

Rapid method for measuring the VOC-adsorption and desorption properties of bamboo and Bincho charcoal

Takahisa TSUGOSHI¹, Maho YOSHIIZUMI², Yuko NISHIMOTO^{2*}, Riko OZAO³

¹ Reference Materials System Division, National Metrology Institute of Japan
National Institute of Advanced Industrial Sciences and Technology (AIST), Tsukuba, Ibaraki 305-8563 Japan
E-mail address: tsugoshi.takahisa@aist.go.jp

² Kanagawa University, Department of Chemistry, Faculty of Science, Hiratsuka, Kanagawa 259-1293 Japan
E-mail address: y24moto@kanagawa-u.ac.jp

³ SONY Institute of Higher Education, Atsugi, Kanagawa 243-8501 Japan
E-mail address: Ozao@ei.shohoku.ac.jp

The volatile organic compound (VOC)-adsorption properties of bamboo and Bincho charcoal were estimated using gas chromatography (GC) based on the finding that the peak area at a predetermined retention time in GC is directly related to the amount of VOC residue that was not adsorbed by bamboo and Bincho charcoal. Bamboo and Bincho charcoal showed strong adsorption of *p*-xylene and citronellol compared to benzene, carvone, geraniol, menthone and pulegone. The VOC-desorption properties of bamboo and bincho charcoal that had adsorbed VOC were investigated by EGA-IAMS using a skimmer interface. The EGA peak of *p*-xylene started to appear at over 60 °C, and showed a maximum intensity at around 180 °C. The EGA peak of carvone started to appear at 30 °C, showed maximum intensity at around 80 °C, and decreased in peak intensity at 130°C. These results suggested that the evolution of *p*-xylene and benzene that had been adsorbed by charcoal was not observed at room temperature. EGA-IAMS using a skimmer interface can be used to monitor VOC desorption from charcoal that has adsorbed VOC.

Key words: wood charcoal, adsorption, desorption, gas chromatography, ion attachment mass spectrometry, volatile organic compounds

1. INTRODUCTION

Wood charcoal differs in physical properties, such as specific surface area, pore structure and pore size, depending on starting materials. Wood-based materials are attracting attention as good absorbers of volatile organic compounds (VOCs). The adsorption properties of wood charcoal and cedar-based woodceramics were evaluated by a rapid method for measuring VOC evolved from wood materials [1, 2]. The adsorption behavior of bamboo charcoal, cedar-based charcoal, cedar-based woodceramics and cedar wood for perfumery materials has been examined. The adsorption behavior of wood materials was shown to depend on the starting materials [1, 3]. The VOC-adsorption behavior of wood materials and VOC-desorption behavior from wood materials are interesting from the viewpoint of indoor air-quality control. The analysis of gas-desorption from an adsorbent usually requires evolved gas analysis-mass spectrometry (EGA-MS), better known as thermogravimetry mass spectroscopy (TG-MS). EGA-MS has generally used a quadrupole mass spectrometer to detect various gaseous species that have evolved from a sample and are carried via a capillary interface between the MS and the furnace. The capillary interface can adsorb the evolved gaseous species. Thus, a skimmer interface, which is useful in an infrared image furnace, has been developed [4]. The fragmentation due to ionization for MS prevents the identification of gaseous species in a furnace. Therefore, the combination of a skimmer interface with no change evolved gaseous species, and ion attachment mass spectrometry

(IAMS), with no fragmentation during ionization, has been expected to the accurate characterization of gaseous species in a furnace. Previous reports have described the application of IA-QMS to EGA for in situ monitoring of porous ceramic processing [5, 6]. In this study, IA-QMS was applied to EGA-MS using a skimmer interface to monitor VOC desorption from wood charcoal that had adsorbed VOC.

2. EXPERIMENTAL

2.1 Reagents

Benzene, carvone, citronellol, geraniol, menthone, and *p*-xylene, as volatile organic compounds, were obtained from Wako Pure Chemical Industries, Ltd. and used without further purification. Pulegone was obtained from Kanto Chemical Industries, Ltd. and used without further purification. The chemical structures and boiling points of these reagents are shown in Figure 1. Wood charcoal manufactured from naturally grown *Quercus phillyraeoides* in Wakayama which was called Bincho charcoal and the bamboo charcoals manufactured from naturally grown bamboo at Matsuzaki-cho in Shizuoka, Odawara and Hiratsuka in Kanagawa were used in this work. All bamboo charcoals used in this study are made from *Phyllostachys pubescens*, and carbonized at about 800~1000°C. The carbonizing temperature of Bincho charcoal was estimated at above 800°C. But the carbonizing temperatures do not controlled exactly. The specific surface areas of these charcoals are as follows, 800 m²/g (Bincho

Charcoal), 500 m²/g (Matsuzaki-cho made), 800 m²/g (Odawara made) and 300 m²/g, (Hiratsuka made), measured by methylene blue adsorption method at room temperature. Because these values are too large for bamboo charcoals and the factor of the difference of these values are not clear, the detailed investigations about pore-size distribution of these samples are carrying out. For pretreatment, charcoal samples were stored at 20% relative humidity (R.H.) for 4 days in order to obtain dry charcoals. [2]

The water contents of all pretreated charcoals proved to be about 1.0 mass% using thermogravimetry.

2.2 Apparatus and Measurements

Rapid adsorption method

A small amount (0.5 μ L) of carvone, citronellol, geraniol, menthone, pulegone, benzene or *p*-xylene was sealed in a vial with a small amount (50 mg) of charcoal, and kept at a 110°C for 1 hour. 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, 7].

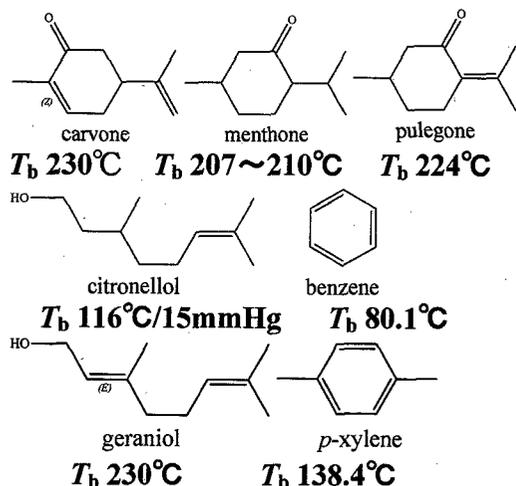


Fig.1 Chemical structures and boiling points of VOCs used in this experiment

VOC desorption process

A small amount (10 mg) of charcoal that had adsorbed VOC was taken out of the vial and measured by EGA-IAMS. All IA-QMS measurements were carried out with a prototype apparatus consisting of a gold image furnace based on TPD type R (Rigaku Corporation) and an IA-QMS instrument (L-241G-IA; Canon ANELVA Technix Corporation), as previously reported [4]. A schematic diagram of the prototype apparatus is shown in Figure 2. The skimmer interface connected the furnace to atmospheric pressure, and the ionization chamber gas helium flowed into the furnace during heating, which was performed at a rate of 10 °C/min.

3. RESULTS and DISCUSSION

Table 1 shows the ratio of VOC adsorbed by charcoal as evaluated by gas chromatography. Three types of bamboo charcoals and one type of bincho charcoal which used in this study showed strong abilities to adsorb *p*-xylene and citronellol compared to benzene, carvone, geraniol, menthone and pulegone.

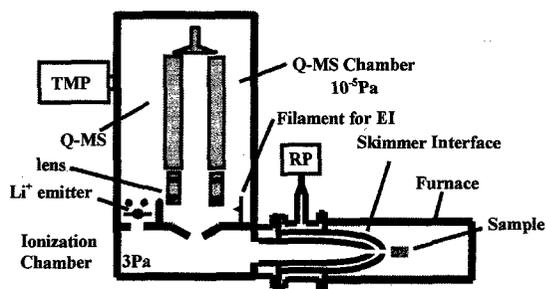


Fig.2 Schematic diagram of the prototype apparatus (TIAS-254)

Table 1 Ratio of VOC adsorbed by charcoal evaluated by gas chromatogram

VOC	adsorption ratio/% (%RSD) (n=3)			
	charcoal A	charcoal B	charcoal C	charcoal D
carvone	89 (5.5)	92 (16)	89 (28)	98 (30)
citronellol	99 (12)	96 (21)	97 (31)	100 (30)
geraniol	66 (17)	82 (19)	54 (15)	98 (26)
menthone	81 (27)	60 (15)	82 (35)	95 (20)
pulegone	88 (40)	85 (39)	91 (4)	98 (19)
benzene	98 (17)	88 (39)	91 (30)	93 (20)
<i>p</i> -xylene	100 (44)	100 (36)	100 (36)	100 (31)

A: bamboo charcoal manufactured from naturally grown bamboo at Matsuzaki-cho

B: bamboo charcoal manufactured from naturally grown bamboo at Odawara

C: bamboo charcoal manufactured from naturally grown bamboo at Hiratsuka

D: Bincho charcoal manufactured from naturally grown *Quercus phillyraeoides* in Wakayama

%RSD: relative standard deviation, standard deviation / mean value X 100

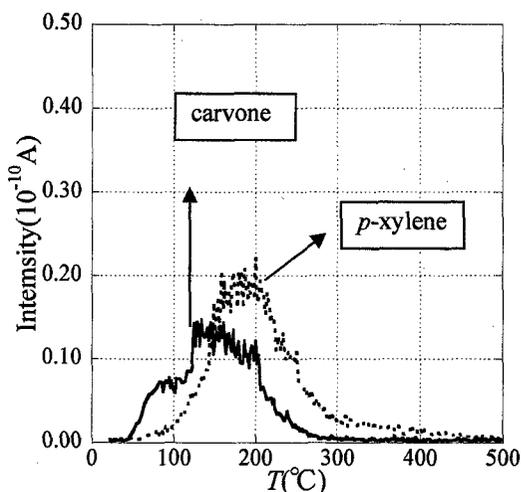


Fig.3 EGA curves of carvone and *p*-xylene desorbed from VOC-adsorbed Bincho charcoal

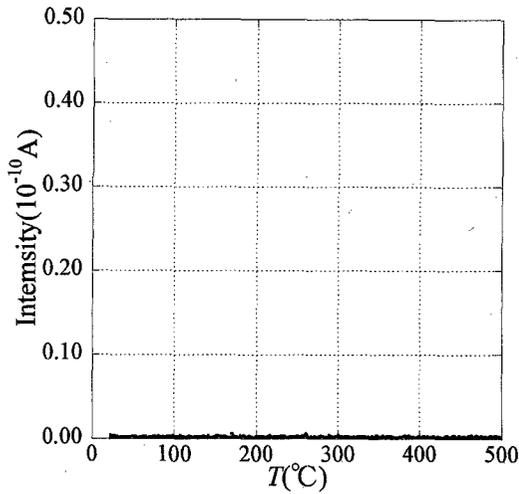
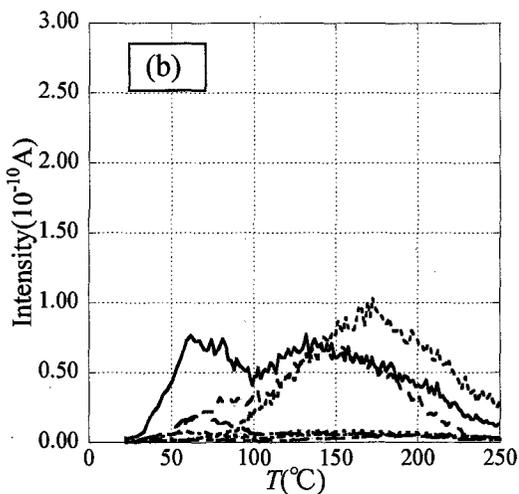
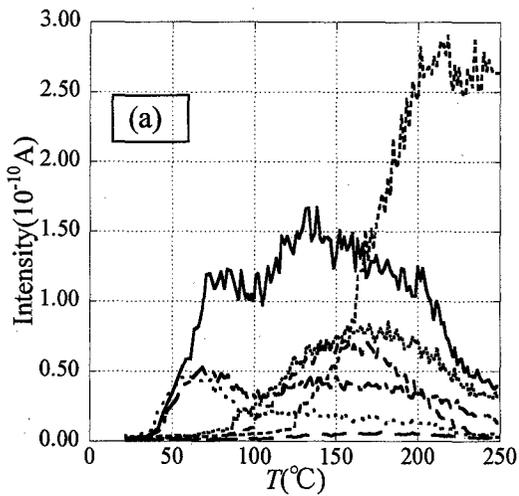
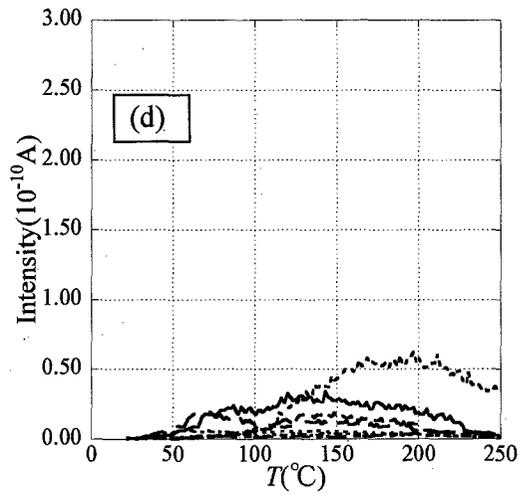
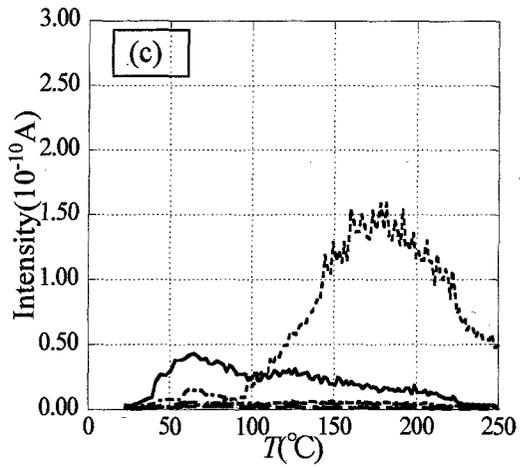


Fig.4 EGA curves of carvone and *p*-xylene desorbed from Bincho charcoal after the 1st measurement



- : carvone + Li⁺ (m/z = 157)
- - - : citronellol + Li⁺ (m/z = 163)
- · — : gelaniol + Li⁺ (m/z = 161)
- · - · - : menthone + Li⁺ (m/z = 161)
- · - · - : pulegone + Li⁺ (m/z = 159)
- : benzene + Li⁺ (m/z = 85)
- - - - : *p*-xylene + Li⁺ (m/z = 113)

Fig.5 EGA-IAMS curves of VOC desorbed from wood charcoal that had adsorbed VOC

(a): bamboo charcoal manufactured from naturally grown bamboo at Matsuzaki-cho

(b): bamboo charcoal manufactured from naturally grown bamboo at Odawara

(c): bamboo charcoal manufactured from naturally grown bamboo at Hiratsuka

(d): Bincho charcoal manufactured from naturally grown *Quercus phillyraeoides* in Wakayama

We expected the influence of the soil on the VOC-adsorption property of bamboo charcoal. The difference of the adsorption ratio of geraniol and menthone was observed among each bamboo charcoals. The reason for this preference is yet to be clarified.

A small amount of charcoal that had adsorbed was taken out of the vial and measured by EGA-IAMS. When it was heated, the adsorbed VOC was released. The mass number of each peak in the IA-QMS spectra included an additional 7 amu as a result of using Li^+ as the ionization source.

Figure 3 shows the EGA curves of carvone and *p*-xylene desorbed from Bincho charcoal. An EGA peak of 113 amu due to *p*-xylene + Li^+ started to appear above 60 °C, and showed a maximum intensity at around 180 °C. On the other hand, the EGA peak at 157 amu due to carvone + Li^+ started to appear at 30 °C, showed a maximum intensity at around 80 °C, and then decreased in peak intensity at 130 °C. The total peak areas of these two curves are almost the same. After the measurement, a sample was taken, and used in a 2nd scan.

Figure 4 shows that the evolved gases were not found. These results suggest that *p*-xylene did not evolve at room temperature. Citronellol, geraniol, menthone and pulegone showed the same tendency as carvone. On the other hand, benzene showed the same tendency as *p*-xylene.

Figure 5 shows the EGA curves of VOC (benzene, carvone, citronellol, geraniol, menthone, pulegone and *p*-xylene) evolved from each VOC-adsorbed charcoal. When charcoal that had adsorbed was heated, the adsorbed gas was released according to its affinity for the charcoal. Charcoal showed strong affinity for *p*-xylene and benzene compared to carvone, citronellol, geraniol, menthone and pulegone. The results suggest that the evolution of *p*-xylene and benzene from charcoal was not observed at room temperature. These results were considered to be related their adsorption mechanism. The detailed adsorption mechanism has not yet been clarified. EGA-IAMS using skimmer interface can be used to monitor VOC desorption from wood charcoal that had adsorbed VOC.

These results suggest that this method is an effective test to estimate the adsorption and desorption abilities of bamboo charcoal for VOCs. It takes 2 hours to estimate the VOC-adsorption and desorption abilities of bamboo charcoals.

4. CONCLUSIONS

A method for rapidly measuring VOC-adsorption and desorption abilities of bamboo and Bincho charcoals was investigated. Three types of bamboo charcoals and one type of wood charcoal (Bincho charcoal) which used in this study showed strong abilities to adsorb *p*-xylene and citronellol compared to benzene, carvone, geraniol, menthone and pulegone. The VOC-desorption properties of bamboo charcoal that has adsorbed VOC were investigated by EGA-IAMS using skimmer interface. The results suggest that the evolution of *p*-xylene and benzene from charcoal was not observed at room temperature. EGA-IAMS with skimmer interface can be used to monitor VOC desorption from wood charcoal that has adsorbed VOC.

5. REFERENCES

- [1] R. Ozao, T. Okabe, T. Ariei, Y. Nishimoto, Y. Cao, N. Whitely and W.-P. Pan, *Materials Transactions*, **46** (2005) 2673-2678
- [2] Y. Nishimoto, Y. Notsu, K. Nakamura, M. Yoshiizumi, R. Ozao and T. Okabe, *Trans. MRS-J*, **31** (2006) 937-940
- [3] R. Ozao, Y. Nishimoto and T. Okabe, *Trans. MRS-J*, **31** (2006), 925-928
- [4] T. Tsugoshi, M. Furukawa, M. Ohashi, Y. Iida, *J. Therm. Anal. Cal.*, **64** (2001) 1127-1132
- [5] T. Tsugoshi, T. Nagaoka, M. Nakamura, Y. Shiokawa and K. Watari, *Anal. Chem.*, **78** (2006) 2366-2369
- [6] T. Tsugoshi, N. Ito, T. Nagaoka and K. Watari, *Talanta*, **70** (2006) 186-189
- [7] Y. Nishimoto, T. Takenouchi, T. Daigo, T. Nakada and H. Kuroyama, *Bunseki Kagaku* **49** (2000) 449-454 (in Japanese)
- [8] T. Tsugoshi, T. Nagaoka, K. Hino, T. Ariei, M. Inoue, Y. Shiokawa and K. Watari, *J. Therm. Anal. Cal.*, **80** (2005) 787-789

(Received February 16, 2007; Accepted July 12, 2007)