Chemical Emission Rates from Building Materials
Measured by a Small Chamber

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Abstract
A small-scale chamber, ADPAC, was developed to measure chemical emission rates from building materials. Measurement results from wall covering adhesives, flooring, and insulation materials were shown in this paper. The test pieces with wall covering adhesives were produced at the day of measurement. First measurement was conducted 15 hours after the production of the test piece, when chemical concentration in the chamber was considered to be steady state. Measurements were repeated after 4, 7, 14, and 28 days. It was found that emission of formaldehyde was observed even for the product indicated of “non-formalin”. Emission rates were higher during the first day, but decreased rapidly after 1 or 2 weeks. Flooring materials and thermal insulation material EPS were also evaluated.

Keywords: chamber; aldehydes; VOCs; emission rate; building materials

Introduction
In Japan problems caused by aldehydes and VOCs have been recognized to be serious especially in new constructed houses. The Ministry of Health, Labor and Welfare, Japan published a first guideline on August 1997, where concentration of formaldehyde in the air should be less than 100µg/m³. Recent study on over 4500 houses in Japan by the Ministry of Land, Infrastructure, and Transport (formally Ministry of Construction) shows that average concentration of formaldehyde is 89µg/m³. For indoor air concentration of formaldehyde, 27% of houses were over the guideline of 100µg/m³. About 12.3% houses were over toluene guideline of 260µg/m³.

From 2000 the Ministry of Health, Labor and Welfare has started to establish guideline on VOCs. Table 1 shows guideline values on the different kinds of chemicals published by January 2002. This guideline has a strong impact on Japanese housing manufactures and industry because more than 1.2 million new houses have been constructed per year (2000). In 1998 the Government Committee on Healthy House (under Ministry of Construction, Ministry of Health, Labor and Welfare, Ministry of International, Trade and Industry, Forestry Agency, formal names at 1998) published a guidebook for architects and builders. They also published a manual for house users and owners. In this guidebook six chemical substances were pointed out. Namely, they are formaldehyde, toluene, xylene, wood preservatives, termite chemicals, and plasticizers. Japanese Home Builders Association published their guidelines on 1999 and 2001. Also a scientific project on indoor chemical pollution (IAPOC) is promoted by the Architectural Institute of Japan. Furthermore, standardization actions on emission test and chemical analysis have been conducted under the Ministry of Economy, Trade and Industry, where small chamber method is applied.

Table 1. Guideline Values for VOCs by the Ministry of Health, Labor and Welfare (Jan. 2002)

| Substance          | Guideline     |
|--------------------|---------------|
| formaldehyde       | 100µg/m³      |
| acetaldehyde       | 48µg/m³       |
| toluene            | 260µg/m³      |
| xylene             | 870µg/m³      |
| p-dichlorobenzene  | 240µg/m³      |
| ethylbenzene       | 3800µg/m³     |
| styrene            | 220µg/m³      |
| chlorpyrifos       | 1(0.1)* µg/m³ |
| DBP                | 220µg/m³      |
| tetradeacane       | 330µg/m³      |
| DEHP               | 120µg/m³      |
| diazinon           | 0.29µg/m³     |
| fenobucarb         | 33µg/m³       |
| TVOC (tentative)   | 400µg/m³      |
| nonanal (tentative)| 41µg/m³       |

*( ) for children

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To prevent “sick house syndrome”, suitable ventilation rate and reduction of emission rates from building products are strongly required. Several small-scale chambers for measuring aldehydes and VOCs emission rates have been proposed in the world (Tichenor, 1987, Wolkoff et al., 1991, Gunnarsen et al. 1994, Brown, 1999). These small test chambers have often been used to determine chemical emission rates from building materials (Colombo et al, 1993, Jensen et al, 1995, Lundgren et al, 1999, Knudsen, et al., 1999, Risholm-Sundman, 1999, Uchiyama et al, 2001). In this study, a small-scale chamber was introduced. Emission rates of aldehydes and VOCs from wall covering adhesives, flooring materials, and EPS (expanded polystyrene form) were measured quantitatively.

Characteristics of Small-Scale Chamber ADPAC

Small-scale chamber, ADPAC, was developed in Japan with its performance in compliance with ASTM (1996, 1997), ECA reports (1989, 1991, 1993, 1995), and ENV 13419-1 (1999). Figure 1 shows the main chamber made of stainless steel (SUS304) and the air control unit. ADPAC chamber has 5 types of size for 20, 45, 100, 150 or 280L. When materials and specimen cannot be cut or cannot be taken into small pieces, the bigger size chamber is used. Although there are several sizes, the same air control system can be used. Twenty-liter chamber was used in this paper, because it was easy to carry and handle. Air control system has an air supplying unit, a humidifier, and pumps. Figure 2 shows the detail of chamber. ADPAC chamber was set up in a temperature-controlled climate chamber. Purified air was used for ventilation. Figure 3 shows schematic diagram of ADPAC system. Figure 4 shows the stainless steel seal box with Teflon sealing. Seal box was used to prevent cut edge effect, which allowed chemical emission only from one side surface of the test piece. When two seal boxes are used, total surface area is 0.044m² and the loading is 2.2m²/m³.

Methods

Before setting up the chamber and seal boxes, they were washed with water, and baked out using oven at 260°C to eliminate any pollutants from the chamber itself. ADPAC System supplied purified and humidified air with a given ventilation rate. Temperature and relative humidity inside the chamber were kept constant. The test conditions were shown in Table 2. Test pieces sealed with seal boxes were set in the chamber, and the air inside the chamber was sampled after 15 hours. Sampling conditions were shown in Table 3. Throughout the measurements, air temperature and relative humidity inside the test chamber were kept constant at 25±1°C and 50±4%, and ventilated at 0.5 h⁻¹. Aldehydes were analyzed by HPLC, and TDS/GC/MS was used for VOCs as shown in Table 4-5. Analysis conditions for VOCs were slightly different among materials, so that for EPS was tabled here. In this paper, TVOC is defined that the all areas of the peaks after n-hexane were converted to concentrations using the toluene response factor. The peak area under 10 was defined as the limit of detection.

| Table 2. Test Conditions |
|--------------------------|
| Chamber Volume           | 20 L               |
| Loading Factor           | 2.2 m²/m³          |
| Temperature              | 25 ± 1 °C          |
| Relative Humidity        | 50 ± 4 %           |
| Ventilation Rate         | 0.5 h⁻¹            |

Fig. 1. ADPAC 20L

Fig. 2. Chamber Detail

Fig. 3. Schematic Diagram of ADPAC System
Table 3. Sampling Conditions

| Sampler       | VOCs                          |
|---------------|-------------------------------|
| Sep-Pak       | Tenax TA (60/80 mesh)         |
| DNPH-Silica   | EPS: Carbopack B (60/80 mesh) |
|               | + Carboxen 1000               |
| Air Flow Rate | 167 mL/min                    |
|               | Adhesive: 50 mL/min           |
|               | Adhesive E: 100 mL/min        |
| Total Volume  | 10 L                          |
|               | 3.2 L                         |

Table 4. Analysis Conditions for Aldehydes

| HPLC           | Waters 2640 Separations Module alliance, Waters 2487 Dual λ Absorbance Detector |
|----------------|--------------------------------------------------------------------------------|
| Column         | Nova-Pak® C18, φ 3.9 x 150 mm                                                  |
| Mobile Phase   | 65% water /30% acetonitrile /5% THF                                           |
| Column Oven Temperature | 40°C                          |
| Sample Injection Volume | 20 µL                        |
| Detector       | UV, operating at 360 nm                                                       |

Table 5. Analysis Conditions for VOCs

| TDS            | Perkin Elmer ATD400 |
|----------------|----------------------|
| GC/MS          | HP6890 /5973B        |
| Column         | HP-VOC, 0.32mm φ 60 x 1.8µm |
| Oven Temperature | 35°C (2min) → 15°C/sec(4min) → 2.5°C/sec(2min) → 5°C/sec → 250°C(1min) |
| Mode           | SCAN                 |

Table 6. Wall Covering Adhesives

| Adhesive | Characteristic             | Main component                          |
|----------|----------------------------|-----------------------------------------|
| A1       | Satisfied Japanese Industrial Standard | Confidential                            |
| A0       | Non formalin type of A1    | Confidential                            |
| R        | Non formalin type          | Vinyl acetate, Starch                    |
| K        | Powder Starch (Japan)     | 90% Ethyl bridge bond, ostatch 10% Vinyl acetate copolymerization |
| E        | Powder Starch (Sweden)    | Confidential                            |

Measurement of Wall Covering Adhesives

Preparation of Test Pieces

Measurements of emission rates were carried out for adhesives A1, A0, R, K, and E shown in Table 6. These were pasted on 12mm-thick plasterboards with and without wall covering. In Figure 5, section view of test pieces is illustrated. Condition 1 means that an adhesive is pasted on the plasterboard without wall covering material. Condition 2 means that an adhesive is pasted on the plasterboard with wall covering materials. Wall covering material was made of polyvinyl chloride (PVC) resin and it contained Diisononyl Phthalate (DINP), which was typically used in Japanese houses.

In order to reproduce realized condition, which was observed during the housing construction, a trained worker produced the test pieces. Adhesive was mixed, and then wall covering was pasted on plasterboard by brush. A roller was used to eliminate the air gap. Size of plasterboard was 165 x 165mm. Total amount of adhesive pasted on plasterboard was 160~180g/m², which was the typical amount for general construction. Adhesive A1 and A0 were used without addition of water. R was diluted with 60% of adhesives weight water. Namely 180g adhesive was diluted with 108g of water. Adhesive K (338g) was put into water (2.3L), and it was mixed with the stirrer for 10 minutes. Adhesive E (100g) was also dissolved with water, 120% of adhesive weight (120g). It was mixed carefully until it dissolved thoroughly into water.

Adhesives A1, A0, R and K were tested from December 8, 1998 to January 7, 1999, and adhesive E was measured from August 18 to September 15, 1999. Test pieces were produced at the day of measurement. The measurements were repeated 1, 4, 7, 14 and 28 days after production.

Results

In Figure 6 emission rates of aldehydes after one day are shown. It was found that emission of formaldehyde for A1, A0 and E was decreased with wall coverings. It was supposed that adhesive A1 should have emitted higher formaldehyde than that from adhesive A0, because A0 indicated “non-formalin”. However, results showed opposite that A0 emitted 34µg/m²h of formaldehyde, which was about three times higher than that of A1. The emission from R and K was very low, therefore the decrement by wall coverings was canceled.

In Figure 7 emission rates of VOCs after one day
are shown. Adhesives A1 and A0 showed high emission rate of aromatic hydrocarbon, especially xylene (50%), and toluene (15%). Powder adhesive K and E emitted very low aldehydes and VOCs.

Figures 8 and 9 show the decay of formaldehyde and VOCs. Emission rates at 1st and 3rd days were higher in both conditions, but they became lower after 1 or 2 weeks. Wall covering material was blocked emission with some extent during the earlier period. It was decreased gradually until it reached a constant value after two weeks. And then emission rate of formaldehyde was 2~3µg/m²·h. That of aromatic hydrocarbon was 10~20µg/m²·h.

Measurement of Flooring Materials
Preparation of Test Pieces
In Japan majority of wooden flooring material in houses is made of plywood. This may be the main source of formaldehyde in houses. Three kinds of flooring materials were tested during 28 days. Table 7 shows the characteristics of flooring materials. Test pieces were cut in the factory before sending to the laboratory by 165mm x 165mm. Test pieces were carefully sealed by aluminum sheet and they were packed in the PET bag. Just before measurements were started, seal was opened. Cut edge of test pieces was sealed by the box shown in Figure 4.

(1) Plasterboard + Adhesive
(2) Plasterboard + Adhesive + Wallcovering

![Fig. 6. Emission Rates of Aldehydes after One Day]

![Fig. 7. Emission Rates of VOCs after One Day]
Table 7. Characteristics of Flooring

| Base      | Grade of JAS* | Surface coating          |
|-----------|---------------|--------------------------|
| A         | Plywood       | F<sub>CO</sub> Urethane type |
| B         | Plywood       | F<sub>CO</sub> UV cure coating |
| C         | Plywood       | F<sub>CO</sub> UV cure coating |

* JAS defines formaldehyde concentration under 0.5mg/L in water by desiccator method as F<sub>CO</sub>

**Results**

Figure 10 shows emission rates of formaldehyde for flooring materials. At the first day emission rates for flooring A and B were almost same as 23µg/m<sup>2</sup>h. That for flooring B was 17µg/m<sup>2</sup>h. After 28 days emission rate of formaldehyde for flooring material A was 15µg/m<sup>2</sup>h and those for flooring B and C were around 10µg/m<sup>2</sup>h. These emission rates are very high, because all of them are classified into F<sub>CO</sub> category by the Japanese Agricultural Standard.

Figure 11 shows the decay of TVOC for three flooring materials. Here TVOC is calculated by toluene equivalent. At the first day TVOC for flooring material A was 570µg/m<sup>2</sup>h and that for flooring B was 490µg/m<sup>2</sup>h and that for flooring C was 300µg/m<sup>2</sup>h.

Table 8 shows main components of VOCs. Ninety four percent of TVOC from flooring material B was toluene. On the other hand for flooring B, ethyl benzene was 20% and xylene was 15%. Flooring A also included aromatic hydrocarbon. For flooring C 20% of them was 1-methoxy butane. Little emission of toluene and ethyl benzene was observed. Even when emission rates of TVOC were same level, characteristics of VOCs were quite different by materials. For three flooring material, even they are made of wood, α-pinene and limonene were under detected limit. We observed α-copaene, β-caryophyllene, β-elemene.

**Measurement of Thermal Insulation Board EPS**

**Preparation of Test Pieces**

Four kinds of expanded polystyrene form (EPS) were measured during 14 days. EPS A was bought at a DIY shop. EPS B was one of the present market products in Japan. EPS C was the improvement product of B. EPS D was made in USA. Just before the measurements were started, test pieces were cut from the board. Cut edge of test pieces was not sealed.
Table 8. Main Component of VOC-Flooring

|                  | [µg/m²h] | 1day | 3day | 7day | 14day | 28day |
|------------------|----------|------|------|------|-------|-------|
| ethyl benzene    | 114      | 95   | 52   | 40   | 24    |
| xylene           | 86       | 77   | 48   | 36   | 20    |
| n-octyl acrylate | 66       | 38   | 44   | N.D. | N.D.  |
| methyl benzoate  | 54       | 19   | 17   | 11   | 7     |
| 1-methoxymethyl benzoate | 43 | 7   | 19   | 9    | 2     |
| toluene          | 37       | 29   | 19   | 12   | 6     |
| benzophenone     | 23       | 24   | 20   | 18   | 11    |
| 2,2-(2-methoxyethoxy)ethoxy ethanol | 23 | 63  | 16   | N.D. | 4     |
| styrene          | 23       | 20   | 10   | 8    | 4     |
| benzaldehyde     | 19       | N.D. | 7    | N.D. | 3     |
| 1-methoxy-2-propanol | 18 | 17  | 15   | 1    | 4     |
| ethyl acetate    | 17       | 17   | 13   | 11   | 8     |
| acetophenone     | 15       | 12   | N.D. | 5    | N.D.  |
| isopropylbenzene | 13       | 32   | N.D. | N.D. | N.D.  |
| trimethylbenzene | 12       | 7    | 4    | 3    | 2     |
| 2-butane         | 11       | 9    | 9    | 7    | 6     |
| trans-caryophyllene | 11  | 4   | 9    | 10   | 5     |
| 4-methyl-2-pentanone | 11  | 3   | 5    | 4    | 3     |
| (-)-.beta.-elemene | 9   | 12  | 7    | 7    | 3     |
| acetic acid      | 7        | 10   | N.D. | 2    | 30    |
| .alpha.-copaene  | 6        | 10   | 5    | 5    | 2     |
| sec-butyl acrylate| 5      | 11   | 9    | 8    | 4     |
| ethyl lactate    | 4        | 11   | 2    | 2    | 4     |
| n-butyl acetate  | 3        | 2    | N.D. | 33   | 17    |

A

|                  | [µg/m²h] | 1day | 3day | 7day | 14day | 28day |
|------------------|----------|------|------|------|-------|-------|
| toluene          | 456      | 378  | 254  | 204  | 161   |
| ethyl benzene    | 111      | 81   | 50   | 40   | 32    |
| hexanal          | 78       | N.D. | N.D. | N.D. | N.D.  |
| xylene           | 77       | 66   | 48   | 39   | 31    |
| styrene          | 32       | 27   | 15   | 11   | 8     |
| n-butyl acetate  | 18       | 63   | 39   | 29   | 25    |
| ethyl acetate    | 11       | 5    | 33   | 27   | 19    |
| 2-butoxyethanol  | 9        | 14   | 7    | 3    | 3     |
| acetic acid      | 8        | 8    | 7    | 7    | 10    |

B

|                  | [µg/m²h] | 1day | 3day | 7day | 14day | 28day |
|------------------|----------|------|------|------|-------|-------|
| methyl tert-butyl ether | 62 | 38  | 17   | 22   | 17    |
| acetic acid      | 27       | 3    | 5    | 4    | 1     |
| trans-caryophyllene | 23  | 22  | 15   | 20   | 18    |
| cyclohexanone    | 21       | 13   | 4    | 10   | 6     |
| benzaldehyde     | 19       | 10   | 3    | 6    | 3     |
| .alpha.-copaene  | 13       | 11   | 7    | 11   | 10    |
| styrene          | 11       | 6    | 4    | 6    | 3     |

C
Results

Figure 12 shows the decay process of TVOC. The emission rate for EPS A was 586µg/m²h after one day and 206µg/m²h after 14 days. That for EPS B was around 40µg/m²h until 7 days. However, after 10 days the emission from EPS B was increased. That of EPS A was 210µg/m²h after 14 days. The reason was not clear. Presumably it may be estimated that the chemical substances inside EPS was diffused to the surface and increased the emission rates. We observed same phenomena for EPS at several different measurements. It was found that the emission of VOCs from EPS A might be continued for long period. At the first day emission rate for EPS C was 42µg/m²h, it was still continued at 10–20µg/m²h level from 5 days after.

Figure 13 shows the decay process of styrene. Styrene was major substances of TVOC. These decay curves were coincide with those of TVOC. As described in the introduction section, the government shows guideline value of styrene (see in Table 1). EPS is made of styrene monomer. Some amount of styrene monomer is still remained in it. Emission rates of styrene for EPS A and B were higher than American EPS D. That for EPS D was observed less than 10µg/m²h during that period. Improvement for Japanese EPS is highly recommended.

![Fig. 12. Decay Process of TVOC –EPS](image)

![Fig. 13. Decay Process of Styrene –EPS](image)

Table 9. Main Component of VOC-EPS

|        | 1day | 3day | 5day | 7day | 10day | 14day |
|--------|------|------|------|------|-------|-------|
| A      |      |      |      |      |       |       |
| toluene| 141  | 125  | 116  | 103  | 95    | 88    |
| styrene| 126  | 110  | 106  | 86   | 80    | 71    |
| trans-1,3-dichloropprene| 20  | 13   | 10   | 10   | 8     | 7     |
| ethyl benzene| 14  | 8    | 6    | 5    | 3     | 3     |
| xylene | 12   | 7    | 5    | 1    | 3     | 2     |
| dichloromethane| 11  | 6    | 7    | 5    | 7     | 6     |
| chloroethane| 8   | 7    | 7    | 6    | 8     | 6     |
| 1,2,4-trimethylbenzene| 7   | 5    | 4    | 2    | 2     | 2     |
| benzene | 4    | 2    | 1    | 1    | 1     | 1     |
| B      |      |      |      |      |       |       |
| chloromethane| 14  | 1    | 5    | 1    | 61    | 62    |
| xylene | 12   | N.D. | 4    | N.D. | 63    | 54    |
| styrene| 12   | N.D. | 3    | N.D. | 64    | 54    |
| ethyl benzene| 5   | N.D. | 1    | N.D. | 22    | 20    |
| dichloromethane| 1  | N.D. | N.D. | 7    | 7     | 7     |
| chloroethane| N.D.| N.D. | N.D. | 9    | 7     | 7     |
| C      |      |      |      |      |       |       |
| chloromethane| 39  | 44   | 22   | 29   | 33    | 39    |
| styrene | 17   | 16   | 9    | 7    | 7     | 9     |
| isopropyl alcohol| 12 | 3    | N.D. | 2    | N.D.  | N.D.  |
| chloroethane| 12  | N.D. | 6    | 7    | 8     | 7     |
| dichloromethane| 7  | 5    | 6    | 4    | 7     | 7     |
| ethyl benzene| 6   | 5    | 3    | 2    | 2     | 3     |
| D      |      |      |      |      |       |       |
| chloroethane| 9   | 6    | 4    | 7    | 6     | 6     |
| dichloromethane| 7  | 5    | 5    | 6    | 6     | 6     |
| isopropyl alcohol| 4  | 2    | N.D. | 1    | 1     | 1     |
| xylene | 3    | 2    | 1    | 1    | 1     | 1     |
| styrene | 2    | 2    | 1    | N.D. | N.D.  | N.D.  |

N.D. not detected

At the 7 days of EPS D was measurement failed.
The main component of VOC was shown in Table 9. Aromatic hydrocarbons such as styrene, toluene, xylene and ethyl benzene were highly emitted, and halocarbons such as chloromethane and dichloromethane were also emitted. Particularly toluene and styrene emission from EPS A was observed. Emission rate of toluene for EPS A was 140µg/m²h at the first day and that of styrene was 125µg/m²h. Although it was decreased after 14 days that of toluene was 87µg/m²h and that of styrene was 70µg/m²h. The emission of styrene from EPS C was low, but emission of chloromethane after one day was observed at 39µg/m²h. Aldehydes were not detected from all EPS.

Conclusions
A small-scale chamber (ADPAC) was developed to measured emission rates of chemical substances from building materials.

By using this small chamber, wall coverings, flooring materials, an expanded polystyrene form was measured. Emission rates from wall covering material at 1st and 3rd day were higher, but they became lower after 1 or 2 weeks. Wall covering material was blocked emission with some extent during the earlier period. It was decreased gradually until it reached a constant value after 2 weeks. Emission rates of TVOC from flooring materials were same level, but characteristics of VOCs were quite different by materials. Styrene was dominant substance of emission from EPS. It was found that the emission from some EPS might be continued for long period.

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