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ORIGINAL ARTICLE

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Evaluation of formaldehyde adsorption by bamboo charcoal using a photoacoustic method

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Abstract This study focuses on a novel, multipass, acoustically open photoacoustic detector designed for fast-response high-sensitivity detection of formaldehyde adsorption by bamboo charcoal in an ambient atmosphere. The detection range, estimated from formaldehyde measurements at a wavenumber of around 2805 cm^{-1}, is 0–2.0 parts per million by volume. In this work, photoacoustic (PA) detection with various bamboo charcoals was analyzed at our laboratory for the detection of a photoacoustic signal using a pulsed laser system and the comparative performances of the charcoals were studied. The PA system is applicable to pollution monitoring and detection of hazardous gases in an indoor environment.

Key words Photoacoustic · Formaldehyde · Charcoal · Adsorption

Introduction

Building materials such as wood-based materials, adhesive, paints, varnish, and vinyl floorings are important sources of volatile organic compounds (VOCs). Wood-based materials are ideal as indoor building materials over a range of temperatures and humidity levels, which are widely used in the indoor environment. Formaldehyde-catalyzed resins are commonly used in the manufacture of engineered wood products such as particleboard, medium-density fiberboard, plywood, oriented strand board, and laminated veneer lumber.[1] Formaldehyde is often considered to be one of the most dangerous toxins that can be found in living spaces.[2] Even at low concentrations, formaldehyde causes health problems and may be associated with various diseases, such as eye/nose irritation, atopic dermatitis, and sick building syndromes.[3] Typical indoor background levels of formaldehyde are of the order of a parts per sub-million by volume (sub-ppmV). Recently, maximum formaldehyde levels have been set in several countries, especially Japan and countries in the European Union.[4] The World Health Organization proposes a minimum-risk formaldehyde level of 0.08 ppmV in the indoor environment.[5] Thus, the concentration of formaldehyde in the indoor atmosphere should be evaluated very carefully.

No formaldehyde emission test methods fulfill the requirements for an ideal detection technique.[6] The application of several different approaches to formaldehyde emission measurements gives a reasonable amount of information to make conclusions concerning formaldehyde emissions and abatement possibilities.[7] The original photoacoustic (PA) system was designed for instantaneous response, low electrical energy consumption, and high sensitivity.[8–10] To facilitate the identification of formaldehyde without a molecule-specific separation step preceding the PA measurement, and to reduce the interference of water absorption, the IR characteristic region was selected for the utility of this experiment design.

Experimental

Preparation of reference formaldehyde

Formaldehyde levels were measured by the open-cell photoacoustic (PA) and acetylacetone photometric method. The reference concentrations of formaldehyde were various ranges of ppbV~ppmV. The standard formaldehyde solution (1000 mg/l) was manufactured by Absolute Standards, USA. Solutions of formaldehyde were prepared in the concentration range 0–1.5 mg/l (0–2.0 ppmV) and used as reference formaldehyde for both the acetylacetone photometric and photoacoustic methods. The laboratory environment condition was recorded under an ambient temperature of 22° ± 2°C and a relative humidity of 65% ± 5%.

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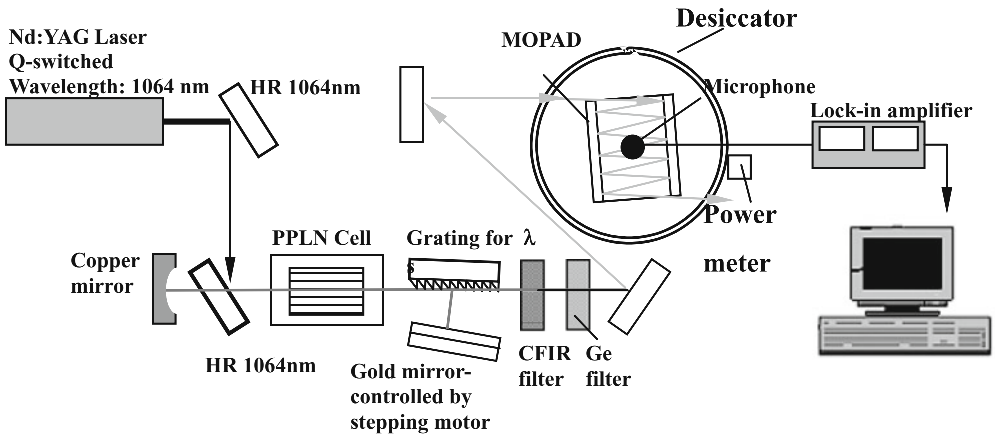

Fig. 1. Schematic of the optical parametric oscillation-multipass acoustically open photoacoustic detector (OPO-MOPAD) measurement setup with a desiccator test cell. *PPLN*, periodically poled lithium niobate crystal; *HR*, highly reflective mirror; *CFIR*, calcium fluoride mirror

Charcoal preparation

In the laboratory, bamboo charcoals were prepared in a stainless steel furnace by CO_2 oxidation and were used to investigate the effect of pore surface chemistry on the adsorption behavior of CO_2-oxidized samples with formaldehyde. The surface area and total pore volume of bamboo was measured by the Brunauer-Emmett-Teller (BET) method (ASAP2020 Micromeritics, USA).[11] Normally this is solved by graphical means by plotting 1/(V[(Po/P)]–1) versus P/Po (where Po is the saturation vapor pressure at the relevant temperature, and P and V are pressure and adsorbed gas quantity). The pore size distribution of the samples was calculated by employing the regularization method according to the density functional theory.[12]

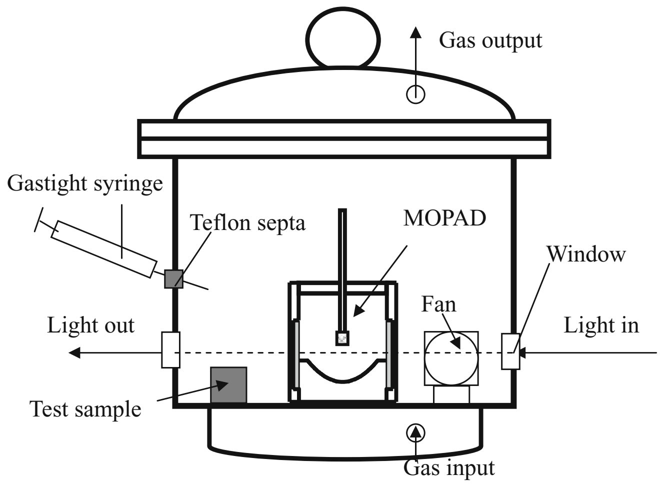

Fig. 2. Schematic of the desiccator cell with multipass acoustically open photoacoustic detector (*MOPAD*)

Photoacoustic methods

A schematic of the setup for measurement is shown in Fig. 1. The utility of an optical parametric oscillation-multipass acoustically open photoacoustic detector (OPO-MOPAD) was demonstrated and measured by the absorption spectrum of atmospheric formaldehyde in a desiccator. The laser light source was a commercial Nd:YAG laser with a multikilohertz tunable optical parametric oscillation source which was a periodically poled lithium niobate crystal (PPLN).[13–15] The laser light was operated at 2800 to 2808 cm^{-1} with a maximum input power of ~105 mW and the time constant of the lock-in amplifier was 300 ms for the spectra measurements.

The desiccator test chamber

The desiccator utilized inert materials/glass as the test chamber with a volume of 10 l. A multipass acoustically open photoacoustic detector (MOPAD) was located at the center of the desiccator on an aluminum sheet as depicted in Fig. 2. Pure nitrogen was used to clean the desiccator before each measurement.

The formaldehyde sample was placed in a gastight syringe with a volume of 10 μl and injected into the desiccator. The acetylacetone photometric method was used as the comparison test. Photometric determination of formaldehyde dissolved in water makes use of the color development when formaldehyde reacts with acetylacetone solution in an acidic medium. The absorbance of the colored solution was read in a spectrophotometer at 415 nm and the reading was proportional to the quantity of formaldehyde in the solution. The concentration was obtained by the absorption spectra at this wavelength and calculated using the Beer-Lambert law.[16]

Adsorption of formaldehyde solution

Bamboo charcoal samples (1 g) were placed in the desiccator to adsorb the vapor from the formaldehyde solution. A 1.5-ppmV standard formaldehyde solution was injected into the desiccator by a gas-tight 10-μl syringe. The mixing fan ran during the experiments to maintain completely mixed conditions. The level of formaldehyde was measured every minute by using the photoacoustic method in the desiccator.

Results and discussion

The PA method was applied to detect formaldehyde concentrations with satisfactory results. The calibration spectra were obtained from published reference libraries such as the high-resolution transmission molecular absorption database (HITRAN).[17,18] There was significant agreement between the measured and calculated spectra in Fig. 3. At 2805 cm^{-1}, water vapor would not affect the detection selectivity so that the PA was able to detect in real time amounts of formaldehyde without water impact in the desiccator. The calibration curve of the PA was obtained at 2805 cm^{-1} by using formaldehyde solutions of various concentrations. Figures 4A and 4B show the formaldehyde calibration curves for both the PA and acetylacetone methods. The results present a linearity of 99% obtained between 0 and 1.5 mg/l (0–2.0 ppmV) and were extrapolated considering a linear dependence on the signal.

The porous structure parameters of the bamboo charcoals prepared at various treatment temperatures are shown in Table 1. The influence of specific surface areas on the adsorption capacity of different charcoal samples allowed us to speculate that the adsorption capacity of the sample increases with increasing surface area.[19] Table 2 shows that both methods obtained adsorption for charcoal samples prepared at 500° and 700°C which were less than the adsorption at 900°C after 24 h. The adsorption capacity of the curve could be described by the exponential curve that could be simply converted into the temporal change of the formaldehyde concentration in the desiccator (Fig. 5). The results reveal that the formaldehyde adsorption capacities shown in tests with 900°C charcoal were better than those with 700°C and 500°C charcoal. As time progressed, the formaldehyde concentration gradually reached equilibrium, in which the measured concentration variation was <10% within 24 h. This may be because the formaldehyde reached adsorption sites through micropores with additional diffusion resistance of charcoal pit size that affected the rate of the controlling step in the charcoal adsorbents.[20] The 900°C samples showed less adsorption than 500°C and 700°C samples in the early stage (from start through the peak) shown in Fig. 6. The adsorption capacity is influenced by the distribution of charcoal pore diameters and hydrophobic/

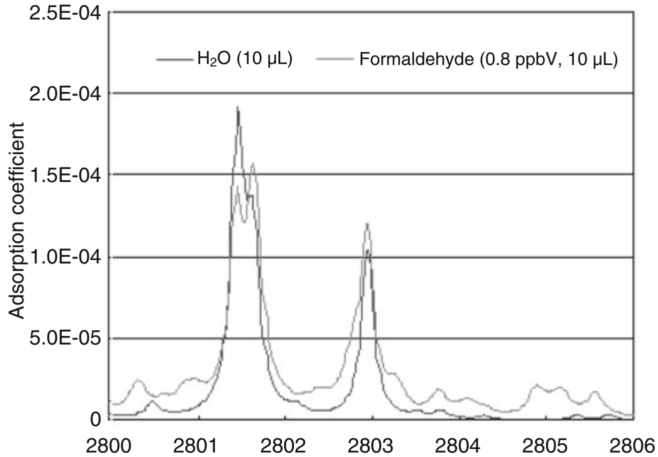

Fig. 3. The photoacoustic spectrum of 10 μl water and aqueous formaldehyde (0.8 ppbV) were calculated using the high-resolution transmission molecular absorption database (HITRAN)

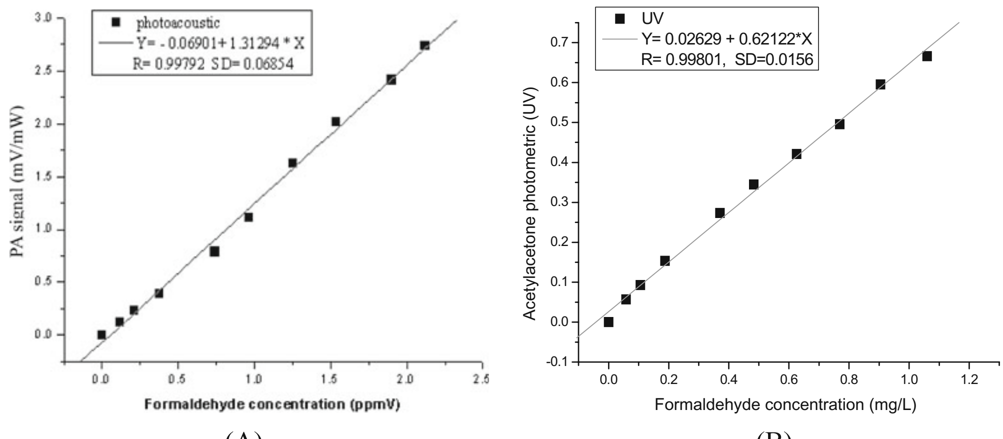

Fig. 4. Calibration curves measured for different formaldehyde concentrations between 0 and 1.5 mg/l (0–2.0 ppmV): **A** photoacoustic (*PA*) and **B** acetylacetone methods

Table 1. The pore properties of bamboo charcoals produced using various carbonization treatments

Specimen	Carbonization Temp (°C)	Pore volume (cm^3/g)			Pore size (nm) Average pore diameter	Surface area BET (m^2/g)
		Macropores	Mesopores	Micropores		
	500	0.0037 ± 0.0011	0.0054 ± 0.0023	0.0023 ± 0.008	10.39 ± 1.79	56.6 ± 17.6
	700	0.0049 ± 0.0006	0.0178 ± 0.0040	0.1240 ± 0.010	3.94 ± 0.17	308.1 ± 13.8
	900	0.0060 ± 0.0036	0.0211 ± 0.0028	0.1300 ± 0.007	4.59 ± 0.33	319.5 ± 20.7

BET, Brunauer-Emmett-Teller method

Table 2. Formaldehyde concentrations in the desiccator and the adsorption capacities for various charcoal specimens after 24 h

Method	Carbonization temperature (°C)		
	500	700	900
Photoacoustic (ppmV)	0.1515 (91.7%)[a]	0.1572 (92.3%)	0.0941 (96.8%)
Acetylacetone[b] (ppmW)	0.80 ± 0.04	0.85 ± 0.05	0.05 ± 0.01

ppmV, parts per million by volume; ppmW, parts per million by weight

[a]The formaldehyde adsorption capacity = $(N_0 - N_{ad}/N_0) \times 100\%$, where N_{ad} is the concentration of formaldehyde molecules after 24 h (ppmV) and N_0 is 1.5 ppmV (level of formaldehyde molecules in the desiccator)

[b]The concentration of these solutions was determined by the acetylacetone photometric method. The concentration was obtained by the absorption spectra at the wavelength 415 nm and calculated using the Beer-Lambert law, $\log \frac{I_0}{I} = \alpha c L$, where I_0 is the reference intensity, I is the measuring intensity, α is the absorption coefficient, c is the concentration, and L is the thickness of the solution

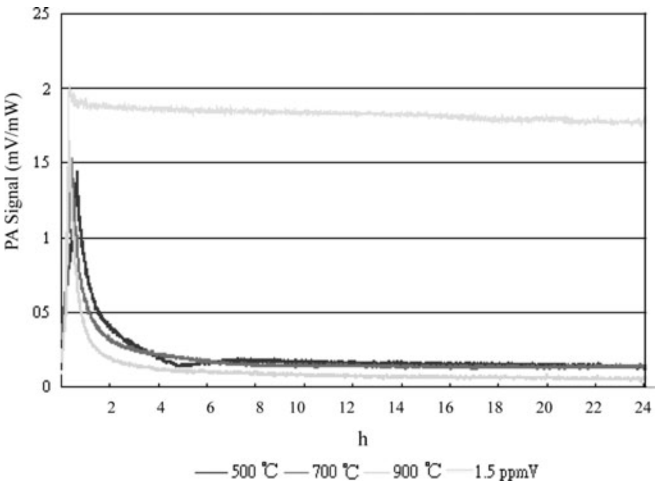

Fig. 5. Qualitative concentration profile of formaldehyde adsorbed onto charcoals prepared at various carbonization temperatures

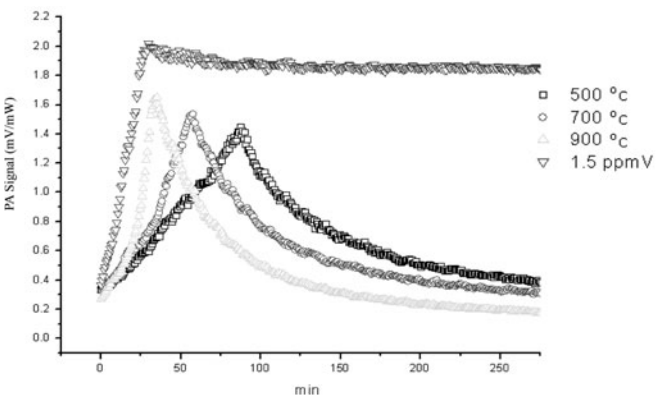

Fig. 6. Formaldehyde adsorption in the desiccator under the laboratory ambient atmosphere (22°C, relative humidity 65%) by charcoals prepared at various carbonization temperatures

hydrophilic surfaces.[21] Formaldehyde is a hydrophilic molecule and can be adsorbed on hydrophilic surfaces more easily than on hydrophobic surfaces. Therefore, the adsorption forces of the hydrophobic surface of charcoal are weaker than hydrophilic surface.[22] At a carbonizing temperature of 500°C, the hydrophobic groups C–H and C=C are formed by the thermolysis of cellulose or lignin, which are the main components of bamboo.[23] Therefore, 500°C samples adsorbed formaldehyde gradually in comparison with the others in the early stage. The adsorption capacities toward formaldehyde increased with increasing carbonization temperature.[24] The micropores still play an important role in formaldehyde adsorption. The formaldehyde adsorption of the 900°C samples decreased more rapidly than those of the 500°C and 700°C samples after reaching the peak and maintained the lowest concentration through to the end. The charcoals can avoid exposure to a peak concentration, which will be a worthwhile trade-off for longer exposure at lower concentrations in the desiccator. The 500°C samples could act as low-pass adsorbents providing exactly this type of desirable protection. Adsorption of formaldehyde to charcoal surfaces further lowers the peak concentration and therefore enhances the indoor air quality.

Conclusions

The high sensitivity of photoacoustic detection and the ability to make measurements in real time allow the characterization of materials and the monitoring of trace gases in a realistic environment. We described an apparatus designed to mimic the indoor environment for the real-time selective monitoring of trace amounts of toxic gas that can readily be applied to characterizing materials used in interior building construction. Central to the apparatus is an open photoacoustic detector that has very high sensitivity, is relatively immune to acoustic noise in the surroundings, and does not require the sampling of gases for its measurements. We demonstrated its sensitivity with trace detection of formaldehyde and the use of the apparatus for time-resolved measurement of the gas adsorption in bamboo charcoal. The formaldehyde levels obtained using the photoacoustic method were similar to those obtained using the acetylacetone method, which is the method typically used. With further refinement, the quantitative analysis of formaldehyde adsorption by the photoacoustic method will become more precise and provide a more advanced technique than the currently used methods.

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