

# Evaluation of emissions in paints: comparison between in-can and test chamber methods

Mikaela Decio<sup>1,\*</sup>, Fabio Abbà<sup>2</sup>, Tiziano Cerulli<sup>1</sup> and Roberto Leoni<sup>1</sup>

<sup>1</sup>Mapei S.p.A. R & D Central Laboratory, Via Cafiero, 22, 20158 Milan, Italy

<sup>2</sup>Vinavil S.p.A. R & D Laboratory, , 28844 Villadossola, Italy

\* *corresponding email: analysis.lab@mapei.it*

## SUMMARY

VOC can be evaluated either as in-can amount in the products or as emissions released by the products in function of time. The European Directive 2004/42/EC defines VOC as every organic compound with a boiling point up to 250°C. We prepared different water-based paints complying with 2004/42/EC. The three paints have different formulation (with or without coalescing agents with different boiling points). Paints were analysed following ISO 11890-2 in order to evaluate the in-can VOC content and then analysed according to ISO 16000-6, for determination of VOC in indoor air using test emission chambers, both on a glass plate and on a sound-deadening panel.

The emissions released by the samples considered were strongly influenced by the presence of the coalescing agents.

## KEYWORDS

Water Based paints, In-can VOC, Emission chambers.

## INTRODUCTION

Different methods are nowadays available to determine the Volatile Organic Compounds (VOC) in many building products. Evaluations of VOC in the product (in-can VOC) can be performed by calculation from the original formulation, gravimetric methods (ISO 11890 part 1, 2006), gas chromatography (ISO 11890 part 2, 2005); VOC emissions as a function of time released by the product can be determined by means of emission chambers (ISO 16000 part 6, 2004).

The aim of this study is to compare different methods, both in-can VOC and emissions, to measure VOC in different water based paints.

To better understand the influence of substrates on the total VOC (TVOC) release, two different substrates have been considered. Firstly a glass plate has been chosen as non adsorbent substrate according to ISO 16000, then paints have been applied also on a sound-deadening panel, an adsorbent surface.

## METHODS

### a) IN-CAN VOC methods

Measurements of in-can VOC are needed at least initially to validate the calculations and gain experience with formulations. In fact calculation methods work well provided formulation is thoroughly understood but there are pitfalls: calculated solvent content is an estimate only; non-solvent additives may volatilise; reactive diluents may volatilise before reacting; actual volatiles content of intermediates (e.g. binder) is not routinely determined prior to use; some oligomers may volatilise; cross-linking reactions may not go according to theory; formation of reaction by-products may be unknown.

Methods for the measurement of VOC content need to be flexible enough to cope with any definition of VOC and VOC content.

There are mainly three different methods that can be used in order to determine in-can VOC content:

- Difference Method (ISO 11890 Part 1,2006; ASTM D3960, 2005)

With these methods some features must be determined before expressing VOC:

weight percentage of non-volatile matter (ASTM D2369,2007; ISO 3251, 2008);

water content using Karl-Fisher titration (ASTM D4017,2002; ISO 760, 1978);

density of paint (ASTM D1475, 2003; ISO 2811 part 1, 1997) if VOC per unit volume is required.

They are applicable to relatively high VOC contents (scope of ISO 11890 Part 1 states weight percent > 15%.)

- Gas-chromatographic methods

1) ISO 11890 - Part 2 - measurement of Low VOC Contents (0.1 wt% < VOC Content < 15 wt%)

It is a split-vent liquid injection Gas Chromatography method that allows identification and quantification of all the volatile components and sums those falling within the relevant definition of VOC. This is the method reported in the European Directive 2004/42/CE.

After preparation of the sample, the VOCs are separated by a gas-chromatographic technique in which either a hot or a cold sample injection system is used, depending on the sample type. After the compounds have been identified, they are quantified from the peak areas using a suitable internal standard

If VOC refers to compounds with a defined maximum boiling point, a marker compound of known purity and a boiling point within  $\pm 3$  °C of the defined maximum boiling point shall be used. According to the European Directive 2004/42/CE the defined maximum boiling point is 250 °C and in this ISO standard diethyl adipate with a boiling point of 251 °C should be used as a marker compound.

This is the method we applied in the determination of in-can VOC content of our products.

2) ISO 17895 - Measurement of very Low VOC Contents (0.01 wt% < VOC Content < 0.1 wt%)

It is a head-space gas chromatographic - total exhaustion technique that gives excellent sensitivity and reduces matrix effects. By means of using of a non-polar column that confers good correlation of retention time with boiling point, a boiling point marker (tetradecane b.p. 252°C) that defines limit for integration, and a suitable mix of standards this method is very powerful in identification and quantification of all the components.

## b) Emission methods

Emission test chambers have been used for years in our analytical laboratory, in order to evaluate the content of volatile organic compounds emitted by building products and adhesives used for flooring installations.

The chambers, made of stainless steel and glass, have a volume of 210 l, controlled relative humidity and temperature ( $T=23 \pm 2^\circ\text{C}$ ;  $\text{RH}= 50 \pm 5\%$ ), and loading factor  $0.45 \text{ m}^2/\text{m}^3$ .

This value is a typical ratio of exposed surface area of the test specimen to the test chamber volume. It simulates the situation in a common installation of a floor in a typical apartment.

The chamber is fluxed by dry nitrogen (in this text we refer to this gas as “air”), with a flow rate of  $0.5 \text{ h}^{-1}$ , which allows a complete change of the air in the chamber every two hours.

The following table (GEV Testing method, 2005) shows the parameters which shall be adjusted before the analysis.

Table 1. chamber parameters

| Parameter                              | Value                                 | Tolerance                             |
|--|---------------------------------------|---------------------------------------|
| Temperature (chamber and incoming air) | 23°C                                  | ±2°C                                  |
| Relative Humidity                      | 50 %                                  | +5%                                   |
| area specific air flow rate            | 1.25 m <sup>3</sup> /m <sup>2</sup> h | 0.125m <sup>3</sup> /m <sup>2</sup> h |
| air exchange rate                      | 0.5 h <sup>-1</sup>                   | 0.025 h <sup>-1</sup>                 |
| loading factor                         | 0.45 m <sup>2</sup> /m <sup>3</sup>   | ±0.02 m <sup>2</sup> /m <sup>3</sup>  |
| air flow                               | max 0.2m/s                            |                                       |

The sample is mixed uniformly, weighed and applied on a glass non adsorbent surface; the test specimen is transferred into the chamber immediately after preparation.

According to the GEV (Gemeinschaft Emissionskontrollierte Verlegenwerksstoffe e.V) testing method, sampling of air for testing should start 24 hours after the application of the adhesive. In our experiment we have collected air samples at 72 hours and 240 hours after the specimen preparation. At the outlet of test chamber, exhaust air is passed through a sample tube filled with a suitable adsorbent material (Tenax TA®)

Tenax tubes are then desorbed by a thermo-desorber; volatile organic compounds are separated by gas-chromatography, identified by MS detector and quantified by FID detector.

After the glass surface prescribed by the ISO method, paints have been applied on a sound-deadening panel and analysed with the same method.

## RESULTS

A water based paint has been prepared with and without coalescing agents, obtaining three different products:

Paint A: paint without any coalescing agent;

Paint B: paint with a coalescing agent having a boiling point lower than 250°C;

Paint C: paint with a coalescing agent having a boiling point higher than 250°C.

The VOC content has been determined using the method described above:

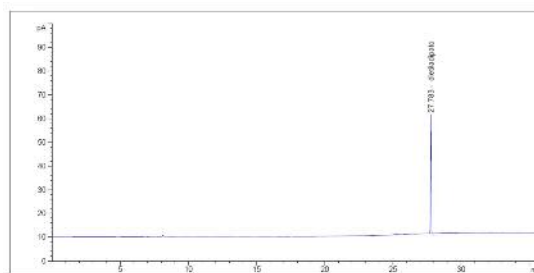


Figure 1. paint A in-can VOC

Chromatogram in figure 1 is the paint A where only the marker peak is evident.

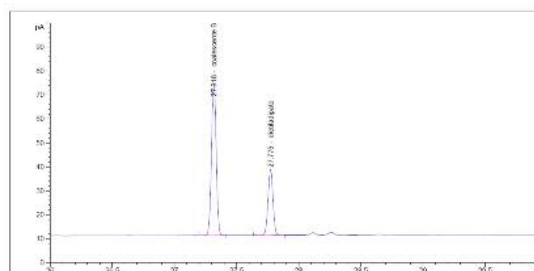


Figure 2. paint B in-can VOC

Chromatogram in figure 2 is the paint B: the main peak is the coalescing agent, with a retention time lower than the marker one.

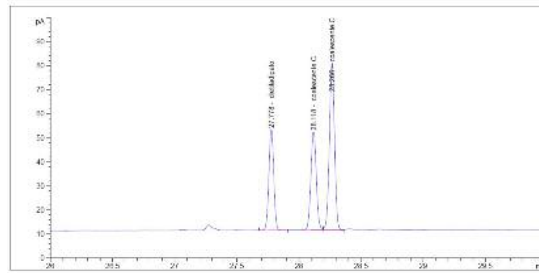


Figure 3. paint C in-can VOC

Chromatogram in figure 3 is the paint C: the coalescing agent shows two peaks, both with a retention time higher than the marker one and for this reason it is not considered as VOC. The next table will sum up the quantitative results on the three samples, expressed in g/L.

Table 2. IN-CAN VOC values

| Sample   | VOC g/L |
|----------|---------|
| Sample A | < 1     |
| Sample B | 8.8     |
| Sample C | < 1     |

According to ISO 11890-2 all the three samples comply with the European Directive 2004/42/CE concerning VOC content, and can be considered as “low-VOC” paints. From the in-can VOC values obtained paint A and C are equivalents.

The same paints have been analysed according to ISO 16000 in order to evaluate their real influence on indoor air quality.

In the first part of the experiment in test emission chambers a film thickness of ~ 100µm of the samples have been applied on a glass plate, as the normative describes. Results are then normalized for a weight of 200g/m<sup>2</sup>.

Following graphs and tables show the content of VOC emissions expressed in µg/m<sup>3</sup> as a function of time, obtained on the three paints (semi logarithmic scale). Concentration of coalescing agents in the first hours is very high, and the peaks might have been saturated.

#### Paint A

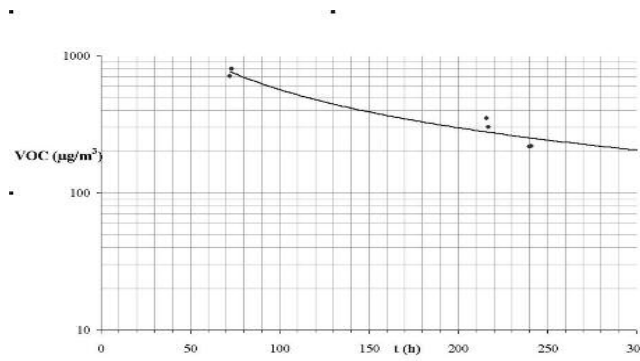


Figure 4. Paint A- glass panel emissions

Table 3. Paint A- glass panel emission compounds

| Compound         | 72 h $\mu\text{g}/\text{m}^3$ | 240 h $\mu\text{g}/\text{m}^3$ |
|------------------|-------------------------------|--------------------------------|
| Propylene glycol | 190                           | -                              |
| Ethylene glycol  | 180                           | -                              |
| Other            | 270                           | 150                            |

Paint A shows very low emissions from the first 72 hours, due to the glycols in the formulations.

After 240 hours, the detected emissions are so low that if the product applied were an adhesive, according to GEV criteria, it would be considered as EC1 (very low VOC emission product).

### Paint B

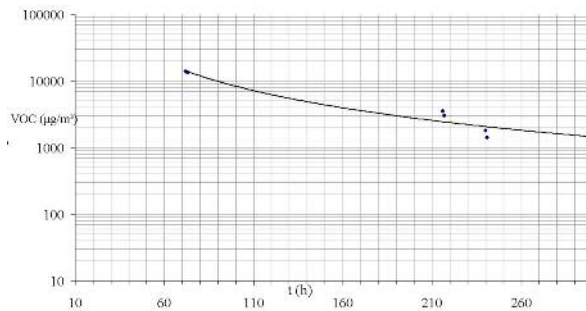


Figure 5. paint B- glass panel emissions

Table 4. Paint B- glass panel emission compounds

| Compound           | 72 h $\mu\text{g}/\text{m}^3$ | 240 h $\mu\text{g}/\text{m}^3$ |
|--------------------|-------------------------------|--------------------------------|
| Coalescing agent B | 8010                          | 1065                           |
| Propylene glycol   | 95                            | -                              |
| Ethylene glycol    | 60                            | -                              |
| Other              | 270                           | 150                            |

Paint B emissions are pretty higher than the ones detected in the first formulation, due to the presence of the coalescing agent B.

Ten days after the application of the product, the emissions only slightly decrease. We could hypothesize that the coalescing agent B will go on releasing VOC for several weeks.

### Paint C

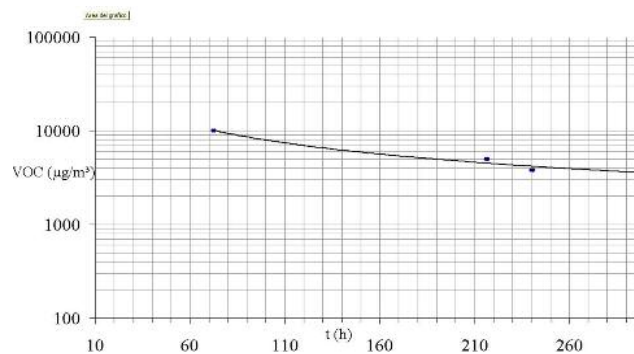


Figure 6: paint C- glass panel emissions

Table 5: Paint C- glass panel emission compounds

| Compound           | 72 h $\mu\text{g}/\text{m}^3$ | 240 h $\mu\text{g}/\text{m}^3$ |
|--------------------|-------------------------------|--------------------------------|
| Coalescing agent C | 10344                         | 3812                           |
| Propylene glycol   | 60                            | -                              |
| Ethylene glycol    | 105                           | -                              |
| Other              | 300                           | 145                            |

Paint C has been formulated adding a high boiling point coalescing agent.

The emissions released by the product are very high after the first 72 hours, due to coalescing agent C.

The emission value after ten days has been strongly influenced by the presence of the coalescent, which hardly decrease in time.

In order to evaluate the influence of a substrate on the emissions, the different paints have been applied on a sound-deadening panel, which has adsorbent characteristics.

Paint A

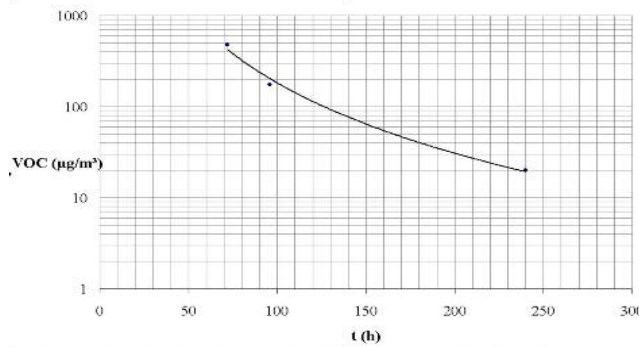


Figure 7. Paint A sound-deadening panel emissions

Table 6. Paint A sound-deadening panel emission compounds

| Compound         | 72 h $\mu\text{g}/\text{m}^3$ | 240 h $\mu\text{g}/\text{m}^3$ |
|------------------|-------------------------------|--------------------------------|
| Propylene glycol | 165                           | -                              |
| Ethylene glycol  | 170                           | -                              |
| Other            | 140                           | 20                             |

The emissions of paint A have been decreased by the adsorbent surface.

Ten days after the application no relevant emissions have been detected.

Paint B

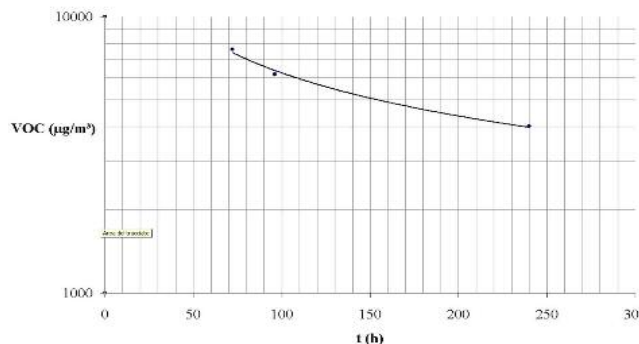


Figure 8. Paint B- sound-deadening panel emissions

Table 7. Paint B- sound-deadening panel emission compounds

| Compound           | 72 h $\mu\text{g}/\text{m}^3$ | 240 h $\mu\text{g}/\text{m}^3$ |
|--------------------|-------------------------------|--------------------------------|
| Coalescing agent B | 7147                          | 3986                           |
| Other              | 475                           | -                              |

Even if the sound –deadening panel reduces the emissions, coalescing agent B has been still detected ten days after the application of paint B.

After 3 days the emissions are lower than the ones observed on glass plate, but they are slowly released into the indoor air.

After ten days all the emissions belong to the coalescing agent, and are higher than the ones on the glass plate.

## Paint C

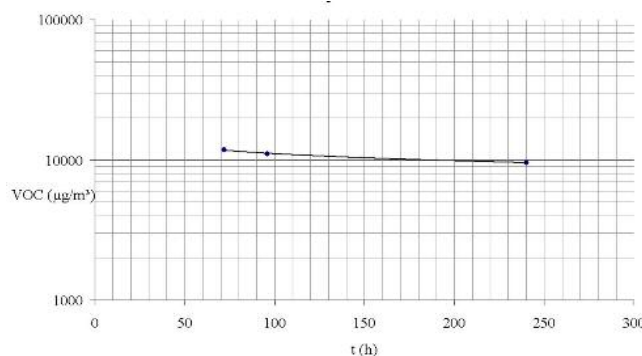


Figure 9. Paint C sound-deadening panel emissions

Table 8. Paint C- sound-deadening panel emission compounds

| Compound           | 72 h µg/m <sup>3</sup> | 240 h µg/m <sup>3</sup> |
|--------------------|------------------------|-------------------------|
| Coalescing agent C | 11403                  | 9571                    |
| Other              | 450                    | -                       |

Results obtained in paint C evaluation are quite higher than the previous ones obtained in the other samples.

It is well evident by the semi-logarithmic graph that the emissions hardly decrease in the first ten days.

## DISCUSSION

The report below sums up all the results found out by applying the various methods:

Table 9. summary

| Samples | IN-CAN VOC (g/l) | TVOC µg/m <sup>3</sup> glass | TVOC µg/m <sup>3</sup> s-d panel |
|---------|------------------|------------------------------|----------------------------------|
| Paint A | < 1              | 150                          | 20                               |
| Paint B | 8.8              | 1215                         | 3986                             |
| Paint C | < 1              | 3957                         | 9571                             |

Paint A and C are considered equivalent from IN-CAN VOC determination while paint B has the highest VOC content.

Considering the emissions according with ISO 16000 both on glass and sound-deadening panel are quite different compared with IN-CAN VOC. The differences are amplified in the case of the sound-deadening panel where an absorbing substrate is used.

The strong influence of the presence of coalescing agents in the paints seems not to be detected by the in-can method but it is relevant considering indoor air quality.

Paint A has low emissions on both substrates due to the absence of additives;

paint B contains a VOC coalescing agent (bp < 250°C) which contributes to a higher in-can value (but inside the limit of European directive): the contribute of the TVOC in the emission at 240 h is entirely due to this additive; paint C has a low VOC value according with IN-CAN

method because contains a coalescing agent which is not considered VOC (bp > 250°C): due to this high boiling point this component is slowly released so the paint has a higher TVOC value at 240h than paint B.

Considering the different substrate used in this experiment it is shown that the release of volatile and semi-volatile compounds is very slow. After 3 days application's paint the detected emissions are comparable between the two substrate; after 10 days the observed emissions are quite higher on the absorbing substrate than on glass.

## **CONCLUSIONS**

The emission test chamber method is applied, according to GEV voluntary scheme only on adhesives, self levellers, primers and sealants.

This scheme foresees applying for instance an adhesive on a glass non adsorbent plate which enhances all the possible emissions coming from the product, even if an adhesive is usually applied on a mortar layer and covered with tiles, wood...In this case the GEV voluntary scheme works ensuring a very good quality of indoor air in our houses.

On the other hand paints are usually applied on a wall (gypsum, sound-deadening panels etc..) and can directly influence the indoor air quality. Nowadays the only method in use to evaluate VOC content in paints is the in-can method.

This work illustrates that an in-can VOC is not sufficient to properly describe indoor air quality, but the complementary emission method is necessary to depict the whole exposure scenario.

Since the coalescing agent is a long time releasing substance a new project is involved in order to evaluate this parameter as well as the influence of other layers such as gypsum, gypsum + primer and so on.

## **ACKNOWLEDGEMENT**

We would like to thank the people that has taken part in this project for their precious contribution, above all Dr. Luigi Mora for the calculation of in-can VOC values, and Mr. Marco Gariboldi for the evaluation of VOC in test emission chambers.

## **REFERENCES**

- ASTM D1475 - 98 Standard Test Method for Density of Liquid Coatings, Inks, and Related Products
- ASTM D2369 - 07 Standard Test Method for Volatile Content of Coatings
- ASTM D3960 - 05. Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings.
- ASTM D4017 - 02 Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method
- GEV (Gemeinschaft Emissionskontrollierte Verlegenwerkstoffe e.V). 2005. GEV Testing method, Determination of volatile organic compounds for control of emissions from products for flooring installation.
- ISO 2811.1988 Paints and varnishes - Determination of density -- Part 1:Pyknometer method
- ISO 3251. 2008. Paints, varnishes and plastics - Determination of non-volatile-matter content
- ISO 11890-1. 2006. Paint and varnishes - Determination of volatile organic compound (VOC) content – Part 1: Difference method
- ISO 11890-2. 2005. Paint and varnishes - Determination of volatile organic compound (VOC) content – Part 2: Gas-chromatographic method
- ISO 16000-6. 2004. Indoor air – Part 6 - Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas-chromatography using MS/FID