

**Part One**  
**Measuring Organic Indoor Pollutants**



# 1

## Application of Solid Sorbents for the Sampling of Volatile Organic Compounds in Indoor Air

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### 1.1 Introduction

The use of building materials, furniture, carpets and household products produces an almost ubiquitous level of volatile organic compounds (VOCs) in indoor air. Several hundred different compounds have been identified in the indoor environment. Since most air pollutants occur in low concentrations of 1–1000  $\mu\text{g}/\text{m}^3$ , highly sensitive detection methods as well as efficient separation methods are needed to analyze air samples (Barro *et al.*, 2009).

Continuously working analytical devices like the flame ionization detector (FID), photo-ionization detector (PID), photo-acoustic detector (PAD) or ion trap mass spectrometer offer a high time resolution, but often lack the required sensitivity and selectivity. Therefore, discontinuous techniques with a sample preconcentration step during or after the sample collection are still preferred, especially regarding toxic substances where detection limits of less than 10  $\mu\text{g}/\text{m}^3$  are demanded. Using discontinuous sampling, the sensitivity can easily be increased by a factor of 1000 to 100 000 by passing an air sample volume of 1 to 100 l through an appropriate 'trap' where the organic ingredients are retained. In general, there are three possibilities for enriching the ingredients of an air sample:

- absorbing target compounds in a suitable liquid;
- condensing target compounds at low temperatures (cryo-trapping);
- adsorbing target compounds on a porous solid material.

Liquid absorption is a common technique for enriching compounds in reactive liquids like solutions of dinitrophenylhydrazine (DNPH) (for aldehydes), acetyl acetone (for formaldehyde) or aqueous carbonate solutions (for organic acids), both procedures which combine trapping and derivatization of the target compound. Another possibility is the use of dissolved alkali or acids to trap certain substances by the formation of salts in the solution.

Cryo-trapping is often used in combination with solid sorbents and therefore is less important as a stand-alone sampling method.

Solid sorbents play an important role for the determination of VOCs in indoor air. They overcome some serious disadvantages of liquid absorbents:

- The direct analysis of the absorption liquid will not normally give the desired sensitivity, so additional steps are required to concentrate the target substances. These may lead to a loss of the more volatile compounds present in the sample. Moreover, the possibility of contamination, for example with phthalates, cannot be excluded when handling with glassware.
- The injection of a solvent into the gas chromatograph makes it difficult to identify and quantify the compounds which are eluted close to the solvent retention time. In addition to that, impurities of the solvent may interfere with the sample compounds and therefore make the quantification more error-prone.
- The use of derivatization agents may increase the sensitivity, but also makes the method specific to a small range of compounds.
- Preconditioning of a solid phase is much easier to achieve than the purification of a liquid phase. Therefore problems with blanks are reduced.
- The handling of solid sorbents, often used in pre-packed tubes, is more convenient than the use of organic solvents to trap VOCs from the air, especially for sampling in the field. The typical laboratory safety procedures required for the handling of organic solvents are not required for solid sorbent samples.

If solid sorbents with a low affinity to water are chosen, they even overcome the main disadvantage of cryo-trapping: Water gets trapped in the device and often leads to serious analytical problems as well as mechanical problems if ice is formed in the trap.

Of the variety of solid sorbents presently available Tenax,<sup>1)</sup> activated charcoal and Carbotrap<sup>1)</sup> are the most widely used ones. This is mostly due to the versatility they offer especially for sampling of VOCs typically found in indoor air (C6 to C16).

## 1.2

### Solid Sorbents – A Brief Overview

Three general types of solid sorbents are mainly used for trapping VOCs in air: inorganic sorbents like silica gels or molecular sieves, carbon-based porous materials and porous organic polymers.

The main types of inorganic sorbents are silica gels, molecular sieves/zeolites, aluminum oxides and magnesium silicates. Carbon-based sorbents include activated charcoals, carbon blacks, graphitized carbon blacks and graphitized molecular sieves. Styrene–divinylbenzene copolymers, ethylvinylbenzene/divinylbenzene

1) For trademarks of commercial products see remarks in Table 1.1.

copolymers, polyvinylpyrrolidone, polyphenylene oxides and polyurethane foams represent the most widely used polymer sorbents. Table 1.1 shows some properties of common sorbents.

The surface area of a sorbent influences the amount of a given substance that can be adsorbed by the medium, whereas the surface polarity determines the general type of compounds a sorbent can be used for. The sorbents offer different suitability for VOC analysis depending on the type and amount of substance to be sampled. The inorganic sorbents are often used to trap hydrocarbons and polychlorinated biphenyls (PCBs). Carbon-based sorbents with large surface area and molecular sieves are useful to trap very low-boiling compounds, but are unsuitable for higher boiling substances; labile or reactive compounds may even decompose on active sites on the sorbent surface. Porous polymers with a comparatively small surface area allow the adsorption and desorption of high-boiling compounds like glycols, phthalates and also the trapping of reactive substances like aldehydes or acrylates. On the other hand it is difficult to sample low-boiling compounds like C<sub>2</sub>-C<sub>5</sub>-alkanes. A special case of the porous polymer sorbents is polyurethane foam (PUF), which can be used to collect large air samples up to 100 m<sup>3</sup> (Ligocki and Pankow, 1985). PUF is often used to trap high-boiling organopesticides like lindane or permethrine.

The different characteristics of the presented sorbents show the need to carefully choose the right adsorption medium for a given VOC mixture.

Several workers have examined the suitability of the available sorbents for general VOC analysis. Figge *et al.* (1987) tested the retention volumes of 26 different adsorbents using a VOC mixture of 29 compounds with boiling points from 21 °C to 361 °C. They rated the sorbents in four groups with decreasing sorption strength. Some of the carbon-based sorbents like Carbosieve SII showed the overall highest ability to retain organic compounds. Adsorbents with good retention properties for higher boiling compounds regardless of their polarity were, Porapak Q, Chromosorb 106 and XAD-4. The third group included Porapak S, Tenax GC and Carbopack B, which showed good retention properties only for higher boiling, non-polar VOCs. For PTFE, Chromosorb T and other weak sorbents only poor retention volumes were found.

Brown (1996) reported the results of a multi-laboratory study concerning the suitability of different sorbents for the measurement of VOCs in the workplace environment. In this study 20 test compounds were used and the sorbents had to fulfill a number of test criteria. Chromosorb 106 was found to be the most versatile sorbent and especially useful for the sampling of very volatile and polar compounds. Other sorbents which satisfied the acceptance criteria were Carbotrap, Tenax TA, Tenax GR and Carbopack B.

Rothweiler, Wäger and Schlatter (1990) and De Bortoli *et al.* (1992) compared two widely used adsorbents: Tenax TA and Carbotrap, regarding their performance for VOC sampling. Both groups found the two sorbents to be convenient for the sampling of non-polar organic compounds regarding background emission and sample recovery. They both agree in reporting significant analyte losses when using Carbotrap with more reactive compounds like terpenes, aldehydes or acrylates.

**Table 1.1** Properties of some solid sorbents according to Quintana, Uribe and Arbeloa (1992), ECA (1994), Zielinska and Fujita (1994), Figge, Rabel and Wreck (1987) and ISO (2001).

Type	Structure	Surface area (m <sup>2</sup> /g)	Products	Desorption	Compounds tested (Starting at b.p.)	Polarity	Thermal stability	Water affinity
Inorganic	Silica gels	1–30	Volosphere, Florisil	Solvent	PCBs, pesticides	High	~400°C	High
	Molecular sieves	500–800		Solvent	Permanent gases	High	<400°C	High
	Aluminum oxides	~300	Alumina F1	Solvent	Hydrocarbons	High	300°C	High
Carbon based	Activated Charcoal	800–1200		Solvent	Non-polar and slightly polar VOCs (>50°C)	Medium	>400°C	High
	Carbon molecular Sieves	400–1200	Carbosieve, Ambersorb, Sphero carb Carboxen	Solvent/ Thermal	Non-polar and slightly polar VOCs (>–80°C)	Low	>400°C	Low – medium
Porous polymers	Graphitized carbon blacks	12–100	Carbotrap, Carbo pack, Carbograph	Thermal	Non-polar VOCs (>60°C)	Low	>400°C	Low
	Styrene, divinylbenzene or polyvinylpyrrolidone polymers	300–800	Porapak Q/N, Chromosorb 106/102, Chromosorb	Thermal/ solvent	Non-polar and moderately polar VOCs (>40°C)	Variable	<250°C	Low
	Phenylphenylen oxide polymers	20–35	Tenax	Thermal	Non-polar VOCs (>60°C)	Low	<350°C	Low
	PU-Foams			Solvent	Pesticides	Low	<200°C	Low

*Remarks:* Tenax® is a registered trademark of Buchem B.V., NV, NL; Carbotrap®, Carbo pack®, Carbograph®, Carbosieve® and Carboxen® are registered trademarks of Sigma-Aldrich Co., USA; Chromosorb® is a registered trademark of Johns-Manville Corp. USA; Porapak® is a registered trademark of Waters Associates Inc., USA; Sphero carb® is a registered trademark of Analabs Inc., USA.; Volosphere®: E.Merck KGaA, Germany; Florisil® is a registered trademark of U.S. Silica Co., USA.

Measurements of the thermal desorption efficiencies of different sorbents were done by Cao and Hewitt (1993). They also noticed the loss of terpenes on Carbotrap.

In the very comprehensive review article of Matisová and Skrabáková (1995) the suitability of various carbon-based sorbents is discussed.

### 1.3

#### Active or Passive Sampling

Two different sampling strategies for collecting air samples exist: actively drawing air through a sorbent-filled cartridge or tube, or passively letting the compounds penetrate a well-defined sorbent bed simply through gradient-driven diffusion. The active sampling process is obviously a faster way to take an air sample and is, especially in cases where a high sensitivity and therefore a large sample volume is needed (e.g., sampling of pesticides), the recommended method. The accuracy of the sample is clearly determined by the sample volume, and measuring the correct air volume is one of the most important quality issues for the whole analysis when doing active sampling. Calibrated pumps, mass flow controllers or pumps in combination with appropriate air meters are often used to control the sample volume. If the sample volume collected is small and sampling time short, active sampling allows the measuring of dynamic processes with a higher sensitivity than continuously working analytical devices (FIDs, PADs). Therefore, it is until now still the preferred method for the study of kinetic experiments in emission test chambers (although with instruments like direct-inlet MS and proton transfer reaction - mass spectrometry (PTR-MS) becoming available this is likely to change in the future).

The use of a passive sampler is characterized by long sampling times, which are needed to allow the airborne compounds to enter the sampler and become trapped on the sorbent surface. Sampling times often exceed several days. The long sampling times show a pitfall of this sampling technique: because the sampler is in contact with the air to be sampled for a long time, very volatile compounds may have the chance not only to enter the sampler, but also to leave it on the same way, if their interaction with the sorbent is low. In this case an underestimation of the very volatile substances can be expected.

Passive samplers are not useful to monitor peak concentrations, but offer a convenient way to regard for example, long term exposure of persons in an indoor environment. A more detailed description of the passive sampling technique is given in Chapter 3.

The decision whether active or passive sampling should be used strongly depends on the type of experiment to be carried out: to measure the mean concentration over a long period of time in a given environment, passive sampling often is the easier way. Lewis *et al.* (1985) even managed to collect an analytically sufficient sample with a special Tenax-based passive sampler within only one hour. For the determination of indoor air concentrations during fast, dynamic processes active sampling normally is preferred.

## 1.4

### Thermal Desorption or Solvent Extraction

After collection on a sorbent the trapped VOCs need to be transferred into the analytic device, which often is a gas chromatography (GC) or a high performance liquid chromatography (HPLC) system.

Depending on the activity of the sorbent and the characteristics of the analyte there are two general possibilities of removing the sample from the sorbent. One of them is solvent extraction, which is commonly used for the inorganic sorbents as well as for PUF and the carbon-based sorbents with high surface activity. For the extraction a suitable organic solvent is selected. Dimethylformamide, carbon disulfide (preferred because it has a low response on a FID), dichloromethane or other polar solvents, often combined with a desorbing agent like methanol or water, are used to recover the trapped substances from the adsorbent. The solvent as well as the desorbing agent need to be carefully chosen; ideally they should not interfere with any of the sample peaks (therefore their purity should be high and their peak on the used separation column should be narrow); they should not react with the sample or the sorbent; their affinity to the sorbent should be high enough to remove the sample compound completely and their response on the used detector should be low.

Thermal desorption, on the other hand, makes use of the fact that the ability of a sorbent to retain compounds dramatically decreases at elevated temperatures. Therefore, heating of the sorbent under a continuous stream of an inert carrier gas can be used to transfer the adsorbed compounds into the GC system. In general the desorption temperature should be at least 20 °C above the boiling point of the adsorbed compounds, so the range of compounds which can be analyzed with thermal desorption is limited by the thermal stability of the sorbent. In order to avoid a loss of analyte due to decomposition on the sorbent's surface at elevated temperatures the surface activity needs to be carefully chosen.

The main advantage of thermal desorption is the greater sensitivity and the absence of a solvent peak, which could interfere with a detector (i.e., mass spectrometer (MS)) or mask potential analyte peaks. Modern thermal desorption units allow the use of multi-bed tubes and traps (see following paragraph).

A method for trapping VOCs on Tenax adsorption tubes with subsequent thermal desorption has been standardized internationally (ISO, 2004, 16000-6).

## 1.5

### Sampler Design

A simple sampler usually consists of a glass or stainless steel tube filled with a certain amount of the sorbent. Typically, 50–500 mg of the sorbent are used. To retain the sorbent in the tubes either glass/quartz wool or small sieves can be used. Both techniques introduce a disadvantage into the sampling system: quartz wool is normally too brittle to be fitted successfully into the tube, and small parts of the



fibers may be released from the tube. Silanized glass wool does not feature that disadvantage, unfortunately at thermal desorption temperatures above 250°C the silanization agent can be released and an increased blank value of siloxanes and similar substance can often be found in the chromatograms. In worse cases, silicon oligomers can coat parts of the thermal desorber tubing or transfer lines and may lead to decreased performance of the instrument.

Stainless steel sieves, which can be fitted into a range of stainless steel sorbent tubes, are usually easier to handle than glass/quartz wool. It is, however, their disadvantage that some very labile compounds may degrade in contact with the metal under thermal desorption conditions. In addition, the sieves will often not completely retain the fines fraction of the used sorbents: this is particularly problematic for the carbon-based sorbents, which are more brittle than the polymers and can therefore be crushed to fine particles by the thermal stress during use of a tube. The presence of a dark residue on the filters inside the thermal desorption unit is an indication of carbon-based sorbent migration from the tubes.

When a sorbent is to be selected for a certain sampling purpose, a number of details need to be addressed:

- Is the sorbent able to retain the targeted analyte at the given conditions (temperature, sample flow rate, target compound concentration etc)?
- What other compounds will be retained during that process, and can they have an adverse effect on the analysis?
- Will the sorbent material be able to withstand the sampling and analysis conditions?

To overcome problems with sorbents either being too weak to retain the very volatiles or too strong to allow for a desorption of the least volatile compounds of a mixture, multi-bed tubes can be used. In such a tube different sorbents of increasing surface area and activity are combined (Figure 1.1). They can be used to trap substances within a wide boiling range. High-boiling compounds get trapped in the first zone of the adsorbent bed (often a porous polymer), the more volatile substances pass through that zone and are collected on an sorbent with greater activity. Therefore, the sampling direction must be accurate under all circumstances. Desorption, in contrast, must occur in the reversed direction (back-flush)

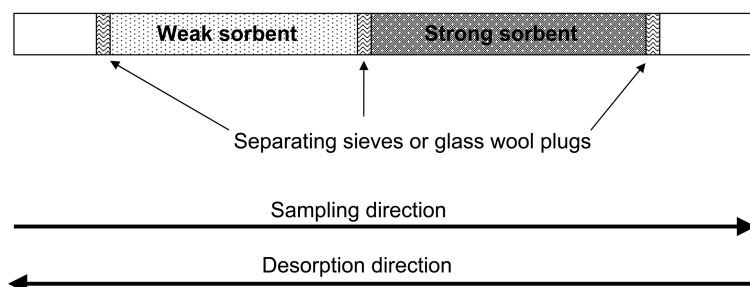
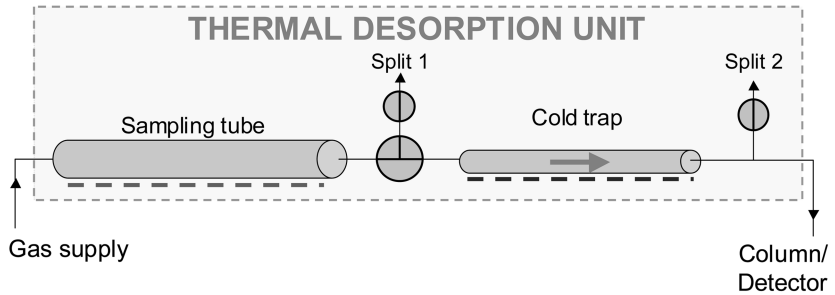
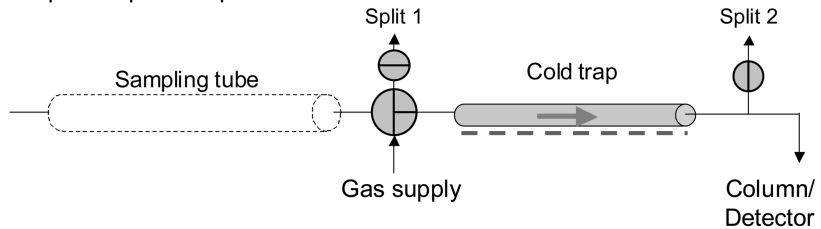


Figure 1.1 A multibed sorbent tube.

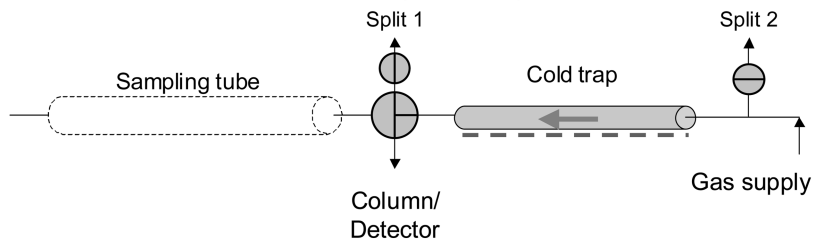
## 1. Tube desorption step:



## 2.a. Trap desorption step – normal flow:



## 2.b Trap desorption step – reversed flow ('backflush'):



**Figure 1.2** Schematic of a thermal desorption process with tube desorption and normal/backflush trap desorption steps.

to prevent the high boiling compounds from getting in contact with the more active sorbent.

Multi-bed tubes can be a perfect solution to analyze a wide range of compounds in known samples. For air samples of unknown composition it is important to consider the possible interactions of two or more sorbents with unexpected compounds in that sample. Therefore, this type of tube is not in widespread use for explorative analysis.

If the thermal desorption unit is able to provide inverted (back-flush) gas flow during trap desorption (Figure 1.2), the same technique described for tubes can also be used for the cold trap. A multi-bed trap can considerably extend the analytical window of the instruments. Commercial cold-traps packed with quartz beads, quartz wool and Tenax TA are reported to cover a substance range from C6 to C40.

## 1.6

### Breakthrough Volumes

The 'breakthrough volume' is defined as the volume of gaseous sample that can be drawn through a sample tube before an analyte is eluted from the tube. Every sorbent has a limited capacity for a given analyte which depends on the characteristics of the sorbent, on the type of compound to be trapped and on certain sampling parameters, like the temperature and the humidity of the air (Bertoni *et al.*, 1981; Brown and Purnell, 1979). Breakthrough of a substance can occur if:

- the sampling speed is too high and the compounds are flushed through the tube without enough time to interact sufficiently with the sorbent surface;
- the concentration is far too high, the sorbent surface gets saturated with the compound and the excess compound passes the sorbent without adequate retention;
- the retention ability for the given amount of substance is not sufficient, the compound is retained, but eluted again in the ongoing sampling procedure.

While the first two cases can easily be avoided by either using a low sampling rate (100 ml/min for Tenax tubes and 1–2 l/min for activated charcoal tubes are usually considered a safe sampling speed) or by using small enough sample volumes (Tenax: 1–6 l, activated charcoal: 5–100 l), the third case can only be overcome by selecting another sorbent or carefully choosing the right sampling temperature and a small sampling volume.

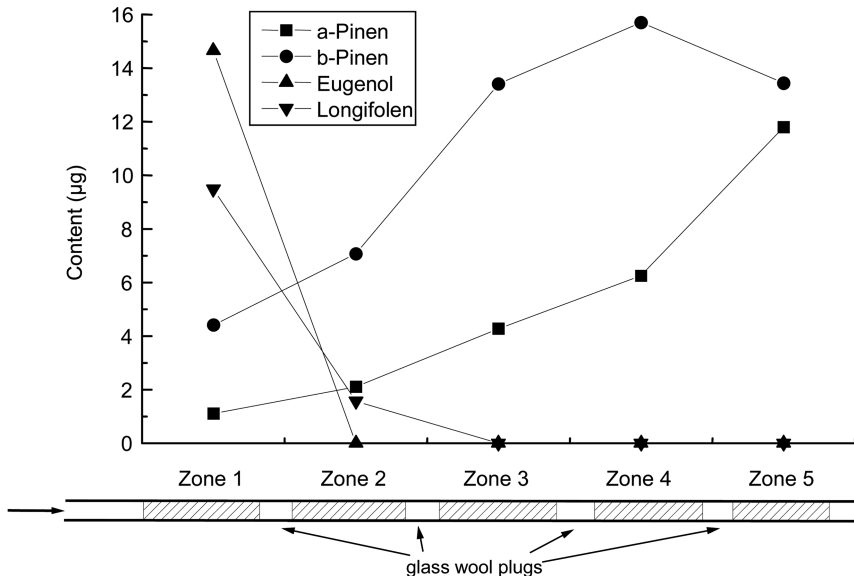
Breakthrough volumes can be determined by a direct method (monitoring the effluent during sampling air with known concentration of a test compound), or by an indirect method, where the sorbent tube is used as a GC column and the retention time of an injected compound is used to calculate the breakthrough volume (Brown and Purnell, 1979).

Figure 1.3 shows the result of an experiment illustrating the breakthrough of volatile terpenes on Tenax TA: the distribution of analytes in a special adsorbent tube filled with Tenax TA in five zones, each separated with a silanized glass wool plug, is determined. After spiking with high concentrations of different terpenes in methanol and sampling two liters of air the content of each Tenax zone was analyzed separately. The effect of chromatography-in-the-tube is clearly visible: The highest boiling compound (longifolene) is completely retained in the first zone, the low-boiling compounds ( $\alpha$ -pinene and  $\beta$ -pinene) have already partially left the tube. While the  $\beta$ -pinene 'peak' is still located inside the tube (zone 4), the  $\alpha$ -pinene concentration rises toward the rear end of the tube which indicates that major amounts of the substance have already left the tube.

## 1.7

### Safe Sampling Volume

The 'safe sampling volume' (SSV) is usually defined as 70% of the 5% breakthrough volume (ISO, 2001, 16017-1). If, for a given air sample, the sample volume



**Figure 1.3** Distribution of volatile compounds on an adsorbent tube after spiking and sampling 2 liters of air with high terpene concentration. The sampling direction is marked with an arrow.

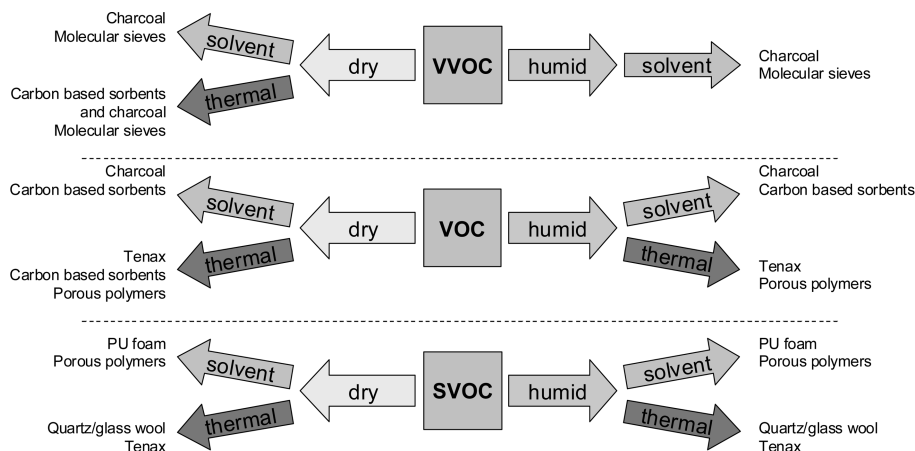
is lower than the SSV of the lowest-boiling compounds in that sample it can be assumed that all compounds were quantitatively retained in the tube. The determination of SSVs is a time-consuming procedure (Martin *et al.*, 2003). Fortunately, a number of SSVs have been published for different combination of sorbents and target compounds (e.g., Ventura, Příhoda and Churáček, 1995). A very helpful resource in this respect is the list of breakthrough volumes of numerous compounds depending on the sampling temperature published on the Scientific Instrument Services website (Sisweb, 1996).

For specific purposes, parallel testing with two different techniques helps to reveal systematic over/underestimation of certain compounds (Salthammer and Mentese, 2008).

## 1.8 Artifacts and Interferences

### 1.8.1 Water Affinity—A Chromatographic Problem

The sampled air inevitably contains a certain amount of water. If water is retained by the sorbent used for sampling it can cause severe problems during gas chromatographical analysis: Formation of ice can lead to a clogging in ‘purge & trap’



**Figure 1.4** Simple selection scheme for a suitable sorbent under different conditions: Boiling point range, humidity of the air sample, desorption type. Please see text for other considerations (artifact formation, surface activity).

samplers and other cryo-focusing units. Water gives a high background noise level in GC–MS chromatograms and can thoroughly influence the signal of other detectors. It is also known to damage fused silica columns due to a hydrolysis of silicon film material at elevated temperatures.

Therefore, the solid sorbent should ideally have a low affinity to water, a characteristic easily met by the porous organic polymers. In contrast, the carbon-based sorbents and molecular sieves as well as some inorganic sorbents show a comparatively high uptake of water. If such sorbents are used in high-humidity environments special measures have to be employed to remove water during or after sampling. Possible methods are:

- dry-purging of the sampler with helium at low temperatures (loss of more volatile organics possible);
- increasing the sampling temperature (Gawrys *et al.*, 2001);
- pre-drying of the sample gas using for example, a Nafion-dryer.

Figure 1.4 shows a scheme to ease the selection of a proper sorbent and desorption considering the target compound range and the humidity of the air to be sampled.

### 1.8.2

#### Sorbent Degradation Products and Sorbent Background

Nowadays solid sorbents can be bought pre-cleaned and less effort is required before the first use. Nevertheless, all sorbents have to be cleaned thermally or by extraction to remove contaminants that formed during production, shipping or storage. For inorganic and carbon-based sorbents this is most easily accomplished by heating

in an inert gas stream (He, N<sub>2</sub>) for some hours, an additional deactivation step may be required for silica gels, magnesium silicates or aluminum oxides depending on the favored use. Tenax can be thermally cleaned as well (280–300°C, 1 h in He or N<sub>2</sub> stream), but the purity of the inert purge gas should be high, otherwise artifact formation can happen with this sorbent if traces of oxygen are present.

Most of the other polymers show only limited thermal stability, so it is recommended that they be cleaned by solvent extraction and dry purging with pure nitrogen.

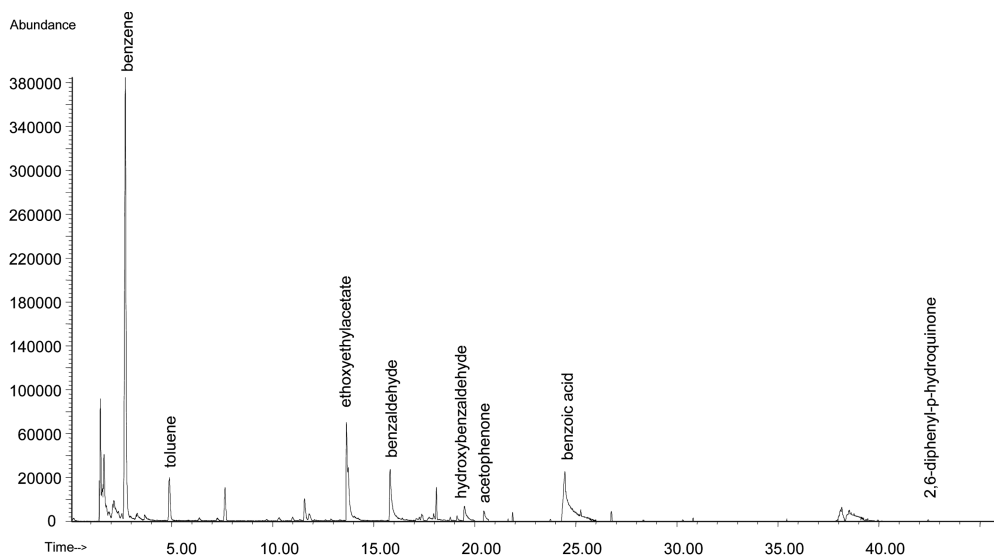
After cleaning, the samplers should be stored tightly sealed and protected from light. Refrigerated storage of the unused samplers is in most cases not required and should be avoided since standard refrigerators can be sources of contaminations. If cold storage is required between sampling and analysis, special attention should be directed to proper sealing of the tubes.

Almost all of the presented solid sorbents show a kind of background emission after a certain period of time. This is due to thermal or photochemical degradation of the sorbent material. Moreover, many sorbents can react with certain adsorbed compounds or reactive gases like O<sub>2</sub>, O<sub>3</sub> or NO<sub>x</sub> and reaction products will show up in the analysis (Hanson *et al.*, 1981; Clausen and Wolkoff, 1997; Klenø *et al.*, 2002).

As long as the degradation products of a used sorbent are known and do not interfere with the collected sample compounds, the sorbent degradation itself is not an analytical problem. But often, especially if the compounds to be sampled are not known in advance, it is difficult to determine whether, for example, benzene is a blank of the used sorbent Tenax TA or a compound trapped from the air sample. Figure 1.5 shows a chromatogram obtained from a glass sampling tube filled with Tenax TA and stored in daylight for two weeks. It presents the important substances to be expected as Tenax blanks. Helmig (1996) suggests methods to avoid such sorbent background peaks. Other adsorbents show a specific background as well, Tirkkonen, Mroueh and Orko (1995) present a compilation of compounds that were found under thermal desorption conditions for seven carbon-based and porous polymer sorbents.

Figure 1.6 presents an example for the formation of a reaction product on the surface of a sorbent. The result of a solvent extraction of activated charcoal with CS<sub>2</sub> and CS<sub>2</sub>/methanol, respectively, shows quite different artifact formation after a 48-hour storage period. Four new compounds could be found in the sample containing methanol as a desorption agent. All of them could be identified as substances formed by the reaction of CS<sub>2</sub> and methanol in the presence of activated charcoal.

The blank problem becomes more severe when volatile organic compounds are sampled in the presence of reactive gases. Pellizzari *et al.* (1984) and Zielinska *et al.* (1986) showed the influence of different reactive inorganic gases on the decomposition of Tenax GC and showed possibilities to protect the adsorbent with mild reduction agents. Clausen and Wolkoff (1997) tried to use the amount of degradation products formed on Tenax as an indicator for the presence of reactive species in indoor air. Helmig (1997) reviews techniques to reduce the adverse effect of ozone on sampled VOCs.



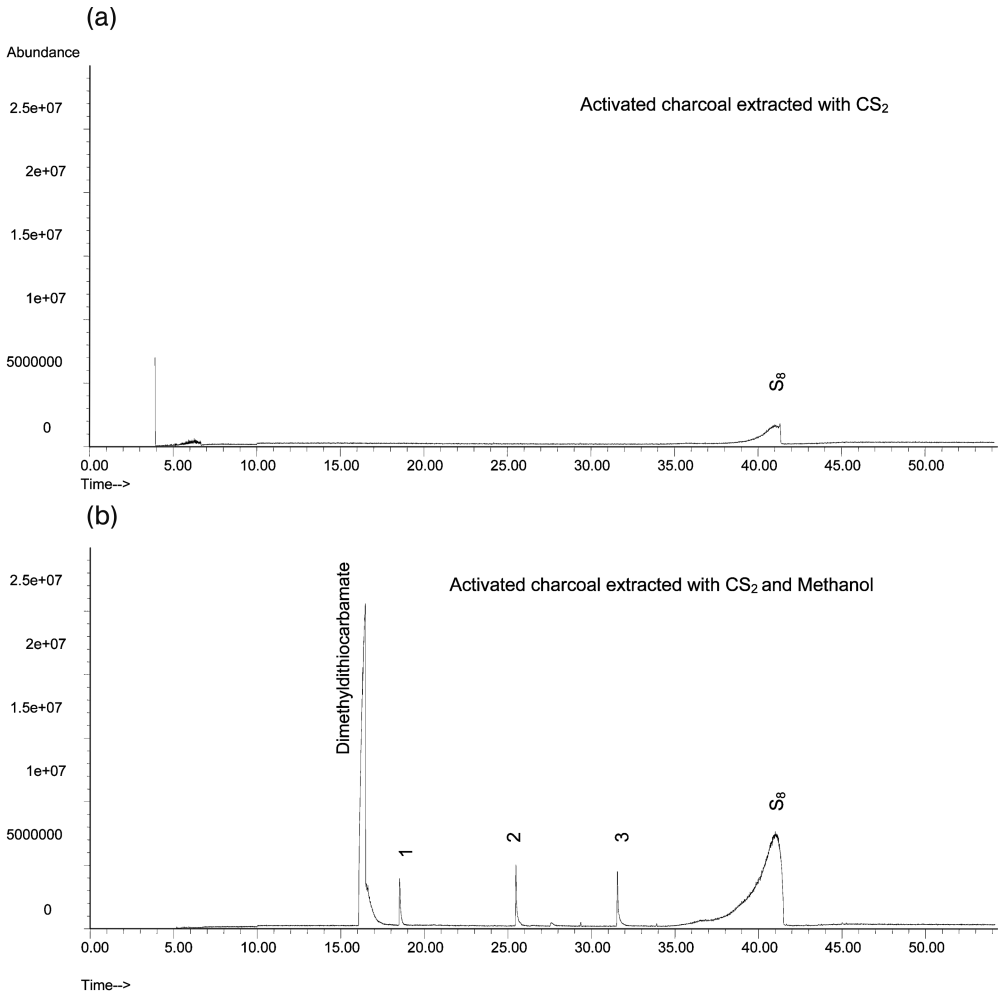
**Figure 1.5** Background of Tenax TA after cleaning and a 2-week storage period. Ethoxyethyl acetate is emitted from the tube cap O-ring.

While for most routine applications (e.g., chamber tests, field sampling in buildings) solid sorbent tubes can be used without having to consider most of these points, it is still important to emphasize the need to tailor the sampling tubes for more special cases, for example, during chamber testing of electronic devices or air cleaners, or during field sampling at sites exposed to sunlight and/or traffic. In the first case additional sampling with carbon-based tubes might be required to avoid ozone-related artifacts (benzene, benzaldehyde) from Tenax TA. In the latter case, the presence of both reactive gases (ozone,  $\text{NO}_x$ ) and labile compounds (terpenes, unsaturated hydrocarbons, aldehydes) requires some pilot testing to find out which sorbent delivers the best performance under the given conditions.

### 1.8.3

#### Target Compound Degradation and Artifact Formation

Whenever organic compounds of limited stability are exposed to high temperature, reactive chemicals (liquids or gases) or active surfaces, degradation and the formation of artifacts is possible. When employing solid sorbents the sampling/storage step as well as the extraction/analysis step may lead to degradation of analytes. Coeur *et al.* (1997) reported the degradation of  $\alpha$ -pinene and sabinene on Tenax and Carboxene. Several other terpenes (camphene, limonene, cymene, terpinolene) were formed as artifacts. The degradation of organo-sulfurous compounds during thermal desorption was studied by Baltussen *et al.* (1999) for several sorbents.



**Figure 1.6** Background of activated charcoal after extraction (a) with CS<sub>2</sub> and (b) CS<sub>2</sub>/Methanol. 1, 2 and 3 are condensation products of CS<sub>2</sub> and methanol.

Especially when long-term storage of samples is required the monitoring of analyte degradation is of special interest (Volden *et al.*, 2005).

## 1.9 Conclusions

Solid sorbents offer a convenient way to enrich the contents of an air sample. The variety of sorbents currently available allows the sampling of gaseous compounds from VVOCs to SVOCs. However, none of the existing sorbents is capable of



retaining all compounds, so either a combination of adsorbents with different characteristics (multi-bed tubes) or one sorbent specially chosen for the actual analytical problem has to be used.

Although new techniques of analyzing VOCs like sensor systems and online mass spectrometers have been introduced in the last decade, the use of solid sorbents in combination with thermal desorption and gas chromatographic separation still seems to be the preferred method due to the sensitivity, selectivity, convenience of use and the reliability that has been proven over the years.

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