



Measurement of in-vehicle volatile organic compounds under static conditions

YOU Ke-wei¹, GE Yun-shan^{1,*}, HU Bin², NING Zhan-wu², ZHAO Shou-tang²,
ZHANG Yan-ni², XIE Peng²

1. School of Mechanical and Vehicular Engineering, Beijing Institute of Technology, Beijing 100081, China. E-mail: awei810715@bit.edu.cn
2. Beijing Municipal Institute of Labor Protection, Beijing 100054, China

Received 28 December 2006; revised 28 February 2007; accepted 7 March 2007

Abstract

The types and quantities of volatile organic compounds (VOCs) inside vehicles have been determined in one new vehicle and two old vehicles under static conditions using the Thermodesorber-Gas Chromatograph/Mass Spectrometer (TD-GC/MS). Air sampling and analysis was conducted under the requirement of USEPA Method TO-17. A room-size, environment test chamber was utilized to provide stable and accurate control of the required environmental conditions (temperature, humidity, horizontal and vertical airflow velocity, and background VOCs concentration). Static vehicle testing demonstrated that although the amount of total volatile organic compounds (TVOC) detected within each vehicle was relatively distinct (4940 $\mu\text{g}/\text{m}^3$ in the new vehicle A, 1240 $\mu\text{g}/\text{m}^3$ in used vehicle B, and 132 $\mu\text{g}/\text{m}^3$ in used vehicle C), toluene, xylene, some aromatic compounds, and various C₇–C₁₂ alkanes were among the predominant VOC species in all three vehicles tested. In addition, tetramethyl succinonitrile, possibly derived from foam cushions was detected in vehicle B. The types and quantities of VOCs varied considerably according to various kinds of factors, such as, vehicle age, vehicle model, temperature, air exchange rate, and environment airflow velocity. For example, if the airflow velocity increases from 0.1 m/s to 0.7 m/s, the vehicle's air exchange rate increases from 0.15 h⁻¹ to 0.67 h⁻¹, and in-vehicle TVOC concentration decreases from 1780 to 1201 $\mu\text{g}/\text{m}^3$.

Key words: volatile organic compounds (VOCs); in-vehicle trim material; static conditions

Introduction

In recent years, the problem of air quality inside the vehicle has become a major concern to people's health. High concentrations of VOCs in the auto-cabin can cause sensory irritation and memory impairments in people, showing that in-vehicle air pollution has become a safety issue for society. Generally speaking, the sources of in-vehicle air pollution include in-vehicle trim material emissions, taking in of outdoor air contaminants and other pollution sources.

Volatile organic compounds associated with in-vehicle trim material emissions include the emission from in-vehicle sealants, carpets, adhesives, paints, leather, plastics, and foam cushions. The main pollutants are benzene, xylene, toluene, formaldehyde, hydrocarbon, and so forth (USEPA, 1976a, b; Akland and Ott, 1987; Brown and Cheng, 2000). Yet, there is scant information concerning in-vehicle trim material emission during static (when the vehicle's engine is off) conditions, an important indoor environment for today's consumer. Fedoruk and Kerger (2003) examined a broader profile of VOCs in the passenger cabin of selected sedan automobiles under static conditions, and the data suggested that the alkyl benzene

pattern was the main pollutant inside vehicles under static conditions. Dropkin (1985) provided some data of in-vehicle VOC emissions, but this study focused primarily on nitrosamine emissions. Grabbs *et al.* (1999) screened four new cars in the USA, all after being closed for one hour. The initial VOC concentrations were approximately 300–600 $\mu\text{g}/\text{m}^3$. However, air sampling in all these published investigations were conducted outdoors or in uncontrolled test conditions. As various kinds of environment factors, such as temperature, humidity, and airflow velocity can influence test results, the in-vehicle pollutants concentration would change a lot when the testing environment change, and finally, result in bad data reproducibility. Yoshida and Matsunaga (2006) also reported that for most of the aliphatic hydrocarbons, the interior concentrations were the same levels as the outdoor concentrations in winter, but in summer, the interior concentrations were higher than the outdoor ones.

Taking in of outdoor air contaminants usually occurs when the vehicle is being driven, and this kind of pollution becomes much more obvious when traffic is heavy. Several investigators have measured in-vehicle VOC concentrations during driving conditions. The main pollutants include hydrocarbon, carbon monoxide, sulfur dioxide, nitrogen oxides, particulate matter, and so forth (Chan *et al.*, 1991; Lofgren *et al.*, 1991; Lawryk and Weisel, 1996;

*Corresponding author. E-mail: geyunshan@bit.edu.cn.

www.jesc.ac.cn

Leung and Harrison, 1999; Chan and Chung, 2003). In these studies, the VOC concentrations inside the vehicle were found to be greatly dependent on driving modes and traffic density, and accordingly, lack of data reappearance. Increased driving speeds led to greater air turbulence and hence more dispersion of pollutants. Heavy traffic problems result in poor air quality in the city, and subsequently cause more serious in-vehicle air pollution problems.

Other sources that affect interior vehicle odors and VOC levels include tobacco smoke, spills of chemicals within the vehicle, climate and altitude change, as well as potential microbial VOC emissions in some instances (Leung and Harrison, 1999; Xie *et al.*, 2003).

The purpose of the current study is to acquire in-vehicle VOC patterns and concentrations under a uniform environment condition, that is, when vehicle is in a static (vehicle's engine is off) condition, and accordingly evaluate the level of air quality inside vehicles. Also, the influence of various kinds of factors, such as vehicle age, vehicle model, temperature, air exchange rate, and environment airflow velocity is discussed in this article.

1 Experimental methods

1.1 Vehicles under study and their pretreatment

The vehicles under study include one new vehicle (named as vehicle A in the following paragraphs) and two old vehicles (named as vehicle B and vehicle C, respectively, in the following paragraphs). Vehicle A and vehicle B are of the same model, except that vehicle A is a new car and vehicle B has been used for no more than one year. Vehicle C is another model, which has been used for approximately five years. All vehicles are well maintained and in good operating condition. Before the test, the following vehicle pretreatments are made: (1) all vehicles are subjected to a detailed mechanical inspection, to verify the absence of any fuel leaks or mechanical problems that could lead to unusual accumulation of exhaust or fuel vapors in the cabin of the vehicle; (2) the covering films (e.g. plastic film, etc.) on the surfaces of vehicle's trim materials were ripped off; (3) the exhaust pipe was wrapped with materials to avoid a hydrocarbon leak during the test.

1.2 Environment test chamber

As many factors can affect in-vehicle VOC concentrations, a room-size, environment test chamber that could provide stable and accurate control of the required environmental conditions was utilized in this test. The size of the chamber was 8 m × 4 m × 3 m, and the exterior surface of the chamber was constructed with stainless steel, which could minimize adsorption and emission of VOCs. The chamber heating, ventilation, and air conditioning (HVAC) system could provide the required environmental conditions, such as temperature, pressure, relative humidity, and airflow velocity, according to set parameters. The clean air supplied to the chamber would be preconditioned by passing the air through a particulate filter, a desiccant

dehumidifier, and activated carbon filters, to reduce the influence of background VOCs on the in-vehicle air quality. On account of the fact that the airflow velocity could affect the vehicle's air exchange rate, and sequentially affect the test result of the in-vehicle VOC concentrations, the chamber's horizontal airflow velocity (at the height of 1.2 m from the chamber's floor) was controlled at no more than 0.3 m/s, and the vertical airflow velocity (at the height of 1.2 m from the chamber's floor) was controlled at no more than 0.5 m/s, to minimize the airflow influence.

Figure 1 shows in-vehicle air sampling in the environment test chamber, Teflon tubing (10 dia.) was used as the sampling line and a small length of silicon tube was used for the joints. The Teflon tubing was led outdoors from the upper corner of the vehicle's door, and the length between the sampling device and the sampling location was no more than 3 m. In this way, the sampling process could be done out of the chamber, thus eliminating the influence of the operator activities on the testing results, and moreover, shorter Teflon tubing could reduce the effect of the VOC adsorption/desorption on the sampling line during the measurement. The Teflon tube was reused after being cleaned with pure nitrogen gas. The sampling position inside the vehicle was set in the middle of the front two headrests, 20 cm away from the car roof to simulate the height of the driver's breathing zone.

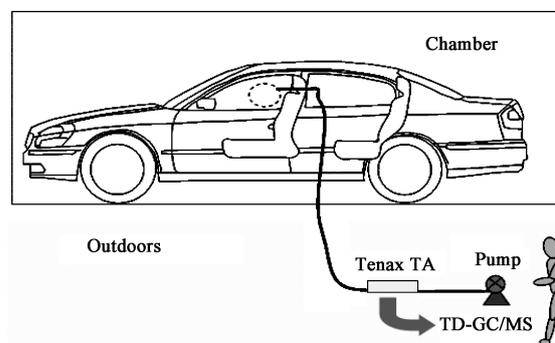


Fig. 1 In-vehicle air sampling in the environment test chamber.

1.3 Vehicle test protocol

A consistent test protocol was utilized with the vehicles when sampling the interior air. This protocol was as follows:

(1) The vehicle was moved (the engine was off) to the environment test chamber, and then the chamber door was closed.

(2) The chamber environmental conditions were adjusted to set parameters, and these environmental conditions were kept for the whole test duration: environment temperature: $25 \pm 0.5^\circ\text{C}$; relative humidity: $(50 \pm 10)\%$; horizontal airflow velocity (at the height of 1.2 m from the chamber floor): ≤ 0.3 m/s; vertical airflow velocity (at the height of 1.2 m from the chamber's floor): ≤ 0.5

m/s; background TVOC concentration: $\leq 100 \mu\text{g}/\text{m}^3$; it was aired with vehicle doors and windows open, for 8 h, to make a good mixture inside/outside vehicle; it was left closed for 16 h so that the vehicle could reach a steady state pollutant concentration in this period; in-vehicle air samples were collected from the middle of the front two headrests, 20 cm away from the car roof, and concurrently outside the vehicle at approximately a 2-m distance; in the course of whole test procedure, the temperature and humidity in the chamber were auto-monitored with the help of a temperature and humidity sensor, to satisfy the required parameters.

1.4 Air sampling and analysis

Air sampling and analysis was conducted under the requirement of the EPA Method TO-17 (USEPA, 1999). Pairs of sorbent tubes were used for in- and out-vehicle sampling. In-vehicle sampling position was set in the middle of the front two headrests, 20 cm away from the car roof, and simultaneously the out-vehicle sample was also collected for blank analysis. Air samples were taken by active sampling, using controlled flow pumps at a rate of 100 ml/min for 30 min. Air was drawn through a stainless steel tube packed with Tenax TA (60–80 mesh). Total sampling volumes were 3 L.

The TD-GC/MS method was employed for identification and quantification of in-vehicle VOC emissions. Sorbent tubes were thermally desorbed by a Perkin-Elmer TurboMatrix Thermal Desorber. This involved eluting the sorbent tube at a temperature of 270°C for 3 min. The desorbed compounds were cryogenically focused in a cold trap at -30°C . After focusing, the trap underwent rapid heating to 280°C, to volatilize the compounds into the gas chromatograph (GC) capillary column through a fused-silica line heated at 250°C. A summary of the equipment parameters is presented in Table 1.

Compounds were identified from their mass spectral data by using the US National Institute of Standards and Technology (NIST). As for benzene, toluene, butyl acetate, ethylbenzene, *p,m*-xylene, *o*-xylene, styrene, and undecane, identifications were confirmed from their chromatographic retention times by using standard compounds, and external standard methods were utilized to make the linear standard curve for quantitative analysis. As for other compounds, the respond factor of toluene was used for concentration calibration. The TVOC concentration was calibrated by identifying as many compounds as possible, particularly those representing the 20 highest peaks and those present at concentrations above $5 \mu\text{g}/\text{m}^3$ between *n*-hexane and *n*-hexadecane.

2 Results and discussion

2.1 Types and quantities of VOCs

Table 2 shows the concentration ($\mu\text{g}/\text{m}^3$) of eight confirmed analytes measured inside three vehicles, and Table 3 presents the concentration ($\mu\text{g}/\text{m}^3$) of the top 20 compounds measured inside three vehicles (unconfirmed compounds were calculated in toluene equivalent). Although the amount of TVOC detected within each vehicle was relatively distinct, toluene, xylene, some aromatic compounds, and various C_7 – C_{12} alkanes were among the predominant VOC species in all the three vehicles tested. These benzene derivatives were common in paints, sealants, carpets, and adhesives used for interior trim material. Styrene, a residue of styrene-butadiene-rubber (SBR) latex glue, was used in the manufacturing of carpets. In addition, tetramethyl succinonitrile, possibly derived from foam cushions was detected in vehicle B.

2.2 Vehicle age influence on VOC concentrations

Vehicle age affects the VOC concentrations. Generally speaking, the in-vehicle VOC concentrations decrease significantly as time goes on, and a used vehicle will have less VOCs than a new one, because of the ventilation after delivering to the customer from the product line. As shown in Fig.2a, vehicle A and vehicle B have the same model, but the TVOC level observed in vehicle A (new vehicle) was about four times that of vehicle B (one year old), and was about forty-fold higher than vehicle C (five years old). Fig.2b illustrates that the number of identified compounds is 82 in vehicle A, 61 in vehicle B, and only 36 in vehicle C.

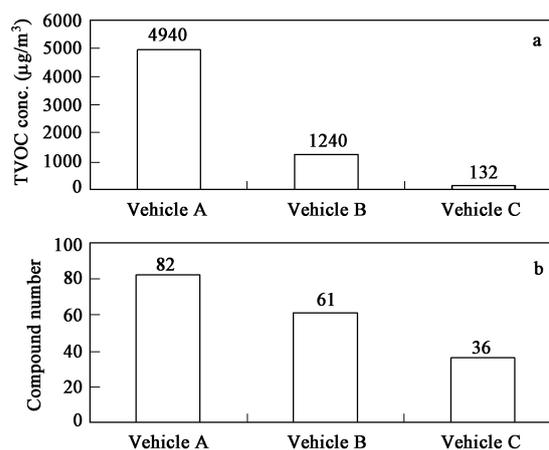


Fig. 2 Influence of vehicle age on TVOC concentration (a) and identified compounds number (b).

Table 1 TD-GC/MS parameters

Thermal desorber	Tube: 270°C (3 min); purge: 1 min; cryotrap: from -30°C at 40°C/s to 280°C (3 min); column pressure: 8.5 psi; split ratio (50:1)
Gas chromatograph (GC)	Capillary column: Rtx-1 (30 m \times 0.25 μm \times 0.25 mm); carrier gas: helium (99.999%); oven temperature program: from 35°C (10 min) at 5°C/min to 250°C
Mass spectrometer (MS)	Transfer line to MS: 250°C; ion source: electron impact (EI); ion source temperature: 200°C; solvent cut time: 2.5 min; scan mode: SCAN; m/z : 35–450 amu; electron multiplier voltage: 1.0 kV; NIST02 library

Table 2 Concentration of eight confirmed analytes measured inside three vehicles

Compound	Conc. in vehicle A ($\mu\text{g}/\text{m}^3$)	Conc. in vehicle B ($\mu\text{g}/\text{m}^3$)	Conc. in vehicle C ($\mu\text{g}/\text{m}^3$)
Benzene	48	10.0	2.4
Toluene	82	50.0	32.2
Ethylbenzene	85	9.9	3.5
<i>p,m</i> -Xylene	346	20.0	10.2
<i>o</i> -Xylene	95	9.9	3.3
Styrene	155	9.8	2.3
Undecane	40	130	9.3
Butyl acetate	225	0	2.3

2.3 Vehicle model influence on VOC concentrations

Fig.3 illustrates the distributing character of aromatic, alkanes, and alkenes inside the three vehicles that were in static condition. The ration of aromatic, alkanes, and alkenes to TVOC is approximately the same between vehicle A and vehicle B (predominated by alkanes), whereas, vehicle C reveals a fairly distinct VOC profile (predominated by aromatic compounds). Fig.4 illustrates the distributing character of BTEX (benzene, toluene, ethylbenzene, and xylene) inside the three vehicles. The concentration ratio of toluene and xylene to TVOC inside vehicle C is much higher than inside vehicle A and vehicle B. Considering that vehicle A and vehicle B have the same model, except that vehicle A is a new car and vehicle B has been used for no more than one year, and vehicle C is another model, these data suggest that the vehicle model has a great influence in VOC profiles.

2.4 Temperature influence on VOC concentrations

It has been commonly found that temperature is one of the most important factors that influence test results. As shown in Fig.5, the concentration level of TVOC and

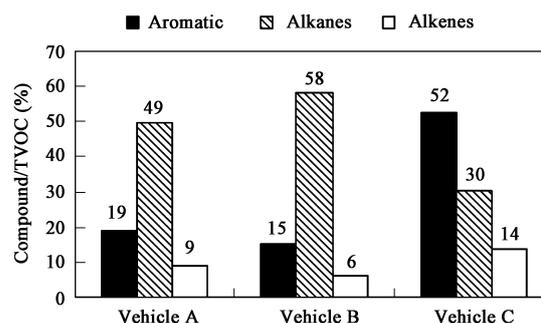


Fig. 3 Distributing character of aromatic, alkanes, and alkenes inside the three vehicles.

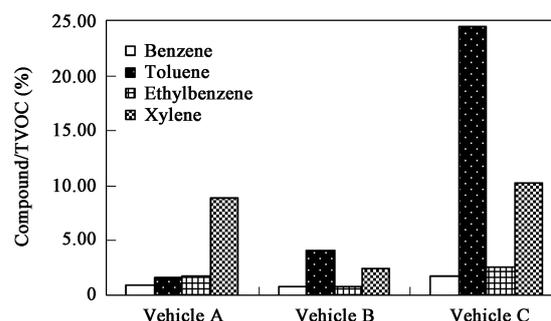


Fig. 4 Distributing character of BTEX inside the three vehicles.

toluene in the auto-cabin increases sharply when temperature rises from 25°C to 60°C. High temperature can be helpful for the evaporation of more VOCs in the material, for the main reason that the release amount of such volatile compositions as organic solvents, adhesives and additives contained in the interior trim material can increase more when in-vehicle temperature rises.

Table 3 Concentration of the top 20 compounds measured inside three vehicles (unconfirmed compounds were calculated in toluene equivalent)

Rank	Vehicle A (new car)		Vehicle B (one year old)		Vehicle C (five years old)	
	Compound	Conc. ($\mu\text{g}/\text{m}^3$)	Compound	Conc. ($\mu\text{g}/\text{m}^3$)	Compound	Conc. ($\mu\text{g}/\text{m}^3$)
1	Decane	345	Dodecane	163.4	Toluene	32.2
2	Nonane	341	Undecane	130.0	<i>d</i> -Limonene	14.4
3	5-Isopropyl-2-methyl-bicyclo[3.1.0]hexan-2-ol	314	Decane	89.3	Butylated hydroxytoluen	14.1
4	Cyclohexanone	301	1-Chloro-2-dodecyl-oxyethane	81.8	<i>p,m</i> -Xylene	10.2
5	Tetrachloroethylene	242	Tetradecane	77.8	Undecane	9.3
6	α -Pinene	200	5-Ethyl-2-methyloctane	52.6	Decane	8.1
7	3-Methylhexane	199	2,4-Dimethyl-1-decene	52.1	Dodecane	6.4
8	Heptane	188	Toluene	50.0	Bicyclo[3.1.1]hept-2-ene	4.2
9	3-Methylheptane	170	Naphthalene	49.3	5-Propyldodecane	4.1
10	2-Methylheptane	134	Tetramethyl succinonitrile	40.1	2-Methyltridecane	4.0
11	Octane	127	<i>trans</i> -Bicyclo[4.4.0]Decane	35.5	Ethylbenzene	3.5
12	Methylcyclohexane	122	1-Chloroundecane	22.7	<i>o</i> -Xylene	3.3
13	2,7-Dimethyloctane	112	2,6-di- <i>tert</i> -butyl- <i>p</i> -Cresol	20.5	1,3,5-Trimethylbenzene	3.1
14	3-Methylnonane	107	<i>p,m</i> -Xylene	20.0	Benzene	2.4
15	2-Methylhexane	105	Nonane	18.3	Butyl acetate	2.3
16	4-Methyloctane	96	Hexanal	15.7	Styrene	2.3
17	2,5-Dimethyl-2-undecene	90	2,6-dimethyl-2-Octene	15.1	2,4-Dimethylpentane	2.1
18	2,5-Dimethyloctane	86	2,2-dimethyl-Propanal	13.2	Nonane	2.0
19	Toluene	82	1,2-Dichloro-ethane	11.8	2-Bromooctane	1.9
20	Cyclohexane	70	Benzene	10.0	2-Methylhexane	1.2
	TVOC	4940	TVOC	1240.0	TVOC	132.8

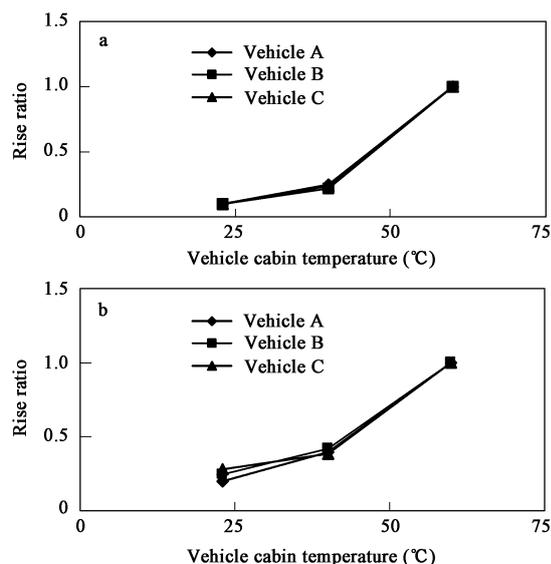


Fig. 5 Influence of temperature on TVOC concentration (a) and toluene concentration (b).

2.5 Environment airflow velocity influence on VOCs concentration

Environment airflow velocity can affect the vehicle's air exchange rate, and sequentially affect the test result of in-vehicle VOC concentration. High environment airflow velocity can accelerate the air exchange rate inside/outside the vehicle. To determine the impact of airflow velocity on VOC concentrations, the vehicle air exchange rate and in-vehicle VOC concentrations were measured under different airflow velocities. The vehicle's air exchange rate was determined by introducing a small amount of CO₂ gas into the vehicle. The concentration of the tracer gas was measured continuously. The absolute value of the slope of the concentration decay curve on a semi-log scale plot was the air exchange rate, because of the air leakage inside vehicle.

Table 4 shows the relationship between environment airflow velocity, air exchange rate, and in-vehicle TVOC concentration of vehicle B. When the airflow velocity increases from 0.1 to 0.7 m/s, the vehicle's air exchange rate increases from 0.15 h⁻¹ to 0.67 h⁻¹, and the in-vehicle TVOC concentration decreases from 1780 to 1201 µg/m³.

Table 4 Relationship between environment airflow velocity, air exchange rate, and in-vehicle TVOC concentration

Airflow velocity (at the height of 1.2 m) (m/s)	Air exchange rate (h ⁻¹)	TVOC concentration (µg/m ³)
0.1	0.15	1780
0.3	0.41	1400
0.7	0.67	1201

3 Conclusions

Although the current study is limited in terms of the number of vehicles, the following general conclusions can be drawn.

High concentrations of VOCs are found inside vehicles, especially new vehicles that reach the market soon after manufacture, showing that the pollution caused by a new vehicle's interiors may be a safety issue.

As many factors could affect in-vehicle VOC concentration, a room-size environment test chamber that could provide stable and accurate control for the required environmental conditions was utilized in this test. Static vehicle testing demonstrated that although the amount of TVOC detected within each vehicle was relatively distinct (4940 µg/m³ in new vehicle A, 1240 µg/m³ in used vehicle B, and 132 µg/m³ in used vehicle C), toluene, xylene, some aromatic compounds, and various C₇–C₁₂ alkanes were among the predominant VOC species in all three vehicles tested.

The types and quantities of VOCs varied considerably according to various kinds of factors, such as vehicle age, vehicle model, temperature, air exchange rate, and environment airflow velocity. For example, high temperature can be helpful for the evaporation of more VOCs from the in-vehicle trim material, and new vehicles have more VOCs than old ones, because of the ventilation after delivering to the customer, and so on.

References

- Akland G, Ott W, 1987. Human exposure assessment: background concepts, purpose and overview of the Washington, DC-Denver, CO field studies[C]. Paper presented at the 77th Annual Meeting of the Air Pollution Control Association.
- Brown S K, Cheng M, 2000. Volatile organic compounds (VOCs) in new car interiors[C]. The 15th International Clean Air & Environment Conference, Nov 26–30, 2000, Sydney, CASANZ, 464–468.
- Chan A T, Chung M W, 2003. Indoor-outdoor air quality relationships in vehicle: Effect of driving environment and ventilation modes[J]. *Atmospheric Environment*, 37: 3795–3808.
- Chan C C, Spengler J D, Ozkaynak H *et al.*, 1991. Commuter exposures to VOCs in Boston Massachusetts[J]. *Journal of Air Waste Manage Association*, 41: 1594–1600.
- Dropkin D, 1985. Sampling of automobile interiors for organic emissions[S]. U.S. Environmental Protection Agency. EPA-600/3-85/008.
- Fedoruk M J, Kerger B D, 2003. Measurement of volatile organic compounds inside automobiles[J]. *Journal of Exposure Analysis and Environmental Epidemiology*, 13: 31–41.
- Grabbs J S, Corsi R L, Torres V M, 1999. A screening assessment of volatile organic compounds in the interior of new automobiles[C]. Proceedings of First NSF International Conference on Indoor Air Health, 3–5 May 1999, Denver, NSF International.
- Lawryk N J, Weisel C P, 1996. Concentration of volatile organic compounds in the passenger compartment of automobiles[J]. *Environ Sci Technol*, 30: 810–816.
- Leung P L, Harrison R M, 1999. Roadside and in-vehicle concentrations of monoaromatic hydrocarbons[J]. *Atmospheric Environment*, 33: 191–204.
- Lofgren L, Persson K, Stromvall A M, 1991. Exposure of commuters to volatile aromatic hydrocarbons from petrol exhausts[J]. *Science of Total Environment*, 108: 225–233.

- Xie J, Wang X, Sheng G *et al.*, 2003. Determination of tobacco smoking influence on volatile organic compounds constituent by indoor tobacco smoking simulation experiment[J]. *Atmospheric Environment*, 37: 3365–3374.
- USEPA (U.S. Environmental Protection Agency), 1976a. Sampling of automobile interiors for vinyl chloride monomer[S]. EPA Office of Research and Development, Industrial Environmental Research Laboratory, EPA-600/2-76-124.
- USEPA (U.S. Environmental Protection Agency), 1976b. Organic emission from automobile interior[S]. Interagency Energy Environment Research and Development Program Report. December (1977), EPA-600/7-77-149.
- USEPA (U.S. Environmental Protection Agency), 1999. Compendium Method TO-17 determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes[S]. U.S. EPA Technical Assistance Document. EPA/625/R-96/010b.
- Yoshida T, Matsunaga I, 2006. A case study on identification of airborne organic compounds and time courses of their concentrations in the cabin of a new car for private use[J]. *Environment International*, 32: 58–79.