# [1]Recommendations for establishing target values and guidance values for volatile organic compounds (VOC) in indoor air

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**ABSTRACT**
Toxicologically derived guidelines for the evaluation of VOC concentrations are still sparse. Therefore a schema is proposed for establishing target or intervention values which includes following basics: i) Guidelines are derived from statistical values of representative studies. ii) Guidelines should refer to standardized analytical methods. iii) Guidelines should exist for all volatile indoor air contaminants. iv) Possibility of dynamic adaptation, if the VOC mixture changes. v) Up-to-dateness. vi) TVOC concept and values for groups of VOC should be included. - As actual data from large surveys are not yet available, target and intervention values were derived for 100 VOC, 12 groups of VOC and for the TVOC (sum of VOC) on the base of 5 studies: Schleibinger et al. (2001), Lux et al. (2001), B.A.U.CH. (2000), Oppl (2000) and Scholz (2000). As long as toxicologically derived values are not obtainable for all VOC encountered indoors these values are proposed for evaluating indoor air situations.

**INDEX TERMS**
VOC, guideline value, target level, intervention level, activated carbon, thermal desorption, GC – MSD, IAQ assessment, TVOC, VVOC, quality assurance

## INTRODUCTION
The impact of volatile organic compounds (VOC) on the residents` health is described in literature. Therefore the residents as a precautionary step or due to reported health complaints often initiate air measurements. The air sampling and the techniques for VOC analysis meanwhile are state-of-the-art and performed generally by GC-MS. But after all measurements done one often encounters a limitation concerning the VOC analysis. When the values obtained have to be interpreted, one will find, that there are only a few guidelines concerning VOC encountered in indoor air. The assessment of the results obtained from the measurements therefore is in many times very difficult and even dissatisfactory.

## AIM OF THIS STUDY
1) In this paper essential points are mentioned for an evaluation concept and for establishing target and guideline values for VOC in indoor air.
2) As toxicologically derived guidelines for VOC are very sparse in literature, a proposition was statistically derived for 100 VOC, 12 groups of VOC and for the TVOC (sum of VOC) on the base of 4 studies.

## METHODS
For the establishment of a comprehensive VOC assessment schema the following points were considered:

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**1. Definition of target and guidance values**

For the evaluation of an indoor VOC mixture target values as well as guidance values should be available. Target values should represent concentrations, which should be aimed at. Below the target values, there should be no adverse health effects, even if a life-long exposition should be considered. These values should be achievable in a technical sense (selection of products, ventilation rate etc.), but preferably be under-runned. If there is no toxicological deduction available, target values are to be derived from environmental surveys, e.g. by the use of the median ($50^{th}$ percentile). For guidance values a level in the range of the $90^{th}$ percentile values is proposed. As a rule an exceeding of guidance values means a noticeable hint for a VOC source.

**2. Methods and standardisation for VOC analysis in indoor air**

The results of chemical analysis are often influenced by the method used. This is true despite all efforts regarding quality assurance, the use of certified standards, carefully running blanks, running standards in different levels etc.. The reason for this is in many cases unclear. Some problems may be due to the different sorption/desorption effects of real samples compared to the situation with a standard mixture. Even the use of so-called "primary calibration standards", i.e. the use of the VOC in question in gaseous form, in contrast to a calibration solution spiked on the sorbent, does not prevent these effects.

The guideline values, which are proposed in this paper, are mainly based on a "classical" method. The indoor VOC are sampled on activated coconut charcoal. This can be done by active sampling or special diffusive samplers. The compounds are eluted by an organic solvent (e.g. carbondisulfide, $CS_2$) and analysed by GC/MS. This method is reliable for the majority of unpolar and slightly polar compounds. For more polar substances like aldehydes and glycol derivates coconut charcoal in combination with $CS_2$ is less applicative. The recovery rates are too low and usually not reproducible. For these compounds the sorbent „anasorb 747" and an elution mixture of methanol/dichloromethane (5:95 v/v) proved to be convenient. Some values for carbonyl compounds like aldehydes and ketones are based on the DNPH method. This method uses silica cartouches impregnated with dinitrophenylhydrazine. The carbonyl compounds are transformed to hydrazones, which are detected by HPLC.

The thermal desorption method uses thermal energy to desorb the VOC from the sorbent, so the VOC are transferred to the GC/MS system without any solvent. The method provides comparatively low detection limits and needs only low sample volumes. This is especially useful if sampling air from cavities, e.g. for MVOC analysis, or from laboratory test chambers. The disadvantages of the method are the higher susceptibility for contaminations (as the aliquot injected is very high) and the need to sample replicates (as it is normally a "one shot only" method. In the schema proposed only a few values refer to the thermal desorption method, e.g. phenols and cresols.

In table 1 the values refer to a proposed method. If other methods are preferred, we recommend strongly that the comparability be checked, as the results are sometimes dependent strongly on the method used.

**3. Comprehensiveness of target and the guidance values**

The aim is to provide target and guidance values for **all** known VOC in indoor air. Otherwise a funded evaluation of a given indoor air situation with a generally complex mixture of VOC is in many times not well founded. The proposition given here consists of 100 compounds or classes of compounds respectively.

**4. Dynamic adaptation**

A concept for the establishment of target and guidance values should provide the possibility of a dynamic adaptation in order to reflect the changes of the VOC mixture. „New“ compounds should be incorporated as fast as possible. But also significantly dropping concentrations of certain VOC, e.g. if substances are banned or due to a change of the consumers` behaviour, might give reason to decrease the respective values as well. In the past 13 years a clear change of the VOC spectrum was observable. While concentrations of classical solvents like aromatic and chlorinated compounds clearly decreased, the concentrations of terpenes, aldehydes, esters and glycol derivates increased in indoor areas (Schleibinger et al. 2001).

**5. Up-to-dateness**

Target and guidance values should consider precaution aspects to protect people in indoor spaces as much as possible. Unfortunately valid toxicological evaluations of VOC are sparse, because they are performed rarely due to the high costs or lack of data. And sometimes there is evidence about adverse health effects only after a long period of exposition. Therefore there is a need for a rapid and simplified derivation of target and guideline levels. One non-toxicological approach is the use of recent and preferably representative studies. Out of them results can be obtained easily by statistical means. Medians and 90$^{th}$ or 95$^{th}$ percentiles can be taken as an approach for target and guidance or even intervention values.

**6. TVOC concept**

TVOC values were already implemented by Seifert (1999) and are widely accepted. The advantage of the TVOC concept is the possibility to limit the sum of VOC. This sum should not be raised with the raising number of VOC occurring indoors. Additionally there should exist values for all or at least the most important groups of VOC. Studies showed, that the number and the total of all analysed substances augmented in the past 15 years significantly. One reason is the increased sensivity, especially due to the establishment of mass selective detectors and the sophistication of the whole analytical procedure. But the other important factor is the increasing variety of chemical compounds in all kind of products.

## RESULTS

As a result of the consideration concerning the points 1 to 6 given in the method’s part we propose a list of guideline and target values for the evaluation of indoor VOC concentrations. This list is also based on 5 studies:

- Schleibinger et al. (2001): VOC concentrations in indoor spaces in Greater Berlin between 1988 and 1999. Here measurements of 744 indoor spaces were statistically evaluated.
- Lux et al. (2001): The indoor burden by VOC in new private buildings. In this study private homes were monitored in the range between 1 and 3 years after completion of the building or the last renovation.
- B.A.U.CH. (2000): The prevalence of esters and ethers of polyvalent alcohols in indoor air. In this study 200 indoor spaces were chosen representatively for a survey of glycol derivates.
- Oppl et al. (2000): Indoor air and TVOC: Analysis, reference and target values, assessment of value. Here indoor air measurements were evaluated. Among other aspects the need of quality assurance and reference values based on defined methods is pointed out.
- Scholz (2000): Personal communication concerning results of indoor air measurements in the period between 1995 and 2000 in Greater Munich, Germany

**Table 1: Proposed scheme for the evaluation of VOC based on indoor surveys**

| **Compound class** compound | **Target value [µg/m³]** | **Guidance value [µg/m³]** | **Compound class** compound | **Target value [µg/m³]** | **Guidance value [µg/m³]** |
|---|---|---|---|---|---|
| **Alkanes**[1] | **50** | **200** | **(Sesqui)Terpenes**[1] | | |
| hexane | 5 | 20 | (continued) | | |
| heptane | 5 | 20 | δ-3-carene | 5 | 20 |
| octane | 5 | 20 | limonene | 10 | 50 |
| nonane | 5 | 20 | camphene | 5 | 20 |
| decane | 5 | 30 | eucalyptol | 5 | 20 |
| undecane | 5 | 30 | isolongifolene | 5 | 20 |
| dodecane | 5 | 20 | longifolene | 5 | 20 |
| tridecane | 5 | 10 | | | |
| tetradecane | 5 | 10 | **Chlorinated** | | |
| pentadecane | 5 | 10 | **Hydrocarbons**[1] | **5** | **20** |
| hexadecane | 5 | 10 | trichloromethane | 1 | 5 |
| cyclohexane | 5 | 20 | tetrachloromethane | 1 | 5 |
| methylcyclopentane | 5 | 10 | 1,1,1-trichloroethane | 1 | 5 |
| methylcyclohexane | 5 | 10 | trichlorethene | 1 | 5 |
| pentamethylheptane | 5 | 20 | tetrachlorethene | 1 | 5 |
| heptamethylnonane | 5 | 10 | 1,4-dichlorobenzene | 1 | 5 |
| **Alkenes**[1] | **5** | **10** | **Aldehydes**[2,3] | **50** | **120** |
| 2-methyl-1-propene | 1 | 5 | formaldeyhde (only [3]) | 30 | 60 |
| 4-vinylcyclohexene | 1 | 3 | acetaldehyde (only [3]) | 30 | 60 |
| 4-phenylcyclohexene | 1 | 5 | benzaldehyde | 5 | 10 |
| | | | furfural | 5 | 10 |
| **Aromatic compounds**[1] | **50** | **200** | butanal | 5 | 10 |
| benzene | 3 | 10 | pentanal | 5 | 10 |
| toluene | 25 | 100 | hexanal | 10 | 25 |
| ethylbenzene | 5 | 15 | heptanal | 5 | 10 |
| m+p-xylene | 10 | 30 | octanal | 5 | 10 |
| o-xylene | 5 | 15 | nonanal | 5 | 10 |
| isopropylbenzene | 5 | 10 | decananal | 5 | 10 |
| n-propylbenzene | 5 | 10 | | | |
| styrene | 3 | 10 | **Ketones**[1,2,3] | **20** | **50** |
| 2-ethyltoluene | 5 | 10 | methylethylketone | 5 | 20 |
| 3-ethyltoluene | 5 | 10 | methylisobutylketone | 5 | 20 |
| 4-ethyltoluene | 5 | 10 | cyclohexanone | 5 | 20 |
| 1,3,5-trimethylbenzene | 5 | 10 | acetophenone | 5 | 20 |
| 1,2,4-trimethylbenzene | 5 | 20 | 2-heptanone | 3 | 10 |
| 1,2,3-trimethylbenzene | 5 | 10 | 3-heptanone | 3 | 10 |
| naphthalene | 3 | 10 | | | |
| | | | **Alkohols**[2] | **20** | **50** |
| **(Sesqui)Terpenes**[1] | **40** | **150** | isobutanol | 5 | 10 |
| α-pinene | 10 | 50 | 1-butanol | 10 | 25 |
| β-pinene | 5 | 20 | 2-ethyl-1-hexanol | 5 | 10 |

| Compound class compound | Target value [µg/m³] | Guidance value [µg/m³] |
|---|---|---|
| **Glycol esters and glycol ethers**[2] | **20** | **100** |
| ethyleneglycol mono-methylether | 5 | 10 |
| ethyleneglycol mono-ethylether | 5 | 10 |
| ethyleneglycol mono-buthylether | 10 | 25 |
| ethyleneglycol mono-phenylether | 5 | 10 |
| diethylenglycol monomethylether | 5 | 10 |
| diethyleneglycol monoethylether | 5 | 10 |
| diethyleneglycol monobutylether | 10 | 20 |
| 1,2-propyleneglycol | 10 | 25 |
| 1,2-propylenglycol monomethylether | 10 | 25 |
| propyleneglycol monobutylether | 10 | 25 |
| propyleneglycol monophenylether | 5 | 10 |
| dipropyleneglycol monobutylether | 5 | 10 |
| tripropyleneglycol monobutylether | 5 | 10 |
| ethyleneglycol mono-methyletheracetate | 5 | 10 |
| propyleneglycol monomethylether-acetate | 5 | 10 |
| ethyleneglycol monoethyletheracetate | 5 | 10 |
| ethylene glycol monobutyletheracetate | 5 | 10 |
| diethylene glycol monobutyletheracetate | 5 | 10 |

| Compound class compound | Target value [µg/m³] | Guidance value [µg/m³] |
|---|---|---|
| **Esters of monovalent alcohols** | **20** | **50** |
| ethylacetate | 10 | 25 |
| isobutylacetate | 5 | 10 |
| n-butylacetate | 10 | 25 |
| methylmethacrylat- | 3 | 10 |
| methylbenzoate | 3 | 10 |
| **Other compounds**[2,4] | **20** | **50** |
| tert.-butylmethylether (MTBE, also [1]) | 5 | 10 |
| 1,4-dioxane (also [1]) | 3 | 10 |
| tetrahydrofuran | 3 | 10 |
| n-methylpyrrolidone | 5 | 10 |
| dibutylmaleinate | 5 | 10 |
| texanol (2,2,4-tri-methyl-1,3-pentandiol monoisobutyrate) | 5 | 10 |
| TXIB (2,2,4-trimethyl -1,3-pentandiol diisobutyrate) | 5 | 10 |
| phenols and cresols (only [4]) | 3 | 10 |
| phthalates | 5 | 10 |
| siloxanes (also [1]) | 5 | 20 |
| **Total of VOC** | **300** | **1000** |

**The values are based on the following methods:**

[1] non-polare to moderate polare compounds: sampling on activated charcoal type NIOSH; desorption by carbondisulfide ($CS_2$), GC-MS

[2] more polar compounds: sampling on Anasorb 747; desorption with methanol and dichloromethane (95:5 v/v), GC-MS

[3] more polare compounds: samling on DNPH silica cartouches, desorption with acetenitrile, HPLC

[4] Particular, polar compounds, sampling on TENAX TA, thermal desorption, GC-MS

## DISCUSSION

Toxicologically derived guidelines for VOC in indoor air are very sparse. 1987 the WHO started to publish air quality guidelines for styrene, toluene, dichloromethane, trichloroethene, tetrachloroethene and formaldehyde. In this connexion interdependencies like synergistic effects between other compounds occurring in indoor air could not be taken into account. In 1977 the German Institute of water, soil and air hygiene released a guideline for formaldehyde of 0.1 ppm (= 0.12 mg/m³). Mølhave (1991) exposed test persons with a defined mixture of VOC and subdivided the physiological reactions in 4 categories. But unfortunately nearly all indoor air measurements are within the category 2 with TVOC values ranging from 0.20 – 3.0 mg/m³. Highly toxic and carcinogen substances were not included in the tests. A schema for the toxicological derivation of guidelines was developed by the German environmental protection agency (Umweltbundesamt 1996). There the guideline II is derived from toxicological and/or epidemiological studies by the use of well defined factors of uncertainty. As a convention the guideline I of the respective VOC is formed usually with the division by 10. Concentrations below guideline I are considered to be safe for the human health even at lifetime exposure. The following guidelines for volatile organic compounds were published:

| VOC | Authors | Guideline I | Guideline II |
|---|---|---|---|
| toluene | Sagunski (1996) | 0.3 mg/m³ | 3 mg/m³ |
| dichloromethane | Witten et al. (1997) | 0.2 mg/m³ | 2 mg/m³ |
| styrene | Sagunski (1998) | 0.03 mg/m³ | 0.3 mg/m³ |
| bicyclic terpenes | Sagunski et al. (2003) | 0.2 mg/m³ | 2 mg/m³ |

Unfortunately the toxicological derivation seems to be very time consuming or impossible due to the lack of data. Furthermore additive and synergistic effects with other VOC cannot be considered as a rule, whereas over 100 compounds are found in indoor air. One answer is the use of TVOC values. But as VOC often reveal unequal toxicological properties, they should be grouped to classes of similar chemical or toxicological characteristics.

## CONCLUSION

As preliminary solution for an enclosing evaluation of indoor air situations the use of statistical values is recommend. These values should be derived preferably from contemporary and representative studies. An example concerning the range of the compounds and the respective values is given in table 1. We emphasize that statistical values give hints on noticeable concentrations or VOC sources, but have no toxicological bases. But they can be very helpful, if adverse health effects are observed in indoor spaces

## LITERATURE

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