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Rapid Method for Measuring the VOC-Adsorption Properties of Woodceramics

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A rapid method for measuring the volatile organic compounds (VOC)-adsorption properties of woodceramics was developed using gas chromatography (GC) based on the finding that the sum of the peak areas at a predetermined retention time in GC is directly related to the amount of VOC residue that were not adsorbed by woodceramics. It takes 2 hours to estimate the VOC-adsorption properties of woodceramics. The mass loss of VOC-adsorbed woodceramics from room temperature to 110°C was compared with the total VOC values obtained by this method. The amount of total VOC evolved from menthone-adsorbed woodceramics stored at 40°C for 3 weeks decreased with the duration of storage because adsorption proceeded gradually. As a result, this method appears to be suitable for investigating the VOC-adsorption properties of woodceramics. The influence of the water content of woodceramics on the VOC-adsorption properties of woodceramics was also examined. As a result, the influence of the water content of woodceramics manufactured from cedar on VOC-adsorption properties was different from that of woodceramics manufactured from apple waste.

Key words: woodceramics, adsorption, gas chromatography, volatile organic compounds

1. INTRODUCTION

It is important that building materials contain only small amounts of volatile organic compounds (VOC) to prevent "sick building syndrome" or "sick house syndrome". Wood has generally been considered to be a valuable building material because only a small amount of formaldehyde is evolved from wood materials. "Woodceramics" are carbon/carbon composite materials consisting of plant-originated amorphous carbon reinforced by glassy carbon generated from phenol resin. Woodceramics (WC) can be produced by impregnating wood-based (lignocellulosic) materials, such as hiba, cedar, pine, medium density fiber boards, waste paper, apple waste, etc., with phenol resin, and then calcining the resulting materials [1].

Wood-based materials are attracting attention as good absorbers of VOCs. Depending on the starting materials, WC differs in physical properties such as specific surface area, pore structure and size. The specific surface area in the BET method for WC manufactured from apple waste (AWC) was much lower than that for WC manufactured from cedar (CWC). AWC showed higher selectivity for oxygen vs. nitrogen gas molecules. On the other hand, CWC has no selectivity for gas species [2]. This result suggests that the gas-adsorption properties of AWC are different than those of CWC.

The adsorption properties of wood charcoal and CWC were evaluated by a rapid method for measuring VOC evolved from wood materials that was recently developed by Nishimoto et al. [3]. In this paper, we investigated this method in detail to establish a rapid method for measuring the adsorption properties of WC. In the case of CWC, the sample size has been reported to affect the adsorption of VOC [2, 4]. In this study, the influence of the water content of wood charcoal and WC was also examined.

2. EXPERIMENTAL

2.1 Samples

Wood charcoal manufactured from cedar (CC) and biomass charcoal manufactured from apple waste (AC) and woodceramics manufactured from cedar (CWC) and apple waste (AWC) were used [2]. The carbonizing temperature of charcoal and woodceramics is 800°C.

2.2 Pretreatment method

As a pretreatment condition of charcoal and woodceramics, these samples were stored at a specific relative humidity (R.H.) (20%, 50% or 75%) for 4 days.

2.3 Rapid adsorption method

A small amount (0.1 μL) of the volatile organic compound sample was sealed in a vial with a small amount (50 mg) of adsorbents such as woodceramics, and kept at a certain temperature (110°C) for 1 hour.

2.4 Long-time adsorption method

A small amount (0.1 μL) of the volatile organic compound sample was sealed in a vial with a small amount (50 mg) of adsorbents such as woodceramics, and kept at a certain temperature (40°C) until 3 weeks. The vial was sampled every 1 week.

2.5 Measurement

One mL of the gas phase in a vial was injected and measured by GC (HP6890, equipped with HP6890 FID and a DB-1 capillary column) using He as the carrier gas [2, 3].

About 5mg of adsorbent in a vial was sampled and measured by thermogravimetry. Thermogravimetric analysis (TGA) was performed with a TG/DTA 320 (SII) in the temperature range of room temperature to 140°C at a heating rate of 5°C/min. The measurements were carried out under Ar gas flow at a rate of 150 mL/min.

3. RESULTS and DISCUSSION

3.1 Acceleration Test

Figure 1 shows the TG curves of CWC and menthone-adsorbed CWC. The TG data of CWC show a smooth one-step mass-loss curve from room temperature to 120°C. In this temperature range, the mass loss from WC can be understood as being due to the desorption of inherent water and CO_2 from WC [5, 6]. In addition, the TG curve of menthone -adsorbed CWC shows another mass-loss step at around 90°C according to the desorption of menthone. In the case of perfume-adsorbed WC, the mass loss at 110°C indicates the amount of VOC, water and CO_2 desorbed from WC. If the amount of water and CO_2 that was adsorbed by WC was the same, it was considered that the value of mass loss at 110°C changed depending on the amount of VOC that was adsorbed by WC.

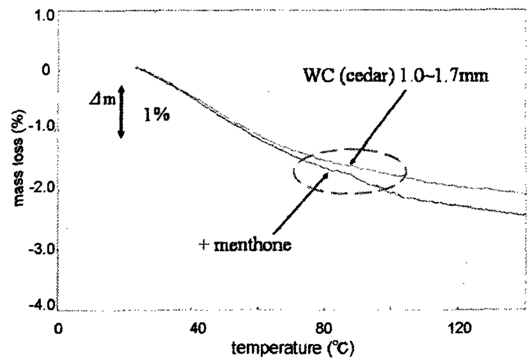

Figure 1 TG curves CWC and menthone-adsorbed CWC.

Table 1 TVOC values for perfumes in the presence of each perfume and CWC obtained by GC.

Perfume	TVOC values (nL)	
	pretreatment condition of CWC	
	without storage	storage at 20% R.H. for 4 days (dry sample)
Pulegone	22.7	15.2
Menthone	16.9	0.3
Geraniol	3.3	1.0
Carvone	0.3	0.7
Citral	0.1	N.D.

N.D.: not detected

Table 1 shows the influence of the pretreatment condition of CWC on the total amount of volatile organic compounds (TVOC) values for perfumes. The TVOC values can be estimated from the sum of the peak areas obtained at a predetermined retention time in the gas chromatogram in a similar way as the method of the description to the literature [2, 3]. The sum of peak areas obtained by GC shows the amount of the perfume remaining in the head space of a vial after storage at 110°C for 1 hour. As the TVOC values indicate the amount of VOCs that were not adsorbed by WC in the vials, the small TVOC values show the high adsorption power of WC for VOCs. All the perfumes except carvone were highly adsorbed by dried (after storage at 20% RH for 4 days)

CWC. Citral was the most adsorbed perfume by dry CWC, whereas carvone was strongly adsorbed regardless of the pretreatment condition of CWC. It was considered that these differences had been caused by the difference of the water solubility of the perfume. The reason for the difference for menthone and carvone is described in 3.3 in detail.

Figure 2 shows the relationship between the mass loss at 110 °C and the TVOC values. The TVOC values for perfumes in the presence of perfumes and CWC are inversely proportional to the mass loss at 110°C. These results show that the TVOC values obtained by this method were related directly to the amount of VOC that remains without being adsorbed. A lower TVOC value is associated with greater adsorption of the perfumes.

These results suggest that this method is an effective acceleration test to estimate the adsorption powers of WC for VOCs.

3.2 Influence of storage at 40°C for 3 weeks

The menthone and AWC or AC put in a vial, and stored at 40℃ until 3 weeks. The vial was sampled every week and kept at a 110°C for 1 hour, and gas phase in a vial was measured by GC. Table 2 shows the TVOC values for menthone in a vial of menthone with AWC or AC. The TVOC values decreased with the duration of storage because adsorption proceeded gradually. These results show that this method is applicable to AC and AWC as well as CWC.

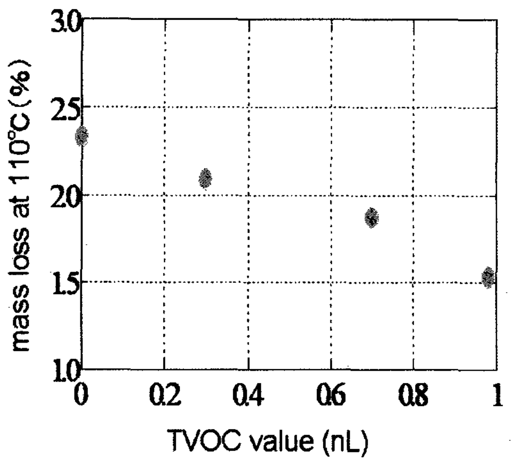

Figure 2 Relationship between the mass loss at 110°C and the TVOC values for perfume (menthone, geraniol, carvone, citral)-adsorbed CWC with storage at 20% relative humidity for 4 days.

Table 2 TVOC values of menthone in the presence of AWC and AC with storage at 40°C for 3 weeks.

storage at 40°C	TVOC values (nL)	
	AWC	AC
Before storage	0.32	0.37
1 week	0.16	0.14
2 weeks	0.14	0.077
3 weeks	0.083	0.082

3.3 Influence of water content of WC on VOC -adsorption properties

Table 3 shows the influence of the pretreatment humid conditions of charcoal and woodceramics. The influence of the water content of charcoal and woodceramics on the adsorption properties for menthone and carvone show a similar tendency. On the other hand, the adsorption properties of charcoal and woodceramics for benzene show an opposite tendency. For example, the adsorption power of AC for menthone or carvone shows the highest value (lowest TVOC value) at 75% R.H. and the lowest value at 50% R.H. The adsorption power of AC for benzene shows the lowest value (highest TVOC value) at 75% R.H. and the highest value at 50% R.H. CC showed strong adsorption ability particularly for benzene independent of its water content. In the dry state, CWC has greater adsorption power for menthone or carvone; on the other hand, AWC has almost identical adsorption power for menthone, carvone and benzene. The influence of the water content of CWC on VOC-adsorption properties differed from that of AWC. R. Ozao et al. reported that the specific surface area obtained by Multipoint BET method using CO_2 molecules as adsorbate of CWC was 555 m^2g^{-1}, and 185 times as large as those of AWC [2]. These results and FE-SEM photograph of CWC suggested the existence of a lot of meso-pores in CWC [2, 7]. There must be a difference of TVOC value of AWC and CWC in distinctness if VOC was adsorbed by the meso-pores of CWC. The VOC was mainly adsorbed by the surface of CWC, and not adsorbed by the meso-pore of CWC because the difference of TVOC values of AWC and CWC in the table 3 is twice or less. Both molecules of carvone and menthone belong to monoterpene ketone. Menthone slightly solves in water though neither carvone nor benzene solves. The difference of the adsorption characteristic of menthone and carvone show the dependency on the difference of the water solubility. In addition, it was suggested that the hydrophilic property on the surface of adsorbent was reflected in the result. The WC shows the lower water affinity than charcoal due to the phenol resin.

Table 3 Influence of the pretreatment humid conditions of wood charcoal and woodceramics on the adsorption power for VOCs

(n=3)

adsorbent	R.H	TVOC values (nL)		
		Menthone	Benzene	Carvone
AC	20%	0.37	0.13	0.38
	50%	0.45	0.11	0.51
	75%	0.22	0.24	0.26
CC	20%	0.16	N.D.	0.30
	50%	0.10	N.D.	0.20
	75%	0.13	N.D.	0.18
AWC	20%	0.31	0.30	0.31
	50%	0.28	0.56	0.42
	75%	0.52	0.39	0.53
CWC	20%	0.33	0.07	0.64
	50%	0.71	0.42	0.47
	75%	0.56	0.27	0.48

4. CONCLUSIONS

A method for rapidly measuring VOC-adsorption properties of woodceramics was developed using GC based on the finding that the sum of the peak areas at a predetermined retention time in chromatogram is directly related to the amount of VOC residue that were not adsorbed by woodceramics. The influence of the water content of woodceramics on the VOC-adsorption properties of woodceramics was examined. The influence of the water content of CWC on VOC-adsorption properties was different from that of AWC. In addition, CC showed strong adsorption ability particularly for benzene independent of its water content.

5. References

[1] T. Okabe and K. Saito, Japanese Patent Laid-Open No. 164806/1922.

[2] R. Ozao, T. Okabe, T. Arii, Y. Nishimoto, Y. Cao, N. Whitely and W-P. Pan, *Materials Transactions*, **46**, 2673-78 (2005).

[3] Y. Nishimoto, T. Takenouchi, T. Daigo, T. Nakada and H. Kuroyama, *Bunseki Kagaku*, **49**, 449-54 (2000) (in Japanese).

[4] R. Ozao, Y. Nishimoto, T. Okabe, *Trans. Mater. Res. Soc. Jpn*, to be submitted.

[5] R. Ozao, Y. Nishimoto, W-P. Pan, T. Okabe, *Thermochimica Acta*, **440**, 75-80 (2006).

[6] R. Ozao, T. Arii, T. Okabe, D. Capogna, M. Ochiai, *Trans. Mater. Res. Soc. Jpn.*, **29**, 2435-38 (2004).

[7] Y. Sawada, S. Sezaki, R. Ozao, Y. Nishimoto, T. Okabe, M. Ide and A. Shida, *Materials Transactions*, **46**, 2685-89 (2005).

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