LABORATORY AND REAL SCALE COMPARATIVE STUDY OF BENZYL ALCOHOL EMISSIONS FROM A TWO-COMPONENT EPOXY PAINT

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ABSTRACT

The benzyl alcohol emissions from a two-component epoxy paint were studied in a 30 litres laboratory test chamber and in a 30 cubic meters real scale test system. The real scale measures were done in a test system realized with concrete and finished with gypsum. The laboratory scale experiments were done in a glass chamber with minimized sink an in another chamber simulating the walls and ceiling sink with gypsum surfaces. The laboratory scale experiment without sink demonstrates a high emission rate during the first hours, and a quick abatement of the emission after the polymerization. The simulated sink laboratory experiments demonstrate lower concentrations during the first hours and higher concentrations after the sample polymerization, due to the secondary emissions from gypsum surfaces. In the real scale experiments however the release effects from walls was were not observed, possibly due to a permeation through the walls under the gypsum layer.

INDEX TERMS

VOC material emission, Benzyl alcohol, Real size chamber, Laboratory ambiental chamber, sink, Gypsum secondary emission

INTRODUCTION

The Volatile Organic Comounds (VOC) emissions of building products are typically measured in laboratory climate chamber, using strictly controlled conditions (Sollinger, Levsen and Wünsch, 1993). Particularly, the ambiental chambers are designed in order to minimize the VOC sinks on the chamber walls, that can interfere with the emission measurements. In the real situations, however, sinks can be very important (Sparks, Guo, Chang et al., 1999), and the time profile of the VOC concentrations in laboratory and real scale measurements could be very different.

We have studied the benzyl alcohol emissions of a two-component epoxy flooring paint in laboratory and in real conditions. For the real conditions experiment we used a full size testing facility (35 m^3), with walls and ceiling finished with gypsum. This testing system is fully described elsewhere (Antonelli, Mapelli, Sanguinetti et al., 2002). For the laboratory scale experiments we used two 30 litres test chambers (Strini, Mapelli and Bignami, 1999). In the former we measured the emissions of the paint alone, while in the latter we simulate the sinking walls of the full-size experiment with three Petri dishes filled with a 3 mm thick gypsum layer.


In all experiments we used the same air change rate and loading factor (surface/volume ratio) as the sample and the sinking surfaces.

METHODS
The laboratory scale emission measurements were carried out with two 30 litres dynamic test chambers operated in parallel.

Qualitative analysis
A sample of the paint was placed in a dynamic headspace chamber (200 ml volume). The emissions were collected with Tenax tubes and analyzed as described hereafter. The primary emission found was benzyl alcohol, followed by glycidyl-2-methylphenyl ether and other minor compounds. The qualitative chromatogram is reported in Figure 1.
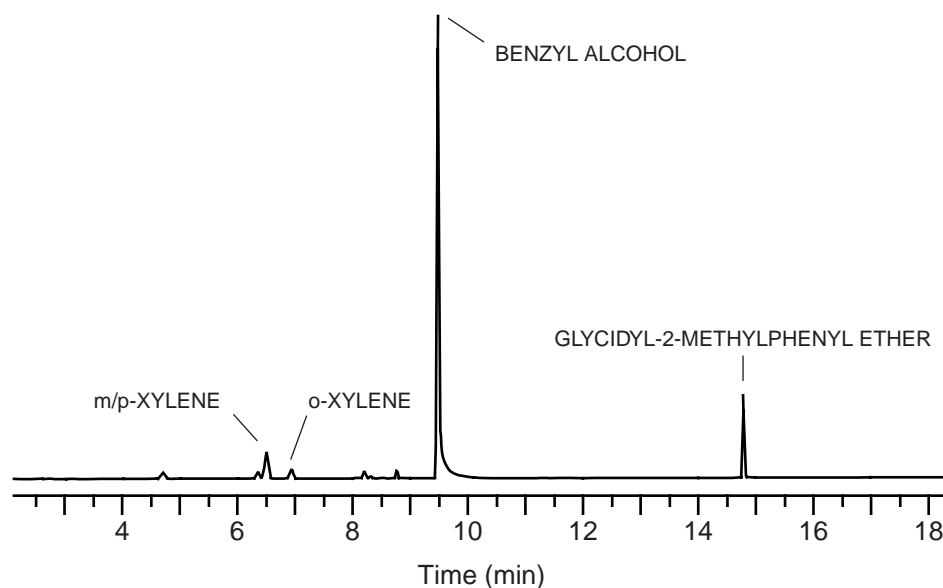
Figure 1. Total ion chromatogram of the paint emissions. Sample in dynamic headspace.

Laboratory experiment with gypsum
Three Petri dishes were prepared applying a mixture of distilled water-gypsum to have a filling thickness of about 3-4 mm. The Petri dishes were allowed to dry, by placing them in a closed desiccator with silica gel to avoid contaminations from the laboratory atmosphere. The drying process lasted seven days, changing the silica gel three times. The Petri dishes were then placed in the 30 litres test chamber supplied with 50 relative humidity and allowed to equilibrate for 24 h. A sample of chamber air was taken and analyzed to assess the absence of contaminants.

The paint sample was prepared by applying a paint aliquot (about 7.5 g) on a inox plate (121 cm^2). The preparation procedure lasted five minutes, then the specimen was exactly weighed and placed in the test chamber.
The experimental conditions are reported in Table 1.

Laboratory measurement without gypsum
A second paint specimen, prepared at the same time and with the same condition was placed in the second test chamber without sinking elements.

Laboratory sampling and analysis
The test chamber atmosphere was sampled with Tenax tubes (Supelco) and analyzed with an automatic thermal desorber (Perkin Elmer ATD 400) coupled with a GC-MS system (Hewlett-Packard HP5973). A HP5-MS column (Hewlett-Packard, 30 m, 250 μm id, 0.25 μm film thickness) was used in all analysis.

The qualitative analysis was obtained with mass spectra library identification followed by pure standard confirmation of both spectra and retention time. The quantitative analysis were performed by acquiring the chromatogram in scan mode and integrating the benzyl alcohol peak with single ion, calibrating the system with 6-8 standard dilution injections.

Table 1. Experimental conditions for the laboratory and real scale experiments

	Laboratory (No sink)	Laboratory (Sink)	Real scale
Chamber volume	0.03 m^3	0.03 m^3	35.6 m^3
Loading factor (Paint)	0.4 m^2/m^3	0.4 m^2/m^3	0.36 m^2/m^3
Loading factor (Gypsum)	---	1.53 m^2/m^3	1.45 m^2/m^3
Air change rate	0.5±0.01 h^{-1}	0.5±0.01 h^{-1}	0.5±0.03 h^{-1}
Temperature	22±1 C	22±1 C	20±2 C
Relative humidity	50±5 %	50±5 %	40~60 % (*)
Paint covering	630±5 g/m^2	635±5 g/m^2	600±50 g/m^2

(*) Not continuosly monitored during the experiment
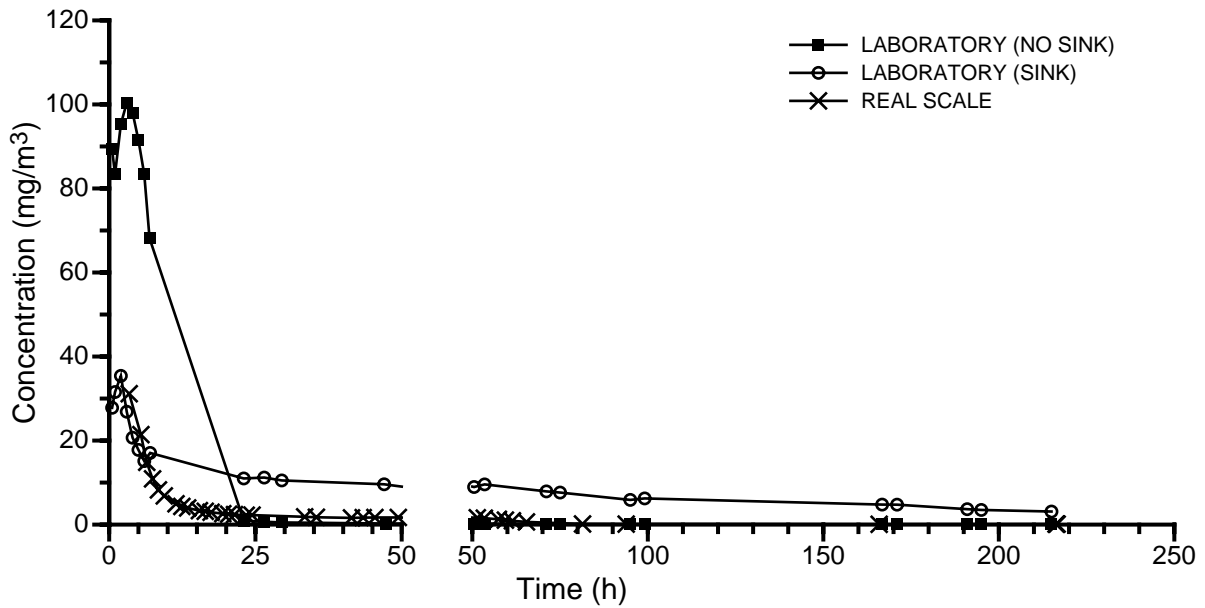
Real scale experiment
The paint was applied to the floor of a real scale system. A single layer of paint was applied. During the application, the cell door was kept open. The application procedure lasted 20 minutes. The cell door was then closed and the air change was set to 0.5 vol/h.

Real scale sampling and analysis
In the real scale experiment an automatic ambient sampler (STS25, Perkin-Elmer) was used allowing unattended sampling operation for 24h (24 samples of 1h each) and 48h (48 samples of 2h each). This allows the overnight sampling of the system. A manual sampling system was also used, as a complement of the automatic one. For all samples Tenax tubes (Supelco) were used. The samples were analyzed with the same procedure as the laboratory ones.

RESULTS
The benzyl alcohol concentrations measured in the three experiments are showed in Figure 2. The concentration measured in the laboratory chamber without the sink surface showed a very high peak during the first hours, followed by a quick decay (note that it was not possible for us to take samples overnight, so we don't have any data over the time range 6.9 to 23 h for the two laboratory scale experiments).

Figure 2. Benzyl alcohol concentration in laboratory and real scale experiments.

In the laboratory chamber with the sinks surfaces however the concentration profile was quite different. The initial peak was lower. It was not observed the fast decay showed without gypsum, and the concentration falls slowly, showing a quite high value at the end of the experiment (215 h).

A third behaviour is showed by the real scale experiment, where the initial peak was comparable to the laboratory experiment with gypsum, but followed by a substantial decay. By integrating the concentration data it is possible to calculate the total amount of a certain compound emitted during a given interval per unit of sample area (Specific Cumulative Emission, *SCE*):

$$SCE(t_1 - t_2) = \frac{C_{flow}}{S_{area}} \cdot \int_{t_1}^{t_2} C_{voc}(t) \cdot dt \qquad (1)$$

where *SCE(t₁-t₂)* is the specific cumulative emission in mg in the interval t_1-t_2, C_{flow} is the chamber air change flow in m^3/h, S_{area} is the sample area in m^2 and $C_{voc}(t)$ is the compound concentration at time t in mg/m^3.

This calculation reflects the amount of compound left from the chamber through the air change process, so if a sink effect is present, the resulting figure represents the compound amount really emitted from the sample minus the amount still adsorbed in the sink and not yet released in the considered time lapse. The calculated *SCE* values for selected time intervals are reported in Table 2.

Table 2. Specific cumulative benzyl alcohol emission calculated from concentration data

Time interval h	Laboratory (No sink) g/m^2	Laboratory (Sink) g/m^2	Real scale g/m^2
0-24	0.74~1.41 (*)	0.47	0.18
24-48	0.014	0.31	0.054
48-215	0.025	1.19	0.046
0-215 (Total)	0.78~1.45 (*)	1.97	0.28

(*) Estimated interval accounting for integration error. See text below.

The specific cumulative emissions were calculated from the concentration data with trapezoid integration (interpolating each data pair with a straight line). This gives some integration errors that are significant in the laboratory experiment without sink, because the manual sampling procedure does not allow the data acquisition during the fast decay part of the emission curve (see Figure 2). The trapezoid integration can cause an overestimation of the *SCE* that was calculated to be 0.67 g/m^2 in the worst case (assuming a vertical decay from the point at 6.9 h to the concentration level found at 23 h). Table 2 reports the minimum and maximum estimated SCE values for the affected time interval

DISCUSSION
At the application time the product is a dense liquid that undergoes a polymerization in few hours. While during the first hours the liquid state allows a high evaporation rate, after polymerization the high compactness of the products accounts for the rapid decrease of evaporation and thus the chamber concentration of benzyl alcohol.

In the presence of gypsum the sink effect decreases the intensity of the initial concentration peak and cause the absorption of a significative amount of emitted benzyl alcohol. However, the gypsum itself acts as secondary emitter after the paint polymerization, and the re-emission keeps the concentration level quite high during the remaining time of the experiment. It is interesting to notice that the total quantity of benzyl alcohol leaving the chamber with gypsum is sensibly higher than the quantity released by the paint. The *SCE* of the system paint and gypsum was about 35% higher than the *SCE* of the paint alone, not accounting for the possible overestimation of the *SCE* for the latter. Moreover, while the chamber with paint alone shows a negligible concentration at the end of experiment (compared to the first hours peak), the chamber loaded with paint and gypsum shows a remarkably high concentration at 215 h, indicating a possible residual emission capability from gypsum. This difference can be explained by an increased benzyl alcohol evaporation during the first hours of the chamber with sink caused by the lower concentration due to the sinking process itself. The increased emission, sank by the gypsum, is released after the paint polymerization, giving rise to an higher cumulative emission.

In the real scale experiment, the first hours concentration profile was remarkably similar to the chamber with gypsum, supporting the hypothesis of analogous sink behaviour. Quite surprisingly however, the sustained concentration showed in the laboratory experiment is not observed in real scale, and the concentration falls to a level comparable to the laboratory experiment without sink. This behaviour could be explained by assuming a permeation through the gypsum to the concrete walls, where the benzyl alcohol was dispersed or irreversibly adsorbed. In the laboratory experiment, the benzyl alcohol can diffuse only in the

few millimetres of the gypsum layer and the presence of the Petri glass prevents the irreversible adsorption.

CONCLUSIONS AND IMPLICATIONS

The VOC adsorption phenomena could have a major impact in the final indoor pollution, and alter the impact of building products foreserable by the standard test chamber experiments, that are carried out without appreciable sink effects. The presence of sinks can cut some peak concentration in case of short time pollution events, as the painting process studied here, but they can at the same time cause a higher evaporation of VOC, resulting in a greater final cumulative emission.

The laboratory simulation of real scale sink behaviour, even in a simple and controlled system like our real scale test environment, puts forward some challenges. Particularly, the simulation of the walls and ceilings sinks with a layer of the same finishing material was not sufficient to recreate the situation found in the real system, even if the same loading factor, ventilation and temperature were maintained in all experiments. The main difference between the real scale and laboratory sinks was the substrate of the gypsum layer, that was concrete in the full scale environment and glass in the laboratory chamber. The data obtained in this work suggest that, at least in the studied case, permeation effects can involve the deep finishing layers and, possibly, the underlying materials. In this hypothesis, the VOCs interacting with the wall materials could permeate and/or be irreversibly or nearly-irreversibly adsorbed.

This suggests the possibility of long term VOC release and permeation from walls, especially considering the case of several contiguous environments.

ACKNOWLEDGEMENTS

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