

# Measurements of Formaldehyde and TVOC Emission from Paints and Coating Materials using Small Chamber Method for Building Composites

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**Abstract:** An optimal test method for paint is proposed; additionally, the Field and Laboratory Emission Cell (FLEC) method used in Europe is applied as a substitute for the 20 L small chamber method. The emission factors of total volatile organic compounds (TVOC) and formaldehyde from oil-based paint, emulsion paint, and water-dispersion paint with a coating weight of 300 g/m<sup>2</sup>, cured for 24/48 hours, were measured using the 20 L small chamber method. The emission rate of TVOC and formaldehyde from all paints began to stabilize after approximately 7 days after 24/48 hours of curing even though Korean standards stipulate that paint should be measured and analyzed after the third day of application. The emission factor of TVOC and formaldehyde from oil-based, emulsion, and water-dispersion paints were also measured using the FLEC method. There was good correlation between the 20 L small chamber method and the FLEC method for oil-based, emulsion, and water-dispersion paint emissions. With the FLEC method, using paints prepared under identical conditions, the emission rate was stable 24 hours after installation of samples because the air flow rate of FLEC is much higher than that of a 20 L small chamber, and the relative cell volume of FLEC is much smaller than that of a 20 L small chamber.

**Key words:** formaldehyde; TVOC; paints; coating materials; FLEC

## 1 Introduction

Many building materials emit volatile organic compounds (VOCs), which can affect the health and comfort of individuals<sup>[1]</sup>. Over the past decade, researchers have developed a variety of techniques for measuring the emissions of volatile organic compounds (VOCs) from building materials. An ASTM standard guide, guideline of the Commission of the European Communities (CEC, 1992), and European preliminary standard (ENV 13419 part 13 (CEN, 1998)) have been published to regulate these tests. Emission test techniques for building materials are important to manufacturers, indoor air quality investigators and researchers. Such validation is important for determining the impact of construction products on

the indoor air quality<sup>[2]</sup>. The perforator method has also been applied, even though it requires a special apparatus<sup>[3]</sup>. The European Particle-board Association originally developed this test procedure in the late 1970s, and it was established in 1984 as the European standard EN 120. However, the desiccator method was adopted in North America, Australia and Asia. The desiccator test was developed in the mid-1970s in Japan, and standardized in the US in 1983. The Japanese industrial standard (JIS) desiccator method and similar procedures employ a closed vessel containing the test material and water reservoir. The formaldehyde released from the material is captured by the water, which is then measured after a standard time interval, e.g., 24 hours<sup>[4]</sup>. Its emission behavior is different from the emission behavior in general interior spaces because this technique measures the formaldehyde emitted from the front, back side, and edges of the materials. A number of chamber methods that introduce air exchange rates ( $h^{-1}$ ) and determine the chemical compounds emitted from the surface of materials are currently used. Building and furnishing materials are

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widely recognized as important sources of VOCs and formaldehyde that contribute to indoor air pollution. A large number of VOCs and formaldehyde are emitted from floor coverings, wall coverings, adhesives, and coating products, and have the potential to cause adverse health effects in building occupants<sup>[5-8]</sup>. In order to prevent "sick house syndrome", suitable ventilation rates and a decrease in emission rates (ERs) from building products are needed. Several small-scale chambers for measuring the aldehyde and VOC ERs have been proposed<sup>[9-13]</sup>. The Korean government began controlling the indoor air quality in 2004. The Ministry of Environment regulates the use of pollutant-emitting building materials. In renovated or completely new buildings, the levels of indoor air pollutants, particularly VOCs, from the emissions from construction and building materials are often several orders of magnitude higher than the VOC levels in buildings with normal use<sup>[14-17]</sup>. In addition, standardization of the emission tests and chemical analyses using the 20 L small chamber has been carried out under the auspices of the Ministry of the Environment. In this study, FLEC was used to measure the formaldehyde and VOC emissions from paint. The results were compared with those obtained from the typical 20 L small chamber method.

## 2 Experimental

### 2.1 Materials

The paints used to determine VOCs and formaldehyde emission are mainly divided into oil-based and water-based paints, with water-based paints categorized as either emulsion or water-dispersion paints. Table 1 lists the characteristics of the different paints. The three types of paints are commercially available. The oil-based paint is an acrylic resin paint with a boiling point > 110 °C, containing 30-40% acryl resin, 10-20% xylene, 20-30% toluene, 20-30% TiO<sub>2</sub>, and other compounds. The emulsion paint generally uses a binder as the solution, which is emulsified boil oil, oil banish, resin, *etc.* in water. The emulsion paint chosen for this study contained 1-10% acryl emulsion resin, 10-20% TiCO<sub>2</sub>, 10-20% CaCO<sub>2</sub>, 10-20% talc, 1-10% kaolin clay, 30-40% water and other

**Table 1 Density and solid content of the paints used**

Materials	Oil-based paint	Emulsion paint	Water-dispersion paint
Density/ (g/cm <sup>3</sup> )	1.16	1.53	10.4
Solid contents /%	57.5	60	37

compounds.

The water-dispersion paint contained 50-60% water, 30-40% water-dispersion urethane resin, 1-10% ethylene glycol monomethyl ether, 1-10% diethylene glycol monobuthyl ether and other compounds.

### 2.2 The 20 L small chamber method for collection of gas samples

Before the chamber and sealed boxes were set up, they were washed with water and baked in an oven at 260 °C to eliminate any pollutants from the chamber itself. The 20 L small chamber was supplied with purified and humidified air at a ventilation rate of 0.5 h<sup>-1</sup> at an air-flow rate of 167 mL/min. The temperature (25 ±1 °C) and relative humidity (RH) (50±5%) inside the chamber were kept constant.

**Table 2 Test conditions of the paints applied to the glass plates**

	Pre-conditioning time/h	Weight /(g/m <sup>2</sup> )	Loading factor /(m <sup>2</sup> /m <sup>3</sup> )	Area /m <sup>2</sup>
Oil-based paint	24			
Emulsion paint		300	4.0	0.008
Water-dispersion paint	48			

The paint was applied to cleaned glass plates, which were then wrapped with aluminum foil using a blush. The glass plates were coated with 300 g/m<sup>2</sup> of paint according to the regulations of the Ministry of the Environment, Korea. The area of paint applied was 6.32 ×6.32 cm, with a 4.0 m<sup>2</sup>/m<sup>3</sup> loading factor. Table 2 lists the pre-conditioning time, weight, area and the loading factor of the individual paints applied. The test pieces sealed in seal boxes were placed in the chamber, and the air inside the chamber was sampled after 15 hours. Table 3 presents the sampling conditions. Throughout testing, the air temperature and relative humidity inside the test chamber were kept constant at 25±1 °C and 50 ±5%, respectively, and the chamber was ventilated at 0.5 h<sup>-1</sup>. The sample gas was taken at 2, 4, 12 hours, and 1, 3, 5, 7, 14, 21, 28 days after installing the samples.

**Table 3 Sampling conditions using the 20 L small chamber method**

	Formaldehyde	VOCs
Sampler	2,4-DNPH cartridge (Supelco, USA)	Tenax-TA (Supelco, USA)
Air flow rate /(mL/min)	167	167
Total volume/L	10	3.2

### 2.3 Field and laboratory emission cell methods

Before the experiments were commenced, the emission cell of the FLEC was cleaned by washing the inner surface with methanol. After the cell was cleaned,

pure air, which was used as a carrier gas, was supplied for approximately 1 day in order to clean the cell completely. The glass plate onto which the paint was applied was washed with dilute water and dried in an oven at 95 °C. The cleaned cells were placed onto the cleaned glass and supplied with pure air.

The paint was applied to the cleaned PET films 300 g/m<sup>2</sup> using blush according to regulations of the Ministry of the Environment, Korea. This area was 0.008 m<sup>2</sup>, which has a loading factor of 4.0 m<sup>2</sup>/m<sup>3</sup>, as used for the 20 L small chamber method, and 0.016 m<sup>2</sup> with a 8.0 m<sup>2</sup>/m<sup>3</sup> loading factor, which is twice as much as that in the 20 L small chamber method. Table 4 lists the weight, area and loading factor of the individual paints applied, and Table 5 provides the sampling conditions.

**Table 4 The samples of PET films coated with paint**

	Weight /(g/m <sup>2</sup> )	Type 1		Type 2	
		Loading factor /(m <sup>2</sup> /m <sup>3</sup> )	Area /cm <sup>2</sup>	Loading factor /(m <sup>2</sup> /m <sup>3</sup> )	Area /cm <sup>2</sup>
Oil-based paint	300	0.008	224.29	0.016	452.25
Emulsion paint					
Water-disper- sion paint					

**Table 5 Sampling conditions using the FLEC method**

Sampler	Formaldehyde		VOCs	
	2,4-DNPH cartridge (Supelco, USA)		Tenax-TA (Supelco, USA)	
Air flow rate /(mL/min)	150	240	50	80
Total volume/L	4.5	7.2	1.5	2.4

## 2.4 Conditions of analysis of GC/MS and HPLC

Volatile organic compounds were analyzed using a thermal desorption system (TDS) combined with gas chromatography-mass spectrometry (GC/MS). Table 6 lists the conditions used for TDS/GC/MS. In this study, TVOC was defined as the conversion of all areas of the peaks between hexane (C<sub>6</sub>) and hexadecane (C<sub>16</sub>) to concentrations using the toluene response factor. The Tenax-TA collected the gas produced by the thermal desorber system in an opposite manner to the gas collected and desorbed VOCs by heating. A peak area under 10 was defined as the limit of detection. Mass spectrometry was performed in scan mode when a type of VOC was identified, and the VOCs were separated according to the mass spectrum. Although some VOCs had identical retention times as some of the standards, they were classified by a comparison with the mass spectrum. Quantitative analyses of

the VOCs were accomplished using total ion current chromatogram (TIC) from GC/MS. Formaldehyde and aldehyde were analyzed using high performance liquid chromatography (HPLC). Table 7 lists the conditions of the HPLC. The DNPH derivative in the 2, 4-DNPH cartridge adsorbed air with formaldehyde and aldehyde was eluted with 5.0 mL of acetonitrile. Quantitative analysis of the eluted solution was accomplished by HPLC.

**Table 6 Analysis conditions for VOCs**

Variables	Condition
TDS	Perkin Elmer ATD400
GC/MS	HP6890/Agilent5973
Column	RTX-1 (105 m × 0.32 mm × 3 μm)
Carrier gas and flow	He (99.99%)
Temperature program	40 °C (5 min) → 70 °C (5 min) → 150 °C (5 min) → 200 °C (5 min) → 220 °C (5 min) → 240 °C (5 min)
MS	Mode EI (Electron ion)
condi-	Electron energy 70 eV
tion	Detection mode TIC (scan), m/z: 35/350

**Table 7 Analysis conditions for formaldehyde**

Variables	Condition
HPLC	Agilent HP110
Detector	UV/Vis 365 (Bw.30), ref. 590 (Bw.10)
Column	Supelco C18 4.6 × 250 mm
Mobile phases	Acetonitrile : Water = 45 : 55
Analysis time	25 min
Injection volume	20 μL
Column temperature	40 °C
Mobile phase flow rate	1.0 mL/min
Purge gas and flow rate	He (99.99%), 100 mL/min

## 3 Results and discussion

### 3.1 20 L small chamber method

Fig.1 shows the TVOC emission results obtained using the 20 L small chamber method for each paint type: oil-based, emulsion, or water-dispersion. The preconditioning time of the paint, which is the time after the paint is applied to the surface, was classified as a 24 hour curing period for oil-based paints and a 48 hour curing period for emulsion and water-dispersion paints, according to the regulations of the Ministry of the Environment, Korea. After the first day, the TVOC emissions from the oil-based paint, emulsion paint and water-dispersion paint was 20.77 mg/m<sup>2</sup>h, 0.05 mg/m<sup>2</sup>h and 2.43 mg/m<sup>2</sup>h, respectively. The emissions from all paints were stabilized after 7 days. After 7 days, the emissions for oil-based paint, emulsion paint, and water-dispersion paint were 4.03 mg/m<sup>2</sup>h, 0.04 mg/m<sup>2</sup>h and 0.07 mg/m<sup>2</sup>h, respectively. The Korean regulations specify that paints should be measured and analyzed 3

days after installing the sample. However, it was found that the emission rates of TVOC from paints only became stable 7 days after installing the samples.

Formaldehyde emission for the oil-based paint reached the maximum emission rate after 6 hours, and was stable after 7 days (Fig.2). The rates of formaldehyde emissions from emulsion paint and water-dispersion paint began to stabilize after 7 days. The emissions of formaldehyde from the different paint types were similar, and as low as 0.12-0.002 mg/m<sup>2</sup>h during the entire test period because these paints contained no source compounds that emit formaldehyde. The emission rates during all periods were quite low but formaldehyde emission was stable after approximately 7 days.

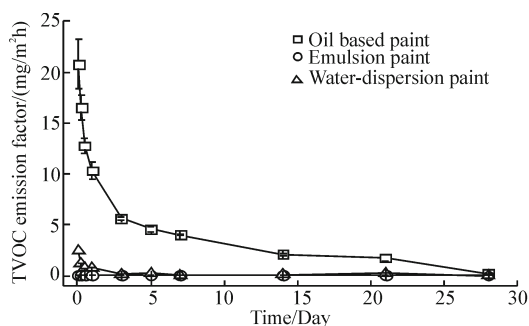


Fig. 1 TVOC emission factors using the 20 L small chamber, 3 days after installing the sample in the small chamber

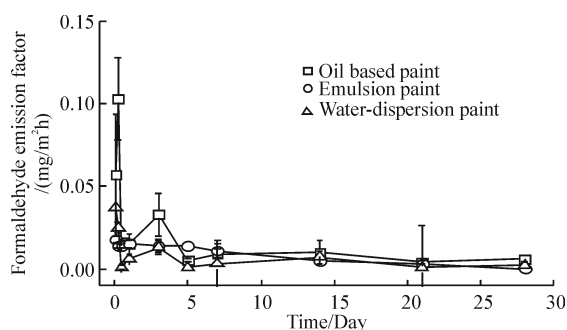


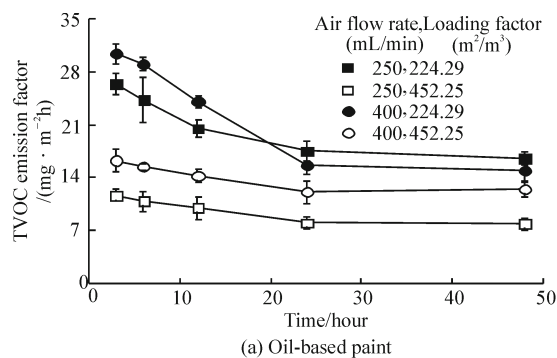
Fig.2 Formaldehyde emission factor of paint using the 20 L small chamber, 3 days after installing the sample in the small chamber

### 3.2 Field and laboratory emission cell

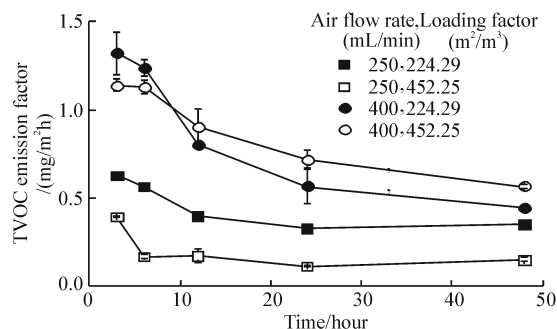
The effect of the loading factor on the rate of VOC emission from each paint sample was greater with a low loading factor than that with a high loading factor, without any impact on the air-flow rate, as shown in Fig.3. However, the rates of formaldehyde emission were affected by the loading factor at an air-flow rate of 250-400 mL/min. Oil-based paint had high emissions when the loading factor was higher. On the other hand, the loading factor had no impact on the emission from the emulsion and water-dispersion paints. The loading factor is affected by formaldehyde

because formaldehyde with a lower concentration of VOCs is emitted slowly with a low emission rate.

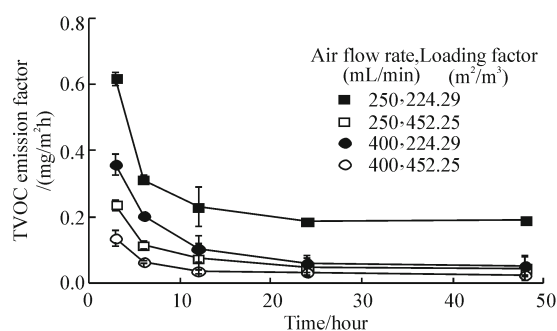
As shown in Fig. 4, the effect of the air flow rates on oil-based paint and emulsion paint VOC emission rates were higher with high air flow rates than that with low air-flow rates. However, with the water-dispersion paint, the VOC emission rates were higher at higher air-flow rates, and the loading factor had no effect. In the case of formaldehyde, the emission rates were affected by air-flow rates of 224.29 and 452.25 m<sup>2</sup>/m<sup>3</sup>. In oil-based paint, low emission rates were observed. In emulsion paints, the air-flow rate had no effect when the air-flow rate was higher. In water-dispersion paints, high emission rates were observed when the air flow rate was high at 224.29 m<sup>2</sup>/m<sup>3</sup>. For all paints, an air-flow rate of 452.25 m<sup>2</sup>/m<sup>3</sup> had no effect on the VOC emission rates. The loading factor is affected



(a) Oil-based paint



(b) Emulsion paint



(c) Water-dispersion paint

Fig.3 Emission factor of TVOC with loading factors of 224.29 and 452.25 m<sup>2</sup>/m<sup>3</sup> at 250 and 400 mL/min by FLEC, respectively



by formaldehyde because formaldehyde, which has a lower concentration than VOCs, is emitted at a low emission rate. There was good agreement between the 20 L small chamber and FLEC methods for oil-based, emulsion and water-dispersion paints. The 20 L small chamber method showed that the emission rate from samples with a coated weight of 300 g/m<sup>2</sup>, a 24 hour (oil-based paint) or 48 hour (emulsion and water-dispersion paint) curing period and an area of 0.008 m<sup>2</sup> was stabilized after 7 days. However, with the FLEC method for identical paint samples, the emission rate stabilized 24 hours after the samples were installed because the air flow rate of FLEC is much higher than that of the 20 L small chamber, and the relative cell volume of the FLEC is much smaller than that of the 20 L small chamber.

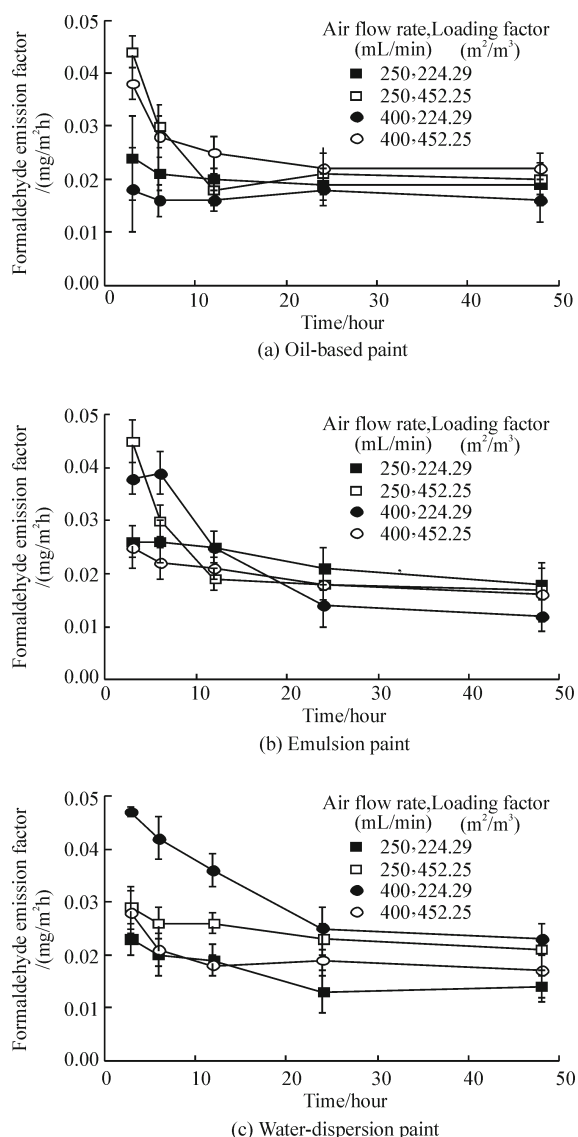


Fig.4 Emission factors of formaldehyde with loading factors of 224.29 and 452.25 m<sup>2</sup>/m<sup>3</sup> at 250 and 400 mL/min, respectively, by FLEC

The value of emission factors for VOC emissions from the oil-based paint measured using the 20 L small chamber method and FLEC method were comparable, as shown in Fig.5. For the FLEC method, the best correlation was observed when the air-flow rate was 250 mL/min with a coating area of 0.008 m<sup>2</sup> (224.29 m<sup>2</sup>/m<sup>3</sup> loading factor).

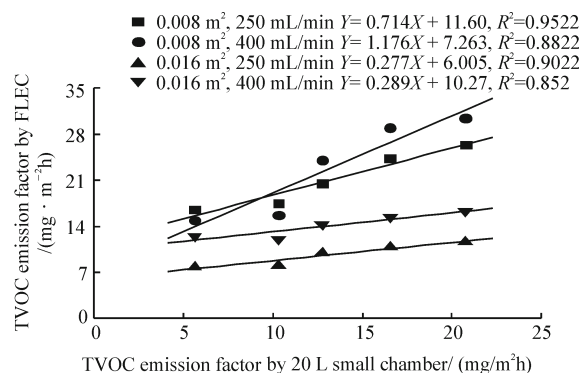


Fig.5 The correlation of the TVOC emitted from oil-based paint between the 20 L small chamber method and FLEC method

## 4 Conclusions

This study examined methods for improving the standardized emissions test methodology for paints in Korea using 20 L small chamber and FLEC tests. After 24/48 hours curing, the TVOC emissions from all paints were stable after 7 days. The rate of formaldehyde emission during all measured times was quite low. However, formaldehyde emission stabilized after 7 days, as was observed with TVOC. The Korean standards state that paints can be measured and analyzed within 3 days of testing. However, this study confirmed that the emission rates of TVOC/formaldehyde from the paints stabilized 7 days after installing the sample.

For all the paints, the VOC emission rates were higher with a low loading factor than that with a high loading factor, and the air-flow rate had no effect on the rate of VOC emission. However, the formaldehyde emission rate was affected by the loading factor at an air-flow rate of 250-400 mL/min. In oil-based paints, high emission levels were observed at a higher loading factor. On the other hand, the loading factor had no effect in emulsion and water-dispersion paints. The loading factor was affected by formaldehyde because it is emitted at low emission rates due to its a lower concentrations than VOCs.

There was good agreement between the emission factors obtained using a 20 L small chamber and FLEC methods for oil-based, emulsion and water-dispersion

paints. Under the conditions of a coating weight of 300 g/m<sup>2</sup> cured for a 24 hour (oil-based paint) or 48 hour (emulsion and water-dispersion paint) curing period, for an area of 0.008 m<sup>2</sup>, the emissions measured using the 20 L small chamber and FLEC methods stabilized after 7 days and 24 hours, respectively, after installing the samples. This is because the air-flow rate of the FLEC is much higher than that of the 20 L small chamber, and because the FLEC has a smaller cell volume than the 20 L small chamber.

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