UNDERESTIMATION OF INDOOR AIR CONCENTRATIONS; COMPARISON OF TENAX-ADSORPTION/THERMAL DESORPTION WITH DIFFERENT SORBENTS/LIQUID EXTRACTION

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ABSTRACT
Reference procedures for determining volatile polar and non-polar organic compounds using different sorbents are compared to additional measurements of air samples adsorbed on Tenax TA followed by thermal desorption (TD). Tendencies for a relationship between absolute concentrations and divergence of measurements could be found. Results differ remarkably within compound classes with higher air-concentrations obtained by TD-analysis. Concentrations of homogeneous groups as aldehydes or terpenes show little variability. In the glycol-derivatives there is a split in a less-polar group with a factor of 1 and a polar group (acetates) with factors around 2. For alkanes and aromates continuously distributed deviations were obtained due to compound structure. Conclusions can be drawn that „real" air-concentrations are underestimated when using the liquid desorption procedures: for example for styrene a loss by a factor of 3 was found. A discussion is needed about how far reference-values and TVOC are concerned from these findings.

INDEX TERMS
Thermal desorption, VOC, TVOC, Reference values, Comparison of sorbents

INTRODUCTION
Nowadays a large and still increasing number of chemicals is present in men's environment. This relates even more to common households than to outdoor environment. Among the quantity of different chemicals occurring indoors and accessible to air sampling some are very volatile while others have quite high boiling points up to 250 degrees Celsius. Moreover there can be found almost non polar and quite polar compounds – mainly derivatives of polyvalent alcohols (glycol-derivatives). With this broad range of chemicals are linked certain analytical problems as it is not possible to choose a single advisory way of sampling and measuring these compounds. It is known, that there is a systematic trend to give low results for polar compounds especially for analyses on charcoal adsorption an elution with CS_2. Further studies (Oppl, 2000) carried out using Tenax consequently came to risen air burdens (TVOC) compared to elder studies. This is supposed to be partly due to an increase in frequency of use of waterborne solvent systems with higher boiling points in building materials (Plieninger and Marchl, 1999) and partly because the definition of the TVOC is changing. It was the aim of this study to quantify the systematic difference of sampling procedures based on liquid extraction from sorbents and TD through correlated measurements in real air samples.

METHODS
A simultaneous sampling of air with up to three different procedures was carried out in some 180 air samples during 2000 and 2001. They were taken at the same time to avoid physical interference (influence of adsorption-desorption, temperature changes, ventilation, etc.) as far

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as possible. The sampling procedure follows indoor air quality guidelines VDI 4300-1 and DIN EN ISO 16017-1, respectively. Examined rooms were left unventilated for a period of at least eight hours and temperatures were set to approximately 20 degrees. Detection limits usually ranged from 1 to 2 $\mu g/m^3$ and from 1 to 20 $\mu g/m^3$ for glycol-derivatives (Anasorb).

Tenax-TA: After sampling, Tenax-tubes were spiked with 5 μl solution of internal standard (trichlorohydrine) and adsorbed analytes were thermally desorbed at temperatures from 100°C to 250°C. Quantification was carried out using external standard solutions spiked on blank tubes and calibration using main fragmentation mass (SIM).

charcoal: VOC samples collected by charcoal-adsorption were subsequently analysed according to VDI 3482. Extraction was carried out with 0,5 ml of CS_2. Separation was carried out on DB-624 column followed by quantification by GC-FID using cyclooctane as internal standard.

Anasorb 747: Polar compounds are correspondingly concentrated on modified charcoal (Anasorb 747) extracted with dichloromethane separated on a DB-624 column and quantified by GC-MS using 4-vinylene-chloride as internal standard (similar to Plieninger and Marchl, 1999)

DNPH: Aldehydes and Ketones were concentrated on DNPH, extracted with acetonitrile and quantified by HPLC UV-DAD according to VDI 3483-3.

Air-concentrations obtained by the different sampling methods were further evaluated: each pair of 818 corresponding values was standardised, expressing the TD value as the percentage deviation against the particular reference measurement. Thus for every certain analyte statistical parameters (median, 1. and 3. quartile) of the obtained deviations were calculated.

RESULTS

Table 1: specific deviation of TD-measurements (median and quartiles) against other analytic methods (reference procedures set to 100%), sorted by compound class

compound class / compared sorbents	compound; number of measurements	mediane [%]	1. quartile [%]	3. quartile [%]
aldehyde / Tenax ↔ Anasorb, DNPH	pentanal; 9	125	93	150
	hexanal; 24	98	80	171
	heptanal; 4	117	71	171
	octanal; 5	125	100	145
	nonanal; 22	171	100	344
	decanal; 8	100	90	152
alkanes / Tenax ↔ charcoal	n-hexane; 7	95	68	307
	n-heptan; 16	227	143	471
	n-octane; 10	107	39	129
	n-nonane; 12	148	99	228
	n-decane; 26	121	78	201
	n-undecan; 32	143	99	250
	n-dodecane; 24	152	100	282
	n-tridecane; 19	300	165	358
	n-tetradecane; 19	142	67	246
	n-pentadecane; 11	154	105	452
	cyclohexane; 3	100	100	416
	methyl-cyclohexane; 5	300	300	447
	methyl-cyclopentane; 2	164	122	206
	4-phenylcyclohexene; 2	183	183	183
	4-vinylcyclohexene; 3	100	96	128
terpenes / Tenax ↔ charcoal	limonene; 50	155	113	250
	δ-3-carene; 18	219	134	298
	α-pinene; 46	181	121	279
	β-pinene; 23	229	147	272
	carvone; 16	200	96	400
	longifolene; 12	450	295	600

compound class / compared sorbents (continued)	compound; number of measurements	mediane [%]	1. quartile [%]	3. quartile [%]
alcohols / Tenax ↔ Anasorb, charcoal	1-butanole; 8	26	20	118
	isopropylalcohol; 4	126	87	151
	2-ethylhexanole; 16	156	117	257
glycol-derivatives [*] / Tenax ↔ Anasorb	EGMB; 11	57	50	87
	EGME; 4	99	76	99
	1,2PG; 3	100	99	100
	1,2PGMM; 6	100	100	107
	1,2PGMMA; 2	173	170	175
	DEGMBA; 7	247	114	400
	DEGMB; 8	230	124	324
	EGMEA; 4	202	189	285
	EGMP; 4	259	108	471
	T3PGMB; 2	473	434	512
esters / Tenax ↔ charcoal	isobutylacetate; 5	105	100	118
	n-butylacetate; 22	200	89	250
	ethylacetate; 24	225	120	383
aromates / Tenax ↔ charcoal	benzene; 14	264	184	321
	toluene; 28	108	67	195
	styrene; 24	269	201	362
	phenole; 2	438	356	519
	ethylbenzene; 31	127	90	192
	i-propylbenzole; 3	119	119	139
	n-propylbenzene; 7	153	126	206
	m,p-xylene; 40	131	87	167
	o-xylene; 23	200	115	250
	1,2,3-tri-methylbenzene; 4	268	229	372
	1,3,5-tri-methylbenzene; 10	119	84	171
	1,2,4-tri-methylbenzene; 16	233	159	254
ketone / Tenax ↔ Anasorb, DNPH	1-butanone; 3	38	38	47
	methyl-isobutyl-ketone; 6	89	44	168
	acetone; 5	478	94	678

[*] for nomenclature refer to Stolz, Weis and Krooss, 1999

When grouped by compound class some distinct rules can be obtained from table 1:

– Taking the reference measurements (charcoal, Anasorb, DNPH) as 100 percent turns out in significantly higher findings for the TD-analysis in almost all cases.
– Within certain compound classes like the aldehydes or terpenes calculated medians of compounds appear to be more ore less similar, while in some groups like aromates and glycol-derivatives the deviations are varying stronger.

Some of the air samples were taken for quality-tests of new building materials. This lead to measurements ranging up to 54 mg/m^3 for single chemicals (limonene). Thus the observed interval of concentrations covered a wide range of some orders of magnitude and gives a good overview of possible indoor concentrations. In order to visualise any effect of analytical uncertainty on the deviations and its possible influence especially on measurements in lower concentrations close to the detection limits an analysis of correlation was carried out (Fig. 1). A regression analysis on all measured concentrations ranked in interval classes and plotted against percentage deviation showed a significant decline. Best fit was exponentially. A similar testing for any compounds individually did never reveal significant correlation. It can be derived, that – because deviations are dependent on concentration - there is a systematic better agreement in analytical methods with elevated concentration. The regression is significant, but nevertheless, it is obviously not steep. A second calculation of medians omitting all concentrations in a range within tree times the particular detection limits therefore showed no considerable improvement on the medians and quartiles compared to table 1. Thus

it was assumed, that the observed deviations between different analytical procedures are not simply an artefact of analytical uncertainty.
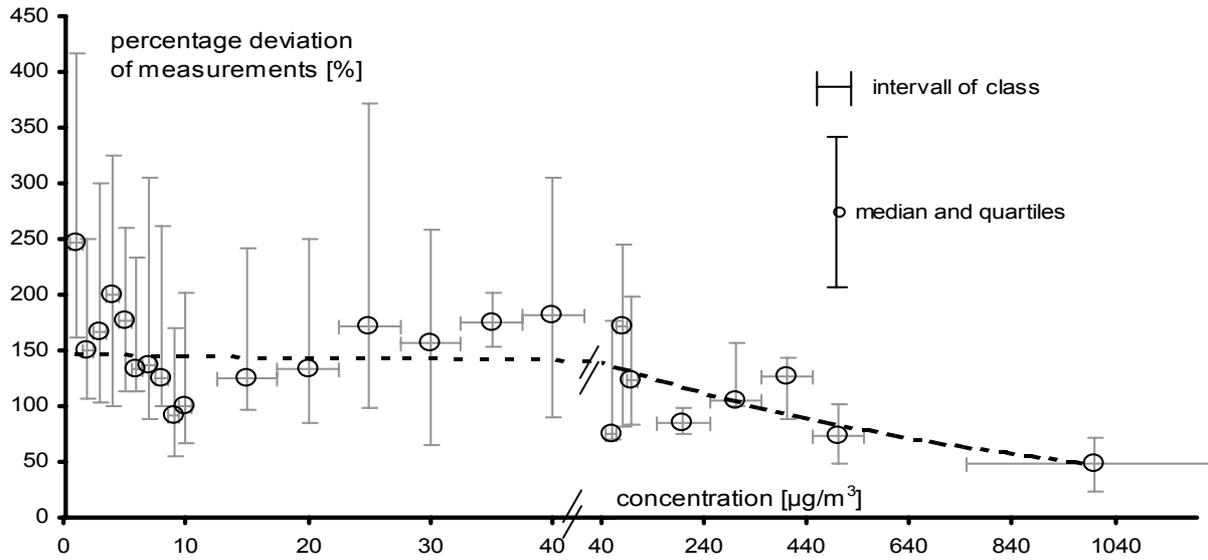

Figure 1: correlation of absolute concentration and percentage deviation between measurements; regression curve: $y = 147,16\ e^{-0,0011\ x}$; $r = 0,692$

Within certain homogeneous groups deviations were summarised by calculating grouped medians and quartiles (fig. 2). As for aldehydes and terpenes (with the exception of longifolene) a collective calculation results in quartiles of acceptable width-span. In the case of not homogeneous classes a dividing in groups is used (glycol-derivatives, alkohols). This correspondingly leads to reduced quartiles, too, as can be seen in fig. 2 compared to table 1. On the other hand it was judged not advisable to summarise aromates or ketones because of not seperated but merging transitions within obtained medians of single compounds. Finally derived conversion factors are listed in table 2.
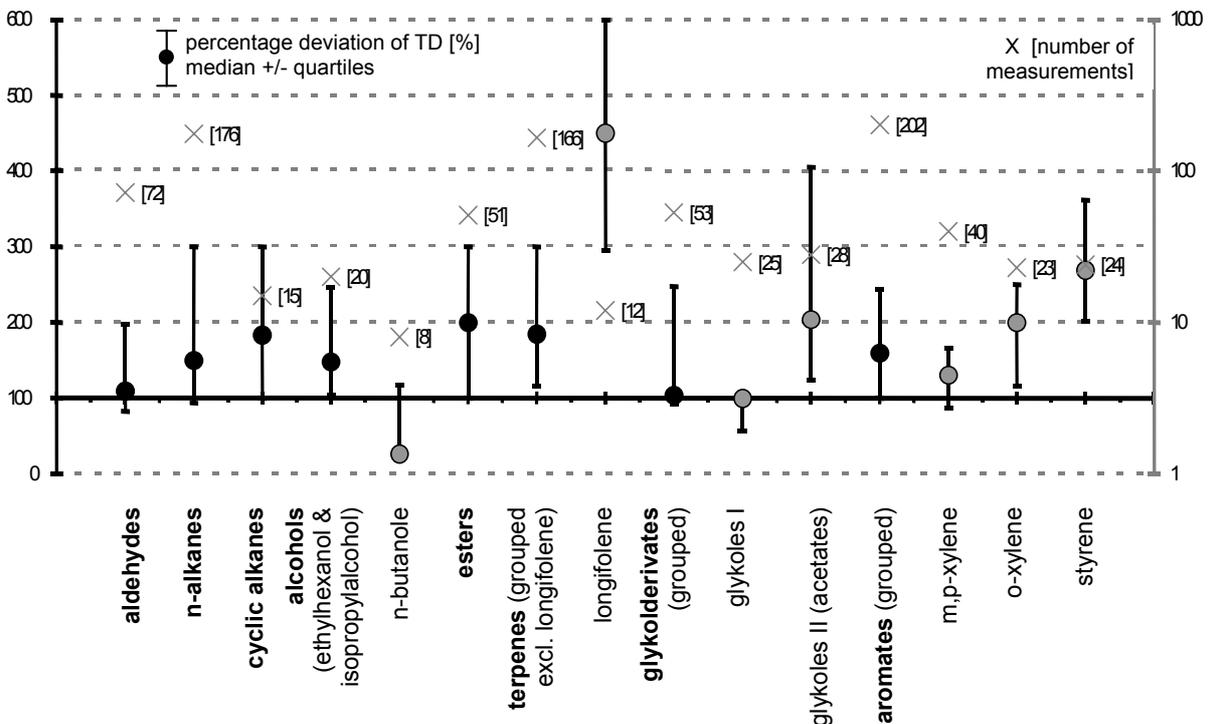

Figure 2: percentage deviation of TD-measurements (median +/- quartiles) compared to other analytic methods (reference procedures set to 100%) grouped by compound classes

Table 2: conversion factors related to thermal desorption and compared sampling procedure

compound	conversion factors	measured air-concentration (TD) min-max [$\mu g/m^3$]
aldehydes	1,2	0 - 76
n-alkanes	1,5	1 - 1.536
cyclic alkanes	2,0	2 - 643
alcohol (ethylhexanol and isopropylalcohol)	1,4	1 - 802
n-butanole	0,3	17 - 700
ester	2,0	1 - 536
terpenes (grouped, longifolene excluded)	1,8	1 - 54.466
longifolene	4,5	56 - 833
glykolderivates (grouped)	1,1	4 - 865
glykoles I	1,0	6 - 344
glykoles II (acetates)	2,0	4 - 865
aromates (grouped)	1,6	1 - 844
m,p-xylene	1,3	2 - 371
o-xylene	2,0	50 - 700
styrene	2,6	2 - 831

DISCUSSION

It is expected, that random distribution of deviations would result in as many deviations lower and higher than 100%. But only butanol, butanone, EGMB, isobutene-trimer and methyl-isobutyl-ketone were underestimated by TD, and most differences were systematically constant and could be expressed by conversion factor >1 and ranged from 1 to 3. In general, far greater systematic deviations belong to data gained from real air samples than to experimental data (Massold *et al.*, 2000; Reiner and Santl, 1999). Inversely, all significant observations in the case of real-samples are of an exclusive value to assessment. As TD is a short-term sampling method compared to other methods, air concentrations can differ with the length of the sampling interval, whenever equilibration in the room is not reached or emission from sources is irregular. In this study all samples were taken simultaneously so these aspects can not lead to the observed deviations with higher values for TD. Conclusions can be drawn, that the deviations are linked to certain chemical quality, rather than methodical differences.

Constant conversion factors within one compound class therefore imply similar interactions between sorbent and compound and comparable recovery rates. On the other hand, regarding longifolen of the terpenes, there are indications that single compounds show independent behaviour. With ketones no grouped conversion factor was calculated as deviations for acetone showed a very high variablity. This supposingly does not reflect reality, because this chemical is far too common and causes great problems with air cross-contamination and blanks. Within glycol-derivatives two distinct groups are proposed. A possible explanation can be found in the dominance of the polar acetate-group, leading to lesser recovery rates when eluted from Anasorb rather than thermally desorbed from Tenax TA. In contrast, within alkanes a split in n-alkanes and cyclic alkanes did not have an improving effect on statistics (cp. fig. 2 and table 1). Moreover, following the homologues of n-alkanes a continuous transition of medians is suggested. Additional testing of the possible influence of chain-length on the analytical divergence a weak positive correlation was found, indicating a rise better recovery for TD against charcoal adsorption with rising chain-length of homologues. Aromates were not summarised as a group. Reduction of quartiles in fig. 2 is more likely an effect of enlarged sample-size. A search for assumed structural features correlated with

deviations did not deliver satisfying results, because any rule of sorting isomers appears far too subjective to be persuading. Even so, through further investigations a significance of the delocated π-system might become evident, as is suggested by higher TD-readings particularly for benzene, phenol and styrene. For styrene an exclusively high conversion factor of 2.6 and a maximum concentration of 831 $\mu g/m^3$ (TD) was derived. Earlier findings particularly point out a loss of styrene on charcoal (Fischer and Böhm, 1994). Further evaluation concerning measured concentrations of these quite hazardous compounds should be carried out, because an underestimation by factors around 3 already might produce potential health risks.

CONCLUSIONS AND IMPLICATIONS

An overall arithmetic mean suggests 2.0 +/- 1.6-times higher concentrations than is indicated by reference methods long-time used for assessing and publishing reference and target values. A rising awareness of the influence of VOC concentrations on health condition has lead to standards for measurement and to target values (Uhde, 1999), but discussion about target values that exclude health risks or affected health condition is still ongoing. The TVOC was generated to analytically summarise indoor air quality. Currently most authors define the non-problem indoor air quality around TVOC sums of 200 to 300 $\mu g/m^3$ (Mølhave and Clausen, 1996; Seifert, 1999). But in spite of the introduction of the ISO/DIS 16.000-6, proposing the standard for calculating TVOC by adding the concentration of 64 compounds, others sum up values obtained by charcoal adsorption (Lux *et al.*, 2001) or prefer the calculation of TVOC using the total chromatographic peak-area in between hexane and hexadecane referred to the response of toluene (Scholz and Santl, 1999). "Real" values will possibly remain unknown, but for postulation of reference values – especially for TVOC - considerable deviations of around twice the measurement are expected. This can be observed (Oppl, 2000) and should be taken into account, when discussing older measurements or comparing differing methods.

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