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# Comparison of Methods to Analyze Chemical Concentrations in Solid Building Materials: Preliminary Results

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**Summary:** To use a mass-transfer based model for the emissions of volatile organic compounds from dry building materials, it is necessary to know several pieces of priori information. One of the important information is the initial concentration ( $C_o$ ) of VOCs in the solid material. In this research, three methods were compared for the extraction of terpenes from plywood to determine  $C_o$ . The tested methods were supercritical fluid extraction (SFE), SFE with methanol (SFE w/ MeOH) and Soxhlet extraction (SE). The qualitative results obtained by the three methods were similar. However, quantitative agreement between methods was poor for all compounds. The applicability of SFE to building materials can be seriously limited by the difficulty in finding optimal extraction conditions.

**Keywords:** material emissions, volatile organic compounds, mass-transfer model, extraction method

## 1 Introduction

As building materials and furnishings are being recognized as major sources of volatile organic compounds (VOC) indoors, the need to use an emission model that accounts for fundamental mass-transfer mechanisms, e.g., diffusion, is getting more attention. To use such a mechanistic model, the amount of chemicals in the source, often called the initial concentration ( $C_o$ ), is essential input data.

The chemicals in solid materials need be extracted before they are quantified with an analytical technique such as gas chromatography/mass spectrometry (GC/MS) to obtain  $C_o$ . A variety of extraction techniques have been developed for food, plant and environmental samples. Conventional methods such as Soxhlet (solvent) extraction (SE) are known to be time-consuming and produce large amounts of waste solvents. Headspace techniques could be an option only for the qualitative analysis, as their extraction yields are low relative to those achieved using SE methods [1]. The fluidized-bed desorption method that was successfully applied to vinyl flooring specimens [2] can be a good candidate. However, the long testing period (e.g., 7 hours) can limit the widespread application of the technique.

More recently, the supercritical fluid extraction technique has been recognized as an enhanced alternative to conventional extraction methods [1]. Super critical extraction typically uses CO<sub>2</sub> as the supercritical fluid. By varying chamber temperature and pressure, the CO<sub>2</sub> density can be modified to provide compound selective extractions [3]. Supercritical CO<sub>2</sub> has several appealing properties that make it a suitable extraction solvent: It has gas-

like diffusivities, allowing for easier penetration into a sample than liquids, and liquid-like solvation properties, allowing it to dissolve analytes from the sample matrix. Furthermore, SFE is safer (non-toxic, non-flammable) and requires shorter extraction times than conventional solvent extraction techniques [4]. It was suggested that the mild extraction conditions of SFE might give a closer indication of the bioavailability of the pollutant in soil matrices [5].

The purpose of this study was to apply the SFE technique to building materials for  $C_o$ . To find the optimal condition for plywood specimens, temperature and pressure of SFE were varied. The role of a modifier (methanol) was also investigated. The results were compared with those by Soxhlet extraction (SE).

## 2 Method

### 2.1 Preparation of test samples

A plywood panel was purchased at a local retail store and immediately cut into pieces and sealed in Tedlar bags until required. A specimen was randomly selected and further cut into a size suitable for grinding to powder using Micromill Grinder (Scienceware). The ground material was transferred to a glass vial, which was stored at -4 °C. A portion (~1 g) of the powder was removed from the vial for each extraction trial.

Although it has been reported that compounds native to the material are extracted much more slowly than the spiked compound [4], spiking materials prior to extraction is a useful means of monitoring extraction efficiency. In this study,  $\alpha$ -

terpinene was chosen as the spiking agent since it was not found in plywood and it is chemically similar to the terpenes, which are major VOCs in plywood. The recovery rate of  $\alpha$ -terpinene was used to determine the actual quantity of compounds of interest.

## 2.2 Supercritical fluid extraction (SFE)

The challenge with *SFE* is that it requires multidimensional calibration for each material/matrix. The variables that need to be optimized include static and dynamic extraction time, chamber temperature and pressure, polarity, and trapping solvent volume. These variables may also be dependent upon the compounds of interest in that material. In this study, the major variables were the operating temperature and pressure. Various temperature and pressure combinations were attempted to determine the appropriate supercritical CO<sub>2</sub> (scCO<sub>2</sub>) density that would deliver a good spike recovery. Once found, several replicates of extractions were performed to assess reproducibility.

The supercritical fluid extraction was performed with the ISCO SFX2-10 with scCO<sub>2</sub> as the extracting fluid. Approximately 1 g of powdered material was placed into the 10 ml cylinder and spiked with 10  $\mu$ l of  $\alpha$ -terpinene. The static extraction time was 20 minutes, allowing the material to rest in the chamber filled with scCO<sub>2</sub>. This was followed by 15 minutes of dynamic extraction, where the CO<sub>2</sub> stream continuously flowed through the chamber, exiting at an approximate flow rate of 1 ml min<sup>-1</sup>. Analytes were collected in 1 ml methanol. Two extracts of the same material were performed and collected separately.

## 2.3 SFE with Methanol (SFE w/ MeOH)

As CO<sub>2</sub> is relatively non-polar, a polar modifier such as methanol can be added (either directly, or premixed in the liquid CO<sub>2</sub> tank) to increase the solubility of polar compounds in the supercritical CO<sub>2</sub> [6]. 300  $\mu$ l of methanol was added directly to the sample in the 10 ml cylinder to test the role of the modifier in the *SFE* method.

## 2.4 Soxhlet Extraction (SE)

Approximately 1g of ground plywood was placed inside the Soxhlet extraction apparatus thimble (Durex Glassware) and spiked with 10  $\mu$ l of  $\alpha$ -terpinene. A volume of 10 ml of the extracting solvent (methanol) was placed in the 25 ml round bottom flask with a magnetic stirrer. Distillation was performed for approximately 1-2 hours at 55 °C.

## 2.5 Extract Analysis

All extracts were analyzed by thermal desorption and gas chromatography/mass spectrometry (TD/GC/MS). 2  $\mu$ l of the extracted solution was injected onto a piece of glass wool blocking a two-bed sorbent tube (Carbopack B and C). Clean air was then drawn through the sorbent tube at a flow rate of 100 ml min<sup>-1</sup> for 2 minutes.

The sorbent tube was thermally desorbed using a Perkin Elmer ATD 400 and analyzed with an Agilent 6890/5973 GC/MS. The temperature program of the ATD 400 was 320 °C for primary desorption, -20 °C for low cold trap temperature and 330°C for cold trap high temperature. The GC temperature program was -20 °C for initial temperature, 5 °C min<sup>-1</sup> to 170 °C and 25 °C min<sup>-1</sup> to 280 °C. The MS temperature levels were 230 °C for source and 150 °C for MS quadrupole. The mass acquisition range was 35-350. The results for each chemical were expressed in nanogram per g of plywood (ng g<sup>-1</sup>).

## 3 Results and Discussion

### 3.1 Optimization of SFE

Many experiments were performed in which the temperature and pressure of the extraction chamber were manipulated in order to achieve a good spike recovery. Extractions were initially performed at 60°C, and it was found that increasing the temperature by increments of 10 °C increased the spike recovery rate. However, decreasing the pressure by increments of 50 atm delivered a more profound effect on the spike recovery. Table 1 shows that the recovery rate of  $\alpha$ -terpinene was best at the scCO<sub>2</sub> density of 0.38 g ml<sup>-1</sup>. Therefore, the extraction condition was set at 90 °C and 150 atm for subsequent extractions.

Table 1. The effect of supercritical CO<sub>2</sub> density on the recovery of  $\alpha$ -terpinene.

Temp (°C)	Press (atm)	scCO <sub>2</sub> density (g ml <sup>-1</sup> )	Spike Recovery (%)
90	100	0.21	78
90	150	0.38	89
90	200	0.54	70
90	250	0.64	20
90	300	0.75	11
80	300	0.79	5

### 3.2 Qualitative Analysis

Fig. 1 presents the chromatograms of extracted ions 93 and 119 for the extracts produced by *SFE*, *SFE w/ MeOH* and *SE*. The chemical compositions were very similar for the three extraction methods with five monoterpenes and one 10-carbon aromatic compound as the main components. The most visible peaks were  $\alpha$ -pinene and *p*-cymene. However, the relative abundance of six compounds was different for the three extract methods.

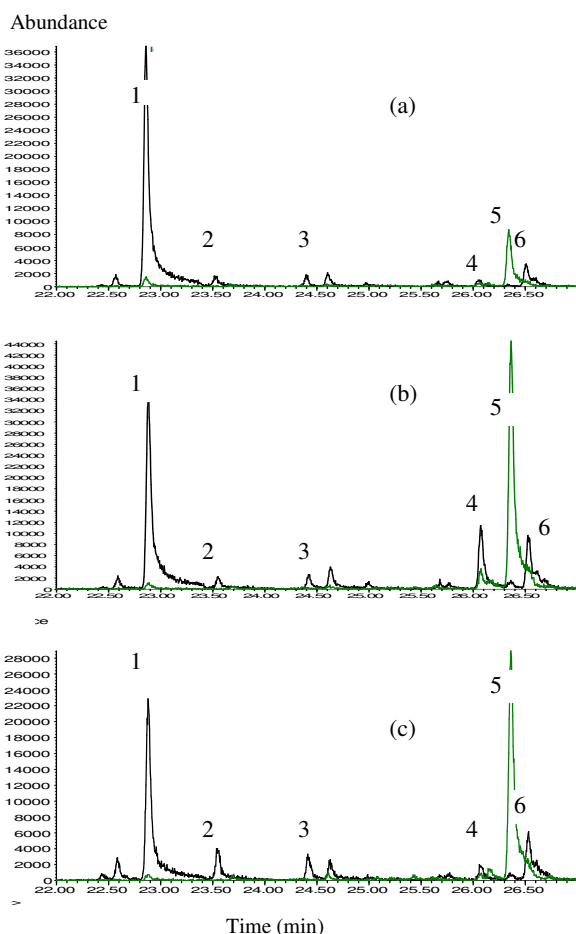


Fig. 1. Chromatogram of the two extracted ions (93 and 119) of the extracted produced by *SFE* (a), *SFE w/ MeOH* (b) and *SE* (c). Peak identification: 1:  $\alpha$ -pinene (aPin), 2: camphene (Cam), 3:  $\beta$ -pinene (bPin), 4: 3-carene (3Car), 5: *p*-cymene (pCym), and 6: limonene (Lim).

### 3.3 Quantitative Analysis

Table 2 summarizes the mean and relative standard deviation (RSD) of the initial concentration measured for the six compounds identified in Section 3.2. Fig. 2 is the graphical presentation of Table 2 with standard deviation levels as error bars. The results show that no two methods agree closely for all compounds. Using methanol as a modifier for *SFE* increased the yields

of the three compounds (aPin, Cam and bPin) by approximately two to three times that obtained with non-modified *SFE*. However, no increase was observed for the other three compounds (3Car, pCym and Lim) by using the modifier. Since the two groups of chemicals have similar chemical characteristics, the difference in the extraction yield is hard to be explained by chemical properties such as polarity.

The extracted amounts by *SFE* were comparable to those by *SE* for the first three compounds (aPin, Cam and bPin). On the other hand, for the second group of compounds, *SFE* yielded 2–3 times the amounts obtained by *SE*. Again, the reason for the improved extraction only for the last three compounds is unknown.

Table 2. Mass of chemicals per gram of plywood ( $\text{ng g}^{-1}$ ).

	aPin	Cam	bPin	3Car	pCym	Lim
<b>SFE<sup>1</sup></b>	<b>8497</b>	<b>722</b>	<b>1791</b>	<b>562</b>	<b>4159</b>	<b>9783</b>
RSD (%)	36	80	37	70	32	93
<b>SFE w/ MeOH<sup>2</sup></b>	<b>24201</b>	<b>1313</b>	<b>4181</b>	<b>478</b>	<b>3945</b>	<b>6865</b>
RSD (%)	37	32	25	39	39	50
<b>SE<sup>3</sup></b>	<b>11327</b>	<b>751</b>	<b>2650</b>	<b>198</b>	<b>2047</b>	<b>3965</b>
RSD (%)	35	17	23	20	9	53

1. Mean from 6 repeats, 2. Mean from 2 repeats for *SEF* with 300  $\mu\text{l}$  of methanol, 3. Mean from 3 repeats.

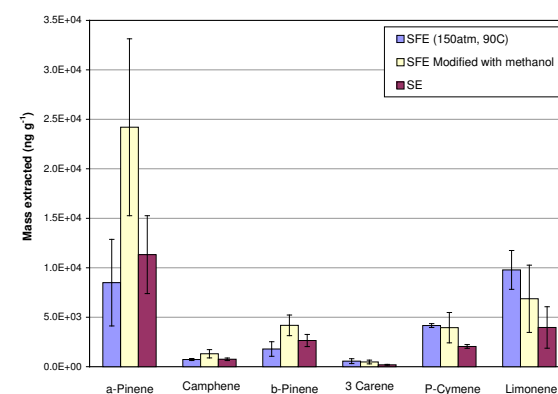


Fig. 2. Graphical presentation of mass extracted ( $\text{ng g}^{-1}$ ).

The relative standard deviation levels in Fig.2 indicate that the reproducibility of all three methods is not very good. In particular, *SFE* is associated with the biggest RSD for most compounds (Table 2) implying that it is necessary to further improve the *SFE* method. Among many variables to be optimized for *SFE*, several experimental variables need particular attention.

First, the optimal extraction condition may need to be found at a lower temperature. The temperature of 90 °C used in this study may be high enough to cause thermal degradation of terpenes or structural

change to the plywood specimen. The importance of using a temperature close to an ambient level can be explained by the dual-mobility model that differentiates the readily mobilized portion from the partially immobilized portion of a VOC in amorphous polymers [2].

Second, the trapping method needs to be improved. A vial containing methanol was used as a trapping method for the SFE extract in this study. Using a solid-phase trap produced a significantly improved repeatability in extracting volatile compounds from spices [1] and successful results in determining petroleum hydrocarbons from soil samples [7]. Various collection methods reviewed in [8] need to be tested for VOCs in solid building materials.

Third, the *SFE* and *SE* extract was injected onto a sorbent tube before it was thermally desorbed and analyzed with GC/MS. This extra step may have induced more variability to the final results and may need to be eliminated with a direct injection technique.

## 4 Conclusion

The extract obtained using the supercritical extraction method was similar in composition to that with the solvent extraction method. However, there was no trend in the relative abundance of six abundant compounds between *SFE* and *SE*. The *SFE* method improved the extraction of only three terpenes. This preliminary study shows that it is not easy to develop an extraction method that can guarantee optimal results even for the chemicals in a single VOC class from one material specimen. It supports the speculation that the extraction method to determine  $C_o$  needs to be tailored to accommodate the differences in chemical and material properties.

The large levels of relative standard deviations imply that the reproducibility of *SFE* is not good at the condition used in this study. More research is needed to optimize the *SFE* method for plywood. In particular, special attention is necessary for variables such as temperature and extract trapping methods. It is important to note that the difficulty in optimizing the *SFE* method can seriously limit the applicability of *SFE* to building materials.

There should be continued effort to find an extraction method that is rapid, simple, and inexpensive to perform and that can provide a good recovery of target analytes without loss or degradation. The starting point would be learning from a pool of existing knowledge on a variety of extraction methods developed for food, plant and environmental samples, including pressurized liquid extraction, microwave and sonic wave-assisted extraction [5], thermal extraction and vacuum distillation extraction. The fluidized-bed desorption method [2] with a shorter testing period

can also be a good candidate for the comparison study.

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