Evaluation of adsorbents for sampling and quantitative analysis of microbial volatiles using thermal desorption–gas chromatography

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Abstract

Eight adsorbents were evaluated for sampling and quantitative analysis of microbially produced volatiles using thermal desorption–gas chromatography. The adsorbents studied were Tenax TA, Tenax GR, Chromosorb 102, Carbotrap C, Carbopack B, Anasorb 727, Anasorb 747 and Porasil C/n-octane (Durapak). The study was performed using a test atmosphere consisting of ten compounds differing in polarity and volatility: 2-propanol, dimethyl disulfide, toluene, furfural, 1-octen-3-ol, 3-octanone, 3-octanol, 2-isopropyl-3-methoxypyrazine, 2-methylisoborneol and geosmin. The adsorbents were tested under conditions found in "sick buildings" – low $\mu g/m^3$ levels and varying humidity. Tenax TA proved to have the best properties considering the amount obtained, breakthrough and standard deviation during sampling/analysis.

1. Introduction

Microorganisms, such as various species of moulds and bacteria, are often found in so-called "sick buildings", where humid building material and/or water damage have created an environment favourable for microbial growth. This can give rise to health problems for the inhabitants [1,2]. The microorganisms produce volatile organic compounds [1,3–7], which sometimes have an unpleasant odour, but the odourless compounds must also be assumed to have a potentially negative health effect.

These volatiles, produced by secondary metabolic pathways, differ in polarity and volatility and are present in the air at low $\mu g/m^3$ levels. A

sensitive analytical method is necessary for determination of these substances. Adsorption on porous polymers and analysis using thermal desorption and high-resolution gas chromatography is an effective method increasingly being used for the determination of low concentrations of volatile compounds in air [8–13]. Chan et al. [8] used multi-sorbent sampling tubes consisting of Tenax, Ambersorb XE-340 and charcoal for sampling volatile organic contaminants in indoor air. The sorbent was evaluated for sampling and thermal desorption–GC analysis of 23 compounds, with reported recoveries of >70%. Heavner, Ogden and Nelson [9] used a multi-sorbent consisting of Tenax and Carbotrap for thermal desorption–GC–MS analysis of 28 volatile organic compounds in indoor air. Reported collection efficiencies were >90% except for

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n-nonane and four halogenated volatile compounds. In a review [10], Rothweiler discusses the advantages and disadvantages of several sorbents for sampling and thermal desorption of volatile compounds in non-industrial buildings. Steudler and Kijowski [11] combined Molecular Sieve 5A and Tenax GC for thermal desorption–GC analysis of six volatile sulfur-containing compounds. Recoveries were 50–80%. For two gases, recoveries decreased with increased humidity. Kawata and Kifune [13] used Tenax GC for collection and thermal desorption of 78 organic compounds differing in polarity and volatility. Recoveries were >90% for most of the compounds; only butylamine, 1-octanol and α-pinene showed recoveries of <70% (40–65%). No clear relationship was found between recovery and boiling point of the compounds, nor between recovery and breakthrough volume.

The ideal adsorbent should 1) be chemically inert, 2) be thermally stable, 3) have a low background, 4) quantitatively adsorb and desorb both very volatile and semi-volatile organic compounds, 5) quantitatively adsorb and desorb both polar and non-polar compounds, 6) be stable on storage, 7) be able to sample very low levels, and 8) the adsorption should be uninfluenced by the humidity of the air. Earlier reported studies show that no adsorbent fulfils all these requirements.

The aim of this study was to evaluate commercially available adsorbents for sampling and analysis of microbially produced volatiles. Eight adsorbents were studied, using a test mixture consisting of ten different compounds, earlier identified or reported as microbial metabolites [1,3–7]. These compounds also differ sufficiently in polarity and volatility to make these studies of general interest.

2. Experimental

2.1. Chemicals

The chemicals used in the test mixture were 2-propanol (Merck, p.a.), dimethyl disulfide (Janssen, p.a.), toluene (Merck, p.a.), furfural (Merck, p.a.), 1-octen-3-ol (Aldrich, 98%), 3-octanone (Aldrich, 99%), 3-octanol (Aldrich, 99%), 2-isopropyl-3-methoxypyrazine (Aldrich, 97%), 2-methylisoborneol (synthesized according to Wood and Snoeyink [14]) and geosmin (synthesized according to Hansson et al. [15,16]). The methanol used as solvent for standards was Merck p.a. The synthesized substances, 2-methylisoborneol and geosmin, had purities >95% and >98%, respectively, as determined by GC (splitless injection).

2.2. Adsorbents

The adsorbents used are presented in Table 1. The sampling tubes were made of glass (Chrompack, length 160 mm × 6 mm O.D., 3 mm I.D.). They were all packed with the same amount of adsorbent (90 mg) and with silanized glass wool (Chrompack) at both ends. The tubes were conditioned overnight before use by heating in a stream of helium (30–40 ml/min). Tenax TA and GR were conditioned at 300°C, Carbotrap C, Carbopack B and Anasorb 747 at 350°C, Chromosorb 102 and Anasorb 727 at 250°C, and Porasil C/n-octane at 170°C.

2.3. Generation of test atmosphere

The sampling atmospheres of the test mixture in two concentrations, 1 and 50 μg/m^3 of each substance, were dynamically generated according to Fig. 1. The compressed air was cleaned through oil and particle filters (Norgren Martonair AB, F50-004-A000 and F13-000-M300). The test mixture was slowly injected (22.7 nl/min for 50 μg/m^3 and 10.4 nl/min for 1 μg/m^3) by means of a micro injection pump (Carnegie Medicin CMA/100). A 10 μl gastight on-column syringe (Hamilton 1701RNFS) was used for the injection. The on-column needle was led through a nebulizer (Meinhard nebulizer TR-30-K3, J.E. Meinhard Associates), the tip ending at the orifice of the nebulizer. The nebulizer was used to improve the vaporization of the test mixture in the mixing chamber [17]. For the 1 μg/m^3 level, the sampling atmosphere generated in the mixing chamber was split in a ratio of 1:20 and diluted (Fig. 1a). For the 50 μg/m^3 level, no splitting of the air was needed (Fig. 1b). The

Table 1
Adsorbents tested

Adsorbent	Mesh size	Polarity	Identity	Surface area (m^2/g)	Max. temp. (°C)	Company
Tenax TA	60–80	nonpolar	2,6-diphenyl-p-phenyleneoxide	35	375	Chrompack
Tenax GR	60–80	nonpolar	ditto mixed with 23% graphitized carbon	24	375	Buchem bv
Chromosorb 102	60–80	slightly polar	polystyrene/divinylbenzene	350	250	Supelco
Carbotrap C[a]	20–40	nonpolar	graphitized carbon black	10	>500	Supelco
Carbopack B[a]	60–80	nonpolar	graphitized carbon black	100	>500	Supelco
Anasorb 727[b]	20–40	nonpolar	cross-linked polystyrene	600–700	250	SKC
Anasorb 747	20–40	nonpolar	synthetic carbon	>1000	>400	SKC
Porasil C/n-octane (Durapak)	80–100	polar	silica coated with n-octane	50–100	175	Supelco

[a] Carbotrap C and Carbopack B are the same adsorbents as Carbopack C and Carbotrap, respectively, but with different mesh size. (Carbotrap and Carbotrap C are 20–40 mesh, Carbopack B and C are 60–80 mesh.)
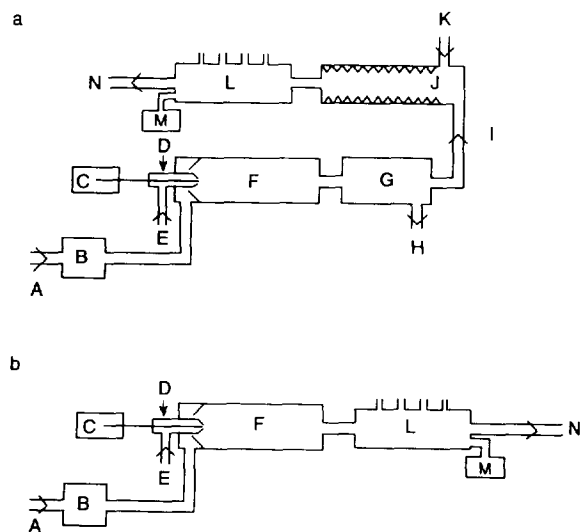[b] Corresponding to Chromosorb 106.

Fig. 1. Generation of test atmosphere at two different levels, (a) 1 μg/m^3 and (b) 50 μg/m^3. A: Cleaned compressed air at (a) 48.5 l/min and (b) 40 l/min. B: Moisturizing outfit consisting of three water-filled dispersion bottles in a thermostated water bath. C: Micro injection pump for continuous injection of the test mixture. D: Nebulizer. E: Air inlet to nebulizer (100 ml/min). F: Mixing chamber. G: Splitting chamber. H: Split air outlet (47 l/min). I: Split air into the system (1.5 l/min). J: Dilution and mixing chamber. K: Dilution air inlet (cleaned and moisturized air, 30 l/min). L: Sampling chamber with four outlets for sampling. M: Relative humidity meter. N: Air outlet (flow measured).

relative humidity of the air was adjusted to 20% and 85%, respectively, using a moisturizing outfit consisting of three water-filled dispersion bottles in a thermostated water bath [18]. Samples were collected on the adsorbents by aspirating the generated atmosphere through the tubes at 100 ml/min for 10 min for 50 μg/m^3 (1 l) and 60 min for 1 μg/m^3 samples (6 l), using a GAST Model MOA-P101-CD pump. The generation equipment was all glass, except the connections to the flow meter (I, Fig. 1) measuring the split air led into the system. These connections were made of Teflon tubing (HABIA, Stockholm, Sweden). Rotameters were ROTA RHN-01 and ROTA L10/400.

2.4. Injection and chromatographic separation

The experiments were run on a commercial thermal desorption injector (Chrompack 16400

purge and trap injector, modified for thermal desorption injection according to the Chrompack modification manual M-16420-85-2).

Tenax TA and GR were desorbed at 220°C for 10 min, Carbopack B, Carbotrap C and Anasorb 747 at 270°C for 15 min, Chromosorb 102 and Anasorb 727 at 170°C for 20 min and Porasil C/n-octane at 160°C for 20 min. For Chromosorb 102, Anasorb 727 and Porasil C/n-octane these temperatures were the highest possible without excessively severe background disturbance caused by adsorbent breakdown. For the other adsorbents, the temperature was chosen such that increasing the desorption temperature by 30°C and redesorbing the just-desorbed tube did not give any more of the adsorbed substances. All the adsorbed substances were then considered to be desorbed at the lower temperature (the temperatures given above).

The gas chromatographic measurements were carried out on an HP 5890 gas chromatograph with a fused-silica column (HP Ultra 2, 50 m × 0.2 mm I.D. coated with cross-linked 5% phenylmethylsilicone, film thickness 0.33 μm) and a flame ionization detector. An HP 3392A integrator was used as a recorder. The injection was run under optimized conditions [19]. The desorption flow was 30 ml/min and the pressure on the injector and column was 3 bar. The cold trap (Chrompack CP-TM-Sil-8CB, film thickness 5.0 μm, I.D. 0.5 mm) was cooled to −125°C during desorption, and the sample was injected onto the column by heating the trap to 130°C for 3 min. The temperature of the detector and injection block was 250°C. The GC temperature programme was 30°C for 5 min followed by a temperature rise of 10°C/min up to 220°C.

2.5. Experimental strategy

All adsorbents were first tested at an atmosphere of 50 μg/m^3 and RH 85%. The four adsorbents showing the best results were then further examined at 50 μg/m^3 and RH 20% and 1 μg/m^3 and RH 20% and 85%. The criteria for evaluation were:
a) recovery of the test substances, which is dependent on both the adsorption and the desorption efficiency of the adsorbent for the

specific compound, compared with reference standard compounds in methanol;

b) background disturbance;

c) relative standard deviation (dependent on both the adsorption and the desorption).

For the four adsorbents investigated further, the storage stability and breakthrough during sampling were included among the criteria for choice of adsorbent. No exact breakthrough values were determined, but sampling with two adsorbents in series (Tenax TA or Chromosorb 102 as second adsorbent) provided a rough indication of the adsorption efficiencies.

Storage stability was investigated for samples generated at an atmosphere of 1 μg/m^3 and RH 85%. The samples to be stored were capped with Swagelok caps and put in a freezer for two weeks immediately after generation. Reference samples generated at the same time were run at once.

As reference standards for quantification and for controlling the stability of the analysis equipment, reference values were obtained by injecting corresponding amounts of the test mixture in methanol onto the adsorbent tubes. Using a gastight syringe (Hamilton 7000.5 KH), 0.3 μl was applied onto the silanized glass wool plug preceding the adsorbent and 100 ml helium (100 ml/min, 1 min) was blown through the tube in order to transfer the substances to the adsorbent and for removal of most of the solvent [20]. Tenax TA was used as adsorbent for the methanol standards and the standards were analysed under the same conditions as the generated samples on the same adsorbent. The standard deviations of the obtained areas of the standards were < 10% (usually 4–6%).

3. Results and discussion

3.1. Screening of adsorbents for further evaluation

The observed amounts of the different substances desorbed onto the column from the eight adsorbents tested at 50 μg/m^3 and RH 85% are presented in Table 2. Problems encountered in the case of a few adsorbents selected for more detailed studies are excess water adsorption,

background disturbance caused by thermal breakdown of the adsorbent, stability of the test compounds during desorption and the recovery found.

Water adsorption

For Anasorb 747, the generation was performed at RH 10%, since the adsorbent adsorbed so much water that it was impossible to analyse samples taken at higher humidity. Attempts at sampling atmospheres with higher water content and then blowing helium (200–500 ml) through the tubes to remove the water still gave rise to problems. Analysis of 2-propanol was not possible at all because of water uptake.

In the case of Chromosorb 102 or Anasorb 727, water uptake caused chromatographic problems unless 100 ml helium (100 ml/min, 1 min) was blown through the tubes after sampling to remove water before analysis. Generally, a high water content in the sample, causing much freezing of water in the cold trap, results in unstable retention times and poor separation at the beginning of the chromatographic analysis. After blowing with helium, analysis of 2-propanol was possible. Some loss of 2-propanol during blowing with helium cannot be ruled out, but the recoveries of 2-propanol on the adsorbents shown in Table 2 are high and the losses caused by helium blowing must be small, if any.

Background disturbances

Both Chromosorb 102 and Anasorb 727 produced background disturbances at retention times close to 2-isopropyl-3-methoxypyrazine in the chromatograms. It was not possible to desorb geosmin from either Anasorb 727 or Chromosorb 102 without increasing the desorption temperature, which causes breakdown of the adsorbents and serious background interferences. Nor did Anasorb 727 desorb 2-methylisoborneol.

Tenax TA and Tenax GR adsorbed and desorbed all substances without severe background disturbances. Toluene, together with benzene, is a known contamination of Tenax [21], but the amount of toluene in the blank was less than 1% of the sampled amount and was therefore neglected.

Porasil C/n-octane proved to be unsuitable as

Table 2
Recovery in per cent of reference standard, 50 $\mu g/m^3$, RH 85%

Substance	Tenax TA	Tenax GR	Chromosorb 102	Carbotrap C	Carbopack B	Anasorb[a] 727	Anasorb[a] 747	Porasil C/ n-octane
2-Propanol	46 (22)	42 (12)	100 (22)	7 (44)	12 (5.3)	86 (27)	n.d.[b]	n.d.
Dimethyl disulfide	103 (11)	89 (13)	83 (14)	11 (23)	62 (13)	90 (26)	149 (10)	n.d.
Toluene	111 (3.6)	105 (12)	114 (13)	99 (4.0)	76 (8.8)	121 (24)	96 (25)	18 (9.5)
Furfural	102 (4.9)	87 (9.0)	102 (12)	98 (8.9)	65 (24)	123 (21)	117 (23)	151 (20)
1-Octen-3-ol	88 (15)	68 (22)[e]	100 (6.0)	99 (3.2)	80 (19)	68 (30)	10 (9.2)	44 (101)
3-Octanone	101 (4.8)	105 (8.9)	107 (11)	91 (3.0)	114 (28)	81 (19)	21 (57)	129 (76)
3-Octanol	88 (15)	100 (14)	101 (12)	84 (2.4)	100 (25)	54 (38)	21 (16)	193 (50)
IPMP[c]	97 (8.8)	92 (7.1)	111 (12)	97 (3.9)	75 (13)	53 (42)	24 (5.0)	47 (173)
2-MIB[d] total[e]	96 (6.0)	58 (13)	62 (3.6)	96 (6.5)	80 (33)	n.d.	20 (22)	103 (33)
Geosmin total[e]	74 (3.8)	63 (6.2)	n.d.	71 (5.6)	64 (56)	n.d.	20 (42)	n.d.
Numbers of samples	6	4	3	3	4	4	3	3

Figures in parentheses are relative standard deviations for the observations given in per cent.
[a] Generation performed at RH 10%.
[b] n.d. = not detected (recovery <2%).
[c] IPMP = 2-Isopropyl-3-methoxypyrazine.
[d] 2-MIB = 2-Methylisoborneol.
[e] Breakdown, see text.

an adsorbent for thermal desorption. Even at 160°C, major background peaks disturbed the chromatogram.

Adsorption

Anasorb 747, Carbopack B and Carbotrap C all needed to be desorbed with the desorption flow in the reverse direction of the sampling flow to remove the sample from the adsorbent.

The adsorptivity for 2-propanol was highest on Chromosorb 102 and Anasorb 727 (Table 2). Using Tenax TA or Tenax GR, 2-propanol was only partly adsorbed. Carbopack B adsorbed 2-propanol only to a small extent, and showed a comparatively high spread in the obtained areas. Carbotrap C showed a low adsorptivity for 2-propanol and dimethyl disulfide, but the recoveries for the other compounds were of the same magnitude as with Tenax and the relative standard deviations of the integrated areas were low. 2-Propanol, dimethyl disulfide and geosmin were not detected at all with the use of Porasil C/n-octane.

Stability of adsorbed components during desorption

2-Methylisoborneol proved to be unstable upon heating during the thermal desorption. The recoveries of 2-methylisoborneol shown in Tables 2, 3 and 5 are based on the sums of two peak areas: the major breakdown product (mass spectrum indicates loss of water from the original molecule) and uninfluenced 2-methylisoborneol. Some additional small breakdown products are also formed (all mass spectra indicate loss of water) but the areas of these components are of the magnitude of 1% or less of the major breakdown product and the original molecule and are therefore neglected. In calculating the recovery, the breakdown product has been assumed to have the same detector sensitivity as original 2-methylisoborneol. Breakdown of 2-methylisoborneol occurs on all adsorbents which desorb it, but is particularly frequent on Tenax GR and Carbopack B. On those adsorbents, geosmin is also degraded into a breakdown product (mass spectrum indicates loss of water). Breakdown of geosmin was also noted to a low

extent in a few samples on Carbotrap C. The geosmin recoveries shown in Tables 2, 3 and 5 are calculated on the peak area of original geosmin plus the area of the breakdown product, if breakdown occurs. As for 2-methylisoborneol, the detector response has been considered to be the same for the original compound and the breakdown product. On Tenax GR, the geosmin breakdown product is of the same magnitude as unaffected geosmin, while on Carbopack B and Carbotrap C original geosmin dominates.

Adsorbents chosen for further investigation

The four adsorbents chosen for further investigation were Tenax TA and GR, Carbotrap C and Chromosorb 102. The Chromosorb was chosen despite its inability to desorb geosmin, since it could be a good complement to the other adsorbents by means of its higher adsorptivity for the most volatile compounds. Carbotrap C was chosen despite its low adsorptivity for the most volatile components because of its good qualities in adsorption and desorption of the less volatile substances.

3.2. Evaluation of Tenax TA, Tenax GR, Carbotrap C and Chromosorb 102

These adsorbents were tested at different values of relative humidity and concentration (Table 3). In addition, breakthrough (Table 4) and storage stability (Table 5) were studied.

Background disturbances and water adsorption

The larger sampling volume for the lower test atmosphere levels (6 l at 1 μg/m^3) increased the water uptake on Chromosorb 102 as compared with the 1 l samples. The determination of such low amounts of 2-propanol is uncertain with the use of any of the adsorbents because of background disturbances caused by the adsorbent, sampling and analysing system.

Adsorption

As shown in Tables 3 and 4, no adsorbent is capable of adsorbing 2-propanol completely. None of the examined adsorbents could be said to work satisfactorily for low (1 μg/m^3) levels of such a low-boiling alcohol. At the lower sam-

Table 3
Recovery in per cent of reference standard

Substance	Tenax TA				Tenax GR				Chromosorb 102				Carbotrap C			
	50 µg/m³		1 µg/m³		50 µg/m³		1 µg/m³		50 µg/m³		1 µg/m³		50 µg/m³		1 µg/m³	
	RH 85%	RH 20%	RH 85%	RH 20%	RH 85%	RH 20%	RH 85%	RH 20%	RH 85%	RH 20%	RH 85%	RH 20%	RH 85%	RH 20%	RH 85%	RH 20%
2-Propanol	46 (22)	40 (7.3)	8 (67)	9 (39)	42 (12)	38 (4.2)	9 (40)	10 (44)	100 (22)	87 (5.3)	34 (12)	46 (12)	7 (44)	n.d.[a]	n.d	n.d.
Dimethyl disulfide	103 (11)	88 (20)	91 (8.9)	93 (4.4)	89 (13)	84 (2.9)	86 (7.1)	84 (7.3)	83 (14)	70 (9.4)	37 (24)	72 (8.5)	11 (23)	n.d.	n.d.	n.d.
Toluene	111 (3.6)	97 (7.3)	110 (12)	102 (4.0)	105 (12)	105 (3.6)	121 (4.7)	97 (17)	114 (13)	95 (11)	97 (10)	120 (24)	99 (4.0)	102 (18)	94 (27)	106 (7.3)
Furfural	102 (4.9)	104 (14)	98 (14)	95 (20)	87 (9.0)	85 (6.4)	70 (19)	94 (60)	102 (12)	95 (16)	83 (36)	63 (24)	98 (8.9)	76 (26)	73 (16)	119 (29)
1-Octen-3-ol	88 (15)	102 (7.0)	96 (8.6)	92 (5.9)	68[d] (22)	50[d] (26)	55[d] (39)	56[d] (68)	100 (6.0)	82 (4.7)	91 (3.8)	100 (14)	99 (3.2)	95 (8.4)	99 (24)	95 (13)
3-Octanone	101 (4.8)	109 (13)	109 (10)	107 (9.7)	105 (8.9)	105 (4.4)	120 (25)	98 (46)	107 (11)	105 (8.4)	110 (6.4)	94 (7.6)	91 (3.0)	105 (8.5)	118 (25)	65 (34)
3-Octanol	88 (14)	101 (7.2)	92 (4.3)	86 (12)	100 (14)	110 (12)	91 (20)	74 (36)	101 (12)	83 (6.5)	97 (8.4)	98 (6.2)	84 (2.4)	95 (9.2)	97 (15)	101 (16)
IPMP[b]	97 (8.8)	101 (7.2)	103 (8.8)	87 (6.3)	92 (7.1)	105 (2.5)	109 (9.9)	80 (14)	111 (12)	95 (12)	113 (5.7)	94 (5.2)	97 (3.9)	112 (10)	95 (16)	76 (8.6)
2-MIB[c] total	96 (6.0)	100 (7.1)	105 (12)	95 (9.6)	58 (13)	63 (4.4)	71 (13)	110 (29)	62 (3.6)	46 (65)	25 (59)	56 (8.1)	96 (6.5)	102 (7.1)	95 (21)	85 (9.9)
Geosmin total	74 (3.8)	86 (7.1)	100 (19)	81 (21)	63 (6.2)	67 (5.8)	74 (23)	58 (22)	n.d.	n.d.	n.d.	n.d.	71 (5.6)	83 (7.4)	77 (22)	70 (3.4)
Numbers of samples	6	5	6	10	4	4	6	8	3	4	5	3	3	4	8	4

Figures in parentheses are relative standard deviations in per cent.
[a] n.d. = not detected (recovery <2%).
[b] IPMP = 2-Isopropyl-3-methoxypyrazine.
[c] 2-MIB = 2-Methylisoborneol.
[d] Breakdown, see text.

Table 4
Breakthrough data

Substance[a]	Tenax TA			Tenax GR			Chromosorb 102			Carbotrap C		
	Tube 1	Tube 2 (T.TA)	Tube 2 (Ch.102)	Tube 1	Tube 2 (T.TA)	Tube 2 (Ch.102)	Tube 1	Tube 2 (T.TA)	Tube 2 (Ch.102)	Tube 1	Tube 2 (T.TA)	Tube 2 (Ch.102)
2-Propanol 50 $\mu g/m^3$	40 (7.3)	32 (4.4)	52 (4.0)	38 (4.2)	30 (4.1)	43 (4.3)	87 (5.3)	n.d.[b]	18 (106)	n.d.	51 (12)	105 (9.8)
2-Propanol 1 $\mu g/m^3$	8 (67)	11 (43)	65 (31)	9 (40)	16 (27)	73 (8.3)	34 (12)	8 (116)	28 (16)	n.d.	14 (50)	56 (61)
Dimethyl disulfide 50 $\mu g/m^3$	88 (20)	n.d.	n.d.	84 (2.9)	n.d.	n.d.	70 (9.4)	n.d.	n.d.	n.d.	111 (10)	65 (17)
Dimethyl disulfide 1 $\mu g/m^3$	91 (8.9)	n.d.	n.d.	86 (7.1)	n.d.	n.d.	37 (24)	n.d.	n.d.	n.d.	79 (2.5)	67 (88)
Toluene 50 $\mu g/m^3$	97 (7.3)	n.d.	n.d.	105 (3.6)	n.d.	n.d.	95 (11)	n.d.	n.d.	102 (18)	19 (38)	33 (86)
Toluene 1 $\mu g/m^3$	110 (12)	n.d.	n.d.	121 (4.7)	n.d.	n.d.	97 (10)	n.d.	n.d.	94 (27)	19 (173)	21 (87)
Furfural 50 $\mu g/m^3$	104 (14)	n.d.	n.d.	85 (6.4)	n.d.	n.d.	95 (16)	n.d.	n.d.	76 (26)	25 (141)	19 (141)
Furfural 1 $\mu g/m^3$	98 (14)	n.d.	n.d.	70 (19)	n.d.	n.d.	83 (36)	n.d.	n.d.	73 (16)	34 (103)	37 (92)
Numbers of samples 50 $\mu g/m^3$	5	2	2	4	2	2	4	2	2	4	2	2
Numbers of samples 1 $\mu g/m^3$	6	3	2	6	3	3	5	3	2	8	3	3

Recovery in per cent of reference standard, 50 $\mu g/m^3$, RH 20% and 1 $\mu g/m^3$, RH 85%. Figures in parentheses are relative standard deviations in per cent. Columns marked with Tube 2 list recoveries in per cent of reference standard of compounds that have broken through the first sampling tube and been trapped by the second tube, in sampling with two tubes in a row. (Tenax TA and Chromosorb 102 used as second adsorbents.)

[a] Other substances in the test mixture did not show any breakthrough.

[b] n.d. = not detected (recovery <2%).

Table 5
Storage stability

Substance	Tenax TA		Tenax GR		Chromosorb 102		Carbotrap C	
	Fresh	Stored	Fresh	Stored	Fresh	Stored	Fresh	Stored
2-Propanol	8 (67)	29 (36)	9 (40)	42 (22)	34 (12)	63 (27)	n.d.[a]	n.d.
Dimethyl disulfide	91 (8.9)	93 (3.8)	86 (7.1)	84 (6.5)	37 (24)	n.d.	n.d.	n.d.
Toluene	110 (12)	120 (3.8)	121 (4.7)	120 (5.7)	97 (10)	77 (20)	94 (27)	99 (14)
Furfural	98 (14)	108 (1.7)	70 (19)	72 (18)	83 (36)	80 (18)	73 (16)	84 (19)
1-Octen-3-ol	96 (8.6)	93 (6.2)	55 (39)[d]	32 (30)[d]	91 (3.8)	74 (19)	99 (24)	105 (12)
3-Octanone	109 (10)	125 (5.6)	120 (25)	103 (16)	110 (6.4)	72 (18)	118 (25)	128 (3.7)
3-Octanol	92 (4.3)	99 (3.0)	91 (20)	80 (18)	97 (8.4)	73 (17)	97 (15)	92 (9.1)
IPMP[b]	103 (8.8)	104 (3.1)	109 (9.9)	104 (5.4)	113 (5.7)	87 (14)	95 (16)	114 (2.8)
2-MIB[c] total	105 (12)	107 (11)	71 (13)	70 (7.7)	25 (59)	31 (29)	95 (21)	116 (7.1)
Geosmin total	100 (19)	92 (7.0)	74 (23)	77 (3.4)	n.d.	n.d.	77 (22)	97 (11)
Numbers of samples	6	4	6	5	5	5	8	5

Recovery in per cent of reference standard of samples run immediately after sampling and samples stored for two weeks in freezer, 1 $\mu g/m^3$, RH 85%. Figures in parentheses are relative standard deviations in per cent.

[a] n.d. = not detected (recovery <2%).
[b] IPMP = 2-Isopropyl-3-methoxypyrazine.
[c] 2-MIB = 2-Methylisoborneol.
[d] Breakdown, see text.

pling volume, breakthrough of 2-propanol on Chromosorb 102 was noted in only one sample, while sampling 6 l of 1 $\mu g/m^3$ atmosphere caused breakthrough of 2-propanol on all Chromosorb sampling tubes.

Carbotrap C is comparable to Tenax for 1-octen-3-ol and compounds with higher boiling points, but obviously has lower adsorptivity than Tenax for the most volatile compounds. The adsorptivity for 2-propanol and dimethyl disulfide is almost negligible, but in the case of toluene and furfural breakthrough is also noted in some samples.

Tenax, the most used adsorbent for sampling low amounts of organic compounds in air and for analysis using thermal desorption, is known to be inert, thermally stable, unaffected by water, has high storage stability and a low background, but has a low breakthrough volume for compounds under C_6 [22]. As expected, this study also showed that both Tenax TA and Tenax GR have low adsorptivity for 2-propanol. On the contrary, despite its volatility, dimethyl disulfide does not show any breakthrough on Tenax under the examined conditions.

Breakthrough or recovery values have previously been published for several compounds on some of the investigated adsorbents [12,23–25]. Rothweiler and co-workers [12] compared recoveries of 24 compounds differing in polarity and volatility on Tenax TA and Carbotrap. They found the recoveries for 2-propanol unsatisfactory on both adsorbents.

Breakdown of adsorbed compounds during desorption

Carbotrap has been reported to have catalytic activity on reactions of α-pinene and aldehydes during thermal desorption [12]. In this study, the adsorbents consisting of graphitized carbon black and Tenax GR, which contains graphitized carbon, proved to have a catalytic effect on breakdown of 2-methylisoborneol and geosmin. Tenax GR also has a catalytic effect on breakdown of 1-octen-3-ol. Several breakdown products in varying amounts are noted (for all, mass spectra indicate loss of water). Because of the complexity of the breakdown products, they are not

included in the recovery values for 1-octen-3-ol on Tenax GR presented in Tables 2, 3 and 5; Tenax GR gives low recovery and high standard deviation for this substance. Breakdown of 1-octen-3-ol was not noted on any of the other adsorbents.

Storage stability

The storage stabilities of samples generated at an atmosphere of 1 $\mu g/m^3$ and RH 85% are shown in Table 5. The Chromosorb 102 tubes were blown with 100 ml helium directly after generation and then capped and stored like the other adsorbents. On Tenax TA and GR and Chromosorb 102, storage caused a varying blank build-up disturbing the analysis of 2-propanol. This explains the increased recovery on storage of this compound. Levels of 3-octanone are generally $> 100\%$, which is also a tendency in Table 5. This could be due to breakdown of 3-octanone in the reference standard in methanol. Samples taken on Chromosorb 102 proved to be unstable on storage. No dimethyl disulfide was detected at all on the stored samples on this adsorbent, and the recoveries of several of the other substances were significantly lower in the stored samples. Both Tenax TA and GR showed high storage stability, except for disturbance of the analysis of the early eluting 2-propanol caused by blank build-up. Carbotrap C also proved to be stable on storage.

4. Conclusions

The data obtained show that none of the examined adsorbents is suitable for all compounds of interest in sampling complex mixtures of volatiles differing in volatility and polarity. Chromosorb 102 gives rise to severe problems because of water adsorption and background disturbance, particularly at high humidity. However, Chromosorb 102 could serve as a reasonable complement to Tenax for analysis of 2-propanol when volumes of 1 l are sampled and the tubes purged with helium before analysis. Carbotrap C does not show any advantages over Tenax, but has a lower adsorption capacity for

the most volatile substances. Tenax TA and GR have equivalent adsorption properties. None of them is suitable for analysis of 2-propanol. The catalytic effect of Tenax GR on thermal breakdown of 2-methylisoborneol, geosmin and 1-octen-3-ol is an important disadvantage of the adsorbent and is most probably not restricted to these three substances. Therefore, of the eight adsorbents tested, Tenax TA is considered to be the adsorbent showing the overall best properties for sampling complex mixtures of volatiles.

Acknowledgements

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