

## **Determination of Chemical Compounds Released from a Natural Wood by Using a Micro-Chamber and Reduction of Carbonyl Compounds**

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**Abstract.** The chemical compounds released from surface of natural wood were analyzed by using a micro-chamber. As a result, we found that they consisted of terpenoids such as  $\beta$ -cadinene,  $\alpha$ -muurolene, calamenene,  $\alpha$ -selinene,  $\beta$ -elemene and copaene as well as carbonyl compounds such as formaldehyde and acetaldehyde. Changes in the release rate of these compounds were observed when the wood was compressed. The release amount of the terpenoids such as  $\beta$ -cadinene,  $\alpha$ -muurolene and calamenene increased by a factor of 5 to 7 with 30% compression and 5 - 8 with 50% compression, but rapidly decreased with a factor of 0.8 with 70 % compression. The release amount of these three substances reached their maximum with 50% compression. In contrast, the release amounts of  $\alpha$ -selinene,  $\beta$ -elemene and copaene reached their maximum with 30% compression. In particular, it was found that  $\alpha$ -selinene was released only with compression. As for the carbonyl compounds, release of formaldehyde, acetone and acetaldehyde increased by a factor of 3 - 10 with 30% compression, 1.8 - 10 with 50 % compression, and 1 - 5 with 70% compression. The release rate of propanal increased by a factor 40 with 30% and 50% compression and by 14 with 70% compression, which was the greatest change in release rate. We treated the carbonyl compounds with urea and examined their release reduction. As a result, it was conformed that the release of each compound was largely reduced. Formaldehyde was reduced most effectively with a maximum reduction factor of 30. This is likely because low steam-pressure methylolurea was produced as a result of the chemical reaction of urea and formaldehyde. Since urea is natural nearly harmless to humans, it can reduce the pollutants if applied to building materials.

**Keywords:** wood materials, carbonyls, micro-chamber, urea

### **1. Introduction**

Recently, with increasing attention to global environmental problems, it has been a serious challenge to create indoor environments that are comfortable as well as energy-saving. However, unlike outdoor environments, indoor environments are closed spaces and thus easily hold in various chemical substances. Typical examples of chemicals that stay in indoor air are volatile organic compounds (VOCs), such as toluene, and carbonyl compounds, such as formaldehyde. The origins of these substances are building materials, construction materials and furniture, but they can also be released from natural wood. In recent years, there are cases where wood is compressed to increase its strength. Thus, in this study we examined the substances released from wood. Also, we measured the change in release amount by compression processes.

### **2. Experiment**

#### **2.1. Three-Bed Sorbent Tube for Collection of VOCs**

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Collection of VOCs was done by the solid sorbent method. An empty glass tube (inner diameter 4 mm and length 60 mm) was packed with 12 mm of Carboxen 1000, 24 mm of Carboxen B and 14 mm of Carboxen 1000, separated by quartz wool. We used a tube conditioner (TC-20, MARKES international LTD) and put the glass tube through an aging process with pure helium gas at 360 °C for 5 hours. The tube was sealed with a stainless cap, making a Carbon tube.

## 2.2. 2,4-Dinitrophenylhydrazine Coated Silica Cartridge (DNPH-Cartridge) for Collection of Carbonyls.

100 g of Silica gel was washed well with water and acetonitrile. This was mixed with 50 mL of acetonitrile, 1 mL of phosphoric acid, and 0.5 g of DNPH hydrochloride mixed solution, and the mixture was dried under reduced pressure using a rotary evaporator (40 °C). This DNPH coated silica particles was weighed at 350 mg and packed in a Resorbian tube (1 mL, Supelco Inc.).

## 2.3. Collection and Analysis of Chemical Compounds.

A micro-chamber, the Field and Laboratory Emission Cell (FLEC, CHEMTEC Inc.) [1]-[3], was used for collection of the chemical compounds. When the FLEC is placed on a wood surface, the wood is like the bottom of a chamber, and it is possible to sample chemical substances released from the wood (Fig. 1). We placed the FLEC at the center of the sample wood in a thermostat chamber and let pure air flow at a certain speed. We then connected either the Carbon tube or DNPH cartridge to the sampling inlet of the FLEC and sampled a certain amount of the released gas from the sample by a suction pump. The Carbon tube was introduced to a gas chromatography (GC/MS) after the sampled substances were removed by heat. DNPH cartridge was eluted by acetonitrile 5 mL, and the DNPH derivative was analyzed by a high-performance liquid chromatography (HPLC).

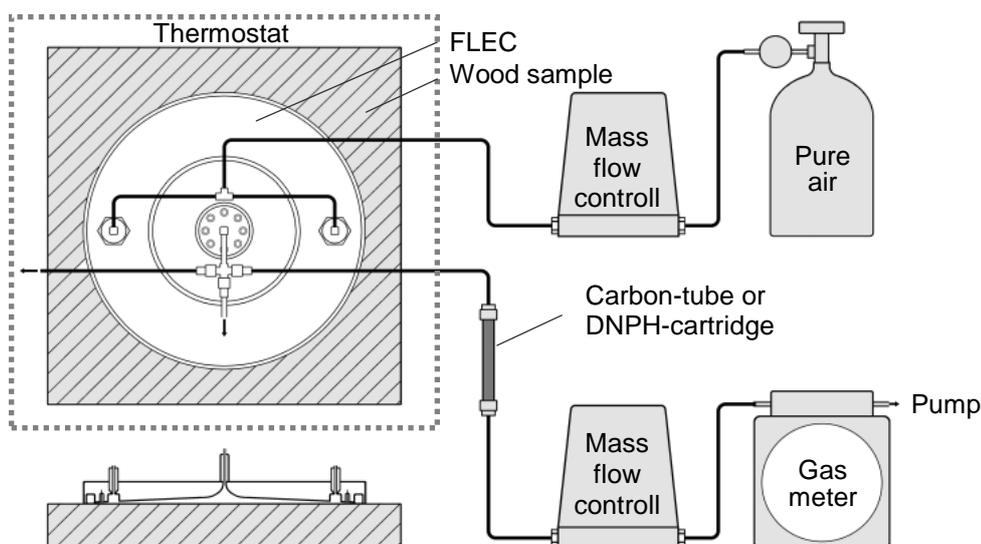


Fig. 1: Schematic drawing of the apparatus for measurement of VOCs or carbonyls emitted from the wood materials.

## 3. Results and Discussion

### 3.1. Examination of the Scavenger Forterpenoids

We used two sorbent tubes. One was an single glass tube packed with carbon absorbent such as Carboxen F, Carboxen C, Carboxen Y, Carboxen B, Carboxen Z, Carboxen X, Carboxen 1016, Carboxen 564, Carboxen 1000, Carboxen SIII, Carboxen S II, or Carboxen G. The other was three-layer sorbent tube packed with 14 mm of Carboxen 1000 for low boiling point substances, 24 mm of Carboxen B for intermediate boiling point substances, and 12 mm of Carboxen C for mid-to-high boiling point substances. We collected the chemical compounds released from wood by the aforementioned method. After the sampling, each sampling tube was placed in a heat desorption furnace, the sampled substances were desorbed, and the tubes were then introduced to gas chromatography-mass spectrometry (GC/MS). Fig. 2 shows typical GC/MS chromatograms of VOC released from wood sampled.

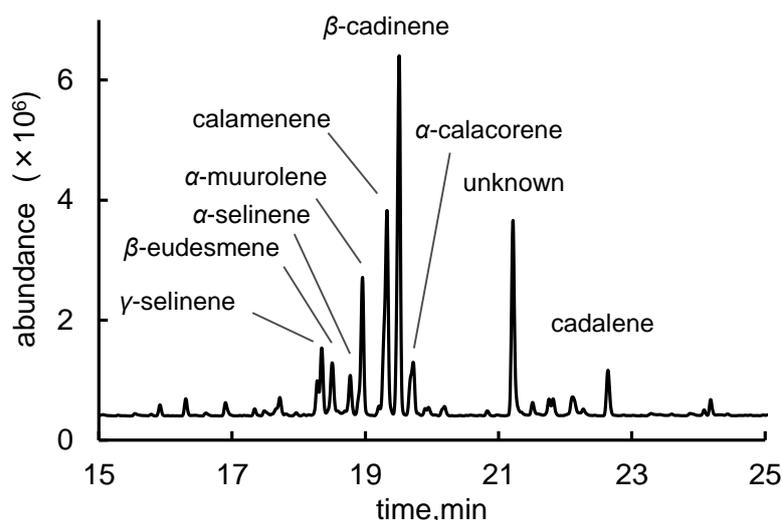


Fig. 2: Chromatographic profile of terpenes emitted from the wood material.

The chromatograms largely changed with different types of adsorbent. The most efficient sampling tubes were the Carboxen 1000 tube and the three-layer sorbent tube, which sampled terpenoids such as  $\beta$ -cadinene, calamenene,  $\alpha$ -muurolene,  $\alpha$ -calacorene, and kardelen. Also, there was little difference between the analysis results of the two sampling tubes. The second most efficient tubes were of Carboxen B and Carboxen 1000, which did not sample many types of chemical substances, but collected high amounts of specific compounds. Carboxen Z was able to collect terpenoids such as  $\beta$ -cadinene, calamenene,  $\alpha$ -muurolene,  $\alpha$ -calacorene, and kardelen as did the Carboxen C tube and the three-layer sorbent tube, but its collected amount was about 60% of the two tubes. The Carboxen X tube collected  $\beta$ -cadinene but did not collect as many types of substance or as high an amount as the other sampling tubes.

### 3.2. Terpenoids Released from Wood

Sanbu cedar was selected as the sample wood. Sanbu cedar is found mainly in the Sanbu region in Chiba (also in Chiba, Inba, Chosei and Isumi regions). It is darker than cedars in other regions, its heartwood deeper, and its material has much resin and stickiness.

In recent years, wood is compressed in order to improve its strength for furniture and construction. In particular, strong compressed wood is often used for flooring. Therefore, we used 10 cm x 4.5 cm x 25 cm pieces of Sanbu cedar compressed by 0%, 30%, 50% and 70% as test samples. The compression treatment was as follows. We first adjusted the moisture content of the samples to the appropriate value for compression by drying either naturally or artificially. The compression was done by a press machine. It was possible to bend or form different shapes when compressing by the press machine. We then collected the chemical substance released from the compressed woods by the Carbon tube and the DNPH cartridge using the FLEC. Each sampling device was then put through heat desorption, solvent desorption, and then analyzed with gas chromatography GC/MS. As a result, high amounts of VOCs and carbonyl compounds were collected from all the samples.

### 3.3. Release of Terpenoids

The major VOCs released from the compressed woods were terpenoids. Particularly prominent were  $\beta$ -cadinene,  $\alpha$ -muurolene, calamenene,  $\delta$ -elemene, copaene,  $\beta$ -Elemene, caryophyllene, and kardelen. Fig. 3 shows the change in release rates of the terpenoids for each compression rate. We could not determine the quantities since there was no standard substance for terpenoids. Therefore, we show on the vertical axis the peak areas of chromatograms as relative release rates. It was revealed that the release rate increased with increasing compression. The release rates of the terpenoids such as  $\beta$ -Cadinene,  $\alpha$ -Muurolene and Calamenene increased by a factor 5 - 7 with 30% compression and 5 - 8 with 50% compression, but it suddenly decreased by a factor of 0.8 with 70% compression. The release rates of these three substances reached their maximum with 50% compression. In contrast, the release rates of  $\alpha$ -Selinene,  $\beta$ -elemene and

copaene reached their maximum with 30% compression. In particular, it was found that  $\alpha$ -selinene was released only with finite compression.

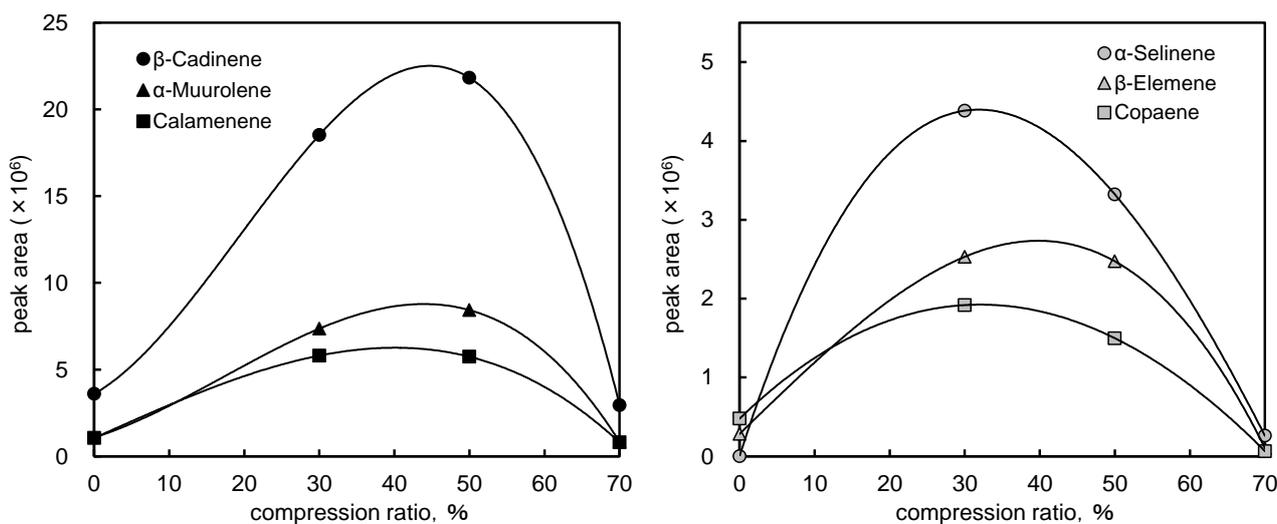


Fig. 3: Changes in emission of terpenes with the compression ratios.

### 3.4. Release of Carbonyl Compounds from Surface of Wood Sample.

The major carbonyl compounds released from the compressed woods were aldehyde and acetone with carbon number 1 - 3. The DNPH cartridge enabled the analysis of 20 components of carbonyl compounds. Fig. 4 shows the representative HPLC chromatogram. Formaldehyde, acetaldehyde, acetones, propanal, butanal, hexanal, nonanol, and decanal were detected. In particular, high amounts of formaldehyde, acetaldehyde, acetones and propanal were found. Unlike the terpenoids, it is possible to obtain standard reagents of carbonyl compounds. Therefore, we measured the concentrations of carbonyl compounds and calculated their release rates. Fig. 5 shows the change in the release rate of the carbonyl compounds at each compression rate.

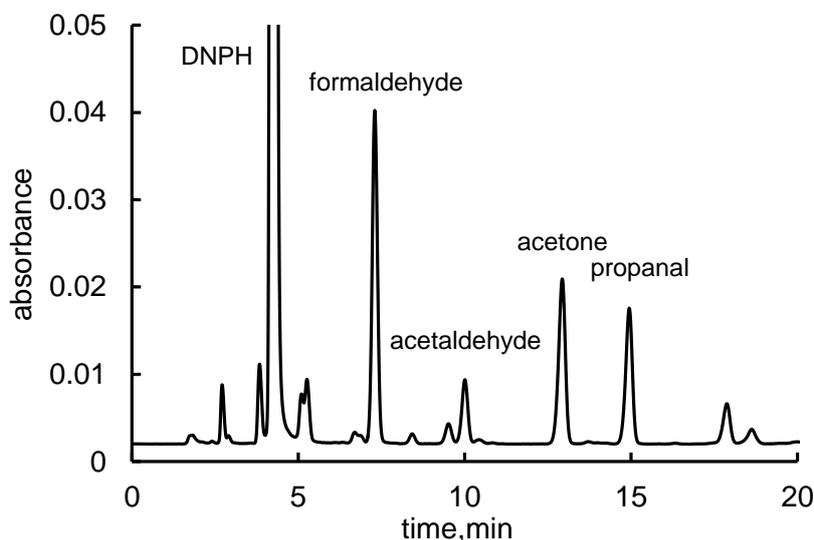


Fig. 4: Chromatographic profile of carbonyl compounds emitted from the wood material.

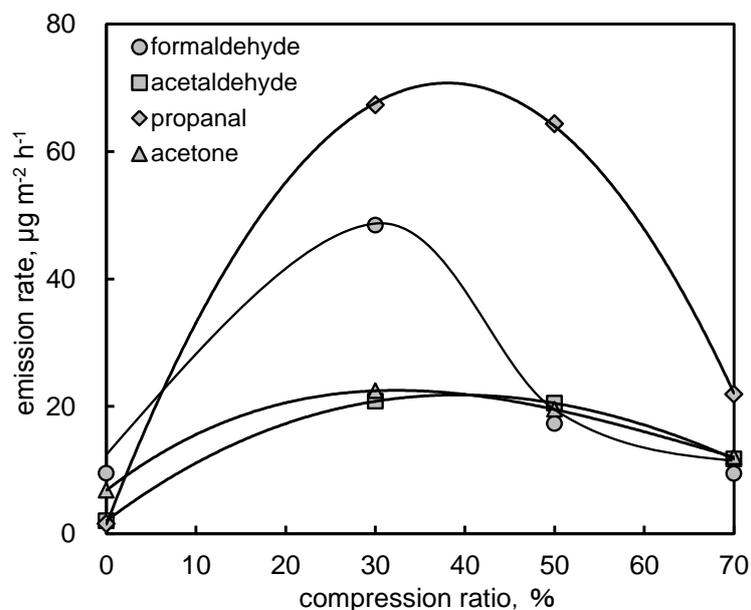


Fig. 5: Changes in emission rates of formaldehyde, acetaldehyde, acetone and propanal with the compression ratios.

The release rates of formaldehyde, acetone and acetaldehyde increased by a factor of 3 - 10 with 30% compression, 1.8 - 10 with 50% compression, and 1 - 5 with 70% compression. As for propanal, whose release rate changed by the most, the release rate increased by a factor of 40 with 30% and 50% compression and by 14 with 70% compression. The increased released rates of carbonyl compounds under compression were supposed to be because cells in the wood break due to the compression, and carbonyl compounds in those cells were released from the wood surface. Compression of the wood increased the release rates of carbonyl compounds such as formaldehyde and acetaldehyde. However, International Agency for Research on Cancer (IARC) reclassified formaldehyde as a Group 1 human carcinogen that causes nasopharyngeal cancer and also concluded that there is a “strong but not sufficient evidence for a causal association between leukemia and occupational exposure to formaldehyde” [4]. Acetaldehyde may be responsible for increased risk of head and neck cancer and esophageal cancer and was classified as a Group 2B substance [5]-[7]. It is therefore imperative to reduce their release.

### 3.5. Reduction of Carbonyl Compounds Release from Wood by Urea Treatment

It is known that formaldehyde is released from a plywood with urea formaldehyde resin as the adhesive. It has been also reported that the formaldehyde release from plywood can be reduced by applying urea [8]. Thus, we applied urea treatment in order to reduce carbonyl compounds released from wood. The wood surface was first soaked in a urea solution (10% concentration) for 2 minutes and then dried at room temperature for 24 hours. The release rate was then measured in the same manner as the pre-treatment wood using the FLEC. Fig. 6 shows the change in the release rate at each compression rate. The wood samples were those used in the experiment shown in Fig. 5. There were dramatic reductions in release rate for all the measured aldehydes. In order to quantify the effect of the urea treatment, we divided the release rate of the post-treatment sample by that of the pre-treatment sample and defined that value as the reduction rate.

Table 1 shows the reduction rate at each compression rate. The largest reduction was obtained for formaldehyde, which was reduced to 2.2% of the release rate of the pre-treatment samples at 70% compression rate. For formaldehyde, the reduction rate was 3.5% with 30% compression, but it was 10% with 50% compression, which was the highest reduction rate. The second largest effect was found in propanal, which, similar to formaldehyde, was reduced the most to 3.5% of the pre-treatment case with 70% compression rate. The reduction rate was 20 - 30% at compression rates between 0% and 50%. For acetaldehyde and acetone as well, the reduction effect was highest with 70% compression rate, and the reduction rates were 3.6% and 5.4%, respectively. However, their reduction rates were 40 - 65% with 0 - 50% compression rate, which were not as low as those of formaldehyde and propanol.



In this study, it was revealed that the release rates of terpenoids and carbonyl compounds changed with the compression rate. Also, the release rates peaked around 30 - 50% compression rates, but rapidly reduced at further compression, and it even became lower than that from the uncompressed sample with 70 % compression rate. Recently, wood compression is done in order to improve its strength, but it leads to increased release rates of harmful carbonyl compounds such as formaldehyde. However, it is possible to significantly reduce the release rate by treating wood with urea. Since urea is a natural substance which is nearly harmless to humans, it can reduce the pollutants if applied to interior building materials.

## 5. References

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