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Evaluation of Volatile Organic Compounds from Asphalt Using UV-visible Spectrometer

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Abstract: In order to evaluate volatile organic compounds (VOC) from asphalt, this paper explored to use ultraviolet and visible spectroscopy (UV-VIS) as the detection method of VOC. 288nm wavelength was selected as the characteristic absorption wavelength of VOC, finding that VOC quality and its absorbance value showed a good linear relationship which could be the basis for evaluation in this research. Experiments were carried out under different conditions, results of which showed that VOC emission was related to temperatures and asphalt specimens. Moreover, VOC emission increased with increasing temperatures. Results under non-high temperatures conditions showed that VOC emission during its service process should not be ignored.

Introduction

Asphalt binders, mainly used in asphalt pavement, are complex mixtures of organic compounds that are produced as a byproduct of petroleum refining [1].During heating, mixing, transfer, and application of asphalt binders, some odor often is perceived in relation to the emission of volatile organic compounds (VOCs) which leads to the deteriorate of asphalt pavement [2]. In additional, VOC could cause occupational exposures suffer from mucosal irritation , skin irritation, rash, nausea, stomach pain, decreased appetite, headaches, and fatigue as reported [3]. Asphalt fumes contain VOC, aerosol and particles, generated by heated asphalt, have been widely reported [4]. However, the researches on VOCs during the service environment are few. The key point in VOC research is detection and evaluation method, which is also a difficult. There is no one standard to evaluation VOCs from asphalt and new analysis methods need to explore. Currently, evaluation methods of asphalt fume are usually by means of gravimetric, fluorescence and UV spectrophotometer. However, methods of gravimetric and fluorescence are not precise enough.VOC emissions form asphalt binders can be evaluation by gas chromatography (GC) or HPLC, problem of which is that device operation conditions are complicated and difficult to determine [5]. This paper tried to explore ultraviolet and visible spectroscopy (UV-VIS) to evaluate VOCs from asphalt generated by conditions of high temperature and non-high temperature respectively.

Test method

An UV-1601 visible spectrometer, produced by Japanese Shimadzu, was used. In the 200-300nm wavelength range, selective ultraviolet light can be aborted by VOC absorption solution collected by cyclohexane. 288nm wavelength was selected as the characteristic absorption wavelength of VOC according to preliminary studies [6]. The evaluation of VOC was based on the linear relationship between VOC quality of the absorption solution and its absorbance value. Analysis steps to evaluate VOC from asphalt by the method of UV-VIS are as follows: 1) Draw the standard curve to determine the specific linear relationship between VOC quality and absorbance. 2) VOC sampling and record experimental data, such as time, temperature and pressure, then detect the absorbance values of samples by UV-VIS. 3) Calculate VOC quality of samples according to the result of step 2, by means of the formulas as showed in Eq1-Eq3:

$$\text{VOC emissions from asphalt : } w=\frac{Y\times V_1}{M\times a\times V_2}\ (\mu g/g) \tag{1}$$

$$\text{Standard volume: } V_0=\frac{P\times v\times T\times 273}{101325\times (t+273)}\ (L) \tag{2}$$

$$\text{Sample concentration: } C=\frac{w\times M}{V_0}\ (\mu g/L) \tag{3}$$

Where ,"M" is asphalt quality(g) ; "a"is the constant of linear curve; "V_1"is volume of cyclohexane dissolved VOC(ml); "V_2" is volume of test sample(ml); "Y"is the absorbance value of the test sample; "P" is sampling atmospheric pressure(Pa); v is sampler flow (ml/min), "T" is sampling time (min) and "t" is sampling temperature (℃).

Standard curve drawing steps are as follows: First, VOC sampling from heated asphalt by glass fiber filter and dissolve in a cleaned Petri dish filled with cyclohexane. Second, after the evaporation of cyclohexane, the disparity quality of Petri dish before and after is just the quality of VOC standard sample. Then dissolve standard sample by cyclohexane to standard solution, the concentration of which is known. Next is drawing different volumes of standard solutions to make up different concentration solutions as different samples by adding different volumes of cyclohexane. Last is detecting samples above by UV-VIS in order to obatin the linear relationship between VOC quality of the absorption solution and its absorbance value.

Experimental

Asphalts chosen for the experiments were provided by KOCH Asphalt Co. Ltd (Hubei Province, China). The installation generated VOC at high temperatures is shown in Fig.1 and at non-high temperature in Fig2. VOC sampling in the experimental used the method of cyclohexane absorption. Start sampling by Airchek 2000 sampler manufactured by SKC Inc when temperature sensor displayed the setting temperature. Sampling flow in the experimental was 500ml/min. As shown in Fig 1, asphalts in conical flask were heated to 120°C, 140°C, 160°C, 180°C, 200°C, 220°C, respectively. Sampling time at high temperature was 15min similarly to STEL (Short-term exposure limit) according to GBZ 159-2004(specifications of air sampling for hazardous substances monitoring in the workplace) [7]. Asphalt in heating oven as shown in Fig 2 were heated to 50°C and 70°C,respectively. Sampling time under these conditions was 8 hours similarly to TWA (Time Weight Average) [7].

Preparations of experiments were as follows: first, clean oven or conical flask by cyclohexane and clean the absorption device, shock absorber, glass fiber filter, clamp, graduated cylinder and Petri dish by distilled water and then by cyclohexane. Second heat above in vacuum oven and dry them at room temperature. Third heat weighed asphalt in the heating oven or conical flask to the setting temperature and connect sampler to start sampling while filling glass fiber filter into shock absorber and cyclohexane in absorption device. Place absorption device and shock absorber in water bath while sampling temperature was above 70℃. When sampling is over, wash the filter in shock absorber with cyclohexane and pour the lotion into absorption device. Last detect the absorbance using UV-VIS while the solution in absorption device evaporating to 10ml (or adding cyclohexane to 10ml if less than 10ml). And calculate the quality of VOC in unit mass of asphalt according to standard curve.

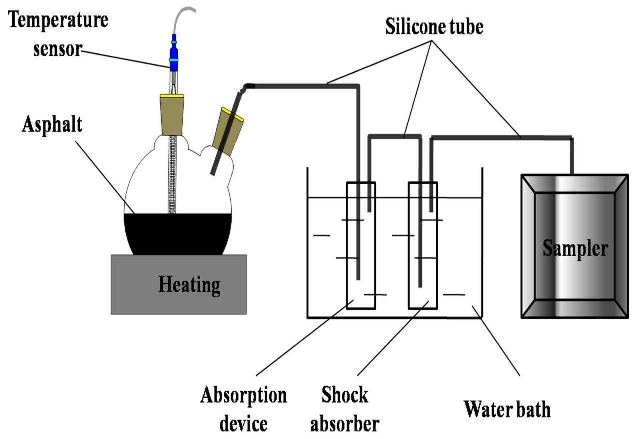

Fig 1 VOC generation device at high temperatures

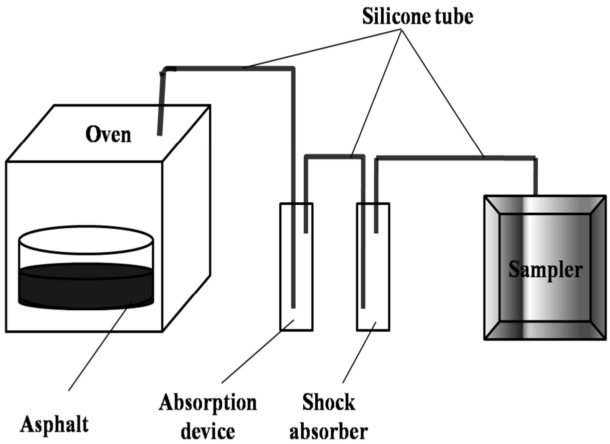

Fig 2 VOC generation device at non-high temperatures

Results and Discuss

Standard curve

Original data of standard curve are presented in Table 1 while the linear relationship between VOC quality of absorption solution and absorbance is shown in Fig 3.

Table1 Original data of the standard curve

NO	Absorbance Y	VOC emission /μg
1	0	0
2	0.176	16.0831
3	0.2806	32.1662
4	0.4036	48.2494
5	0.5328	64.3325
6	0.6420	80.4156
7	0.7660	96.4987
8	0.8691	112.5818
9	0.9982	128.6649
10	1.1154	144.7481
11	1.2919	168.8727
Mathematical solver	Y=0.00793793X (Y=aX,R^2=0.9997)	

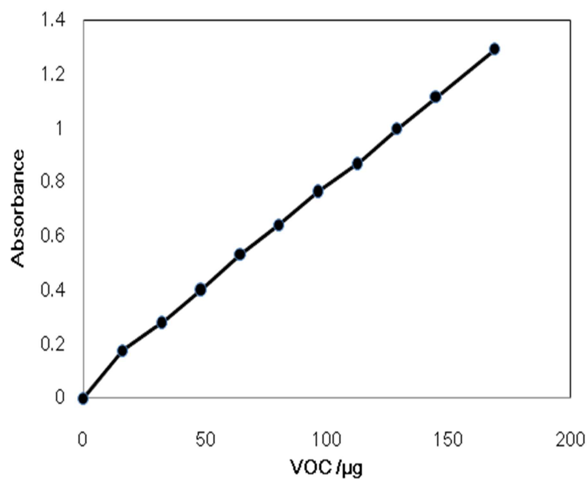

Fig 3 Standard curve between VOC quality and absorbance

As presented in Table 1 and Fig3, VOC quality and its absorbance show a good linear correlation. Besides, the constant of the linear curve, "a" value as shown in Eq1 is 0.00793793. For the certain absorbance value, VOC quality can be calculated according to Eq1-Eq3.

VOC emission at high temperatures

Five asphalts chosen in the experiments were SK70, SK90, PJ90, KL90 and HC90, respectively. VOC emissions and VOC sampling concentrations from different asphalts are presented in Fig 4, Fig 5. Figures show that VOC emission increases with the increasing temperatures. The increment of VOC emission is more pronounced while temperature is higher than 140℃ or more. In these five asphalts, trends of VOC emission and VOC sampler concentration are similar. VOC emission (or sampling concentration) of asphalt grade 70 is smaller than the other asphalts graded 90 at the same temperature. While higher than 180°C, emission difference (or sampling concentration difference) between SK70, PJ90 and SK90 is small. In conclusion, asphalt labeled 90 emissions is greater than asphalt labeled 70 with the same brand SK. In different brand asphalts with the same label 90, the law of VOC emission (or sampling concentration) is as descending: HC90, KL90, PJ90, and SK90, reason of which may be that distribution and components of different asphalts are not the same, so do different levels of light components in asphalts.

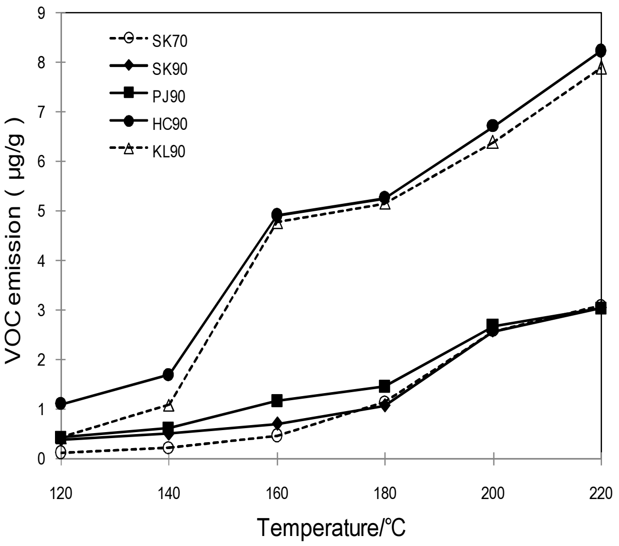

Fig 4 VOC from different asphalts under different temperatures conditions

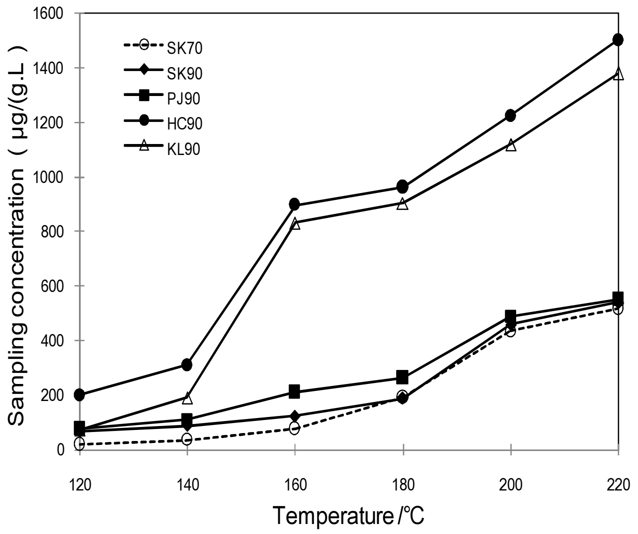

Fig 5 Sampling concentration from different asphalts under different temperatures conditions

VOC emission at non-high temperatures

Asphalts chosen in this experiment are SK70 and PJ90. VOC emissions and sampling concentration under non-high conditions, temperatures of which were 50°C and 70 °C respectively , are presented in Fig6 and Fig7.

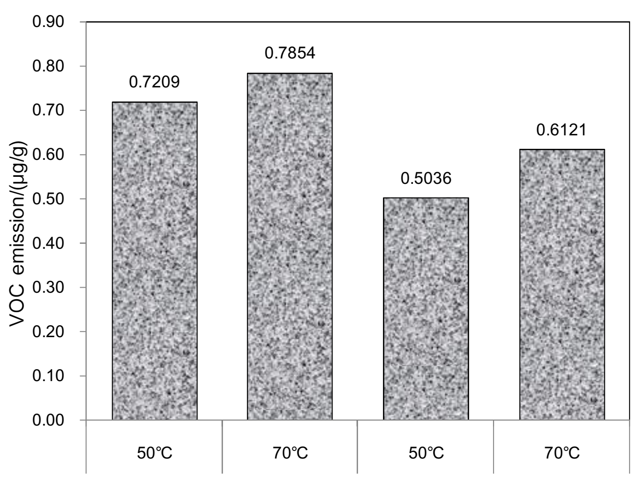

Fig 6 VOC emission under non-high temperature condition

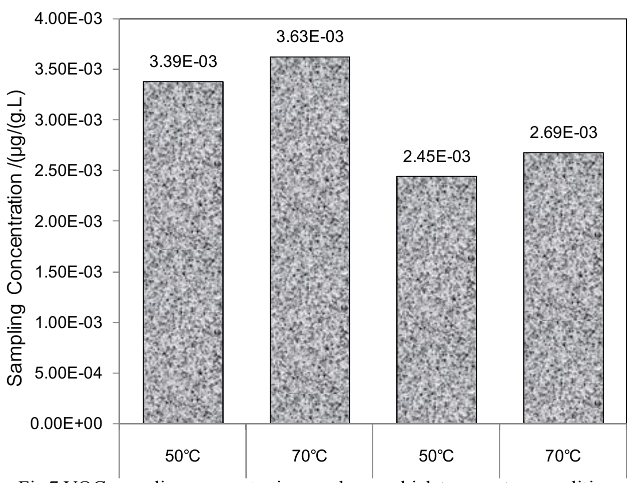

Fig 7 VOC sampling concentration under non-high temperature condition

As shown in Fig6 and Fig7，trends with different asphalts and temperatures of VOC emission are the same as trends of sampling concentration. VOC emission and VOC sampling concentration from PJ90 are greater than SK70,both at the temperature of 50℃ and 70℃.Compared to 50℃, VOC emission from PJ90 was increasing about 9% at 70℃,while SK70 was more than 20%; VOC sampling concentration from PJ90 was increasing about 7% while SK70 was more than 9%. Results indicate that asphalt could volatile even if under non-high conditions, which need attract more attention in future. Reason of VOC emission under non-high condition may be that light components in the asphalt can evaporate to odor. Light components in PJ90 are more than SK70, which leads that VOC emission from PJ90 is greater than SK70.

Conclusions

This paper tries to explore UV-VIS to evaluate VOC emission from asphalts under different conditions. Generally conclusions that can be drawn from this research are as follows:

1) VOC quality of absorption solution and its absorbance values showed a good linear relationship, which is the basis for VOC evaluation method in this research. Moreover, trends of VOC emission are the same as trends of VOC sampling concentration which can also be a method to evaluate VOC from asphalt.
2) VOC emissions from different asphalts are different depends on asphalt species and temperatures. VOC emission increases with the increasing temperatures, and VOC emission from asphalt labeled 70 is smaller than asphalt labeled 90 in these asphalts. The law of VOC emission from asphalts labeled 90 of different brands is as descending: HC90, KL90, PJ90, and SK90 under high temperatures conditions.
3) Under the conditions of non-high temperatures, VOC emissions from asphalts in this paper can also be detected by UV-VIS, which indicates that VOC emission from asphalt at non-high temperatures should not be ignored

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