Development of Colorimetric Type Passive Flux Detector for Formaldehyde

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Introduction

Which building material or furniture have to be taken off to improve the polluted indoor air?
Previous methods to measure the emission flux of volatile chemicals -1

- **Emission Chamber Method**
  - **Advantage**
    - Temperature and humidity are adjustable
    - Measurable the flux from any kind of materials
    - Correlate with the real environment
  - **Limitations**
    - Measurable only in laboratory
    - Instrument is Large

- **Desiccator Method**
  - **Advantage**
    - Simple method
  - **Limitations**
    - Measurable only in laboratory
    - 100% humidity
    - Applicable only to water-soluble compounds

Impossible to measure the emission in a residential house
Previous methods to measure the emission flux of volatile chemicals -2

Field and Laboratory Emission Cell (FLEC)

- Advantage: Measurable in laboratory and a residential house
- Advantage: Highly precise
- Limitations: Instrument is Large
- Limitations: High cost

Passive Flux Sampler (PFS)

- Advantage: Measurable in laboratory and a residential house
- Advantage: Low cost and easy to handle
- Limitations: Need GC or HPLC analysis
- Limitations: (Common limitation for the four methods)
Objectives

To Develop a Passive Type Detector for the On-site Measurement of Formaldehyde Flux

- Low cost
- Easy operation
- Lightweight and small
- Short monitoring time
- Precise and accurate
Detector design

Inside of the detector is coated with DLC (Diamond like Carbon) to prevent contamination. Water-retaining grass filter is set in the detector to provide water to the test sheet for the reaction.
Reaction on the test sheet

Formaldehyde-specific reaction using an enzyme reaction

\[
\text{Formaldehyde} \rightarrow \text{Formate} + \text{NADH} \quad (1)
\]

\[
\text{NADH} + \text{INT} \rightarrow \text{NAD} + \text{Reduced INT} \quad (2)
\]

- Two step enzyme reaction in the presence of water
- Color appearance result from the reaction (2)
- Water is necessary for the reaction and for keeping the color
Measurement procedure

(1) The aluminum seal lid is peeled off from the body

(2) 2 drops of pure water is put into the detector

(3) The detector is placed on each indoor material

(4) Leave the detector for 30 minutes
    (Formaldehyde emitted from material diffuse to the inside of the detector and reacted on the test sheet)

(5) The detector is lidded with the aluminum seal and determined the color of the test sheet
Development of colorimetric determination devise

Emission flux

\[ \text{Absorbance} = \log \left( \frac{I_0}{I} \right) \]
\[ = \log \left( \frac{V_0}{V} \right) \]  \hspace{1cm} \text{(Bouguer-Beer's law)}

- \( I_0 \): Incidence light intensity, \( I \): Receiving light intensity,
- \( V_0 \): Initial voltage, \( V \): Output voltage
Colorimetric determination with formaldehyde solution – Method-

Formaldehyde solution was put into the detector

- Concentration: 0, 0.3, 0.6, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 10 μg/mL
- Volume: 80 μL
- Number: 3 for each concentration

Colorimetric determination by using the developed devise
Colorimetric determination with formaldehyde solution – Results -

- Absorbance was correlated with the concentration of the solution between 0.5 and 8.0 μg/mL
- Reaction was saturated at 8.0 μg/mL
- Precision of the detector was good
- Sensitivity was very low

Sensitivity have to be improved

RSD (N=3) 0.3%-3%
Comparison with the flux measured by the desiccator method

Desiccator method

Passive flux detector

Absorption by pure water

Acetylacetone method

Visual observation
Comparison with the desiccator method
- Visual observation -

<table>
<thead>
<tr>
<th>JIS category</th>
<th>F★★★★</th>
<th>F★★★</th>
<th>F★★</th>
<th>F★</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desiccator value [mg/L]</td>
<td>0.3</td>
<td>0.5</td>
<td>1.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Flux [μg/m²/hour]</td>
<td>&lt; 5</td>
<td>5 - 20</td>
<td>20 - 120</td>
<td>120&lt;</td>
</tr>
</tbody>
</table>

Concentration in the Desiccator method [mg/L]

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>0.08</th>
<th>0.31</th>
<th>1.42</th>
<th>3.06</th>
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</thead>
<tbody>
<tr>
<td>Converted flux [μg/m²/hour]</td>
<td>&lt;=5</td>
<td>&lt;5</td>
<td>20-120</td>
<td>120&lt;</td>
<td></td>
</tr>
</tbody>
</table>

JIS category
Comparison with the flux measured by the desiccator method

Desiccator method

Passive flux detector

Absorption by pure water

Acetylacetone method

- Ten pieces of 4 types plywood were tested
- Ten detectors were used for each plywood

Colorimetric determination
Comparison with the desiccator method
- Colorimetric determination -

Absorbance was correlated with the results of the desiccator method.

\[ y = 0.0440 x + 0.110 \]

\[ R^2 = 0.995 \]
**Blank test**

**Method**

Two drops of pure water were put into the detectors (N=10)

After 30 minutes

Colorimetric determination by using the developed devise

This blank test was conducted twice

**Results**

Mean of the absorbance: 0.0990, 0.101

SD of the absorbance: 0.00556, 0.00363

\[\text{Absorbance} = \log \left( \frac{V_o}{V} \right)\]

10SD = 0.0556

LOD > F☆☆☆☆☆

The variation have to be low to determine the Flux of F☆☆☆☆☆ plywood precisely
Conclusion

A passive Flux detector for On-site Measurement was developed. Photometer was developed to determine the color variation of the detector.

- The color variation of the detector was visible. Flux can be measured by the detector only with a color sample.
- The color variation of the detector was correlated with the results of desiccator method.
- The sensitivity and variability have to be improved. Light emitting element and detector cover will be improved.