Comparison of Tenax and Carbotrap for VOC Sampling in Indoor Air

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Abstract

The most important features of Tenax and Carbotrap, solid sorbents used widely for sampling organic pollutants in air, have been tested under the conditions requested for surveys in indoor spaces and for determinations of VOC emitted from indoor sources by chamber experiments. The performances of samplers, tested with 10 nonpolar and polar (mostly lipophilic) hydrocarbons, present as vapours in 0.5 to 2.0 litre air samples, include: (a) accuracy and reproducibility of the measured concentration, (b) background or "blank" of samplers, (c) stability upon storage (at ambient and below ambient temperatures) of clean samplers and of samplers loaded with VOC, and (d) performance stability after several sampling desorption cycles. The results fulfil the requirements for both adsorbents, though each presents some different drawbacks. In particular (a) Tenax samplers show a "blank" (90 percentile) of 16 ng of benzene and 5 ng of toluene, Carbotrap samplers roughly twice as much; (b) the samplers may be stored for one month either before or after use and (c) they may withstand many cycles without discernible deterioration.

Introduction

The most common technique for sampling volatile organic compounds (VOC) in air is retention on solid sorbents. Adsorption on activated charcoal and desorption by solvent elution has been the preferred choice of most analysts in the past. The sensitivity of this method suffers, however, from the dilution of the sampled compounds in the solvent; only a small fraction of the eluent, i.e. of the sampled compounds, can be used for gas chromatographic analysis. Whereas the limited sensitivity of the method has not been a problem for industrial hygiene applications where only relatively high pollutant concentrations are of concern, environmental applications require the sampling of large air volumes in order to detect much lower concentrations. Over the past two decades, however, adsorbents have become available from which VOC may be thermally desorbed; the entire amount of collected pollutants can thus be made available for a single analysis, yielding a considerably higher sensitivity. Therefore thermal elution is more widely adopted for environmental analysis of VOC. The availability of commercial devices performing thermal desorption-injection and cold trap focusing contributed to this change.

Another important improvement in the sensitivity of environmental VOC analysis was made by the replacement of packed columns with open tubular capillary columns, with a highly increased separation. The combination of thermal desorption and capillary columns brought about a drastic reduction in the volume of air required for the analysis, with a corresponding decrease in sampler size (from 2 g or more to 100 mg for Tenax).

Advantages and disadvantages of Tenax, the most commonly used absorbent that can be thermally eluted, have been evaluated in our laboratory in the past (Versino et al., 1974; Schlitt et al., 1979). The detected artifacts were due to an interaction of ozone and UV light with Tenax when sampling outdoor

air. Further reported artifacts (Pellizzari and Krost, 1984; Pellizzari et al., 1984) refer also to outdoor air sampling. However, criticism regarding the reliability of Tenax sampler when tested with calibrated VOC mixtures, in particular a high scattering of the results and a bias towards certain compounds, has been published (Crist and Mitchell, 1986). On the other hand, comparing concentrations obtained by sampling different air volumes on Tenax in a test house, as proposed by Walling (1984), showed perfectly consistent data (Spicer, 1986).

In view of these somewhat contradictory experiences we decided to perform a series of experiments aimed at assessing the reliability of Tenax and of Carbotrap – a more recently introduced adsorbent, which has been used as an alternative to Tenax – for VOC sampling in indoor air. Some limitations of Carbotrap, concerning quantitative recovery of certain compounds, have already been reported (De Bortoli et al., 1989). The experiments described here have been performed mostly with nonpolar but also with some polar lipophilic hydrocarbon compounds. Experiments with a mixture of polar hydrophilic compounds will be published separately. The different experiments are briefly outlined in the following section. Experimental details are given in the section "Methods".

Experimental Design

The *accuracy and reproducibility of VOC sampling* and analysis were assessed using two different types of gas text mixture: a dry cylinder mixture obtained by dilution of known amounts of five compounds in GC grade nitrogen, and environmental chamber mixtures consisting of humidified zero air to which 10 compounds were added using permeation devices. The second is believed to be a good model of indoor air. Comparison of the results obtained with both mixtures was aimed at revealing a potential influence of humidity and of a sink effect in the environmental chambers on sample analysis.

The cylinder mixture contained five nonpolar, lipophilic compounds: benzene, n-heptane, toluene, 1,3-xylene and n-decane. The concentrations of the individual compounds ranged from about 15-50 ng/l (see Table 1).

The compounds contained in the chamber atmospheres are shown in Table 2 in GC elution order. The selection of these compounds was based on the following criteria: they are representative of classes of nonpolar and polar lipophilic compounds typically occurring in indoor air (only 1-butanol was added as a hydrophilic compound) and some of them have been included in earlier investigations mentioned above (Crist and Mitchell, 1984; Walling, 1984). The expected chamber concentrations (calculated from the weight loss of the diffusion vials and the carrier gas flow rate) are also given in Table 2 and ranged from approximately 15 µg m^{-3} for α-pinene to 170 µg m^{-3} for tetrachloroethene. Bromopentane (only for experiments with the stainless steel chamber) entered the sampling manifold without flowing through the test chamber and was used as an internal standard.

In order to assess any bias introduced by the operator or any irregular performance of the analytical instrumentation, test mixtures were always sampled by three operators using three different GC instruments. Moreover, each operator repeated each measurement with a second sampler yielding a total of six measurements for each test. Samples from the environmental test chambers were always taken simultaneously by the three operators.

Two different air volumes (0.5 litre and 2.0 litres) were sampled from each test atmosphere in order to detect any breakthrough, i.e. incomplete retention on the sampling tubes. The selection of the two

Table 1 Concentrations of test compounds in cylinder air determined by sampling on Tenax and Carbotrap

Compound	Tenax					Carbotrap					rel. difference [%] between mean concentrations measured with Carbotrap and Tenax samplers	
	0.5 l air sample		2 l air sample		rel. difference of means [%]	0.5 l air sample		2 l air sample		rel. difference of means [%]	0.5 l air samples	2 l air samples
	mean [ng/l]	RSD [%]	mean [ng/l]	RSD [%]		mean [ng/l]	RSD [%]	mean [ng/l]	RSD [%]			
benzene	52.9	6.7	53.3	4.1	0.8	66.0	15.6	54.2	3.5	19.6	22.0	1.7
n-heptane	42.2	2.2	43.7	6.5	3.5	41.0	9.7	45.6	2.9	10.6	2.9	4.3
toluene	29.2	3.6	30.5	6.0	4.3	33.0	8.4	31.8	3.5	3.7	12.2	4.2
1,3-xylene	14.2	6.5	15.0	5.3	5.5	17.5	9.7	16.1	4.7	8.3	20.8	7.1
n-decane	14.2	7.2	14.5	3.7	2.1	14.4	8.8	15.5	3.5	7.3	1.4	6.7
average	–	5.2	–	5.1	3.2	–	10.4	–	3.6	9.9	*11.9*	*4.8*

sample volumes was made in order to cover the range of sample volumes which in our laboratory are used for indoor air monitoring and for the analysis of vapours emitted from materials in test chambers, 1 litre being the normally used sample volume.

Capillary columns with methylsiloxane coatings (OV 1) were used for all analyses. These nonpolar columns have excellent chromatographic performance for all of the selected lipophilic test compounds.

The *background* from freshly cleaned Tenax and Carbotrap sampling tubes and its stability upon storage of the cleaned tubes has been analysed. Moreover, the *stability upon storage* of samples of the chamber atmosphere collected on both adsorbents has been investigated and some experience with the *repeated use of samplers* is reported.

Methods

Sampling of Cylinder Atmosphere
VOC were sampled from the cylinder by direct attachment of the samplers, regulating the sample flow by a needle valve. The sampled air volumes were determined by displacement of water out of a container and weighing the displaced water (0.5 litre volumes) or by an integration gas counter (2 litre volumes).

Sampling of Chamber Atmospheres
Atmospheres containing nine lipophilic compounds and 1-butanol (see Table 2) were prepared by means of calibrated diffusion sources. These consist of 2-5 cm^3 vials with a septum cover through which a stainless steel capillary of appropriate diameter and length is inserted to obtain the desired source strength, which is determined by regularly weighing the vials. The calibrated sources are placed in an aluminium container, flushed by a small flow of zero air, carrying the vapours into the chamber. A variable split on this line enables the selection of the fraction entering the chamber and, hence, control of the concentration therein. Two environmental chambers with glass walls (0.45 m^3, see Colombo et al. 1990), and an electropolished stainless steel cham-

Table 2 Concentrations of a test mixture [µg/m³] in chamber air determined by sampling on Tenax and Carbotrap

Compound	Samplers	0.5 l air samples		2.0 l air samples		expected		$\frac{2.0\,l - \text{expected}}{\text{expected}} \times 100$
		mean[1]	RSD [%]	mean[1]	RSD [%]	mean[2]	RSD [%]	[%]
1-butanol	Tenax	17.3	25.6	17.0	8.3	21.2	6.2	−19.8
	Carbotrap	10.6	42.7	14.9	12.5			−29.7
toluene	Tenax	88.8	5.6	90.7	5.7	87.8	10.9	3.2
	Carbotrap	91.0	10.4	93.1	3.4			6.0
tetrachloro-ethene	Tenax	166	6.0	178	5.7	170	1.6	4.7
	Carbotrap	172	12.2	183	3.4			7.7
bromopentane	Tenax	485	10.5	495	13.1	483	0.9	2.5
	Carbotrap	464	19.5	505	10.8			4.6
ethylbenzene	Tenax	26.9	10.0	28.1	5.5	29.0	2.5	−3.1
	Carbotrap	27.1	12.9	29.2	3.5			0.7
n-nonane	Tenax	20.4	20.4	22.0	4.8	24.1	2.4	−8.7
	Carbotrap	19.9	17.6	22.9	4.4			−5.8
bromobenzene	Tenax	55.3	6.7	58.6	5.5	69.5	1.3	−15.7
	Carbotrap	57.6	11.8	60.5	4.0			−13.0
α-pinene	Tenax	15.9	6.2	16.9	4.8	15.3	5.6	10.5
	Carbotrap	15.1	13.7	17.6	6.2			15.0
1,4-dichloro-benzene	Tenax	16.0	14.7	15.6	4.8	19.7	2.8	−20.8
	Carbotrap	18.5	25.3	17.1	9.2			−13.2
n-decane	Tenax	18.2	9.9	22.1	5.5	21.4	3.5	3.3
	Carbotrap	18.3	14.5	22.6	5.2			5.6
average	Tenax	-	11.6	-	6.4	-		9.2
	Carbotrap	-	18.1	-	6.3		3.8	10.1

[1] three operators, each analysing two samplers for a total of six;
[2] derived dividing the weight loss rate (five weekly weighings) of the diffusion vials by the airflow rate.

ber (0.28 m³ capacity) with a sampling manifold on the outlet were used. The chambers were supplied with "zero" air to which the vapour mixture was added as described above and were operated at 23 °C and 50% relative humidity.

VOC were sampled from the environmental test chambers using constant flow pumps or peristaltic pumps. A sampling flow between 100 and 200 cm³/min was used. Previous experience in our laboratory had shown that in this flow range adsorption is quantitative. The sampled air volumes were measured with integrating gas counters or by bubble flowmeters. When a direct comparison of adsorbents was made, air samples were collected simultaneously with the different samplers at the sampling manifold of the chamber.

Preparation of Sampling Tubes

The following adsorbents were tested: Tenax TA 60-80 mesh (Chrompack, Middelburg, Netherlands) and Carbotrap 20-40 mesh (Supelco Inc., Bellefonte PA, USA). The adsorbents were contained in glass tubes, 160 mm length, 6 mm o.d., 3 mm i.d., filled up to about 8 cm with the adsorbent, which corresponds to about 100 mg for Tenax and 200 mg for Carbotrap. Some tests were carried out with glass tubes of 100 × 6 mm containing the same adsorbent quantities. The Tenax used was from one lot or batch only, whereas Carbotrap from different lots was used; differences observed are reported in the next section. The adsorbent was held in place with metal grids (described later) or silanized glass wool "pesticide grade". The samplers were cleaned by heating overnight at 280 °C (Tenax) or 350 °C (Carbotrap), under a flow of helium roughly 10 cm³/min. More details (e.g. on sampler conservation) are given in the following section.

Thermal Desorption

Most samplers were desorbed using the thermodesorption-cold-trap-injector model TCT produced by Chrompack (Middelburg, Netherlands), working with 160 × 6 mm sampling tubes. Some analyses were carried out using the TDAS 5000 thermal desorption autosampler produced by Carlo Erba Strumentazione (Rodano, Milano, Italy) and designed for 100 × 6 mm sampling tubes. Desorption time was 20 min and desorption temperature 250 °C for Tenax and 330 °C for Carbotrap. Cryofocusing was carried out at –120 °C and the trapped compounds were injected into the GC column by heating the trap to 250 °C.

Analysis

The analyses were carried out by capillary GC-FID with 25 m × 0.32 mm OV-1 fused silica columns. Quantification based on the internal standard turned out to yield larger standard deviations than using external calibration with the test mixture; consequently the quantification of compounds was based on the comparison with liquid test mixtures (methanol as solvent), of which 1 µl was deposited on a sampler. The solvent was removed by purging the sampler with ≃ 100 cm³ of helium.

Whenever the parameter TVOC (= total volatile organic compounds) is reported, this refers to the sum of all the GC peaks, recorded by the FID detector, with a retention time greater than or equal to that of n-hexane, transformed into a concentration using the toluene response factor.

In order to test the stability of the vapour concentrations in the chamber and the overall analytical reproducibility obtained by a single operator using a single instrument, eighteen 2-litre air samples were collected and analysed in the course of eight days with the following result: out of the ten compounds (Table 2), six showed a standard deviation of 3.3% or smaller, two between 3.3% and 4.7% and two (1-butanol and 1,4-dichlorobenzene) up to 9.4%.

Results and Discussion

Analysis of the Cylinder Atmosphere

The aim of this first test was to assess and compare the reproducibility of Tenax and Carbotrap sampling for nonpolar compounds in the absence of water. Results are summarized in Table 1. For the two-litre samples, the relative standard deviations of the six concentration measurements are low for all compounds and slightly lower for Carbotrap (mean 3.6%, range 2.9-4.7) than for Tenax (mean 5.1%, range 3.7-6.5). Moreover, the measured mean concentrations on the two adsorbents agree well with each other (mean difference 4.8%, range 1.7-7.1; see last column in Table 1).

For the 0.5 litre samples Tenax performs significantly better than Carbotrap; the standard deviations of the mean concentrations measured for the five compounds are on average for Tenax half as high as for Carbotrap (5.2% compared to 10.4%) and the mean concentrations measured for the two sample volumes differ for Tenax on the average by 3.2% (range 0.8-5.5) and for Carbotrap by 9.9% (range 3.7-19.6). The largest differences occur for benzene which for both sorbents contributes the most to

Table 3 Background emission of freshly cleaned samplers [ng/sampler]

Compound	Tenax (~100 mg, 23 samplers) percentile			Carbotrap (~200 mg, 44 samplers) percentile		
	50	90	100	50	90	100
benzene	5.6	16	20	11	30	67
toluene	1.9	5.0	14	2	8	87
TVOC[1]	9.6	30	93	15	45	106

[1] Sum of the FID signal counts of all peaks eluting after and including n-hexane, divided by the response factor of toluene

sampler blanks. In absolute terms, however, the amount of benzene eluting from a clean Carbotrap sampler is twice as high as from a Tenax sampler. As reported in Table 3 below, the 50 percentile of the benzene background concentration for Carbotrap is 11 ng/sampler and for Tenax 5.6 ng/sampler compared to about 27 ng of benzene in the 0.5 litre samples of cylinder air. This observation suggests that the somewhat higher blank values of Carbotrap are the main reason for its greater scattering at small sampling volumes for benzene (no background or blank values have been subtracted from the measured concentrations).

Apart from this limitation for Carbotrap, however, the results confirm a good reproducibility for sampling nonpolar hydrocarbons from a dry atmosphere on Tenax and Carbotrap.

Analysis of the Chamber Atmosphere

In order to test the two sorbents for a wider range of pollutants and under more realistic conditions, chamber tests with the mixture shown in Table 2 were performed at a relative humidity of 50%. Again, on each sorbent six samples of 0.5 litre and of 2 litres were collected. Three samples were always taken simultaneously as described above.

The results of these measurements are reported in Table 2. The reproducibility of the measurements in terms of their relative standard deviation (RSD) for the 2 litre sample is about 6% or better, except for 1-butanol, bromopentane and 1,4 dichlorobenzene (the latter only on Carbotrap) and on average the same for Tenax and Carbotrap (6.4% and 6.3%). Compared to the reproducibility of the cylinder samples, these values are on average only slightly higher for Tenax (6.4% vs 5.2%) and somewhat more for Carbotrap (6.3% vs 3.6%).

The chamber concentrations determined from the 0.5 litre samples are considerably less reproducible

for both Tenax and Carbotrap, but as for the cylinder samples, the RSDs are on average significantly higher for Carbotrap than for Tenax (18.1% vs 11.6%).

In the last column of Table 2 the test chamber concentrations as determined by the 2 litre samples are compared to the expected concentrations derived from the weight loss of the diffusion vials, the fraction of the compounds transferred to the chamber and the dilution in the airflow through the chamber. The two concentrations agree within ± 10% except for 1-butanol, bromobenzene and 1,4-dichlorobenzene, the measured concentrations of which are significantly ($p < 0.01$) smaller (13%-30%) than that expected. Insufficient retention by the sorbent cannot be the reason for these differences; results from a comparison of the concentrations determined by the 0.5 litre and 2 litre samples are not significantly different. There is also no significant difference between the concentrations and the apparent losses obtained with the two sorbents, except for 1-butanol determined on the 0.5 litre samples. In this case the loss for Carbotrap is significantly ($p < 0.05$) higher than for Tenax. This may be an indication of irreversible adsorption or reaction of 1-butanol on Carbotrap. The other observed losses may also be due to irreversible adsorption in the chamber or in the analytical system.

Background or Blank Emission of Tenax and Carbotrap Samplers

An important feature of samplers is their background or blank emission, i.e. the number and amount of compounds released from cleaned samplers upon thermal desorption, an emission which should ideally be zero. The lower this background emission, the more sensitive measurements can be made with a sampler. Two aspects have been investigated: (a) the background of freshly cleaned sampling tubes and (b) the period of time for which a cleaned tube can be stored without a significant increase of its blank emission under different storage conditions.

(a) Freshly Cleaned Sampling Tubes

Twenty-three freshly cleaned Tenax tubes and 44 Carbotrap tubes have been analysed. Benzene and toluene contribute most to the background of both sorbents. Whereas the structure of Tenax (polyterphenylether) suggests decomposition of the adsorbent as the origin of this background for Carbotrap, a graphitized carbon black, incomplete graphitization may be its origin. Table 3 reports for both sor-

bents the 50, 90 and 100 percentiles of the amounts of benzene, toluene and TVOC, thermally eluted from the freshly cleaned sampling tubes. The background from the Carbotrap tubes is higher and has a wider distribution than that of Tenax tubes. However, normalized to the same weight of adsorbent, only the maximum amounts of benzene and toluene eluted from the Carbotrap samplers are larger than those of the Tenax samplers. The results show anyway that the detection limit and error of benzene and toluene is increased by the background elution of both adsorbents, somewhat more for Carbotrap than for Tenax. For other compounds no significant limitation of this kind has been observed.

The distribution of the background values of Carbotrap samplers appears to depend on the history of the individual tubes rather than on characteristic differences between sampling tubes; the background emissions of one single tube determined 26 times after sampling different atmospheres showed a distribution which was strikingly similar to the distribution shown in Table 3.

Also for Carbotrap, significant quantitative differences of the background emission have been observed between different batches of the adsorbent: from one batch of Carbotrap, but not from others, n-undecane and n-dodecane were eluted in a characteristic ratio and both compounds could not be removed by repeated thermal elutions.

(b) Stability of the Background upon Storage

Six Tenax and six Carbotrap tubes after cleaning were stored for 55 days, three of each at room temperature and three at –15 °C. The samplers were capped with PTFE caps and enclosed in glass test tubes with screw caps and PTFE-lined rubber seals in order to reduce diffusion sampling from the storage environment (De Bortoli et al., 1989). The results are shown in Table 4. After about 8 weeks' storage at –15 °C the background of the three Tenax samplers agree well with the background distribution of freshly cleaned samplers, whereas the background of the Carbotrap samplers shows a slight increase. Upon storage at room temperature, all background values are significantly increased. As a result, it can be concluded that clean samplers should not be stored at room temperature, but that they may be stored for several weeks in a freezer at –15 °C without a significant increase of their background.

Storage Capability of Loaded Samplers

Samples of VOC taken in the field often cannot be analysed immediately; therefore it has to be determined whether storage of loaded samplers before analysis has an influence on the recovery of the sampled compounds. Therefore, six Tenax and six Carbotrap samplers were loaded with 1 litre of chamber air containing a similar mixture of compounds as used previously (and shown in Table 2). Of each set of six samplers, two were analysed immediately, two after 50 days' storage at room temperature and two after 50 days' storage at –15 °C. The results are reported in Table 5. Only some of the concentrations determined after 50 days' storage are significantly different from those determined immediately, but only at the 0.05 confidence level. They have been labelled by an asterisk. Of these, tetrachloroethylene (on Carbotrap) and n-nonane (on Tenax) are higher than the concentrations determined immediately after sampling, but only in the samples stored at room temperature. In view of the results obtained with blank samplers, these deviations may be caused by increased blank values of these compounds or of compounds coeluting during GC analysis.

Small but significant ($p < 0.05$) losses have been observed for ethylbenzene (Carbotrap, storage at –15 °C), Br-benzene (Carbotrap, storage at room temperature and at –15 °C), α-pinene (Tenax, room temperature) and n-decane (Carbotrap, room temperature). Of these, only the loss of ethylbenzene and Br-benzene has been observed at –15 °C and is acceptably low as can be seen from the standard deviations of all six concentration measurements reported in the last column of Table 5 (3.6% for ethylbenzene and 5.6% for Br-benzene).

Higher deviations occur for 1-butanol and α-pi-

Table 4 Background TVOC* released from Tenax and Carbotrap samplers after 55 days of storage

Room temperature		–15°C	
TENAX Sampler nr.	ng*/sampler	TENAX sampler nr.	ng*/sampler
1	189	4	43
2	203	5	6.9
3	115	6	1.8
CARBOTRAP sampler nr.	ng*/sampler	CARBOTRAP sampler nr.	ng*/sampler
1	219	4	27
2	102	5	65
3	386	6	70

* TVOC (see footnote of Table 3); roughly equivalent amounts are also detected in the chromatogram portion between time zero and the elution time of n-hexane

Table 5 Vapours adsorbed on Tenax and Carbotrap samplers analysed immediately after sampling and after 50 days' storage at room temperature and at –15 °C [µg/m³]

Compound	Sampler	Measured immediately		50 days at room temp.		50 days at –15 °C		Mean	RSD [%]
		sample 1	sample 2	sample 3	sample 4	sample 5[1]	sample 6		
1-butanol	Tenax	20.6	21.3	19.4	17.6	17.6*	18.3*	19.1	8.2
	Carbotrap	23.1	20.5	18.4	19.3	17.8	15.5	19.1	13.5
toluene	Tenax	212	223	237	241	228	232	228.8	4.5
	Carbotrap	230	227	245	239	232	235	234.7	2.8
tetrachloroethene	Tenax	441	462	488	489	467	473	470	3.8
	Carbotrap	471	474	514*	504*	489	480	488.7	3.5
Br-pentane	Tenax	1746	1812	1933	1820	1794	1783	1814	3.5
	Carbotrap	1816	1822	1735	1872	1844	1747	1806	3.5
ethylbenzene	Tenax	41.8	44.5	41.4	41.4	40.4	41.3*	41.8	3.3
	Carbotrap	45.9	45.3	44.3	43.3	42.4*	41.9*	43.9	3.6
n-nonane	Tenax	51.7	55.0	60.8*	61.4*	53.9	54.8	56.3	7.0
	Carbotrap	56.3	56.1	60.1	58.3	56.0	55.0	57.0	3.3
Br-benzene	Tenax	87.6	92.4	84.7	85.3	80.4	82.2	85.4	5.0
	Carbotrap	95.1	93.2	84.7*	85.5*	85.7*	83.2*	87.9	5.6
α-pinene	Tenax	37.1	39.0	33.5*	32.6*	36.1	36.9	35.9	6.7
	Carbotrap	40.9	25.9**	32.4	37.0	23.5**	36.6	36.7	9.5
n-decane	Tenax	31.3	33.2	33.6	33.3	31.1	31.1	32.3	3.7
	Carbotrap	34.3	33.9	32.8*	32.9*	31.8	29.5	32.5	5.3

[1]   for Carbotrap: same sampler as for sample 2 (see text)
*   values significantly (p < 0.05) different from values measured immediately after sampling
**   excluded from the mean calculation: incomplete desorption of α-pinene (see text)

nene. Both Tenax and Carbotrap show losses of 1-butanol which are even higher (although not significantly) at –15 °C than at room temperature. This finding suggests irreversible adsorption or reaction as the cause, rather than loss by desorption which could be suspected in view of the volatility of 1-butanol (De Bortoli et al., 1989) but should be more pronounced at room temperature than at –15 °C.

For α-pinene one of the Carbotrap samplers shows results that deviate greatly. The same sampler used to collect sample n. 2, immediately after the analysis, was also used to collect sample n. 5. Both analyses yielded similar values, which are distinctly lower than all other values and significantly lower than the three remaining values, measured immediately after sampling on Tenax and Carbotrap. At first we attributed this factor to the presence in the adsorbent of active sites on which α-pinene may either react or be irreversibly adsorbed. This hypothesis was supported by even greater losses of α-pinene observed by Rothweiler (1990) on all samplers prepared with a certain batch of Carbotrap.

Subsequently, however, we could clearly attribute the effect to the stainless steel grids which kept the adsorbent in position. The same explanation is valid for the smaller, but significant losses of α-pinene deter-

mined after storage of Tenax samplers at room temperature as reported in Table 5. Substituting the stainless steel grids with gold plated grids eliminated the effect.

No losses were observed for bromopentane after storage. However, earlier experience in our laboratory with bromoalkane mixtures – used as internal references for the calculation of retention indices – injected on Carbotrap of different batches has shown losses and the appearance of new compounds upon gaschromatographic analysis. The losses were different for different batches of Carbotrap. A similar finding has recently been reporteed also by researchers of the Supelco Corporation, the producer of Carbotrap (Shirey et al., 1991). For Tenax a similar effect has never been observed in our laboratory.

According to the reported results, α-pinene and bromoalkanes appear to be good test substances for the performance of Carbotrap and Tenax samplers.

In the light of the results described in this section, loaded Tenax and Carbotrap samplers can be stored at –15 °C for several weeks before analysis, without significant alterations, if normally performing samplers are used.

Repeated Use of Tenax and Carbotrap

For economic reasons and for quality control considerations it is important to know how often and

Table 6 FID response factors [counts/ng] for the compunds of a test mixture injected on a Tenax and a Carbotrap sampler at approximately one month interval after previous use [1]

| Compound | Tenax sampler | | | | Relative difference between Tenax means [%] | Carbotrap sampler | | | | Relative difference between Carbotrap means [%] | Relative difference between Tenax and Carbotrap means[2] [%] |
| | 5-10 April 7 values | | 30 April-2 May 4 values | | | 5-10 April 5 values | | 30 April-2 May 4 values | | | |
	mean	RSD [%]	mean	RSD [%]		mean	RSD [%]	mean	RSD [%]		
1-butanol	8.27	6.8	8.94	3.2	7.8	8.65	7.1	9.22	2.3	6.4	3.8
toluene	9.79	6.2	9.77	1.6	0.2	10.00	5.3	9.63	6.2	3.8	0.4
tetrachloroethene	1.84	5.1	1.74	1.8	5.6	1.78	4.8	1.72	6.4	3.4	2.3
bromopentane	4.44	6.3	4.61	2.2	3.8	4.36	5.6	4.41	5.0	1.1	3.1
ethylbenzene	11.66	6.5	12.29	2.0	5.3	11.94	5.5	12.27	4.4	2.7	1.1
n-nonane	9.22	6.3	9.29	1.8	0.8	9.41	5.6	9.20	5.5	2.3	0.5
bromobenzene	6.70	6.7	7.22	1.9	7.5	6.92	5.6	7.24	3.7	4.5	1.7
α-pinene	11.10	6.8	11.66	1.7	4.9	11.45	5.5	11.59	4.8	1.2	1.2
n-decane	10.64	6.9	11.20	1.8	5.1	10.89	5.9	11.19	4.0	2.7	1.1

[1] The Tenax sampler has been used at least 11 times before and 16 times between the reported measurements, the Carbotrap sampler more than 800 times before and 21 times between the measurements
[2] Difference between the means of all 11 Tenax measurements and all 9 Carbotrap measurements

under what conditions a sampler can be re-used without appreciable deterioration. For the time being the causes for the observed artifacts in Carbotrap samplers are not known and there is only marginal evidence for possible causes in the deterioration of the performance of Tenax and Carbotrap samplers. These may be due to the presence of oxygen during thermal elution of samplers, high elution temperatures (e.g. because of defective temperature control), or sampling of reactive compounds (e.g. ozone, Schlitt et al., 1979).

The following experiments were performed with accurately controlled desorption temperatures, using test solutions without oxidizing constituents in order to test the stability of Tenax and Carbotrap. Under these conditions, a test mixture was injected on a Tenax and a Carbotrap sampler several times at the beginning and at the end of April 1991. Prior to making these analyses, the Tenax sampler had been used at least 11 times and the Carbotrap sampler more than 800 times. Between the analyses the samplers were loaded and analysed 16 and 21 times respectively. The GC-FID response [counts/ng] of the different compounds in the test mixture was used as an indicator for potential performance changes of the sampling tubes. Table 6 reports the mean responses obtained for the analyses of the Tenax and Carbotrap samplers at the beginning and at the end of April, their relative standard deviations and the percent differences between them. In addition, the percentage difference between the reported Tenax and Carbotrap means is given in the last column of the table.

Using the "t"-test, none of the reported differences is significant (p = 0.05 confidence level). The two-sampler mean response factors agree within 3% for all compounds except 1-butanol, for which the response factors differ by 3.8%; the "t"-test (with 18 degrees of freedom) for the difference between these means is largely nonsignificant (p varying from 0.15 for 1-butanol to 0.80 for toluene).

We conclude that under the conditions described, the Carbotrap sampler has exceptional stability and the Tenax sampler did not show any deterioration after 38 analyses. This is contrary to results obtained by Rothweiler (1991) injecting liquid solutions.

Conclusions

Under the testing conditions described above, the samplers based on Tenax and Carbotrap appear adequate for sampling nonpolar and lipophilic polar VOC in indoor air. They show good reproducibility and accuracy, low background or blank values, stability upon storage for one month (at –15 °C) either before or after use, and performance stability after several tens (Tenax) or hundreds of sampling-desorption cycles. Occasional artifacts have been observed for Carbotrap, such as decomposition of bromoalkanes, which appear linked to particular batches of the adsorbent. These drawbacks should be detected by good quality assurance programmes and the compounds mentioned above appear to be particularly good indicators.

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