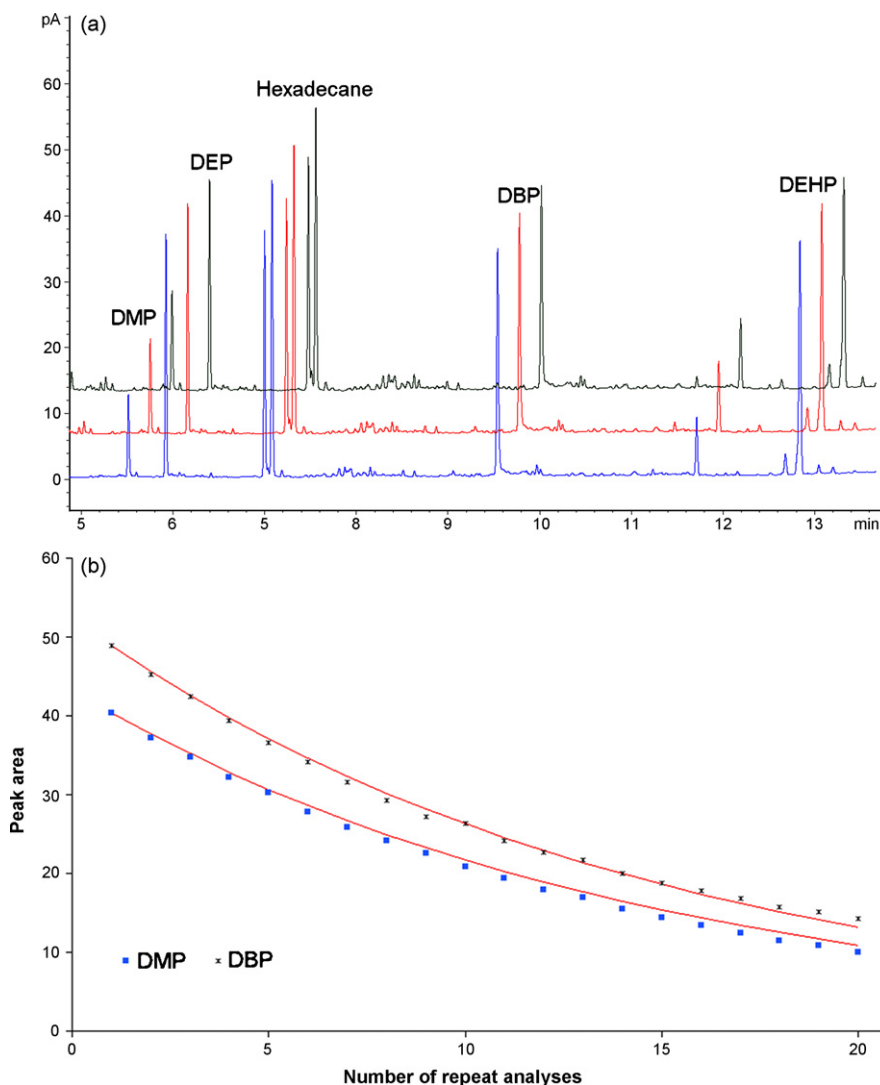

Fig. 2. (a) Sequence of chromatograms showing re-analysis of re-collected phthalate mixture using an automated ULTRA 50:50™ thermal desorber from Markes International Ltd., UK. (b) Plot showing the theoretical (lines) and measured (points) peak areas for multiple re-collection and repeat analyses of the sample shown in a.

Fig. 3. RFID tags attached to thermal desorption sorbent tubes.

Another more recent innovation is 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 Fig. 2a 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. This approach has now been adopted into some of the most recent thermal desorption standards [36].

Electronic labeling has recently been introduced for sorbent tubes (Fig. 3) 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 permanently attached to the same tube (or canister) throughout its life. 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 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 [16].

9. 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.

Fig. 4. Child's plastic toy inside a micro-chamber prior to analysis. (a) Schematic of a single micro-chamber as used for bulk emission testing.

9.1. Rapid assessment of chemical emissions from products and materials

Recent legislative activity – e.g. under REACH [17], the California 'formaldehyde rule' [18] plus the European Construction Products Directive (CPD) [19] and its successor the Construction Products Regulation (CPR) [20] – is driving increased evaluation of vapour-phase chemical emissions from products and materials [21,22]. 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'. 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-GC(MS) analysis [36,23,24]. These procedures are effective and increasingly well validated [25] but time consuming and expensive. Each test takes between 3 and 28 days. While feasible for certification, faster and simpler tools and procedures are required for in-house emissions screening as part of routine quality control.

Micro-chamber technology (Fig. 4) 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 [26,27] and is undergoing rapid standardisation [28,29]. 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 micro-chambers could provide a versatile interface for many natural and man-made materials allowing the power of sorbent tubes/traps and TD-GCMS air monitoring technology to be

Fig. 5. Bio-VOC breath sampler (Markes International Ltd., UK) developed by UK HSL.

Fig. 6. 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.

applied to vapour profiling an almost universal range of real world solid or liquid samples.

9.2. Breath sampling

A number of breath samplers have been developed over recent years to interface to sorbent tubes [30,31]. The example shown in Fig. 5 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 [32]. 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 [33].

9.3. In situ sampling of VOCs in soil

Soil probes fitted with sorbent tubes were initially developed in the petrochemical industry [34] for rapid screening of large industrial sites. Fig. 6 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 [34,35] 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
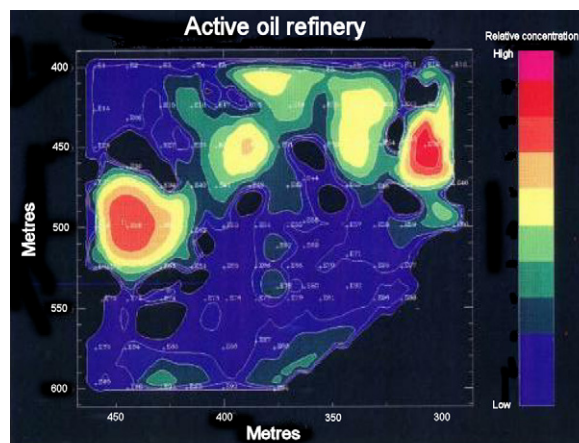
true picture of the level and spread of underground contamination to be built up.

10. 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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