

## **EVALUATION OF INDOOR PRODUCTS BY SENSORY AND CHEMICAL TESTING. PART II: COMPARISON OF OLFACTOMETRIC AND VOC ANALYSIS**

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### **ABSTRACT**

Evaluation of building products for indoor use with respect to an influence on human well-being is a topic of multi-disciplinary concern. Climatic parameters, inorganic and organic contaminants as well as psychological factors, etc., are frequently discussed as contributors to an impact on indoor air quality and SBS. Two approaches were compared for their usability for evaluation of emissions from indoor products in emission test chambers. The first is olfactory testing in which odor units, odor intensity and hedonic effects are determined by a sensory panel. The second is VOC analysis in which concentrations of compounds in the test chamber are quantified by sampling on Tenax TA and thermal desorption GC/MS. The latter also employs the TVOC<sub>GC/MS</sub>-method according to ECA-report no. 19. No simple correlation between VOC analysis and sensory testing was found. Both methods bear their assets and drawbacks and for that reason complement one another.

### **INDEX TERMS**

Measurement methods, Perceived air quality, VOCs and SVOCs, Test chamber, Olfactometry

### **INTRODUCTION**

It is a matter-of-fact that evaluation of building products with respect to health and comfort is not trivial and must take into account measures of diverse nature (Wolkoff, 1999; Fang et al., 1999, Knudsen et al., 1999). For this reason indoor products were investigated by sensory testing and for their VOC emissions. While olfactory analysis is a comparably simple method and permits evaluation of acceptable materials with regard to perceptual well-being, chemical testing records substances which are, for example, detrimental to occupants' health. In some cases both methods may be equally useful, e.g. when the odor threshold of an emitting compound is in a concentration range where it can be easily detected by chemical testing as well. Sometimes, however, the human nose is much more sensitive than chemical testing while other compounds do not exhibit characteristic odors and chemical analysis is therefore more informative. Materials examined in emission test chambers were cork adhesive and parquet adhesive. Odorous compounds could be expected to be released from this test specimen. The measurement of odor units, hedonic effects, and type of odor are described in part I (Salthammer and Kühn, 2002). The measurement of VOC and TVOC<sub>GC/MS</sub> according to ECA-report no. 19 (CEC, 1997) also has been previously described (Massold et al., 2000a,b). However, the method is varied in so far as emitting substances that could be found in the analytical window between n-hexane and n-hexadecane but were not part of the list of 64 compounds stated in the report were also quantified and included in the value of  $S_{id}$  (= sum of identified substances;  $S_{un}$  = sum of unidentified substances) (CEC, 1997). A ratio of  $S_{id}/TVOC_{GC/MS} > 0.67$  ensures that most compounds detected are quantified by their own response factors. This demand is therefore a major criterion for the validity of the TVOC<sub>GC/MS</sub>-value.

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## METHODS

The samples were tested in 1 m<sup>3</sup>-chambers made of glass and had a surface area of 0.4 m<sup>2</sup>. The adhesives were scraped on a glass piece and put into the chamber immediately after application. Measurement took place over periods of 28 days (cork adhesive) and 17 days (PUR) until constant emission was reached. The loading to air exchange ratio was 1 m<sup>3</sup>/(m<sup>2</sup>h). Temperature was 23 °C and r.h. 50 %. Sampling of chamber air for VOC-analysis was carried out with FLEC-pumps (CHEMATEC) on stainless steel tubes filled with 250 to 300 mg Tenax TA 60-80 mesh. Sampling volumes were 4 - 6 l of chamber air at a flow rate of 100 ml/min. Analysis of sampling tubes was done by using a GC/MS-system (Hewlett Packard 5890) with a 60 m HP5MS column equipped with a thermal desorber – cold trap injector (Perkin-Elmer ATD 400). Sampling for olfactory tests (ECOMA) was performed with cylinders equipped with a fan which causes vacuum and thus draws the chamber air into a sampling bag.

Liquid standards were prepared by dissolving the compounds in methanol. Gas standards were used for more volatile compounds which were found to undergo a loss when prepared as liquid standard. The combination of liquid and gas standards for calibration of VOC has previously been described (Massold et al., 2001). In addition, a liquid standard of completely deuterated n-alkanes (n-hexane, n-heptane, n-octane, n-decane, n-dodecane, n-tetradecane, n-pentadecane, n-hexadecane and n-heptadecane) was also dosed onto the tubes as internal standard. Calibration was established by relating obtained areas of appropriate extracted ion currents (EIC) of substances investigated to EIC of m/z 34 obtained for n-dodecane.

Earlier experiments showed inter laboratory discrepancies for analysis of VOC in test chambers which were partly caused by poor calibration curves in the lower and upper concentration range (Massold et al., 2000a). Extension of the calibration range for the 64 compounds improved quantification and was specifically beneficial for low concentrations.

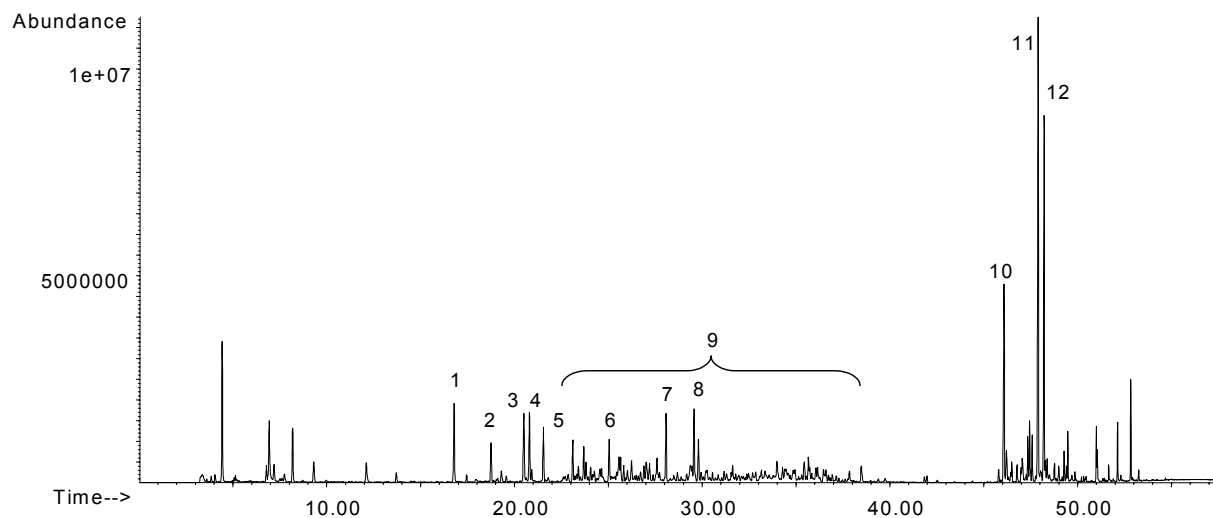
## RESULTS

The two investigated samples yielded quite different results. The cork adhesive showed a high variety of emitting compounds. Figure 1 shows a chromatogram of a sample taken 5 h after loading. Besides numerous iso-alkanes, cycloalkanes, alkenes and terpenes, the major emissions found in the first sample were 4-phenyl-cyclohexene, 4-vinyl-cyclohexene, isolongifolene and some aromatic compounds. For chemical analysis and with regard to calculation of TVOC<sub>GC/MS</sub> this sample is highly challenging because of the multitude of compounds that would have to be calibrated for exact quantification of their sum.

Quantification of some selected compounds of such a complex sample would always be insufficient for evaluation of emissions. After 24 hours high emissions of diethylamine and CS<sub>2</sub> could be detected. These substances are degradation products of diethyl carbamate which is used for cross-linking the polymer chains. Both of them cause problems with their quantification. CS<sub>2</sub> elutes before n-hexane and cannot be trapped quantitatively on Tenax TA. Diethylamine does elute in the respective analytical window between n-hexane and n-hexadecane. However, it does not exhibit a sharp peak but an extremely broad band of approximately 7 min. in retention time units. The shapes were too diffuse to be integrated correctly.

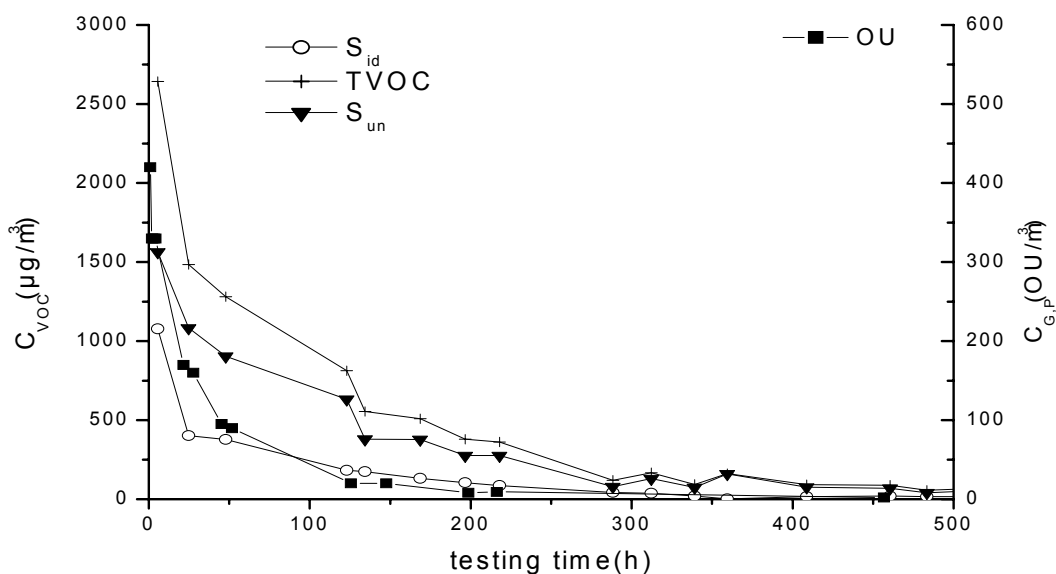
The TVOC<sub>GC/MS</sub>-method is only of limited use for overall emissions of this sample. Because of the high concentration of some compounds they were additionally calibrated and added to the S<sub>id</sub> value. These were 4-vinyl-cyclohexene, di-n-butyl ether, allylbenzene, p-cymene, decanal and isolongifolene. Figure 2 shows the decay of the thus obtained values for S<sub>id</sub>, S<sub>un</sub>

and  $TVOC_{GC/MS}$ . Both  $S_{id}$  and  $S_{un}$  have a high concentration (1078 and 1564  $\mu\text{g}/\text{m}^3$ , respectively) at the beginning of the experiment.



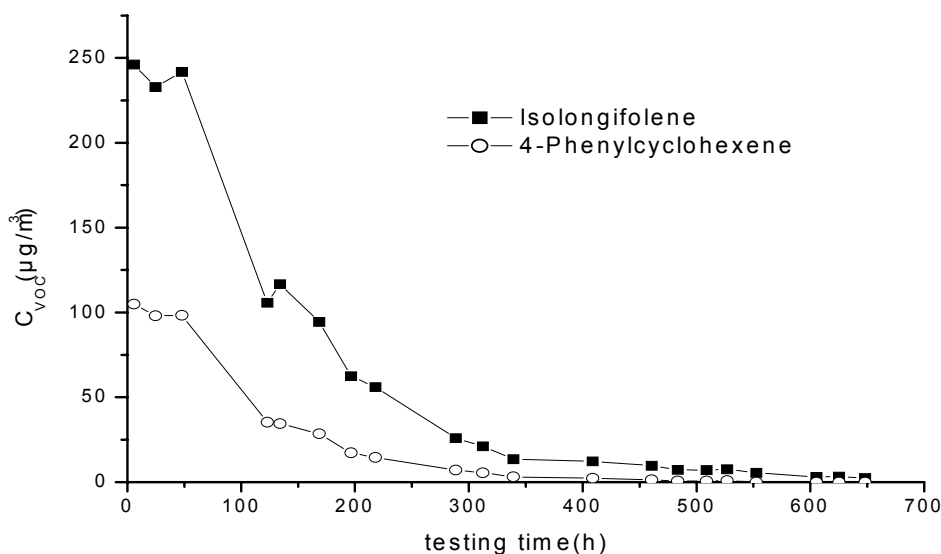
**Figure 1.** Chromatogram of a sample of chamber air of cork adhesive on glass surface taken 5 h after loading.

1) 4-vinyl cyclohexene, 2) ethyl benzene, 3) di-n-butyl ether, 4) styrene, 5) n-nonane, 6) n-propyl benzene, 7) n-decane, 8) p-cymene, 9) various hydrocarbons, 10) 4-phenyl-cyclohexene, 11) isolongifolene, 12) unknown sesquiterpene (not identifiable).



**Figure 2.** Decay of  $S_{id}$ ,  $S_{un}$ ,  $TVOC_{GC/MS}$  and odor units of cork adhesive.

Figure 2 shows that the requirement given for the ratio of  $S_{id}/TVOC_{GC/MS}$  being two third is not met for the emissions of this sample.  $S_{un}$  is higher than  $S_{id}$  at all times. If diethylamine could be quantified more reliably the situation would be different as this is a major emittent. In Figure 3 the decay of isolongifolene and 4-phenyl-cyclohexene is shown. They are very different types of components and show the diversity of emitting compounds for the cork adhesive.

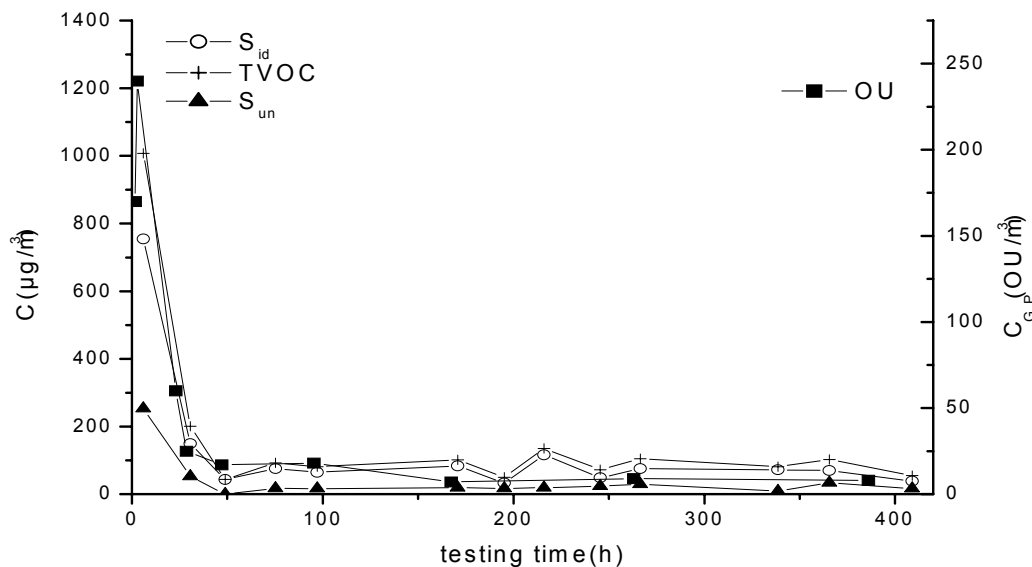


**Figure 3.** Concentration versus time plots for some selected compounds emitted from PUR adhesive.

Sensory evaluation resulted in equally diverse descriptions of the emissions. In Figure 2 odor units can also be seen. Odor types at the beginning of the experiment (within four hours, 420 – 330 OU/m<sup>3</sup>) were characterized as solvent like, glue like, detergent like and ammoniac like. Furthermore, a pungent, rancid odor was noticed. The hedonic effect was described as being unpleasant or extremely unpleasant and the intensity as distinct or strong. After 22 and 28 hours (170 and 160 OU/m<sup>3</sup>, respectively) they were attributed a rancid, sour and glue-like odor. At this time the hedonic properties were still unpleasant and the intensity had not changed. Towards the end of the test period (126 and 148 hours, both 20 OU/m<sup>3</sup>) they are described as being increasingly solvent like, rubber like and glue like. From this time on the hedonic effect was said to be indifferent (neither/nor) and the intensity was low to very low. At the end of the experiment a glue like, musty, wood glue like, earthy, and sour smell, according to the test panel, was described.

In Figure 4 the decay of  $S_{id}$ ,  $S_{un}$  and  $TVOC_{GC/MS}$  is shown for the parquet adhesive (poly urethane). This sample exhibited some comparably uncommon emissions such as cyclic ethers, e.g. 2-methyl-1,3-dioxolane, siloxanes but also acetic acid ethyl ester, acetic acid vinyl ester and very high amounts of acetic acid methyl ester. The two latter compounds do not elute in the analytical window between n-hexane and n-hexadecane and hence are not to be included into the  $TVOC_{GC/MS}$ -value. However, a vague quantification of acetic acid vinyl ester would yield 63 µg/m<sup>3</sup> at the beginning and 1.3 µg/m<sup>3</sup> after 4 days.

Tentative quantification of acetic acid methyl ester is not possible because the concentration is so high that it lies far outside the calibration range. It must be assumed that it is the major emitting compound. Very high emissions of acetic acid could also be detected. They ranged from 533 µg/m<sup>3</sup> at the beginning of the experiment to 21 µg/m<sup>3</sup> on the second day. Acetic acid caused the unsteady decay of the  $S_{id}$  and  $TVOC_{GC/MS}$  curve. It was also included into the



**Figure 4:** Decay of  $S_{id}$ ,  $S_{un}$ ,  $\text{TVOC}_{\text{GC/MS}}$  and OU of cork adhesive

$S_{id}$  value as additional compound, because it elutes in the analytical window. This substance produces a very broad band on the unpolar column what made integration and quantification difficult. The calibration curve had a poor fit ( $r^2 = 0.98$ ). Fluctuations in concentrations are nonetheless observed. At the end of the experiment acetic acid could still be detected ( $37 \mu\text{g}/\text{m}^3$ ).

Both, the VOC concentrations and the odor concentration were much lower than in the case of the cork adhesive. The chromatogram exhibited distinctive peaks and most of them could be identified. Nevertheless, the ratio of compounds which would not be in the list of the 64 compounds is quite high and additional calibration of some selected compounds was necessary in order to achieve a higher ratio of  $S_{id}/\text{TVOC}_{\text{GC/MS}}$ .

The odor was in this case described glue like, solvent like and musty. At the end it was only characterized as being musty. Especially glue like and musty odors are said to be pungent. Within one day the hedonic effect was said to be extremely unpleasant and the intensity strong. At all other times they were unpleasant. The intensity was strong at 28, 47 and 95 hours and weak to very weak at later times of the test period. In this case the quick decay of the odor units at the beginning correlates well with the  $\text{TVOC}_{\text{GC/MS}}$  decay which is mainly due to the decay of acetic acid. However, the concentration of acetic acid vinyl ester also decreased very quickly to  $< 2 \mu\text{g}/\text{m}^3$  at day four. A major contribution to the pungent odor must supposedly also be attributed to the very high amounts of acetic acid methyl ester.

## DISCUSSION

The overall estimation of building products is still difficult. Different approaches of validation aim at specific properties. Influence parameters such as VOCs, VVOCs, SVOCs, POMs and sensory impacts can influence indoor air quality. Taking into account their contribution demands employment and interaction of different disciplines. The presented methods of olfactory testing and  $\text{TVOC}_{\text{GC/MS}}$  analysis complement one another and both show an important contribution towards a better understanding of material emission and hence indoor air quality.

The presented results showed parallel decays for both OU and VOC concentration. This, however, can also be a coincidence and is not necessarily the case for different samples.

### **CONCLUSION AND IMPLICATIONS**

Both, olfactory and chemical analysis, provide important information about the acceptability of building products for indoor use. For the samples investigated there is a rough correlation between high odor concentrations and high VOC concentrations at the beginning of the experiments and also for the shape of the decay curves. However, the measurement of one value does not entail a redundancy of the other. The correlation is not that high that this could be permitted and furthermore both methods bear information the other does not offer.

While olfactory testing is a comparably simple method that gives quick results about an influence of indoor products on perceptual well-being, the TVOC<sub>GC/MS</sub> method is more sophisticated and time-consuming but supplies exact data about type and concentrations of VOC with relevance to indoor air quality. The method which was so far only used for evaluation of outdoor air has proved to be valuable also for indoor air (Salthammer and Kühn, 2002). Both adhesives are rather difficult to assess for their TVOC<sub>GC/MS</sub> -values and the TVOC-method according to the ECA-report No. 19 shows its limitations.

### **ACKNOWLEDGEMENTS**

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