

# Sampling of volatile terpenes in indoor air

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## ABSTRACT

Monoterpenes are substances commonly found in indoor air, they are released by wood products or certain consumer products that contain scents. Depending on the type of source the concentrations of the volatile monoterpenes (e.g.  $\alpha$ -pinene, limonene) can easily exceed  $1000 \mu\text{g}/\text{m}^3$ . In indoor air samples these substances are usually analysed together with other volatile organic compounds by thermal desorption GC/MS or thermal desorption GC/FID, with Tenax being the preferred solid sorbent for the collection of the air samples. After noticing a certain breakthrough of limonene during field measurements, a number of experiments to study the breakthrough behaviour of several monoterpenes were carried out. Standard Tenax tubes were used for sample collection, both gas phase sampling and liquid spiking of the target compounds were used. Significant breakthrough of  $\alpha$ -pinene and  $\beta$ -pinene was determined for air concentrations larger than  $600 \mu\text{g}/\text{m}^3$  on standard Tenax TA filled sampling tubes. As expected, the sampling volume was found to be an important factor for the breakthrough rate. Some experiments were carried out to assess the distribution of several substances in the tube during the sampling process; additionally improvements to sorbent tubes by adding another sorbent type were tested and the results are discussed.

## INDEX TERMS

Terpenes; Sampling; VOC; Desorption

## INTRODUCTION

The low boiling monoterpenes are well-known indoor air pollutants. The main sources of this group of compounds are wooden furniture and wooden panels, especially items made of fresh spruce or pine, but they are also in widespread use as solvents in paints. Other sources of these substances in the indoor environment are various household products, where they are used as fragrance producers/odourizers. Despite their comparatively pleasant odour, the effects of at least some of the terpenes ( $\Delta^3$ -carene, longifolene) for indoor air quality are in discussion. Additionally, the health effects of reaction products of terpenes with active species like ozone, nitrogen oxide or radicals under indoor conditions (indoor chemistry) is nowadays being evaluated and first results (Wolkoff *et al.*, 1999; Salthammer, 2000) indicate that reaction products like pinenoxide, pinonaldehyde, caronaldehyde or limonenoxide are stronger airway irritants than the terpenes.

Of the different methods existing to assess the variety of organic compounds in indoor air many involve the preconcentration of airborne substances on a solid sorbent and thermal or solvent desorption of the collected compounds prior to a GC analysis. Although the trapping of monoterpenes (but not of their oxidation products) is possible on active charcoal or carbon-based sorbents, nowadays the use of Tenax is most widespread due to its many beneficial properties, namely the high thermal stability, the low background noise (Tirkkonen *et al.*, 1995) and the good sorption/desorption properties. The retention volumes for many non-polar organic compounds are excellent at room temperature and decrease rapidly at elevated temperatures, a fact that encourages the application of thermal desorption techniques with this sorbent.

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Since the composition of an air sample is often unknown at sampling time, the use of Tenax as a sorbent is a good choice to identify most of the compounds in the range of C6 to C16. For the same reason Tenax TA was chosen as the sorbent for the TVOC analysis procedure suggested by the European Community (ECA Report No. 19) and is described in the ISO standard 16000-6.

Terpenes are quite common compounds in the indoor environment and they too are often identified and quantified by use of Tenax sampling tubes—but experimental results presented in this article will show some drawbacks of the sorbent for the quantitative determination of the low-boiling monoterpenes.

## METHODS

Terpene standard substances in GC quality were used to produce the desired chamber air concentrations ( $\alpha$ -pinene,  $\beta$ -pinene,  $\Delta^3$ -carene: Fluka, Buchs; longifolene, myrcene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, p-cymene,  $\alpha$ -phellandrene, limonene, 1,8-cineneol, linalool, ocimene, *cis/trans*-carveol, eugenol, geraniol, farnesol, caryophyllene, longipinene: Aldrich, Weinheim). All experiments were carried out in a 23.5 l emission test chamber (dessiccator type) either statically (injection of a weighed amount of the terpene mixture in the sealed chamber) or dynamically (using a capillary emission tube and an air exchange rate of 1 h<sup>-1</sup>). Stainless steel tubes as well as glass tubes (Perkin-Elmer) were used for trapping and thermal desorption. The packing of the tubes is described for each experiment.

The used solid sorbents are Tenax TA (60/80 mesh, Chrompack), Carbotrap (60/80 mesh, Supelco), Carbosieve (60/80 mesh, Supelco), Chromosorb 106 (60/80 mesh, Chrompack) and XAD-4 (60/80 mesh, Supelco). The tubes were thermally desorbed with an ATD 400 thermal desorption unit (Perkin-Elmer) and analysed with a GC/MS-System (6890/5972, Hewlett-Packard) on a HP-5MS column (0.25  $\mu$ m, 60 m, Agilent Technologies).

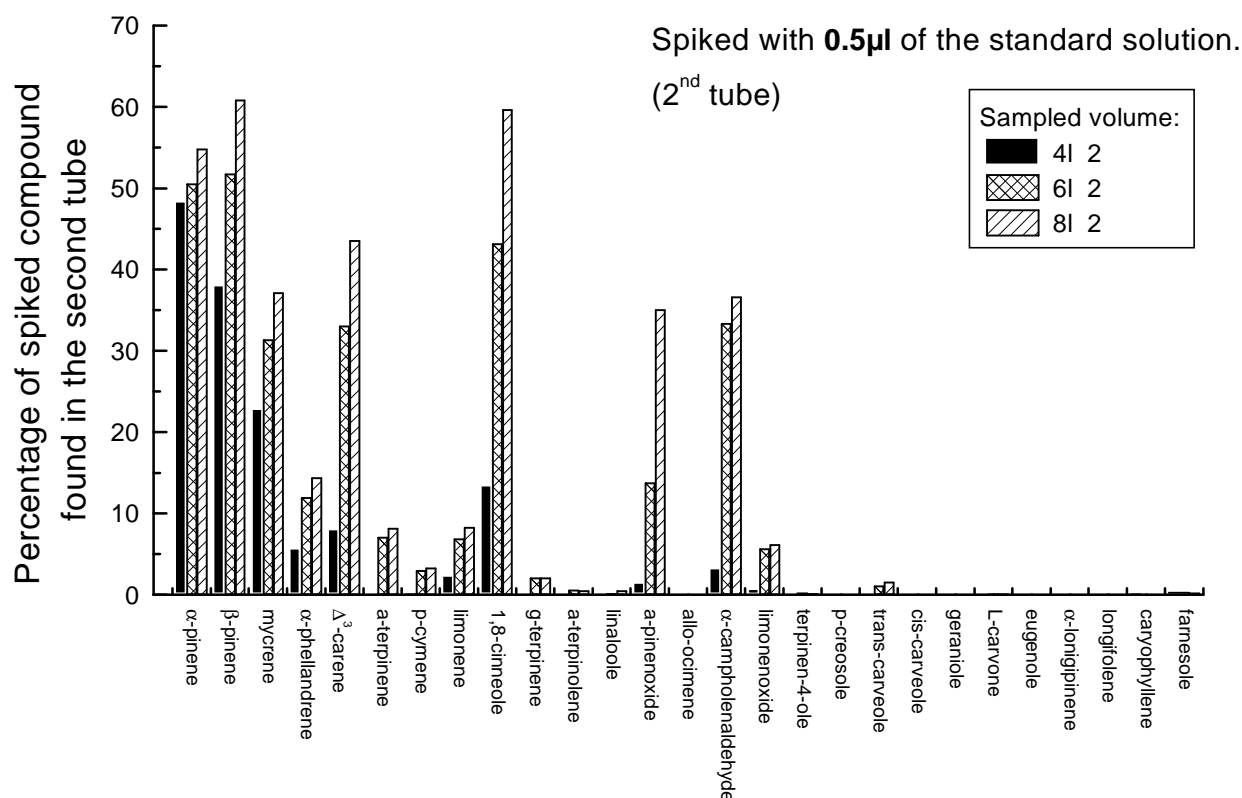
A temperature program optimized for terpenes was used: 34°C (5 min)  $\xrightarrow{4^\circ\text{C/min}}$  140°C  $\xrightarrow{8^\circ\text{C/min}}$  200  $\xrightarrow{20^\circ\text{C/min}}$  280 (4 min).

## RESULTS

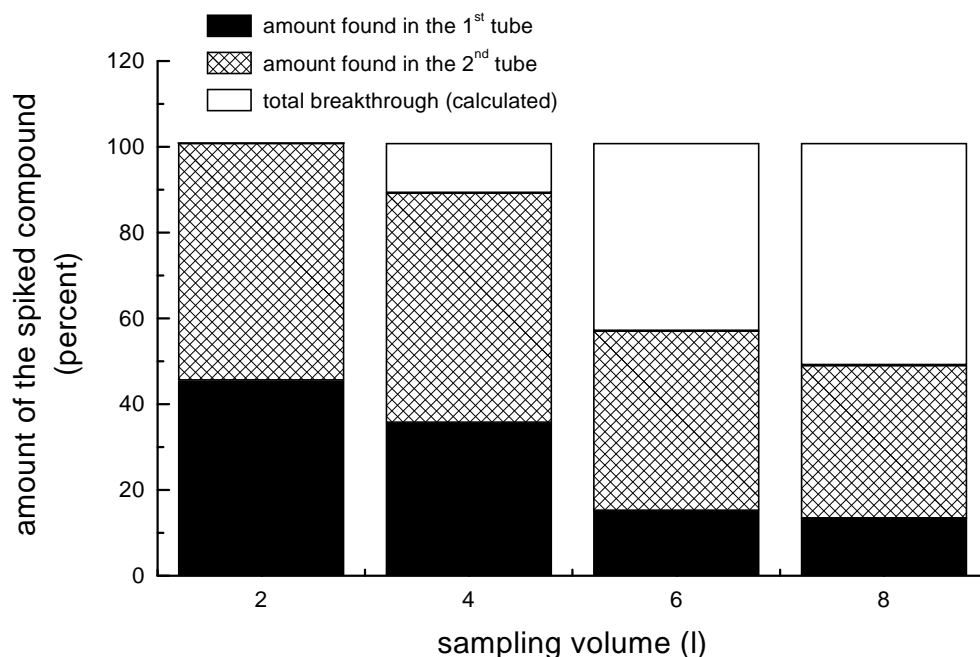
### Breakthrough Screening

To determine the breakthrough capabilities of the different terpenes Tenax tubes (0.3 g Tenax TA in stainless steel tubes) were spiked with a methanolic solution of 29 terpenes commonly found in indoor air and the amount found in a backup -tube (see Figure 1) was measured for different sample volumes. The amount of each compound on the tube was 1250 ng (0.5  $\mu$ l standard solution) and 2500 ng (0.5  $\mu$ l standard solution), calculated air concentration for tubes spiked with 0.5  $\mu$ l and a sampling volume of 2–8 l would be 625–158  $\mu$ g/m<sup>3</sup>, respectively. The experiment proved a significant breakthrough of the most volatile monoterpenes  $\alpha$ -pinene,  $\beta$ -pinene, myrcene and 1,8-cineneol. Some other terpenes, namely phellandrene,  $\Delta^3$ -carene and  $\alpha$ -pinene oxide, showed less dramatic breakthrough in the range of 5–10%.

It is interesting to note that the amount of terpenes recovered from the second tube increases with rising sampling volume when the first tube is spiked with 0.5  $\mu$ l, but decreases when it is spiked with higher concentrations. This effect is due to a breakthrough in the second tube which leads to a complete loss of the lower boiling terpenes. The experiment was repeated with  $\alpha$ -pinene and the percentage recovered from the first and the second tube is shown in Figure 2. The total loss is calculated with the known amount of  $\alpha$ -pinene injected onto the tube. An increasing total loss is detectable.



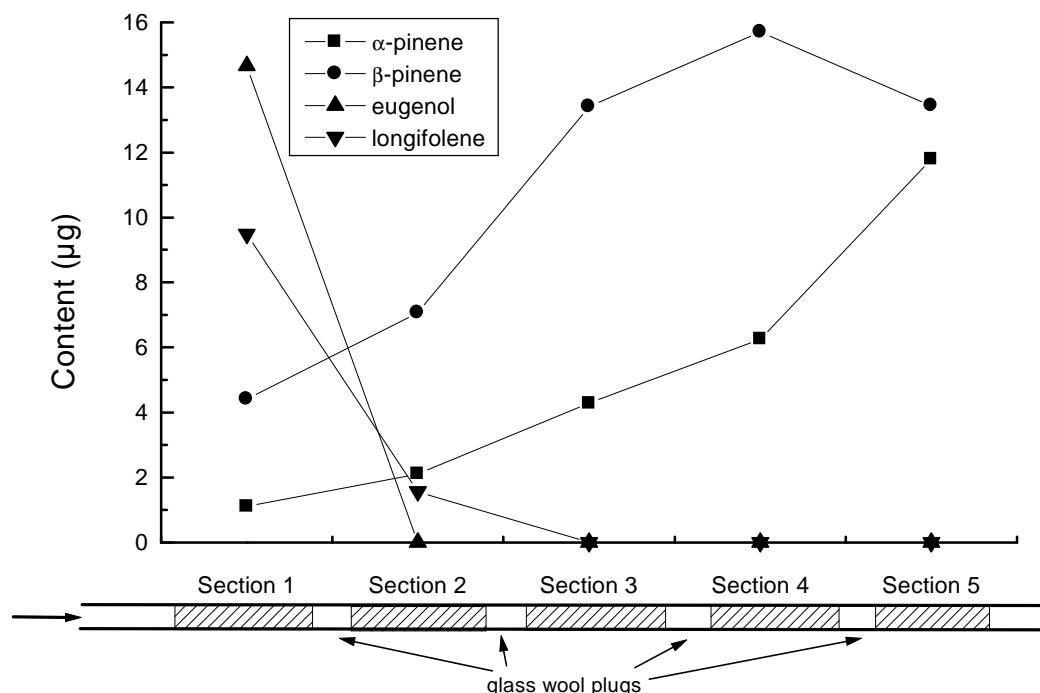
**Figure 1** Screening of different terpenes concerning breakthrough on Tenax TA.



**Figure 2** Dependency of the  $\alpha$ -pinene breakthrough on different sampling volumes.

When a compound has entered a sampling tube and is trapped on the sorbent, on further drawing of air through the tube it actually becomes a chromatographic system. The sorbent acts as the stationary phase, the air as the fluid phase: this effect has been visualized with a specially designed sampling tube, which contained five zones of Tenax TA, each separated with a glass wool plug. After spiking the tube with 1  $\mu$ l of a high-concentration mixture of  $\alpha$ -pinene,  $\beta$ -pinene, eugenol and longifolene a total volume of 2 l of clean air was drawn through the tube. Each zone was then transferred into standard glass sampling tubes and the terpene

content was determined by thermal desorption GC/MS. Figure 3 shows the results of such an experiment.



**Figure 3** Distribution of some terpenes in a Tenax tube. Sampling direction as marked.

The results show that a kind of 'chromatography-in-the-tube' occurs, a major part of  $\alpha$ -pinene has already left the tube, whereas eugenol is still retained exclusively in the first section. For  $\beta$ -pinene the formation of a 'peak' is visible.

### Experiments with Multibed Tubes

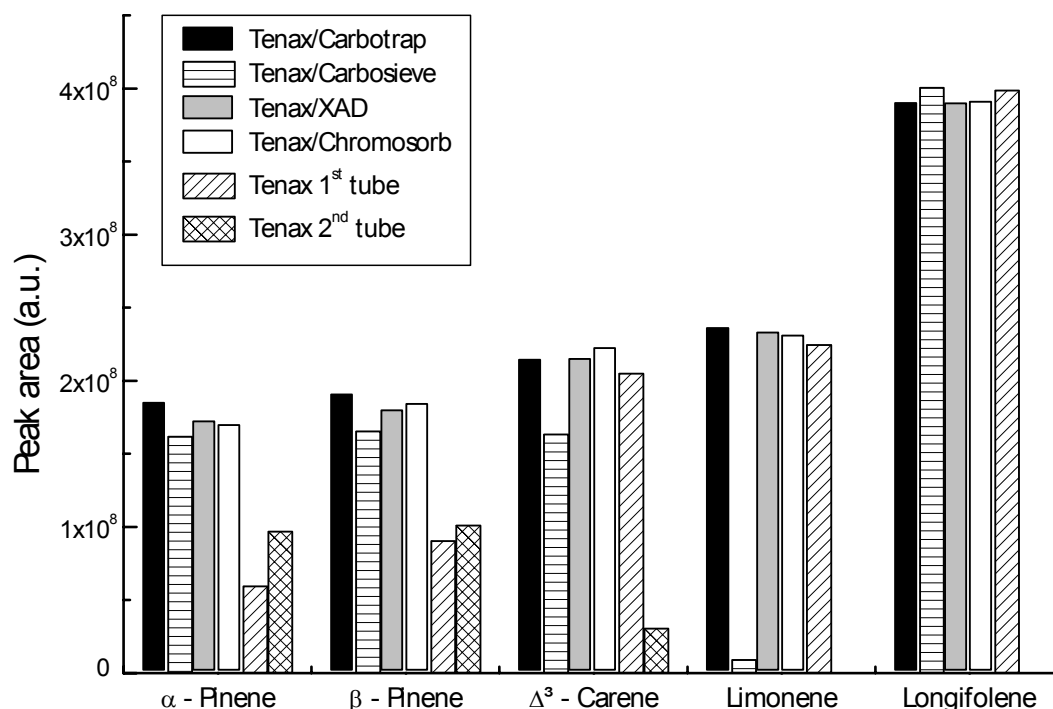
Multibed tubes are a means to overcome the limitations of a certain sorbent by adding a second (and sometimes a third) one. They have been successfully used to quantitatively trap some VVOC and VOC in one sampling step. Adding a second, more active sorbent to a tenax tube may increase the breakthrough rate of certain volatile substances significantly. Unfortunately, the negative properties of two sorbents also add up, e.g. Tenax/XAD tubes can only be heated to up to 220°C, Tenax/Carbosieve tubes will collect significant amounts of water. The blank signal of a multibed tube will be dominated by the least stable sorbent. It is thus important to point out that although multibed tubes can greatly improve the sampling performance for certain substances, the versatility of such tubes for a wide range of compounds might be reduced compared to a single bed tube. Figure 4 shows results of some experiments with multibed Tenax tubes, the signal intensity found in a backup tube after the single-bed Tenax tube is also presented.

Both carbon-based and porous polymer sorbents were successfully used to enhance the breakthrough volume for some terpenes.

### Carbon-based Sorbents

While almost all the tested carbon sorbents reduced the breakthrough of monoterpenes through the tube significantly, only Carbotrap led to an improved recovery rate. The desorption of terpenes from carbon-based sorbents is sometimes difficult, the recovery rates are often poor (e.g. less than 8% limonene from Tenax/Carbosieve). Artefact formation during thermal desorption of less stable terpenes is described by several authors (Rothweiler *et al.*,

1991). Mainly decomposition reactions (alpha pinene to isoprene), rearrangements (alpha pinene to beta pinene) and oxidations (limonene to limonenoxide) are described.



**Figure 4** Breakthrough experiments with different multibed tubes.

No such artefact formation could be observed during the use of the tubes with a second sorption zone, even at high terpene concentrations. Probably other factors are also controlling the artefact formation.

### Porous Polymer Sorbents

The main advantage of porous polymer sorbents is the weaker interaction between the sorbent and the analyte, thus allowing the thermal desorption of compounds which would decompose on carbon-based sorbents. Unfortunately, these sorbents often show a higher background signal and a lower thermal stability. While the background noise (although it often has a negative influence on the detection limits) can be dealt with by careful preconditioning, a low thermal stability definitely reduces the range of compounds to be analysed with this sorbent: The thermal desorption temperature should ideally exceed the boiling point of the least volatile compound by 20°C. For this reason the porous polymer sorbents like Chromosorb and XAD are limited for trapping compounds with boiling points of less than ~220°C. Tenax TA, with a thermal limit of 350°C, is therefore one of the most widely used porous polymer sorbents.

### DISCUSSION

A significant breakthrough of the most volatile monoterpenes could be detected on Tenax TA. α-Pinene and β-pinene showed a breakthrough of 45 and 30%, respectively. For the higher boiling monoterpenes Δ<sup>3</sup>-carene and limonene the breakthrough was less than 5%.

An underestimation of the volatile monoterpenes during VOC sampling can therefore be expected to occur at higher air concentrations. During emission testing air concentrations of 800–1000 μg/m<sup>3</sup> were found to be sufficient to detect a measurable breakthrough with 3-l samples. If bigger samples are collected, breakthrough may even influence measurements of

concentrations below 500  $\mu\text{g}/\text{m}^3$ . The use of backup tubes or the collecting of two independent tubes with different sample volumes is therefore highly recommended.

In this context a selection of suitable sorbents is once again an important question for VOC analysis. The breakthrough problems can also be solved by either reducing the temperature of the tube during sampling or increasing the amount of sorbent used in the sampling tubes. Unfortunately, the temperature reduction is most often only possible in laboratory tests and not applicable for field tests. The use of a larger amount of Tenax is limited by the tube length/diameter which is used for the thermal desorption unit.

Using a second sorbent in a multitube tube is an appropriate way to enhance the suitability of a Tenax tube, but it should be noted that, apart from the Tenax/Carbotrap combination, all tested multitube tubes had serious disadvantages, regarding either the thermal stability/background noise or recovery rate considerations. In cases where only volatile terpenes are to be analysed, XAD or Chromosorb are good choices as sorbents.

## CONCLUSIONS AND IMPLICATIONS

As a consequence of these experiments multitube (Tenax/Carbotrap) tubes have been successful in use at WKI for 4 years to sample terpenes and other VOC in chambers and in the field. These tubes will also enhance the collection of other volatile hydrocarbons (e.g. pentane). No formation of artefacts during sampling of sensitive substances could be detected.

## ACKNOWLEDGEMENTS

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