Int. J. Environ. Sci. Technol. (2016) 13:1685–1696
DOI 10.1007/s13762-016-1003-6

ORIGINAL PAPER

Development of low-cost passive sampler from cow bone char for sampling of volatile organic compounds

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Received: 8 July 2015 / Revised: 12 February 2016 / Accepted: 13 April 2016 / Published online: 4 May 2016

Abstract A simple and low-cost passive sampler for collection of volatile organic compounds, specifically benzene, toluene, ethylbenzene and xylene (BTEX), from the ambient air has been developed by using cow bone char (CBC) as an adsorbent with desorption by solvent extraction prior to analysis by gas chromatography–mass spectrometry (GC–MS). The laboratory-made CBC was prepared by calcination process in a partially oxidative atmosphere. The developed passive sampler was tested for a suitable amount of CBC used, diffusion tube type and size, and sampling duration, in a closed chamber saturated with each of the BTEX vapors. With the optimum amount of 250 mg CBC packed in a glass bottle (82.6 mm height × 11.1 mm i.d.) and the exposure time of 168 h, detection limits (μg/m^3) for BTEX determination using this developed sampler together with GC–MS were 0.28 (benzene), 0.79 (toluene), 0.58 (ethylbenzene), 0.28 (p-xylene) and 0.54 (o-xylene). The proposed method was applied to sampling BTEX from selected petrol stations, traffic congestion areas and a rural area in Chiang Mai Province, Thailand. The BTEX concentrations detected were well correlated with their sources as they were the highest at the petrol station sites, lower at the traffic congestion area sites and the lowest at the rural area site. The laboratory-made passive sampler containing CBC has thus opened up a possibility of having a simple and effective device for sampling of BTEX in the ambient air.

Keywords Benzene · Ethylbenzene · Gas chromatography–mass spectrometry · Toluene · Xylene

Introduction

Volatile organic compounds (VOCs) are hazardous compounds, which are contributed to various reactions in the atmosphere, i.e., the formation of photochemical oxidants (Haagen-Smit and Fox 1956; Atkinson 1997; Atkinson et al. 1999; Hoque et al. 2008) associated with smog, secondary organic fine particles and ground-level ozone (Tolnai et al. 2000; Kim 2002; Truc and Oanh 2007). A group of compounds including benzene, toluene, ethylbenzene and xylenes (BTEX) belong to are a particular group of VOCs. They are mainly emitted from road traffic in urban areas, and they could be found up to 60 % of non-methane VOCs (Lee et al. 2002; Parra et al. 2006) and 35 % of total VOCs (Perry and Gee 1995; Fernández-Villarrenaga et al. 2004). Vehicle exhaust is well known to be the main VOCs source in the atmosphere (Fujita et al. 1994; Thijesse et al. 1999; Na 2006; Hoque et al. 2008), especially the emission of BTEX which are probably the most serious effects on air quality (Laowagul et al. 2008). Despite their very low (ppb-ppt) concentrations, BTEX can affect both short and long terms to human health. Benzene, in particular, is classified as a human carcinogen compound group A (USEPA 2012) and a probable human carcinogens class 1 (IARC 2012).

Generally for VOCs adsorption, solid sorbents are often combined with either passive or active samplers. However,

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passive samplers are widely used due to their simple construction, low cost, no electricity requirement (energy saving) and acceptable accuracy (Zabiegała et al. 1999).

There are various types of solid sorbents used for VOCs adsorption such as activated carbon (AC) (Odabasi et al. 2005; Khoder 2007), Anasorb 747 (Seethapathy and Górecki 2010, 2011), Tenax TA (Parra et al. 2008; Hsu and Huang 2009) and Chromosorb106 (Suwanttiga and Limpaseni 2005; Pekey and Yilmaz 2011). These commercial solid sorbents are quite expensive. Therefore, various types of adsorbents for BTX have been introduced; these include semipermeable membrane (Esteve-Turrillas et al. 2007), solid phase membrane (SPM) (Esteve-Turrillas et al. 2009), Tenax TA contained in a screw cap glass bottle for BTX (Thammakhet et al. 2006) and Anasorb 747® contained in a permeation passive air sampler for VOCs (Seethapathy and Górecki 2010, 2011).

Bone char is a low-cost adsorbent as it can be obtained directly from carbonization of animal bones. The bone can be collected from various sources such as slaughterhouses, ranchlands, restaurants and markets in general (Akinyi 2013). Kawasaki et al. (2009) reported fluoride adsorption capacities of bone chars produced from different animals, including cattle, pigs, chickens and fishes. They revealed that yielding of bone char from cattle was the highest and it provided higher capacity for fluoride adsorption than bone char from pigs, chickens and fishes. It has been examined as an effective adsorbent for elimination of various pollutants, including decolorizing agent for sugar cane (Girgis et al. 1997), defluoridation from water (Leyva-Ramosa et al. 2010), adsorption of dyes (Ip et al. 2010a, b) and removal of heavy metals in wastewater (Choy and McKay 2005). All these applications of bone char have been attributed to its adsorption taking place in the liquid condition. However, the capability of bone char for gas adsorption has hardly been reported in publication. This work was therefore an attempt to extend the use of a suitable type of bone char, utilizing its adsorption capacity in the condition other than liquid, i.e., in ambient air, with an initial goal of BTEX sampling in various sites in Chiang Mai, the largest city in the northern region of Thailand, where air pollution has been a serious problem each year.

This study was conducted with the aim to produce laboratory-made bone char from cow bones available locally and use it as the adsorbent for sampling of BTEX, a particular group of volatile organic compounds, in ambient air from various sources in the city of Chiang Mai, Thailand. The whole experiment was conducted in 2011–2012. The field experiment alone (sampling of BTEX from ambient air) was carried out in the wet season from July 21–27, 2012.

Materials and methods

Chemicals

Preparation of stock standard solutions

Standard solutions of BTEX (benzene, toluene, ethylbenzene, p-xylene and o-xylene), internal standards (1,4-difluorobenzene and 4-bromofluorobenzene) and surrogate standard (toluene-d8) were supplied by Dr. Ehrenstorfer GmbH (Germany). Methanol was purchased from Merck (Germany). Each solution was prepared in methanol to obtain the concentration of 1000 µg/mL as stock solution. In order to limit losses by evaporation and photooxidation, all solutions were stored in the amber glass-stopped bottles in the freezer compartment of a refrigerator.

Preparation of working standard solutions

Working standards of BTEX were routinely prepared by accurate dilution from stock standard solutions. Benzene, toluene-d8 and toluene were prepared in a range of 5.0–60 ng/mL, while ethylbenzene, p-xylene and o-xylene were prepared from 1.0 to 60 ng/mL. A 20 µL of 2 µg/mL of internal standards (1,4-difluorobenzene and 4-bromofluorobenzene) was added in all series of solutions.

Materials

Preparation of laboratory-made cow bone char (LM-CBC)

LM-CBC production Cow bones were crushed to 2–5 mm size and soaked in 5 % of hydrogen peroxide for 24 h to remove fatty acids and dried at 105 °C in an oven overnight. They were calcinated under the control temperature set from 500 to 850 °C in a muffle furnace for 8 h. After that, they were ground into powder and sieved to the 1–2 mm grain size and kept in desiccators at room temperature. The cow bone char powder prepared as such is to be referred to as laboratory-made cow bone char (LM-CBC) (Fig. 1) in this work.

LM-CBC decontamination The LM-CBC powder had to be cleaned up through a heating process before use. Fifty milligrams portion of LM-CBC was used for each of the testing conditions: (a) non-treated CBC, (b) preheating at 110 °C for 12 h, (c) preheating at 150 °C for 3 h, (d) soaking in methanol for 12 h followed by heating at 150 °C, (e) preheating at 180 °C for 3 h. The LM-CBC in each condition was then tested for BTEX contaminants by GC–MS.

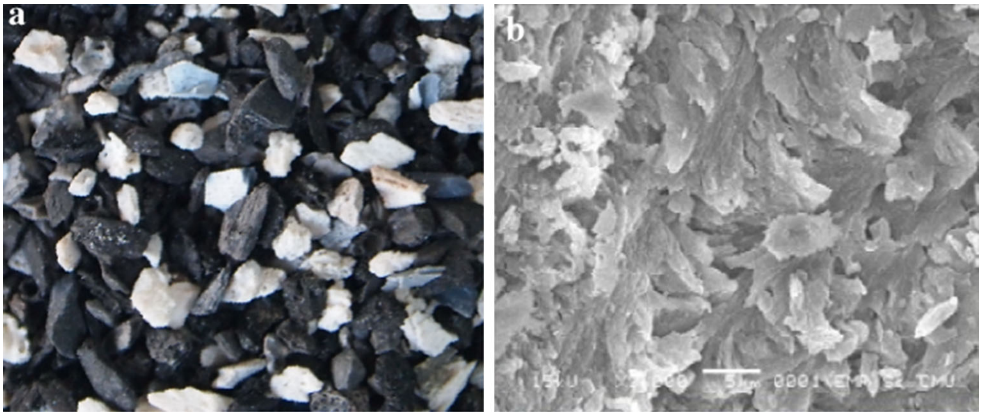

Fig. 1 **a** Image of LM-CBC, **b** scanning electron microscope (SEM) of LM-CBC (30,000X)

Gas chromatographic conditions

Analysis of BTEX was performed using a gas chromatograph (GC-6850, Agilent Technology, USA) combined with a mass selective detector (MSD-5973, Agilent Technology, USA). The injection was done in the splitless mode with HP5-MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness), using ultra-high pure helium at a constant flow rate of 0.80 mL/min. The column temperature program was held at 36 °C for 6 min, increased at 30 °C/min to 120 °C, and held at 120 °C for 5 min. Ionization mode of the mass spectrometer was electron impact (EI) operated at 70 eV. The ion source, quadrupole mass analyzer and GC/MSD interface temperatures were 230, 150 and 280 °C, respectively. A mass scanning ranging from 35 to 500 m/z was used for full scan acquisitions. The selected masses of the analytes (Table 2) were monitored for quantification and confirmation of each compound.

Quality control of BTEX analysis

In order to confirm the reliability of BTEX determination by GC–MS, detection limit, precision and linearity were examined when the optimum conditions of GC–MS were obtained. The instrument detection limits (IDLs) of GC–MS for BTEX analysis were obtained by multiplying the standard deviation (SD) of the ten replications by three of the lowest concentrations of the working solutions. The method detection limits (MDLs) were calculated from field blanks (the same kind of sampler that used for sampling, but the bottle was capped all the time during exposure). The values of MDLs were then calculated by multiplying SD values ($n = 18$) by 3. The precision of this method was calculated from repeatability and reproducibility which was determined by seven repetitive measurements of 15 ng/mL mixed standard solutions and presented in terms of percent relative standard deviation (% RSD). The linearity was examined by analysis of solution concentrations from 5 to 2500 ng/mL (benzene, toluene-d8 and toluene) and 1–2500 ng/mL (ethylbenzene, p-xylene and o-xylene), which were the ranges expected to be found in the ambient air.

Selection of organic solvent for BTEX extraction

Generally, carbon disulfide (CS_2) was commonly used as an extraction solvent for VOCs adsorbed by solid sorbents from solid sorbents (Odabasi et al. 2005; Khoder 2007). However, CS_2 is highly toxic, flammable and easy to explode (ASTDR 2011). Therefore, methanol was selected as an alternative solvent for extraction of BTEX adsorbed on the surface of the LM-CBC. Its efficiency was investigated by spiking method. Low, medium and high amounts (6, 29 and 52 ng) of mixed BTEX standards and toluene-d8 standard were spiked on 50 mg of the conditioned LM-CBC ($n = 5$ for each batch) and incubated at 20–25 °C for 24 h. Before analysis, each vial was accurately weighed, and weighed again after adding 1.0 mL of methanol which was used as extraction solvent (ASTM 1988). After that, the solutions were extracted using ultrasonicator for 15 min. Then, each extracted solution was added with 40 μL of 1 μg/mL internal standards (1,4-difluorobenzene and 4-bromofluorobenzene), adjusted to 1 mL volume and filtered by 0.45 μm of nylon syringe filter. The extracted solutions were kept in the refrigerator prior to analysis by GC–MS.

Fabrication of laboratory-made BTEX passive sampler

To prepare a laboratory-made BTEX passive sampler (LM-BTEX-PS), a screw cap glass bottle was packed with an appropriate amount of activated LM-CBC. The bottle was then closed with a cap and wrapped with parafilm, and stored in a desiccator at room temperature prior to a sampling. At the sampling site, one set of passive sampler containing five opened and three closed bottles was packed in the protective shelter and then hung at a height between 1.5 and 2.0 m. After the end of the sampling period, it was recapped tightly with a lid and parafilm. It was placed in double layers of the amber ziplock plastic bags for protection from photooxidation before being stored in the refrigerator until analysis.

Method validations

Adsorption capacity of LM-CBC

In order to obtain an appropriate amount of LM-CBC used in the sampler, five replicates of different amounts of LM-CBC (50, 150 and 250 mg) were tested. A 50 μL of 20 μg/mL of mixed BTEX and toluene-d8 standards were spiked into a petri dish and placed inside a testing chamber. Then, one glass bottle (0.52 cm i.d. × 3.21 cm height) containing LM-CBC was placed in the testing chamber. The system was settled at room temperature (about 25–30 °C) for 24 h. After that, extraction was carried out and the extracted solution was analyzed for BTEX by GC–MS.

Testing of various sizes of glass bottles for passive sampler

Different sizes of screw cap glass bottles including type I (32.4 mm height × 11.1 mm i.d.), type II (41.7 mm height × 10.0 mm i.d.), type III (62.8 mm height × 10.5 mm i.d.) and type IV (82.6 mm height × 11.1 mm i.d.) were tested. Each bottle size was packed with 250 mg of activated LM-CBC. One set of an experiment contained three sampling bottles and one blank bottle. Each of them was put in the testing chamber (2.4 L). Based on the report from the Pollution Control Department (PCD) of Thailand in 2008 (PCD 2009), the highest concentration of BTEX was about 50 μg/m^3 at Chiang Mai station. However, concentrations of BTEX from pollution sources such as petrol stations have not been reported. It could be expected that such sources would have higher concentrations of BTEX than the traffic congestion areas. Therefore, two times of the maximum reported concentration were used in this experiment. The 100 μg/m^3 of mixed BTEX and toluene-d8 standard solution was prepared and diluted. Then, a solution (100 μL of 2.4 μg/mL) was spiked into a vial inside the chamber and the chamber lid was immediately closed and wrapped with silicone glue. The system was set up at controlled temperature (20–25 °C) for 24 h. After that, extraction was carried out and the extracted solution was analyzed for BTEX by GC–MS.

Influence of temperature on BTEX adsorption

One set of the sampler contained three sampling bottles and one blank bottle. Four sets of LM-BTEX-PS were prepared by using two sizes of sampling bottles (type I: 32.4 mm height × 11.1 mm i.d. and type II: 41.7 mm height × 10.0 mm i.d.). Then, they were simultaneously exposed for 24 h in the testing chambers containing 100 μg/m^3 of mixed BTEX and toluene-d8 standards and kept at the room temperatures (27–32 °C) and at the controlled temperatures (20–25 °C) in the air-conditioning room for comparison. After that, they were extracted and analyzed by GC–MS.

Sampling duration of LM-BTEX-PS for BTEX adsorption

The sampling duration was tested to find out the capacity of the LM-CBC for adsorption of BTEX from air. Thirteen sets of LM-BTEX-PS were exposed in the chamber containing 100 μg/m^3 of mixed BTEX and toluene-d8 standards. The sampling durations were 8, 16, 24, 32, 40, 48, 96, 120, 168, 336, 504, 672 and 840 h. This experiment was set up at room temperature in accordance with a real environment.

Use of LM-BTEX-PS in the real environment

One set of the LM-BTEX-PS (five sampling tubes and three blank tubes fixed in a plastic shelter) was used for sampling of BTEX in ambient air at each sampling site. There were five sampling sites including two traffic congestion areas, two petrol stations and one background site. The samplers were hung at the sampling sites at a height between 1.5 and 2.0 m above ground level. The sampling was carried out from July 21–27, 2012 (7 days). The air temperature during the sampling was in the range 24.0–28.2 °C. After that, they were kept in cooling boxes and transferred back to the laboratory for further analysis.

Results and discussion

Physical properties of LM-CBC

The LM-CBC was produced by calcination process using partially oxidative atmosphere by controlling the amount of fuel (liquid petroleum gas) and oxidant (air) ratio to avoid any oxidation on the bone char surface. Due to quite a large-scale production, the calcination temperatures were varied from 500 to 850 °C. In each batch, various colors of CBC (black, gray and white) were observed, but black color was a major appearance. Color changing is generally related to the thermal degradation of the organic matrix (i.e., collagen, protein and fat tissue) of bone char. White color indicates the complete degradation of organic matter, whereas dark color indicates the remaining of organic compounds (Ooi et al. 2007). However, the specific surface area is decreased at high-temperature treatment due to an increase in hydroxyapatite crystallite size and loss of elemental carbon (Rojas-Mayorga et al. 2014). According to the literature (Buxbsum 1998; Rojas-Mayorga et al. 2014), when the specific surface area (S_{BET}) is increased, the chance of adsorbent–adsorbate interaction is also increasing. This is a positive effect to adsorption process. Many researchers have tried to synthesize bone char under a hypothesis that the experimental parameter of heat treatment plays a significant influence on adsorption property. However, most of the heat treatment optimum condition was that low temperature and black bone char represented the best adsorption property (Mwaniki 1992). The bone char physical properties, i.e., specific surface areas and pore volumes, from various research works are shown in Table 1. The physical properties of LM-CBC from this study could be estimated based on the temperature used in the heat treatment and color appearance.

Removal of contaminants from LM-CBC

Use of the LM-CBC for BTEX sorbent in the air passive sampler was started from the cleanup step of the CBC by various conditions. Bone char is produced by carbonization of cow bone, and it contains about 10 % carbon and 90 % hydroxyapatite. Its application as air pollutant adsorbent was reported only for formaldehyde but without decontamination. Kaseva (2006) varied the temperature (100–800 °C) for bone char regeneration by using the heating method. The recommended temperature limits used for the commercial solid sorbents are 190 °C (XAD2), 250 °C (Anasorb 727), 350 °C (Anasorb 727 and Tenax TA and 250–275 °C (Chromosorb). In this work, low temperatures were used because the reaction between BTEX compounds and bone char is physical adsorption and their interaction is quite weak. In addition, using low temperatures could protect changes of bone char characteristic and save cost from using high energy. Temperatures applied for decontamination were 110, 150 and 180 °C. After the treatment, low concentration of BTEX (71 ng/g)

Table 1 Summary of some physical properties of bone char from some research studies

Raw material	Thermal treatment		Textural parameters of bone char			Color	Application	References
	Temperature (°C)	Condition	S_{BET} (m^2/g)	V_{Total} (cm^3/g)	Pore size (nm)			
Bovine bone	350	Heat treatment	–	–	–	Black	Removal of fluoride in water	Mwaniki (1992)
	450					Gray		
	600					White		
Cow femur bone	400	Annealing under ambient condition	85	–	–	–	Removal of cobalt in water	Dimović et al. (2009)
	600		71.7	–	–	–		
	800		7	–	–	–		
	1000		2.4	–	–	–		
Cattle and sheep bone	450	Pyrolysis in a rectangular furnace	105.24	0.367	13.95	–	Removal of formaldehyde in air	Rezaee et al. (2013)
Cow femur bone	650	Pyrolysis in an inert atmosphere (N_2 400 ml/min)	118	0.24	8.13	–	Removal of fluoride in water	Rojas-Mayorga et al. (2013)
	700		110	0.233	8.47	–		
	800		96	0.224	9.33	–		
Cow femur bone	650	Carbonization using a partially oxidative atmosphere (CO_2 400 ml/min)	62	0.2	–	Black	Removal of fluoride in water	Rojas-Mayorga et al. (2014)
	700		69	0.23	–	Black		
	800		9	0.16	–	Gray		
	900		4	0.04	–	White		
	1000		2	0.02	–	White		
Cow bone (laboratory-made)	500–850	Calcination using a partially oxidative atmosphere	–	–	–	Mostly black (a bit of gray and white mixture)	Used as absorbent for sampling of BTEX from ambient air	This study

S_{BET} specific surface areas, V_{Total} total pore volume was still detected as contaminant in the LM-CBC. Therefore, the detected value was subtracted from the BTEX concentrations detected in the samples in every routine experiment.

Analytical feature of the method

Chromatogram of BTEX and toluene-d8 analyzed by GC–MS in this experiment is shown in Fig. 2. All peaks were completely separated from each other, and the analysis time was about 9 min. The detection limit, precision and linearity of the GC–MS for BTEX analysis are shown in Table 2.

The values of the instrument detection limits (IDLs) of GC–MS for BTEX analysis ranged from 0.38 to 1.44 ng/mL, while the values of the method detection limits (MDLs) of the laboratory-made BTEX passive sampler (LM-BTEX-PS) ranged from 0.28 to 0.79 μg/m^3.

The precision of the analysis of BTEX and toluene-d8 was assessed from repeatability and reproducibility. Relatively high precision was obtained (1.8–7.3 %RSD for repeatability and 3.1–13 %RSD for reproducibility).

GC–MS presented excellent linearity for all of the analytes (Table 2) with the coefficient of determination higher than 0.995 for BTEX in the concentration range 1–2500 ng/mL.

Efficiency of methanol for BTEX extraction

Use of methanol for BTEX extraction provided relatively good percent recoveries for all ranges of the spiked concentrations (low, medium and high). Their recoveries were 71–86 % (benzene), 74–89 % (toluene-d8), 64–70 % (toluene), 84–110 % (ethylbenzene), 73–92 % (p-xylene) and 82–104 % (o-xylene). These results indicated that intermolecular force between LM-CBC with BTEX and toluene-d8 was quite weak (van der Waal force). It can be revealed that methanol is an optional solvent, which provided high efficiency of BTEX extraction.

Validation of LM-BTEX-PS

Adsorption efficiency of LM-CBC

The amount of LM-CBC packed in the diffusion bottle should be suitable with the quantity of BTEX in the ambient air. Figure 3 shows the concentration of BTEX adsorbed on different LM-CBC in terms of percent recoveries.

It was found that BTEX concentrations found in each condition with various amounts of LM-CBC ($n = 5$) packed were not significantly different ($p > 0.05$). Thus, a 50 mg quantity of LM-CBC was selected for BTEX adsorption from ambient air in this experiment. However, recoveries of the BTEX were still low, possibly due to inappropriate size of diffusion bottles, low amount of LM-CBC used and too short sampling time. To confirm the adsorption efficiency based on the availability of diffusion bottle and Fick's law (Górecki and Namiesnik 2002; Seethapathy et al. 2008), size of diffusion bottle was optimized for better recoveries of the analytes. The amount of LM-CBC used was also increased from 50 to 250 mg.

Comparison of diffusion bottles

Four sizes of diffusion bottles (types I, II, III and IV) were examined ($n = 3$) to be used as a passive sampler for BTEX. In each bottle, 250 mg of LM-CBC was packed. It was found that the recoveries of all analytes sampling by the diffusion bottle types III and IV were obviously higher than types I and II (Fig. 4). Between types III and IV, it was found that recoveries obtained from type IV were slightly better than type III. Type IV was therefore chosen for the further experiment. However, it was found that percent recoveries of benzene (15.4 %), toluene-d8 (32.0 %),

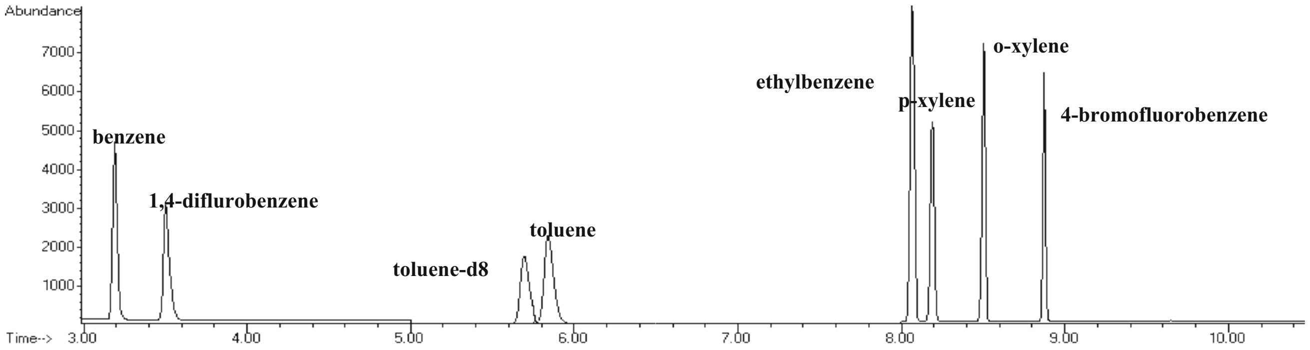

Fig. 2 Chromatogram of 1 μg/mL BTEX standards and toluene-d8 standard in SIM mode

Table 2 Analytical characteristics of BTEX analyzed by GC–MS

Compound	Retention time (min)	Confirm ion (m/z)	Linearity	R^2	IDL (ng/mL)	MDL (μg/m^3)	Repeatability % RSD	Reproducibility % RSD
Benzene	3.156	78	5–2500	0.9984	0.82	0.28	3.7	6.9
1,4-difluorobenzene*	3.470	114	–	–	–	–	–	–
Toluene-d8**	5.707	98	5–2500	1.0000	1.05	–[a]	4.0	12
Toluene	5.854	91	5–2500	0.9996	1.44	0.79	7.3	13
Ethylbenzene	8.067	91,106	1–2500	0.9993	0.46	0.58	1.8	3.1
p-Xylene	8.189	91,106	1–2500	0.9998	0.49	0.28	2.4	5.8
o-Xylene	8.506	91,106	1–2500	0.9995	0.38	0.54	3.5	8.7
4-Bromofluorobenzene*	8.875	95,174	–	–	–	–	–	–

[a] It is not found in the real sample

* Internal standard and ** surrogated standard

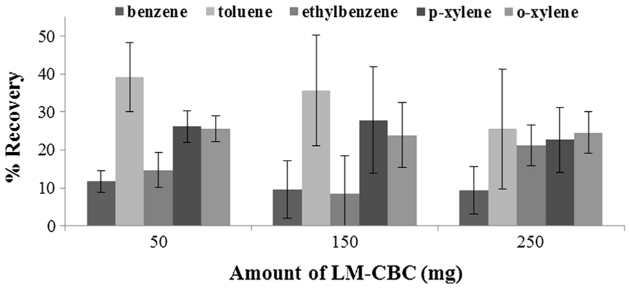

Fig. 3 Percent recoveries of BTEX from different amounts of LM-CBC used

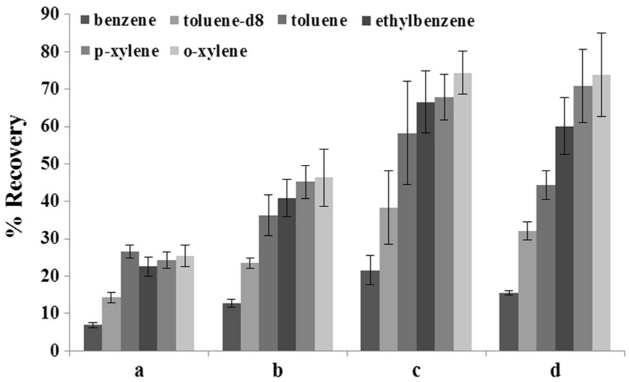

Fig. 4 Percent recoveries of BTEX on the different type of diffusion tubes: **a** type I, **b** type II, **c** type III and **d** type IV

toluene (44.3 %), ethylbenzene (60.1 %) were lower than 70 %. The results were the same for all testing conditions. It is probably because the adsorption process is based on the nature of the adsorbent (LM-CBC) and adsorbate (BTEX and toluene-d8). The chemical properties of adsorbate, i.e., polarity, molecular weight, boiling point, vapor pressure and log K_{OW} (Table 3), are elemental factors in the interaction between the different BTEX and toluene-d8 for the active sites on the LM-CBC. On the other hand, the adsorption can rely on the number and type of substitute group on benzene ring. They play an important role with steric hindered groups (i.e., –CH_3 or –CH_2CH_3) which contribute to increase the distance between the plane of the ring and surface of the adsorbent (Daifullah and Girgis 2003) and also protect different type of compounds to interact with active sites within the deepest of adsorbent (micropore). Therefore, the compounds have more chance to be adsorbed on the active site by non-specific attraction (van der Waal force). The CBC contains about 10 % elementary carbon and 90 % hydroxyapatite (Medellin-Castillo et al. 2014). The inorganic part presents the ability to adsorb ions, while the organic part presents the ability to nonpolar organic compounds (Rojas-Mayorga et al. 2014). The activated carbon has been reported to possess high affinity to adsorb BTEX compounds (Daifullah and Girgis 2003). Relatively high molecular compounds (i.e., BTEX and toluene-d8) could thus pass easily through the pore and physically adsorb on the active site of LM-CBC.

Temperature dependency of BTEX adsorption

Percent recoveries of all compounds obtained from the controlled temperature (20–25 °C) were 2–13 times higher than those in the un-controlled temperature (27–32 °C) for both two types of diffusion bottles (Fig. 5). Increase in

Table 3 Selected physical and chemical properties associated with BTEX and toluene-d8 *Sources* Esteve-Turrillas et al. (2007), Rowe et al. (2005)

Compound	Log K_{OW}	Boiling point (°C)	Vapor pressure (torr at 25 °C)	Molecular weight (g/mol)	Diffusion coefficient in air (m^2/s)	Henry's law constant (kPa m^3/mol)
Benzene	2.15	80.1	100.84	78.11	0.93	0.55
Toluene	2.69	110.6	28.47	92.14	0.84	0.67
Ethylbenzene	3.15	136.3	9.51	106.17	0.75	0.80
m-Xylene	3.20	139.3	8.29	106.17	0.68	0.50–0.78
p-Xylene	3.15	137.5	8.75	106.17	0.67	0.51–0.88
o-Xylene	2.77	144.0	6.62	106.17	0.73	0.50
Toluene-d8*	2.73	110.0	27.70	100.18	–	0.67

* http://www.guidechem.com/reference/dic-9768.html

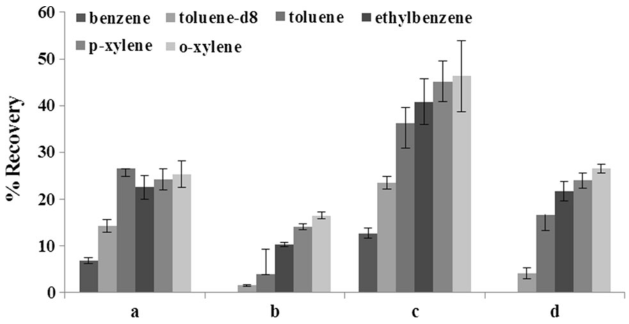

Fig. 5 Percent recoveries of BTEX from different conditions: **a** type I controlled temperature, **b** type I ambient temperature, **c** type II controlled temperature, **d** type II ambient temperature

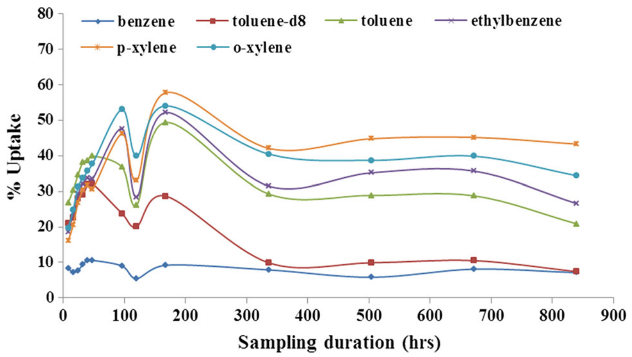

Fig. 6 Capacities of LM-CBC on BTEX and toluene-d8 adsorption

temperature can basically be explained by the hypothesis that the process of gas–solid adsorption is a physical adsorption and an exothermic reaction (Attard and Barnes 2008). The BTEX and toluene-d8 molecules are attracted with weak intermolecular force (van der Waals force) toward the LM-CBC, and they have low enthalpy value (less than 30 kJ/mol) (Kolasinski 2008). Reversing the adsorption process (desorption process) without high activation energy could be facile in this case, and an exothermic process could occur when the temperature was increased. The system was adjusted to remove the amount of heat in the system for restoring the heat of reaction by presenting the endothermic reaction which is reversely an exothermic reaction according to the Le Chatelier's principle. Therefore, the amount of LM-CBC combined with BTEX compounds was reduced.

$$M_{(g)} + S_{(\text{surface site})} \underset{k_d}{\overset{K_a}{\rightleftarrows}} M{-}S_{(\text{Associative adsorption})}$$

where $M_{(g)}$, $S_{(\text{surface site})}$, $M{-}S_{(\text{Associative adsorption})}$, k_a and k_d are molecule of gas, solid sorbent, molecule of gaseous combined with solid sorbent, rate constants for the adsorption and desorption, respectively (Attard and Barnes 2008).

Moreover, increasing temperature has influenced the diffusion coefficient of a compound in the air (D) and pressure (P) (Pennequin-Cardinal et al. 2005) as follows:

$$D\alpha\frac{T^{\frac{3}{2}}}{p}$$

When the temperature rises up for 1 °C, the diffusion rate of each compound is slightly increased about 0.5 %. Therefore, BTEX and toluene-d8, which are normally present in a gaseous phase at room temperature, preferred to distribute in the air more than being adsorbed on the adsorbent.

Influence of sampling duration on the operation of LM-BTEX-PS

Sampling duration was tested in order to obtain the maximum adsorption of BTEX compound by GC–MS. The results in Fig. 6 showed that all of analytes (toluene-d8, toluene, ethylbenzene, p-xylene and

Table 4 Mean concentrations (SD) of BTEX obtained from different sampling sites by LM-BTEX-PS

Compound	Concentration (μg/m^3)				
	Benzene	Toluene	Ethylbenzene	p-Xylene	o-Xylene
Petrol station 1 ($n = 5$)	0.80 (0.15)	9.33 (0.68)	1.00 (0.22)	10.7 (0.74)	4.21 (0.40)
Petrol station 2 ($n = 5$)	1.97 (2.09)	5.51 (0.47)	0.68 (0.14)	7.22 (0.60)	2.75 (0.28)
Traffic congestion 1 ($n = 5$)	0.94 (0.56)	0.86 (0.13)	N.D.	0.94 (0.29)	0.44 (0.09)
Traffic congestion 2 ($n = 5$)	1.04(0.74)	N.D.	N.D.	N.D.	N.D.
Background site ($n = 5$)	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. not detected

o-xylene) were adsorbed rapidly within 72 h, which indicated high adsorption rates of the LM-CBC for BTEX in this period. The maximum adsorption was obtained at 168 h, where adsorption capacity of the LM-CBC was reached. After that, the uptake rate was reduced. The uptake rate of benzene by the LM-CBC was low, which is probably because it has high vapor pressure and low log K_{OW} (Table 3) which indicated that it prefers to distribute in the gaseous phase more than being adsorbed on LM-CBC. The optimum sampling duration in this work was 168 h as the highest amounts of BTEX were obtained from this sampling duration.

Use of the developed passive samplers for real sampling

Five selected sampling sites in Chiang Mai Province, Thailand, were two petrol stations, two traffic congestion areas, which are expected to be major BTEX emission sources, and one background site in the rural area. One set of the LM-CBC-PS was set up at each sampling site. The BTEX concentrations (Table 4) detected at both petrol stations in descending order were p-xylene > toluene > o-xylene > ethylbenzene > benzene (except at the petrol station 2, where concentration of benzene was slightly higher than ethylbenzene). The difference in order might be due to type and quantity of fuel sale in each petrol station. The concentrations of benzene, toluene, ethylbenzene, p-xylene and o-xylene detected at the petrol station 1 were 0.80, 9.33, 1.00, 10.7 and 4.21 μg/m^3, whereas they were 1.97, 5.51, 0.68, 7.22 and 2.75 μg/m^3 at petrol station 2. The concentrations were significantly different between the petrol stations ($p > 0.05$), which was due to different fuel loads at the two petrol stations. The petrol station 1 was reported to have a higher fuel load than the petrol station 2 (Sopajaree et al. 2011); therefore, the BTEX values (except benzene) measured at both stations were well reflected their fuel loads.

In the traffic congestion area 1, the compound concentrations in descending order were benzene ~ p-xylene (0.94 μg/m^3) > toluene (0.86 μg/m^3) > o-xylene (0.44 μg/m^3), whereas only benzene (1.04 μg/m^3) was detected in the traffic congestion area 2. Regarding the above air pollutants detected in the traffic congestion areas of Chiang Mai, it is worth discussing this study in comparison with the earlier work conducted by the Pollution Control Department (PCD) of Thailand, which collected samples in 2008 at the air quality monitoring station (about 2 km from the study sites in this work). The air sampling had been done using a canister for 24 h, once a month for a whole year and transported for analysis by GC–MS in Bangkok. The reported annual concentrations (min–max) were 1.3–6.6 μg/m^3 (benzene), 8.1–46 μg/m^3 (toluene), 0.58–11.0 μg/m^3 (ethylbenzene), 0.47–0.53 μg/m^3 (p-xylene) and 0.67–5.9 μg/m^3 (o-xylene) (PCD 2009). In this study, concentrations of BTEX compounds were obviously lower than those reported by the PCD. Such discrepancies were possibly attributed by meteorological factors during the sampling period (July 21–27, 2012), when it rained almost every day (0.6–42.2 mm) with 75–95 % relative humidity and 24.0–28.2 °C temperature (Thailand Meteorological Department 2012). These factors could reduce air pollutant levels by the washout effect.

Concentrations of BTEX at the traffic congestion area 2 (23,697 vehicles/day) were higher than those at the area 1 (34,265 vehicles/day). The BTEX concentrations were well related to the traffic volume recorded. None of the BTEX was detected at the background site. It can be concluded that the LM-CBC passive sampler performed well in collecting volatile organic compounds from ambient air.

Based on the results, LM-BTEX-PS can be used for sampling of BTEX from ambient air, in which the LM-CBC was used as solid sorbent. The BTEX concentrations in this work were higher in petrol stations than in traffic congestion areas. No similar pattern of BTEX was found between three groups of sampling sites. These could be described on the association of type of fuel, age and speed of vehicle, design of engine, fuel control, combustion condition, driving mode, refueling time and evaporation process (Brocco et al. 1997; Na et al. 2004) as well as the basis of meteorological conditions, including temperature and wind velocity (Esteve-Turrillas et al. 2007; Seethapathy et al. 2008).

Conclusion

The combined method of using LM-BTEX passive sampler, solvent extraction and analysis by GC–MS can be effectively used for determination of BTEX in ambient air. The results obtained from various sampling sites including the petrol stations, traffic congestion areas and background site were clearly classified. This sampling method was simple, easy to use and effective. Therefore, the cost of BTEX determination for air quality assessment can be reduced through the cost of the sampler. The LM-BTEX-PS developed in this study to be used as an air passive sampler although yielded low recoveries of BTEX adsorption on LM-CBC, the study as a whole could still be mentioned as a pioneering work with regard to the use of CBC for air pollution monitoring purposes. Future work in line with this study should further modify the active sites of CBC for specific adsorption of BTEX in order to improve sampling efficiency.

Acknowledgments Financial support from the Center of Excellence for Innovation in Chemistry (PERCH-CIC) and Graduate School of Chiang Mai University is gratefully acknowledged.

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