

## Chemical fingerprinting of volatile organic compounds from asphalt binder for quantitative detection

Chang, Xiwen; Long, Yongshuang; Wang, Chen; Xiao, Yue

**DOI**

[10.1016/j.conbuildmat.2023.130766](https://doi.org/10.1016/j.conbuildmat.2023.130766)

**Publication date**

2023

**Document Version**

Final published version

**Published in**

Construction and Building Materials

**Citation (APA)**

Chang, X., Long, Y., Wang, C., & Xiao, Y. (2023). Chemical fingerprinting of volatile organic compounds from asphalt binder for quantitative detection. *Construction and Building Materials*, 371, Article 130766. <https://doi.org/10.1016/j.conbuildmat.2023.130766>

**Important note**

To cite this publication, please use the final published version (if applicable). Please check the document version above.

**Copyright**

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

**Takedown policy**

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

***Green Open Access added to TU Delft Institutional Repository***

***'You share, we take care!' - Taverne project***

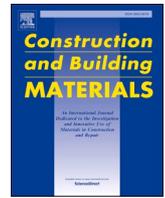
**<https://www.openaccess.nl/en/you-share-we-take-care>**

Otherwise as indicated in the copyright section: the publisher is the copyright holder of this work and the author uses the Dutch legislation to make this work public.



Contents lists available at ScienceDirect

# Construction and Building Materials

journal homepage: [www.elsevier.com/locate/conbuildmat](http://www.elsevier.com/locate/conbuildmat)

## Chemical fingerprinting of volatile organic compounds from asphalt binder for quantitative detection

Xiwen Chang<sup>a</sup>, Yongshuang Long<sup>a</sup>, Chen Wang<sup>b</sup>, Yue Xiao<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China

<sup>b</sup> Civil Engineering and Geosciences, Delft University of Technology, Delft 2628CN, The Netherlands

### ARTICLE INFO

#### Keywords:

Asphalt VOCs  
Quantitative analysis  
Fingerprint components  
Release characteristic  
VOCs dependency

### ABSTRACT

Asphalt material is an irreplaceable material in road construction. However, it releases VOCs (Volatile Organic Compounds), which do cause pollution to the surrounding environment, during its full life cycle, especially in high-temperature paving stage and summer service time. Asphalt VOCs release mechanism and effective emission reduction technologies are therefore urgently needed. The chemical analysis of VOCs from asphalt binder always invariably excludes a vast number of compounds of unknown relevance, making the quantitative analysis lower data accuracy. In order to address this problem, fingerprint database was developed and introduced in this study, with the detected VOCs data from 104 kinds of asphalt binders. The analysis parameters, including fingerprint components and calibration curves were optimized through quantitative study. With the help of a self-developed fingerprint database, the calculation formulas of single VOC and total released VOCs were established for quantitative analysis of VOCs from asphalt binder. In addition, the influencing mechanism of heating temperature and asphalt types on VOCs volatilization characteristic were explored to achieve emission reduction in asphalt industry.

### 1. Introduction

Asphalt materials are widely used in road construction for low noise and comfortable traffic driving [1,2]. Huge asphalt usage confirms that there will be much serious environmental pollution to be solved [3].

Asphalt materials are often heated to more than 150 °C to make it easy for mixing with aggregates in engineering. There are a large number of volatile organic compounds (VOCs, Volatile Organic Compounds) [4] and black smoke particles [5,6] released from asphalt materials during heating, mixing, paving in road construction. In addition, there is still some volatilization escaping slowly during road service stage due to the influences of weather and environment. In general, asphalt material can be regarded as a VOCs source during its full life cycle. These VOCs will be a sustainable and serious harm to the environment, construction workers' health and economy on a global scale [7].

In addition to the environmental pollution caused by asphalt VOCs, the odor in the air is serious due to sulfides. Asphalt binder contains complex components, including high molecular hydrocarbons and their derivatives of non-metallic elements (such as O, N, S) [8], which means that high temperature makes VOCs more complex. Polycyclic aromatic

hydrocarbons (PAHs) are one type of the most toxic asphalt VOCs, which are considered as human carcinogens. Their toxicity increases with the number of benzene rings. For construction workers, long-term exposure to PAHs and sulfides will cause extremely strong damage to nerve center [9,10], eyes and respiratory, such as bronchitis, even asphyxiation [11]. For the environment, the volatilization of VOCs into atmosphere will lead to environmental problems such as acid rain and global warming. Smoke particles will also escape from asphalt with VOCs, such as PM<sub>2.5</sub>, which will aggravate smog and other pollution problems. Therefore, it is urgent to explore volatilization mechanism firstly to achieve higher asphalt VOCs reduction.

Many researchers have studied asphalt VOCs by different testing methods. Some researchers have collected VOCs in actual construction site for detection analysis. Brandt Martin H. et al [12] collected and estimated the total emissions during construction by Flame Ionization Detector. Paniz Possebon E. et al [13] used electron capture detector to collect VOCs and quantify amounts of PAHs by Liquid Chromatography-Mass Spectrometry. Cui P. et al [14] found out that volatile components include toluene, m-xylene, butanone and n-hexane, and used photo ionization detector (PID) to analyze the concentration of VOCs around workers. At the same time, a health risk assessment model based on

\* Corresponding author.

E-mail address: [xiaoy@whut.edu.cn](mailto:xiaoy@whut.edu.cn) (Y. Xiao).

<https://doi.org/10.1016/j.conbuildmat.2023.130766>

Received 3 April 2022; Received in revised form 30 January 2023; Accepted 15 February 2023

Available online 24 February 2023

0950-0618/© 2023 Elsevier Ltd. All rights reserved.

**Table 1**  
Basic Performance of Asphalt Materials.

Basic Performance	70A	70B	90A	90B	SBS
Penetration (25 °C, 100 g, 5 s)/0.1 mm	68	67	92	97	75
Softening Point/ °C	46	46	45	44	60
Ductility (5 cm/min, 15 °C/5 °C)/cm	>100	>100	>100	>100	30.8
Density (15 °C)/g/cm <sup>3</sup>	1.03	1.02	0.93	0.98	1.00

Monte Carlo simulation was proposed to evaluate carcinogenic risks of workers during pavement construction.

Collecting VOCs in construction site is susceptible by external factors, as a result more and more researchers tended to simulate asphalt heating process in laboratory to improve the accuracy. Mo S.C. et al [15] analyzed total particles by Thermo-Gravimetric analysis and identified composition of VOCs by Gas Chromatography-Mass Spectrometry (GC-MS). They also compared the differences of VOCs amount and chemical composition between different asphalt binders and temperatures. Lei M. et al [16] characterized the VOC emission as a function of temperature by GC-MS. Cui P.Q. et al [17-19] explored some new equipment, including Thermo-Gravimetric Mass Spectrometry (TG-MS) and Ultraviolet Spectrophotometry (UV-Vis). Harrison E.K. [20], Liu X. J. [21] and others also used UV-Vis to draw the curve between quality with absorbance. GC-MS has good multi-component analysis capability, so more researchers started to combine GC-MS with other equipment to improve detection accuracy [22]. Yang X. et al [23] studied asphalt VOCs at 120, 140 and 160 °C respectively by Dynamic Headspace Gas Chromatography-Mass Spectrometry. Long Y.S. et al [24] reflected the release law of asphalt VOCs through the combination of pyrolysis gas chromatography-mass spectrometry (PY-GC-MS) and TG-MS. Borinelli J.B. et al [25] proposed a standardize measurements on a lab scale, Proton-Transfer Reaction Time-Of-Flight Mass Spectrometry (PTR-TOF-MS), to monitor VOCs emissions, which can analyze VOCs in real time at different production process.

These studies provide an important theoretical basis and method support for the study on asphalt VOCs release mechanism [26], but research data also show that owning no unified calculation method is a big obstacle to achieve quality analysis of asphalt VOCs in different temperatures and different asphalt binders.

Fingerprint components can be used as a reference standard for analysis [27-30]. "Fingerprint" originated from forensic medicine and can identify component characteristics through subtle differences. In modern medicine, "fingerprint" is widely used in traditional Chinese medicine [31,32] to analyze their characteristic and pathology [33]. In the field of material science, "fingerprint" frequently appears in Fourier transform infrared spectrometer to give the information of measured material [34,35]. Sometimes, fingerprint region is more complex and difficult to identify, but it can sensitively reflect the material information [36]. Defining fingerprint components of asphalt VOCs and establishing fingerprint database can provide a unified quantitative evaluation system for calculating VOCs from different researches.

In this paper, specimen location and temperature dependency of asphalt VOCs were analyzed to explore the VOCs release mechanism, including VOCs composition and release amount. Based on the VOCs data from 104 kinds of asphalt binders, asphalt fingerprint VOCs were defined to for an accurate and unified analysis. The calculation formulas of individual component and total components of asphalt VOCs were established to provide the data basis for follow-up research on VOCs reduction.

**2. Materials and method**

**2.1. Materials**

The asphalt production techniques will influence the asphalt VOCs. Five asphalt binders, produced from the same plant with the same production techniques were first analyzed to establish the VOCs release mechanism. The studied SBS asphalt binder was produced with 90A binder and SBS modifier with linear structure. Physical parameters of five kinds of asphalt in this study are shown in Table 1. The penetrations of the five asphalt binders are different, in which asphalt 70A and 70B represent two types of Pen 60/80 asphalt binder, asphalt 90A and 90B are two types of Pen 80/100 asphalt binder, while asphalt SBS represents SBS modified asphalt.

**2.2. Research methodologies**

This study adopts two parallel testing schemes to explore the similarities and differences between the results when the sampling amount is small and sufficient. Two different detection technologies were used to establish an effective analysis method for asphalt VOCs.

**2.2.1. Research program**

Fig. 1 shows the detail technical scheme of this study. Firstly, the optimization of GC-MS analysis was conducted by two parallel testing detection, PY-GC-MS and TD-GC-MS. In PY-GC-MS test, the VOCs from asphalt at different depths is analyzed. It can simulate with or without air contact during heating and explore volatilization capacity of asphalt at different depths. In PY-GC-MS test, asphalt from 12 different sampling depths were heated to 180 °C. The VOCs were analyzed to explore the volatilization capacity of asphalt at different depths. It can simulate the volatilization capacity of asphalt with or without air contact during heating. The data shows the volatilization of asphalt blocks is related to depth. In TD-GC-MS test, 100 g of asphalt binder was heated to different temperatures to simulate the whole heating process. VOCs release in this state was detected to summarize volatilization law of asphalt VOCs in different temperatures. Secondly, fingerprint components of asphalt VOCs were proposed for unified quantification of asphalt VOCs. In total 104 asphalt binders, with different source location, production process and physic properties, were included to finalize the fingerprint components. Based on the linear relationship between concentration and peak

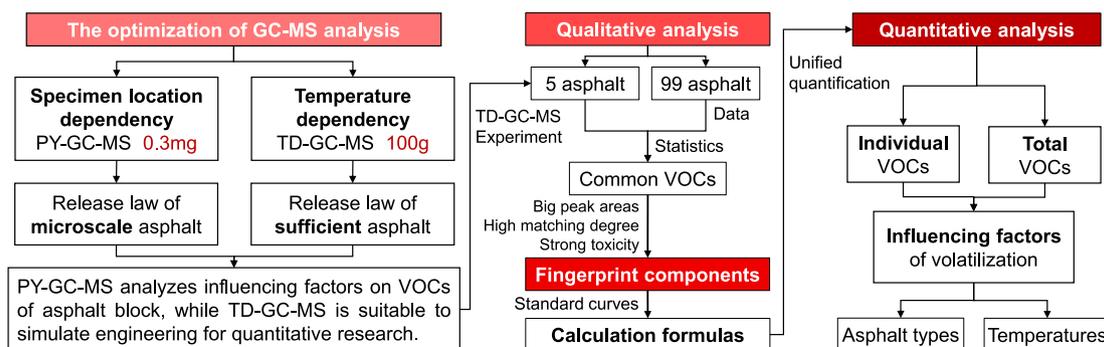


Fig. 1. Detailed technical scheme.

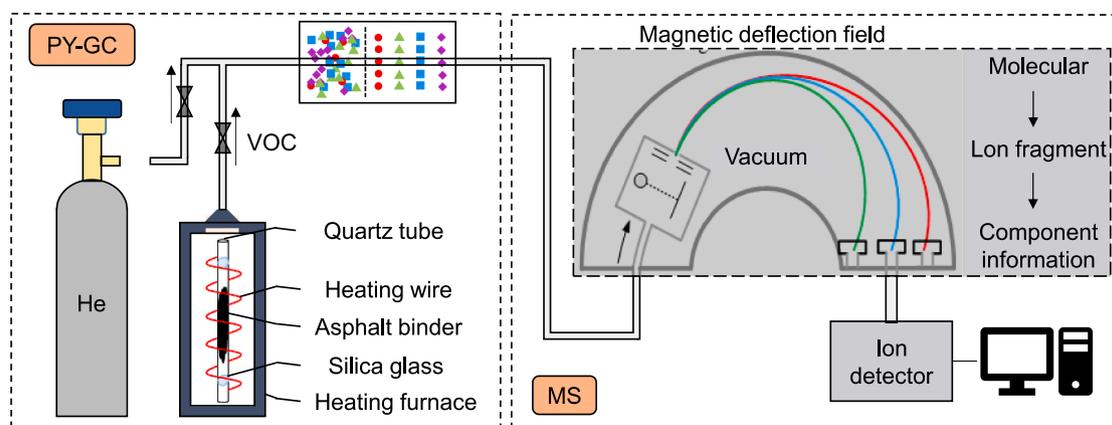


Fig. 2. Detected diagram of specimen location dependency.

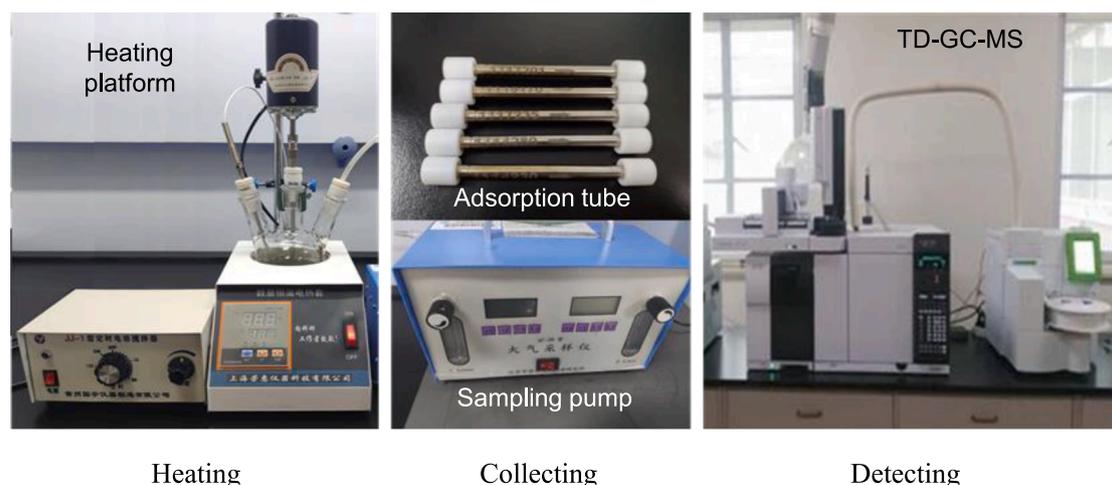


Fig. 3. TD-GC-MS equipment.

area, the standard curve of fingerprint components was drawn. With the help of fingerprint components and their corresponding standard curves, the calculation formulas of individual component and total components were established. Finally, TD-GC-MS analyze the VOCs released from five different sources (asphalt 70A, 70B, 90A, 90B and SBS) at four different heating temperatures (50, 100, 130 and 160 °C). According to the calculation formula, VOCs amounts of independent components and total components were calculated quantitatively.

Based on the whole technical scheme, the steps can be divided into three steps: optimization of detection method, fingerprint components and quantitative analysis.

## 2.2.2. Optimization of detection method

### 2.2.2.1. Specimen location dependency.

Previous study indicated that VOCs characteristics were significantly affected by the specimen itself [37]. Specimens from different positions of the same asphalt binder would result in far different VOCs characteristics. Therefore, the specimen location dependency was studied by comparing VOCs information of 12 specimens from different depth of an asphalt binder block which is 10 cm × 6 cm × 3 cm. There are three sampling variables, including specimen location, depth and weight. The sample locations are divided into three categories: middle, corner and edge of the asphalt block. Sampling depth are from surface to 15 mm inside, as shown in Appendix Table A1. The sample weight is varying from 0.1 mg to 0.29 mg. In order to ensure the consistency of the experiment, the sampled asphalt was uniformly coated on the inner wall of the quartz tube.

Fig. 2 shows the detection diagram of PY-GC-MS. The sample was rapidly heated to 180 °C at the rate of 10 °C/s by PY system. With the high heating rate and micro sample weight, VOCs generation by PY-GC-MS can be so quick and accurate that is not like the actual construction. However, due to the slow heating rate in normal construction, part of asphalt binder is heated higher than 160 °C. Therefore, in this experiment, a higher temperature, 180 °C, was selected for more accurate simulation of the actual situation. Then, the released VOCs were separated and detected by GC-MS system. The model number of PY-GC-MS used in this study is the ENTECH 7100-CDS 5150-Agilent 6890 N/5975 instrument produced by American Agilent company.

### 2.2.2.2. Testing temperature dependency.

Thermal Desorption Gas Chromatography-Mass Spectrometry (TD-GC-MS) was used to quantitatively analyze the asphalt VOCs, while the temperature dependence of asphalt VOCs was also analyzed.

An independent heating platform was set up to heat 100 g asphalt 70A sample to 50, 100, 130 and 160 °C respectively. The last three temperatures have 30 °C interval to explore the VOCs release rule at the same temperature interval. Meanwhile, 130 and 160 °C are actual construction temperatures of warm and hot mix. Since 50 °C is less than the boiling points of most asphalt VOCs, it was used to verify that VOCs volatilization at low temperature is mainly affected by its boiling point. The ATD (Automatic Tube Dispenser) tubes adsorbed VOCs and were desorbed and detected by TD-GC-MS. The effect of thermal temperature on the release of asphalt VOCs was analyzed according to the final chromatogram and mass spectrum. Equipment utilized in this study are

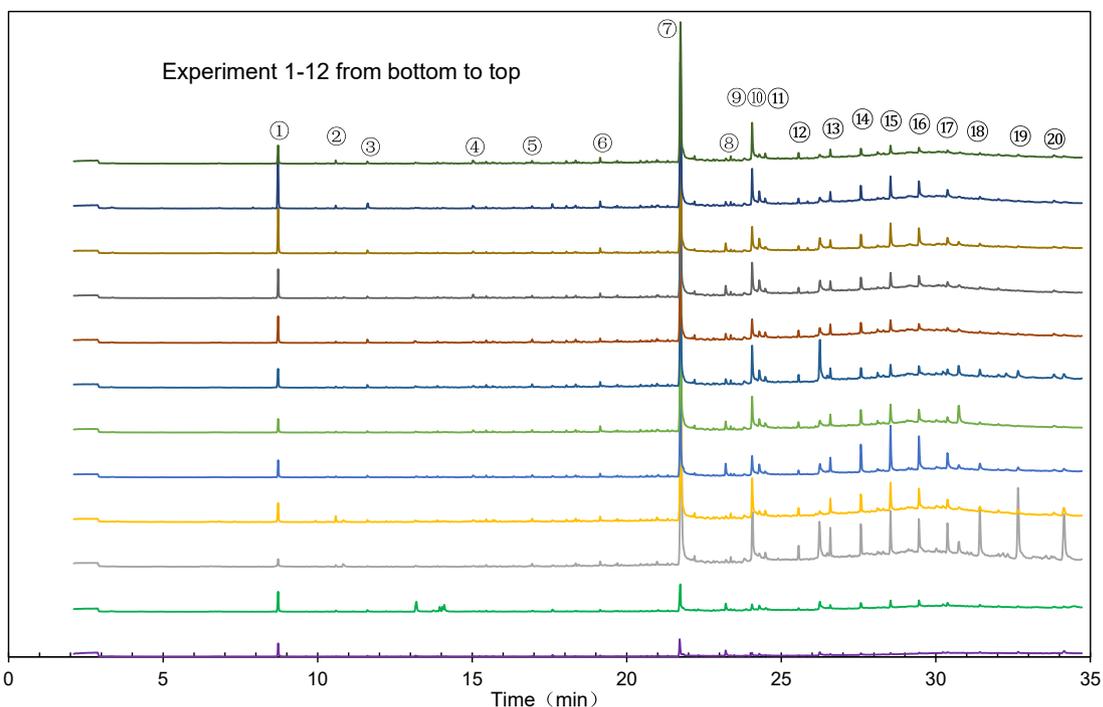


Fig. 4. Chromatograms of experiment 1–12 detected by PY-GC-MS.

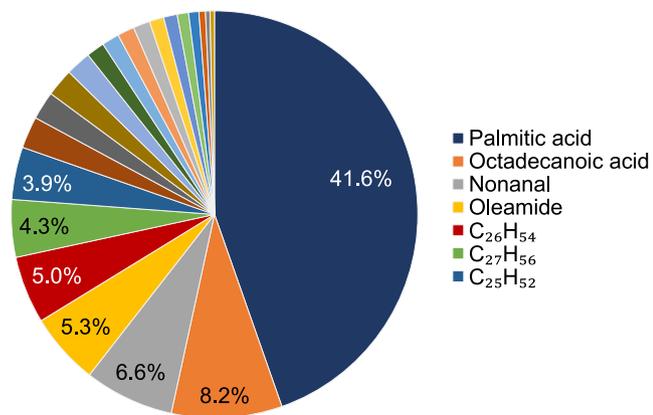


Fig. 5. The percentages of 20 components with bigger average peak areas.

shown in Fig. 3. The thermal desorption equipment used in this paper is Turbomatrix ATD 350, which is characterized by 50-tube automatic sampler and programmable gas path control. GC-MS is a product of Agilent Company, AtomxP&T-Agilent 7890B-5977B.

### 2.2.3. Fingerprint components

Generally, asphalt VOCs consist of more than one hundred types of components, while these components vary with different asphalt binders. Therefore, the fingerprint component of asphalt VOCs was defined, which summarizes the common characteristics of various VOCs for subsequent unified research. The data confirmed that the main VOCs components will not be significantly different although asphalts that having different raw materials and production processes. VOCs from different asphalts include unique components, but the release amounts of unique components are generally small, not the main volatiles of VOCs. Fingerprint components are proposed to represent the major components of asphalt VOCs. Verified by the volatilization data of 104 kinds of asphalt binders, fingerprint components can represent the main volatiles of asphalt. The fingerprint database can be established to guide

the quantification of asphalt VOCs.

The fingerprint components were selected from the VOCs released by 104 kinds of asphalt binders, of which 15 kinds are from the testing data of our experiments, and 89 kinds are the VOCs data of literatures, whose VOCs are under the actual construction temperature with a high qualitative accuracy. The selection of fingerprint components follows these four principles: ① they should have big chromatographic peak area, ② or higher matching degree of mass spectrometry, ③ or more toxic, ④ representative and can be found in asphalt VOCs as much as possible.

The peak area of the chromatogram analyzed by GC-MS is dimensionless, so the unconverted peak area does not represent the release amount. In this study, a linear relationship between the release amount of a single fingerprint component (x) and the chromatographic peak area (y) was constructed. A standard curve was drawn to provide a formula for the quantitative calculation of asphalt VOCs.

### 2.2.4. Quantitative analysis

Same as the method of temperature dependency experiment, 100 g asphalt 70A, 70B, 90A, 90B and SBS samples are heated to 50, 100, 130 and 160 °C respectively. VOCs are collected by ATD tubes and detected by TD-GC-MS. The amount of asphalt VOCs from different sources at different temperatures is calculated by the formula library to analyze the release law.

## 3. Results and analysis

In general, the substance with the highest matching degree of each peak is selected as the VOC component corresponding to this peak. The asphalt VOCs composition can be accurately analyzed through Mass-database, while the amount of asphalt VOCs can be quantitatively calculated by the peak areas of chromatogram.

### 3.1. GC-MS analysis optimization

#### 3.1.1. Specimen location dependency by PY-GC-MS

Twelve asphalt samples with different specimen locations were tested by PY-GC-MS. Substance volatilization can be compared by the

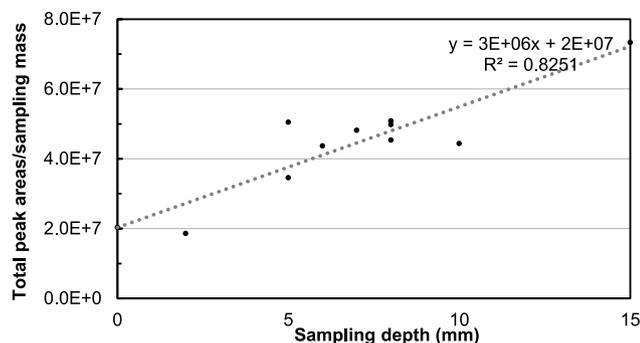


Fig. 6. Specimen location dependency fitting curve of total VOCs amount.

peak area. Specimen location dependency can be inferred by the relationship between VOCs amount and sampling depth.

Peak positions of the 12 chromatograms are basically the same, but their relative values are different, as illustrated in Fig. 4. Through Mass-database, 20 substances with the largest peak area in the 12 chromatograms were obtained, as shown in Appendix Table A2. There are 17 same substances among 12 chromatograms, most of them are long-chain alkanes and hydrocarbon derivatives. The other 3 substances are different, which are benzene series with low matching degree. Therefore, the sampling depth has little effect on the composition of asphalt VOCs, which means the VOC composition from asphalt binder is depth-independent.

Fig. 5 compares the average peak areas of the proportion of 20 substances. The pie chart shows that the peak area of palmitic acid accounts for 41.6%, which is much larger than that of other substances, followed by octadecanoic acid, nonanal and oleamide.

Fig. 6 shows the relation diagram between sampling depth and the peak area per unit sample mass (the total peak area divided by sample mass). All data points are uniformly distributed on both sides of the fitting line and the distance between them is small. The  $R^2$  value is 0.825, so it can be considered that there is a linear relationship between the peak area per unit sample mass and the sampling depth. It means that the VOC volatilization per unit mass of asphalt increases linearly with the increase of sampling depth.

Comparing the asphalt with the sampling depth of 0 mm (asphalt surface) and sampling depth of 15 mm, it is found that the VOCs amount of 15 mm depth is about 3.5 times as the surface emission. It indicated that asphalt surface had released VOCs during the service so that the

volatilization was much smaller than the inner asphalt binder.

Twenty linearly fitting curves of single component were drawn to study the specimen location dependency of individual component. K value is the slope of the curve. The larger the K value of is, the greater the variation of peak area per unit sample mass with the sampling depth is. The absolute increase rate of peak area to depth is defined as depth sensitivity coefficient  $D_n$ . It can analyze the depth dependency of every component, as shown in Eq. (1). The higher the  $D_n$  is, the stronger the depth dependence of the substance is.

$$D_n = K_n / Y_{n7.5} \tag{1}$$

where  $K_n$  is the K value of No. n substance's fitting line,  $Y_{n7.5}$  is the

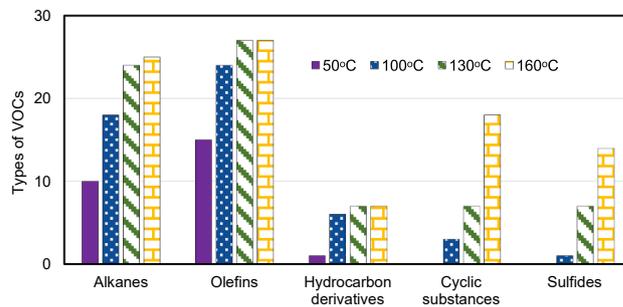


Fig. 8. Classification of five types of VOCs at different heating temperatures.

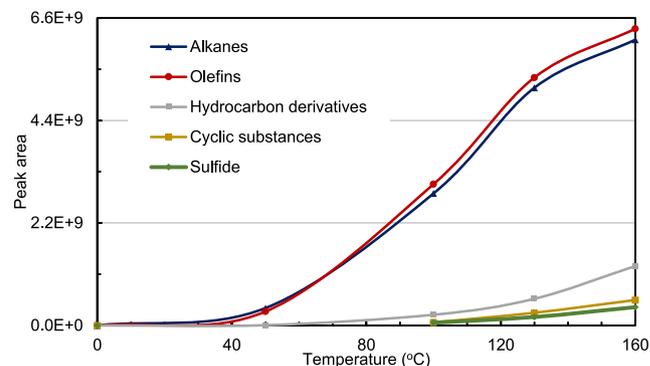


Fig. 9. The trend of chromatogram peak area of five types of VOCs.

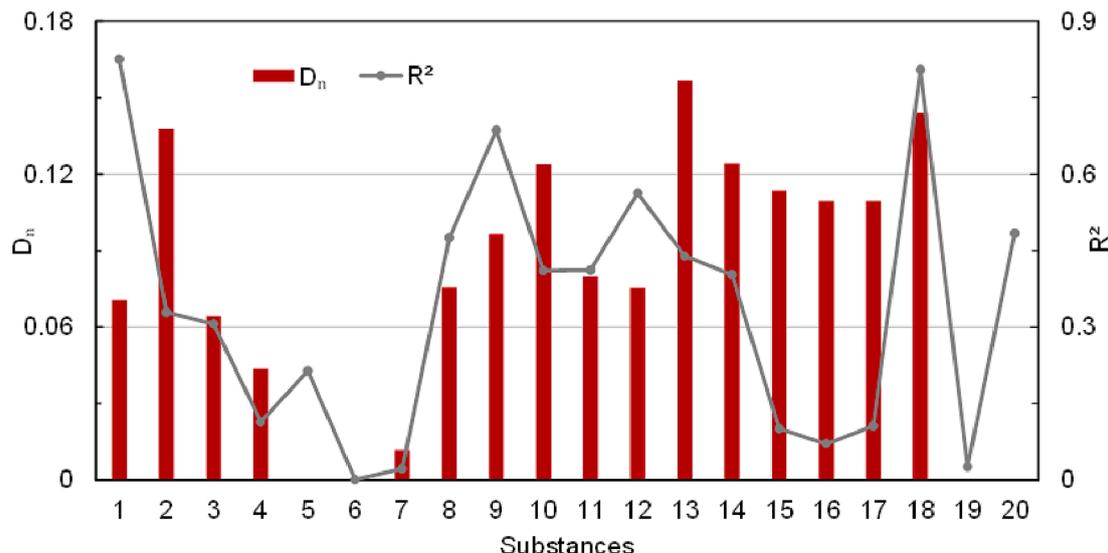


Fig. 7. Fitting line  $R^2$  and depth sensitivity coefficient  $D_n$  of the of individual component.

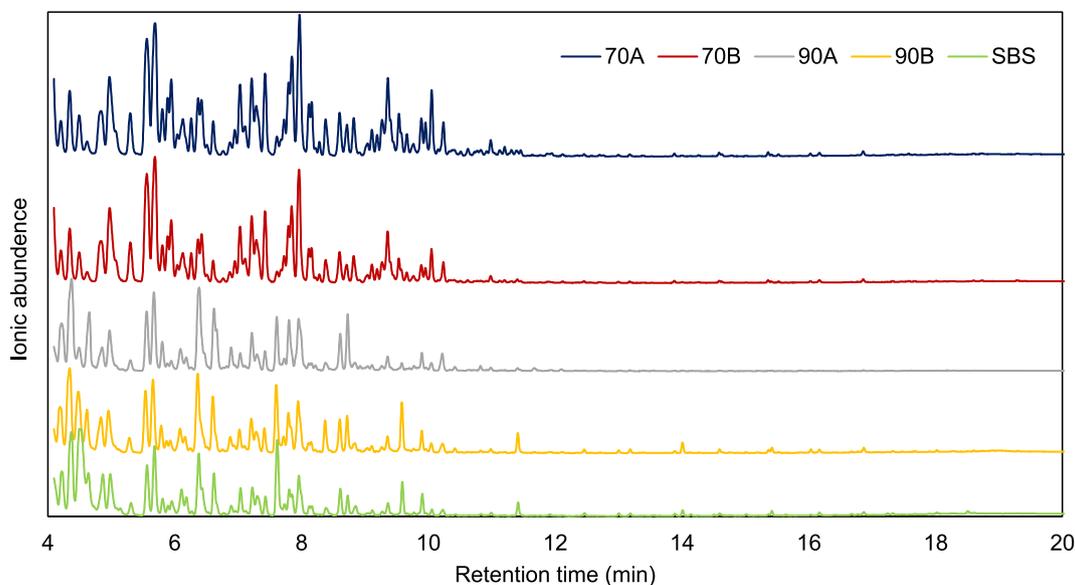


Fig. 10. Chromatograms of VOCs from five asphalt binders detected by TD-GC-MS.

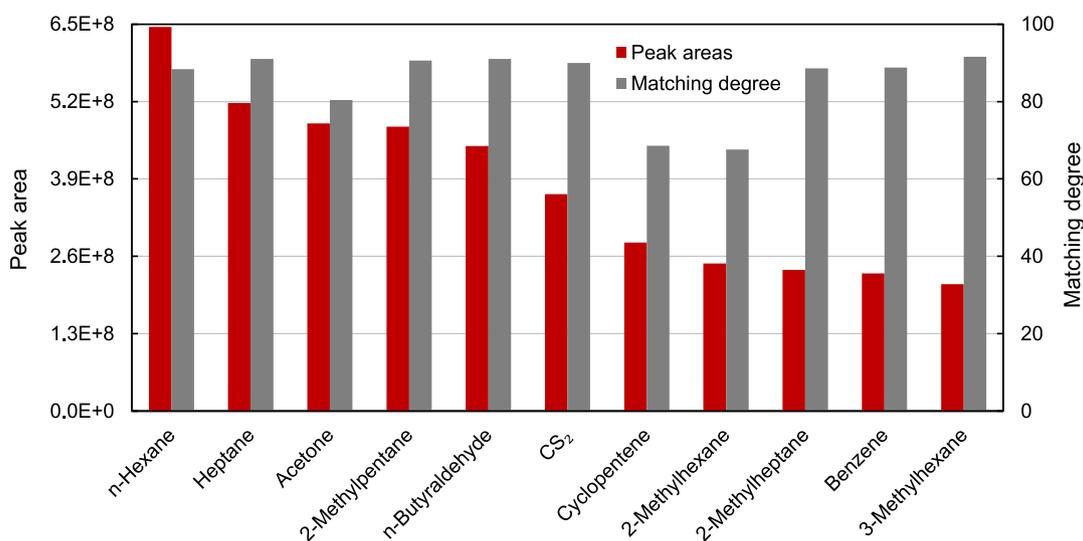


Fig. 11. Coexisting components with an average peak area greater than  $2.1 \times 10^8$ .

median of No. n substance in fitting line.

Fig. 7 shows the  $R^2$  value of fitting lines and depth sensitivity coefficient for the studied 20 components. The No. 1, 18 and 9 substances have the highest  $R^2$  values, which are nonanal,  $C_{29}H_{60}$  and octadecanoic acid, respectively (refer to **Appendix** Table A2). Compared with total VOCs, the  $R^2$  values agree with acids and aldehydes > long-chain alkanes > halogenated hydrocarbons.

The No. 13, 18 and 2 substances have the biggest  $D_n$ , which are oleic acid amide,  $C_{29}H_{60}$  and decanal, respectively. Generally, the depth dependency of VOCs agrees with amines > alkanes > hydrocarbon derivatives (long-chain > short-chain) > PAHs and halogenated hydrocarbons.

At the same time, PY-GC-MS results showed that most of fitting line  $R^2$  values are lower than 0.6, indicating that the peak area is also related to other factors in addition to sample mass and sampling depth due to the complex heating process. So the quantitative analysis by PY-GC-MS will be disturbed by many factors and PY-GC-MS is suitable for asphalt

VOCs composition analysis, but not for the quantitative calculation of VOCs amount.

### 3.1.2. Testing temperature dependency by TD-GC-MS

3.1.2.1. *Types of VOCs in different temperatures.* Released VOCs types at four heating temperatures (50, 100, 130 and 160 °C), analyzed by Mass-database, were 26, 52, 72 and 91 respectively, as shown in **Appendix** Table A3. VOCs released at 50 °C can be regarded as common VOCs because these components are all released and can be detected at other three temperatures. Results also showed that the types of VOCs increase and the components become more complex and toxic with the increment heating temperature. At 160 °C, the released VOCs types was about 3.5 times as that of 50 °C and VOCs toxicity was higher than other temperatures, including substances with 1 or 2 benzene rings, such as 4-pyridine methanol, 2-*tert*-butyl anthraquinone, 1-aminoindene and methanosulfuran.

**Table 2**  
Comparison of VOCs from 104 types of asphalts.

Asphalt VOCs	Asphalt types	Data sources
n-Hexane, heptane, acetone, 2-methylpentane, n-butylaldehyde, carbon disulfide, etc	5 types	This paper
Dichloroethane, octane, naphthalene, methylphenanthrene, etc	4 types	Cui Peiqiang [26]
Decane, 1-tridecene, pentadecanoic acid, octadecanoic acid, tetracosane, etc	2 types	Long Yongshuang [24]
2-Methylheptane, 3-methylheptane, 4-methylheptane, n-octane, methylcyclohexane, ethylcyclopentane, dimethylbenzene, 9 types of PAHs	4 types	Zhang Honghua [38]
Carbon dioxide, butane, n-octane, 3-methylthiophene, 2-methylheptane, 3-methylheptane, etc	1 type	Fan Chengzheng [39]
Benzo[a]pyrene	1 type	Luo Haoyuan [40]
11 types of PAHs and Benzene solubles	17 types	Benjamin Sutter [41]
PAHs containing N, S and/or O	3 types	Stephane Binet [42]
2-Butanone, n-hexane, cumene, ethylbenzene, toluene, m-xylene, p-xylene, o-xylene	12 types	Cui Peng [14]
PAHs	3 types	Bolliet [43]
	4 types	Brudi Leticia C. [44]
Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, benzo(a)anthracene, fluorene, benzo[a]pyrene, phenanthrene, etc	6 types	Mo Shicong [15]
16 types of PAHs with 3–4 rings	1 type	Cao Jiahui [45]
Naphthalene, alkene, diene, fluorene, benzene [a]anthracene, etc	4 types	Park Hyunhee [46]
Nonanal, naphthalene, tridecane, pentadecane, hexadecane, heptadecane, eicosane, film, diethyl propionic acid, diisooctyl maleate, 1-pentadecene, etc	3 types	Li Liping [47]
1,1,1-trichloroethane, benzene, toluene, tetrachloroethylene, styrene, o-xylene, formaldehyde, butylaldehyde, etc	11 types	Ajit Sharma [48]
Isobutylaldehyde, hexane, n-butylaldehyde, 2-ethylacrolein, isovaleraldehyde, hexadiene, benzene, toluene, 2-methylpentane, heptane, etc	3 types	Grzegorz Boczkaj [49]
Naphthalene, anthracene, phenanthrene and its derivatives	3 types	Yongjie Xue [50]
Benzothiazole, toluene, ethyltoluene or trimethylbenzene, styrene, isopropyltoluene, ethylbenzene or xylene, benzene, undecane, pentadiene, methyl-heptane, decane, butanone or butenal, etc	3 types	Jaffer Bressan Borinelli [25]
2-Methylpentane, 3-methylpentane, hexane, heptane, toluene, etc	9 types	Javier Espinoza [51]
1,3-butadiene, benzene and trichloroethylene, m-/p- xylene, o-xylene, 1,2,4-trim-benzene, n-hexane, acetone, methyl chloride, methyl bromide, acetonitrile and carbon tetrachloride, etc	1 type	Li Na [52]
Cyclopentene, 2-methyl-pentane, 4-methyl-2-pentene, 3-methyl-pentane, 1-hexene, n-hexane, 1,1,2-trimethyl-cyclopropane, 1-heptene heptane, etc	1 type	Li Na [53]
Polycyclic aromatic sulfur heterocycles (PASHs)	3 types	Rejane Secretti Cargnin [54]

According to the toxicity of different functional groups, asphalt VOCs were divided into five categories: alkanes, olefins, hydrocarbon derivatives, cyclic substances and sulfides. Asphalt VOCs at different temperatures were classified as following five categories (Fig. 8). It illustrated that alkanes and olefins are the main substances of asphalt VOCs. The growth trend of olefins was similar to that of alkanes. Mostly alkanes and olefin released below 130 °C with a high increase speed from 50 to 130 °C. When temperature is higher than 130 °C, their volatilization rate slows down. Since the boiling point of alkenes and olefin molecules is lower than 130 °C, their number of species are greatly

**Table 3**  
Detail information of selected fingerprint components of asphalt VOCs.

Classification	Components	Structural formula	Relative molecular mass	Characteristic
Aldehydes	2-Methylpentane	C <sub>6</sub> H <sub>14</sub>	86	Big peak area High repetition rate
	n-Hexane	C <sub>6</sub> H <sub>14</sub>	86	Big peak area High repetition rate
	3-Methylhexane	C <sub>7</sub> H <sub>16</sub>	100	Big peak area High repetition rate
Derivative	Heptane	C <sub>7</sub> H <sub>16</sub>	100	Big peak area
	2-Methylheptane	C <sub>8</sub> H <sub>18</sub>	114	Big peak area
	Acetone	C <sub>3</sub> H <sub>6</sub> O	58	Strong toxicity Big peak area
	Methacrolein	C <sub>4</sub> H <sub>6</sub> O	70	Strong toxicity
Benzene series	n-Butylaldehyde	C <sub>4</sub> H <sub>8</sub> O	72	Strong toxicity Big peak area
	Isovaleraldehyde	C <sub>5</sub> H <sub>10</sub> O	86	Strong toxicity Big peak area
	Benzene	C <sub>6</sub> H <sub>6</sub>	78	Strong toxicity High repetition rate
Sulfide	Toluene	C <sub>7</sub> H <sub>8</sub>	92	Strong toxicity High repetition rate
	Carbon disulfide	CS <sub>2</sub>	76	Strong toxicity Big peak area

affected by the temperature when the temperature is lower than 130 °C. When temperatures are higher than 130 °C, the volatilization trend of alkenes and olefin became stable, and increasing rate with temperature slowed down. Types of alkanes at the four heating temperatures are respectively 10, 18, 24 and 25. Olefin species of VOCs released at 160 °C is about twice as that at 50 °C.

Species of hydrocarbon derivatives was less than that of alkanes and olefins. They were mainly derived from the interaction of asphalt and oxygen in the air at high temperatures. The growth rate of cyclic substances was the highest during 130 to 160 °C. About 12 kinds of benzene ring substances and 7 kinds of heterocyclic substances were detected at 160 °C. Sulfides and cyclic substances had similar volatilization trends, which increased rapidly from 130 to 160 °C.

The data also indicated that not only types of VOCs, but also complexity of VOCs would gradually increase with the increase of heating temperature. According to the actual process of asphalt in engineering, warm mixing agent which reduce the mixing temperature can effectively reduce the diversity and structural complexity of asphalt VOCs.

**3.1.2.2. Relative volatilization of VOCs in different temperatures.** VOCs amounts, by means of chromatogram peak area, in different temperatures were compared roughly by peak area of chromatogram in this chapter. At four heating temperatures, the peak areas of five VOCs categories followed this order (Fig. 9): olefins > alkanes > hydrocarbon derivatives > cyclic substances > sulfides.

Peak areas of olefins and alkanes increased rapidly from 80 to 120 °C and grew slowly, which were much larger than that of other three categories. In contrast, peak area of hydrocarbon derivatives increased rapidly since 130 °C, and would continue to increase when changed to 160 °C. Compared with chapter 3.2.1, species of hydrocarbon

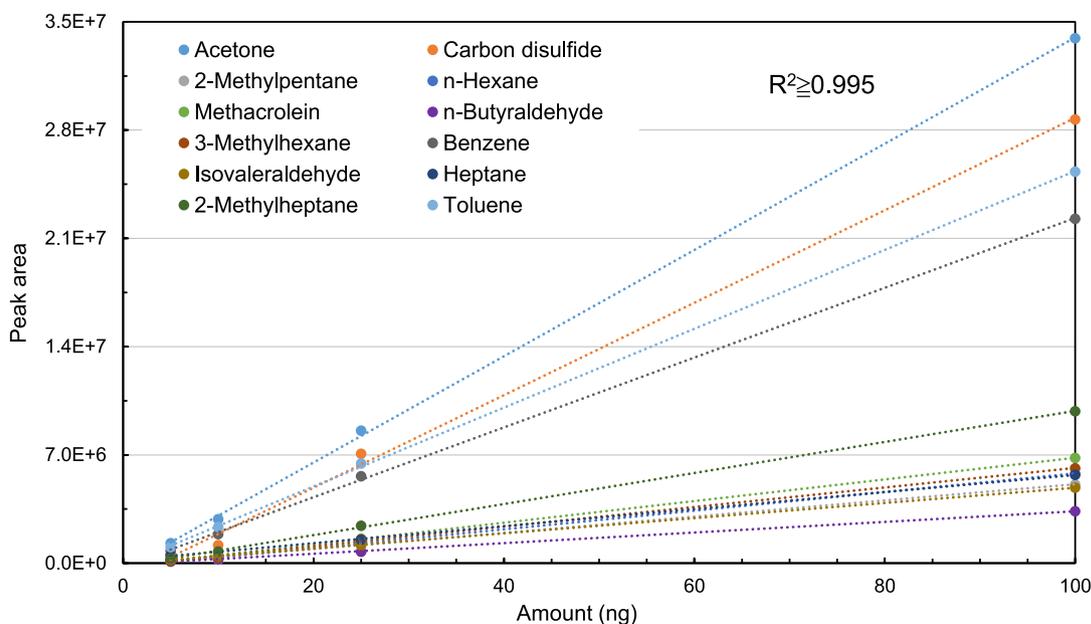


Fig. 12. Fingerprint Component Standard Curves.

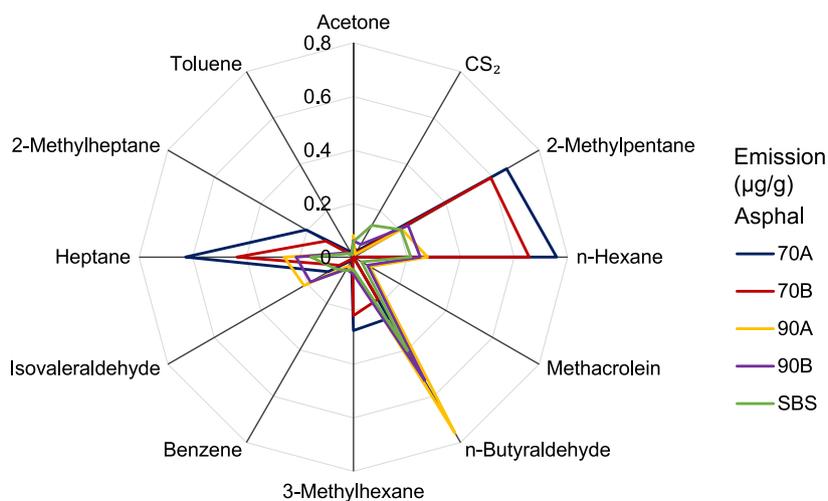


Fig. 13. The release amount of fingerprint components from five asphalt.

derivatives did not change from 130 to 160 °C, but peak areas increase a lot. This data implied that it is easier for alkanes to react with oxygen when temperature increases. Cyclic substances and sulfides accelerated to release since 100 to 160 °C.

Appendix Table A4 compares individual VOCs with top highest peak area at different heating temperatures, including top 10 substances at 160 °C, and one substance with significant change of peak area at different temperature. These substances contain 5 kinds of olefins and 6 kinds of alkanes, so the main components of asphalt VOCs are alkanes and olefins. The substance with largest peak area at four temperatures is n-hexane, while 1-hexene, 2-methylpentane, 2-methylhexane and 3-methylhexane are almost top substances at different temperatures.

Compare with the two GC-MS method, PY-GC-MS showed that the sampling depth would influence the volatilization capacity of asphalt. PY-GC-MS is suitable for asphalt VOCs composition analysis, but not for the quantitative calculation of VOCs amount. TD-GC-MS simulated the actual construction process and obtained more universal result. In order to unify the detection results of asphalt VOCs and establish a quantitative standard, TD-GC-MS method is more appropriate.

### 3.2. Fingerprint components of asphalt VOCs

VOCs compositions generally varied with types of asphalt due to their complex manufacture process and source area. In this experiment, VOC from five types of asphalt binders at 160 °C was detected by TD-GC-MS, VOCs chromatograms shown as Fig. 10 with the similar shapes. The mass spectrometry data confirmed that the main VOCs released from the five asphalt binders are basically the same. It can be considered that although different asphalt binders will release some unique VOCs components, the main VOCs components are uniform due to the light components in asphalt binders. Summarizing common components with larger volatilization from various asphalt VOCs can effectively achieve quantitative analysis on asphalt VOCs.

In order to ensure accurate and unified analysis, fingerprint component of asphalt VOCs were proposed and defined. They released from most of asphalt binder with big peak areas, which are representative in the field of environmental load research. Two critical parameters were used for setting fingerprint components, which are matching degree and peak area. The higher the matching degree of mass

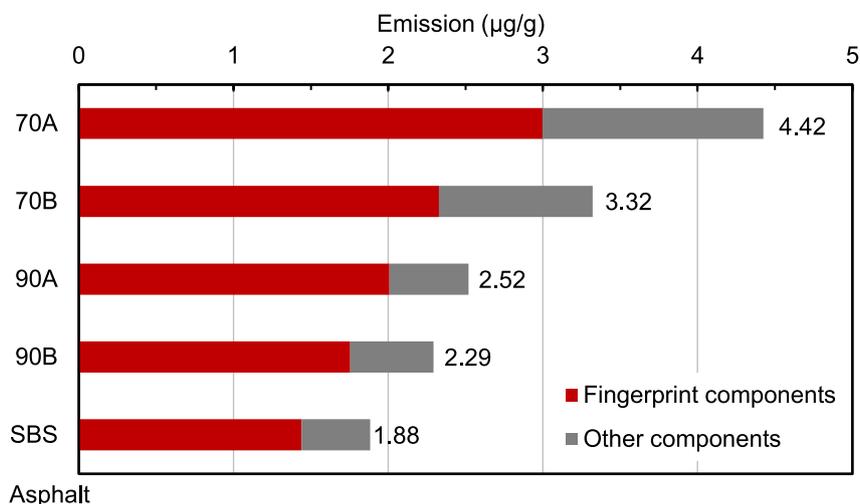


Fig. 14. Total released VOCs of five asphalt at 160 °C.

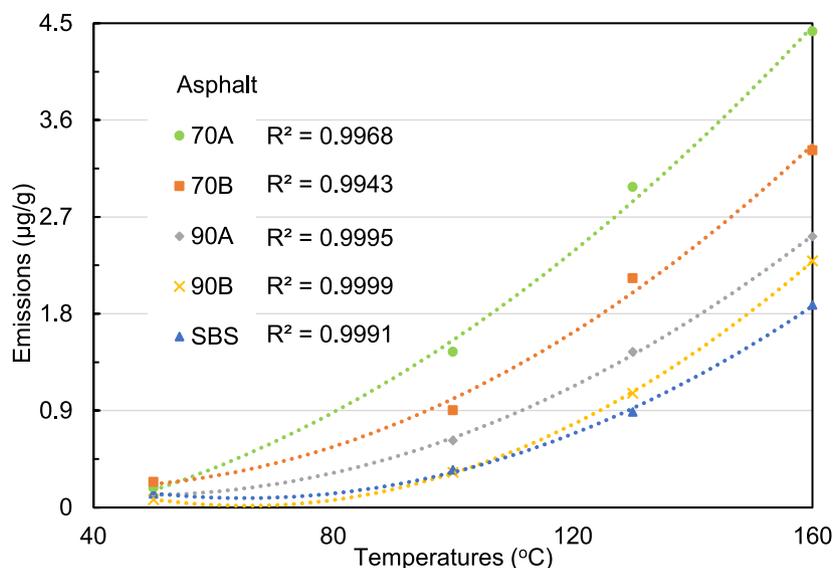


Fig. 15. The influence of heating temperature on the total asphalt VOCs release.

spectrometry is, greater the purity of detected VOCs is and more accurate the qualitative is. The peak area of the chromatogram is proportional to its concentration. So it can be used to quantitative analysis asphalt VOCs, with the help of standardized relation between peak area and detected concentration.

### 3.2.1. Definition and selection of fingerprint components

In this experiment, **Appendix** Table A5 shows the common VOCs released from five asphalt binders at the heating temperature of 160 °C. The peak areas of these components account for a large proportion of the total peak area. About 11 substances with higher average peak areas (ionic abundance is more than  $2.1 \times 10^8$ ) can be detected as common VOCs (Fig. 11), which can be representative components of asphalt VOCs. They are alkanes, aldehydes, ketones, olefins and benzene. Matching degrees of cyclopentene and 2-methylhexane are less than 80, indicating that these two substances are too inaccurate to be selected as fingerprint component for quantitative analysis. The other nine substances, including n-hexane, heptane, acetone, 2-methylpentane, n-butylaldehyde, carbon disulfide, 2-methylheptane, benzene and 3-methylhexane, own high matching degree and big peak area.

The fingerprint components are selected by comparing VOCs

volatilized from 104 types of asphalt binders at 160 °C, as concluded in **Table 2**. These data are derived from 5 sets of VOCs obtained from TD-GC-MS in this study, 10 sets of data from previous published studies, and 89 sets of data from other researchers. The nine substances summarized from Fig. 11 also appear frequently in **Table 2**, indicating that they are universal and with big peak areas. They are suitable for selected as fingerprint components of asphalt VOCs.

Compared with alkanes and olefins, aldehydes and those substances containing benzene ring are more toxic. For instance, aldehydes can cause pathological changes of eyes, mucosa and upper respiratory tract [55,56]. Asphalt VOCs in **Appendix** Table A5 and **Table 2** display that toluene, isovaleraldehyde and methacrolein all have big peak areas and strong toxicity. So, these three substances are selected as the toxic fingerprint components of asphalt VOCs.

In summary, **Table 3** lists the detail information of fingerprint components. According to the definition of fingerprint component, these fingerprint components have the following characteristics: (1) peak area of chromatogram is large, (2) matching degree is more than 80 in mass spectrometric analysis, (3) peak area of chromatogram is not large but the toxicity is strong. In any asphalt binder, the total release amount can be calculated based on standard curves of fingerprint components. The

more types of fingerprint components appear in analyzed asphalt, the higher the total release accuracy is.

### 3.2.2. Standard curves of fingerprint components

The peak area of chromatogram is dimensionless, so unconverted peak area only represents relative amounts of components, not the absolute value of emission. In this study, release amount (x-axis, ng) of single selected fingerprint component was confirmed to have linear relationship with peak area (y-axis, dimensionless) of chromatogram. Standard solution, representing relation between peak area and detected concentration were demarcated by GC–MS test and finalized in Fig. 12.

The slope which reveals the corresponding relationship between peak area and release amount of these substances of each standard curve is different. K values of acetone, CS<sub>2</sub>, toluene and benzene are much higher than that of other alkanes and aldehydes. It indicated that peak areas of these four substances are the most sensitive to the concentration of components. On the contrary, K value of n-butyraldehyde and isovaleraldehyde standard curves are the smallest, indicating that their peak areas of per unit mass are smaller than that of other fingerprint components. The more standard curves are established, the more accurate quantitative analysis is.

### 3.2.3. Calculation formulas for individual and total VOCs

With the help of fingerprint components and their standard curves, the release amounts of individual VOCs and total VOCs from asphalt or asphalt mixture can be further proposed. Standard curve reflects the linear relationship between amount and peak area, so the calculation formula of a single fingerprint component is directly derived from corresponding standard curve, as Eq. (2).

$$m_i = \frac{S_i - b_i}{K_i} \quad (2)$$

where  $m_i$  is the release amount of fingerprint component  $i$ , ng;  $S_i$  is the peak area of fingerprint component  $i$ , dimensionless;  $K_i$  and  $b_i$  are the K and b values in the standard curve of corresponding fingerprint component  $i$ , dimensionless, as shown in Appendix Table A6.

Total VOCs include 12 fingerprint components and other components, so it is a formula of summation, as Eq. (3) shows. Release amount of fingerprint components are directly derived from corresponding standard curves,

while release amount of other un-calibrated components is derived by standard curve of toluene standard curve according to the document HJ644-2013[57].

$$m = \sum_{i=1}^{12} \frac{S_i - b_i}{K_i} + \frac{S_t - \sum S_i + 132876}{254898} \quad (3)$$

where  $m$  is the release amount of total VOCs components, ng;  $S_i$  is the peak area of fingerprint component  $i$ , dimensionless;  $S_t$  is peak area of total components, dimensionless;  $K_i$  and  $b_i$  are the K and b values in the standard curve of fingerprint component  $i$ , dimensionless, as shown in Appendix Table A6.

## 3.3. Quantitative analysis on independent component

### 3.3.1. Release amount from different asphalt binder

Fig. 13 compared the release amounts of fingerprint components from the studied asphalt binder, according to Eq. (2). Among the five asphalt binders, release amounts of 2-methylpentane, n-hexane, n-butyraldehyde and heptane were all more than 0.1 µg/g. Their amounts are also related to the asphalt binder type. Pen 80/100 asphalt and SBS modified asphalt released much more n-butyraldehyde than from than Pen 60/80 asphalt, and n-butyraldehyde emission from asphalt 90A was about 4 times that of asphalt 70B. The emission of the other three alkanes from Pen 60/80 asphalt were much higher than that of Pen 80/100 asphalt and SBS modified asphalt, and amount ratio was about 2–3 times.

Pen 60/80 asphalt released more alkanes, while Pen 80/100 asphalt and SBS modified asphalt released more aldehydes and CS<sub>2</sub>, respectively. The alkanes released from Pen 60/80 asphalt included n-hexane, 2-methylpentane and heptane, with the release amounts all above 0.40 µg/g. In Pen 80/100 asphalt and SBS modified asphalt, VOCs were more toxic (such as acetone, CS<sub>2</sub>, isovaleraldehyde, benzene and toluene) and the top VOC was n-butyraldehyde, with 0.76 µg/g emission from asphalt 90A. Pen 60/80 asphalt released much less high-toxicity substances than other asphalts, such as acetone, benzene, toluene and methacrolein.

According to Eq. (3), the total VOCs release amount from five asphalt binders heated at 160 °C were 4.42, 3.32, 2.52, 2.29 and 1.88 µg/g, respectively, while release amounts of fingerprint components were 3.00, 2.33, 2.01, 1.75 and 1.44 µg/g, respectively, as shown in Fig. 14. The release amount of fingerprint components in the histogram accounted for more than 60% of total asphalt VOCs, indicating that fingerprint components proposed in this study can effectively guide the quantitative analysis of asphalt VOCs. Fig. 13 and Fig. 14 also illustrated that the VOCs release amounts are affected by the types of asphalt binders. The total VOCs amount from Pen 60/80 asphalt is generally higher than VOCs from Pen 80/100 asphalt, and is more than twice of VOCs from SBS modified binder.

Yang Xu [23] found that the volatilization limitation of acetone, toluene and thiophene from 1 ml asphalt sample by HS-GC–MS is about 2.94–9.87 µg/g, which is twice as much as VOCs in this study. Cao Jiahui [45] quantitatively analyzed PAHs in asphalt VOCs by GC–MS. The release amount of PAHs was about 0.86–1.09 µg/g. Rasoulzadeh Y. [58] reported that PAHs volatilization of Pen 60/80 asphalt was about 0.2 µg/g by GC-FID. Yu Man [59] and Zhang Honghua [60] attained that total amount of VOCs detected was respectively 0.4–3.1 µg/g and 0.7–1.3 µg/g by drawing quantitative curve based on UV–Vis. These published data proved that fingerprint components and standard curves in this study can provide accurate and unified quantitative analysis on asphalt emission.

### 3.3.2. Release amount in different temperatures

Heating temperature is also a key factor affecting asphalt VOCs, so VOCs at different temperature were analyzed to indicate the release law of temperature. The detected total VOCs amounts from asphalt binders at different heating temperature were presented in Fig. 15.

When heating temperature increases, VOCs release amount increases rapidly in a quadratic function, as shown in Fig. 15. The derivative of curve function represents the sensitivity of VOCs amount with temperature increasing. At 50–160 °C, sensitivity of the release amount follows this order: 70A greater than 70B greater than 90B greater than 90A > SBS, which means that VOCs from SBS modified asphalt is hardly affected by temperature. At same time, asphalt 70A emission at 160 °C was 4.42 µg/g, which was about 3 times as that of 100 °C.

The release of individual fingerprint components also has the same tendency. Most of the release of VOCs showed a quadratic function growth trend, while the emissions of CS<sub>2</sub>, 2-methylpentane, n-hexane and 3-methylhexane showed a gentle trend with heating temperature increasing. The fitting relationships of the four substances were linear, indicating that with the increase of temperature, the release of these substances showed a steady growth trend.

## 4. Conclusions

In this study, the release mechanism of asphalt VOCs was discussed with self-developed fingerprint component database. The quantitative calculation formulas of individual released fingerprint component and total amount of released asphalt VOCs were introduced. Besides, release amount with different asphalt types at different heating temperatures were detected. According to the presented research data, the following conclusions were obtained.

1. The depth dependency of asphalt VOCs was analyzed by PY-GC-MS at different sampling locations. Results showed that their compositions are not related to sampling depth, but their detected release amount is linearly related to sampling depth. The depth sensitivity of different VOC could be ranked as: amines > alkanes > hydrocarbon derivatives (long chain > short chain) > PAHs and halogenated hydrocarbons.
2. The temperature dependency of VOCs was detected by TD-GC-MS at different testing temperatures. With temperature increasing, the types and amount of asphalt VOCs increase and individual component becomes more toxic. The emissions of alkanes and olefins were always more than other VOCs, which increased rapidly at 100–130 °C. At 130 °C, hydrocarbon derivatives, cyclic substances and sulfides increased sharply, while alkanes and olefins reduced, which was resulted from intensified oxidation since 130 °C.
3. According to VOCs statistics from 104 kinds of asphalt binder, 12 substances were selected as asphalt VOCs fingerprint components. Standard curves showed that the amount is linear to the peak area of chromatogram, which can be used to quantitative calculate release amounts of individual VOC and total VOCs. The more fingerprint components appear during the quantitative analysis, the more accurate the calculation of total VOCs is.
4. Based on the quantitative formula, the total emissions from asphalt binders heated at 160 °C were between 1.88 and 4.42 µg/g. Fingerprint components account for more than 60% of total release amount. In addition, the total VOCs release amount followed a binomial growth with temperature. Different asphalt binders owned different increasing rates with temperature.

### CRedit authorship contribution statement

**Xiwen Chang:** Conceptualization, Investigation, Validation, Formal analysis, Writing – original draft. **Yongshuang Long:** Methodology, Investigation. **Chen Wang:** Investigation, Resources. **Yue Xiao:** Conceptualization, Supervision, Writing – review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Acknowledgements

The financial supports by the National Natural Science Foundation of China (51878526) are gratefully acknowledged. The authors would also like to thank Fok Ying Tung Education Foundation for their honorary support.

### Appendices for Chemical fingerprinting of volatile organic compounds from asphalt binder for quantitative

**Table A1**  
Sampling information of specimen location dependency (Asphalt 70A).

Exp.	1	2	3	4	5	6
Weight (mg)	0.10	0.26	0.29	0.27	0.22	0.23
Depth (mm)	0	2	5	10	8	5
Position	middle	middle	middle	corner	middle	middle
Exp.	7	8	9	10	11	12
Weight (mg)	0.23	0.17	0.23	0.23	0.23	0.18
Depth (mm)	15	5	8	6	8	7
Position	middle	middle	corner	corner	edge	middle

**Table A2**  
Asphalt 70A VOCs with the largest peak area in the 12 chromatograms.

No.	Matching degree	Substances
1	91	Nonanal
2	91	Decanal
3	47 or 49	2,3-Dihydrobenzofuran or Benzylamine
4	86	Nonanoic acid
5	47	Alpha-nicotine or nicotine
6	83	Chlorinated 12-alkane
7	46	Di- <i>tert</i> -butylphenol
8	99	Hexadecanoic acid
9	99	Octadecanoic acid
10	93	Tridecamide
11	90	Docosane
12	96	Trisane
13	99	Oleamide
14	97	Pentacosane
15	96	Hexadecane
16	99	Heptadecane
17	97	Octacosane
18	60	Nonacosane
19	38 or 98	2,4-Dimethylbenzo[h]quinoline or alkane
20	53 or 95	2-Ethylacridine or alkane

**Table A3**  
Asphalt 70A VOCs at four heating temperatures (50, 100, 130 and 160 °C).

No.	Substance	50°C	100°C	130°C	160°C
1	Propionaldehyde		√	√	√
2	Acetone	√	√	√	√
3	Carbon disulfide		√	√	√
4	2-Propanol		√	√	√
5	Cyclopentene	√	√	√	√
6	2-Methylpentane	√	√	√	√
7	3-Methylpentane	√	√	√	√
8	1-Hexene	√	√	√	√
9	Hexane	√	√	√	√
10	2-Ethyl-1-butene	√	√	√	√
11	2-Hexene	√	√	√	√
12	4-Methyl-2-pentene	√	√	√	√
13	3-Hexene	√	√	√	√
14	3-Methyl-2-pentene	√	√	√	√
15	n-Butyraldehyde		√	√	√
16	Methylcyclopentane	√	√	√	√
17	Isobutyraldehyde		√	√	√
18	3,4-Dimethyl-1-pentene		√	√	√
19	2,4-Dimethyl-1-pentene		√	√	√
20	3-Methyl-1-hexene	√	√	√	√
21	1-Methylcyclopentene	√	√	√	√
22	5-Methyl-1-hexene	√	√	√	√
23	2-Methylhexane	√	√	√	√
24	4-Methyl-1-hexene	√	√	√	√
25	3-Methylhexane	√	√	√	√
26	benzene		√	√	√
27	Cyclohexene	√	√	√	√
28	Heptane	√	√	√	√
29	4,4-Dimethylcyclopentene	√	√	√	√
30	2-Methyl-3-hexene	√	√	√	√
31	3-Methyl-2-hexene		√	√	√
32	2-Heptene	√	√	√	√
33	Methylcyclohexane	√	√	√	√
34	Isovaleraldehyde		√	√	√
35	Ethylcyclopentane	√	√	√	√
36	1,2,4-Trimethylcyclopentane		√	√	√
37	4-Methyl-1-cyclohexene		√	√	√
38	1,2,3-Trimethylcyclopentane		√	√	√
39	2,4-Dimethyl-1-hexene		√	√	√
40	3-Methylcyclohexene		√	√	√

(continued on next page)

Table A3 (continued)

41	2-Methylheptane	√	√	√	√
42	3-Methylheptane		√	√	√
43	1-Methylcyclohexene		√	√	√
44	1,4-Dimethylcyclohexane		√	√	√
45	Toluene		√	√	√
46	1-Octene		√	√	√
47	Octane		√	√	√
48	2-Methyl-3-heptene			√	√
49	3-Methylthiophene		√	√	√
50	1,2-Dimethylcyclohexene		√	√	√
51	1,3-Dimethylcyclohexene			√	√
52	2,4-Dimethylheptane		√	√	√
53	2,6-Dimethylheptane			√	√
54	Propylcyclopentane			√	√
55	Ethylcyclohexane			√	√
56	1,1,3-Trimethylcyclohexane		√	√	√
57	2-nonene			√	√
58	2,3-Dimethylheptane		√	√	√
59	4-Methyloctane			√	√
60	4-Pyridinemethanol			√	√
61	2,5-Dimethylheptane			√	√
62	2-Methyltetrahydrothiophene				√
63	Ethylbenzene				√
64	1-Methyl-1-ol-2-cyclohexene			√	√
65	O-xylene			√	√
66	Nonane			√	√
67	3,4-Dimethylthiophene			√	√
68	2,3-Dimethylthiophene				√
69	Paraxylene				√
70	Methyl isopropyl disulfide				√
71	1,4-Dimethylthiophene				√
72	1-Methyl-2-ethylheptane				√
73	Diethyl disulfide			√	√
74	Methylpropyl disulfide				√
75	2-Tert-butylanthraquinone			√	√
76	Ethyl isopropyl disulfide			√	√
77	Dimethyl trisulfide				√
78	Methyl isobutyl disulfide				√
79	Diisopropyl disulfide			√	√
80	3-Thiophenecarboxaldehyde				√
81	4-(Methylthio)phenol				√
82	Ethyl isobutyl disulfide				√
83	Dipropyl disulfide			√	√

(continued on next page)

Table A3 (continued)

84	Propyl isobutyl disulfide			√	√
85	p-Aminobenzonitrile				√
86	Methiocarb				√
87	Diisobutyl disulfide			√	√
88	4-Methylthiobenzoic acid				√
89	1-Aminoindan				√
90	Dibutyl disulfide				√
91	Dipropyl trisulfide				√

Table A4

Asphalt 70A VOCs with top highest peak area among four temperatures.

No.	Components	50 °C	100 °C	130 °C	160 °C
1	n-Hexane	1	1	1	1
2	1-Hexene	3	2	2	2
3	Heptane	11	9	4	3
4	2-Methylpentane	2	3	3	4
5	2-Methylheptane	17	12	7	5
6	3-Methylhexane	7	6	8	7
7	2-Methylhexane	9	8	9	8
8	Cyclopentene	5	5	6	9
9	Methylcyclopentene	13	14	12	10
10	4-Methyl-2-pentene	10	7	10	11
11	4,4-Dimethylcyclopentene	4	4	24	26

Table A5

Common VOCs released from five asphalt binders at 160 °C.

No.	Common VOC	Peak area				
		70A	70B	90A	90B	SBS
1	Propionaldehyde	2.28E + 08	1.73E + 08	2.15E + 08	1.85E + 08	1.27E + 08
2	Acetone	3.68E + 08	2.89E + 08	6.57E + 08	5.72E + 08	5.31E + 08
3	Carbon disulfide	2.36E + 08	1.64E + 08	1.06E + 08	4.29E + 08	8.86E + 08
4	2-Propanol	7.05E + 07	5.22E + 07	3.34E + 08	2.28E + 08	2.64E + 08
5	Cyclopentene	3.89E + 08	3.65E + 08	1.54E + 08	2.44E + 08	2.64E + 08
6	2-Methylpentane	7.70E + 08	7.27E + 08	2.75E + 08	3.23E + 08	2.95E + 08
7	3-Methylpentane	2.57E + 08	2.44E + 08	5.70E + 07	8.32E + 07	6.64E + 07
8	n-Hexane	1.03E + 09	9.32E + 08	4.61E + 08	4.24E + 08	3.80E + 08
9	2-Hexene	2.57E + 08	2.03E + 08	3.16E + 07	5.28E + 07	4.14E + 07
10	4-Methyl-2-pentene	3.86E + 08	3.15E + 08	5.51E + 07	6.65E + 07	9.07E + 07
11	n-Butyraldehyde	2.77E + 08	1.99E + 08	6.94E + 08	6.02E + 08	4.55E + 08
12	3,4-Dimethyl-1-pentene	1.77E + 07	1.60E + 07	1.45E + 07	1.72E + 07	1.15E + 07
13	1-Methylcyclopentene	3.86E + 08	2.87E + 08	9.20E + 07	1.18E + 08	1.31E + 08
14	5-Methyl-1-hexene	1.62E + 08	1.37E + 08	2.74E + 07	3.86E + 07	2.39E + 07
15	2-Methylhexane	4.13E + 08	3.49E + 08	1.92E + 08	1.48E + 08	1.36E + 08
16	3-Methylhexane	4.23E + 08	3.56E + 08	8.89E + 07	1.14E + 08	8.55E + 07
17	Benzene	9.05E + 07	4.94E + 07	2.60E + 08	3.63E + 08	3.93E + 08
18	Cyclohexene	2.20E + 08	1.21E + 08	5.56E + 07	7.36E + 07	5.31E + 07
19	Heptane	8.92E + 08	6.49E + 08	4.21E + 08	3.64E + 08	2.61E + 08
20	4,4-Dimethylcyclopentene	4.19E + 08	3.89E + 08	3.14E + 07	3.96E + 07	5.92E + 07
21	Isovaleraldehyde	1.61E + 08	9.23E + 07	2.52E + 08	1.71E + 08	8.77E + 07
22	2-Methylheptane	5.72E + 08	3.54E + 08	8.22E + 07	1.02E + 08	7.50E + 07
23	1-Methylcyclohexene	9.70E + 07	4.55E + 07	2.79E + 07	3.21E + 07	1.27E + 07
24	Dimethylcyclohexane	8.07E + 07	5.42E + 07	2.83E + 07	2.13E + 07	1.55E + 07
25	Toluene	1.78E + 08	8.19E + 07	8.40E + 07	1.06E + 08	9.78E + 07
26	1,1,3-Trimethylcyclohexane	8.32E + 07	3.29E + 07	1.47E + 07	2.29E + 07	1.72E + 07
27	Xylene	1.65E + 07	9.61E + 06	2.30E + 06	9.00E + 06	7.08E + 06
28	Methylpropyl disulfide	8.75E + 06	4.66E + 06	2.93E + 06	1.44E + 07	1.13E + 07
29	Dimethyl trisulfide	3.61E + 06	3.25E + 06	2.61E + 06	3.67E + 07	1.97E + 07

**Table A6**  
Standard curves of fingerprint VOC.

Fingerprint VOC	Standard curve	R <sup>2</sup>	K	b
Acetone	$y = 3.44E + 5x - 3.64E + 5$	0.9997	3.44E + 05	-3.64E + 05
Carbon disulfide	$y = 2.99E + 5x - 1.00E + 6$	0.9980	2.99E + 05	-1.00E + 06
2-Methylpentane	$y = 5.25E + 4x - 1.36E + 5$	0.9950	5.25E + 04	-1.36E + 05
n-Hexane	$y = 6.02E + 4x - 2.21E + 5$	0.9989	6.02E + 04	-2.21E + 05
Methacrolein	$y = 6.99E + 4x - 1.81E + 5$	1.0000	6.99E + 04	-1.81E + 05
n-Butyraldehyde	$y = 3.43E + 4x - 7.23E + 4$	0.9996	3.43E + 04	-7.23E + 04
3-Methylhexane	$y = 6.33E + 4x - 1.66E + 5$	0.9990	6.33E + 04	-1.66E + 05
Benzene	$y = 2.26E + 5x - 2.52E + 5$	0.9998	2.26E + 05	-2.52E + 05
Isovaleraldehyde	$y = 4.92E + 4x - 3.48E + 4$	0.9999	4.92E + 04	-3.48E + 04
Heptane	$y = 5.51E + 4x + 1.92E + 5$	0.9996	5.51E + 04	1.92E + 05
2-Methylheptane	$y = 1.00E + 5x - 1.86E + 5$	0.9998	1.00E + 05	-1.86E + 05
Toluene	$y = 2.55E + 5x - 1.33E + 5$	0.9998	2.55E + 05	-1.33E + 05

## References

- X.W. Chang, R.H. Zhang, Y. Xiao, X.Y. Chen, X.S. Zhang, G. Liu, Mapping of publications on asphalt pavement and bitumen materials: A bibliometric review, *Constr. Build. Mater.* 234 (2020), 117370.
- Y. Xiao, X.W. Chang, B.X. Yan, X.S. Zhang, M. Yunusa, R. Yu, Z.W. Chen, SBS morphology characteristics in asphalt binder and their relation with viscoelastic properties, *Constr. Build. Mater.* 301 (2021), 124292.
- S. Qu, S. Fan, G. Wang, W. He, K. Xu, L. Nie, Y. Zhao, Q. Zhu, T. Li, G. Li, Air pollutant emissions from the asphalt industry in Beijing, China, *J. Environ. Sci.* 109 (2021) 57–65.
- I. Burstyn, H. Kromhout, Are the members of a paving crew uniformly exposed to bitumen fume, organic vapor, and benzo(a)pyrene? *Risk Analysis* 20 (5) (2010) 653–664.
- M.P. Mendez, Asphalt fumes, *Vis. Tecnol.* 9 (1) (2001) 51–56.
- V.P. Piracelli, I.R. Amador, F.C. Sabino, J.P. Pinto, C.R. Silva Jr, M.C. Solci, Air pollutants emissions in real conditions of asphalt paving. Particulate matter (PM), black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs), *Quim. Nova* 43 (4) (2020) 404–412.
- M. Wang, P. Li, T. Nian, Y. Mao, An overview of studies on the hazards, component analysis and suppression of fumes in asphalt and asphalt mixtures, *Constr. Build. Mater.* 289 (2021), 123185.
- L.B. Jaycox, L.D. Olsen, Determination of total sulfur compounds and benzothiazole in asphalt fume samples by gas chromatography with sulfur chemiluminescence detection, *Applied occupational and environmental hygiene* 15 (9) (2000) 695–704.
- G. Reinke, M. Swanson, D. Paustenbach, J. Beach, Chemical and mutagenic properties of asphalt fume condensates generated under laboratory and field conditions, *Mutat. Res. Genet. Toxicol. Environ. Mutagen.* 469 (1) (2000) 41–50.
- L.V. Osborn, J.T. Kurek, A.J. Kriech, F.M. Fehsenfeld, Luminescence spectroscopy as a screening tool for the potential carcinogenicity of asphalt fumes, *J. Environ. Monit.* 3 (2) (2001) 185–190.
- P.J. Boogaard, J. Buschmann, R. Fuhst, K. Bluemlein, W. Koch, D. Schaudien, K. Schwarz, C. McAlinden, L. Deferme, M. Vaissiere, H.B. Ketelslegers, A. Stenholm, Prenatal developmental toxicity studies on fumes from oxidised asphalt (OA) in the rat, *Reprod. Toxicol.* 102 (2021) 67–79.
- H. Martin, Z. Kerstin, M. Joachim, Reduced emissions of warm mix asphalt during construction, *Road Mater. Pavement Des.* 20 (2019) S568.
- E.P. Possebon, L.P. Specht, D.S. Pereir, L.M.R. Ferraz, P.C. Nascimento, F. T. Sacramento Aragao, PAHs emissions by 12 Brazilian bitumens: procedure and results, *Road Mater. Pavement Des.* 20 (6) (2019) 1481–1499.
- P. Cui, G. Schito, Q. Cui, VOC emissions from asphalt pavement and health risks to construction workers, *J. Clean Prod.* 244 (2020), 118757.
- S. Mo, Y. Wang, F. Xiong, C. Ai, Effects of asphalt source and mixing temperature on the generated asphalt fumes, *J. Hazard. Mater.* 371 (2019) 342–351.
- M. Lei, S. Wu, G. Liu, S. Amirkhanian, VOCs characteristics and their relation with rheological properties of base and modified bitumens at different temperatures, *Constr. Build. Mater.* 160 (2018) 794–801.
- P. Cui, H. Zhang, S. Wu, Influence of high-temperature volatilization on performance of bituminous binder, *Annual Meetings of Chinese-Society's-Building-Materials, Professional Committees of Stone and Aggregate and Utilization of Solid Waste, Wuhan, China* 599 (2013) 164–167.
- P. Cui, S. Wu, Y. Xiao, M. Wan, P. Cui, Inhibiting effect of Layered Double Hydroxides on the emissions of volatile organic compounds from bituminous materials, *J. Clean Prod.* 108 (2015) 987–991.
- P.Q. Cui, S.P. Wu, Y. Xiao, H.H. Zhang, Experimental study on the reduction of fumes emissions in asphalt by different additives, *Mater. Res. Innov.* 19 (2015) S158.
- E.K. Harrison, B.S. Thomas, R.L. Sun, et al., Spectrometric determination of volatile content of coal tar pitch, *The Administration and Technique of Environmental Monitoring* 2 (1993) 65–66.
- X.J. Liu, Y.J. Wang, X.Q. Ma, Research on testing asphalt smoke by ultraviolet spectrophotometry (Chinese), *Green, Living* 10X (2014) 20. In Chinese.
- X.S. Zhang, Y. Xiao, Y.S. Long, Z.W. Chen, P.Q. Cui, R. Wu, X.W. Chang, VOCs reduction in bitumen binder with optimally designed Ca(OH)<sub>2</sub>-incorporated zeolite, *Constr. Build. Mater.* 279 (2021), 122485.
- X. Yang, Z. You, D. Perram, D. Hand, Z. Ahmed, W. Wei, S. Luo, Emission analysis of recycled tire rubber modified asphalt in hot and warm mix conditions, *J. Hazard. Mater.* 365 (2019) 942–951.
- Y.S. Long, S.P. Wu, Y. Xiao, P.Q. Cui, H. Zhou, VOCs reduction and inhibition mechanisms of using active carbon filler in bituminous materials, *J. Clean Prod.* 181 (2018) 784–793.
- J.B. Borinelli, J. Blom, M. Portillo-Estrada, P. Kara De Maeijer, W. Van den Bergh, C. Vuye, VOC emission analysis of bitumen using Proton-Transfer Reaction Time-of-Flight Mass Spectrometry, *Materials* 13 (17) (2020) 3659.
- P.Q. Cui, S.P. Wu, Y. Xiao, H.H. Zhang, Study on the deteriorations of bituminous binder resulted from volatile organic compounds emissions, *Constr. Build. Mater.* 68 (2014) 644–649.
- F. Autelitano, E. Garilli, R. Pinalli, A. Montepara, F. Giuliani, The odour fingerprint of bitumen, *Road Mater. Pavement Des.* 18 (2017) 178–188.
- I.R. Kaplan, S.T. Lu, H.M. Alimi, J. MacMurphey, Fingerprinting of high boiling hydrocarbon fuels, asphalts and lubricants, *Environmental Forensics* 2 (3) (2001) 231–248.
- M.N. Siddiqui, NMR fingerprinting of chemical changes in asphalt fractions on oxidation, *Pet. Sci. Technol.* 28 (4) (2010) 401–411.
- W. Wu, C. Wang, P. Zhao, L. Xiu, L. Fan, F. Bi, X. Song, X. Zhou, The fingerprint identification of asphalt aging based on H-1-NMR and chemometrics analysis, *Materials* 15 (19) (2022) 6825.
- M. Jiang, J. Cao, C. Zhang, B. Su, S. Wang, N. Ning, T. Lei, P. Li, A comprehensive strategy for quality evaluation of Wushe Zhiyang Pills by integrating UPLC-DAD fingerprint and multi-ingredients rapid quantitation with UPLC-MS/MS technology, *Journal of Pharmaceutical and Biomedical Analysis* 210 (2022), 114556.
- T.L. Yoon, Z.Q. Yeap, C.S. Tan, Y. Chen, J. Chen, M.F. Yam, A novel machine learning scheme for classification of medicinal herbs based on 2D-FTIR fingerprints, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy* 266 (2022), 120440.
- H. Feng, S. Li, Y. Hu, X. Zeng, P. Qiu, Y. Li, W. Li, Z. Li, Quality assessment of Succus Bambusae oral liquids based on gas chromatography/mass spectrometry fingerprints and chemometrics, *Rapid Communications in Mass Spectrometry* 35 (24) (2021) e9200.
- W.F. Zhang, K.F. Fan, J.W. Lei, L. Ji, Infrared fingerprint and multivariate statistical analysis of rehmanna glutinosa, *Spectroscopy and Spectral Analysis* 41 (11) (2021) 3392–3398.
- X. Bai, W. Yang, W. Song, N. Liao, Latent fingerprint residue detection method using Sagnac Fourier transform imaging spectroscopy, *Applied Optics* 60 (19) (2021) 5534–5539.
- G.L. Li, H.H. Zhao, Y.Q. Liu, P. Zhao, X.L. Pei, Y.J. Sun, X.Y. Tang, Study on Chinese herb astragalus membranceus by FTIR Fingerprint, Spectroscopy and Spectral Analysis 30 (6) (2010) 1493–1497.
- M. Wang, C. Wang, S. Huang, H. Yuan, Study on asphalt volatile organic compounds emission reduction: A state-of-the-art review, *J. Clean Prod.* 318 (2021), 128596.
- H. Zhang S. Wu L. Pang K. Jenkins M. Yu P. Cui Grey system theoretical analysis on the influence of volatile organic compounds emission from asphalt on its performance 3rd International Conference on Advanced Engineering Materials and Technology (AEMT 2013) 753 2013 Zhangjiajie, China 481 485.
- C.Z. Fan, The study of composition of asphalt smoke and its inhibition (Chinese), *China University Of Petroleum.* (In Chinese).
- H. Luo, H. Leng, H. Ding, J. Xu, H. Lin, C. Ai, Y. Qiu, Low-temperature cracking resistance, fatigue performance and emission reduction of a novel silica gel warm mix asphalt binder, *Constr. Build. Mater.* 231 (2020), 117118.
- B. Sutter, E. Pelletier, M. Blaskowitz, C. Ravera, C. Stolze, C. Reim, E. Langlois, D. Breuer, Sampling and analysis of bitumen fumes: Comparison of german and french methods to determine a conversion formula, *Ann. Work Expos. Health* 62 (6) (2018) 721–732.
- S. Binet, A. Pfohl-Leszczkovic, H. Brandt, M. Lafontaine, M. Castegnaro, Bitumen fumes: review of work on the potential risk to workers and the present knowledge on its origin, *Sci. Total Environ.* 300 (1–3) (2002) 37–49.
- C. Bolliet, A.J. Kriech, C. Juery, M. Vaissiere, M.A. Brinton, L.V. Osborn, Effect of temperature and process on quantity and composition of laboratory-generated bitumen emissions, *J. Occup. Environ. Hyg.* 12 (7) (2015) 438–449.

- [44] L.C. Brudi, F.R. Adolfo, P.C. do Nascimento, R.S. Cargnin, D. Bohrer, L.M. de Carvalho, T.A.L. Burgo, M.C. Cravo, L.A.H. do Nascimento, Emission and collection of polycyclic aromatic hydrocarbons from raw asphalt samples heated at 130 degrees C, *Energy Fuels* 34 (9) (2020) 11248–11257.
- [45] J.H. Cao, J. Shen, Y.G. Wang, G. Liu, Y.X. Liu, Release of 16 kinds of polycyclic aromatic hydrocarbons in blended asphalt fume (Chinese), *Coal Conversion* 42 (5) (2019) 88–96. In Chinese.
- [46] H. park, E. Hwang, S. Kim, Asphalt fumes and polycyclic aromatic hydrocarbons (PAHs) exposure assessment among asphalt road paving workers, *Journal of Korean Society of Occupational and Environmental Hygiene* 28 (3) (2018) 257–266.
- [47] L.P. Li, S.P. Wu, G. Liu, T.W. Cao, S. Amirkhanian, Effect of organo-montmorillonite nanoclay on VOCs inhibition of bitumen, *Constr. Build. Mater.* 146 (2017) 429–435.
- [48] A. Sharma, B.K. Lee, A novel nanocomposite of Ca(OH)<sub>2</sub>-incorporated zeolite as an additive to reduce atmospheric emissions of PM and VOCs during asphalt production, *Environ.-Sci, Nano* 4 (3) (2017) 613–624.
- [49] G. Boczkaj, A. Przyjazny, M. Kaminski, Characteristics of volatile organic compounds emission profiles from hot road bitumens, *Chemosphere* 107 (2014) 23–30.
- [50] Y. Xue, X. Wei, H. Zhao, T. Wang, Y. Xiao, Interaction of spent FCC catalyst and asphalt binder: Rheological properties, emission of VOCs and immobilization of metals, *J. Clean Prod.* 259 (2020), 120830.
- [51] J. Espinoza, C. Medina, A. Calabi-Floody, E. Sanchez-Alonso, G. Valdes, A. Quiroz, Evaluation of reductions in fume emissions (VOCs and SVOCs) from warm mix asphalt incorporating natural zeolite and reclaimed asphalt pavement for sustainable pavements, *Sustainability* 12 (22) (2020) 9546.
- [52] N. Li, Q. Jiang, F. Wang, J. Xie, Y. Li, J. Li, S. Wu, Emission behavior, environmental impact and priority-controlled pollutants assessment of volatile organic compounds (VOCs) during asphalt pavement construction based on laboratory experiment, *J. Hazard. Mater.* 398 (2020), 122904.
- [53] N. Li, Q. Jiang, F. Wang, P. Cui, J. Xie, J. Li, S. Wu, D.M. Barbieri, Comparative assessment of asphalt volatile organic compounds emission from field to laboratory, *J. Clean Prod.* 278 (2021), 123479.
- [54] R.S. Cargnin, F.R. Adolfo, P. Cicero do Nascimento, P. Schmidt, L.C. Brudi, L. Machado de Carvalho, D. Bohrer do Nascimento, M.C. Coutinho Cravo, L.A. Herrmann do Nascimento, Collection of polycyclic aromatic sulfur heterocycles from asphalt fumes and quantification by an HPLC-DAD method, *Analytical Methods* 13(29) (2021) 3307–3315.
- [55] J. Yang, J. Lee, Y. Lim, S. Park, C. Hong, C. Kim, D. Shin, Factors related to aldehydes exposure and symptoms in residential indoor air, *Environmental Health and Toxicology* 22 (1) (2007) 37–47.
- [56] R.M. LoPachin, T. Gavin, Molecular mechanisms of aldehyde toxicity: A chemical perspective, *Chemical Research in Toxicology* 27 (7) (2014) 1081–1091.
- [57] J.M. Qu, N.S. Ye, X.K. Qi, X.X. Wang, Determination of VOCs in ambient air by thermal desorption-GC/MS, *Analytical Instrumentation* 4 (2021) 58–65. In Chinese.
- [58] Y. Rasoulzadeh, S.B. Mortazavi, A.A. Yousefi, A. Khavanin, Decreasing polycyclic aromatic hydrocarbons emission from bitumen using alternative bitumen production process, *J. Hazard. Mater.* 185 (2–3) (2011) 1156–1161.
- [59] M. Yu S. Wu M. Chen H. Zhang Evaluation of volatile organic compounds from asphalt using UV-Visible spectrometer 3rd International Conference on Manufacturing Science and Engineering (ICMSE 2012) 472 2012 Xiamen, China 432 436.
- [60] H.H. Zhang, P.Q. Cui, L. Qiu, S.P. Wu, Influence of VOC emission on asphalt components, Annual Meetings of Chinese-Society's-Building-Materials, Professional Committees of Stone and Aggregate and Utilization of Solid Waste, Wuhan, China, 599 (2013) 178–181.