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Determination of volatile organic compounds in child care centers by thermal desorption gas chromatography-mass spectrometry†

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Children are among the most vulnerable to certain air pollutants, such as volatile organic compounds. Analysis of indoor air has been analytically challenging and costly. The objectives of this study were to (1) develop and validate a sensitive analytical method for assessing the exposure of children to volatile organic compounds at child care centers and (2) characterize the indoor concentrations of target volatile organic compounds in classrooms at child care centers. The volatile organic compounds were sampled by using thermal desorption samplers and the concentrations of the volatile organic compounds were determined by a thermal desorption gas chromatography-mass spectrometry method. Among the 73 target indoor volatile organic compounds, 47 were identified and quantified in the air samples collected from the selected child care center. The limits of detection and limits of quantitation ranged from 0.001 to 0.123 μg m^{-3}, and 0.002 to 0.406 μg m^{-3}, respectively. The correlation coefficients (R^2) of the calibration were between 0.982 and 0.999. The mean recoveries of the analytes ranged from 87% to 112%. The precision expressed as the coefficient of variation was between 0.6% and 16.2%. The volatile organic compounds identified in our pilot study include a wide range of potential toxic chemicals and endocrine disruptors, such as the ingredients in dry cleaning agents (*e.g.*, tetrachloroethylene), surfactants (*e.g.*, butoxyethanol), and personal care products (*e.g.*, homosalate). Due to the portability, affordability, and flexibility, the developed sampling and analytical method has several advantages over conventional techniques for large-scale multi-position air quality monitoring studies at child care centers.

Introduction

Children spend as many as ten hours per day and five days per week in child care and preschool centers. Recent studies reported children's potential exposure to harmful volatile organic compounds (VOCs), which could be released by flame retardants, cleaning supplies, personal care products, toys, air fresheners, school supplies, wood preservatives, furniture, and unvented stoves in early childhood education centers and primary schools.[1–5] School maintenance activities, renovations and painting can also contribute to high levels of VOCs.[6–9] Children are particularly susceptible to chemical exposures for several reasons: (1) children breathe more air per unit of body weight compared to adults, (2) children have more direct exposure by direct contact with contaminated surfaces, and (3) children have less developed immunological, physiological, and neurological systems that are sensitive to environmental perturbations with potential for long term negative health impacts.[10]

The major constituents of indoor air VOCs include a wide variety of chemicals such as benzene, toluene, ethylbenzene, and xylenes also known as BTEX, naphthalene, tetrachloroethylene (PERC), chloroform, and formaldehyde.[11,12] These VOCs are known to be environmentally hazardous, human carcinogens, or to have adverse health impacts on endocrine function or deleterious effects on the central nervous system. Exposure to these chemicals has been shown to be associated with reproductive disorders, thyroid effects, autism, depression, obesity, diabetes, hyperactivity disorders and other endocrine-related diseases.[13,14]

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The development of a multi-residue analytical method for a large-scale multi-position air quality monitoring study at child care centers continues to be a challenging scientific endeavor. Several sampling and analytical techniques have been developed for the analysis of indoor VOCs. For example, many sampling techniques including (1) solid-phase micro-extraction (SPME), and use of (2) canisters and (3) Teflon and Tedlar air sampling bags have been developed to collect VOCs for indoor air quality studies.[15–17] Following air sampling, the concentrations of VOCs were determined by using gas chromatography coupled with mass spectrometry, a flame ionization detector, and a thermal conductivity analyzer. Recently, colorimetric sensors[18,19] and molecularly imprinted polymer based[20] and electrochemical sensors[21,22] have been developed for the analysis of VOCs. However, these analytical tools have similar drawbacks and challenges for the analysis of indoor air VOCs such as limited portability, reusability, durability, versatility, and flexibility of the sampling equipment, or low adsorption capacity of the sorbent materials. Therefore, they are not ideal for multi-position air quality monitoring at child care facilities. Thermal desorption (TD) has gained increasingly wide acceptance in air sampling[23–25] by offering an excellent option that is superior to the above extraction techniques. Specifically, it has several advantages over the conventional VOC procedure, such as low cost, an easy regeneration process, high adsorption capacity, high sensitivity, and versatility. Sampling tubes are small, and therefore they can be easily transported, regenerated, stored, and implemented/hidden in the class rooms without attracting the children's attention or triggering their curiosity. The sorbent material can be easily customized for the quantitation of VOCs with a wide range of concentrations, volatility and polarity.[26] Thermal desorption is a process of collection and desorption of analytes from solid sorbents using heat and a flow of inert gas. Analytes are then focused on a cold trap prior to entering the analytical column, resulting in higher responses and narrow, more symmetric peaks. It is more efficient than conventional extraction methods and allows the selective concentration of target analytes, making it ideal for the trace-level analysis of VOCs by gas chromatography-mass spectrometry (GC-MS) across a wide range of applications.[23–25]

Despite the growing recognition of the potential risks to children associated with exposure to VOCs, limited information is available about environmental quality in child care facilities and its impacts on young children's health, learning, and development. The objectives of this study were (1) to develop a sensitive multi-residue analytical method for large-scale, multi-position air quality monitoring studies at child care facilities (i.e., facilities of Head Start programs) and (2) to validate the analytical method at selected child care centers.

Materials and methods

Sample collection

The VOCs were sampled by passing approximately 74 liters of air at a flow rate of 0.18 L min^{-1} through pre-conditioned sampling tubes (70 mm long and 6 mm in outer diameter) containing layers of sorbent material (CDS 20:35 mesh Tenax-TA/Carboxen 1000/Carbosieve). The air pump (SKC Model 222-3, SKC Inc., Pennsylvania, USA) was placed at a location within the child care room which was not covered or obstructed by furniture or teaching supplies. The sampling tube connected to the pump was positioned at 1 meter above the floor (near the heights of children's noses). After six-hour sampling, the tubes were removed from the samplers and sealed in clean glass tubes, and stored at −20 °C until analysis. The analysis of the VOCs was conducted within 7 days.

Thermal desorption and GC-MS analysis

The VOCs were analyzed using a thermal desorption unit (TDU) interfaced with gas chromatography-mass spectrometry. In brief, air sampling tubes were loaded in a CDS Model 7500 Thermal Desorption Autosampler (Oxford, PA) which was followed by a Dynatherm 9300 TDA (Oxford, PA) interfaced with an Agilent 6890N gas chromatograph. The VOCs were thermally desorbed by the TDU at 300 °C for 5 min. Helium was used as a carrier gas at a flow rate of 20 mL min^{-1}. Following the desorption process, the VOCs were concentrated by using a focusing trap packed with a 60:80 mesh Tenax-TA/Carboxen 1000/Carbosieve SIII. The focusing trap was initially set at 45 °C, and the oven temperature was then raised to 300 °C. The analytes were then transferred to an Agilent 6890N gas chromatography system coupled with an Agilent 5973 quadrupole mass spectrometer (GC-MS) through a transfer line set at 225 °C. The VOCs were separated by using a 5% phenyl 95% dimethylarylene siloxane Agilent DB-5MS capillary column (30 m × 0.25 mm I.D.). The GC temperature was initially set at 45 °C for 3 minutes, and then increased to 250 °C at 15 °C min^{-1}, and was held for 10 minutes, using split injection with a split ratio of 5 : 1 and a constant carrier gas flow (He, 1.0 mL min^{-1}). The injector temperature was held at 275 °C, the transfer line between the GC and mass spectrometer was held at 150 °C, and the MS source (quadrupole) was held at 230 °C. The mass spectra of each peak identified in chromatograms were characterized by comparison with the mass spectra of commercially available reference standards and mass spectral libraries supplied by the National Institute for Standard and Technology (NIST/EPA/NIH). Acquisition was started after a 3 minute solvent delay.[27]

Ion selection for qualitative and quantitative purposes

Ions with m/z ranging from 50 to 400 were monitored. Primary or secondary ions were selected for qualitative and quantitative identifications of VOCs by injecting an analytical standard of each VOC into the TDU-GC-MS system. One microliter of 30 µg mL^{-1} standards prepared in GC grade methanol was spiked in a sampling tube for the development of the retention time profile and identification of the diagnostic ions. The primary ion, which is the most abundant ion generated during electron ionization (EI) of each VOC analyte, was recorded and used for the quantitative purpose. If interference was present, a secondary ion was used as the quantitative ion. Background spectrum subtraction was subsequently carried out, and thus the selectivity and sensitivity could be optimized. The

chromatographic data were processed with MSD Chemstation software (Agilent Technologies, Inc.).

Chemicals

The analytical standards for these target VOCs (Table S1†) including an indoor air standard 50 component premix (1000 μg mL^{-1}), a VOC calibration standard 54 component premix (200 μg mL^{-1}), an EPA 554 12 carbonyl compound premix (1000 μg mL^{-1}), benzaldehyde, acetophenone, benzothiazole, 2-butoxyethanol, homosalate, 2-ethylhexyl salicylate, and α-methylstyrene were purchased from Sigma-Aldrich, USA. GC grade methanol and acetonitrile used in these experiments were purchased from Fisher Scientific. Tenax TA sorbent tubes (part no. MX062131) were purchased from SKC Inc., Pennsylvania, USA.

Calibration, sensitivity, repeatability, and recovery

Calibration curves were constructed using seven concentrations (1.0, 2.5, 5.0, 10, 25, 50, and 100 μg mL^{-1}) of the standard samples. The construction of calibration curves was performed by spiking 1 μL of the mixed standards into TD sampling tubes followed by thermal desorption and GC-MS procedures as described above. The calibration curves plotted depicted the relationship between mass (ng) and peak areas.[25] The concentration (C) of a certain VOC detected in the air samples was calculated as follows:

$$C = (m - m_{\mathrm{B}})/V, \text{ μg m}^{-3}$$

in which m (μg) is the amount of an individual compound trapped on the sorbent material in the sampling tube, and m_{B} (μg) is the mass of the analyte in a blank tube, which was calculated using the appropriate calibration curve of that compound, V (m^3) is the volume of air pumped through the sorbent material during the period of sampling time. The volume of air was determined from counter readings and the stroke factor of the air pump provided by the manufacturer as follows:

$$V = (\text{final counter reading} - \text{initial counter reading}) \\ \times \text{stroke factor, m}^3$$

Blank samples were used to determine background contamination and sample-to-sample carryover. Assessment of the sensitivity of the analytical method was conducted by calculating the limit of detection (LOD) and limit of quantification (LOQ). The signal-to-noise ratios of three and ten were used for calculating the LOD and LOQ, respectively.[28]

The precision of the analytical method expressed as the coefficient of variation (CV) for the VOCs was examined using five injections of the spiked mixed standard solutions. The formula used to calculate the CV of the VOCs is as follows:

$$\text{CV\%} = \text{SD}/\mu \times 100\%$$

in which SD is the standard deviation for concentration measurements, and μ represents the arithmetic mean.

The recovery of an individual compound was tested using the mixed standard solution with blank samples. Recoveries were calculated according to the formula:

$$\text{recovery} = (\text{MC} - B)/\text{SC} \times 100\%,$$

in which MC represents the mean concentration value obtained from replicate measurements, B is the concentration of the VOC in the blank sample, and SC stands for the spiked concentration of the VOC.

Method validation and field study

The analytical method was tested and validated by a field study conducted at a selected child care center in Kansas City, Missouri to examine the applicability of the air sampling method using a Tenax TA tube. The field study was conducted in a classroom at this Head Start child care center. All the air samples were collected from October 2014 to March 2015.

Results

TDU-GC-MS analysis

In total, 107 VOCs (Table S1†) were screened based on the potential emission sources of VOCs (*e.g.* toys, school supplies, furniture, cleaning supplies, *etc.*) in indoor educational buildings and child care centers. The results of the ion selection and optimization are demonstrated in Table 1. Among the selected 107 VOCs, 73 VOCs were successfully quantified using the thermal desorption unit coupled with GC-MS (Table 1).

GC separation

The results demonstrated that 73 VOCs can be chromatographically separated using a DB-5MS capillary column (30 m length × 0.25 mm I.D. × 1 μm film thickness, Agilent Technologies, Santa Clara, CA). Fig. 1 illustrates the total ion chromatogram obtained for a mixed standard of 30 ng of each compound. Our results also indicated that the GC method with a temperature ramp rate of 15 °C min^{-1} helped increase the speed of analysis without compromising compound separation or reducing the sensitivity. All the monitored VOCs have symmetric peaks with widths less than 0.1 min, and they were eluted within the first 17 min.

Ion selection and optimization

The results for the ion selection and optimization of the examined 73 VOCs are shown in Table 1. Five of the VOCs, *n*-nonane, heptanal, 2-butoxyethanol, 4-ethyltoluene and *n*-butylbenzene, were identified and quantified with secondary ions while the rest were quantified using primary ions. There were several coeluting analytes as demonstrated in Table 1 and Fig. 1. The retention time (RT) of benzene was as early as 3.15 min while homosalate was the last compound to elute (RT = 15.68).

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Table 1 Summary of retention times, monitored ions, calibration curves, recoveries, precisions and detection limits of the target VOCs[a]

No.	Compounds	Retention time (min)	Monitored primary[b] and secondary ions	Equation	Coefficient of determination R^2	Recovery	CV%	LOD, µg m^{-3}	LOQ, µg m^{-3}
1	Benzene	3.11	78, 77	$y = 13665x$	0.9948	89	4.9	0.003	0.010
2	Trichloroethylene	3.45	130, 132	$y = 5200x$	0.9899	103	3.6	0.015	0.050
3	Methyl methacrylate	3.56	69, 100	$y = 4701x$	0.9892	93	14.7	0.026	0.086
4	Bromodichloromethane	3.63	83, 85, 129, 127	$y = 650x$	0.9919	91	9.5	0.020	0.065
5	4-Methyl-2-pentanone[a]	3.88	58, 57	$y = 1857x$	0.9996	94	3.5	0.031	0.101
6	1,4-Dioxane[a]	3.88	88, 58	$y = 333.9x^2 + 3281x$	0.9815	88	16.2	0.035	0.116
7	trans-1,3-Dichloropropene	3.97	75, 77	$y = 10474x$	0.9956	99	1.5	0.027	0.089
8	2-Hexanone	4.00	58, 57	$y = 2250x$	0.9877	93	9.2	0.030	0.098
9	Toluene	4.23	91, 92	$y = 31497x$	0.9964	96	2.8	0.001	0.003
10	cis-1,3-Dichloropropene	4.27	75, 77	$y = 10509x$	0.9913	99	1.5	0.021	0.069
11	1,2-Dichloroethene[b]	4.40	61, 96	$y = 3254x$	0.9997	96	2.1	0.002	0.007
12	1,1,2-Trichloroethane[b]	4.40	97, 99, 132	$y = 8185x$	0.9994	98	6.4	0.018	0.061
13	Octane	4.64	57, 85	$y = 2066x$	0.9989	97	1.4	0.036	0.120
14	Hexanal[c]	4.76	56, 57	$y = 4846x$	0.9991	96	2.6	0.011	0.035
15	Tetrachloroethylene[c]	4.78	166, 164, 131, 129	$y = 12434x$	0.9971	98	4.6	0.002	0.005
16	Dibromochloromethane	4.85	127, 129	$y = 10191x$	0.9989	98	2.2	0.007	0.022
17	1,2-Dibromoethane[d]	4.94	107, 109	$y = 13141x$	0.9993	95	1.1	0.006	0.020
18	Butyl acetate[d]	4.95	56, 73	$y = 7747x$	0.9995	87	3.7	0.008	0.026
19	Chlorobenzene	5.45	112, 77	$y = 37647x$	0.9999	99	4.6	0.002	0.006
20	Ethylbenzene	5.65	91, 106	$y = 57609x$	0.9997	99	1.7	0.001	0.004
21, 22	m/p-Xylenes	5.80	91, 106	$y = 89296x$	0.9999	98	3.2	0.001	0.004
23	n-Butyl ether	5.95	57, 87	$y = 26655x$	0.9996	98	3.0	0.003	0.008
24	Styrene[e]	6.12	104, 103	$y = 41767x$	0.9992	96	2.5	0.001	0.004
25	o-Xylene[e]	6.12	91, 106	$y = 45728x$	0.9989	102	2.8	0.002	0.006
26	Bromoform[f]	6.15	173, 171	$y = 16393x$	0.9999	97	1.7	0.001	0.004
27	n-Nonane[f]	6.17	57, 85[c]	$y = 11857x$	0.9996	98	1.2	0.002	0.006
28	Heptanal	6.26	55, 70[c]	$y = 7682x$	0.9994	95	1.8	0.008	0.026
29	2-Butoxyethanol	6.33	57, 87[c]	$y = 13.99x^2 + 1858x$	0.9918	100	3.6	0.059	0.196
30	Cumene	6.56	105, 120	$y = 61123x$	0.9998	100	3.5	0.001	0.004
31	2-(2-Methoxyethoxy)ethanol (22MEE)	6.75	59, 58	$y = 130x^2 - 1269x$	0.9933	95	3.5	0.123	0.406
32	α-Pinene	6.74	93, 92, 91	$y = 2896x$	0.9943	112	3.3	0.011	0.037
33	n-Propylbenzene	6.98	91, 120	$y = 75400x$	0.9995	99	1.9	0.001	0.003
34	3-Ethyltoluene	7.08	105, 120	$y = 49855x$	0.9997	100	2.3	0.001	0.002
35	4-Ethyltoluene[g]	7.12	105, 120[c]	$y = 46462x$	0.9995	100	2.3	0.001	0.002
36	Benzaldehyde[g]	7.14	77, 105, 106	$y = 17250x$	0.9972	103	7.0	0.001	0.005
37	1,3,5-Trimethylbenzene	7.19	105, 120	$y = 52493x$	0.9999	101	2.4	0.001	0.003
38	2-Ethyltoluene	7.31	105, 120	$y = 63099x$	0.9994	93	1.2	0.001	0.003
39	α-Methylstyrene	7.35	118, 117	$y = 48083x$	0.9991	99	2.5	0.002	0.006
40	1,2,4-Trimethylbenzene[h]	7.52	105, 120	$y = 54917x$	0.9999	100	2.2	0.001	0.003
41	Decane[h]	7.54	57, 71	$y = 20525x$	0.9999	96	0.7	0.002	0.006
42	2-(2-Ethoxyethoxy)ethanol (22EE)[k]	7.61	59, 72	$y = 65.48x^2 + 3620x$	0.9904	102	5.0	0.035	0.116
43	Octanal[k]	7.62	57, 84	$y = 5236x$	0.9998	97	6.7	0.007	0.023
44	1,3-Dichlorobenzene	7.69	146, 148	$y = 37794x$	0.9999	99	0.6	0.001	0.003
45	3-Carene	7.73	93, 91	$y = 17190x$	0.9952	102	1.4	0.002	0.008
46	Benzyl chloride	7.81	91, 126	$y = -20\,960x^2 + 684\,600$	0.9949	92	6.5	0.001	0.002
47	1,4-Dichlorobenzene	7.81	146, 148	$y = 37795x$	0.9999	100	2.0	0.002	0.008
48	1,2,3-Trimethylbenzene	7.86	105, 120	$y = 54054x$	0.9999	97	1.2	0.001	0.004
49	2-Ethylhexanol-1[m]	7.94	57, 70	$y = 45.87x^2 + 7875x$	0.9968	103	2.4	0.045	0.149
50	D-Limonene[m]	7.96	68, 93	$y = 13980x$	0.9979	100	1.7	0.002	0.006
51	1,2-Dichlorobenzene	8.04	146, 148	$y = 36780x$	0.9999	100	0.8	0.002	0.005
52, 53	m-/o-Diethylbenzenes	8.17	119, 105	$y = 13020x$	0.9989	102	2.3	0.003	0.009
54	p-Diethylbenzene[n]	8.28	119, 105, 134	$y = 16690x$	0.9989	101	2.6	0.002	0.008
55	n-Butylbenzene[n]	8.28	91, 92, 134[c]	$y = 54683x$	0.9996	96	2.8	0.001	0.004
56	g-Terpinene[n]	8.30	93, 91, 121, 136	$y = 20990x$	0.9980	99	1.5	0.002	0.005
57	Acetophenone[p]	8.45	105, 77	$y = 41628x$	0.9990	96	4.4	0.003	0.010
58	Heptanoic acid[p]	8.48	60, 73	$y = 88.6x^2 - 82.5$	0.9965	103	4.4	0.104	0.343
59	1,2-Dibromo-3-chloropropane[q]	8.72	157, 155	$y = 14306x$	0.9999	98	0.8	0.002	0.005
60	Undecane[q]	8.74	57, 71, 85	$y = 23380x$	0.9998	99	0.6	0.001	0.002
61	Nonanal	8.82	57, 56, 70, 82, 98	$y = 8722x$	0.9997	100	6.8	0.002	0.008

Table 1 (*Contd.*)

No.	Compounds	Retention time (min)	Monitored primary[b] and secondary ions	Equation	Coefficient of determination R^2	Recovery	CV%	LOD, µg m^{-3}	LOQ, µg m^{-3}
62	Decamethylcyclo-pentasiloxane	9.03	73, 267	$y = 40960x$	0.9997	100	2.4	0.001	0.002
63	Dodecane[r]	9.82	57, 71, 85	$y = 24562x$	0.9996	98	1.1	0.002	0.006
64	Naphthalene[r]	9.82	128	$y = 100288x$	0.9995	97	1.8	0.002	0.005
65	Decanal	9.91	57, 55, 70, 82, 112	$y = 4692x$	0.9992	93	2.3	0.003	0.009
66	Hexachlorobutadiene	10.02	225, 190	$y = 29626x$	0.9995	98	2.4	0.001	0.002
67	Benzothiazole	10.26	135, 108	$y = 53458x$	0.9947	99	2.4	0.007	0.022
68	Tridecane	10.81	57, 71, 85	$y = 25188x$	0.9997	94	1.6	0.001	0.004
69	Tetradecane	11.74	57, 71, 85	$y = 25920x$	0.9997	99	2.5	0.001	0.003
70	Pentadecane	12.61	57, 71, 85	$y = 25960x$	0.9985	101	4.0	0.001	0.003
71	Hexadecane	13.43	57, 71, 85	$y = 24896x$	0.9999	99	3.2	0.001	0.005
72	2-Ethylhexyl salicylate	15.06	120, 138	$y = 30650x$	0.9919	96	3.6	0.001	0.003
73	Homomenthyl salicylate	15.68	138, 109	$y = 18420x$	0.9929	101	3.0	0.001	0.003

[a] a–h, k, m, n, p–r: The same letter represents the analytes coeluting. [b] The first values represent primary ions. [c] Secondary ions used for the quantitative identification of VOCs.
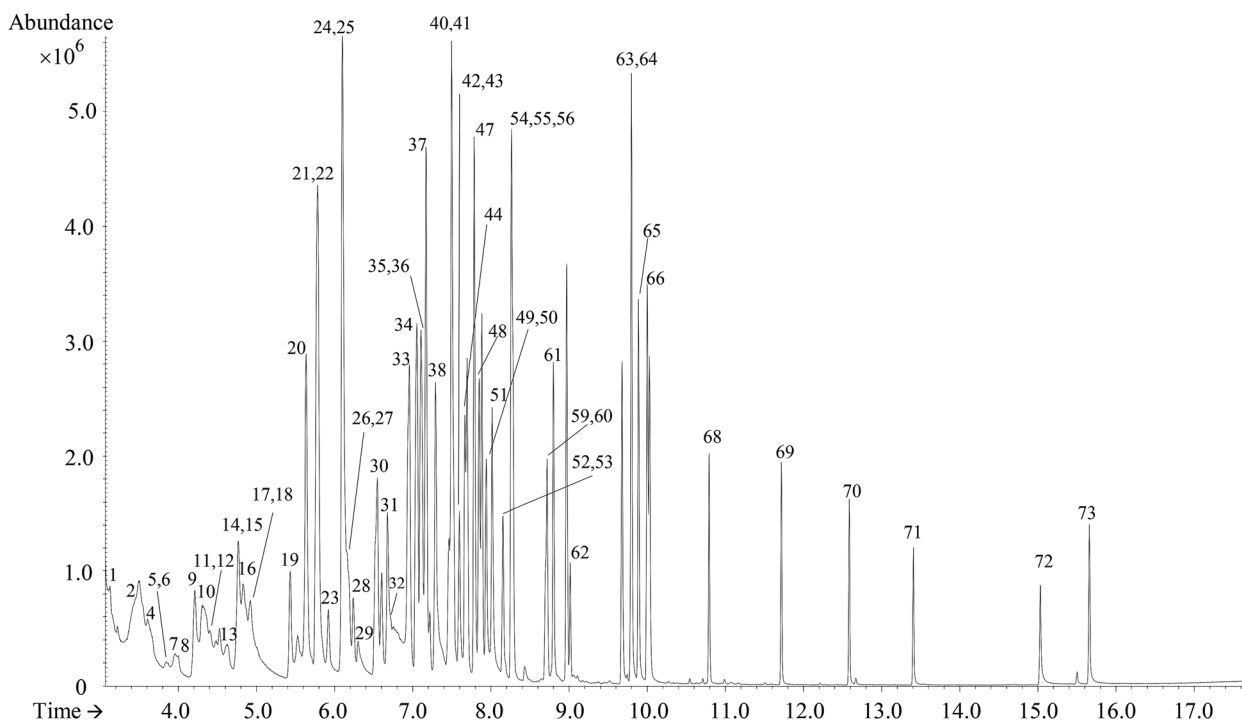

Fig. 1 Total ion chromatogram of the volatile organic compounds on a DB-5MS column (1 µL injection, 30 µg mL^{-1}).

Thermal desorption system

As shown in Table S1,† the thermal desorption sampling method allowed sampling of a wide range of volatile and semi-volatile, moderately hydrophobic and non-polar organic compounds. The recovery rates of all the spiked VOCs ranged between 87% (butyl acetate) and 112% (α-pinene) at a level of 25 ng (Table 1). Of these VOCs, 61 compounds were found with recovery falling within the range of 95 to 105%.

As demonstrated in Table 1, the linear relationship successfully fitted every calibration curve, except 22-MEE, 1,4-

dioxane, 22-EE, 2-butoxyethanol, 2-ethylhexanol-1, heptanoic acid and benzyl chloride. Non-linear correlations were developed at the low calibration levels of the compounds including 22-MEE, 1,4-dioxane, 22-EE, 2-butoxyethanol, and 2-ethylhexanol-1 when the standard concentration approached the detection limit. For benzyl chloride, a quadratic polynomial fit was used for the whole range because a non-linear effect was found above 10 ng. A calibration curve of a typical VOC (*n*-propylbenzene) and its mass spectrum are shown in Fig. 2 and 3. The developed calibration equation for every compound in the
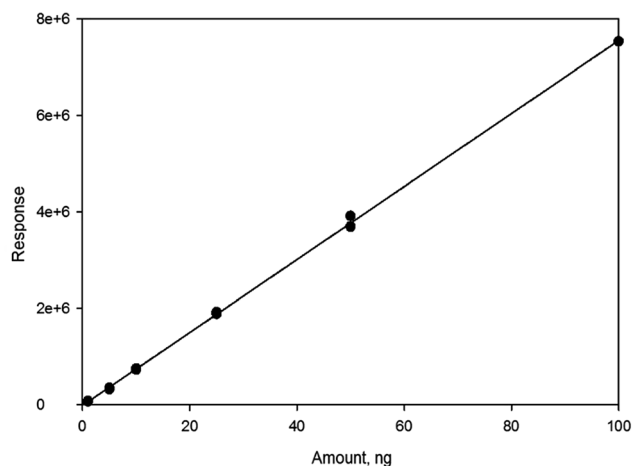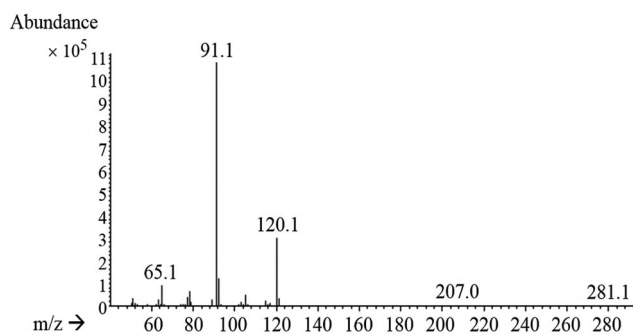
Fig. 2 Calibration curve of *n*-propylbenzene.

Fig. 3 MS spectrum of *n*-propylbenzene.

study had correlation coefficients (R^2) greater than 0.99, except for trichloroethylene, methyl methacrylate, 2-hexanone and 1,4-dioxane whose R^2 values were slightly lower than 0.99 (Table 1). As for *m*-/*p*-xylenes and *o*-/*m*-diethylbenzenes, two calibration curves were collectively constructed for the two pairs unresolved under the separation conditions with the DB-5MS capillary column.

The LOD, LOQ and precision of the method for each of the VOCs are shown in Table 1. The LOD and LOQ ranged between 0.001 (3-ethyltoluene and 4-ethyltoluene) and 0.123 (2,2-methoxyethoxyethanol) μg m^{-3}, and 0.002 and 0.406 μg m^{-3}, respectively. The precision expressed as the coefficient of variation (CV) for the VOCs ranged between 0.6% and 16.2%.

Field study and method validation

The developed TDU-GC-MS method was successfully validated by the field study. The VOCs in the air samples were collected from the selected child care center and their concentrations were successfully determined. In total, 47 VOCs were detected in the child care center as summarized in Table 2. Among the chemical classes, aromatic hydrocarbons (*i.e.* benzene derivatives) and alkanes account for 54% of the total detected VOC compositions. Aldehydes, chlorinated hydrocarbons, alcohols, esters, compounds of mixed functions (containing hydroxyl and

Table 2 Indoor concentrations (μg m^{-3}) of VOCs detected in the child care center

Compounds	Mean	SD	Outdoor concentration[a]	I/O ratio
1,1,2-Tricholorethane	nd	—	nd	n/a
1,2,3-Trimethylbenzene	0.1	0.1	nd	n/a
1,2,4-Trimethylbenzene	0.5	0.2	nd	n/a
1,2-Dibromo-3-chloropropane	nd	—	nd	n/a
1,2-Dibromoethane	nd	—	nd	n/a
1,2-Dichlorobenzene	nd	—	nd	n/a
1,2-Dichloroethene	nd	—	nd	n/a
1,3,5-Trimethylbenzene	nd	—	nd	n/a
1,3-Dichlorobenzene	nd	—	nd	n/a
1,4-Dichlorobenzene	1.6	1	0.006	258
1,4-Dioxane	nd	—	nd	n/a
2(2-Ethoxyethoxy) ethanol	nd	—	nd	n/a
2(2-Methoxyethoxy) ethanol	nd	—	nd	n/a
2-Butoxyethanol	1.7	2.8	nd	n/a
2-Ethylhexanol-1	1.4	1.5	0.098	14.3
2-Ethylhexyl salicylate	0.2	0.2	nd	n/a
2-Ethyltoluene	0.2	0.1	nd	n/a
2-Hexanone	nd	—	nd	n/a
3-Carene	nd	—	nd	n/a
3-Ethyltoluene	0.2	0.1	nd	n/a
4-Ethyltoluene	0.1	0.1	nd	n/a
4-Methyl-2-pentanone	nd	—	nd	n/a
Acetophenone	0.3	0.2	3.0	0.1
α-Methylstyrene	0.01	0	nd	n/a
α-Pinene	0.2	0.3	0.10	2
Benzaldehyde	1.4	0.6	1.40	1
Benzene	0.3	1.1	0.007	42
Benzothiazole	0.1	0	0.02	5
Benzyl chloride	nd	—	nd	n/a
Bromodichloromethane	nd	—	nd	n/a
Bromoform	nd	—	nd	n/a
Chlorobenzene	0.01	0	0.002	5
cis-1,3-Dichloropropene	nd	—	nd	n/a
Decamethylcyclopentasiloxane	nd	—	nd	n/a
Decanal	0.5	0.2	0.029	17
Decane	1.2	0.7	0.014	85
Dibromochloromethane	nd	—	nd	n/a
ᴅ-Limonene	6.2	9	0.006	1032
Dodecane	1.4	0.9	0.008	186
Ethylbenzene	0.4	0.3	0.024	17
g-Terpinene	nd	—	nd	n/a
Heptanal	nd	—	nd	n/a
Heptanoic acid	0.7	0.5	nd	n/a
Hexachlorobutadiene	nd	—	nd	n/a
Hexadecane	0.4	0.1	0.003	118
Hexanal	nd	—	nd	n/a
Homomenthyl salicylate	0.1	0.1	nd	n/a
Cumene	0.1	0.1	nd	n/a
o/m-Diethylbenzenes	0.1	0	nd	n/a
m/p-Xylenes	0.4	0.2	0.031	13
Methyl methacrylate	nd	—	nd	n/a
Naphthalene	0.2	0.1	0.011	18
n-Butyl acetate	0.3	0.2	nd	n/a
n-Butyl ether	0.01	0	nd	n/a
n-Butylbenzene	nd	—	nd	n/a
Nonanal	0.9	0.3	0.045	20
Nonane	0.8	0.5	0.013	63
n-Propylbenzene	0.2	0.1	nd	n/a
Octanal	0.2	0.2	0.022	9.3
Octane	0.6	0.7	nd	n/a
o-Xylene	0.3	0.1	0.025	12

Table 2 (*Contd.*)

Compounds	Mean	SD	Outdoor concentration[a]	I/O ratio
p-Diethylbenzene	0.2	0.1	nd	n/a
Styrene	0.6	0.9	0.007	92
Tetrachloroethylene	0.7	0.5	0.010	70
Tetradecane	1.7	0.7	0.004	424
Toluene	2.7	1.1	0.18	15
trans-1,3-Dichloropropene	nd	—	nd	n/a
Trichloroethylene	0.5	0.4	nd	n/a
Tridecane	0.6	0.5	0.007	92
Undecane	1.3	0.6	0.016	79
Pentadecane	0.7	0.3	0.004	164

[a] : Arithmetic mean outdoor concentrations of VOCs ($\mu g\ m^{-3}$). Mean and SD stand for the arithmetic mean and standard deviation of indoor concentration values ($n = 6$). nd: below LOD. —: not calculated.

alkoxy groups) and other cyclic hydrocarbons constitute the remaining. The VOC concentrations calculated as the arithmetic mean ranged from 0.01 to 6.2 $\mu g\ m^{-3}$. D-Limonene, toluene, *n*-nonanal, α-pinene, 2-ethylhexanol, benzaldehyde, and *n*-decanal were found to be the most common components among the target VOCs. Particularly, D-limonene which has the highest concentration in indoor air was detected in all classrooms in the monitored child care center. The results also indicated that benzene was present in the air samples at concentration levels averaging 0.3 $\mu g\ m^{-3}$. The concentrations of other BTEX components including toluene, ethylbenzene and xylenes varied between 0.3 and 2.7 $\mu g\ m^{-3}$.

The results also showed the presence of chlorinated hydrocarbons such as 1,4-dichlorobenzene, trichloroethylene, and tetrachloroethylene in the child care center. While the former was commonly used in pesticides or personal products to control moths and molds, the latter two were commonly used as dry-cleaning agents. These results also yielded evidence of several aldehydes such as octanal, nonanal, decanal, and benzaldehyde which are often used as components in flavors, perfume and cosmetic products.[29] As seen in Table 2, the concentrations of these compounds range between 0.2 and 1.4 $\mu g\ m^{-3}$. Among the VOCs found in the child care center, 13 compounds, namely 2-butoxyethanol, 2-ethylhexanol-1, benzaldehyde, cumene, ethylbenzene, homosalate, *m*- and *p*-xylenes, *o*-xylene, naphthalene, styrene, tetrachloroethylene, and toluene, were previously reported to have endocrine disrupting activities.[30–34] To our knowledge, the present study is one of only two studies that documented the presence of homosalate (0.1 $\mu g\ m^{-3}$), 2-ethylhexanol-1 (1.4 $\mu g\ m^{-3}$) and 2-butoxyethanol (1.7 $\mu g\ m^{-3}$) in child care facilities. The other study reporting the presence of the three endocrine disrupting compounds was conducted by Bradman *et al.* (2012).

To assess the relationship between the indoor and outdoor emission sources of VOCs, our study used indoor/outdoor (*I/O*) concentration ratios (mean indoor concentration/mean outdoor concentration). As seen in Table 2, *I/O* ratios varied between 0.1 and 1032.

Discussion

Thermal desorption system

Thermal desorption sampling and analysis involve the use of a sorbent-based tube, air sampling pump and two-stage thermal desorption system. First, the sorbent tube is thermally desorbed to transfer the analytes to a small, cooled, secondary sorbent trap (focusing trap). The second desorption process subsequently transfers the pre-concentrated analytes to the GC-MS. This helps minimize band-broadening and generate capillary-compatible peaks, leading to a greater sensitivity of this method. Canisters and sampling bags are generally employed for organic compounds which are too volatile to be trapped by using sorbent tubes. However, the analysis of the VOCs retained by canisters or sampling bags requires system leak check, cleaning, and 12 hour equilibration before direct injection into the GC-MS. Also, for air analysis using canisters, special equipment and a modified injection port are needed to concentrate and pressurize the analytes into the GC-MS.

Sampling of VOCs

Selection of air samplers. The findings suggest that TD sampling tubes are ideal for air sampling at child care centers because of their simplicity, portability, flexibility and affordability. The use of TD sampling tubes in the present study required less space than that of canisters. The sampling tubes and pre-charged pumps were quickly and easily installed. Importantly, neither an electrical supply nor a vacuum system is required during the sampling period. Moreover, the integrated TD tubes and pump system are highly portable, and are less likely to draw children's attention compared to other collection devices due to their smaller size and simpler installation. In addition, the sampling tubes are much more affordable than canisters, leading to cost reduction in the analysis of air samples. More importantly, the TD tubes can be easily regenerated and implemented at any desired sampling elevation, based on the height and nose position of the children, when a simple rack or tower is used.

Specificity of sorbent materials and absorption capacity. For air monitoring, there are three types of commonly used sorbent-based sampling tubes including pumped sampling tubes, axial diffusive tubes and radial diffusive tubes. Among these tubes, pumped samplers are more suitable for the measurement of VOCs at a wide concentration range of approximately 0.1 $\mu g\ m^{-3}$ to 1 $g\ m^{-3}$.[25] The present study chose to deploy pumped sampling tubes packed with a 20:35 mesh Tenax-TA/Carboxen 1000/Carbosieve, air pump and two-stage thermal desorption system for the sampling and preparation of air samples.

Our results indicated that the selected sorbent-based sampling tubes coupled with TDU-GC-MS analysis demonstrate high recovery rates for 73 compounds (Table 1). The combination of the three sorbents with a high adsorption capacity and surface area allows the sampling tubes to capture a wide range of VOCs in air, including alkanes, aromatic hydrocarbons, halogenated hydrocarbons, esters, and aldehydes. The Tenax-TA™ is designed to capture the VOCs with molecular weight ranges from C6 to C30s and C2 to C5

depending on the functional group. It provides a surface area of 35 m^2 g^{-1} (CDS Analytical). The Tenax-TA does not react with materials and has low affinity for water. During the thermal desorption process, the adsorbed VOCs were quickly released. A Carbosieve SIII was used to adsorb C2 to C6 VOCs. The Carbosieve SIII has a high capacity/breakthrough volume for low boiling compounds and has a low desorption efficiency for polar compounds. The Carboxen 1000 has a surface area of 1200 m^2 g^{-1}. It was designed to adsorb C2 to C6 volatile organic compounds with a better desorption efficiency than the Carbosieve SIII (CDS Analytical). The combination of these sorbents can facilitate the sampling of a wide range of highly volatile, higher molecular weight, semi-volatile, and polar analytes.[25,35] Particularly, the Tenax-TA has a high temperature stability which allows it to be conditioned to obtain a very low background, and helps improve the recovery rates of semi-volatile compounds.[35,36] The arrangement of the sorbents is to enhance the sorbent strength, with the weakest sorbent (Tenax-TA) nearest to the sampling inlet end of the tube to trap least volatile compounds. More volatile compounds are retained by stronger sorbents which are separated by unsilanized (deactivated) glass wool along the tube.

A study previously conducted by Koziel *et al.* (2005) showed that canisters and sampling bags provided sample recoveries for VOCs as low as 4.2% and 47.3–71.7%, respectively, while Tenax-TA packed tubes provided much higher recoveries for VOCs of up to 94.8%.[37] There are several factors affecting recovery rates if canisters or sampling bags are used for air sampling. For example, canisters that are insufficiently cleaned will produce high background contaminants. The wall of sampling bags can potentially adsorb VOCs, resulting in the loss of analytes. The use of sorbent-based tubes can help avoid these drawbacks, thereby improving recovery rates.

The results demonstrated that the universality of the sorbent materials used in our study made the sorbent tubes an effective sampling tool for monitoring the air quality at child care centers. In contrast, other sampling techniques like SPME and use of canisters have disadvantages over sorbent tubes for exploratory studies in which the concentrations of the target analytes in ambient air are unknown. While SPME has a capability of trapping a limited range of VOCs due to the high specificity of polymer- or sorbent-coated SPME fibers, canisters are only suitable for the analysis of highly volatile C1–C6 hydrocarbons.[38] For monitoring of less volatile hydrocarbons, particularly cyclic aromatic hydrocarbons and semi-volatile organic and polar compounds, sorbent tubes are a better choice.

The multi-sorbent bed tubes used in the present study could be applied to a broad range of volatile organic compounds with a much wider range of hydrophilicity and concentration levels. This also aims to overcome the adsorption issue experienced by other conventional VOC sampling techniques such as the compound-specific and surface-limited SPME sampling method.

GC separation. The selected column DB-5MS in the present study was designed for the analysis of volatiles and semi-volatiles as well as halogenated hydrocarbons. As seen in

Table 1 and Fig. 1, seventeen chlorinated and brominated compounds were successfully separated and analyzed. The 30 m chromatographic column yielded excellent efficiency, and accomplished the analysis of complex air samples collected in child care centers. Although longer columns (60 m, 75 m, and 105 m) might have further improved the peak resolution, the additional cost could not be justified due to the increased analysis time.[39] The use of medium I.D. columns (0.25 mm–0.32 mm) can facilitate the analyses of complex samples with a wide concentration range.[40] With a film thickness of 1 μm, the DB-5MS has a high sample loading capacity and high resolution for volatiles and low molecular weight compounds, facilitating the analysis of high concentration air samples. For 0.25 mm I.D. columns, a film thickness of 0.18–0.25 μm is average or standard, and can be used for most analyses.[39] The column was employed with a higher film thickness which has higher solute capacities, and helps reduce peak broadening (Fig. 1). Previous studies (unpublished data) suggested that the thickness of 0.25–0.5 μm was less effective in the analysis of volatile and low molecular compounds as thinner films would be less efficient in preventing the diffusion of the analytes in the column and, therefore, result in broader signals with much lower signal to noise ratios.

Ion selection and optimization. In the present study, a mass spectrometry-based analytical method was developed for indoor air monitoring in child care facilities. Simply, mass spectrometry is an analytical technique that is used to qualitatively and quantitatively identify molecules based on their mass to charge (m/z) ratio. In mass spectrometry, the molecules must be subjected to ionization to form molecular ions and fragment ions. The formation of the latter takes place during the dissociation of energetically unstable molecular ions. For instance, the ionization of styrene in a mass spectrometer generates the molecular ion at m/z 104 and fragment ions at m/z 103 and 78. As described earlier, among these ions, the primary and secondary quantitation ions, which can be either molecular or fragment ions, are the most and second most abundant ions in the mass spectrum. For examples, the mass spectrum of styrene has the primary ion and secondary ion at m/z 104 and 103, respectively. The primary and second ions of each target VOC are summarized in Table 1. Through careful selection of the quantitative ions, it allows the separation and quantitation of the coeluting VOCs such as styrene and *o*-xylene. The quantitation of the other co-eluting pairs of VOCs can rely on the ratios between their primary or secondary ions. For the three co-eluting VOCs nonane, heptanal and 2-butoxyethanol whose mass spectra have the same primary ion at m/z 57, quantitative identification was carried out using secondary ions at m/z 85, 70 and 87, respectively. Compounds that shared primary and secondary ions such as *m*-xylene and *p*-xylene cannot be separately quantified by mass spectrometry. As a result of the identical fragmentation patterns of the isomers and their retention time, it only allows the determination of the total concentration of the two *m*- and *p*-xylenes. As illustrated in Fig. 1, 4A and B, the extracted ion chromatograms of *m*- and *p*-xylene (m/z 91), styrene (m/z 104) and *o*-xylene (m/z 91), which
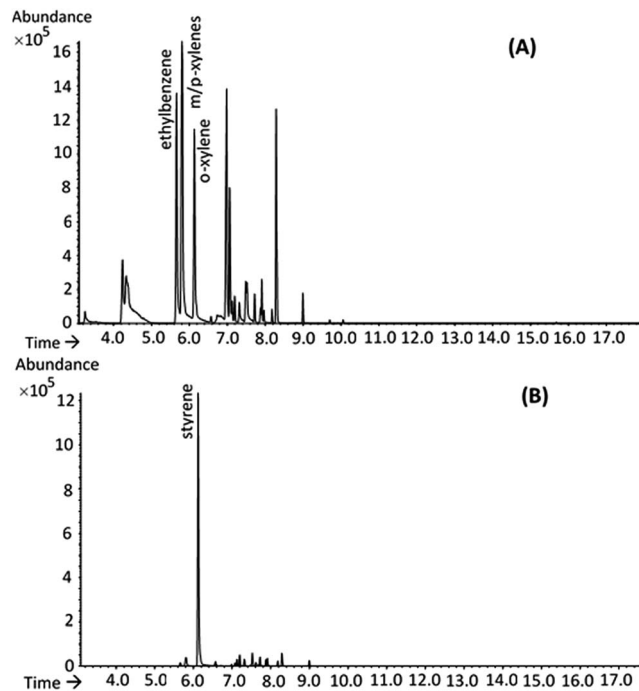
Fig. 4 Extracted ion chromatograms at *m/z* 91 (A) and extracted ion chromatograms at *m/z* 104 (B). The thermal desorption sampling tube was spiked with 1 μL of 30 μg mL^{-1} mixed VOC standards.

could not be chromatographically separated, were displayed to compare with the total ion chromatograms.

Despite the identification of VOCs using their secondary ions which were not the most abundant ions observed in mass spectra, the selectivity and distinctive characteristics of these selected ions significantly reduce the background noise generated by co-eluting interferents.

Our findings suggest that mass spectrometry is a more definitive analytical technique used for indoor air monitoring in child care centers than other detectors such as flame ionization detectors and electron capture detectors. Based on the high sensitivity, selectivity, and complementary comprehensive mass spectral libraries, the detection technique significantly improves the accuracy of identification and quantification of VOC analytes when compared to other detection techniques.

Detection limits and precision. According to the calculated LODs (Table 1), the developed method is more sensitive than other similar methods reported in previous research. Compared with prior research,[41–43] the calculated LODs for the analysis of BTEX in the present study were much lower. Furthermore, these previous studies used either Tenax-TA packed diffusive sampling tubes or pumped sampling tubes for VOC sampling. The low LODs and high precision of the developed method in the present study are mainly attributed to: (1) large air sampling volume (74 L) due to the high adsorption capacity of the 3-layer Tenax-TA/Carboxen 1000/Carbosieve design, (2) high levels of analytes introduced into GC by the thermal desorption process, (3) focused analytes on a trap prior to entering the analytical column, resulting in higher responses and narrow, more symmetric peaks, (4) the highly sensitive and selective MS ion

trap mass spectrometer, and (5) reduced potential analytical errors due to the fully automated design.

Field study and method validation. The presently developed analytical method was successfully tested and validated by a pilot study to assess the exposure of children to VOCs at the selected child care center located in Kansas City. From the results shown in Table 2, the broad range of VOCs detected were categorized into various chemical classes, reflecting the complex chemical composition of indoor air in the child care center. Among these compounds, D-limonene was the prominent VOC detected in the child care center. This cyclic terpene is often used in air fresheners, botanical insecticides and personal care products such as hand cleansers, which smell like citrus. D-limonene and its oxidation products are known as skin and respiratory irritants.

A variety of endocrine disrupting chemicals (EDCs) were also found among the detected 47 VOCs. Exposure to these chemicals may adversely affect the hormone system in animals and/ or humans.[44] Benzene, toluene, ethylbenzene and xylene (BTEX), which were detected in the monitored child care center, are among these EDCs. BTEX are often used as solvents in consumer products including cleaning agents, paint thinners, and vanishes, and in petrochemical additives. The International Agency for Research on Cancer (IARC) has also classified benzene and ethylbenzene as a human carcinogen and possible human carcinogen, respectively. BTEX have raised public concerns over the past few decades due to their toxicity and carcinogenicity.[45] As described earlier, the major contributors to atmospheric BTEX concentrations are emissions from cigarette smoke, motor vehicles, indoor combustion sources, paints, and cleaners. In the present study, lower concentrations of BTEX were observed as compared to the concentrations reported previously (Fig. 5).[4,5,46] The variations in the concentration values may be attributed to differences in sampling and analytical methods, temperature, humidity, and indoor ventilation systems in the studied child care center, building structures, and center maintenance activities. For the effects of ventilation systems on indoor VOCs in child care centers,
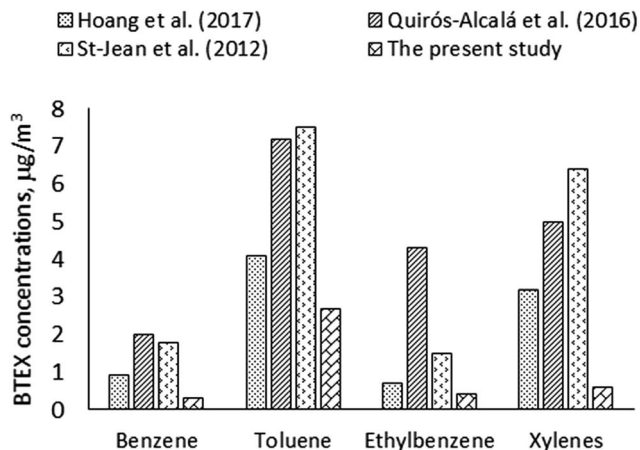

Fig. 5 Mean concentrations of BTEX components in child care centers in the present study and in other studies.

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Zuraimi et al. (2008) showed that ventilation systems with lower air exchange rates could lead to higher VOC exposures and risks.[47] We also observed lower BTEX levels compared to those reported in North American homes (Table 3). Particularly, the concentrations of m/p-xylenes in studies by Chin et al. (2014) and Bari et al. (2015) were 85 times higher than those in our study.[48,49] The differences in BTEX levels between the child care center and homes may be due to the use of household products, combustion processes (cooking, smoking, etc.), deodorizers and emission of VOCs from building materials which are the major contributors to VOC sources in homes.[49] Additionally, these authors found that household products and combustion processes accounted for 44% and 10.5% of VOC sources in homes, respectively. As seen in Table 2, I/O values for BTEX ranging from 12 to 42 indicate that the concentrations of BTEX components were found to be 12 to 42 times higher in indoor air samples than in outdoor air samples. Consistent with prior studies, in general, the indoor concentrations of BTEX were higher than outdoor concentrations in child care centers.[3,50] In other words, our results indicated that indoor sources were preponderant over outdoor sources for BTEX.

To evaluate the health risk from chronic exposure to BTEX, we compared the concentrations of indoor BTEX components to chronic Reference Exposure Levels (cRELs) developed by the California Office of Environmental Health Hazard Assessment (OEHHA).[51] The cREL is an airborne level of a VOC at or below which non-cancer health effects are not anticipated for a continuous exposure over a lifetime. Longer term exposure to benzene can cause human hematological problems.[52] Chronic exposure to ethylbenzene has been linked to adverse effects on the respiratory system and the liver and kidneys.[30,53,54] Chronic exposures to toluene and xylenes have been linked to adverse effects on the nervous system, the liver and the kidneys.[54] Table 4 shows that the indoor concentrations of BTEX components were lower than cRELs.

Among the target chlorinated hydrocarbons detected in the child care center, tetrachloroethylene is known to be a probable human carcinogen[55] and an EDC.[33] Because of its partial degradation by hydrolysis leading to the formation of two human carcinogens, namely trichloroethylene and vinyl chloride, its presence in child care facilities and other man-made structures has been a growing public health concern. In this study, it was found in the child care center with an average concentration of 0.7 $\mu g\ m^{-3}$. Compared with the OEHHA chronic Reference Exposure Level for tetrachloroethylene (30 $\mu g\ m^{-3}$), the concentrations of this compound detected in the child care center in our study were significantly lower.

This chemical is widely used in dry cleaning agents and consumer products such as paint strippers and spot removers. Another organochloride compound found in the child care center is trichloroethylene. Similar to tetrachloroethylene, trichloroethylene is often used in spot removers and metal degreaser. Its presence in child care centers is a matter of health concern because trichloroethylene has been associated with kidney and liver cancer.[55] The third chlorinated hydrocarbon found in the present study is 1,4-dichlorobenzene which is often used in mothballs and deodorizers. Due to its high volatility, it can readily sublime near ambient temperature. This compound is currently classified as "reasonably anticipated to be a human carcinogen" by the National Toxicology Program of the USA.[56]

The findings also showed the detection of naphthalene, which is one of the most commonly found VOCs in indoor and outdoor air. This pollutant, commonly used as an ingredient in deodorizers, moth and pest repellents, is classified as a possible human carcinogen.[57] Exposure to naphthalene at high levels may cause red blood cell damage.[58] The detection of this VOC in child care facilities and elementary schools was previously reported.[5,42,46] Compared with prior research conducted in child care centers in North America,[5,46] lower concentrations of naphthalene in the present study were observed (Fig. 5). We also observed lower naphthalene levels compared to those reported in North American homes (Table 3). As suggested by Batterman et al. (2012), differences in naphthalene levels may be due to the use of naphthalene-containing products such as deodorizers and moth and pest repellants.[59] Table 2 shows that the concentrations of naphthalene were found to be 18 times higher in indoor air than in outdoor air samples. To our knowledge, I/O values for naphthalene have not been reported in child care centers. We thus compared our result with that reported in primary and middle schools.[60,61] Consistent with those studies, our result demonstrated that the indoor sources of naphthalene predominated over outdoor sources. Chronic exposure to naphthalene has been associated with adverse effects on the respiratory system.[51] As seen in Table 4, our result did not exceed the cREL for naphthalene developed by the California Office of Environmental Health Hazard Assessment.

Table 3 Indoor levels of BTEX and naphthalene in studies conducted in North America

Compounds	Edmonton, Canada (Bari et al., 2015)[a]	Detroit, Michigan (Chin et al., 2014)[a]	Detroit, Michigan (Johnson et al., 2010)[a]	New Jersey (Weisel et al., 2008)[a]	Kansas city, MO (the present study, 2014–2015)[b]
Benzene	1.2	2.3	3.0	4.01	0.3
Toluene	18.3	11.6	18	25.1	2.7
Ethylbenzene	1.5	1.7	2.3	3.7	0.4
m/p-Xylenes	34	34	7.9	10.2	0.4
o-Xylene	5.7	2.0	2.7	3.9	0.3
Naphthalene	1.4	7.88	0.5	—	0.2

[a] Data for indoor VOC concentrations ($\mu g\ m^{-3}$) in homes. [b] Data for indoor VOC concentrations ($\mu g\ m^{-3}$) in the child care center. " — ": not reported or detected.

Table 4 Potential health risk from chronic exposure to BTEX and naphthalene

BTEX components	Indoor concentrations[a], µg m^{-3}	Chronic reference exposure levels (cRELs)[b], µg m^{-3}	Hazard index target organs	Species
Benzene	0.3	3	Hematologic system	Human
Toluene	2.7	300	Nervous and respiratory systems	Rat
Ethylbenzene	0.4	2000	Liver and kidneys; endocrine system	Mouse, rat
Xylenes	0.7	700	Nervous and respiratory systems; eyes	Human
Naphthalene	0.2	9	Respiratory system	Human

[a] Indoor concentrations of BTEX and naphthalene in the present study. [b] Chronic reference exposure levels for BTEX and naphthalene (adapted from the OEHHA, 2016).

Another EDC, 2-butoxyethanol, was also detected in our study. The compound is widely used as an ingredient in paint thinners, liquid soaps, cosmetics, household cleaners, dry-cleaning agents, inks and spot removers. Accordingly, its presence in indoor air may be attributed to emissions from these sources. While reports conducted by the American Conference of Governmental Industrial Hygienists (ACGIH) indicated that 2-butoxyethanol is a rodent carcinogen, it is not evident that the chemical is carcinogenic to humans.[62] Cometto-Muñiz and Abraham (2015) reported indoor concentrations of this VOC at slightly higher (2.3 µg m^{-3})[63] amounts than our study (1.7 µg m^{-3}).

Despite its common use as an active ingredient in sunscreen, homosalate has rarely been reported in previous research on indoor air monitoring. In the present study, this VOC was found in the monitored child care center. Growing concern about skin cancer has led to an increased use of sunscreens in children, and child care centers have policies regarding application to their charges during outdoor play time.[64–66] Although homosalate is an effective chemical ultraviolet filter it was identified as an antiandrogen and an estrogen agonist *in vitro*.[32]

According to the results for I/O ratios (Table 2), the indoor and outdoor concentrations of 37% (27/73) of the identified VOCs were detected at different levels between indoor and outdoor samplings. Only one VOC, acetophenone, was detected at higher concentration in the outdoor sample compared to the indoor sample. The remaining VOCs ranged from a one-fold (*i.e.*, benzaldehyde) increase to 1032 times (*i.e.*, D-limonene) higher concentration in the indoor air sample than in the outdoor air sample. This indicates that indoor sources played an influential role in VOC emission.

Advantages of the thermal desorption system over other techniques for the analysis of VOCs at child care centers. As reviewed earlier, several sampling and analytical techniques have been developed for the analysis of indoor VOCs. However, these analytical tools face similar drawbacks and challenges for the analysis of indoor air VOCs such as limited portability, reusability, durability, versatility, flexibility of the sampling equipment, or low adsorption capacity of the sorbent materials. Particularly, they are not ideal for multi-position air quality monitoring at child care facilities. For example, the SPME sampling technique has been widely used for the analysis of VOCs. However, SPME has been considered a passive sampling technique and it has a very limited adsorption surface area, high selectivity of SPME fibers towards VOCs, and low

reproducibility due to the ageing of SPME fibers.[67] They often lead to inaccurate results in quantitative measurements. The collected air samples are not time-integrated, and require to be desorbed as soon as possible after sampling.[68] Thus, the technique is more suitable for qualitative or semi-qualitative rather than quantitative purposes. The major drawbacks of using metal canisters in air sampling include their high cost (4 to 12 times more expensive than a TD sampling tube) and requirement of maintaining vacuum conditions prior to sampling. Canisters are also much larger and heavier than sorbent sampling tubes, making them costlier to ship. In addition to physical space which limits the number of samplers that can be transported and implemented simultaneously, canister samplers do not offer the flexibility to sample VOCs at target elevations. Canisters also have time-consuming regeneration and conditioning processes, and complicated installation when performing the gas chromatography analysis of collected samples. For example, canister cleaning requires a separate system as an additional step prior to background certification and sampling. Compared to sorbent sampling tubes, canisters have a limited sampling volume (1–15 L). Teflon and Tedlar bags are relatively expensive and have a high VOC background, making them difficult to re-use. Colorimetric and electrochemical sensors used in VOC analysis are suitable for the specific detection of VOCs, leading to a small range of chemicals detected. As an option that is superior to the above extraction techniques in terms of simplicity, rapidity, and affordability, sorbent tubes have gained increasingly wide acceptance in air sampling. Moreover, the integrated TD tubes and pump system are highly portable and do not draw children's attention compared to canisters which often trigger the children's curiosity due to their shape and size. They can be easily regenerated and conditioned before use and easily implemented in classrooms. In addition, sampling tubes are much more affordable than canisters, leading to cost reduction in the analysis of air samples. More importantly, TD tubes can be implemented at any desired sampling elevation, based on the height and nose position of the children, when a simple rack or tower is used.

Conclusions

Thermal desorption sampling techniques coupled with a mass spectrometry-based analytical method proved to be a sensitive

and precise approach for the qualitative and quantitative analysis of a broad range of indoor VOCs in air samples collected in child care centers. The technique demonstrated greater simplicity, and offered much higher detection sensitivity and recovery rates as compared to traditional analytical techniques. Furthermore, its suitability for the determination of organic analytes with a wide range of volatility and polarity has been validated by this pilot study. The developed sampling and analytical method has several advantages over conventional techniques for large-scale multi-position air quality monitoring studies at child care centers, due to the portability, affordability, and flexibility of the sampling technique.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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